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INTERNATIONAL SERIES IN PHYSICS
F. K. RICHTMYER, CONSULTING EDITOR

QUANTUM MECHANICS

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Condon and Morse—

Quantum Mechanics

Ruark and Urey—

Atoms, Molecules and Quanta

Pauling and Goudsmit—

The Structure of Line Spectra

QUANTUM MECHANICS

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FIRST EDITION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK: 370 SEVENTH AVENUE
LONDON: 6 & 8 BOUVERIE ST., E. C. 4
1929

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

To

KARL TAYLOR COMPTON

DISTINGUISHED PHYSICIST,
VALUED FRIEND OF PHYSICISTS.

PREFACE

This book aims to give an account of some of the leading developments in our knowledge of atomic structure and the interpretation of spectroscopic and electronic phenomena which have been made in the past four years. This period has probably been the most exciting in the history of theoretical physics. About 1923 and 1924 there was a pause in the rapid advances which occurred in the decade immediately following Bohr's theory of 1913. It seemed that all the advances that could be made with that patchwork theory had been made, and the difficulties which it had always involved came more and more to the front.

Then came the discovery by Heisenberg of the matrix mechanics. This started the vast activity of which we here attempt to give some account. De Broglie had published his thesis on phase waves somewhat earlier but practically no attention had been paid to it. Some comments had been made on his ideas concerning light quanta, but the ideas concerning matter waves were ignored. The story is told that someone asked Schrödinger to report de Broglie's thesis to the colloquium at Zürich, and that thus he came to read it and to build his famous series of papers on "undulatory mechanics" upon it.

The matrix mechanics demands a mathematical technique which is strange to physicists and with which it is exceedingly difficult to clothe the steps of a calculation with physical meaning. Therefore, in this book the matrix mechanics is omitted almost entirely. The wave mechanical equation of Schrödinger stands in its place.

Soon it was recognized that the mathematical methods of wave mechanics and of matrix mechanics were formally equivalent and, therefore, would lead to the same results with regard to allowed energy levels and other observable properties of atoms. But there was a wide difference between the attitudes of two parties toward this set of quantum mechanical equations. Schrödinger sought to regard the atom as a set of charges smeared into a volume distribution and obeying laws otherwise not radically different from those of classical electrodynamics.

Heisenberg, Dirac, Jordan and Born, and others of the Göttingen and Copenhagen schools showed the untenability of Schrödinger's interpretation and brought forward the idea that we are dealing with a statistical theory in which the equations give probabilities rather than precise answers to most questions. There seems now to be no question that this second interpretation lies closer to the real truth. It is now the one adopted by all the leading theoretical physicists.

The intention has been here to give an account of the theory which builds inductively from the phenomena to be explained, along the lines of Schrödinger's wave methods, but giving to them the statistical interpretation. The work has been kept on as elementary a plane as possible in order that it may be useful to a wide circle of readers. This has made necessary the omission of many topics of fundamental importance, such as, especially, the problem of quantization of the electromagnetic field and Dirac's theory of the magnetic electron. The book is, rather, intended to be an outline of the results obtained by the quantum mechanics, and a manual of various methods which are used in arriving at these results. An attempt has been made to standardize the notation, to unify the treatment of normalizing factors and of the polynomials, and to correlate the various exact solutions of the Schrödinger equation, so that the book can be used as a reference work when dealing with any of the known wave functions.

The subject is growing at such a pace that almost every number of the leading research journals has at least one contribution of importance to the theory, and many have several. In such a situation it is manifestly impossible to write a book that is in any sense complete. All that can be done is to pick out interesting and important topics and treat them. In making the selection, an author is naturally influenced by his personal interests. There is no need to apologize for that, for the reader wants an author to write on those things that he knows best, if he is to function in any higher capacity than merely as editor of a compilation.

Especially incomplete is our Chapter VII in which only a very few of the more elementary results of the theory for aperiodic phenomena could be incorporated. For a supplementary account of collision processes the reader is referred to a report which is to appear in the January, 1930 issue of the *Physical Review Supplement.*

The authors have had the privilege of seeing the manuscript of two other books of this series. Ruark and Urey's "Atoms, Molecules, and Quanta" is to be recommended for the details of the experimental results which are the basis of the theory treated in this volume. Goudsmit and Pauling's "The Atomic Model and the Structure of Line Spectra" will be valuable in supplementing the sections on atomic spectra, and references to it have been made from place to place.

The book as it appears here is an outgrowth of the lectures which the senior author has been privileged to give during the spring term of 1928 at Columbia University, and during the academic year, 1928–1929, at Princeton University. The authors are much indebted to their colleagues for suggestions and criticisms, especially to Prof. H. P. Robertson, Dr. J. E. Mack, and Dr. E. C. G. Stueckelberg.

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CONTENTS

CHAPTER I

GENERAL INTRODUCTION

CHAPTER II

SIMPLE MECHANICAL PROBLEMS BY THE WAVE METHOD

CHAPTER III

RADIATION AND EXTERNAL FIELDS OF SIMPLE MECHANICAL SYSTEMS

CHAPTER IV

APPROXIMATE METHODS OF HANDLING THE WAVE EQUATION. PERTURBATION THEORY

DEGENERATE SYSTEMS

CHAPTER V

DIATOMIC MOLECULES

CHAPTER VI

GENERAL FORMULATION OF THE THEORY

CHAPTER VII

APERIODIC PHENOMENA

QUANTUM MECHANICS

CHAPTER I

GENERAL INTRODUCTION

During the first quarter of the twentieth century physics has been chiefly concerned with the disheartening task of showing that the classical laws and concepts of dynamics and electrodynamics do not hold in the region of atomic dimensions; and with the more pleasant concomitant task of discovering the new laws and concepts which are valid in this region. These new laws and concepts, as originally formulated in the "classical quantum theory," have encountered grave difficulties in their interpretation and in their wider application, difficulties only recently obviated by the "quantum mechanics," which has restated these laws in a better and more elegant form, and has clarified to some extent the philosophical difficulties in the concepts. This chapter will briefly enumerate[1] the difficulties encountered in the classical theories, their partial explanation by the "classical quantum theory," and the consequent difficulties encountered in this theory. The leading ideas of a theory which proposes to mitigate these difficulties will then be given and discussed.

1. Quantum Physics before 1925.—The field in which the failure of classical laws was first acutely felt was in that of radiation. It had been quite reasonably assumed that the atoms of any material were electrical harmonic oscillators, and general arguments of statistical equilibrium had shown that in this case $\overline{W}$, the average energy of motion possessed per atom per degree of freedom, would necessarily be kT, where k is a universal constant, and T is the absolute temperature. Such matter would, of

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[1] For a more detailed account, see Richtmyer, "Introduction to Modern Physics," McGraw-Hill Book Company, Inc. (1928); Darrow, "Introduction to Contemporary Physics," D. Van Nostrand (1926). Andrade, "Structure of the Atom," Harcourt Brace & Company (1927). Sommerfeld, "Atomic Structure and Spectral Lines," E. P. Dutton & Company (1923).

course, give off radiation, and each different frequency of the radiation would represent a different degree of freedom. It was proved that the average energy density of radiation inside a cavity in this material for radiation of a frequency between ν and $\nu + d\nu$ would be $\rho(\nu)d\nu$, where

$$\begin{aligned}\rho(\nu) &= 8\pi\nu^2\overline{W}/c^3 \\ &= 8\pi\nu^2 kT/c^3 \text{ if } \overline{W} = kT.\end{aligned}$$

This law agreed with experiment only for small values of ν. Also a serious fundamental difficulty became apparent. Even if $\overline{W}$ were not exactly equal to kT, there would be a disproportionate amount of energy resident in radiation of very high frequency, and sooner or later all the energy in the universe would be drained off into such radiation—an event known as the "violet catastrophe." But such a consummation has not yet occurred, and the universe has been going on for some time . . .

In an effort to circumvent these difficulties, Planck, in 1900, hit upon a formula

$$\rho(\nu) = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/kT} - 1},$$

where h is another universal constant. This coincided with experiment for all frequencies. But when he developed a theoretical justification for such a formula in terms of statistical mechanics, he was forced to make two radically new assumptions about the interaction between matter and radiation. The first was: *Each degree of freedom of each oscillator can have only an energy equal to an integral multiple of some unit* W_0. Previously these oscillators were supposed to be able to possess instantaneously any value of energy from zero up to the total energy of the body.

When this assumption was made it was found that the average energy, instead of equalling kT, was

$$\overline{W} = \frac{W_0}{e^{W_0/kT} - 1},$$

and to make this correspond to the correct formula when $\overline{W}$ is substituted into $\rho(\nu) = 8\pi\nu^2\overline{W}/c^3$, Planck was forced to make a second assumption: *The energy unit* W_0 *connected with a given frequency* ν *is related to* ν *by the equation* $W_0 = h\nu$. No satisfactory theoretical derivation of Planck's formula involving assumptions fundamentally different from the above two has ever been published.

Thus was the idea of discrete quantum states introduced into physics. The oscillator could exist only in certain states whose energy was an integral multiple of $h\nu$. In radiating and absorbing light, it follows that the oscillator cannot slowly radiate away its energy as the classical electrodynamics requires, for it would thus be led into states other than the allowed ones. Instead, there must be an abrupt transition from one allowed state to another, in which the energy radiated or absorbed is an integral multiple of $h\nu$. There is thus a lower limit $h\nu$ put on the amount of energy involved in the interaction between matter and the electromagnetic field where waves of frequency ν are involved.

The newly explored field of photoelectricity was also showing marked divergences from the expectations of classical physics. If ϕ_0 is the energy required to separate an electron from a metal surface or from a gas molecule, v is the electron's velocity after separation, and W the energy of the absorbed light, then

$$\frac{mv^2}{2} = W - \phi_0.$$

W in the classical theory is proportional to the square of the amplitude of the incident light (the intensity) and to the square of its frequency. Experiment showed that this was not at all correct. Einstein, in 1905, applied Planck's assumptions to the phenomenon and showed that W must equal $h\nu$ and that the intensity of the incident light affected only the number of electrons expelled and not their velocity. The resulting formula, $mv^2/2 = h\nu - \phi_0$, was approved by experiment. Since the absorption, as well as the radiation, of light seems thus to occur in quanta of energy it began to be clear that the amount of light energy $h\nu$ had some sort of unitary existence.

Einstein also showed that another difficulty could be circumvented by the use of Planck's assumptions. The empirical rule of Dulong and Petit states that solids have a molar specific heat of $3R$. This is explained by classical statistics if each atom is an oscillator with three degrees of freedom. Then its total average energy would be $3\overline{W} = 3kT$, as we have seen above, and the total energy for N atoms in a mol would be $3NkT = 3RT$. The derivative of this with respect to the temperature is the specific heat $3R$, which is independent of the temperature.

But it was found that Dulong and Petit's rule does not hold at low temperatures, for the specific heat of all solids diminishes as the temperature approaches absolute zero. Einstein showed that if Planck's formula for $\overline{W}$ given above were used, and $3N\overline{W}$ were differentiated with respect to T, the resulting formula showed fairly good agreement with experiment: an agreement which has been made quite satisfactory by refinements of the theory that do not, however, affect the basic idea of the discreteness of the energy states.

The next important development for quantum physics came with the publication, in 1913, of Bohr's theory of the spectrum of atomic hydrogen. This is not the place for a complete discussion of the experiments on scattering of cathode rays and of alpha particles which led to the nuclear model of the atom. According to this model, the atom which is Zth in the list in the periodic system has a positively charged central nucleus of charge $-Ze$ surrounded by Z electrons each of charge $+e$.[1] The dimensions of the nucleus are, from scattering experiments, of the order of 10^{-12} centimeter while the space occupied by the electrons is roughly a sphere of radius 10^{-8} centimeter. Earlier models had supposed that the positive electricity made up a sphere of about this latter size in which the electrons were imbedded. There was a period in which attempts were made to apply the theory of elasticity to rigid distributions of charge, the aim being to find a model whose elastic vibrations would have the same frequencies as the lines in the spectrum of an atom. These attempts have now only historic interest.

If the atom be a set of electric charges in dynamic equilibrium, then Maxwell's equations demand that the atoms continually radiate energy, and even if the atom does not eventually collapse, the frequency of the oscillations will continually change, and the spectrum of the light radiated from such a body will be continuous. But all gases radiate light which gives a spectrum at least partially composed of discrete lines.

Ritz showed that the frequency of the lines in any spectrum could be classified by the relation

$$\nu_n{}^m = T_m - T_n,$$

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[1] Throughout the book it will be understood that e stands for the charge on the electron, and since this charge is negative, the letter e stands for -4.77×10^{-10} e.s.u. of electric charge.

where the T's are constant "terms." Thus a large number of frequencies could be correlated by a relatively small number of terms, and, while not all the frequencies given by the various term differences are present in the radiated light, all that are present are included in the system. In particular, T_n for the hydrogen atom was found to be R/n^2, where R is a general constant for every term, and n is an integer. These relations for radiated light have not yet been satisfactorily explained from the standpoint of classical electrodynamics.

Bohr applied Planck's ideas to the recently promulgated nuclear atom model put forward by Rutherford. He saw that if *an atom did not radiate whenever it had one of a discrete set of energy values* E_n, and that if *it radiated only when for some reason it changed from one of these "stationary states" to another* then by Planck's assumption the radiant quantum

$$\epsilon_n{}^m = h\nu_n{}^m = E_m - E_n.$$

Then $T_m = E_m/h$, and Ritz's equation is immediately satisfied.

Further, assuming that the single electron in the hydrogen atom revolves in a circular orbit about its nucleus under the influence of the usual electrostatic forces, and that the *atom is in a stationary or non-radiating state when the angular momentum of the electron is* $nh/2\pi$, he obtained the required value R/n^2 for the various terms. He also obtained a value for R which is within about 0.02 per cent of the experimental value, an astounding agreement.

This great result was soon followed by many others. The lines of the hydrogen spectrum show a very close fine structure: Sommerfeld introduced "quantized" elliptical orbits and related them to small variations of the energies with the eccentricity of the orbits arising from the relativistic variation of the mass of the electron with its velocity. The lines are split up into components by an electric field, a fact known, after its discoverer, as the "Stark effect." Epstein related this to the perturbation of the quantized energy levels due to the action of the field as well as the nuclear attraction on the moving electron. The Zeeman effect was explained by several investigators in terms of alteration of energy levels by the magnetic field.

The higher atoms consisting of many electrons presented insuperable difficulties in the way of exact calculation of energy levels. But in the hands of Sommerfeld, Bohr, and many others, the Bohr principles led soon to a semiquantitative description of the energy levels of these atoms. This, in turn, gave a great impetus to the experimental study of these spectra. Similarly the simple model of two masses which could rotate about their center of mass and could execute small oscillations along their line of centers greatly clarified the study of the band spectra emitted by diatomic molecules, relating these complicated spectra to the forces which bind the atoms together into molecules. The success of such investigations served to emphasize the breakdown of Maxwell's equations in the regime of atomic physics, at least in the matter of radiation.

The next problem was a discussion of the relative and absolute intensities of spectral lines. The investigation of absolute intensities is difficult and even now there is but a small amount of such data. But there was a wealth of data on relative intensities that needed explanation. The foremost problem was that of the so-called "selection rules" expressing the fact that the frequencies corresponding to certain differences of terms do not occur. Thus, in the spectrum of neutral sodium it is possible to label certain terms as s, p, d, f . . . terms and to make the rule that s terms combine only with p terms, p only with s or d, d only with p or f, etc. In the hydrogen spectrum such selection rules must be employed to get agreement between theory and experiment in the relativistic fine structure and in the Stark and Zeeman effects. Otherwise the theory would give too many lines.

While there were various arguments leading to the necessary selection rules, by far the most important development was that known as the "correspondence principle," put forward by Bohr in 1918. It would lead too far afield to attempt an exposition of this principle in detail in this introductory resumé of the subject. The main idea consists in the observation that for large quantum numbers the frequencies given for transitions between neighboring states by Bohr's rule become asymptotically equal to the actual orbital frequencies of the motion and to linear combinations of integral multiples of them. These latter frequencies are, of course, the ones which would be radiated if Maxwell's electrodynamics were fully correct. This asymptotic agreement for the *frequencies* suggests that for states of the atom associated with large quantum numbers the actual radiation *intensities* may approach to those given by application of classical electrodynamics to the model. This connection Bohr postulates.

In the realm of large quantum numbers and small changes in them, this amounts to a definite statement concerning intensities, since then the classical rate is about the same no matter for which of the two energy states involved it is computed. But for small quantum numbers the classical intensities computed for the two states involved are quite different. It is natural to suppose the true intensity is some sort of an average between these; but what kind of average to take could never be clearly read into the principle in spite of numerous attempts. In case the classical rate of radiation vanishes for both states involved in a given pair of energy levels, however, it seems natural to suppose that the actual intensity is zero, even though the quantum numbers are not large. This rule actually gives the empirical selection rules correctly. Moreover, in certain cases the intensities are fairly well predicted by the correspondence principle—a noteworthy example is Kramers' discussion of the relative intensities of the Stark effect components of the hydrogen lines.

By and large, the main principles of the quantum theory were those outlined, up to about 1924. In the meantime, the Compton effect had been discovered—another phenomenon which is easily discussed, at least so far as frequencies go, in terms of the light-quantum idea. Here the momentum as well as the energy of the light quantum plays a role.

The successes of the theory built on Bohr's lead are conspicuous. Nevertheless, it was marred by serious defects and beset with numerous difficulties. Until about 1924 and 1925, theoretical physicists were so concerned with the working out of the many successes of the theory that the fundamental difficulties were, for the time, left out of mind. These difficulties then began to make themselves felt as serious impediments to further progress. It was coming to be realized that progress probably depended on a revision of the basic principles of quantum physics—a revision which to be successful would probably be quite radical.

One can find this need expressed by various writers. For example, Born,[1] writing the preface to his lectures on atom mechanics, in November, 1924, says:

> In bringing out the thought that the theory is still unripe, I want to mention that we are concerned with an attempt, a logical experiment,

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[1] Born, "Vorlesungen über Atommechanik," Berlin (1925).

> the plan of which is to stake out the limits of the present quantum theory and to seek the ways by which these limits are to be passed. To bring out this program clearly in the title, I have called this book volume I; the second will contain a higher approximation to the finally valid atom mechanics . . . At present we have but a few vague indications about the kind of deviations from classical laws which must be introduced for the explanation of atomic properties . . . Therefore perhaps the second volume so-planned will remain for many years unwritten . . .

These sentences have always seemed to the present writers a particularly apt statement of the mood which preceded the revolutionary reformulation of quantum physics that started shortly afterward. In the next section more attention will be devoted to the difficulties of the old quantum theory and to the first attempts at overcoming them.

2. Some Difficulties.—The difficulties which led to a reformulation of the principles of quantum physics are really of two sorts.[1] Even when it gave correct results as in the case of the hydrogen energy levels and their alteration in the Stark and Zeeman effects, there was an unsatisfactory looseness about the principles. The quantum conditions were added to ordinary mechanics as an afterthought, so to speak, instead of being an integral part of it. Besides the laws of mechanics there were (*a*) the rule connecting spectral frequencies with energy level differences, (*b*) the quantum conditions for picking out the allowed states, and (*c*) the correspondence principle which gave only incomplete information about radiation intensities. All three of these things were supplementary to classical mechanics and not closely tied to it.

The first kind of difficulty is just this lack of coherence in the structure of the principles, a feature which led many to seek a more unified formulation of the mathematical laws governing atom models.

The other kind of difficulty, while no more important, was of the sort that gave greater immediate cause for concern. At about the critical period, several applications of the principles had been carried through that had definitely failed to agree with experiment. One of the most glaring examples of this sort is

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[1] VAN VLECK, "Quantum Principles and Line Spectra," National Research Council *Bull.* 54 (1926); PAULI, "Quantentheorie, Handbuch der Physik," Vol. 23, Berlin (1926).

in the case of dispersion theory. For the discussion of the propagation of light through matter it is necessary to know how the atoms of the matter will react to the alternating electric field of the light wave. By the perturbation theory of classical mechanics, it is possible to do this with the result that the critical point in the frequencies around which anomalous dispersion occurs are the *orbital* frequencies of the periodic motions in the atom and not the frequencies of the spectral lines as given by Bohr's rule. Experimentally, however, anomalous dispersion is known to be intimately connected with the frequencies of the spectral lines. (The experiments of Wood on the dispersion of sodium vapor in the neighborhood of the D-lines are an oft-cited instance of this.)

Other examples are the calculation of the energy levels of H_2^+ by Pauli and by Niessen, of the normal state of He by Kramers and by Van Vleck, of the excited states of He by Born and Heisenberg and of the normal state of H_2 by Hutchisson. After the two-body problem, the three- and four-body problems could be treated only by approximate methods. Nevertheless, they gave results decidedly not in accord with experiment. More detail on the numerical results of such calculations will be reserved for the places where the contributions of the newer methods are discussed. A full account of them is to be found in the National Research Council *Bulletin*, by Van Vleck on "Quantum Principles and Line Spectra," especially Chaps. VII and VIII.

The breakdowns in dispersion theory and in the more complicated atoms are really closely related. The failure of the former tells that electrons do not react to rapidly varying electric fields in the classical way. In atoms containing several electrons, the force on each electron arises not only from the virtually fixed nucleus but also from the other rapidly moving electrons and so it is also a field which varies rapidly with the time. From this point of view, one sees the possibility that the atomic state calculations may fail for the same reason as the dispersion theory.

The anomalous Zeeman effect proved another stumbling block for the older atomic mechanics. According to the latter, the effect of a magnetic field on any atomic system would be to set up a precessional movement of the system as a whole about the direction of the lines of force with an associated alteration of energy levels in just such a way that the effect on any line would be simply to split it into the normal Lorentz triplet. While many spectral lines do behave according to the simple theory worked out by Lorentz, in 1896, there are many more which show a much more complicated behavior. Nevertheless, the theory persists in giving the Lorentz triplet for all atomic models. With the help of the hypothesis that electrons possess a magnetic moment, the new developments of quantum mechanics have reached the explanation of the so-called anomalous Zeeman effect.

In the field of impacts between electrons and gas atoms, it was also recognized that atomic mechanics was in difficulty. Especially is this the case in the experiments of Ramsauer, in which it is shown that electrons of very low speed are deflected less in atomic collisions than those of higher speed.

From consideration of such difficulties as these Bohr was therefore led in 1925 to express the conviction that:

> . . . From these results it seems to follow that, in the general problem of the quantum theory, one is faced not with a modification of the mechanical and electrodynamical theories describable in terms of the usual physical concepts, but with an essential failure of the pictures in space and time on which the description of natural phenomena has hitherto been based.

3. A New Rule for the Energy Levels.—Because of difficulties of the sort just mentioned and others which it seems best to reserve until later, it was recognized that quantum phenomena would call for a rather radical modification of the principles of physics. Heisenberg[1] set up a scheme for dealing with mechanical quantities which in the hands of Born and Jordan led to the so-called matrix mechanics.[2] Soon afterward Schrödinger,[3] working from another direction, built up a system which was based on earlier work of de Broglie and which has come to be known as "wave mechanics."

Developments have shown that the two are equivalent, in so far as predictions of the frequencies and intensities in the

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[1] HEISENBERG, *Zeit. für Phys.*, **33**, 879 (1925).

[2] For a general review see BIRTWISTLE, "The New Quantum Mechanics," Cambridge (1928); BORN, "Problems of Atomic Dynamics," Cambridge, Mass. (1926).

[3] SCHRÖDINGER, *Ann. der Phys.*, **79**, 361 (1926); *Ann. der Phys.*, **79**, 489 (1926); *Ann. der Phys.*, **79**, 734 (1926); "Collected Papers on Wave Mechanics," London (1928); *Phys. Rev.*, **28**, 1,049 (1926).

spectrum of a system goes, and that both of these schemes are but a part of a still more general point of view for which the name "quantum mechanics" in the broad sense will be reserved. It is essential to keep distinct those parts of the theory which provide equations which are successful in a formal way, independently of their interpretation, and those parts which attempt to interpret the equations. This will be done in what follows, the intention being to present the working equations in as naked a form as possible at first, reserving until later the question of their interpretation.

There is no question of *proving* these equations any more than there has been a need of *proving* Newton's laws. We shall see that the equations merge into those of classical mechanics for values of energy much larger than those involved in atomic processes, and that for atomic energy values, they give results much more in accord with experimental data than any earlier set of equations. Thus, we have not questioned the older theories in fields where they are known to work, and we have provided ourselves with a theory which does work in a region where the older ones did not. This is all the *proof* which is needed for any theory.

Since some of the mentioned difficulties are concerned with the failure of the old methods to give the right energy levels, a good starting place is to seek a new rule by which the energy levels are to be found. In this form, Schrödinger attacked the problem, making use of ideas of de Broglie on "phase waves" associated with matter, Sec. **4.** As will be seen later, de Broglie discovered reasons for supposing that there is some sort of wave motion associated with a moving particle and that the wave length of the motion is $h/\mu v$, where μ is the mass of the particle and v its velocity.

The equation of wave propagation as it is familiar to physicists from the theory of electric waves or of elastic waves is

$$\Delta\Psi - \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = 0,$$

in which Ψ is a quantity measuring the wave amplitude and c is the velocity of the waves. Thus in electric waves Ψ may be the vectors $\boldsymbol{E}$ or $\boldsymbol{H}$, in acoustic waves it may be the scalar pressure. If the phenomenon is a purely periodic one so that

$$\Psi = \psi(x, y, z).e^{2\pi i\nu t},$$

the equation for the space part of Ψ, *i.e.* ψ, becomes

$$\Delta\psi + \frac{4\pi^2\nu^2}{c^2}\psi = 0.$$

But the ratio c/ν occurring here is the wave length, so the coefficient can as well be written $4\pi^2/\lambda^2$. Building on the idea that there is some sort of wave, whose wave length is $h/\mu v$, associated with a particle, it is natural to seek the equation which governs the propagation of this new sort of wave—variously called de Broglie waves, matter waves, phase waves, etc. If one is dealing with a state of motion of the particle in which the total energy is W and the potential energy as a function of position is $V(x, y, z)$, then the momentum at any point is $\sqrt{2\mu(W - V)}$ and possibly then the matter waves of wave length $h/\mu v$ are governed, so far as the space variation goes, by the equation

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}(W - V)\psi = 0, \tag{3.1}$$

which is gotten by putting this value of the wave length into the preceding wave equation.

Suppose that this is done. Then there is a partial differential equation for ψ, the as-yet uninterpreted quantity which characterizes the amplitude of the wave disturbance. Now a closer consideration of this equation shows that for certain force fields, *i.e.*, certain particular functions $V(x, y, z)$, there are only discrete values of W such that the quantity ψ is everywhere a finite and single-valued function of position. If ψ is ever to be given much physical significance, it seems likely that only cases in which ψ is finite and single valued everywhere will be admissible.

At any rate, if this assumption is made: *namely, the allowed quantum-mechanical energy levels are the values of W for which ψ as determined by equation* (3.1) *is finite and single-valued throughout space,* it is found that in a great many cases the levels so defined are in agreement with the experimental facts. The consideration of the technique of solving this equation in various special cases is the subject of the next chapter. Here it must suffice to say that the new rule gives the same levels as the method of Bohr in cases where this method was right and is in agreement with experiment in several instances where the old method was not.

The equation for $\psi(x, y, z)$ thus provides a new rule for finding the allowed energy levels of a particle of mass μ moving in a field of potential energy $V(x, y, z)$. The new method dispenses entirely with the necessity of determining the orbits according to classical mechanics, and suggests that these orbits may not have the clear cut significance they formerly had.

In obtaining equation (3.1) it was supposed that the system consisted of just one particle in a force field. A natural generalization of this to a system of f degrees of freedom described by $q_1 q_2 \dots q_f$ is easily obtained. For such systems the kinetic energy T is a quadratic form in the velocities $\dot{q}_i$, where, in general, the coefficients depend on the q's, that is,

$$T = \sum_{ij} a_{ij}(q)\dot{q}_i\dot{q}_j,$$

or expressed in terms of the $p_i = \partial T/\partial \dot{q}_i$, the kinetic energy is still a quadratic form with new coefficients

$$T = \sum_{ij} A_{ij}(q)p_i p_j.$$

In the simple case of three dimensions, the wave equation can be written as

$$-\frac{1}{2\mu}\frac{h^2}{4\pi^2}\left[\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right] + V\psi = W\psi,$$

an equation which bears a great resemblance to the equation

$$\frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V = W,$$

of classical mechanics. In fact, one observes that from this latter equation the wave equation could have been gotten by replacing p_x by the operator $\frac{h}{2\pi i}\frac{\partial}{\partial x}$ and, similarly, for p_y and p_z and then letting each term of the resulting operational equation operate on ψ. This formal process often gives the wave equation which is needed for working out a special example. Hence, one often sees the basic wave equation in the general form for a system whose Hamiltonian function is $H(p_1, p_2, p_3, \dots ; q_1, q_2, q_3 \dots)$ written as,

$$\left\{H\left(\frac{h}{2\pi i}\frac{\partial}{\partial q_1}, \frac{h}{2\pi i}\frac{\partial}{\partial q_2}, \dots ; q_1 q_2 \dots\right) - W\right\}\psi = 0 \qquad (3.2)$$

The formal replacing of each p by the corresponding $\frac{h}{2\pi i}\frac{\partial}{\partial q}$ has given a differential operator involving second derivatives when H is a quadratic form in the p's which is often the analogue of the Laplace operator. But this is not always so. A simple example is in the case of spherical polar coordinates for a particle of mass μ. Here the kinetic energy function is

$$T = \frac{1}{2\mu}\left(p_r{}^2 + \frac{p_\theta{}^2}{r^2} + \frac{p_\varphi{}^2}{r^2 \sin^2 \theta}\right),$$

so the corresponding operator would be

$$-\frac{1}{2\mu}\frac{h^2}{4\pi^2}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta . \partial \varphi^2}\right),$$

which is not the same as the Laplace operator gotten by transforming the previous wave equation directly from the Cartesian x, y, z, to the polar r, θ, φ.

This discrepancy has its origin in the fact that we are replacing p_r, say, by $\frac{h}{2\pi i}\frac{\partial}{\partial r}$, a thing which does not combine commutatively with r itself. In other words, the operation of multiplying ψ by r is not commutative with the operation $\frac{h}{2\pi i}\frac{\partial}{\partial r}$ acting on ψ. It is readily seen that the difference is simply

$$\frac{h}{2\pi i}\frac{\partial}{\partial r}(r\psi) - r\frac{h}{2\pi i}\frac{\partial}{\partial r}\psi = \frac{h}{2\pi i}\psi, \tag{3.3}$$

the rule which expresses the non-commutivity of the operation which passes for p in the wave equation and its associated q. The difficulty is that one did not need to pay attention to this in setting up the expression for T in the old theory in which p and q were interchangeable, and, therefore, the direct replacement may not come out right. But it is interesting to note that the quadratic form for T can always be written in such a way that this formal replacing process gives the correct Laplace operator. Thus, if T had been written

$$T = \frac{1}{2\mu}\left[\frac{1}{r^2}\, p_r r^2 p_r + \frac{1}{r^2 \sin \theta} p_\theta \sin \theta p_\theta + \frac{1}{r^2 \sin^2 \theta} p_\varphi{}^2\right],$$

the substitution would have given

$$-\frac{1}{2\mu}\frac{h^2}{4\pi^2}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial}{\theta \partial}\right) + \frac{1}{r^2 \sin^2 \theta}\frac{\partial^2}{\partial \varphi^2}\right],$$

which is the correct Laplace operator.

The rule thus loses its usefulness somewhat since, in general, one does not know how to rewrite the T-function in order to get the correct differential operator.

The complete rule now to be presented provides a convenient method for computing the generalized Laplace operator for any sort of coordinates. Suppose the Hamiltonian is $H(p, q)$. The wave equation is obtained by the following formal process: Let A be the determinant of the A_{ij} occurring in the expression for $T(q, p)$. Then one must demand of ψ that it minimize the integral

$$\int\left\{\frac{h^2}{4\pi^2}T\left(q, \frac{\partial\psi}{\partial q}\right) + V\psi^2\right\}\sqrt{A}\,dq_1dq_2 \cdots dq_f,$$

when one requires of ψ that

$$\int\psi^2A^{½}dq_1dq_2 \cdots dq_f = 1.$$

It is to be understood that in this equation each p^2 in $T(q, p)$ becomes $\left(\frac{h}{2\pi}\right)^2\left(\frac{\partial\psi}{\partial q}\right)^2$ and not $-\left(\frac{h}{2\pi}\right)^2\left(\frac{\partial^2\psi}{\partial q^2}\right)$, as in the previous equations, where p is replaced by the operator $\frac{h}{2\pi i}\frac{\partial}{\partial q}$. Both integrals are extended over all values of the q's which correspond to possible configurations. This variation problem requires that ψ satisfy the Eulerian differential equation,

$$\frac{h^2}{4\pi^2}\frac{1}{\sqrt{A}}\sum_i\frac{\partial}{\partial q_i}\left(\sqrt{A}\sum_k A_{ik}\frac{\partial\psi}{\partial q_k}\right) + (W - V)\psi = 0. \qquad (3.4)$$

This partial differential equation for ψ is the analogue, in the case of several independent variables, of the ordinary Eulerian differential equations.[1]

Numerous applications of the general method of setting up the wave equation will be treated in later sections so an example need not be given here.

To conclude, it is perhaps well to remark that the form of the wave equation is in no sense an inescapable conclusion from the argument that matter is associated with phase waves of wave length $h/\mu v$. Nevertheless the form here presented and the rule for finding the allowed energy levels have been extraordinarily

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[1] The discussion of such problems is given, for example, in Courant-Hilbert, pp. 171 and 194.

successful as will appear in Chaps. II and III. Therefore, the postulate has value for theoretical physics and will be adopted in what follows.

4. de Broglie's Phase Waves.—In getting at the rule just formulated for the energy levels, use was made of the idea that a sort of wave motion is associated with the moving particles such that its wave length is equal to Planck's constant divided by the momentum of the particle. The idea is due to L. de Broglie.[1] Concerning the nature of the waves little can be said.

One of the most elementary applications of the idea is to an alternative to the Bohr rule for picking out the circular orbits in hydrogen. Here it is supposed that these phase waves travel around in a circle in the same path as the electron. The allowed orbits are those which put an integral number of wave lengths into one revolution—in analogy with the fact that the allowed frequencies of vibration in a stretched string are those for which an integral number of half wave lengths is contained in the length of the string. The potential energy is $-\frac{e^2}{r}$, so in a state of energy W the kinetic energy is $\left(W + \frac{e^2}{r}\right)$. In the circular orbits, the centrifugal force balances the attraction, *i.e.*, $\mu\omega^2 r = e^2/r^2$. hence $\frac{1}{2}\mu\omega^2 r^2 = \frac{1}{2}e^2/r = T$. The wave length $\lambda = h/\sqrt{\mu e^2/r}$, and this must equal $1/n$th of the circumference $2\pi r$. This fixes the allowed radii at $r = n^2h^2/(2\pi)^2\mu e^2$, agreeing with the Bohr values and so gives the Bohr values for W.

Considering more complicated cases, de Broglie showed that the same requirement of an integral number of wave lengths in the orbit is a quite general interpretation of the quantum conditions, $\int p dq = nh$, as will appear later in the more detailed consideration of the Schrödinger wave equation.

The introduction of waves associated with matter completes the duality of the wave and particle viewpoint in quantum physics. For many years, it was thought that the simplest element of mechanical theory was the particle. In optics, the corresponding simple element was the plane monochromatic wave. In the early history of the quantum theory, a duality appeared in the form of the introduction of a discrete light quan-

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[1] DE BROGLIE, *Phil. Mag.*, **47**, 446 (1924); *Ann. de Phys.*, **3**, 22 (1925). DE BROGLIE and BRILLOUIN, "Selected Papers on Wave Mechanics," London (1928).

tum or particle on an equal footing with the extended light wave. This situation appeared to be intolerable and was followed by a program of attempts to understand the quantum as a composite of these plane waves. These attempts cannot be said to have had any success.

Matter wave theories do just the other thing. They recognize something basic in the particle-wave duality in light and seek to extend it to the mechanics of small particles. At the time of de Broglie's work, and for some time after, the understanding of this basic duality was wholly lacking. Recently, it has become clearer due to profound speculations of Heisenberg, Bohr, Dirac, and Jordan so that it will be possible greatly to improve the exposition of the theory by departing at once from the historical order and giving at once the meaning of the wave-particle duality as it is coming to be understood.

5. Inaccuracy of Empirical Knowledge.—To anyone who has ever made any measurements whatever, it is unnecessary to insist on the point that these are always affected by a certain inaccuracy or uncertainty. It is easy to determine experimentally that the length of your desk is more than 5 feet and less than 5 feet and 1 inch. To find out experimentally that the length is surely within much narrower limits is also not difficult. But there is a limit to the accuracy of the measurement which can be carried out and which therefore makes it impossible for me to assign an exact mathematical number which expresses how many times the unit of length is contained in the length of my desk.

Below the limit that is set merely by technical difficulties, another limit makes its appearance which has its origin in the nature of things. It is to this sort of uncertainty that we must now direct our attention, for it proves to be fundamental for quantum physics. In thinking about all physics, especially in connection with the problems of quantum theory, the operational point of view stressed by Bridgman[1] in his "The Logic of Modern Physics" is a most important aid. He emphasizes that in physics we should observe that "the concept is synonymous with the corresponding set of operations." Thus, "if the concept is physical, as of length, the operations are actual physical operations, namely, those by which length is measured . . . "

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[1] Bridgman, "The Logic of Modern Physics," The Macmillan Company (1927).

Discussing in more detail the measurement of length, it is clear that length on the ordinary macroscopic scale of experience is the set of operations involved in counting the number of times a stick of unit length need be laid end to end to traverse the length being measured. On a larger scale, say the astronomical, length becomes a quantity inferred from other lengths measured in the preceding way by the use of Euclidean geometry and measurements of certain angles of direction of light rays. From the operational standpoint, such a set of operations is quite different from the first one and so the concept is a different one. The two concepts may have many elements in common but we must not be surprised if their physical relationships are not identical.

Bridgman's discussion of the concept of small lengths forms an illuminating introduction to one of the important new results of quantum physics. He says:

> Down to the scale of microscopic dimensions a fairly straightforward extension of the ordinary measuring procedure is sufficient, as when we measure a length in a micrometer eyepiece of a microscope. This is, of course, a combination of tactual and optical measurements, and certain assumptions, justified as far as possible by experience, have to be made about the behavior of light beams. These assumptions are of a quite different character from those which give us concern on the astronomical scale, because here we meet difficulty from interference effects due to the finite scale of the structure of light, and are not concerned with a possible curvature of light beams in the long reaches of space . . . As the dimensions become smaller, certain difficulties become increasingly important that were negligible on a larger scale . . . About the time that we discover the necessity for a complete vacuum, we discover that the gauges themselves are atomic in structure, that they have no definite boundaries, and therefore no definite length, but that the length is a hazy thing, varying rapidly in time between certain limits . . . But as the dimensions get smaller continually the difficulties due to this haziness increase indefinitely in percentage effect, and we are eventually driven to give up altogether. We have made the discovery that there are essential physical limitations to the operations which defined the concept of length . . .
>
> What is the possible meaning of the statement that the diameter of an electron is 10^{-13} centimeters? Again the only answer is found by examining the operations by which the number 10^{-13} was obtained. This number came by solving certain equations derived from the field equations of electrodynamics, into which certain numerical data obtained by experiment had been substituted. The concept of length

has therefore now been so modified as to include that theory of electricity embodied in the field equations, and, most important, assumes the correctness of extending these equations from the dimensions in which they may be verified experimentally into a region in which their correctness is one of the most important and problematical of present-day questions in physics. To find whether the field equations are correct on a small scale, we must verify the relations demanded by the equations between the electric and magnetic forces and the space coordinates, to determine which involves measurement of lengths. But if these space coordinates cannot be given an independent meaning apart from the equations, not only is the attempted verification of the equations impossible, but the question itself is meaningless. If we stick to the concept of length by itself, we are landed in a vicious circle. As a matter of fact, the concept of length disappears as an independent thing, and fuses in a complicated way with other concepts, all of which are themselves altered thereby, with the result that the total number of concepts used in describing nature at this level is reduced in number. A precise analysis of the situation is difficult, and I suppose has never been attempted, but the general character of the situation is evident. Until at least a partial analysis is attempted, I do not see how any meaning can be attached to such questions as whether space is Euclidean in the small scale.

This sort of difficulty with the extension of ordinary concepts to the scale of atomic dimensions has been recognized for a long time but probably no critic has put it so clearly as Bridgman.

Another writer who has given us an excellent account of the importance of the unavoidable inaccuracy of empirical knowledge is Felix Klein[1] in the third volume of his "Elementarmathematik vom höheren Standpunkt aus." Klein is there concerned with the difference between the mathematics of precision, whose program is the exact deduction of consequences from logically independent postulates, and the mathematics of approximation, which is the only kind needed for practical applications. The failure to recognize this point is the commonest stumbling block of pure mathematicians in their studies in physics. Further, it may be said that the idea is usually so repulsive to them that its recognition sooner or later spoils their interest in natural science. Klein's discussion of the inference of a complete determinism from the laws of classical mechanics is especially good, so a review of it is introduced here.

[1] Klein, "Elementarmathematik vom Höheren Standpunkt aus," Vol. 3, Berlin (1924).

Analytic functions, that is, those whose Taylor's series converge in the neighborhood of a given point, have such important precise mathematical properties and have so many of the properties of *smoothness* which we instinctively desire for the functions in the laws of nature that it is a common idea that perhaps *in nature only analytic functions present themselves.* Such functions, through the process of analytic continuation, are known for all values of their argument when their values in any small range of the argument values are known.

Thus, the postulate that the laws of nature involve analytic functions leads at once to a complete mechanistic determinism for the world, for if every quantity of interest in nature is an analytic function of the time, its value at all future and past times is fully determined by those, for instance, during any particular second of time. Everyone knows how repellent to some minds is such a complete determinism. Therefore, for example, Boussinesq was led to try to escape the conclusion by supposing that the laws of nature are not given by analytic functions but are solutions of differential equations with analytic coefficients. This leads to an escape while still honoring the analytic functions with a high place, inasmuch as the solutions of such differential equations may branch into two curves. Which branch is to be followed is decided by a higher will of a biological or ethical nature and thus the loophole from determinism is provided.

The answer both to the complete determinism argument and Boussinesq's escape is evidently connected with the unavoidable inaccuracy of empirical knowledge. Natural science always deals with approximate data which can be fitted on in various ways to the subject matter of precise mathematics. Finally, "*Überhaupt bleibt es fraglich, ob das Wesen einer richtigen Naturerklärung auf präzisionsmathematiker Basis zu suchen ist, ob man je über eine geschickte Verwendung der Approximationsmathematik hinausgelangen kann.*" (It remains doubtful whether the essence of a correct explanation of nature is to be sought on the basis of precise mathematics, whether one can go above and beyond a skillful application of approximate mathematics.)

The trend taken by quantum physics has brought such questions more to the forefront than ever because it now appears that a great many of the difficulties in applying classical mechanics to quantum phenomena lay in a kind of naive overprecise application of these laws to nature. Quantum mechanics consists partly in the recognition of the nature of a limitation on the application of classical mechanics which appears now to be an actual failure of the methods of the old theory and not merely a failure of particular models for atomic phenomena.

6. The Quantum Uncertainty Principle.—This limitation asserts that no physical measurements are capable of providing information of unlimited precision about the simultaneous values of the position and momentum of a particle. All measurements of position in the x direction are affected by an error Δx and the simultaneous measurement of momentum is affected by an error Δp_x and in the most favorable case these are such that

$$\Delta x \cdot \Delta p_x \nless \frac{h}{4\pi}.$$

The same thing holds true for the simultaneous measurement of any two mechanical quantities which are conjugate to each other in the sense of the Hamiltonian theory of dynamics. This principle was first clearly enunciated by Heisenberg[1] although it was recognized as a fundamental characteristic of the new methods by Dirac[2] at almost the same time.

It was at first recognized in a more limited form, namely, that any physical experiment can, at most, determine with perfect accuracy but f independent quantities in a system of f degrees of freedom. The number needed to make the motion definite in the sense of the old mechanics is, of course, $2f$. The later formulation of the principle is that $2f$ quantities can be measured but there will always be an uncertainty in the measurements of a quantity and its conjugate given by the rule

$$\Delta p \cdot \Delta q \nless \frac{h}{4\pi}, \tag{6.1}$$

where p and q are conjugate momentum and coordinate.

This principle is to be understood in the spirit of the second law of thermodynamics: It is a generalization from physical experience and like all such it is to be abandoned if a single exception to it can be found. A clear example of the way in which coordinate and momentum are associated is furnished by a

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[1] HEISENBERG, *Zeits. für Phys.*, **43**, 172 (1927).

[2] DIRAC, *Proc.* Roy. Soc. 113A, 621 (1927).

proposed microscopical measurement of the sort discussed by Heisenberg and Bohr.

To measure the position (say in the x direction) of a particle, shine light on it and look at it in a microscope of semiaperture, ϵ. From our knowledge of the resolving power of a microscope, it is known that if λ is the wave length of the light, positions whose separation is as little as $\lambda/\sin\epsilon$ cannot be separated. This quantity measures the uncertainty of position. The corresponding uncertainty in momentum arises, as we know empirically, from the Compton effect. In scattering, the light behaves as if it carried momentum of amount h/λ. In order that the full aperture of the microscope can function, we have to admit the possibility that light can be scattered into any part of the whole objective. This means an admitted uncertainty in the direction of the scattering and an associated uncertainty in the amount of the momentum imparted to the particle. This uncertainty is clearly of the order of the extreme variation of the x-component of momentum of the scattered quantum which ranges between

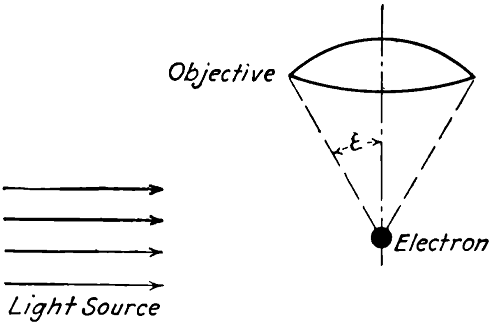

FIG. 1.—A gamma ray microscope.

$$\frac{h}{\lambda}(1 - \sin\epsilon) \text{ and } \frac{h}{\lambda}(1 + \sin\epsilon),$$

the range being $2h/\lambda \sin\epsilon$. The product of the uncertainty of measured position and measured momentum is thus

$$\frac{\lambda}{\sin\epsilon}\,\frac{2h}{\lambda}\sin\epsilon = 2h,$$

which is not less than $h/4\pi$ and is, in fact, in this ideal case, of the order of magnitude of h. Other concrete examples of this limitation will be discussed in later sections.

7. Wave Interference and the Uncertainty Principle.—We have now to examine the way in which the existence of the de Broglie waves for matter and the quantum-wave dualism in optics can be understood as a manifestation of the principle enunciated in the preceding section. The discussion of this fundamental relation is due to Bohr.[1] It shows how the interplay of wave

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[1] BOHR, *Nature*, **121**, 580 (1928).

and particle concepts has its origin in the uncertainty of physical measurements and how the mathematical formalism is an expression of this unavoidable uncertainty. In Secs. **3** and **4,** we have seen that the new rule for finding the allowed energy levels is in some way a manifestation of the fact that there is some sort of wave motion associated with a moving particle. With a moving free particle of energy E and momentum $\mathbf{p}$ is associated a plane wave of frequency ν and wave number $\boldsymbol{\sigma}$, the wave function being given by

$$\psi = Ae^{2\pi i(\nu t - \boldsymbol{\sigma}\cdot\mathbf{r})},$$

in which the connection of E and $\mathbf{p}$ with ν and $\boldsymbol{\sigma}$ is given by

$$\begin{aligned} E &= h\nu, \\ \mathbf{p} &= h\boldsymbol{\sigma}. \end{aligned} \tag{7.1}$$

For the moment, we do not specify the physical meaning of the quantity ψ nor just what is meant by the wave being "associated" with the particle. Concerning the plane wave just written down one observes that it has infinite extension in space and so seems to bear no relation whatever to a particle. But the simple wave expression has in it a definite value of σ corresponding to a definite value of the momentum. Here is a property of the wave which is consistent with one phase of the principle of uncertainty. It suggests itself that this wave is associated with a particle of which one knows with absolute precision its momentum. As a consequence, one knows nothing about its position. This is expressed by the infinite extension in space of the wave function.

Thus we take the standpoint that *such a plane wave is to be associated* not simply with a particle but *with a state of our knowledge about a particle,* the state of knowledge being exact information about momentum and complete lack of information about position. To carry through this view consistently naturally demands that one be able to represent by waves other intermediate states of knowledge about a particle. Thus it is possible to know the position with some uncertainty and to know the momentum with some uncertainty. The natural thing to take as the representative of knowledge that a particle is in a certain locality, is a wave function which has a value in that locality and is zero elsewhere.

Such a wave function can be constructed purely mathematically as the result of the superposition of waves having different wave lengths. Suppose one considers the resultant of a number of different plane waves all having somewhat different values of $\boldsymbol{\sigma}$. If they are added in such a way that they are in phase at a particular point, the resultant will have an appreciable value in the neighborhood of that point. But away from that point the phases will become quite different, resulting in destructive interference. The size of the space in which the resultant has appreciable value depends on the range of values of $\boldsymbol{\sigma}$ involved. Since σ is the number of waves in unit length. The distance Δx which one must go in order to get from the condition of being in phase to that of being out of phase is such that the difference in the number of waves of the two trains in the distance is one-half. If $\Delta\sigma_x$ is the difference of the x component of $\boldsymbol{\sigma}$ between two interfering waves, then this is the difference in the number of waves per unit length of the two trains. Then $\Delta\sigma_x \cdot \Delta x = \frac{1}{2}$ gives the distance Δx that it is necessary to go in order to pass from an in-phase to an out-of-phase condition.

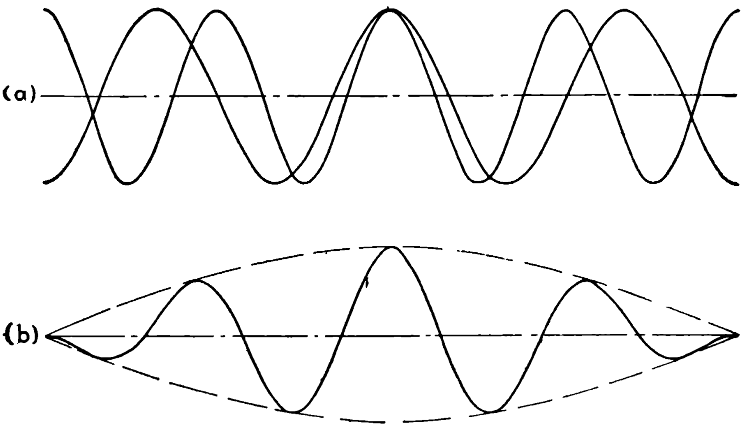

Fig. 2.—Wave interference. (*b*) is a portion of the wave train resulting from the superposition of the two wave trains shown in (*a*).

The same relations are true for $\Delta\sigma_y \Delta y$ and $\Delta\sigma_z\, \Delta z$, as expressing the range of values of $\boldsymbol{\sigma}$ which must enter into a wave composed of different plane waves in order to produce interference localized in a space of the approximate dimensions Δx, Δy, Δz. Thus, just out of the properties of wave interference, one sees that to build up a packet of waves which signifies a certain knowledge of position in space it is necessary to superpose waves of different values of $\boldsymbol{\sigma}$. Moreover in building a packet of small extension (small Δx, Δy and Δz) it is necessary to admit a large range in the wave-number values, $\Delta\sigma_x$, $\Delta\sigma_y$, $\Delta\sigma_z$.

This reciprocal connection between the size of the packet and the range in $\boldsymbol{\sigma}$ coupled with the mode of associating $\boldsymbol{p}$ and $\boldsymbol{\sigma}$

suggested by de Broglie is clearly just the behavior needed if the waves are to symbolize in the mathematics the physical principle of the finite precision of the measurements of position and momentum. For if we remove the idea of a particle, as such, from our thinking and substitute for it a packet of waves which represents not merely the particle but the state of knowledge about the particle, then there is no danger that the principle of uncertainty of measurements will be overlooked.

The mode of association between $\boldsymbol{\sigma}$ and $\mathbf{p}$ is clearly such a one that the condition

$$\Delta\sigma_x\Delta x = \tfrac{1}{2},$$

dictated by laws of wave interference leads exactly to

$$\Delta p_x \cdot \Delta x = h/2$$

on multiplying through by Planck's constant.

8. Dependence of the Wave Equation on the Time.—We have seen that the natural counterpart for the associative relation

$$\mathbf{p} = h\boldsymbol{\sigma}$$

is the relation $W = h\nu$, where W is the total energy of the associated classical motion. Since W plays the role of a constant of integration, it must not appear explicitly in the fundamental equations of the theory. In Sec. **3** the equation for the wave function's dependence on space coordinates was set up as

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}(W - V)\psi = 0$$

for the case of one particle of mass μ. If one supposes that the complete function contains a factor $e^{-2\pi i\nu t}$, where $W = h\nu$, then one can eliminate W from this equation by observing that

$$\frac{\partial\Psi}{\partial t} = -2\pi i\nu\Psi = -\frac{2\pi i}{h}W\Psi,$$

so that the equation with W eliminated becomes

$$\Delta\Psi - \frac{8\pi^2\mu}{h^2}V\Psi + \frac{4\pi i\mu}{h}\frac{\partial\Psi}{\partial t} = 0. \tag{8.1}$$

A striking thing about this equation, if it be regarded as fundamental for the wave function associated with a particle, is the explicit appearance in it of the imaginary unit i. Since in the physical interpretation of the results only real quantities can be involved, one sees that the conjugate complex function $\overline{\Psi}$ must be on a par with the function Ψ throughout the theory. The differential equation satisfied by $\overline{\Psi}$ is gotten by reversing the sign of i in the equation for Ψ:

$$\Delta\overline{\Psi} - \frac{8\pi^2\mu}{h^2}V\overline{\Psi} - \frac{4\pi i\mu}{h}\frac{\partial\overline{\Psi}}{\partial t} = 0.$$

Another point to be noticed is that the equation is not of the form of a wave equation and so one cannot expect the behavior of the Ψ function always to be like that of a wave amplitude. The ordinary wave equation in an inhomogeneous medium involves, besides the Laplacian, the *second* time derivative with a coefficient which is a function of position. Here one has, besides the Laplacian, the unknown function itself multiplied by a function of position, and the *first* time derivative with a constant imaginary coefficient.

There is another way of arriving at this result for the basic equation and that is by the consistent substitution of each p by $\frac{h}{2\pi i}\frac{\partial}{\partial q}$ where p and q are conjugated coordinate and momentum. In the Hamilton-Jacobi theory of dynamics, the negative energy W, and the time t satisfy all the relations demanded of conjugate canonical variables and so one should naturally replace W in the Hamilton-Jacobi equation by $-\frac{h}{2\pi i}\frac{\partial}{\partial t}$. If this be done, following the procedure of Sec. **3**, one obtains the same basic equation with the *first* time derivative as was obtained in this section by the simple device of eliminating W.

9. Particle in a Magnetic Field.—One can obtain a differential equation for the wave function associated with a charged particle in a magnetic field by the method of replacing the momenta by the corresponding $\frac{h}{2\pi i}\frac{\partial}{\partial q}$ in the classical Hamilton-Jacobi equation just as has been done in preceding sections. If a particle of charge e moves in an electric field $\boldsymbol{E}$ and a magnetic field $\boldsymbol{H}$ the force on it, according to classical electrodynamics is

$$\boldsymbol{F} = e\left(\boldsymbol{E} + \frac{1}{c}\boldsymbol{v}\times\boldsymbol{H}\right)$$

The problem is that of taking into account the second term in this expression in the Hamiltonian function for the particle.

This can be done in the following way. One supposes the potentials A and V of the field to be known so that

$$\boldsymbol{H} = \text{curl } A$$
$$\boldsymbol{E} = -\text{ grad } V - \frac{1}{c}\frac{\partial A}{\partial t}.$$

Then the Lagrangian equations of motion will correspond to the foregoing expression for the force if one uses the following form of the Lagrangian function

$$L = \frac{1}{2}\mu(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - e\left[V - \frac{1}{c}A \cdot v\right].$$

That the form gives the correct equations of motion is easily seen. For example, the equation for the x-coordinate becomes:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = 0,$$
$$\frac{\partial L}{\partial \dot{x}} = \mu\dot{x} + \frac{e}{c}A_x;$$
$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) = \mu\ddot{x} + \frac{e}{c}\left[\frac{\partial A_x}{\partial t} + \dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_x}{\partial y} + \dot{z}\frac{\partial A_x}{\partial z}\right];$$
$$\frac{\partial L}{\partial x} = -e\frac{\partial V}{\partial x} + \frac{e}{c}\left[\dot{x}\frac{\partial A_x}{\partial x} + \dot{y}\frac{\partial A_y}{\partial x} + \dot{z}\frac{\partial A_z}{\partial x}\right];$$

hence,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = \mu\ddot{x} + e\left(\frac{\partial V}{\partial x} + \frac{1}{c}\frac{\partial A_x}{\partial t}\right) + \frac{e}{c}\left[\dot{y}\text{ curl}_z A - \dot{z}\text{ curl}_y A\right]$$
$$= \mu\ddot{x} - eE_x - \frac{e}{c}(v \times \boldsymbol{H})_x.$$

Using this form for the Lagrangian function the momenta, defined as $p = \partial L/\partial \dot{q}$, become

$$p_x = \mu\dot{x} + \frac{e}{c}A_x.$$

. . .

The Hamiltonian function is

$$H = \dot{x}p_x + \dot{y}p_y + \dot{z}p_z - L,$$

when expressed as a function of the p's and x, y, z. Eliminating $\dot{x}$, $\dot{y}$, $\dot{z}$ from this form, one has

$$H = \frac{1}{2\mu}\left[\left(p_x - \frac{e}{c}A_x\right)^2 + \left(p_y - \frac{e}{c}A_y\right)^2 + \left(p_z - \frac{e}{c}A_z\right)^2\right] + eV.$$

The wave equation is now to be obtained formally by replacing each p by the corresponding $\frac{h}{2\pi i}\frac{\partial}{\partial q}$ as in preceding sections. Here some ambiguity comes in, however, since in expanding such a term as $\left(p_x - \frac{e}{c}A_x\right)^2$, one does not know whether to write the cross-product term as $2\frac{e}{c}p_xA_x$ or as $2\frac{e}{c}A_xp_x$. For the present, we shall assume that we know the correct order to be the latter so that the formal substitution for each p gives the following wave equation:

$$-\frac{h^2}{8\pi^2\mu}\Delta\Psi - \frac{eh}{2\pi\mu ic}A\cdot\text{grad }\Psi + \left(\frac{e^2A^2}{2\mu c^2} + eV\right)\Psi + \frac{h}{2\pi i}\frac{\partial\Psi}{\partial t} = 0.$$

9 .1)

The magnetic field thus manifests itself principally by the introduction of a term in grad Ψ and also through the small term $e^2A^2\cdot/2\mu c^2$.

Here again there is an explicit appearance of the imaginary unit i in the equation. The equation for the conjugate complex function $\overline{\Psi}$ is

$$-\frac{h^2}{8\pi^2\mu}\Delta\,\overline{\Psi} + \frac{eh}{2\pi i\mu c}\;A\cdot\text{grad }\overline{\Psi} + \left(\frac{e^2A^2}{2\mu c^2} + eV\right)\overline{\Psi} - \frac{h}{2\pi i}\frac{\partial\overline{\Psi}}{\partial t} = 0.$$

These equations suffice to give the theory of electronic motions when effects corresponding to the so-called "spin" of the electron are neglected.

10. The Charge and Current Expressions.—In Secs. **6** and **7**, it was seen how the interference properties of the waves associated with a particle expressed the limitation of the accuracy of definition of the concepts of position and momentum which is recognized as a law of physics in the uncertainty principle. From the standpoint there introduced, the definite statements of classical mechanics are now to be replaced by vaguer predictions as to probability of being in a certain locality. The wave function Ψ whose interference properties are consistent with the uncertainty principle must therefore be connected with the probability that a particle is in a certain region of space.

Any probability function must be everywhere positive and this in itself shows that Ψ itself cannot be used for this purpose. A natural suggestion is that Ψ^2 be used or, in case Ψ is a complex function, $\Psi\bar{\Psi}$. This expression fulfills all the requirements which such a probability function must meet, a statement which will receive numerous confirmations later. In particular, it will be shown later that this probability function for states of large quantum number agrees asymptotically with the relative probabilities of being at different parts of the classical orbit.

From the standpoint presented by Schrödinger in his original work on wave mechanics it was supposed that the electron was actually broken up when it was in the low quantum orbits. According to this view it no longer remained a particle of radius about 10^{-13} centimeters but became a volume distribution of electricity. This view requires either the giving up of the theory of electromagnetic mass, which fixes the size at 10^{-13} centimeters, or needs some kind of a modification of the electromagnetic equations which gives more inertia to a given charge density than does the present theory. In this view one regards the charge density of the distributed electron as actually proportional to $\Psi\bar{\Psi}$. On the probability view, the mean amount of charge in the volume element dv, *in the long run,* will be proportional to $\Psi\bar{\Psi}$, but that is different from Schrödinger's supposition. If $\Psi\bar{\Psi}$ is to function as the actual charge density distribution it is necessary to suppose that some other combination of the Ψ's will represent the electric current associated with the given motion. The chief guide for finding such a current expression is the requirement that the equation of continuity must be satisfied. If ρ is the charge density and $\boldsymbol{i}$ the current density, one must have,

$$\frac{\partial\rho}{\partial t} + \operatorname{div}\boldsymbol{i} = 0.$$

Such an expression can be derived as a consequence of the wave equation for one particle in a combined electric and magnetic field, as will now be seen. One writes down the equations satisfied by Ψ and $\bar{\Psi}$, as given in the preceding section. Multiply the one for Ψ by $\bar{\Psi}$ and the one for $\bar{\Psi}$ by Ψ and subtract. The result is

$$-\frac{h^2}{8\pi^2\mu}(\bar{\Psi}\Delta\Psi - \Psi\Delta\bar{\Psi}) + i\frac{eh}{2\pi\mu c}\boldsymbol{A}\cdot\operatorname{grad}(\Psi\bar{\Psi}) + i\frac{h}{2\pi}\frac{\partial(\Psi\bar{\Psi})}{\partial t} = 0.$$

Using the identity,

$$\bar{\Psi}\Delta\Psi - \Psi\Delta\bar{\Psi} \equiv \operatorname{div}(\bar{\Psi}\operatorname{grad}\Psi - \Psi\operatorname{grad}\bar{\Psi}),$$

and the relation

$$A\cdot \text{grad}\,(\Psi\overline{\Psi}) = \text{div}\,(A\Psi\overline{\Psi}) + \Psi\overline{\Psi}\frac{1}{c}\frac{\partial V}{\partial t},$$

the equation can be written,

$$\frac{\partial(e\Psi\overline{\Psi})}{\partial t} + \text{div}\left[\frac{eh}{4\mu\pi i}(\overline{\Psi}\,\text{grad}\,\Psi - \Psi\,\text{grad}\,\overline{\Psi}) - \frac{e^2}{\mu c}\,A\Psi\overline{\Psi}\right] - \frac{e^2}{\mu c^2}\frac{\partial V}{\partial t}\Psi\overline{\Psi} = 0.$$

If the last term can be neglected, because $\partial V/\partial t = 0$ or, in general, because it is small on account of the $1/c^2$ factor, then this is in the form of the equation of continuity. Supposing this term negligible, one sees that if there is any significance to the use of $(e\Psi\overline{\Psi})$ as charge density then the associated current distribution can be taken to be

$$\boldsymbol{i} = \frac{eh}{4\pi\mu i}(\overline{\Psi}\,\text{grad}\,\Psi - \Psi\,\text{grad}\,\overline{\Psi}) - \frac{e^2}{\mu c}A\,\Psi\overline{\Psi}. \qquad (10.1)$$

For the present it will be assumed *that in computing the external fields due to a moving charge, these expressions for charge and current density in terms of the wave functions are to be used.* It will turn out that this working rule will suffice to give some idea of the relative intensity of spectral lines emitted by atoms, of the magnetic moment of the atoms in the various stationary states, etc. But when such applications are made, it is to be understood that they are only provisional and to be regarded as an intermediate stage preceding the extension of quantum mechanical laws to the energy and momentum of the electromagnetic field itself.

Of course, when $\Psi\overline{\Psi}$ is to be used as probability it has to be so normalized, by choice of a constant multiplier for Ψ, that

$$\int \Psi\overline{\Psi}dv = 1,$$

where the integral extends over the entire range of all the coordinates, to express the fact that the system is certainly in some configuration. The same normalization is required from the distributed charge standpoint to express the fact that the total charge is e.

CHAPTER II

SIMPLE MECHANICAL PROBLEMS BY THE WAVE METHOD

The host of rather radical ideas which have been sketched in the last chapter will perhaps be clarified if the attention be now directed to the study of a number of important special cases by this method. Perhaps the most interesting feature of the wave equation is the way in which the requirement of finiteness and single valuedness can provide discrete energy levels in some cases and a continuous range in others. This chapter is, therefore, devoted to the discussion of a number of important simple mechanical problems by the wave method, especially to showing how the quantization of the energy comes about and to pointing out the connections between the wave functions and the orbits of classical mechanics.

11. General Mathematical Remarks.—Suppose a wave equation is given by the processes outlined in the preceding chapter and it is desired to find those values of the parameter W for which the equation possesses a solution which is everywhere finite and continuous. In addition, it is desired to find these finite and continuous solutions. There are some elements which all such problems have in common.[1]

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[1] For the general mathematical theory underlying the next two sections see:

COURANT-HILBERT, "Methoden der Mathematischen Physik," Chaps. II, V, VI and VII, Berlin (1924).

RIEMANN-WEBER, "Differentialgleichungen der Physik," Vol. I, Chaps. VII, VIII, and IX, Braunschweig (1925).

GOURSAT, "Mathematical Analysis," Vol. II, Part II, Chap. III, Ginn & Company (1917).

INCE, "Ordinary Differential Equations," Chaps. X and XI, Longmans, Green and Co. (1927).

SCHLESINGER, "Einführung in die Theorie der Gewöhnlichen Differentialgleichungen auf funktionentheoretischer Grundlage," Berlin (1922).

WHITTAKER and WATSON, "A Course of Modern Analysis," Cambridge (1920).

WATSON, G. N., "A Treatise on the Theory of Bessel Functions," Cambridge (1922).

If the mechanical system under discussion has more than one space coordinate or degree of freedom, then the wave equation is a partial differential equation. The only method which has been used in quantum mechanics for dealing exactly with the partial differential equations thus arising consists in reducing them to sets of equivalent ordinary linear differential equations. The process for doing this is known as "separation of variables," and is the same as that used in the treatment of the classical boundary value problems of physics which arise in the theory of heat conduction, diffusion, elasticity theory, and so forth. Although it is fairly well-known, some remarks on it may not be amiss here.

The process proceeds as follows: Suppose, for example, that there are three independent variables, x, y, and z. The assumption is made that the dependent variable ψ can be found in the form of a product of three functions, each of which depends on just one of these independent variables. The wave equation is entered with this hypothesis and one attempts to impose conditions on each of the factors by requiring each of them to satisfy a linear differential equation in such a way that if they do, then the wave equation itself will be satisfied by their product. Many examples of this process will be found in this chapter. It should be observed that the property of separation of variables is a property of a particular coordinate system. No rule is known for testing a given wave equation as to whether there exists a set of coordinates which permit separation of the variables. Nor is there any sure way of finding the correct variables even when they do exist. Usually, the variables which "separate" have a suggestive relationship to the geometry and symmetry of the problem. Thus, central-force field problems, Sec. **14**, separate in spherical polar coordinates as is suggested by the spherical symmetry. The problem of the single particle under the motion of two fixed centers of Coulomb force separates in elliptic coordinates whose foci are the two fixed centers. Some problems separate in several quite different coordinate systems. Thus, the problem of a spacially symmetric harmonic oscillator separates not only in spherical polar coordinates, but also in ordinary rectangular coordinates. The equation for the hydrogen atom (Sec. **19**) separates in parabolic coordinates as well as in spherical polar coordinates, but not in rectangular coordinates. For the helium-atom problem, no coordinates are known which allow a separation of variables.

Having applied the method of separation of variables, one is then confronted with several ordinary linear differential equations of the second order. The type form is the following:

$$\frac{d^2y}{dx^2} + f_1(x)\frac{dy}{dx} + [Ef_2(x) + f_3(x)]y = 0.$$

The variable x ranges between certain values conditioned by the geometry of the problem. For instance, if it is an ordinary linear coordinate, its range is from $-\infty$ to $+\infty$, while if it is $\cos\theta$ where θ is the colatitude of a spherical polar coordinate system, then its range is from -1 to $+1$. The problem is to find the values of the parameter E for which a solution $y(x)$ exists which is finite and continuous in the specified range of values of x.

The ordinary theory of differential equations, as given in elementary courses, is concerned mostly with the finding of a solution in the neighborhood of a given point. The usual form is that of a power series expansion around the point. What is here required is a form of solution which will enable one to determine whether y remains finite throughout the whole range of values of x. For this purpose it is desirable to have a closed expression for the solution, for example, to have the solution in the form of a definite integral. The power-series method is a good one for gaining an insight with regard to some features of the problem, even though it has not proven to be a very valuable tool in the actual solution of the problems of wave mechanics.

In the neighborhood of any point, say x_0, there are two linearly independent solutions of a linear differential equation of the second order. The general solution is then representable in terms of two such linearly independent solutions as follows:

$$y = c_1y_1(x) + c_2y_2(x).$$

Two linearly independent solutions, $y_1(x)$ and $y_2(x)$, are said to form a fundamental system. Clearly, a necessary condition that two solutions form a fundamental system is contained in the negation,

$$y_1(x)y_2'(x) - y_2(x)y_1'(x) \neq 0.$$

Thus, the problem of finding the general solution consists in finding a fundamental system of solutions. The problem is somewhat simplified by the fact that when one solution is known, another forming with it a fundamental system may be found by quadratures. Suppose $y_1(x)$ is known, then it is easy to show that $y_2(x)$ satisfies this linear differential equation of the first order,

$$y_2(x)y_1'(x) - y_1(x)y_2'(x) = ce^{-\int_{x_0}^{x} f_1(x)dx}$$

and, therefore, may be obtained by quadratures. It is interesting also to note that the differential equation by means of which y_2 is obtained from y_1 does not involve the energy parameter E.

For the problem of finding which solutions remain finite everywhere, it is helpful to know that the solution of a differential equation is finite wherever the coefficients $f_1(x)$ and $Ef_2(x) + f_3(x)$ remain finite. Usually these become infinite in only two or three places, so that if a given solution remains finite at these places, assurance is given that it is finite everywhere. Any point at which the two coefficients in question are finite is called an "ordinary" point of the equation. Other points are called "singular."

Singular points themselves are conveniently divided into two classes—regular (Punkte der Bestimmtheit) and irregular (Punkte der Unbestimmtheit). The former are those in which $f_1(x)$ and $Ef_2(x) + f_3(x)$, although they become infinite, do so in such a way as to possess poles of at most the first and second order, respectively. It is important to notice that the value $x = \infty$ is often a singular point. The rule for deciding on this is to transform to a new independent variable $z = 1/x$ and investigate the new equation to see if $z = 0$ is a singular point for it. The importance of the classification of singular points into regular and irregular lies in the fact that in the series expansion of the general solution in the neighborhood of the regular point, say x_0, only a finite number of negative powers of $(x - x_0)$ occurs. For an irregular point an infinite number of negative powers occurs, that is, this point is an essential singularity for the general solution.

From function theory, it is known that the power-series expansion of any function converges in a circle in the complex plane of the independent variable extending from the center of the development out to the nearest singularity of the function. Unfortunately, however, it may not converge right at the other singular point and that causes a good deal of difficulty in obtaining the energy levels for a quantum mechanical problem.

With these facts in mind, it is now possible to make some remarks which bear more specifically on the solution of the wave equation. Suppose, for example, that the equation has two regular singularities, at $x = -1$ and at $x = +1$, and that it is desired to find values of E, if any, for which a solution exists that is finite at both of these. An attempt to solve the equation formally, first by means of a power series around $x = +1$, *i.e.*, in powers of $x - 1$, will give two series forming a fundamental system. It may be that both of these become infinite for $x = 1$, and for all values of E. In this case, there are no allowed values of E. Or it may happen that for any value of E, one of these is finite at $x = +1$ while the other becomes infinite. The determination of a power series around $x = -1$ is then to be carried out. Suppose that here, too, it is found that one of the series remains finite at $x = -1$ while the other becomes infinite.

Consider now the solution which is finite at $x = -1$. It is known that this can be expressed as a linear combination of the two solutions valid around $x = +1$. That is, it is known that such a mode of expression is possible. Unfortunately, however, there seems to be no simple way of finding the relation in specific examples. Let the solution finite at $x = -1$ be denoted by $y_1(E, x)$ because it depends on E parametrically. Similarly, let the two solutions at $x = +1$ be denoted by $z_1(E, x)$ and $z_2(E, x)$, the first being the one that remains finite at $x = +1$, while the other becomes infinite, then the general relation is

$$y_1(E, x) \equiv c_1(E)z_1(E, x) + c_2(E)z_2(E, x),$$

as an identity in x. The trouble is that there is no practicable general way of finding the functions $c_1(E)$ and $c_2(E)$. But if they were known, then clearly the energy levels would be the roots of the equation

$$c_2(E) = 0,$$

this being the condition which insures that the solution which remained finite at $x = -1$ will also do so at $x = +1$.

Even though the method just sketched has little practical value in the absence of a good way to find the function $c_2(E)$, it is nevertheless useful in showing how different possibilities may arise. For instance, suppose that it so happened that both $z_1(E, x)$ and $z_2(E, x)$ remained finite at $x = +1$. Then it would not matter what linear combination of them $y_1(E, x)$ was, with the result that E would be unrestricted, that is, a continuous spectrum of energy levels would present itself. This is exactly the case that occurs in dealing with the radial equation for hydrogen-like atoms. Here the singular points are at $r = 0$ and at $r = \infty$. For negative values of E it will be seen that only one of the fundamental solutions remains finite at $r = \infty$. For positive values of E both of them remain finite at $r = \infty$. On the other hand, for $r = 0$ only one of the solutions is finite for all values of E. Hence, by the argument of the foregoing paragraphs, it follows that the positive energy levels will form a continuous spectrum while the negative ones are discrete.

In the case of one-dimensional problems where the range of the independent variable x is symmetric about the origin, a little more can be said about the behavior of the wave function.

Change the independent variable so that its upper and lower bounds are plus and minus infinity. When x is positive, the Schrödinger equation can have two independent solutions $f_+(x, W)$ and $g_+(x, W)$, and when x is negative, the two solutions will be $f_-(x, W)$ and $g_-(x, W)$. If W is greater than V at both upper and lower bounds of x, then all four solutions will be finite and W can have any value. But if W is less than V at both bounds of x, only one of each of these pairs will be finite. Suppose f_+ is finite from $x = \infty$ to $x = 0$ and f_- is finite from $x = -\infty$ to $x = 0$.

Then

$$\Psi = \begin{cases} A_+f_+(x, W) & (0 \le x \le \infty) \\ A_-f_-(x, W) & (0 \ge x \ge \infty) \end{cases}$$

where A_+ and A_- are constants whose values are such that Ψ and its derivatives are continuous at $x = 0$. That is,

$$A_+f_+(0, W) - A_-f_-(0, W) = 0$$
$$A_+f_+'(0, W) - A_-f_-'(0, W) = 0$$

where the primes indicate differentiation with respect to x.

In order that these two equations for the A's be satisfied, the determinant

$$\begin{vmatrix} f_+(0, W) & f_-(0, W) \\ f_+'(0, W) & f_-'(0, W) \end{vmatrix} = 0,$$

which gives an equation whose roots are the allowed values of W. It is difficult to say, in general, just what roots this equation would have, whether the roots would be finite or infinite in number. It seems probable that unless f_+ and f_- were independent of x, these roots would be discrete; and also it seems that for most of the wave functions which are of importance in wave mechanics the number of roots is infinite.

When the potential energy V is symmetrical about the origin [*i.e.*, $V(x) = V(-x)$] then $f_-(-x)$ can be set equal to $f_+(x)$ by reason of this symmetry. Then of course $f_-'(-x) = -f_+'(x)$. In this case the only possible solutions of the equations for the A's are that $A_+ = A_-$ or that $A_+ = -A_-$. In the first case, the wave function is even about the origin

$$[\Psi(x, W) = \Psi(x, W); \Psi'(x, W) = -\Psi'(-x, W); \Psi'(0, W) = 0]$$

and the resulting equation, $\Psi'(0, W) = 0$, has a set of discrete roots for W. In the second case, the function is odd

$$[\Psi(x, W) = -\Psi(-x, W); \Psi'(x, W) = \Psi'(-x, W); \Psi(0, W) = 0]$$

and the equation,

$$\Psi(0, W) = 0,$$

gives the energy levels. These even and odd solutions occur alternately as W is allowed to take on successively its allowed values.

12. Orthogonal Functions.—The wave functions occurring to characterize the different quantum states form sets of orthogonal functions in the sense in which this term is used in the theory of Fourier analysis. This property is of fundamental importance for the theory.

The designation, orthogonal, is based on a far-reaching analogy with simple coordinate geometry and vector analysis. A function $f(x)$ in a certain interval is a quantity of infinitely many values, namely, one for each of the infinitely many values of x. This can be spoken of in geometric language by speaking of a function space of infinitely many dimensions and, saying, that each function is a vector in this space which needs then to be specified by infinitely many components. In order to make anything more out of this analogy, what is meant by the components of a function must be understood.

Components, in analogy with ordinary geometry, imply a coordinate system, the fundamental relation being that a vector r can be represented as a sum of its components multiplied by the unit vectors. In the function space the set of unit vectors defining a coordinate system must themselves be functions. Thus, any expansion of a function in a series of other functions may be looked upon as a representation of a function in terms of its components multiplied by the basis vectors defining a coordinate system.

Thus let the interval be $0 \leqslant x \leqslant 2\pi$.

If

$$f(x) = \tfrac{1}{2}A_0 + A_1 \cos x + A_2 \cos 2x + \cdots \\ + B_1 \sin x + B_2 \cos 2x + \cdots$$

is written, this equation can be regarded as the expression of the function $f(x)$ in terms of the coordinate functions $\frac{1}{2}$, $\cos x$, $\sin x$, $\cos 2x \ldots$; the components being A_0, A_1, B_1, $A_2 \ldots$ In vector analysis, each component of a vector is equal to the scalar product of the vector with the corresponding unit vector of the coordinate system. The analogous expression here is the equation determining the coefficients,

$$A_n = \int_0^{2\pi} f(x) \cos nx dx,$$

which suggests that the scalar product of two functions $f(x)$ and $g(x)$ should be defined by the equation

$$f \cdot g = \int f(x)g(x)dx,$$

the integration being extended over the fundamental region. With this definition the natural criterion for *orthogonality* of two functions is that their scalar product shall vanish.

$$\int f(x)g(x)dx = 0$$

is the condition that $f(x)$ and $g(x)$ be orthogonal functions. Similarly, the length of a function would naturally be defined as the square root of its scalar product with itself, *i.e.*,

$$|f|^2 = \int f(x)f(x)dx.$$

A function is said to be a unit function, if its length, so defined, is equal to unity. Any function when divided by its length is a unit function, and if this has been done, the function is said to have been normalized.

Thus, the analogy of an expansion like the Fourier expansion is made complete, for it is the important characteristic of the sines and cosines of multiples of x that they form an orthogonal function system in the interval $0 \leqslant x \leqslant 2\pi$.

There are many other orthogonal function systems known to mathematics, many of which will be encountered in this chapter as the wave functions associated with mechanical problems.

It is important to notice that in basing the discussion on the Fourier series there was a limitation on the set of unit functions to being, although infinite in number, nevertheless denumerable. That is, it was possible to set the unit functions in one-to-one correspondence with the integers. But this seeming limitation is not a real one. In the case of the Fourier integral the set of functions is cos νx and sin νx where ν is not restricted to integral values but takes on all values in the continuous range $0 < \nu < \infty$. The Fourier integral, which expresses a function as

$$f(x) = \int_0^\infty [A(\nu) \cos \nu x + B(\nu) \sin \nu x]\, d\nu,$$

is thus the analogue of the Fourier series where the functions of the basic coordinate system are the infinite and *non-denumerable* set of orthogonal functions sin νx and cos νx.

An interesting case of a non-denumerable set of orthogonal functions will now be discussed which will pave the way for some of the more elaborate developments of quantum mechanics. Let $\delta(x - \nu)$ be defined as a function which is zero if $x \neq \nu$ and is infinite for $x = \nu$ to such a degree that

$$\int \delta(x - \nu) dx = 1,$$

where the integration extends from $x < \nu$ to $x > \nu$. (The exact limits, of course, do not matter.) It is clear that two functions $\delta(x - \nu)$ for different values of ν will be orthogonal, for the integrand in $\int \delta(x - \nu_1)\delta(x - \nu_2)dx$ will be everywhere zero. Now evidently the value of

$$\int f(\nu)\delta(x - \nu)\, d\nu$$

will be simply $f(x)$ if $f(x)$ is continuous, for the integrand will vanish everywhere except at $\nu = x$ and here it will suffice to replace $f(\nu)$ by its value at $\nu = x$ and take $f(x)$ out from under the integral sign. In other words, $f(\nu)$ gives the components of $f(x)$ in regard to the non-denumerable orthogonal function system $\delta(x - \nu)$.

This fact perhaps makes appropriate some remarks on the nature of a function. (Mathematicians will probably find them rather naive, but to the writers as physicists these ideas have been helpful.) A function of x is an assemblage of values each one associated with a definite value of x. From the function space standpoint each function is a vector in a space of infinitely many dimensions. The function is then to be regarded, *funda-*

mentally, as this vector which is capable of representation in terms of its components in regard to a large variety of different coordinate systems (*i.e.*, sets of coordinate functions). This general concept of the function *as a vector* is denoted by the usual symbol $f(x)$. This is an extension of meaning of the symbol $f(x)$ which usually means just the ensemble of values of the function associated with each value of x. The function in the larger sense is then the ensemble of its components relative to *any* set of coordinate functions. The usual sense which regards it as the set of values associated with each value of x, places undue emphasis on the resolution of the function into components with regard to the particular functional coordinate system formed by the $\delta(x - \nu)$ for various ν.

This viewpoint, in turn, leads to a more general view of the definition of the scalar product of two functions. In vector analysis the scalar product is the sum of the products of corresponding components, quite independently of the particular coordinate system employed. It is now seen that the definition

$$\int f(x)g(x)dx, \text{ or better } \int f(\nu)g(\nu)d\nu$$

is simply the sum of the products of corresponding components $f(\nu)$ and $g(\nu)$ of the functions $f(x)$ and $g(x)$ when represented in the $\delta(x - \nu)$ system of orthogonal functions. The more general definition is, if $A_f(\nu)$ represents the components of f, and $A_g(\nu)$, those of g in any coordinate system,

$$\sum_\nu A_f(\nu) \cdot A_g(\nu)$$

where the sign Σ means summation, if the values of ν are denumerable, and integration, if the values of ν are non-denumerable.

Finally, it may be mentioned that sets of orthogonal functions present themselves which include a set of denumerable functions and a set of non-denumerable functions in the complete system. By a complete system is meant a system such that there does not exist any function that is orthogonal to every member of the system.

To show that the various wave functions of a specific Schrödinger equation are orthogonal to each other, set down the equations for two of them

$$\Delta\psi_i + K^2(W_i - V)\psi_i = 0.$$
$$\Delta\bar{\psi}_j + K^2(W_j - V)\bar{\psi}_j = 0.$$

Multiply the first by $\bar{\psi}_j$ and the second by ψ_i and subtract.

$$\bar{\psi}_j\Delta\psi_i - \psi_i\Delta\bar{\psi}_j = K^2(W_j - W_i)\psi_i\bar{\psi}_j.$$

Integrate both sides throughout a sphere

$$\int\!\!\int\!\!\int(\bar{\psi}_j\Delta\psi_i - \psi_i\Delta\bar{\psi}_j)dv = K^2(W_j - W_i)\int\!\!\int\!\!\int\psi_i\bar{\psi}_j dv.$$

But the left side of the equation is, by Green's theorem, equal to a surface integral.

$$\int\!\!\int(\bar{\psi}_j \operatorname{grad} \psi_i - \psi_i \operatorname{grad} \bar{\psi}_j)_n ds = K^2(W_j - W_i) \int\!\!\int\!\!\int\psi_i\bar{\psi}_j dv \tag{12.1}$$

where the integral is taken over the surface of the sphere.

Now increase the radius of the sphere to infinity. At infinity the wave function can be expressed by a series of the type $\psi = F(\theta, \phi)\sum_{n=1}^{\infty}(C + a_n r^n + b_n/r^n)$, where r is the distance from the origin and θ and ϕ are the angles which r makes with some axes. In order that ψ be finite at $r = \infty$, the a's must be zero, and in order that $\int\!\!\int\!\!\int\psi_i\bar{\psi}_i dv$ be unity, C must equal zero. Since the normal component of the gradient over the sphere is $\partial\psi/\partial r$, the first term in the series for the product $\psi \operatorname{grad}_n \psi$ is proportional to $1/r^3$. The area of the sphere is proportional to r^2, and so the first term in the series representing the left-hand integral will be proportional to $1/r$. Therefore, at infinity this integral will always be zero.

This means that

$$\int\!\!\int\!\!\int\psi_i\bar{\psi}_j dv = 0 \quad (W_i \neq W_j)$$

when the integral is taken over all space. If $i = j$, then $(W_j - W_i) = 0$ and the volume integral can have a finite value. This shows that the wave functions are orthogonal.

Since in Sec. **10** we have shown that $\int\!\!\int\!\!\int\psi_i\bar{\psi}_i dv = 1$, the arbitrary constant multiplier which occurs in ψ must be adjusted so that this is satisfied. ψ_i should thus be written, in general, as

$$\psi_i = \frac{F_i}{\sqrt{\int\!\!\int\!\!\int F_i\bar{F}_i dv}}$$

where F_i is a finite solution of the Schrödinger equation for the energy level W_i. In the case where $\int\!\!\int\!\!\int F_i\bar{F}_i dv$ is a product of several separable integrals $\int X_i dx \int Y_i dy \int Z_i dz$, each of which include but one coordinate, F_i is also separable into factors

$\Xi_i(x)$, $H_i(y)$, $\Omega_i(z)$. The wave function will then be most conveniently written as

$$\psi_i = \frac{\Xi_i}{\sqrt{\int X_i dx}} \cdot \frac{H_i}{\sqrt{\int Y_i dy}} \cdot \frac{\Omega_i}{\sqrt{\int Z_i dz}} \tag{12.2}$$

and the wave functions dealt with in this chapter will be thus "normalized" wherever possible.

13. The Free Particle.—By a free particle is meant one for which the potential energy is quite independent of position. It may therefore be set equal to zero everywhere so that the wave equation becomes

$$\Delta\psi + \frac{8\pi^2\mu}{h^2} W\psi = 0. \tag{13.1}$$

If the particle is quite free to move anywhere, the boundary condition on ψ is simply that ψ be finite everywhere in space. The equation is one for which the variables are separable in many coordinate systems. For instance, in ordinary rectangular coordinates, x, y, z, one has on writing $\psi = X(x)Y(y)Z(z)$ where X, Y, Z are functions of their respective coordinates alone,

$$\left(\frac{1}{X} X'' + \frac{8\pi^2\mu}{h^2} W_x\right) + \left(\frac{1}{Y} Y'' + \frac{8\pi^2\mu}{h^2} W_y\right) + \left(\frac{1}{Z} Z'' + \frac{8\pi^2\mu}{h^2} W_z\right) = 0.$$

Each term in parenthesis may be separately set equal to zero, the process yielding three ordinary differential equations of the form,

$$X'' + \frac{8\pi^2\mu}{h^2} W_x \cdot X = 0,$$

of which the solutions are

$$X = e^{\pm 2\pi i x \sigma_x} \text{ with } \sigma_x = \frac{\sqrt{2\mu W_x}}{h} \tag{13.2}$$

and similarly for the factors depending on y and z.

If W_x were negative then the wave number σ_x would be imaginary, making the solution be the exponential function of a real coefficient times x. But this would become infinite for either $x = +\infty$ or $x = -\infty$; therefore, negative values of W are inadmissible. For any positive value of W_x the exponential function has an imaginary argument, and is finite for all real values of x. Therefore, any positive value of W_x is allowed. Similarly, any positive value of W_y and W_z is allowed.

Thus, the characteristic functions and energy levels of the free particle are

$$\psi = X \cdot Y \cdot Z = e^{\pm 2\pi i \sigma_x x} \quad e^{\pm 2\pi i \sigma_y y} \quad e^{\pm 2\pi i \sigma_z z},$$
$$W = W_x + W_y + W_z,$$

where σ_y and σ_z are defined in terms of W_y and W_z just as σ_x is defined in terms of W_x. The complete characteristic function with the time factor can be written as the product of three factors, each of the form,

$$e^{2\pi i\left(\pm\sigma_x x - \frac{W_x t}{h}\right)} \cdot e^{2\pi i\left(\pm\sigma_y y - \frac{W_y t}{h}\right)} \cdot e^{2\pi i\left(\pm\sigma_z z - \frac{W_z t}{h}\right)}.$$

Such a factor clearly corresponds to a progressive wave moving from left to right when the plus sign is taken and from right to left when the minus sign is taken. The phase velocity of the waves is simply

$$\frac{W_x}{h\sigma_x} = \sqrt{\frac{W_x}{2\mu}} = \frac{v_x}{2}$$

where v_x is the velocity of a particle according to the classical mechanics whose energy of translation along the x coordinate is equal to W_x.

The characteristic functions here found are to be regarded as the representative of a beam of electrons moving in a single direction. They correspond to a stream of particles whose components of momentum in the x, y and z directions are, respectively,

$$\sqrt{2\mu W_x}, \quad \sqrt{2\mu W_y}, \quad \sqrt{2\mu W_z}.$$

Problems

1. Using the ideas of Sec. **10** compute the space distribution of charge and current density associated with the foregoing characteristic functions. Show that the forms sin $2\pi\sigma_x x$ and cos $2\pi\sigma_x x$ are solutions for the free particle, but that the current is zero for these forms. Hence they must represent two streams of equal flow in opposite directions, and are, therefore, not as simple physically as the exponential forms.

2. Set up and solve the wave equation for free particles whose motion is described in cylindrical coordinates, and in spherical polar coordinates, instead of in rectangular coordinates.

3. Compute the charge and current-density expressions associated with the characteristic functions of Problem **2**, and discuss their physical meaning.

Although the absolutely free particle is not quantized, in the sense that the energy levels form a continuous set, quantization may occur if the particle is not entirely free but is constrained to remain in a box. Thus suppose the particle must stay in the box specified by the ranges of coordinates,

$$0 \leqslant x \leqslant a, \quad 0 \leqslant y \leqslant b, \quad 0 \leqslant z \leqslant c$$

The question arises, how are these boundary conditions to be made effective? The particle must remain in the box. That means that the expressions for charge and current density must vanish outside the box. This can be effected by making ψ vanish at the walls of the box and setting it equal to zero outside. If ψ represents a probability of being in a certain coordinate range, then if the walls are really impenetrable, the probability of being outside the box must vanish; therefore, ψ must vanish outside the box.

The problem of finding which values of the energy are allowed and the associated characteristic functions is now exactly like the problem of finding the possible standing acoustic waves in a rectangular box and is, therefore, well known to classical mathematical physics. The details need not be given here, the result being,

$$W = \frac{h^2}{8\pi^2\mu}\left[\left(\frac{n_1}{a}\right)^2 + \left(\frac{n_2}{b}\right)^2 + \left(\frac{n_3}{c}\right)^2\right] \qquad (n_1,\ n_2,\ n_3,\ \text{integers})$$

for the energy levels, the associated characteristic function being,

$$\psi = \sin\frac{2\pi n_1 x}{a}\sin\frac{2\pi n_2 y}{b}\sin\frac{2\pi n_3 z}{c}.$$

This result is one of importance for the theory of the monatomic gas.

Problems

4. Discuss the quantization of the motion of a free particle constrained to remain in a cylindrical enclosure and in a spherical enclosure, using the results of Problem **2** of this section.

5. Find the expressions for charge and current density associated with these quantized problems. Why does the current vanish for the rectangular box, but not, necessarily, for the cylindrical and spherical enclosures?

14. The Freely Falling Particle.—Next in simplicity to the free particle, is the case of the particle moving under the influence of a constant force.[1] The force being constant, the potential energy is a linear function of the rectangular coordinates x, y,

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[1] Breit, *Phys. Rev.*, **32**, 273 (1928).

and z. If the x-axis is chosen in the direction of the force, then the potential energy is given by $V = -kx$. The wave equation separates immediately giving for the $Y(y)$ and $Z(z)$ factors the same differential equation as in the case of the free particle. For the $X(x)$ factor the equation is,

$$X'' + \frac{8\pi^2\mu}{h^2}(W_x + kx)X = 0. \tag{14.1}$$

Suppose that W_x is an allowed energy level and that $\psi_0(x)$ is the corresponding characteristic function. If the coordinate origin is shifted, by writing $x = x' - x_0$, the equation becomes,

$$X'' + \frac{8\pi^2\mu}{h^2}(\overline{W_x - kx_0} + kx')X = 0.$$

Since this is of the same form as the preceding, it may be concluded that if any value of W is allowed, then every other value, positive or negative, is allowed, and that the associated characteristic functions differ only by a shift of origin. Therefore, the equation may be conveniently investigated for the case $W = 0$. By showing that this is an allowed value, it will follow that any value of W is allowed; giving a continuous spectrum quite in accord with expectations.

The solution of equation (14.1), with $W = 0$, is known to be,

$$X(x) = \sqrt{\frac{x}{a}}\, J_{1/3}\left[\left(\frac{x}{a}\right)^{3/2}\right] \tag{14.2}$$

in which

$$a = \sqrt[3]{\frac{9h^2}{32\pi^2\mu k}}$$

and in which $J_{1/3}(z)$ is the Bessel function of order one-third.[1]

It is of interest to examine the behavior of this function and to note the relation of its behavior to what one would expect in analogy with classical mechanics. The corresponding classical motion is one in which the particle comes from $x = +\infty$ to $x = 0$ and then turns and goes back to $x = +\infty$ according to the law, $x = \frac{1}{2}\frac{k}{\mu}(t - t_0)^2$, where t_0 is the time of being at the origin. As t_0 plays the rôle of an indeterminate phase constant,

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[1] G. N. Watson's treatise on Bessel functions, p. 189.

the quantum mechanical solution might be expected to represent the average condition of a stream of particles executing such a motion, but with all different phases of the motion equally likely.

Hence, for negative values of x the characteristic function should approach zero rapidly, for the particles, behaving almost classically, will not be found much beyond the classical limit of their motion. For positive values of x, it should start to oscillate, with the spacing between zeros at first being of the order of magnitude of a and gradually becoming less and less, for as the particle goes faster its de Broglie wave length will decrease. Moreover, the amplitude of the approximately sinusoidal oscillations should decrease, as x continues to increase to large values. The approach of the amplitude of ψ to zero should approximate to the way in which $x^{-1/4}$ approaches zero for large x. This is inferred from the fact that ψ^2 is to measure the probability of being at x, and this will classically vary inversely as the velocity of the motion at that point and, hence, as $x^{-1/2}$ from the elementary theory of the falling body.

These expectations are seen to be true by applying known results from the theory of Bessel functions. For large values of x, the Bessel function, $J_p(x)$, is given by the asymptotic formula,

$$J_p(x) \sim \sqrt{\frac{2}{\pi x}}\left[\cos\left(x - \frac{2p+1}{4}\pi\right) - \frac{4p^2-1}{8x}\sin\left(x - \frac{2p+1}{4}\pi\right) + \cdots\right]$$

so that for very large values of x only the first term need be considered. Around $x = 0$ the function is given by,

$$J_p(x) = \left(\frac{x}{2}\right)^p \sum_{\nu=0}^{\infty} \left(\frac{ix}{2}\right)^{2\nu} \frac{1}{\nu!\,\Gamma(p+\nu+1)}.$$

For large imaginary values of the argument, one has the asymptotic formula

$$J_p(ix) = \frac{i^p e^x}{\sqrt{2\pi x}}\left(1 - \frac{4p^2-1}{8x} \cdots\cdots\right).$$

By means of these formulas, the reader may readily verify that the characteristic function has all of the properties which one expects it to have by reasoning from the nature of the associated classical motion. Figure 3 is a plot of the function $[\sqrt{x}\,J_{1/3}(x^{3/2})]$, and its square over the most interesting part of the range of the independent variable.

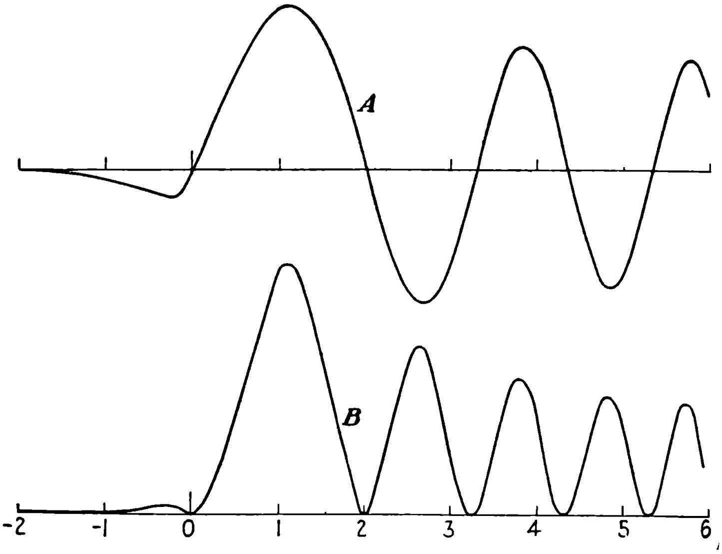

FIG. 3.—Curve A represents $X(x)$. Curve B represents $X^2(x)$.

15. Harmonic Oscillator.—In contrast to the two preceding examples, the harmonic oscillator[1] has a wholly discrete spectrum of energy levels. By a harmonic oscillator is understood, a particle which moves in a straight line and is attracted to a fixed point in that line by a force which is proportional to its distance from that point. If x is the distance from the center of attraction, then the potential energy function is $\frac{1}{2}kx^2$, so that the wave equation for a particle of mass μ is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}\left(W - \frac{1}{2}kx^2\right)\psi = 0. \qquad (15.1)$$

This equation is not a new one to theoretical physics, for it occurs in problems connected with the parabolic cylinder,[2] for example, in the diffraction of light at a straight edge, when the straight edge is regarded as of the form of a parabolic cylinder.

Nevertheless, it will be well to discuss the equation here to illustrate one method of dealing with the wave equation. It is desired to find the values of W for which solutions exist that are finite from $x = -\infty$ to $x = +\infty$, and to find these solutions. Observe that as $x \rightarrow \infty$, the coefficient of ψ becomes very large

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[1] SCHRÖDINGER, *Ann. der Phys.*, **79**, 361 (1926).

[2] WHITTAKER and WATSON, "Modern Analysis," p. 347.

and negative, so that by analogy with the differential equation satisfied by the exponential function, a non-oscillatory solution is expected. If $\psi = A \cdot e^{\frac{2\pi S}{h}}$ is written, the differential equation becomes

$$\frac{4\pi^2}{h^2}(S')^2 + \frac{4\pi}{h} S'(\log A)' + \frac{2\pi}{h} S'' + (\log A)'^2 + (\log A)'' + \frac{8\pi^2\mu W}{h^2} - \frac{4\pi^2\mu k}{h^2} x^2 = 0,$$

which can be satisfied by satisfying each of the three equations,

$$\left(\frac{dS}{dx}\right)^2 = \mu k x^2,$$

$$\frac{dS}{dx}\frac{d\,log\,A}{dx} + \frac{2\pi\mu W}{h} + \frac{1}{2}\frac{d^2S}{dx^2} = 0,$$

and

$$\left(\frac{d\log A}{dx}\right)^2 + \frac{d^2\log A}{dx^2} = 0.$$

The first of these gives

$$S = \pm\tfrac{1}{2}\sqrt{\mu k}x^2,$$

where the negative sign must be taken in order to have a solution that is finite at infinity. With this value for S the second equation determines A:

$$A = x^n, \text{ with } n = \frac{2\pi}{h}\sqrt{\frac{\mu}{k}}\,W - \frac{1}{2}.$$

The third equation, with this value of A reduces to

$$\frac{n(n-1)}{x^2} = 0,$$

so that the form found for the solution is rigorously correct for n equal to zero or unity, and is asymptotically correct for large values of x, for any n. Thus two of the allowed energy levels are $W_0 = \frac{1}{2}h\omega$ and $W_1 = \frac{3}{2}h\omega$ where $\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, and is seen to be the same as the frequency of the oscillator reckoned classically. Writing $a^2 = \frac{h}{2\pi\sqrt{\mu k}} = \frac{h\omega}{k}$, the asymptotic form of the solution for large x is

$$\psi \sim x^n e^{-\frac{1}{2}\left(\frac{x}{a}\right)^2}.$$

It can easily be seen that the length a, as defined, is equal to the classical amplitude of motion when the oscillator has the energy $\frac{1}{2}h\omega$.

This result suggests studying the original equation by writing $x = as$ and $\psi = U(s)e^{-\frac{1}{2}s^2}$.

The differential equation for u is then

$$U'' - 2sU' + \left(\frac{2W}{h\omega} - 1\right) U = 0.$$

This equation has the remarkable property that when an attempt is made to solve it by power series

$$U = a_0 + a_1 s + a_2 s^2 + \cdot\cdot\cdot ,$$

the recursion formula connecting successive coefficients involves only two of the a's.

It is

$$a_{n+2}(n + 2)(n + 1) + \left(\frac{2W}{h\omega} - 2n - 1\right) a_n = 0.$$

From this it is clear that if W have one of the values

$$W_n = \left(n + \frac{1}{2}\right)h\omega \qquad n = 0, 1, 2 \cdot\cdot\cdot \quad (15.2)$$

there will be a solution for which U reduces to an nth degree polynomial. For each of these values of W, the original equation therefore has a solution which is finite everywhere, so these are allowed energy levels.

Besides the polynomial solution, which is an odd or even function according as n is odd or even, there is an infinite series solution which is an even or odd function. For values of W other than those specified, the power-series solution is a sum of an even function defined by a power series and an odd function defined by a power series. Of these really infinite power series it may be shown that they tend to infinity as e^{+s^2} for large s so that the corresponding ψ tends to infinity as $e^{+s^2/2}$; in other words, they are not finite. Since this is the case, the values of W found are seen to be the only allowed energy levels.

The theory of these polynomials from the recursion relation between their successive coefficients could be built up further from this, but enough has been said to indicate how the discrete spectrum of energy levels is required by the wave equation, and it is better simply to quote the necessary results.

The polynomials defined by this problem are known as the "Hermitian" polynomials, and are commonly designated as $H_n(s)$. The first five of them are:

$$H_0(s) = 1. \qquad H_1(s) = 2s.$$
$$H_2(s) = 4s^2 - 2. \qquad H_3(s) = 8s^3 - 12s.$$
$$H_4(s) = 16s^4 - 48s^2 + 12.$$

The higher ones can be written down in order from these by means of the recursion formula,

$$H_{n+1} - 2sH_n + 2nH_{n-1} = 0.$$

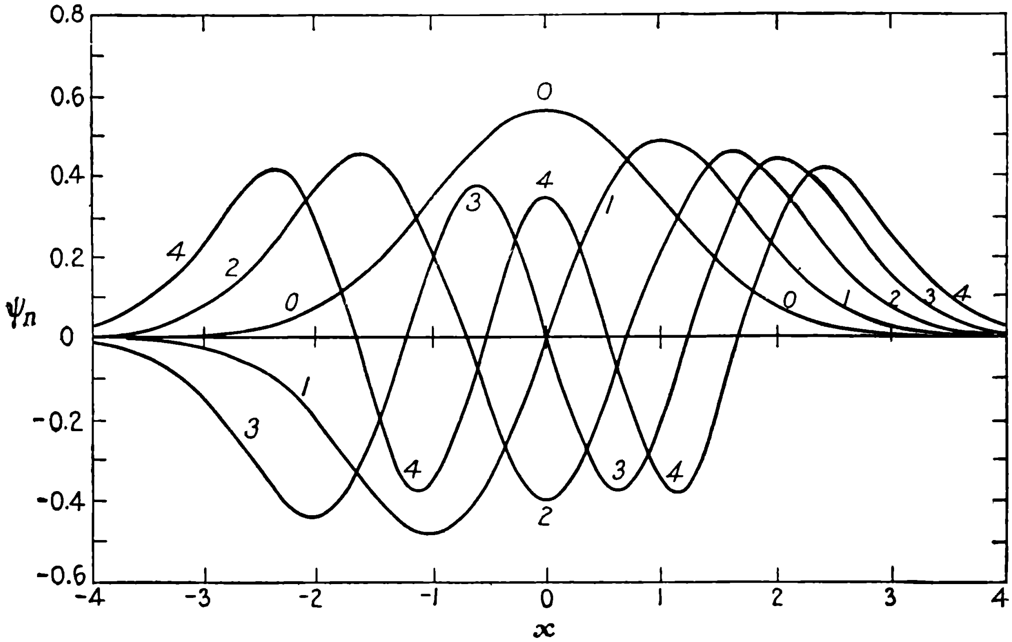

FIG. 4.—$\psi_n = \sqrt{\dfrac{1}{2^n n! \sqrt{\pi}}} \cdot e^{-\frac{1}{2}x^2} \cdot H_n(x)$ for $n = 0, 1, 2, 3$ and 4.

For some purposes the following relation is useful

$$H_n(s) = (-1)^s \cdot e^{s^2} \cdot \frac{d^n}{ds^n}(e^{-s^2});$$

also,

$$H'_n(s) = 2nH_{n-1}(s).$$

Using this formula and making successive integrations by parts, it can be verified that the functions have the orthogonal property

$$\int_{-\infty}^{+\infty} e^{-s^2} \cdot H_m(s) \cdot H_n(s)\, ds = \begin{cases} 0 & (m \neq n) \\ 2^n n! \sqrt{\pi} & (m = n). \end{cases}$$

The normalized wave function for this equation is therefore,

$$\psi_n = \frac{1}{a}\sqrt{\frac{1}{2^n n!\sqrt{\pi}}}\cdot e^{-\frac{1}{2}\left(\frac{x}{a}\right)^2}\cdot H_n\left(\frac{x}{a}\right). \tag{15.3}$$

Figure 4 shows ψ_n for $n = 0, 1, 2, 3$ and 4.

Turning back to the physical problem, it is observed that the energy levels are spaced just as they were in classical quantum theory, but that they have all been increased by $\frac{1}{2}h\omega$. Otherwise expressed, the results are the same as in the old theory if "half-integral" quantum numbers are used there. It is also instructive to consider the relation between the characteristic functions and the classical motion. Classically, the probability of finding the particle between x and $x + dx$ is equal to Adx/v where A must be chosen so that the integral over the classical motion is unity, for the particle must be somewhere on its path. This yields as the classical formula for being between x and $x + dx$ the probability,

$$\frac{1}{\pi}\frac{dx}{\sqrt{a_n^2 - x^2}} \qquad \text{with } \tfrac{1}{2}ka_n^2 = W_n.$$

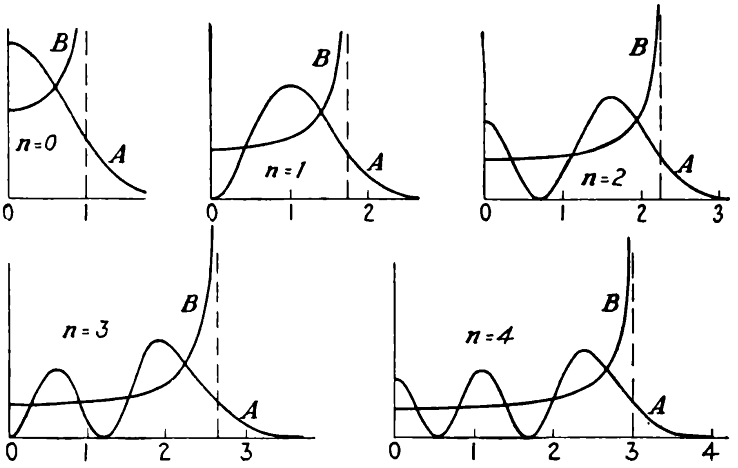

Fig. 5.—Curves A represent $[\psi_n]^2$. Curves B represent $\dfrac{1}{\pi}\dfrac{1}{\sqrt{a_n^2 - x^2}}$.

This classical result is to be compared with that obtained by interpreting $\psi_n^2 dx$ as the probability of being between x and $x + dx$. In Fig. 5 the classical and quantum expressions are plotted together for the first five states. The wavy ones are those for "wave" mechanics. It is seen that there is quite a good correspondence even for n as small as three and four.

Problems

1. Show that, asymptotically for large n and small x, one has the formula,

$$\psi_n{}^2 \sim \frac{2}{\pi}\frac{1}{\sqrt{a_n{}^2 - x^2}}\,\frac{\cos^2}{\sin^2}\left(\frac{a_n x}{a^2}\right),$$

in which cos appears for even n and sin for odd n. Hence for large n, since the trigonometric factor oscillates very rapidly, it may be averaged out. Replacing it by its mean value one-half, one has a complete correspondence between the classical and wave-mechanical formulas.

2. From the asymptotic formula of Problem 1 show that the distance between neighboring zeros of ψ at $x = 0$ is just half the de Broglie wave length for a particle whose momentum is that of a classically moving particle at this part of its path.

3. Show that the values of the matrix component integrals for x are

$$\int_{-\infty}^{+\infty} x\psi_n\psi_m dx = \begin{cases} a\sqrt{\tfrac{1}{2}(n+1)} & m = n+1 \\ a\sqrt{n/2} & m = n-1 \\ 0 & m \neq n \pm 1. \end{cases}$$

This is most readily done by using the recursion formula which connects three successive Hermitian polynomials.

16. Central Forces.—The case of the motion of a particle under the action of forces directed to or from a fixed center is one of great interest for atomic theory. It is also of theoretical interest since it covers the quantum mechanical analogue of the integral of angular momentum and the theory of space quantization of the old quantum theory. In this section the theory of central forces in general will be developed leaving to other sections the consideration of special centrally symmetric problems. Let the particle, of mass μ, be located by the spherical polar coordinates r, θ, and φ. The potential energy function, depending on r alone will be denoted by $U(r)$.

For such a problem the wave equation becomes,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{8\pi^2\mu}{h^2}[W - U(r)]\psi = 0. \quad (16.1)$$

This equation can be separated into an equation for a factor of the characteristic function depending only on the two angles and a factor depending on the radius. Writing

$$\psi = S(r)\cdot Y(\theta, \varphi)$$

the equations for the angular and radial factors of the characteristic function are found to be

$$\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+CY=0, \qquad (16.2)$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial S}{\partial r}\right)-\frac{C}{r^2}S+\frac{8\pi^2\mu}{h^2}[W-U(r)]S=0. \qquad (16.3)$$

The equation for the angular coordinates has been long known in mathematical physics. It has occurred in all of the problems where the Laplace operator is involved and where the boundary conditions have spherical symmetry. It is known that solutions of it which are finite and continuous over all values of the coordinates of geometrical significance exist only for certain values of the parameter C namely for

$$C=l(l+1) \qquad l=0,1,2\cdots$$

Any solution corresponding to a particular value of l is then known as a spherical harmonic of order l. As is known, the lth order spherical harmonic is not one definite function but contains $2l+1$ arbitrary constants.

It is interesting to observe that the quantum constant h, does not appear in the angular equation, nor does the energy W. The only way, therefore, that W can be affected by the angular part of the solution is through the value of the parameter C which also appears in the radial equation. But to every allowed value of $C=l(l+1)$, there are $2l+1$ linearly independent angular characteristic functions. The result is that every centrally symmetric problem is degenerate, the order of the degeneracy being $2l+1$ in the state characterized by the quantum number l. This result is in agreement with the result of classical quantum theory: this is the degeneracy of random space orientation in a centrally symmetric field, and gives the multiplicity into which the terms are split when a non-symmetric perturbing field removes the degeneracy.

It is of importance to find explicit functions in terms of which the spherical harmonics can be written. This can be done by observing that the angular equation itself can be separated into two ordinary differential equations for each angle separately. These are

$$\Phi''+m^2\Phi=0. \qquad (16.4)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left[l(l+1)-\frac{m^2}{\sin^2\theta}\right]\Theta=0. \qquad (16.5)$$

The equation in φ is to be solved with the requirement that the solution have the period 2π. This requires that m be an integer and gives the complex exponential function $e^{\pm im\varphi}$ as the factor of the characteristic function which depends on φ.

This exponential factor is orthogonal, for

$$\int_0^{2\pi} e^{i(m-n)\phi}d\phi = \begin{cases} 0, & (m \neq n) \\ 2\pi, & (m = n) \end{cases}$$

and, therefore, in accordance with the remarks in Sec. **12** this factor can be normalized separately

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \tag{16.6}$$

The equation in θ is that of the associated Legendre polynomials. These will be denoted by $P_{lm}\ (\theta)$. These are known to be simply related to the ordinary Legendre polynomials as follows

$$P_{lm}(\theta) = \sin^m \theta \cdot \frac{d^m}{d\ (\cos\theta)^m}\,[P_l\ (\cos\theta)] = \sin^m \theta \cdot P_l^m\ (\cos\theta).$$

Since the simple Legendre polynomials $P_l\ (\cos\theta)$, are of degree l in their argument, it follows that these functions vanish identically unless $m \lesseqq l$. Since two different Φ factors are associated with each value of m except $m = 0$, one has the result stated before that there are $2l + 1$ different angular factors associated with a given value of l. The first ten of these polynomials are given here:

$$\begin{array}{lll}
P_0^0(x) = 1 & & \\
P_1^0(x) = x; & P_1^1(x) = 1 & \\
P_2^0(x) = \frac{1}{2}(3x^2 - 1); & P_2^1(x) = 3x; & P_2^2(x) = 3 \\
P_3^0(x) = \frac{1}{2}(5x^3 - 3x); & P_3^1(x) = \frac{3}{2}(5x^2 - 1); & P_3^2(x) = 15x; \\
 & & P_3^3(x) = 15
\end{array}$$

where x stands for $\cos\theta$. The higher polynomials can be obtained by the recursion formulas

$$\begin{aligned}
(l - m)P_l^m(x) &= xP_l^{m+1}(x) - P_{l-1}^{m+1}(x), \qquad (16.7)\\
(l + m + 1)P_l^m(x) &= P_{l+1}^{m+1}(x) - xP_l^{m+1}(x),\\
(l + m)P_{l-1}^m(x) &= (2l + 1)xP_l^m(x) - (l - m + 1)P_{l+1}^m(x),\\
(2l + 1)P_l^m(x) &= P_{l+1}^{m+1}(x) - P_{l-1}^{m+1}(x).
\end{aligned}$$

The functions $P_{lm}(\theta)$ are orthogonal, for

$$\int_0^\pi \sin^{2m}\theta \cdot P_l^m(\cos\theta)\, P_k^m(\cos\theta)\cdot \sin\theta\cdot d\theta \begin{cases} =0 & (l\neq k) \\ =\dfrac{2}{(2l+1)}\dfrac{(l+m)!}{(l-m)!} & (l=k) \end{cases}$$

The wave-function factor for the θ coordinate can thus be normalized separately and is

$$\Theta_{ml} = \sqrt{\frac{(2l+1)\cdot(l-m)!}{2\cdot(l+m)!}}\cdot \sin^m\theta P_l^m(\cos\theta). \tag{16.8}$$

Figure 6 shows Θ_{ml} for several values of m and l.

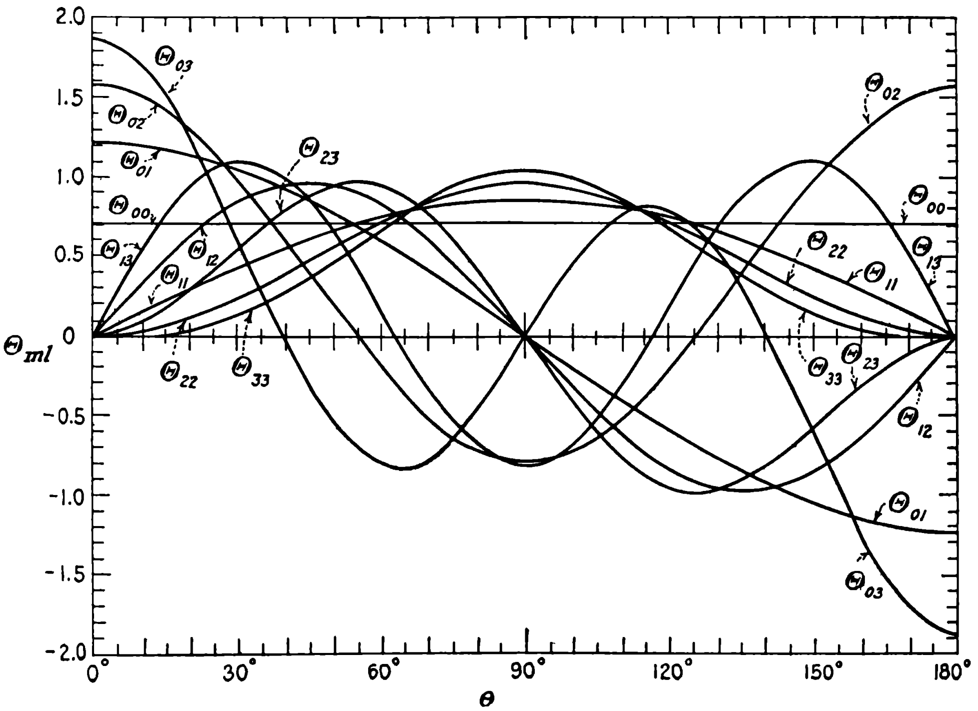

FIG. 6.—Θ_{ml} for several values of m and l.

17. Relation to Oriented Orbits.—Consideration of the characteristics of these various angular factors in central-force field problems throws some light on their relation to the orbits of classical mechanics. If $m = 0$, the ϕ factor is simply a constant. This is to be understood as meaning that there is no motion in the ϕ coordinate in the corresponding classical orbit. But, classically, if there is no motion in ϕ, the orbit would lie entirely in *some one* meridian plane through the polar axis. A satisfactory interpretation of the fact that the characteristic function is independent of φ can be obtained by supposing that this function corresponds not to a motion in a definite meridian plane, but to all classical motions in meridian planes, all meridian planes being of equally probable occurrence.

Similarly if $m = l$, the factor $P_{lm}(\theta)$ has no zeros, implying that there is no motion in the θ-coordinate. In this case the φ factor becomes $e^{\pm il\varphi}$. This case is expected to correspond to the classical orbits in the equatorial plane, the two signs corresponding to opposite senses of rotation relative to the pole of the coordinates. For large l, the wave function here takes on appreciable values only near the equatorial plane, as is shown in Fig. 7.

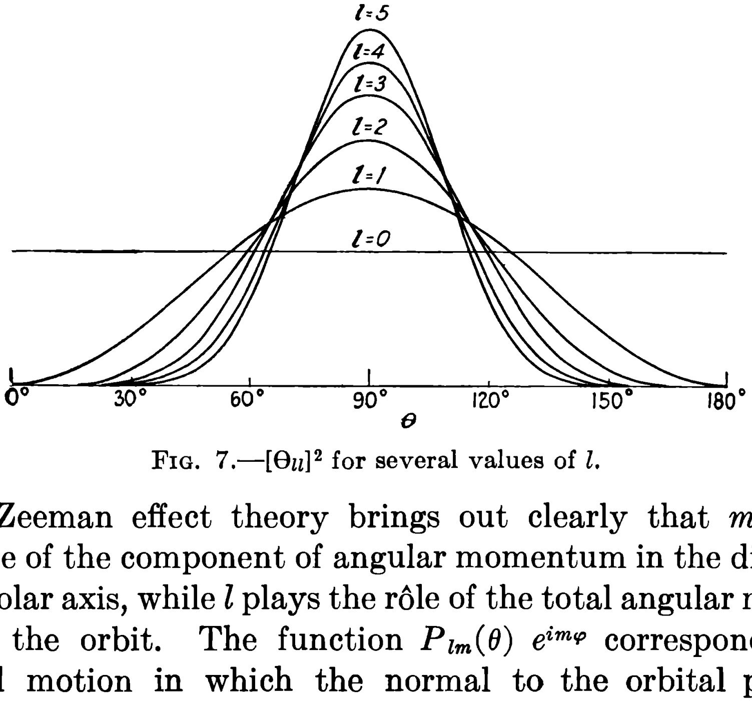

FIG. 7.—$[\Theta_{ll}]^2$ for several values of l.

The Zeeman effect theory brings out clearly that m is the analogue of the component of angular momentum in the direction of the polar axis, while l plays the rôle of the total angular momentum of the orbit. The function $P_{lm}(\theta)\ e^{im\varphi}$ corresponds to a classical motion in which the normal to the orbital plane is inclined to the polar axis, by an angle given by $\cos\theta = \frac{m}{l}$ where, however, the azimuth of this normal to the orbit plane is indeterminate. A more detailed consideration of the quantum mechanics of angular momentum is reserved for Sec. **64**.

Problem

1. Using the asymptotic formula, for large l,

$$P_{l0}(\cos\theta) \sim \frac{2}{\sqrt{2\sin\theta}}\,\frac{1\cdot 3\cdot 5\cdots(2l-1)}{2\cdot 4\cdots\quad 2l}\cos\left[\frac{3\pi}{4}-\left(l-\frac{1}{2}\right)\theta\right]$$

show that the probability of being between θ and $\theta + d\theta$ becomes independent of the value of θ, except for the fine serrations arising from the cosine-squared factor. Interpret these as due to the interference between orbits traversed in opposite senses in each meridian plane.

18. The Radial Equation in Central-force Problems.—The equation for the radial coordinate remains to be considered. Writing the value $l(l+1)$ for C, it is, from equation (16.3),

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial S}{\partial r}\right) - \frac{l(l+1)}{r^2}S + \frac{8\pi^2\mu}{h^2}(W - U(r))S = 0.$$

Here it is expected that the amplitude of the characteristic function will fall off with r, roughly inversely proportional to r just to compensate for the increasing amount of volume of space enclosed between r and $r + dr$ for increasing values of r. Therefore, it should help to make the transformation

$$S = \frac{1}{r}R,$$

yielding as the equation for R,

$$R'' + \frac{8\pi^2\mu}{h^2}\left[W - U(r) - \frac{h^2}{8\pi^2\mu}\frac{l(l+1)}{r^2}\right]R = 0. \tag{18.1}$$

This equation greatly resembles one for a particle moving along one straight-line coordinate, under an effective potential energy $V(r)$ related to the actual potential energy as follows

$$V(r) = U(r) + \frac{h^2}{8\pi^2\mu}\frac{l(l+l)}{r^2}.$$

The analogy is not quite complete for the boundary conditions are different. Here R must vanish at $r = 0$ in order that $S(r)$ remain finite there; a condition that is not necessary in the ordinary problem of one-dimensional motion.

This sort of equivalence of the central-force field problem to the linear oscillator also existed in the old theory.[1] The analogy shows even more how l plays the rôle of the total angular momentum. Of course, the identification cannot be carried too far. For example for $l = 0$ the centrifugal-force effect would be zero. This is the case in the normal state of the hydrogen atom and, yet, the characteristic function shows that the electron manages to keep outside of the nucleus. From this point of view, the normal state of hydrogen is a zero-point energy like the $\frac{1}{2}h\omega$ in the lowest

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[1] It is presented, for instance, in VAN VLECK, "Quantum Principles and Line Spectra," p. 294.

state of the harmonic oscillator; in both cases, the lowest energy level is not coincident with the minimum of the effective potential energy curve.

19. Hydrogen-like Atoms.—The model of a single electron moving about a nucleus under the influence of the Coulomb attraction is by far the most important problem for the application of quantum mechanics to the theory of atomic structure. The results to be obtained in this section are of fundamental importance for the theory, since they cover the main features of the spectrum of all atoms having but 1 electron. They are also the starting point for qualitative and semi-quantitative discussions of all atomic spectra as will be seen in Chap. IV.

Let the mass of the nucleus be M and that of the electron μ_1, and the charges $-Ze$ and $+e$, respectively. Then the potential energy function is $V = -\frac{Ze^2}{r}$, where r is the distance from nucleus to electron. The complete wave equation for the space part of the characteristic functions is

$$\frac{1}{2M}\Delta_1\psi + \frac{1}{2\mu_1}\Delta_2\psi + \frac{4\pi^2}{h^2}\left(W + \frac{Ze^2}{r}\right)\psi = 0,$$

in which Δ_1 and Δ_2 are the Laplace operators referring to the nuclear and electronic coordinates, respectively. This equation in six independent variables may be reduced at once by introducing the coordinates of the center of mass and the coordinates of the electron relative to the nucleus. Then, since the potential energy is independent of the position of the center of mass, these coordinates may be separated out by splitting off a factor which depends only on them and which merely represents the free translational motion of the atom as a whole. The factor corresponding to the free motion will, of course, be of the same form as that found in Sec. 12 for a particle of mass $M + \mu_1$. The equation for the factor depending on the other coordinates becomes

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}\left(W + \frac{Ze^2}{r}\right)\psi = 0, \tag{19.1}$$

where Δ is now the Laplace operator with respect to the coordinates of the electron relative to the nucleus and $\mu = \frac{\mu_1 M}{\mu_1 + M}$ is the so-called reduced mass that also appears in a corresponding way in classical mechanics. The W of the original equation is equal to that of this equation plus the energy of the translational motion. The latter part need not be considered further; it is usually very small compared to the spectroscopic energy levels and contributes only a small broadening of the lines. The equation for the relative coordinates is that of a central-force field problem so that the results of the preceding section may be applied at once. The ψ splits into a factor depending on the two angles $\theta\varphi$ of a system of spherical polar coordinates and a function of the radius alone which will be denoted by $\frac{1}{r}R(r)$. If the case is considered in which the angular factor is a surface harmonic of order l, the equation for $R(r)$ is,

$$R'' + \left(\frac{8\pi^2\mu W}{h^2} + \frac{8\pi^2\mu Ze^2}{h^2 r} - \frac{l(l+1)}{r^2}\right)R = 0. \qquad (19.2)$$

What is required are the values of W for which this equation has a solution which is finite at infinity and zero at the origin, and to find the solutions themselves.

Unlike the equations which have thus far arisen, this boundary-value problem was quite new to mathematical physics when first discussed by Schrödinger.[1] He used the method of complex integration in arriving at the results which are about to be obtained here by more elementary methods. It is convenient to introduce a new variable n in place of W and a new independent variable x, defined by the following relations,

$$W = \pm\frac{2\pi^2\mu e^4 Z^2}{n^2h^2},\ r = \frac{nh^2}{8\pi^2\mu e^2 Z}x, \qquad (19.2a)$$

because these make the equation take on a neater form,

$$R'' + \left(\pm\frac{1}{4} + \frac{n}{x} - \frac{l(l+1)}{x^2}\right)R = 0. \qquad (19.3)$$

So far n is unrestricted. The results that are expected, in order to get agreement with experiment and with the Bohr theory, are that for the positive sign n may take any value, whereas for the negative sign, n must be an integer greater than or equal to $l + 1$. The inequality arises from the fact that n plays the rôle of the "total" quantum number of the old theory while $l + 1$ plays the role of k, the old azimuthal quantum number, in Bohr's notation.

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[1] SCHRÖDINGER, *Ann. der Phys.*, **79**, 361 (1926).

An attempt to solve this equation by a power series around the origin brings out the fact that there is always one solution which is equal to zero at the origin. The one that vanishes at the origin begins with x^{+l}, the other with x^{-l}.

For $x \rightarrow \infty$, two cases are to be distinguished for the two signs appearing in the equation. Striking out the terms which tend to zero as $x \rightarrow \infty$, the equation becomes

$$R'' \pm \tfrac{1}{4}R = 0,$$

which, in the case of the positive sign has both of its fundamental solutions remaining finite for large x, namely, $\sin\frac{x}{2}$ and $\cos\frac{x}{2}$. On the other hand, in the case of the negative sign, only one of the two solutions, $e^{+x/2}$ and $e^{-x/2}$, remains finite.

As already mentioned (Sec. **11**) a general theorem tells that either of the two solutions expressed as series around the origin is equal to a particular linear combination of the two forms valid at infinity. In the case of the positive sign, therefore, that solution which is zero at the origin will be finite at infinity, because it is a linear combination of two functions both of which are finite at infinity. But in the case of the negative sign, the solution will not be finite if the linear combination really involves that one of the two solutions which behaves like $e^{+x/2}$ at infinity. Only for certain values of n will the solution which vanishes at the origin fail to have the undesirable solution in it at infinity. These are the allowed values of n, and hence of W, for negative energies.[1]

To complete the determination of allowed values of n along these lines, it would be necessary to have an expression for the coefficient of the function that becomes infinite at infinity in the representation of the particular solution which vanishes at the origin. This would be a function of n. Equated to zero, the roots of the equation would give the allowed values of n. There does not seem to be any direct method, however, by which this coefficient as a function of n can be found. Therefore, another procedure will be adopted.

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[1] VAN VLECK (*Phys. Rev.*, **33**, 122, 1929) has given an interesting discussion of this result by considering the classical behavior of a particle whose equation of motion is similar to the equation for the radial function, where S represents the particle's position, and the independent variable is the time.

Considering the negative W case, corresponding to the discrete states, suppose $R = yx^{l+1}e^{-x/2}$ is written, then the differential equation for y becomes,

$$xy'' + [2(l + 1) - x]y' + [n - l - 1]y = 0. \qquad (19.4)$$

This equation has a two-term recursion formula for successive coefficients in a power-series solution and, therefore, admits of polynomial solutions as did the similar equation in the harmonic oscillator problem. The relation between successive coefficients is readily found to be

$$a_{j+1}(j + 1)(j + 2l + 2) = a_j(j + l + 1 - n).$$

Hence the series breaks off and gives a polynomial solution of degree j if n is set equal to $j + l + 1$. The possible values of j being 0, 1, 2 . . . it is seen that the allowed values of n associated with any l are the integers satisfying the relation,

$$n \geq l + 1.$$

The letter j, the degree of the polynomial, evidently plays the rôle of the old radial quantum number.

The notation $L_{n+l}^{2l+1}(x)$ will be adopted for the polynomial of degree $n - l - 1$ which corresponds to the integers n and l. This function will be discussed in the next section. Recalling all the various substitutions and writing

$$a = \frac{h^2}{4\pi^2\mu e^2 Z} = 0.532 \times 10^{-8}\text{cm} \times \frac{1}{Z},$$

it is seen that the (not yet normalized) characteristic functions are

$$R(r) = \left(\frac{2r}{na}\right)^{l+1} \cdot e^{-\frac{r}{na}} \cdot L_{n+l}^{2l+1}\left(\frac{2r}{na}\right).$$

Turning now to the consideration of the relation of these functions to the classical orbits, one recognizes that the length a, which was just defined, is equal to the radius of the smallest circular orbit on the Bohr theory. The relation to the classical orbits is seen most easily in the case of the circular orbits. For these one sets the radial quantum number equal to zero so that the polynomial is simply a constant. For the radial factor of the characteristic functions corresponding to a circular orbit one has

$$R(r) \sim \left(\frac{2r}{na}\right)^n e^{-\frac{r}{na}}.$$

Since one interprets the probability of being between r and $r + dr$ as the square of the characteristic function, several of these squared functions have been plotted in Fig. 8 where it is seen how closely related to the corresponding circular Bohr orbit these functions are. It is readily found that the maximum of R^2 occurs for $r = an^2$, which is exactly the value of the radius of the nth circular orbit on Bohr's theory.

By a consideration of the general formula in which the radial quantum number is not zero, one can readily see that the functions in general bear a close relation to the corresponding Keplerian ellipse.

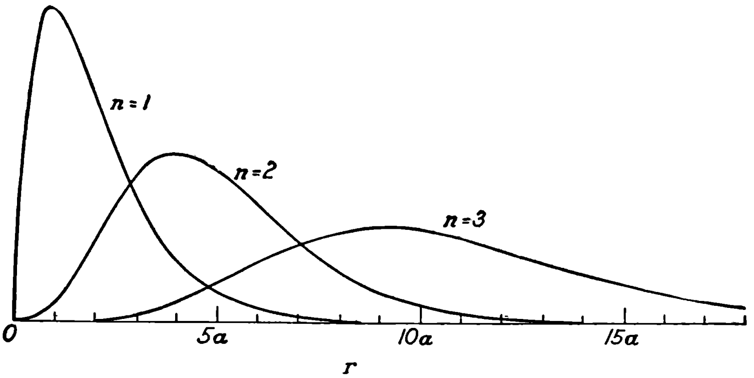

FIG. 8.—The probability function $r^2[S_{n,n-1}(r)]^2$ for $n = 1, 2, 3$.

20. The Radial Functions for Hydrogen.

—The polynomials $L^{2l+1}_{n+l}(x)$ are related to the Laguerre polynomials, a system of orthogonal functions which has been much studied by mathematicians. These polynomials $L_n(x)$ can be defined by the equation

$$L_n(x) = e^x \frac{d^n}{dx^n}(x^n e^{-x}), \tag{20.1}$$

and they can easily be written down in succession by making use of the recursion formula,

$$L_{n+1}(x) - (2n + 1 - x)L_n(x) + n^2 L_{n-1}(x) = 0.$$

When multiplied by the factor $e^{-x/2}$ they form a set of orthogonal functions in the interval zero to infinity, that is,

$$\int_0^\infty e^{-x} \cdot L_n(x) \cdot L_m(x) dx \begin{cases} = 0 & (m \neq n) \\ = (n!)^2 & (m = n) \end{cases}$$

so that they would need to be multiplied through by the reciprocal of $n!$ to form a normalized set. The Laguerre polynomial of order n is a solution of the following second order differential equation

$$xy'' + (1 - x)y' + ny = 0.$$

The connection of the polynomials involved in the hydrogen-atom problem with the Laguerre polynomials is given by the equation,

$$L_{n+l}^{2l+1}(x) = \frac{d^{2l+1}}{dx^{2l+1}}[L_{n+l}(x)]. \qquad (20.2)$$

This relation can be verified easily by writing down the differential equation satisfied by $L_{n+l}(x)$. Differentiating that equation $(2l + 1)$ times there results a second order differential equation which is satisfied by the $(2l + 1)^{st}$ derivative of $L_{n+l}(x)$. It will be found that this differential equation is identical with the one which the polynomials have to satisfy in the hydrogen-atom problem.

The first ten of these polynomials are:

$$\begin{array}{ll}
L_0^0(x) = 1 & \\
L_1^0(x) = -x + 1; & L_1^1(x) = -1 \\
L_2^0(x) = x^2 - 4x + 2; & L_2^1(x) = 2x - 4; \\
 & L_2^2(x) = 2 \\
L_3^0(x) = -x^3 + 9x^2 - 18x + 6; & L_3^1(x) = -3x^2 + 18x - 18; \\
 & L_3^2(x) = -6x + 18; \\
 & L_3^3(x) = -6
\end{array}$$

and the others can be found by means of the general formula

$$L^{\alpha}_{\beta+\alpha}(x) = (-1)^{\alpha+\beta}\frac{(\alpha+\beta)!}{\beta!}\left[x^{\beta} - \frac{(\alpha+\beta)\beta}{1!}x^{\beta-1} + \frac{(\alpha+\beta)(\alpha+\beta-1)\beta(\beta-1)}{2!}x^{\beta-2} - \cdots\right] \qquad (20.3)$$

The differential equation which the polynomial $L^{\alpha}{}_{\beta+\alpha}(x)$ satisfies is

$$xL'' + (\alpha + 1 - x)L' + \beta L = 0, \qquad (20.4)$$

where β must be an integer greater than zero for the polynomial to be finite. The integral

$$\int_0^{\infty} x^{2l+1} \cdot e^{-x} \cdot L_{n+l}^{2l+1}(x) \cdot L_{m+l}^{2l+1}(x) \cdot dx$$

$$\begin{cases} = 0 & (n \neq m) \\ = \dfrac{[(n+l)!]^3}{(n-l-1)!} & (n = m) \end{cases} \qquad (20.5)$$

displays the orthogonal properties of these functions. However, the function which is to be integrated to give part of the integral $\int \Psi\overline{\Psi}dv$ is

$$\int_0^\infty x^{2l} \cdot e^{-x} \cdot L^{2l+1}_{n+l}(x) \cdot L^{2l+1}_{m+l}(x) \cdot x^2 dx,$$

which has an additional factor of x over the above integral, and thus is not orthogonal.

This fact seems to be in contradiction to the statements of Sec. **12,** but when the equation which was used to determine R is examined

$$R_n'' + \left[-\frac{1}{4} + \frac{n}{x} - \frac{l(l+1)}{x^2}\right]R_n = 0.$$

On multiplying this by R_m and multiplying a similar equation for R_m by R_n, subtracting the two, and integrating as before

$$\left[R_n R'_m - R_m R'_n\right]_0^\infty = 0 = (n - m)\int_0^\infty \frac{R_n R_m}{x} dx$$

it is seen that the function which is orthogonal is $R/\sqrt{x}$, corresponding to the orthogonal conditions found above.

The reason for this is that x is not only a function of r, but also includes the quantum number n, and so this transformation from r to x disguises the orthogonal properties of the R function, although it has facilitated the derivation of the form of R.

To find the actual value of $\int R^2 dx$, use is made of the general formula[1]

$$\int_0^\infty x^p \cdot e^{-x} \cdot L^a{}_{a+b}(x) \cdot L^{a'}{}_{a'+b'}(x) \cdot dx$$
$$= p! \cdot (a+b)! \cdot (a'+b')! \cdot \sum_{\tau=0}^{\leq b \text{ or } b'} \left[(-1)^{a+b+a'+b'+\tau} \cdot \binom{p-a}{b-\tau} \cdot \binom{p-a'}{b'-\tau} \cdot \binom{-p-1}{\tau}\right] \qquad (20.6)$$

where τ runs from zero to the smaller of the two numbers b, b', and

$$\binom{r}{s} \begin{cases} = \dfrac{r!}{(r-s)!s!} & \text{if } r \text{ is positive} \\[2ex] = (-1)^s \dfrac{(-r+s-1)!}{(-r-1)!s!} & \text{if } r \text{ is negative.} \end{cases}$$

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[1] SCHRÖDINGER, *Ann. der Phys.*, **80,** 483 (1926).

Using this formula,

$$\int_0^\infty x^{2l} \cdot e^{-x} \left[L_{n+l}^{2l+1}(x) \right]^2 x^2 dx = \frac{2n[(n+l)!]^3}{(n-l-1)!}. \qquad (20.7)$$

The normalized radial function is therefore,

$$S_{nl}(r) = \sqrt{\frac{(n-l-1)!}{2n[(n+l)!]^3}\left(\frac{2}{na}\right)^3} \cdot \left(\frac{2r}{na}\right)^l \cdot e^{\frac{-r}{na}} \cdot L_{n+l}^{2l+1}\left(\frac{2r}{na}\right). \qquad (20.8)$$

Figure 9 shows S_{nl} for several values of n and l.

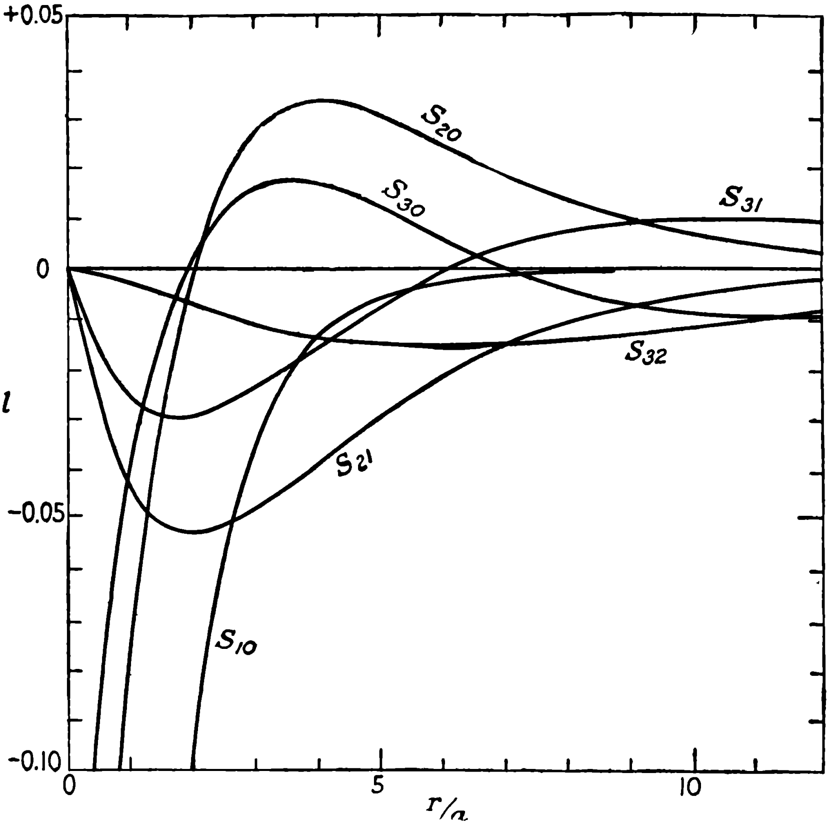

FIG. 9.—$S_{nl}(r)$ for several values of l and n.

The complete wave function for the hydrogen atom is

$$\Psi_{nlm}(\varphi, \theta, r) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{1}{2\pi} \frac{2l+1}{2} \frac{(l-m)!}{(l+m)!} \frac{(n-l-1)!}{2n[(n+l)!]^3}}$$
$$\cdot\, e^{im\phi} \cdot \sin^m \theta \cdot P_l{}^m(\cos\theta) \cdot \left(\frac{2r}{na}\right)^l \cdot e^{-\frac{r}{na}} \cdot L_{n+l}^{2l+1}\left(\frac{2r}{na}\right). \qquad (20.9)$$

The conjugate function $\overline{\Psi}$ has only the exponential term $e^{im\phi}$ changed to $e^{-im\phi}$. When these two functions are multiplied together they are to be multiplied by the usual volume element $r^2 \sin \theta dr d\theta d\phi$, before they are integrated.

The allowed energy levels for the hydrogen atom

$$W = -\frac{2\pi^2 \mu e^4 Z^2}{h^2 n^2} \tag{20.10}$$

where $n = j + l + 1$. (j and l integers), are the same as Bohr obtained by the older quantum theory.

21. A Simple Molecular Model.—In the preceding section it was seen that equation (20.4), which the associated Laguerre polynomial $L^{\alpha}{}_{\beta+\alpha}(x)$ satisfies is

$$xL'' + (\alpha + 1 - x)L' + \beta L = 0,$$

where β must be a positive integer for the polynomial to be finite. So far the number α has also been an integer, but this restriction is not necessary. The general formula (20.3) for $L^{\alpha}{}_{\beta+\alpha}(x)$ can be generalized

$$L^{\alpha}{}_{\beta+\alpha}(x) = e^{i\pi(\alpha+\beta)}\frac{\Gamma(\alpha+\beta+1)}{\beta!}\left[x^{\beta} - \frac{(\alpha+\beta)\beta}{1!}x^{\beta-1} + \frac{(\alpha+\beta)(\alpha+\beta-1)\beta(\beta-1)}{2!}x^{\beta-2} - \cdots\right] \tag{21.1}$$

where now α can have any positive value, integral or non-integral.

The differential equation satisfied by the function

$$F = x^{\gamma/2} \cdot e^{-x/2} \cdot L^{\alpha}{}_{\beta+\alpha}(x)$$

is

$$F'' + \frac{\alpha + 1 - \gamma}{x}F' + \left[-\frac{1}{4} + \left(\beta + \frac{\alpha+1}{2}\right)\frac{1}{x} - \gamma(2\alpha - \gamma)\frac{1}{4x^2}\right]F = 0. \tag{21.2}$$

Thus, to fit this general equation to equation (19.3) for the hydrogen-atom radial function, γ must equal $\alpha + 1$, α must equal $2l + 1$, and n must equal $\beta + l + 1$ where β is an integer.

This shows that

$$R = e^{-x/2}\, x^{l+1} L^{2l+1}_{n+l}(x),$$

which corresponds to the solution obtained previously. This equation will be found useful in several other cases.

In finding the energy levels associated with the rotation and nuclear vibration of a diatomic molecule it is convenient to start with the exact solution for a particular model. Then the solution for models in which the law of force between the two nuclei is slightly different from the one assumed may be found approximately by perturbation theory, as will be seen in Chap. IV. Such a model which can be solved exactly[1] and which is useful as a starting point for the theory of the rotation and vibration spectrum of a diatomic molecule is the central-force problem in which the potential energy function contains an inverse square repulsive term as well as a Coulomb attraction

$$V(r) = \frac{B}{r^2} - \frac{Ze^2}{r}.$$

In this section this particular central-force problem will be treated. It will be seen that the essential difference between the old and the new mechanics will consist in the introduction of so-called half-integral quantum numbers, both in the rotation and the vibration terms. This result is an improvement over the old integral quantum numbers as it is now generally agreed that the half-integral quantum numbers are correct in those cases in which it is possible to distinguish empirically between integral and half-integral quantum numbers.

If the problem is that of two particles of masses M_1 and M_2 whose mutual interaction is given by the potential energy function just written down, then the first stages of this problem parallel closely that of the hydrogen-like atoms given in the preceding section. One can introduce the coordinates of the center of mass and separate off a factor corresponding to the translational motion. The equation for the factor which depends on the motion of one of the atoms relative to the other is similar to that for the hydrogen case in which μ is now the harmonic mean of the masses of the two atoms, and in which the extra repulsive term in the potential energy function appears. As before, the angular factor is simply the spherical harmonic say, of order j, so that the equation for $R(r)$ where $\frac{1}{r}R(r)$ is the radial factor is simply,

$$R'' + \frac{8\pi^2\mu}{h^2}\left[W + \frac{Ze^2}{r} - \frac{B}{r^2} - \frac{h^2 j(j+1)}{8\pi^2\mu r^2}\right]R = 0. \quad (21.3)$$

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[1] Fues, *Ann. der Phys.*, **80,** 367 (1926).

This differs from that of the hydrogen-like atoms only in that a repulsive inverse square term in the potential energy is present to strengthen the inverse square term which represents the effect of "centrifugal force." To discuss this equation it is convenient to introduce the same change of variables as before, namely,

$$W = -\frac{2\pi^2\mu Z^2e^4}{h^2\sigma^2};\ r = \frac{\sigma h^2 x}{4\pi^2\mu e^2} = \sigma a x;\ B = \frac{h^2}{8\pi^2\mu}b$$

so that the equation becomes,

$$R'' + \left[-\frac{1}{4} + \frac{\sigma}{x} - \frac{j(j+1)+b}{x^2}\right]R = 0. \qquad (21.4)$$

This equation is of the general form of (21.2) if $\alpha + 1 = \gamma$, and $(\alpha + 1)(\alpha - 1) = 4j(j + 1) + 4b$

This means that

$$\alpha = 2\sqrt{b + (j + \tfrac{1}{2})^2}$$

and, if β be called n, an integer

$$\sigma = n + \frac{(\alpha + 1)}{2} = n + \tfrac{1}{2} + \sqrt{b + (j + \tfrac{1}{2})^2}.$$

The wave function is therefore,

$$R = \frac{1}{\sqrt{N}} \cdot e^{-x/2} \cdot x^{(\alpha+1)/2} \cdot L^{\alpha}_{n+\alpha}(x)$$

where α has the values given above, and N is the generalization of the normalizing factor given in equation (20.7). Therefore, the normalized radial factor of the wave function is

$$S = \frac{R}{r} = \sqrt{\left(\frac{2}{\sigma a}\right)^3 \frac{n!}{(2n + \alpha + 1)[\Gamma(n + \alpha + 1)]^3}} \cdot \left(\frac{2r}{\sigma a}\right)^{\frac{\alpha-1}{2}} \cdot e^{-\frac{r}{\sigma a}} . L^{\alpha}_{n+\alpha}\left(\frac{2r}{\sigma a}\right), \qquad (21.5)$$

a generalization of equation (20.8).

The energy is found by substituting the allowed values for σ in the equation for W given above

$$W = \frac{2\pi^2\mu e^4 Z^2}{h^2[n + \frac{1}{2} + \sqrt{b + (j + \frac{1}{2})^2}]^2}.$$

The notation here has been changed somewhat from the preceding section to conform more closely to the usual notation for molecular spectra. The n of these formulas is, as will be seen, the analogue of the vibrational quantum number, and the j or $j + 1$ the analogue of the rotational quantum number. If $B = 0$ it is seen that the energy levels just obtained reduce to the ones found for hydrogen (Equation 20.10), as, of course, they should.

When b is large compared to $j(j + 1)$, the effective potential energy curve is almost independent of the rotation. This is the case in the spectrum of diatomic molecules. In this case one can expand the rigorous formula for W in powers of the small quantity $\frac{(j + \frac{1}{2})^2}{b}$. For simplicity, rejecting all but the constant and linear terms one has,

$$W = -\frac{2\pi^2\mu e^4Z^2}{h^2b} + (n + \tfrac{1}{2})\frac{4\pi^2\mu e^4Z^2}{h^2b^{3/2}} + (j + \tfrac{1}{2})^2\frac{2\pi^2\mu e^4Z^2}{h^2b^2} + \cdots \tag{21.7}$$

Already this looks like the result of classical quantum theory, with its term linear in the radial or vibrational quantum number, and its quadratic term in the angular or rotational quantum number. One observes, however, that the formula shows both n and j appearing as effectively half-integral. All that remains to complete the identification with the old theory is to show that the constant term is equal to the value of the potential energy at its minimum, and that the coefficients of $(n + \frac{1}{2})$ and $j(j + 1)$ are, respectively, $h\omega$ and $\frac{h^2}{8\pi^2I}$ in which ω is the frequency, reckoned by classical mechanics, for small oscillations in the neighborhood of the potential energy minimum, and I is the moment of inertia of a dumb-bell the separation of whose masses is equal to the separation of the two atoms corresponding to the minimum of the potential energy curve. This identification will be made in Chap. V, where molecular spectra are more fully dealt with.

It is thus seen how a formula of the right form for molecular energy levels comes out of this simple model. Later the energy levels will be found for a more general law of force between the two atoms by applying the perturbation theory using the results of this section as a starting point.

This form of solution is also applicable in dealing with the alkali metal atoms. Here one electron does the radiating, and due to the inner shell of electrons the outer electron is in a non-Coulomb field.

The potential energy due to the nucleus, plus the inner shells, is very approximately expressed by

$$V = -\frac{C}{r^2} - \frac{e^2}{r}$$

if the electron is not in what was termed a "penetrating orbit."

The analysis of the Schrödinger equation arising from such a potential energy field is the same as that for the molecule carried out above, where now $C = \frac{h^2c}{8\pi^2\mu}$
and

$$k = \tfrac{1}{2} + \sqrt{(l + \tfrac{1}{2})^2 - C},$$

where l is used instead of j, since now atomic levels are considered again. This fixes a lower limit to l, for l can never be less than $(\sqrt{c} - \frac{1}{2})$ or k would become complex.

But c is usually small compared to $\frac{1}{4}$; and, expanding the radical and keeping only the first power of c,

$$k = l + 1 - \frac{c}{(2l + 1)} = l + 1 - \delta_l.$$

This gives us the familiar Rydberg formula for series

$$W = -\frac{2\pi^2\mu Z^2e^4}{h^2(n + \delta_l)^2}. \tag{21.8}$$

This potential energy function was studied by classical mechanics.[1] There C was taken to be e^2Zc_1a, where a is the smallest Bohr orbit of hydrogen, as before. In this case the classical quantum theory gave $\delta_l = Zc_1/(l + 1)$, and the above shows that the quantum mechanics gives $\delta_l = Zc_1/(l + \frac{1}{2})$ illustrating the introduction of the "half-quantum number" which in many cases is the sole difference between the new and the old quantum mechanics.

This approximation, however, for the potential energy is not at all close to the actual potential function for the alkali metal atoms, and so the above discussion has little value except as it illustrates another possible solution of the Schrödinger equation.

Problems

1. Make a table of the radial characteristic functions for the model of this section for several small values of n and j.

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[1] SOMMERFELD, Atomic Structure and Spectral Lines, Dutton (1923), p. 596.

2. Investigate the connection between the characteristic functions for hydrogen and for this problem and the confluent hyper-geometric function, $W_{km}(z)$ as defined in Chap. XVI of "Modern Analysis," Whittaker and Watson.

3. Show that the characteristic functions of this problem, for small values of n, and $b >> j(j+1)$, rapidly approach zero away from the minimum of the potential energy curve, *i.e.*, they correspond to the classical "small oscillations" in the neighborhood of the potential energy minimum.

22. Another Molecular Equation.—In the chapter on molecular spectra it will be seen that the potential energy for nuclear motion of a diatomic molecule is closely approximated by the function[1]

$$V(r) = De^{-2ar} - 2De^{-ar}. \qquad (22.1)$$

Such an energy function has a minimum value of $-D$ at $r = 0$, a value of zero at $r = \infty$ and of infinity at $r = -\infty$. Typical curves are shown in Fig. 16. The classical frequency of small vibrations about the minimum of such a potential energy function is

$$\omega_0 = \frac{a}{2\pi}\sqrt{\frac{2D}{M}}, \qquad (22.2)$$

where M is the harmonic mean of the nuclear masses, $M_1M_2/(M_1 + M_2)$. This function is to be introduced into the usual radial equation, which becomes from (18.1)

$$R'' + \frac{8\pi^2M}{h^2}\left[W + 2De^{-ar} - De^{-2ar} - \frac{h^2j(j+1)}{8\pi^2Mr^2}\right]R = 0. \qquad (22.3)$$

Consider the allowed W's when $j = 0$, *i.e.*, when the molecule does not rotate. First make the transformation $y = e^{-ar}$,

$$\frac{d^2R}{dy^2} + \frac{1}{y}\frac{dR}{dy} + \frac{8\pi^2M}{a^2h^2}\left[\frac{W}{y^2} + \frac{2D}{y} - D\right]R = 0,$$

and if

$$x = 4\pi y\sqrt{2MD}/ah \text{ and } k = 2\pi\sqrt{2MD}/ah,$$

the equation becomes

$$\frac{d^2R}{dx^2} + \frac{1}{x}\frac{dR}{dx} + \left(-\frac{1}{4} + \frac{k}{x} + \frac{k^2W}{Dx^2}\right)R = 0,$$

which resembles equation (21.2) for the generalized Laguerre polynomial if α equals γ, and $\alpha^2/4$ equals $-k^2W/D$, or

$$W = -\alpha^2D/4k^2.$$

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[1] MORSE, *Phys. Rev.* **34**, 57, (1929).

Also, since β in equation (21.2) must be n a positive integer,

$$n + (\alpha + 1)/2 = k \quad \text{or} \quad \alpha = 2k - 1 - 2n$$

where α must be positive, since it is the superscript of the Laguerre polynomial. This means that n can only range from zero to the largest number less than $k - \frac{1}{2}$. This solution of a wave equation, therefore, has a finite number of allowed energy levels,

$$\begin{aligned} W &= -D(k - n - \tfrac{1}{2})^2/k^2 \\ &= -D + \frac{ha}{2\pi}\sqrt{\frac{2D}{M}}\left(n + \frac{1}{2}\right) - \frac{a^2h^2}{8\pi^2M}\left(n + \frac{1}{2}\right)^2 \\ &= -D + h\omega_o(n + \tfrac{1}{2}) - (h^2\omega_o{}^2/4D)(n + \tfrac{1}{2})^2, \end{aligned} \tag{22.4}$$

for the allowed values of n.

The wave function is

$$R = \frac{1}{\sqrt{N_{nn}}} e^{-\frac{x}{2}} x^{k-n-\frac{1}{2}} L_{2k-n-1}^{2k-2n-1}(x), \tag{22.5}$$

where N is the normalizing factor

$$N_{nm} = \int_0^\infty R_nR_m\frac{dx}{x}\begin{cases} = 0 & (n \neq m) \\ = [\Gamma(2k - n)]^2 \displaystyle\sum_{t=o}^{n}\frac{\Gamma(2k - 2n + t - 1)}{\Gamma(t + 1)} & (n = m) \end{cases}$$

which is obtained by generalizing equation (20.6). Therefore, the normalized radial function for this problem is

$$S = \frac{R}{r} = \sqrt{\frac{2ba}{N_{nn}}} \cdot e^{-be^{-ar}}\left(\frac{1}{r}\right) \cdot (2be^{-ar})^{k-n-\frac{1}{2}} \cdot L_{2k-n-1}^{2k-2n-1}(2be^{-ar}) \tag{22.6}$$

where

$$b = 2\pi\sqrt{2MD}/ah.$$

The equation obtained here for the allowed energies is a good representation of the actual energy levels of diatomic molecules, and it is therefore reasonable to suppose that the function V is a good representation of the potential energy function of the molecule.

23. Cyclical Coordinates.—In the classical dynamics a cyclical coordinate may be defined as one which does not appear explicitly in the Hamiltonian function. For such a coordinate an integral of the equations of motion may be obtained at once. Suppose q_0 is cyclical in this sense. Then since q_0 does not appear in the Hamiltonian function $H(p, q)$, the classical Hamilton's equation for p_0 becomes

$$\dot{p}_0 = \frac{\partial H}{\partial q_0} = 0,$$

giving at once the integral $p_0 =$ constant.

A cyclical coordinate may or may not also have the property that the configuration of the system is a periodic function of it, when it is varied while the other coordinates are held fixed. Those of most interest in quantum theory do have this property. By proper choice of measure of such a coordinate, q_0, the period may be equal to 2π. If this is done, the old quantization process for this coordinate can be carried out at once, yielding the result that the associated momentum p_0 can take on only the values

$$p_0 = \frac{nh}{2\pi} \quad n = 0, 1, 2, \cdot \cdot \cdot$$

Cyclical coordinates also appear in a simple rôle in the wave mechanical approach to the problem. If the Hamiltonian function from which one starts is independent of q_0, then the wave equation will not involve q_0 explicitly although it will involve derivatives of the wave function with respect to q_0 of the following forms,

$$\frac{\partial^2\psi}{\partial {q_0}^2}, \quad \frac{\partial^2\psi}{\partial q_0 \partial q_i}, \quad \frac{\partial\psi}{\partial q_0}.$$

Now if one assumes that the wave function depends on q_0 only through a factor e^{ikq_0} where k is a constant, so that $\psi = Fe^{ikq_0}$, then these derivatives become, respectively,

$$-k^2F, \quad ik\frac{\partial F}{\partial q_i}, \quad ikF.$$

The result is a wave equation for F which is entirely freed of q_0, that is, the hypothesis of separation has been successful.

Here again, if the coordinate is such a one that the configuration is periodic in q_0 with period 2π, then one must impose this condition on the wave function, with the result that it is seen that k must be equal to zero or a positive or negative integer. On the other hand, if the configuration is not a periodic function of q_0, then k may take on any value.

24. The Symmetrical Top.—The case of a freely rotating body having two of its three principal moments of inertia equal is of importance in the theory of molecular spectra and furnishes an interesting example of the quantization by the wave equation.[1] Let the position of the top be denoted by Euler's angles θ, φ, ψ, the first two being the ordinary polar coordinates of the axis of symmetry, and the third, the angle which the plane through some point fixed in the body and the axis of symmetry makes with another plane through the axis of symmetry and the line of intersection of the plane normal to the axis of symmetry with the xy plane.

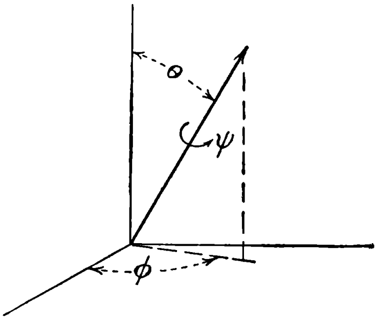

Fig. 10.—Eulerian angles.

The kinetic energy function is then

$$T = \tfrac{1}{2}A\dot{\theta}^2 + \tfrac{1}{2}A\dot{\varphi}^2 \sin^2\theta + \tfrac{1}{2}C(\dot{\psi} + \dot{\varphi}\cos\theta)^2,$$

giving for the associated momenta,

$$p_\theta = A\dot{\theta}, \quad p_\varphi = A\dot{\varphi}\sin^2\theta + C(\dot{\psi} + \dot{\varphi}\cos\theta)\cos\theta$$
$$p_\psi = C(\dot{\psi} + \dot{\varphi}\cos\theta)$$

so that the kinetic energy in terms of the momenta becomes,

$$T = \frac{1}{2A}p_\theta^2 + \tfrac{1}{2}\left(\frac{1}{C} + \frac{\cos^2\theta}{A\sin^2\theta}\right)p_\varphi^2 + \frac{1}{2A\sin^2\theta}p_\psi^2 - \frac{\cos\theta}{A\sin^2\theta}p_\varphi p_\psi.$$

The details of the derivation are omitted since this is well-known from classical mechanics. The wave equation is best obtained by the method of Sec. **3** which applies for the general quadratic form for T. The result is (letting U represent the wave function to avoid confusion with the coordinate ψ),

$$\frac{\partial^2 U}{\partial\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial U}{\partial\theta} + \left(\frac{A}{C} + \frac{\cos^2\theta}{\sin^2\theta}\right)\frac{\partial^2 U}{\partial\varphi^2} + \frac{1}{\sin^2\theta}\frac{\partial^2 U}{\partial\varphi^2}$$
$$- \frac{2\cos\theta}{\sin^2\theta}\frac{\partial^2 U}{\partial\varphi\partial\psi} + \frac{8\pi^2 AW}{h^2}U = 0 \quad (24.1).$$

Evidently both φ and ψ are cyclical coordinates, and the configuration of the top is periodic in them with the period 2π, so one can write

$$U = \Theta(\theta) \cdot e^{i(n\varphi + m\psi)}.$$

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[1] Kronig and Rabi, *Phys. Rev.*, **29,** 262 (1927).
Reiche, *Zs. für. Phys.*, **39,** 444 (1926).
Reiche and Rademacher, *Zs. für Phys.*, **41,** 453 (1927).

The resulting equation for $\Theta(\theta)$ is then

$$\Theta'' + \frac{\cos\theta}{\sin\theta}\Theta' - \left(\frac{A}{C} + \frac{\cos^2\theta}{\sin^2\theta}\right)\cdot n^2\Theta - \frac{m^2}{\sin^2\theta}\Theta + \frac{2\cos\theta}{\sin^2\theta}mn\Theta + \frac{8\pi^2AW}{h^2}\Theta = 0.$$

Introducing the abbreviation

$$\sigma = \frac{8\pi^2AW}{h^2} - \frac{An^2}{C},$$

this can be written

$$\Theta'' + \frac{\cos\theta}{\sin\theta}\Theta' - \frac{(m - n\cos\theta)^2}{\sin^2\theta}\Theta + \sigma\Theta = 0. \tag{24.2}$$

This equation has singularities at $\theta = 0$ and $\theta = \pi$ and the problem is now to find the values of σ for which the equation possesses solutions that are finite at both of these places.

If one writes

$$s = |m + n| \text{ and } d = |m - n|$$

and introduces a new independent variable, $t = \frac{1}{2}(1 - \cos\theta)$ and a new dependent variable F where $\Theta = t^{d/2}(1 - t)^{s/2}F$ the differential equation for F turns out to be

$$t(1 - t)\frac{d^2F}{dt^2} + [\gamma - (\alpha + \beta + 1)t]\frac{dF}{dt} - \alpha\beta F = 0; \tag{24.3}$$

that is, the well-known hypergeometric equation, the relation of the parameters α, β, γ to the parameters of the problem being,

$$\gamma = 1 + d,$$
$$\alpha + \beta = 1 + d + s,$$
$$\alpha\beta = \frac{d + s}{2}\left(\frac{d + s}{2} + 1\right) - \frac{8\pi^2AW}{h^2} + \left(\frac{A}{C} - 1\right)n^2.$$

The new variable ranges from $t = 0$ to $t = 1$ so what is desired is a solution which remains finite at both ends of this interval which are singular points of the equation. The solution of the equation which remains finite at $t = 0$ is $F(\alpha, \beta, \gamma, t)$ commonly known as the "hypergeometric function,"

$$F(\alpha, \beta, \gamma, t,) = 1 + \frac{\alpha\beta}{1\cdot\gamma} + \frac{\alpha(\alpha + 1)\beta(\beta + 1)}{1\cdot 2\gamma(\gamma + 1)}t^2 + \cdots$$

It can be shown that only in case α is a negative integer or zero say, $\alpha = -p$ ($p = 0, 1, 2, 3, \cdots$), do the solutions satisfy the finiteness requirements. These allowed values of α determine the allowed values of the energy as

$$\frac{8\pi^2 W}{h^2} = \frac{1}{A}\left(\frac{d+s}{2}\right)\left(\frac{d+s}{2}+1\right) - \alpha\beta + \left(\frac{1}{C}-\frac{1}{A}\right)n^2$$
$$= \frac{1}{A}j(j+1) + \left(\frac{1}{C}-\frac{1}{A}\right)n^2, \quad (24.4)$$

where j is equal to p plus the larger one of the two quantities $m|$ or $|n|$. This expression for the allowed energy levels differs only from that of the old quantum conditions by the appearance of $j(j+1)$ where j^2 appeared before.

The dependence of the wave function on θ or t is therefore given by

$$t^{d/2}(1-t)^{s/2}F(-p, 1+d+s+p, 1+d, t).$$

Since the "volume" element of the configuration space is $\sin\theta d\theta d\varphi d\psi = 2dtd\varphi d\psi$ the following integral is needed in order to effect the normalization of the factor depending on t:

$$\int_0^1 t^d\,(1-t)^s\,[F(-p, 1+d+s+p, 1+d, t)]^2dt$$
$$= \frac{1}{1+d+s+p}\,\frac{p!(d!)^2(s+p)!}{(d+s+p)!(d+p)!}.$$

Two of these functions for equal d and s but unequal p are orthogonal, *i.e.*,

$$\int_0^1 t^d(1-t)^s\cdot F(-p_1, 1+d+s+p_1, 1+d, t)$$
$$\cdot F(-p_2, 1+d+s+p_2, 1+d, t)\cdot dt = 0 \text{ if } p_1 \neq p_2.$$

The function $F(-p, 1+d+s+p, 1+d, t)$ is a polynomial of degree p and the set for all values of p is known as the "Jacobi polynomials." The set of Jacobi polynomials, $G_p(a, b, t)$ is connected to these by the relations

$$G_p(a, b, t) = F(-p, a+p, b, t),$$

hence, in this notation, the characteristic functions become

$$t^{d/2}(1-t)^{s/2}G_p(a, b, t)$$

in which

$$a = 1+d+s$$
$$b = 1+d.$$

Therefore, the complete wave function for the symmetrical top is

$$\Psi_{mnp}(\psi, \phi, \theta) = \sqrt{\frac{(1 + d + s + p)(d + s + p)!(d + p)!}{8\pi^2 p!(d!)^2(s + p)!}}$$
$$\cdot e^{i(n\psi + m\phi)} \cdot \left(\frac{1 - \cos\theta}{2}\right)^{d/2} \cdot \left(\frac{1 + \cos\theta}{2}\right)^{s/2}$$
$$\cdot F\left(-p,\ 1 + d + s + p,\ 1 + d,\ \frac{1 - \cos\theta}{2}\right) \cdot \qquad (24.5)$$

It would lead too far to give here a complete discussion of the relation of this wave function to the classical motions. By way of indicating the nature of the connection, it may be pointed out that if m and n are both zero, this means that there is no motion in the ϕ and ψ coordinates, all of the motion must, therefore, be in the θ-coordinate. Now, classically if the top is not spinning (p_ϕ and p_ψ zero) the motion of the top in the θ coordinate is just like that of the free rotator. We should therefore expect the wave functions in this case to correspond to those of a free rotator. This, in fact, is true. If $m = n = 0$, then $d = s = 0$, and the θ factor becomes simply $G_p(1, 1, t)$ which is equal to the Legendre polynomial $P_p(\cos\theta)$, the θ-factor of the characteristic function of a free rotator, as it should be.

Problem

Show that for the case in which $m = 0$, *i.e.*, in the absence of axial spin, the wave functions reduce to those of the rotator.

25. The Physical Pendulum.—If a mass particle is constrained to move in a circle while acted on by a uniform force field, the mechanical problem so presented is that of the physical pendulum.[1] This problem is one whose wave functions were known to mathematicians before the development of quantum mechanics, being in fact the Mathieu functions of even order.

Denoting the position of the particle in the circle by the angle θ, the potential energy function becomes $-eEa\cos\theta$ and the kinetic energy is $\frac{1}{2}\mu a^2\dot{\theta}^2$, so that the wave equation becomes

$$\frac{d^2\psi}{d\theta^2} + \frac{8\pi^2\mu a^2}{h^2}(W + eEa\cos\theta)\psi = 0, \qquad (25.1)$$

the requirement being that the solution have the period 2π in θ.

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[1] Condon, *Phys. Rev.*, **31**, 891 (1928).

Introducing these changes,

$$x = \frac{1}{2}\theta, \quad \alpha = \frac{8\pi^2\mu a^2 W}{h^2}, \quad q = \frac{2\pi^2\mu a^2 eE}{h^2},$$

the equation for ψ takes on the form

$$\frac{d^2\psi}{dx^2} + (4\alpha + 16q\cos 2x)\psi = 0 \tag{25.2}$$

which is the standard form of the Mathieu equation. The Mathieu functions, denoted by $Ce_n(x, q)$ and $Se_n(x, q)$, have the period 2π in x and those of even order (n even) have the period π in x, or 2π in θ, and so are the characteristic functions of the problem.

This mechanical problem differs from those already considered in that the potential energy function contains a parameter E, the field strength, on which both the energy levels and the characteristic functions depend. For $E = 0$, the problem is that of a free rotator so the energy levels go over into $W(n, 0) = n^2\frac{h^2}{8\pi^2\mu a^2}$ where $n = 0, 1, 2 \cdots$ and the wave functions are $e^{\pm in\theta}$. For E large, the lower energy levels should be almost equally spaced, corresponding to the harmonic-oscillator-like small amplitude motion which is the classical result for this case. The wave functions, moreover, should be essentially zero everywhere except in the neighborhood of $\theta = 0$ where the corresponding classical motion takes place. These properties, predicted from the pendulum problem, are, in fact, possessed by the Mathieu functions as analytical investigations of them have shown. The problem will not be discussed here in fuller detail because it is without application in the field of atomic physics and its value as an illustrative example is limited by the fact that the Mathieu functions are not widely known.

26. Spatial Harmonic Oscillators.—If a particle can move in two or three dimensions, and is attracted to a fixed point by a force that is proportional to the distance, one has to do with the spatial analogue of a linear harmonic oscillator. The problems are readily solvable.

Thus let the particle be free to move in a plane, the potential energy function being

$$V = \tfrac{1}{2}k_1x^2 + \tfrac{1}{2}k_2y^2.$$

The variables are separable in the wave equation in rectangular coordinates, the separate equations for the two coordinates being just those already discussed for the linear harmonic oscillator. Similarly, for three degrees of freedom and a potential energy function,

$$V = \tfrac{1}{2}k_1x^2 + \tfrac{1}{2}k_2y^2 + \tfrac{1}{2}k_3z^2,$$

the problem is separable in rectangular coordinates and presents no new features.

If $k_1 = k_2 = k_3$, the problem can be regarded as one in central forces and can be solved not only in rectangular coordinates, but in cylindrical and spherical coordinates as well. The carrying through of the details proceeds on the same lines as the other problems discussed, and furnishes a good illustrative example whose solution can be left to the reader.

In cylindrical coordinates, r, ϕ, z, one finds that the z-factor is simply that of linear harmonic oscillations in this coordinate. The φ-factor is that of a cyclic coordinate. The new feature lies in the r-factor for which the equation is

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dR}{dr}\right) - \frac{m^2}{r^2}R + \frac{8\pi^2\mu}{h^2}\left(W_r - \frac{k}{2}r^2\right)R = 0. \qquad (26.1)$$

Introduce the same change of unit of r as in the linear oscillator, *i.e.*,

$$r = a\rho \text{ with } a^2 = \frac{h}{2\pi\sqrt{\mu k}},$$

and find that

$$R = \rho^m e^{-\frac{\rho}{2}} C_{nm}(\rho), \qquad (26.2)$$

in which the $C_{nm}(\rho)$ are a set of polynomials.

The energy levels turn out to be

$$W = h\omega(m + n + p + \tfrac{3}{2}), \qquad (26.3)$$

in which p is the quantum number of the motion in the z coordinate. $C_{nm}(\rho)$ is of the nth degree.

Similarly in spherical polar coordinates, the angles θ, φ may be treated as in any central-force problem, the new feature again lying in the equation for the radial factor. Denoting the radial factor by $\frac{1}{r}R(r)$, as in earlier sections, the equation for R is now

$$R'' + \frac{8\pi^2\mu}{h^2}\left(W - \frac{1}{2}kr^2\right)R - \frac{l(l+1)}{r^2}R = 0, \qquad (26.4)$$

which is similar to, but not identical with, the equation of this problem in cylindrical coordinates. The same change from r to ρ is again convenient and one finds for the radial function $R(r)$,

$$R(r) = \rho^l e^{-\frac{\rho^2}{2}} B_{nl}(\rho) \tag{26.5}$$

in which the $B_{nl}(\rho)$ are another set of polynomials. The energy levels in this case are

$$W = h\omega(n + l + \tfrac{3}{2}). \tag{26.6}$$

It will be observed that in all cases the energy levels coincide, no matter in which coordinate system the problem is solved, and that the degree of multiplicity of a degenerate state is the same for the different forms of solution.

The $B_{nl}(\rho)$ have a simple relation to the hypergeometric function,

$$B_{nl}(\rho) = \lim_{b \to \infty} F\left(-n, b; l + \frac{3}{2}, \frac{\rho^2}{b}\right).$$

27. Hydrogen in Parabolic Coordinates.—The problem of hydrogen-like atoms is also separable and easily solved in parabolic coordinates,[1] a form of solution which is of importance in studying the influence of an external electric field on the energy levels. The wave equation, as in Sec. **18,** for this problem is

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}(W + \frac{Ze^2}{r})\psi = 0.$$

The transformation equations,

$$x = \sqrt{\xi\eta}\cos\varphi,$$
$$y = \sqrt{\xi\eta}\sin\varphi,$$
$$z = \tfrac{1}{2}(\xi - \eta),$$

serve to introduce a new set of orthogonal coordinates, ξ, η, φ $(0 \leqslant \xi \leqslant +\infty,\ 0 \leqslant \eta \leqslant +\infty,\ 0 \leqslant \varphi \leqslant 2\pi)$, which have the property that the surfaces of constant ξ or η are paraboloids of revolution, their axis of symmetry being the z-axis. For the wave equation the Laplace operator is needed in these coordinates, also the expression for r. The former can be obtained by the usual methods, while the latter is, simply,

$$r^2 = x^2 + y^2 + z^2 = \tfrac{1}{4}(\xi + \eta)^2.$$

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[1] Schrödinger, *Ann. der Phys.*, **80,** 457 (1926).

The transformation expression for the volume element is

$$dxdydz = \tfrac{1}{4}(\xi + \eta)d\xi d\eta d\varphi,$$

so that the wave equation for the problem can be written

$$\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \psi}{\partial \xi}\right) + \frac{\partial}{\partial \eta}\left(\eta \frac{\partial \psi}{\partial \eta}\right) + \tfrac{1}{4}\left(\frac{1}{\xi} + \frac{1}{\eta}\right)\frac{\partial^2 \psi}{\partial \varphi^2} + \frac{2\pi^2\mu}{h^2}\,[W(\xi + \eta) + 2\,Ze^2]\,\psi = 0. \quad (27.1)$$

Evidently, the coordinate φ is cyclic and the equation is separable with regard to ξ and η. Writing

$$\psi = F(\xi)G(\eta)e^{im\varphi},$$

it is found that the equations for F and G are:

$$\frac{\partial}{\partial \xi}\left(\xi \frac{\partial F}{\partial \xi}\right) + \frac{2\pi^2\mu}{h^2}\left(W + Ze^2 - \beta Ze^2 - \frac{m^2h^2}{8\pi^2\mu}\frac{1}{\xi}\right)F = 0,$$

$$\frac{\partial}{\partial \eta}\left(\eta \frac{\partial G}{\partial \eta}\right) + \frac{2\pi^2\mu}{h^2}\left(W + Ze^2 + \beta Ze^2 - \frac{m^2h^2}{8\pi^2\mu}\frac{1}{\eta}\right)G = 0.$$

Each of these is to be solved in the range from 0 to $+\infty$.

The equations can be discussed in detail following the general methods of this chapter. The results will be outlined, leaving the details as an exercise for the reader. As in Sec. **18**, restricting the treatment to the negative energy levels, one may write

$$W = -\frac{2\pi^2\mu e^4Z^2}{n^2h^2}, \quad (\xi, \eta) = \frac{nh^2}{4\pi^2\mu^2e^2Z}(x, y),$$

then the two differential equations become,

$$x\frac{d}{dx}\left(x\frac{dF}{dx}\right) + \left[-\frac{x^2}{4} + \frac{n(1 - \beta)}{2}x - \frac{m^2}{4}\right]F = 0,$$

$$y\frac{d}{dy}\left(y\frac{dG}{dy}\right) + \left[-\frac{y^2}{4} + \frac{n(1 + \beta)}{2}y - \frac{m^2}{4}\right]G = 0. \quad (27.2)$$

The substitutions,

$$F = x^{m/2}\,e^{-x/2}\,u \text{ and } G = y^{m/2}\,e^{-y/2}\,v$$

yield as the equations for u and v:

$$xu'' + (m + 1 - x)u' + \tfrac{1}{2}[n(1 - \beta) - m - 1]u = 0,$$

$$yv'' + (m + 1 - y)v' + \tfrac{1}{2}[n(1 + \beta) - m - 1]v = 0. \quad (27.3)$$

Set $n(1 - \beta) - m - 1 = 2k_1$ and $n(1 + \beta) - m - 1 = 2k_2$, so that $n = k_1 + k_2 + m + 1$. The resulting equation is seen to be equivalent to equation (20.4) given for the radial component of the wave function for hydrogen. The solution is a generalized Laguerre polynomial, given in equation (20.3), and

$$\begin{aligned} F(x) &= x^{m/2}e^{-x/2}L^m{}_{k_1+m}(x) \\ G(y) &= y^{m/2}\,e^{-y/2}\,L^m{}_{k_2+m}(y). \end{aligned} \qquad (27.4)$$

Inasmuch as the volume element in these coordinates is $\frac{1}{4}(\xi + \eta)d\xi d\eta d\phi$, it is not possible to normalize each factor of the wave function separately. The inseparable factors give

$$\int\int F^2(x)G^2(y)(x + y)dxdy = \frac{2(k_1 + k_2 + m + 1)[(k_1 + m)!]^3[(k_2 + m)!]^3}{k_1!\ k_2!}$$

and therefore the complete, normalized wave function for hydrogen in parabolic coordinates is

$$\Psi_{k_1k_2m}(\xi,\,\eta,\,\phi) = \frac{2}{\sqrt{2\pi(na)^3}}\sqrt{\frac{k_1!\ k_2!}{2n[(k_1 + m)!]^3\cdot[(k_2 + m)!]^3}} \qquad (27.5)$$
$$\cdot\,e^{im\phi}\left(\frac{\xi\eta}{n^2a^2}\right)^{m/2}\cdot e^{-(\xi + \eta)/2na}\cdot L^m{}_{k_1+m}\left(\frac{\xi}{na}\right)\cdot L^m{}_{k_2+m}\left(\frac{\eta}{na}\right)\cdot$$

It will be observed that n appears here as one greater than the sum of the three quantum numbers k_1, k_2 and m. This expression for n is the exact analogue of a similar one in polar coordinates,

$$n = (n - l - 1) + (l - m) + m + 1,$$

where the terms are, respectively, the quantum number in the r, θ, ϕ coordinates instead of the ξ, η, ϕ system. The reader will find it an interesting example to discuss the relation of the characteristic functions in these coordinates to the classical orbits.

It is easily seen that, although the energy levels for the various n's are exactly the same as for the problem in spherical coordinates, the wave function itself is considerably different in form for the two problems. This is a typical case of a *degenerate* system, where the energy is independent of one or more of the quantum numbers; which systems will be more fully discussed in Chap. IV. In hydrogen, the energy is dependent only on the quantum number n, and there are n^2 different wave functions, corresponding to the various l and m values (or k_1 and k_2 and m values) which will give the n considered, all having the same energy.

Inasmuch as it is the energy which is actually measured, and not the wave function, it seems reasonable to consider that the actual wave function of a degenerate system is not any particular wave function for a particular value of the degenerate quantum numbers, but the ensemble of all possible linear combinations of all the wave functions having the same energy. It can be shown that the wave functions obtained by using parabolic coordinates are particular linear combinations of those wave functions obtained by using spherical coordinates, and, therefore, the ensemble of all linear combinations of the parabolic wave functions will be the same as the ensemble of all linear combinations of the spherical wave functions.

As will be shown later, any slight change, or *perturbation*, in the potential field about the atom will "remove the degeneracy" in one or more of the quantum numbers (*i.e.*, will cause the energies for the various values of these numbers to differ slightly from one another). As soon as this happens, the wave function of the atom is no longer the ensemble of all linear combinations, but consists of those particular linear combinations which are peculiar to the perturbation.

Thus, in the unperturbed hydrogen atom, it is meaningless to state that the atom has quantum numbers $n = 2$, $l = 1$, $m = 0$, say, for l and m have no effect on the energy value and, therefore, have no meaning; it can only be stated that $n = 2$. Similarly, it would have no meaning to assign definite values of k_1, k_2 and m for this same state.

If, however, the potential field be made slightly non-Coulomb, as in the alkali-metal atoms, then the particular combination of wave functions applicable to such a system will be the spherical ones, and the value of l will have a meaning.

On the other hand, if a uniform electric field is superposed on the Coulomb field, as in the Stark effect, the particular wave functions then applicable are the parabolic ones, and the k_1 and k_2 quantum number values will have meaning, but the m value will not. The problem will be further discussed in the chapter on perturbation theory.

28. Some Oscillatory Properties of the Wave Function.—If curves be examined of the wave function for a one-dimensional problem giving a discrete energy spectrum, as, for instance, the harmonic oscillator, several properties will be noticed. First, that the wave function for a given quantum number n has n nodes or points where the real part of Ψ changes sign. Second, that the wave function has no nodes in the region where W is less than V.

To prove that these properties are true of any one-dimensional wave function, or any one-dimensional factor of a separable n dimensional wave function, consider the equation

$$\frac{d}{dx}\left[p(x)\frac{d\Psi}{dx}\right] + r(x, W)\cdot\Psi = 0$$

which, with the requirement that Ψ be finite at some singular points a and a', is the general form which includes the equation of all such wave functions. $r(x, W)$ usually has the form $K[W - V(x)]$.

Now take another equation

$$\frac{d}{dx}\left[\pi(x)\frac{d\Phi}{dx}\right] + \rho(x, W')\cdot\Phi = 0,$$

with the same requirements of finiteness. Sturm's First Comparison Theorem[1] states that, if throughout an arbitrary interval $b < x < a$, where a is one of the singular points, if $p \geq \pi > 0$ and $r < \rho$ throughout this interval, then Φ has at least as many nodes in the interval as Ψ has.

To apply this most easily to the case at hand, change the independent variable x so that one of the singular points is at $+\infty$, if it is not already there. Then in any interval (a, b), where V is always greater than W, choose π to be a constant less than any value of p in the interval (if π comes out negative it is possible to change the position of the origin of x so that π is positive). Let ρ be some negative constant greater in magnitude than the magnitude of any value of r in the interval. Then Φ is an exponential of the form $Ae^{\pm kx}$. But Φ must be finite at $x = a = \infty$ and so only one of the solutions can be used, Ae^{-kx}. Therefore, Φ has no nodes in the interval (a, b), and since Φ has at least as many nodes as Ψ, Ψ has no nodes in this interval.

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[1] INCE, "Ordinary Differential Equations," p. 231, Longmans, Green and Co.

Therefore: In any interval (a, b) where a is a singular point of the Schrödinger equation, if V is greater than W everywhere in the interval, then Ψ has no nodes in this interval.

Now, consider the interval (a, c) where W is sometimes greater than V. The allowed wave functions may or may not have a node in this interval. Suppose that for the allowed energy level $W = W_0$, the wave function Ψ_0 has no node in the whole interval from a to a'. Also, suppose that for $W = W_1$ the wave function Ψ_1 has but one node in (a, a'), and let that node be at d.

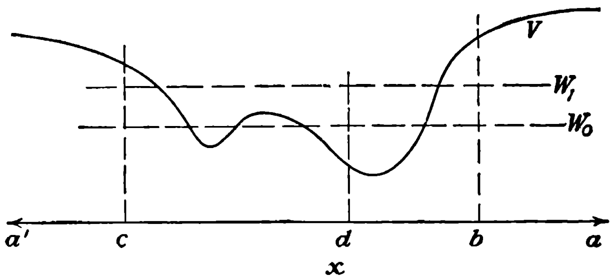

FIG. 11.—Potential energy function V_1 with two of its allowed energy levels, W_o and W_1.

Suppose that there were another allowed level W' corresponding to the wave function Ψ', where W' lies between W_0 and W_1. If such a function exists, it can have no more than one node; for since its p equals the p for W_1 and since its r is everywhere less than the r for W_1, then the wave function Ψ_1 must have at least as many nodes as Ψ'.

If it has one node, by considering the interval from a' up to d, and then from a to d, it is seen that this node must be at d. But this means that $\int_{a'}^{a} \Psi_1 \Psi' dx$ cannot be zero, and, since these functions must be orthogonal (for W' is different from W_1), therefore Ψ' cannot have a node. If it cannot have a node, then $\int_{a'}^{a} \Psi_0 \Psi' dx$ is different from zero. This also cannot be; therefore there can be no allowed wave functions corresponding to an energy between W_0 and W_1.

The process of reasoning to show that there can be no allowed wave function whose energy lies between the energies for Ψ_n, having n nodes and Ψ_{n+1} having $n + 1$ nodes, is similar.

Thus it has been shown that if the allowed energy levels are arranged in an ascending series, W_0, W_1, W_2, . . . , and the corresponding wave functions be Ψ_0, Ψ_1, Ψ_2 . . . , and if Ψ_0 has no nodes, then Ψ_n has n nodes.

Since W must be less than V at both the upper and lower bounds of x, in order that the energy levels be discrete, then a general process of reasoning shows that Ψ_0 must have no nodes. For the form of Ψ at both the upper and lower portions where W is less than V must be similar to an exponential, with amplitude decreasing toward each bound (*i.e.*, with curvature upward), and it is always possible to choose a W such that the inner portion of Ψ where W is greater than V and the curvature is downward, has no nodes and yet fits both outer portions of Ψ in value and in slope.

In the intervals where W is less than V, which do not include a singular point, Ψ is approximately of the form $ae^{kx} + be^{-kx}$. If the plus sign be taken between the terms, then Ψ has no node in the interval, but, if the minus sign be taken, then it has one node. Therefore, in these intervals Ψ cannot have more than one node.

Consider the case of a particular Ψ_{no} for the equation

$$\frac{d}{dx}\left[\,p(x)\frac{d\Psi}{dx}\right] + K[W_{no} - V_0(x)]\Psi = 0.$$

If V_0 be slightly changed to V_1, W_{no} will be perturbed, becoming W_{n1}, and Ψ_{no} will be slightly changed to Ψ_{n1}, but will never increase the total number of nodes it possesses.

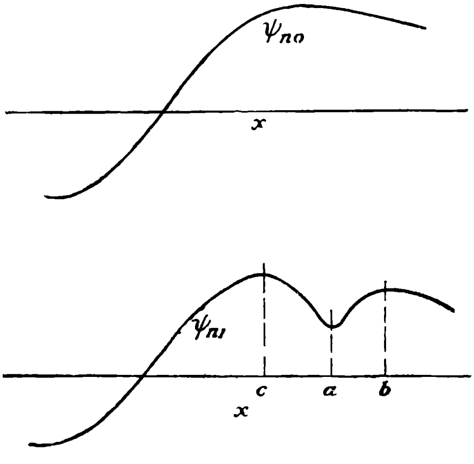

Fig. 12.—Unperturbed wave function Ψ_{no}, and an assumed perturbed wave function Ψ_{n1}.

For, in order to change the number of nodes, Ψ_{n1} must decrease in some such manner as at the interval (c, a, b), or until the minimum at a is less than zero. If this were true two more nodes would result, and, since any interval where $W < V$ can at most have but one node, this must occur where $W - V$ is positive.

Integrate the above equation with respect to x.

$$\left[p\frac{d\Psi}{dx}\right]_b - \left[p\frac{d\Psi}{dx}\right]_a = -K\int_a^b (W - V)\Psi dx.$$

Then if a be the minimum point, and b the next point where $d\Psi/dx$ is zero, the left side of the equation will be zero, but in the interval (a, b), Ψ is always positive, and, if $(W - V)$ is positive, the integral will be positive, and the right side of the equation will be a negative quantity, not zero. An extension of this reasoning will show that if $(W - V)$ is negative enough in this interval to make the integral zero, then b will not be the first point after a where $d\Psi/dx$ is zero, and this intermediate point must be taken for b.

Therefore, as V is slowly changed, no nodes can disappear, or no new nodes can be formed in Ψ_n. Since the number of nodes corresponds to the quantum number, this theorem is equivalent to the Principle of Adiabatic Invariance, which postulates that for a particular energy level W_n, represented by the quantum number n, if V be changed slowly, W_n will slowly change, and will not jump discontinuously to another level represented by another quantum number.

For two, three, or more dimensions, these nodal points become nodal lines, nodal surfaces, and nodal hypersurfaces. For any problem where the variables are separable, these theorems are applicable, and even if the variables are not separable, it seems likely that similar proofs can always be given by means of Green's theorem.

For instance, for three dimensions, there can be no more than one nodal surface lying wholly within a region where W is everywhere less than V; no nodal surfaces can be formed or can disappear from a wave function if V is slowly changed; and if the energy levels, corresponding to a series of wave functions having the same number of nodal surfaces in two coordinates, but various numbers of nodal surfaces in the third coordinate, be arranged in an increasing series, W_0, W_1 . . . , then the wave function Ψ_n corresponding to W_n will have n nodes in that coordinate.

In other words, in n dimensions there will be as many different W's corresponding to the same total number of nodal surfaces as there are different ways of allotting these nodal surfaces to the n coordinates. The number of nodes, however, in any particular coordinate still corresponds to the quantum number for that coordinate, and, therefore, the total number of nodes corresponds to the total quantum number, if such a number is used in the problem considered.

In the hydrogen atom, $n = 1$ for the lowest energy level, so that the total number of nodal surfaces in the wave function will be $n - 1$.

In spherical coordinates, these nodal surfaces can be either in r, θ, or ϕ. For $n = 2$, for instance, the node can be in r, where it is a sphere, with Ψ positive within and negative outside; or it can be in θ, where it is a plane perpendicular to the axis of coordinates; or it can be in ϕ, where it is a plane in which the axis is. The nodal surfaces for the hydrogen atom in parabolic coordinates are paraboloids of revolution in ξ and η and planes in ϕ.

CHAPTER III

RADIATION AND EXTERNAL FIELDS OF SIMPLE MECHANICAL SYSTEMS

In Sec. **10** the postulate was made that the external electromagnetic fields, due to charges moving in a mechanical system, could be computed from Maxwell's equations, using for the charge and current density certain expressions in terms of the wave functions which were there developed. This chapter will be devoted to the consideration of some important consequences of this postulate in connection with the mechanical problems whose wave equations were treated in Chap. II.

29. The General Wave Function.—It has been seen that sometimes the wave equation leads to a continuous spectrum of energy levels (free particle) sometimes to a wholly discrete set (harmonic oscillator, symmetrical top) and sometimes to a set that is partly continuous and partly discrete (hydrogen atom). Since the fundamental equation with W eliminated,

$$\Delta\Psi - \frac{8\pi^2\mu}{h^2}V\Psi + \frac{4\pi i\mu}{h}\frac{\partial\Psi}{\partial t} = 0, \tag{29.11}$$

is linear, it is clear that the general solution for Ψ is a sum of the individual solutions each multiplied by an arbitrary constant. Thus if the allowed energies are $W_n (n = 0, 1, 2 \cdots)$ and the corresponding space functions are $\psi_n(x, y, z)$, the general solution for Ψ is evidently

$$\Psi = \sum_n c_n\psi_n(x, y, z)e^{-\frac{2\pi i W_n t}{h}}, \tag{29.12}$$

in which the c's are wholly arbitrary. We have now to consider the physical interpretation of such a quantity Ψ. A more complete answer to this question will emerge gradually as the theory develops; here will be given just a preliminary discussion of the question.

The fact that the energy levels agree with those found experimentally through spectroscopy, and through electron impact experiments, and the fact that the wave function $\psi_n(x, y, z)$

usually bears a recognizable resemblance to the classical orbit of the same quantum numbers, makes us want to hold on to the old idea of stationary states as much as possible. Forming the expression $\Psi\bar{\Psi}$ from the general solution one has

$$\begin{aligned}\Psi\bar{\Psi} &= \sum_{nm} c_n\bar{c}_m\psi_n\bar{\psi}_m \cdot e^{\frac{2\pi i}{h}(W_n - W_m)t} \\ &= \sum_{n} c_n\bar{c}_n\psi_n\bar{\psi}_n + \sum_{m<n}\Bigg(c_n\bar{c}_m\psi_n\bar{\psi}_m e^{\frac{2\pi i}{h}(W_n - W_m)t} \\ &\qquad\qquad + c_m\bar{c}_n\psi_m\bar{\psi}_n e^{\frac{-2\pi i}{h}(W_n - W_m)t}\Bigg).\end{aligned}$$

The second form of the sum brings out clearly the fact that the general expression involves terms not varying with the time, and terms which vary harmonically with the time with frequencies just equal to the frequencies of the spectrum lines

$$\nu_m^n = \frac{1}{h}(W_n - W_m).$$

This suggests at once that somehow or other the first terms are to be associated with atoms *while in* each of the stationary states, and the second set of terms are to be associated with atoms *that are jumping* between two stationary states.

Thus

$$c_n\bar{c}_n\psi_n\bar{\psi}_n$$

is the effective charge distribution for finding the external field of an atom while in the nth state and,

$$\left(c_n\bar{c}_m\psi_n\bar{\psi}_m e^{\frac{2\pi i}{h}(W_n - W_m)t} + c_m\bar{c}_n\psi_m\bar{\psi}_n e^{-\frac{2\pi i}{h}(W_n - W_m)t}\right),$$

is that which is to be associated with the field due to an atom while a transition from state n to state m is taking place.

This is the way in which the wave functions will be used in this chapter for computing the radiation properties of atoms. This use, it will be seen, is sufficient to give the important selection rules of spectroscopy and other features of the atomic fields correctly. A better foundation for this method in regard to radiation problems will be taken up in Chap. VII when the interaction between atoms and radiation is discussed.

Schrödinger's viewpoint here is that the ψ functions represent different possible "modes of vibration" of the atom.[1] When

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[1] SCHRÖDINGER, *Ann der Phys.*, **81,** 134 (1926).

only one of these is "excited," the atom functions in the same way as if it were in a stationary state. But when two different "states of vibration" are functioning at once, then radiation can be emitted which has the frequency equal to the beat frequency of the two modes of vibration. But this amounts simply to a use of the language of the elasticity theory in describing the method of computing radiation from the wave functions and really contributes nothing to an understanding of the processes involved.

Against this view it can be objected that it regards the atoms as being in two different states at once, which is contrary to the usual view. Klein has ignored this difficulty and treated the problem in a slightly different way.[1] He sets every $c_n = 1$ and then considers the double array of quantities

$$\rho_{nm} = \psi_n \bar{\psi}_m e^{\frac{2\pi i}{a}(W_n - W_m)t}. \tag{29.2}$$

Suppose the numbering of the states has been made so that W_n increases with n, then he takes as the charge density associated with the nth state the following group from the double array:

$$\rho_n = \rho_{nn} + \sum_{m=0}^{n-1} (\rho_{mn} + \rho_{nm}).$$

This makes the charge density associated with the nth state contain terms which will make the atom, while in the nth state, radiate *at once* the frequencies corresponding to *all* of the lower energy levels to which, according to the old view, it might jump. This view seems rather unsatisfactory.

In discussing the effective electric currents due to the atom, proceed in the same way as with the charge densities. The current expression of Sec. **10** formed with the general solution which is the sum of various separate solutions will also lead to expressions which are constant and which can be associated with the properties of the atoms in individual stationary states and other terms which vary harmonically with the time, with frequencies equal to the spectral-line frequencies.

Probably the best interpretation of Ψ in the radiation problem, as well as in others, is that the effective charge densities determine not what every atom must do in a fully determinate way, but only the probability that it will do certain things.

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[1] Klein, *Zeits. für Phys.*, **41,** 407 (1927).

This interpretation was first introduced by Born in his studies of the wave mechanical treatment of collision problems and is the one which fits in with the modern ideas connected with the uncertainty principle.[1]

For the purposes of this chapter the external electromagnetic field of an atom will be computed from the terms in the general expression for the effective charge and current density distribution. The terms of the form $\psi_n\bar{\psi}_n$ will then be associated with the behavior of the atom while in the nth stationary state and terms of the form $(\psi_n\bar{\psi}_m + \psi_n\bar{\psi}_m)$ with the behavior during a transition from the nth to the mth state.

30. Classical Radiation from Oscillating Charges.—Since the radiation from an oscillator is usually treated, following Hertz, by studying the field of an infinitesimal dipole which varies harmonically with the time, it is necessary here that the field of a varying volume distribution of charge and currents be considered from the standpoint of the classical electromagnetic theory. Suppose the charges and currents are confined to within a sphere of radius, a, about the origin. Let the charge and current densities be given by the real parts of the expressions $\rho(x, y, z)$ $e^{2\pi i\nu t}$ and $\boldsymbol{i}(x, y, z)$ $e^{2\pi i\nu t}$ where ρ and $\boldsymbol{i}$ are connected by the equation of continuity,

$$2\pi i\frac{\nu}{c}\rho(x, y, z) + \operatorname{div}\boldsymbol{i} = 0.$$

The fields may be most conveniently found from the potentials $\boldsymbol{A}$ and φ by the relations,

$$\boldsymbol{H} = \operatorname{curl}\boldsymbol{A}$$
$$\boldsymbol{E} = -\operatorname{grad}\varphi - \frac{1}{c}\frac{\partial\boldsymbol{A}}{\partial t},$$

after the potentials have been computed by the formulas,

$$\varphi(x'y'z', t') = \int\frac{\rho(x, y, z)e^{2\pi i\nu t}}{R}\,dxdydz, \tag{30.1}$$

$$\boldsymbol{A}(x'y'z', t') = \int\frac{\boldsymbol{i}(x, y, z)e^{2\pi i\nu t}}{R}\,dxdydz, \tag{30.2}$$

in which t' and t are connected by the retardation relation

$$t' = t - \frac{1}{c}R,$$

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[1] Born, *Zeits. für Phys.*, **37,** 863 (1926) and **38,** 803 (1926).

and R is the distance from xyz to $x'y'z'$. If d is the distance of $x'y'z'$ from the origin, the field may be expressed as a series of inverse powers of d of which only the one involving d^{-1} contributes to the radiation. If a is small compared to R then one can replace R by $d - r\cos\theta$ which is correct to the first power in r/d. Moreover, if ν is small enough that c/ν is large compared to a, then a good approximation to the potentials is obtained by expanding the exponential term and retaining only the first two terms. The first of these approximations is always legitimate for one can make d as large as is necessary. The second begins to break down in the case of X-radiation, since X-ray wave lengths are of the same order of magnitude as the size of atoms. We have in the usual case, however, to retain only the terms in $1/d$ and only those that involve λ in order to get the radiation field. This means that one can replace R by d in the denominator of the integrand so that the potential expressions become

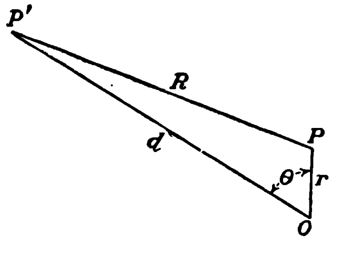

FIG. 13.

$$\varphi(x', y', z', t) = \frac{1}{d}e^{2\pi i\nu\left(t - \frac{d}{c}\right)}\int \rho(x, y, z)e^{\frac{2\pi i r\cos\theta}{\lambda}}dxdydz,$$

$$A(x', y', z', t) = \frac{1}{d}e^{2\pi i\nu\left(t - \frac{d}{c}\right)}\int i(x, y, z)e^{\frac{2\pi i r\cos\theta}{\lambda}}dxdydz.$$

If, moreover, the radius a is small compared to λ, then one can expand the exponential function and retain only the first few terms.

Since the total charge inside the sphere does not change with time, one must have

$$\int \rho dxdydz = 0,$$

so the first term vanishes in the expression for φ. It is the next term which corresponds to the so-called dipole radiation of the charges and which is the only one which need be considered if a/λ is small. It is

$$\frac{2\pi i}{\lambda}\frac{1}{d}e^{2\pi i\nu}\left(t-\frac{d}{c}\right)\int \rho(x, y, z)r\cos\theta dxdydz.$$

If $\boldsymbol{d_0}$ is a unit vector in the direction of the point $x'y'z'$, then $r\cos\theta = \boldsymbol{d_0}\cdot\boldsymbol{r}$ and if one define the electric moment of the oscillating charge as

$$\boldsymbol{M} = \int \rho(x, y, z)\,\boldsymbol{r}dxdydz, \tag{30.3}$$

then this term in the scalar potential becomes,

$$\frac{2\pi i}{\lambda d}e^{2\pi i\nu\left(t-\frac{d}{c}\right)}\boldsymbol{d}_0\cdot\boldsymbol{M}.$$

Similarly the first term in the expanded expression for A also involves $\boldsymbol{M}$, the measure of the effective dipole moment. One has

$$\begin{aligned} M_x &= \int \rho x dxdydz = i\frac{c}{2\pi\nu}\int x \operatorname{div} \boldsymbol{i}\, dxdydz \\ &= i\frac{c}{2\pi\nu}\left[\int \operatorname{div}(x\boldsymbol{i})\, dxdydz - \int \boldsymbol{i}\cdot\operatorname{grad}x\, dxdydz.\right. \end{aligned}$$

The first of these integrals must vanish for it is equal to the surface integral of the normal component of $x\boldsymbol{i}$ on the sphere enclosing the charges, while the second is equal to $\int i_x dxdydz$.

Hence the relation,

$$\int \boldsymbol{i} dxdydz = \frac{2\pi i\nu}{c}\boldsymbol{M}.$$

Therefore, the expression for the vector potential which involves the effect of the dipole moment of the charge is given by

$$A = \frac{2\pi i}{\lambda d}e^{2\pi i\nu\left(t-\frac{d}{c}\right)}\boldsymbol{M}. \tag{30.4}$$

In calculating the fields from these expressions for the potential, the possibility of the direct emission of circularly or elliptically polarized light is contained in the fact that the real and imaginary parts of the vector $\boldsymbol{M}$ need not be parallel. The electric vector will be found always to lie in the plane of $\boldsymbol{M}$ and the line joining the position in space to the origin, so that if the real and imaginary parts of M are not parallel but are, say, $\boldsymbol{M}_r$ and $\boldsymbol{M}_i$, the resultant real part

$$\boldsymbol{M}_r \cos 2\pi\nu t - \boldsymbol{M}_i \sin 2\pi\nu t,$$

will have in general an elliptic variation in space giving rise to elliptically polarized spherical waves.

It is thus seen that the main part of the radiation, if the size of the distribution is small compared to a wave length of the light, is the so-called dipole radiation and is measured entirely by the dipole moment of the oscillating charge

$$\boldsymbol{M} = \int \rho(x, y, z)\boldsymbol{r}dxdydz.$$

The average rate of radiation of energy associated with such a dipole moment the classical formula shows to be

$$I = \frac{(2\pi\nu)^4}{3c^3}\boldsymbol{M}\cdot\overline{\boldsymbol{M}}.$$

Throughout the book, unless the contrary is explicitly stated, it is supposed that only the dipole radiation is considered. Accordingly, the radiation due to a transition from state 1 to state 2 will be measured by the amplitude of the electric moment associated with that transition, *i.e.*,

$$\boldsymbol{M}_{12} = \int r(x, y, z, \cdot \cdot \cdot)(\Psi_1\overline{\Psi}_2 + \Psi_2\overline{\Psi}_1)dV. \qquad (30.5)$$

Because of their relation to the original Born-Heisenberg-Jordan matrix mechanics,[1] these quantities will be referred to as the "matrix components" of the electric moment. The "matrix" of the electric moment is simply the ensemble of all of the matrix components corresponding to all possible transitions.

It must be borne in mind, however, that although the terms in the general series beyond that corresponding to the dipole moment are very small compared to the dipole term, when the amplitude $\boldsymbol{M}_{12}$ in equation (30.5) is zero it cannot be said there is no radiation whatever until these further terms are investigated.

31. Harmonic Oscillator.—The simplest case is that of a harmonic oscillator supposed constrained to move in the x direction. In this case, the electric moment associated with a transition between states n and m is in the x direction and is equal to

$$e\int_{-\infty}^{+\infty} x\psi_n\psi_m dx$$

where the ψ_n and ψ_m are supposed to be normalized so that the total charge distribution associated with either state is e, that is,

$$e\int_{-\infty}^{+\infty} \psi^2 dx = e.$$

The calculation of the electric moment integral has already been proposed as a problem in Sec. **15** where the result is given as

$$\int_{-\infty}^{+\infty} x\psi_n\psi_m dx = \begin{cases} 0 & m \neq n \pm 1 \\ a\sqrt{\tfrac{1}{2}(n+1)} & m = n + 1 \\ a\sqrt{\tfrac{1}{2}n} & m = n - 1. \end{cases}$$

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[1] BORN, and JORDAN, *Zeits. für Phys.*, **34,** 858 (1925); BORN, JORDAN and HEISENBERG, *Zeits. für Phys.*, **35,** 557 (1926).

The vanishing, except for $m = n \pm 1$, means that the quantum number of a harmonic oscillator can only change by unity during a radiation process. From energy considerations it is known that the spontaneous jumps will all be downward, so if n is the initial number and m the final, the spontaneous transitions will be those for which $m = n - 1$. This example is quite simple owing to the fact that the wave functions are wholly real.

The intensity of radiation associated with this amplitude using the classical formula of the preceding section is then,

$$\frac{(2\pi\nu)^4}{3c^3}[2ae\sqrt{n/2}]^2 = \frac{(2\pi\nu)^4}{3c^3}(2na^2e^2), \tag{31.1}$$

the factor 2 in the brackets occurring because of the appearances of both $\psi_n\bar{\psi}_m$ and $\psi_m\bar{\psi}_n$ in the effective charge density expression. This expression is to be compared with the classical rate of radiation by an oscillator. This is simply $\frac{(2\pi\nu)^4}{3c^3}A^2e^2$ where A is the amplitude of the oscillation at the moment in question. Since it was seen in Sec. **15** that a is equal to the amplitude of the classical motion of the same oscillator when it has the energy $\frac{1}{2}h\nu$, and, since the classical amplitude is proportional to the square root of the energy, the classical amplitudes corresponding to the nth and $(n - 1)st$ energy levels are $\sqrt{2n + 1}\, a$ and $\sqrt{2n - 1}a$, respectively, which makes the corresponding classical rate of radiation be something between $\frac{(2\pi\nu)^4}{3c^3}(2n + 1)\, a^2e^2$, and $\frac{(2\pi\nu)^4}{3c^3}(2n - 1)a^2e^2$ which agrees, for large n, with that given by the quantum mechanical formula.

32. The Bohr Magneton.—The simplest mechanical system in which there are discrete states and for which the current expression does not vanish is the rotator with fixed axis.[1] Suppose a particle is constrained to move in a circle of radius a but with no forces acting on it. Its wave equation is then

$$\frac{d^2\psi}{d\theta^2} + \frac{8\pi^2\mu a^2}{h^2}W\psi = 0,$$

and, since the solutions must be periodic in 2π, the allowed energy levels are

$$W_m = \frac{h^2}{8\pi^2\mu a^2}m^2 \qquad m = 0, 1, 2 \cdots$$

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[1] Compare Fermi, *Nature*, **118,** 876 (1926).

and the normalized wave functions are

$$\psi = \frac{1}{\sqrt{2\pi}}e^{im\theta}, \qquad \bar{\psi} = \frac{1}{\sqrt{2\pi}}e^{-im\theta}.$$

For any state the charge density (charge per unit angle, here) comes out to be simply $e/2\pi$, that is, the charge functions as though it were distributed uniformly over the circle. To apply the current expression the coordinate must be a length, $x = a\theta$ so that the normalized functions become $\psi = \frac{1}{\sqrt{2\pi a}} \cdot e^{im\frac{x}{a}}$ and $\bar{\psi} = \frac{1}{\sqrt{2\pi a}}e^{-im\frac{x}{a}}$. The gradient will always be directed along the circle and will be

$$\text{grad } \psi = \frac{im}{a}\psi \text{ and grad } \bar{\psi} = -\frac{im}{a}\bar{\psi}.$$

Therefore, the magnitude of the current expression associated with the mth state is

$$\begin{aligned} j &= \frac{eh}{4\pi\mu i}(\bar{\psi} \text{ grad } \psi - \psi \text{ grad } \bar{\psi}) \\ &= \frac{eh}{2\pi\mu}\frac{m}{2\pi a^2}. \end{aligned}$$

This value bears a very simple relation to what would be expected from classical mechanics. In the mth state, classically, the angular momentum is $mh/2\pi$ so the linear speed is $mh/2\pi\mu a$. The charge distribution has a linear density $e/2\pi a$ along the circle and the classical current is the product of this and the velocity, a value which agrees exactly with the magnitude of the current given by the quantum mechanical current expression.

The important external effect of this current distribution is its magnetic moment. By simple electrodynamics, a current in a small circular circuit will have a magnetic field that at some distance from itself is the same as that of a bar magnet whose moment is equal to the product of the current by the area of the circuit. The magnetic moment of the rotator in the mth state is, therefore,

$$m \cdot \frac{eh}{4\pi\mu c},$$

the c coming in to change the previous expression for current in electrostatic units to electromagnetic units, the more usual unit for magnetic moment.

It thus appears that in each state of the rotator it will have a magnetic field (except $m = 0$) which is that of a little magnet whose magnetic moment is an integral multiple of $eh/4\pi\mu c$. If the moving particle which constitutes the rotator is the electron so that e and μ are the charge and mass of the electron then this unit of magnetic moment is called the *Bohr magneton*. It will be seen later that magnetic moment, associated with the currents due to moving electrons, always occurs in integral multiples of this amount according to quantum mechanics. This result has many points of agreement with experience especially in the Stern and Gerlach experiment[1] which is a direct proof of the possession by atoms of magnetic moments of this amount.

33. Central Forces: Magnetic Field.—The result of the preceding section that the magnetic moment of a particle of charge e and mass μ moving as a rotator with fixed axis is an integral multiple of $eh/4\pi\mu c$ can be extended readily to the general case of central-force motions. For such systems the wave function is of the form

$$\psi = R_{nl}(r) \cdot \Theta_{lm}(\theta) \cdot \frac{e^{im\varphi}}{\sqrt{2\pi}}.$$

The factor depending on θ is a real function and so is that depending on the radius.

The gradient in spherical coordinates is given by

$$\text{grad}\,\psi = \boldsymbol{i}_1\frac{\partial\psi}{\partial r} + \boldsymbol{i}_2\frac{1}{r\sin\theta}\frac{\partial\psi}{\partial\varphi} + \boldsymbol{i}_3\frac{1}{r}\frac{\partial\psi}{\partial\theta},$$

in which at any point $\boldsymbol{i}_1\boldsymbol{i}_2\boldsymbol{i}_3$ are unit vectors in the directions of increasing r, φ, θ, respectively. Thus, if $R_{nl}(r)$ is real, the only component of grad ψ which is different from that of grad $\bar{\psi}$ is that in the φ-direction. Hence the current expression will all be in this direction, and its amount in electromagnetic units will be

$$\frac{eh}{4\pi^2\mu c}\frac{m}{r\sin\theta}\psi\bar{\psi}$$

in the direction of increasing φ, *i.e.*, the lines of flow are circles around the polar axis. The magnetic moment of this volume

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[1] PAULING and GOUDSMIT, "The Structure of Line Spectra," McGraw-Hill Book Company, Inc. (1929) (hereafter designated as Pauling and Goudsmit) Sec. 54.

distribution is again equal to the integral of the current in each ring of cross-section area $rd\theta dr$ multiplied by $\pi(r \sin \theta)^2$ the area of the circuit of the line of flow. That is, the total magnetic moment is

$$m\frac{eh}{4\pi\mu c}\int_0^\infty\int_0^\pi \psi\bar{\psi}r^2 \sin \theta \, dr d\theta, \tag{33.1}$$

which is equal to $\frac{eh}{4\pi\mu c}m$ since the integral appearing is simply the normalizing integral and is equal to unity. The magnetic moment is again equal to an integral number of Bohr magnetons, the axis of the magnetic moment being in the direction of the polar axis.

This result is quite in accord with the discussion of Sec. **16** on the relation of the various wave functions to the corresponding classical motions. The conclusion was that l plays the rôle of the total angular momentum (in units $h/2\pi$) and m measured the component of angular momentum in the direction of the polar axis. The factor $P_{lm}(\theta)e^{im\varphi}$ characterizes states whose classical orbits are oriented with the normals to their planes making the angle $\cos \theta = m/l$ with the polar axis but otherwise distributed uniformly with regard to φ. Magnetically, this would mean that although any one such orbit had its full magnetic moment of l Bohr magnetons, this particular function characterizes such an ensemble of orbits that the components of the magnetic moment, perpendicular to the polar axis, neutralize each other, leaving only the component along the polar axis which was given by the preceding calculation.

34. Central Forces: Selection Rules.—One of the most important characteristics of radiation from centrally symmetric models (hydrogen atom, diatomic molecule) is the fact that many of the pairs of energy levels are not connected with observed lines in the spectrum. This fact is expressed in the statement that such transitions are forbidden, and in certain so-called selection rules which tell which transitions are forbidden.[1] The simplest example of this sort occurred in Sec. **31** where it was found for the harmonic oscillator that the quantum transitions by radiation could only occur between adjacent energy levels. But the harmonic oscillator is such an idealized model that the workings of this rule are not observed in nature so the example has only theoretical interest.

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[1] PAULING and GOUDSMIT, Chap. VIII, for general discussion.

In the old quantum theory the selection rules were given theoretically, as were the approximate answers to all questions about intensities of radiation, by appeal to the correspondence principle. Here they are given at once by the use of the classical theory for the rate of radiation from the quantum mechanical charge distribution associated with the transition in question. The classical result was, that if k is the quantum number measuring the angular momentum, only transitions for which $\Delta k = \pm 1$ were allowed. If m is the quantum number which gives the orientation of the orbit, *i.e.*, the component of k which is in the direction of some fixed axis in space, then only the transitions in which $\Delta m = 0, \pm 1$ were allowed. We shall now see that these rules are given by the new methods together with additional definite information about the relative intensity of the different allowed transitions.

In any central-force field problem the normalized wave function may be written in the form

$$\psi_{nlm} = N_r \frac{1}{r} R_{nl}(r) \cdot N_\theta P_{lm}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\varphi},$$

as was found in Sec. **16.** Here N_r and N_θ stand for the factors which normalize the radial and θ-factors, respectively. For the intensity of the transition between the states (n, l, m) and (n', l', m') one needs the integral,

$$\boldsymbol{M}(n,\ l,\ m,\ n',\ l',\ m') = \int \boldsymbol{r}(\psi_{nlm}\overline{\psi}_{n'l'm'})dxdydz.$$

Using polar coordinates it is observed that the different components of the integrand can be split into factors depending separately on r, θ, and φ. The relation of x, y, z to r, θ, φ is conveniently summarized in the formulas,

$$\begin{aligned} z &= r \cos \theta \\ u = x + iy &= r \sin \theta e^{i\varphi} \\ v = x - iy &= r \sin \theta e^{-i\varphi}, \end{aligned}$$

in terms of which $\boldsymbol{r}$ is given by

$$\boldsymbol{r} = \frac{u + v}{2}\boldsymbol{i} + \frac{u - v}{2i}\boldsymbol{j} + z\boldsymbol{k},$$

so that the intensity integral is given by the consideration of the separate integrals for u, v, and z.

The triple integrals can be written as the product of three simple integrals over each coordinate. Of these, the one involving r will depend on the particular central-force field problem under consideration, while the factors depending on θ and φ will be common to all central-force field problems. It is to these latter factors that attention is now directed.

The factor for φ is the simplest of all. For z it is simply

$$\frac{1}{2\pi}\int_0^{2\pi}(e^{im\varphi}\cdot e^{-im'\varphi})d\varphi,$$

which is equal to zero, unless $m' = m$, in which case, the value is 1. The integral for the case of u is

$$\frac{1}{2\pi}\int_0^{2\pi}e^{i\varphi}e^{im\varphi}e^{-im'\varphi}d\varphi,$$

which is equal to zero unless $m' = m + 1$, the value in this case being 1. Similarly, the integral for v vanishes unless $m' = m - 1$, the value in this case being 1. This completes the deduction of the selection rule for m, for all components of the electric moment vanish if $\Delta m \neq 0, \pm 1$.

Consideration of the θ-factor yields the selection rule for l. The θ-factor integral for z is

$$N_\theta(lm)N_\theta(l'm')\int_0^{\pi}\cos\,\theta\cdot P_{lm}(\theta)P_{l'm'}(\theta)\,\sin\,\theta d\theta.$$

This needs to be evaluated only for $m = m'$, because of the selection rule for m. The evaluation is readily effected by using the recursion relation which can be derived from equations (16.7),

$$(2l + 1)\cos\,\theta\cdot P_{l,m} = (l + m)P_{l-1,m} + (l - m + 1)P_{l+1,m}.$$

Because of the orthogonality property of the $P_{lm}(\theta)$ it is then seen that the integral vanishes unless $l' = l \pm 1$.

The values are

$$\left.\begin{aligned}&\frac{N_\theta(l,\,m)}{N_\theta(l-1,\,m)}\,\frac{l+m}{2l+1}\text{ if } l' = l - 1,\\ \text{and}\quad&\\ &\frac{N_\theta(l,\,m)}{N_\theta(l+1,\,m)}\,\frac{l-m+1}{2l+1}\text{ if } l' = l + 1.\end{aligned}\right\}\tag{34.1}$$

Similarly, the θ-factor integrals for u and v require evaluation of the integrals

$$\int_0^{\pi}\sin\theta\;P_{lm}(\theta)P_{l,m+1}(\theta)\,\sin\theta\;d\theta.$$

These can be evaluated in the same way with the use of the recursion relation,

$$(2l + 1) \sin \theta \, P_{lm} = P_{l+1,\, m+1} - P_{l-1\, m+1},$$

so that again the result is evident that the integrals vanish unless $l' = l \pm 1$. The detailed calculation for this case will be left to the reader. This completes the deduction of the selection rule for l, *i.e.*, $\Delta l = \pm 1$.

35. Central Forces: Intensities.—We have now to consider the nature of the radiation from the allowed transitions. The complete calculation requires the value of the normalizing factor,

$$[N_\theta(l, m)]^{-2} = \int_0^\pi P_{lm}^2(\theta) \sin \theta d\theta = \frac{(l + m)!}{(l - m)!}\frac{2}{2l + 1}.$$

With the aid of this value, a table of the values of the nonvanishing intensity factors can be readily constructed.

The polarization of the light associated with any transition can be found by considering the preceding results. Consider first the case $\Delta m = 0$. The integrals for u and v vanish which means that the electric moment is entirely in the z direction. In Sec. **30** it was decided that the complete $\boldsymbol{M}$ to be used is

$$e\int r(\Psi_1\bar{\Psi}_2 + \Psi_2\bar{\Psi}_1)dxdydz,$$

the large Ψ's including the time factors $e^{2\pi i\nu_{12}t}$ and $e^{-2\pi i\nu_{12}t}$, respectively. For the case $\Delta m = 0$, only the z component has a value, and, since complex quantities do not occur in the r and θ factors, the complete result for $\boldsymbol{M}$ for such a transition will be just the factors arising from the r and θ integrations multiplying into

$$(e^{2\pi i\nu_{12}t} + e^{-2\pi i\nu_{12}t}) = 2 \cos 2\pi\nu_{12}t.$$

Thus, the complete result is that the transitions for which $\Delta m = 0$ will have their radiation exactly like that of a Hertz dipole whose axis is in the direction of the polar axis of the coordinate system, that is, linearly polarized with the electric vector in the meridian planes through the polar axis.

For the case $\Delta m = \pm 1$, the z component vanishes, leaving values for both the x and y components. These values are associated in such a way that the radiations are right and left circularly polarized, respectively. Consider in detail the case $\Delta m = +1$. Here one has for the u component

$$e^{2\pi i\nu_{12}t}\frac{1}{2\pi}\int_0^{2\pi} e^{-i\varphi}e^{i(m-m')\varphi}d\varphi + e^{-2\pi i\nu_{12}t}\frac{1}{2\pi}\int_0^{2\pi} e^{i\varphi}e^{i(m-m')\varphi}d\varphi$$

when the time factors are included. For $m' = m + 1$, the second of these vanishes and the first has the value $e^{2\pi i\nu_{12}t}$. Similarly, for the v component, the complete φ factor with the time factors is,

$$e^{2\pi i\nu_{12}t}\frac{1}{2\pi}\int_0^{2\pi} e^{-i\varphi}e^{i(m-m')\varphi}d\varphi + e^{-2\pi i\nu_{12}t}\frac{1}{2\pi}\int_0^{2\pi} e^{-i\varphi}e^{-i(m-m')\varphi}d\varphi$$

so that for $m' = m + 1$, the first term vanishes, and the second has the value $e^{-2\pi i\nu_{12}t}$. The x component of the electric vector thus has the time variation of $\frac{u+v}{2}$ or $\cos 2\pi\nu_{12}t$, while the y component varies as $\frac{u-v}{2i}$ or $\sin 2\pi\nu_{12}t$. This result means that in a transition, $\Delta m = +1$, there is oscillating electric moment in which there is a definite phase relation between the x and y components. Viewed from the direction of positive z, the resultant electric moment will appear as constant in amount but revolving counterclockwise with frequency ν_{12}. Such a mode of variation of the electric vector is that which is associated on the classical theory with the emission of light that is circularly polarized when viewed in the z direction. Evidently, the case $m' = m - 1$ gives the same sort of relation between the x and y components of the electric moment except that the direction of revolution is reversed, corresponding to circular polarization in the opposite sense.

This completes the combined consideration of the φ and time factors. To summarize:

$\Delta m = 0$.—The electric moment is entirely in the z direction and the radial and θ factors have to be multiplied by $2 \cos 2\pi\nu t$ to give the magnitude of the electric moment.

$\Delta m = + 1$.—The electric moment is in the x, y plane, the x component being given by multiplying the radial and θ factors by $\cos 2\pi\nu t$, while the time factor for the y component is $\sin 2\pi\nu t$.

$\Delta m = -1$.—Like the preceding case. Here the time factor of the x component is $\cos 2\pi\nu t$, and of the y component is $-\sin 2\pi\nu t$.

We have next to consider the numerical value of the θ factors of the electric moment associated with each allowed transition. The mode of the calculation of these has been indicated in the preceding section.

The values are:

for z,

$$+i\sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}} \qquad \begin{pmatrix}\Delta l = \pm 1\\ \Delta m = 0.\end{pmatrix} \tag{35.1}$$

for u or v,

$$-i\sqrt{\frac{(l-m)(l-m')}{(2l-1)(2l+1)}} \begin{pmatrix}\Delta l = -1\\ |m'| = |m| + 1\end{pmatrix} \text{or} \begin{pmatrix}\Delta l = +1\\ |m'| = |m| - 1\end{pmatrix}. \tag{35.2}$$

for u or v,

$$+i\sqrt{\frac{(l+m)(l+m')}{(2l-1)(2l+1)}} \begin{pmatrix}\Delta l = -1\\ |m'| = |m| - 1\end{pmatrix} \text{or} \begin{pmatrix}\Delta l = +1\\ |m'| = |m| + 1\end{pmatrix}. \tag{35.3}$$

In the formulas, m and m' stand for the numerical magnitude of the m's of the initial and final states, while l stands for the larger of the two l values involved. The appearance here of the imaginary unit is without effect on the intensities.

It has already been seen (Sec. **16**) that all central-force field problems are degenerate in that the energy levels do not depend on the quantum number m. This merely expresses the obvious fact that, in the case of spherical symmetry, the energy levels do not depend on the orientation of the orbits in space. On symmetry grounds it would also be expected that the radiation of a given frequency would not show any resultant polarization in any direction. This result can be readily derived from the preceding intensity formulas, for the light from different changes of the quantum number m corresponds to different kinds of polarization, although all such different transitions have the same emitted frequency since the energy levels are independent of m.

The total intensity of a line, as observed experimentally, is proportional both to the number of atoms in the excited state and to the probability of the transition in question, the probability measuring the frequency with which the transition happens. If the emitting model has spherical symmetry, the intensity in any given line is really the sum of the intensities due to a number of different transitions for which the quantum numbers n and l (which determine the energy levels) are the same but for which the m's are different. In order to get unpolarized light one sees, therefore, that the spherical symmetry of the situation must extend to the means by which the atoms are excited. If the atoms are put in the excited state by some means which puts the atoms more frequently into a state of one particular value of m, this represents a deviation from complete spherical symmetry. Therefore, we suppose that the conditions are such that equal numbers of atoms are put into all of the states associated with the same initial energy level but having different values of m. The different possible transitions which give rise to the total intensity of a line are supposed to happen quite independently, so that to find the total intensity, the sum of the separate *intensities* must be taken rather than of the separate amplitudes, as when dealing with coherent radiation.

It will suffice to consider the radiation in the x direction in order to show that the resultant radiation is unpolarized. In this direction, the radiation is that from the y and z components of the electric moment. Also, it will be sufficient to consider a transition in which $\Delta l = -1$, the other change of l behaving similarly. The total intensity of light polarized in the z direction is that corresponding to the $\Delta m = 0$ transitions. The intensity is given by

$$\frac{4}{(2l-1)(2l+1)} \sum_{m=-(l-1)}^{m=l-1} (l-m)(l+m).$$

Using the formula,

$$\sum_{m=-a}^{+a} m^2 = \tfrac{1}{3}a(a+1)(2a+1)$$

this becomes simply, $\frac{4}{3}l$.

The total intensity of light polarized in the y direction is the sum of that coming from the $|m'| = |m| + 1$ and from the $|m'| = |m| - 1$ transitions. Using the formulas this amounts to,

$$\frac{2}{(2l-1)(2l+1)}\left\{ \sum_{m=0}^{l-2} (l-m)(l-m-1) + \sum_{m=1}^{l} (l+m)(l+m-1) \right\}.$$

The two sums can be rearranged in the form.

$$\sum_{m=1}^{2l-1} n(n+1) = \tfrac{1}{3}(2l-1)(2l)(2l+1),$$

so that the total intensity of the light polarized in the y direction comes out proportional to $\frac{4}{3}l$ and is, therefore, of the same intensity as that polarized in the z direction.

To conclude, it is interesting to observe that in Sec. **16** the forms $P_{lm}(\theta) \cdot \cos m\varphi$ or $P_{lm}(\theta) \sin m\varphi$ might, with equal right, have been taken as fundamental solutions of the wave equation for the θ and φ factors. If this had been done, the appearance of the preceding intensity calculations would have been changed considerably. But the selection rules and the intensity formulas would have been just the same. The only thing that would be changed would be the discussion concerning the state of polarization of the light emitted in such transitions as $\Delta m = \pm 1$. In getting the selection rule for m, it is now more convenient to deal directly with x and y, expressed in polar coordinates. One has now to distinguish moreover, between transitions involving the two different functions associated with the same value of m. The detailed discussion of these formulas for this case and their comparison with those given by the complex exponential function will be left to the reader.

This equivalence of the trigonometric form and the complex exponential form touches on a point of fundamental importance in quantum mechanics. This is that in dealing with degenerate systems one can work with any set of linear combinations of the wave functions connected with the same energy level so long as the linear combinations are orthogonal to each other. The importance of the point will be developed later in connection especially with the spectrum of atoms involving more than one electron.

In the above rules, that the radiation intensity is zero for $\Delta m \neq$, 0, ± 1 $\Delta l \neq \pm 1$, the reservation made at the end of Sec. **30** must be remembered. A more correct statement of the selection rules would be that when the dipole moment is zero, the probability of transition, due to the further terms in the series (called quadrupole, etc.), is so small that very few atoms in gas at the usual pressures have time enough between collisions to perform a "forbidden" transition. In nebulæ, however, where atoms travel several days between collisions, radiation has actually been observed corresponding to transitions for which the dipole moment is zero. An evaluation of the quadrupole radiation from hydrogen atoms has recently been carried out by Rubinowicz.[1]

36. Hydrogen Atom Intensities.—The complete calculation of the relative intensities of various transitions in a model governed by central forces requires the evaluation of the integral

$$\int_0^\infty rR_{nl}(r)R_{n'l'}(r)r^2dr,$$

where the $R_{nl}(r)$ are the radial factors of the wave functions for the initial and final states, respectively. Thus for the relative intensities of the different lines in a spectral series due to hydrogen, one needs to calculate these integrals using the known normalized forms for the wave functions of Sec. **20.** As the actual integration calls for quite a lengthy calculation, the details will not be reproduced here.

It will suffice to remark that the calculation differs from those of the preceding sections in that, if n' differs from n, there exists no formula relating $rR_{n'l'}$ to a few terms involving constant coefficients multiplying into R_n functions for various values of n. Instead, the expression involves an infinite series of such functions ranging over all values of n. This is as it should be; otherwise, one would be led to a selection rule in the total quantum number, contrary to the experimental evidence.

For the Lyman series, the integrals in which $n' = 1$, $l' = 0$ for the final state, and $l = 1$ for the initial state, while n takes on different values for the various members of the series are to be computed. Omitting a factor of proportionality, the result for the relative *intensities* (square of the integral) comes out

$$\frac{(n-1)^{2n-1}}{n(n+1)^{2n+1}}.$$

For large n this becomes asymptotically $1/n^3$, a result which had been obtained for all the series by the application of Bohr's correspondence principle before the development of quantum mechanics.

The Balmer series in hydrogen is really the superposition of three distinct spectral series corresponding, respectively, to the changes in l: $1 \rightarrow 0$, $0 \rightarrow 1$, $2 \rightarrow 1$, that is, $P \rightarrow S$, $S \rightarrow P$,

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[1] Rubinowicz, *Phys. Zeits.*, **29**, 817 (1928).

$D \rightarrow P$ series in the usual spectroscopic notation. As it may be desired to use the hydrogen-intensity formulas for approximate comparison with the alkali metals, it is better to give the theoretical intensities separately. The results are

$$\begin{array}{ll} P \rightarrow S & \dfrac{4(n^2-1)(n-2)^{2n-2}}{n(n+2)^{2n+2}}, \\ D \rightarrow P & \dfrac{32n(n^2-1)(n-2)^{2n-3}}{3(n+2)^{2n+3}}, \\ S \rightarrow P & \dfrac{n(n-2)^{2n-2}}{3(n+2)^{2n+2}}, \end{array}$$

where n is the total quantum number of the initial state. The sum of these three series, giving the total intensity of the Balmer lines is

$$\frac{(n-2)^{2n-3}}{n(n+2)^{2n+3}}(15n^4 - 32n^2 + 16).$$

There is apparently no experimental data in existence for hydrogen with which these formulas may be compared. Trumpy has made measurements of absorption of various lines in the vapor of the alkali metals which have been compared with the theory by Kupper on the assumption that the hydrogen-like wave functions are applicable, with fairly satisfactory results.[1]

37. The Radiation Problem.—To conclude this chapter it is necessary to point out that the simple standpoint adopted at the beginning in no way corresponds to an adequate treatment of the problem of emission of radiation by atoms. From Einstein's theory of the black-body radiation, it is known that this cannot be treated as a simple continuous classical process arising from oscillating charge distributions as here contemplated. Instead, it is necessary to distinguish two types of emission process as happening.

According to Einstein, there is a certain probability that an atom in an excited state will radiate by the emission of a quantum of energy in time dt, which is dependent only on the nature of the atom. This is known as the spontaneous emission probability coefficient for the transition in question. In addition, in order to get the Planck black-body radiation law, it is necessary to assume that there is another probability of emission which is

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[1] KUPPER, *Ann. der Phys.*, **86**, 511 (1928), TRUMPY, *Zeits. für Phys.*, **42**, 327 (1927) and **44**, 575 (1927).

proportional to the existing density of radiation of the frequency involved in the transition. As to absorption probabilities there can be no probability of absorption which is independent of the radiation density, since the probability must be zero if the radiation density is zero. Considering the interaction of the radiation of frequency ν, with an atom which has two energy levels so spaced that it is capable of emitting and absorbing this frequency, one has for the number of absorption acts per second,

$$N_1 B_{12} \rho(\nu),$$

where N_1 is the number of atoms in the first state, and B_{12} is a constant dependent on the nature of the atom. Evidently, if one set simply $N_2 A_{21}$ for the number of emission acts per second, and then equated the two to express the existence of the equilibrium, he would not get A_{21} and B_{21} to be constants and at the same time have $N_1/N_2 = e^{h\nu/kT}$, as it should by the Maxwell-Boltzmann law, and also have the Planck formula holding for $\rho(\nu)$. To avoid this difficulty, Einstein sets the number of emission acts proportional to

$$N_2[A_{21} + B_{21}\,\rho(\nu)].$$

Equating the two rates and solving for $\rho(\nu)$,

one has

$$\rho(\nu) = \frac{A_{21}/B_{12}}{\dfrac{N_1}{N_2} - \dfrac{B_{21}}{B_{12}}},$$

which leads to the Planck formula, if

$$\frac{A_{21}}{B_{12}} = \frac{8\pi h\nu^3}{c^3} \text{ and } \frac{B_{21}}{B_{12}} = 1,$$

in view of the fact that

$$N_1/N_2 = e^{h\nu/kT}.$$

In this way, the necessity of the two types of emission process is seen. A satisfactory theory of the interaction between radiation and matter must give a complete account of the two kinds of emission and the quantitative relations of the different probability coefficients involved. Plainly, such a result is quite impossible of attainment from the standpoint of the preceding sections. The next development in the treatment of the problem is to study the effect on the atom of a perturbation by an incident light wave. This calls for a knowledge of the perturbation theory and will be put off until Chap. VII.

The fuller treatment will show, however, that the probability coefficients are measured by the square of the matrix components of the electric moment for the transition in question, and, thus, assures the validity of the results of this chapter for relative intensities, even though the phenomenon is not as simple as Sec. **29** seems to imply.

CHAPTER IV

APPROXIMATE METHODS OF HANDLING THE WAVE EQUATION

PERTURBATION THEORY

Now that it has been seen, in a number of instances, how the Schrödinger wave equation provides the quantization of the energy levels, it is important to study approximate methods of solving the equation. By such arguments one can see the relation of the new method to the old Bohr-Sommerfeld rules for quantization. Also, by the development of a rational perturbation theory, the scope of important physical problems to which the wave equation is applied can be greatly extended.

38. Bohr-Sommerfeld Quantization.—Let x be the coordinate of a mass μ free to move in a straight line under forces given by the potential energy function $V(x)$. Then the wave equation can be written

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2 p^2}{h^2}\psi = 0,$$

in which p is the amount of momentum which the particle would have classically at the position x, *i.e.*,

$$\frac{1}{2\mu}p^2 + V(x) = W,$$

where W is the total energy of the motion. We first remark the similarity of this equation to that satisfied by the exponential function. If p^2 is positive, the equation resembles that satisfied by $\begin{smallmatrix}\cos\\ \sin\end{smallmatrix} \frac{2\pi p}{h}x$, and the solution is expected to be oscillatory in character. In fact, if p is practically constant over a distance h/p, it is expected that this will be a good approximation to the true solution. If p^2 is negative, then ip is real, the equation is like that satisfied by $e^{\pm\frac{2\pi ipx}{h}}$ and a non-oscillatory behavior of the solution in such a region is to be expected.

The region of x values, in which p^2 is positive, is that in which p has a real value and so is the region in which the particle moves classically. It is the region in which the potential energy is less than the total energy. The situation is illustrated in the figure. Classically, the motion is confined to $x_1 < x < x_2$. In this same range the wave function shows the oscillations and dies off rapidly outside of this range ($x < x_1$ or $x > x_2$), provided the value of W is really one for which the wave equation possesses an admissible solution.

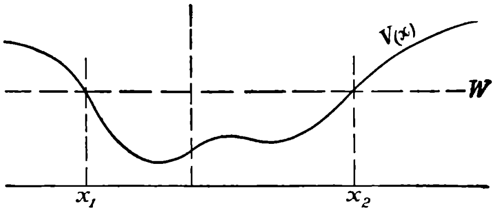

FIG. 14.—A potential energy function $V(x)$, with an allowed energy level W.

An approximate solution, valid inside the limits $x_1 < x < x_2$ and not too near the end points, may be obtained by writing

$$\psi = e^{2\pi i S(x)/h}$$

and regarding $S(x)$ as developed in powers of $h/2\pi$,

$$S(x) = S_0(x) + \frac{h}{2\pi}S_1(x) + \left(\frac{h}{2\pi}\right)^2 S_2(x) + \cdot\cdot\cdot$$

Substituting this form in the equation and equating successive powers of $h/2\pi$ to zero,

$$S_0'(x) = \pm p \text{ or } S_0(x) = \pm\int_{x_1}^{x} pdx + C$$

$$S_1' = \frac{i}{2}\frac{S_0''}{S_0'}, \text{ or } S_1 = \frac{i}{2}\log p + \text{constant.}$$

Neglecting the higher powers of h, this gives

$$\psi \sim \frac{1}{\sqrt{p}}e^{\pm\frac{2\pi i}{h}\int pdx}$$

suppressing the integration constants for simplicity. This dependence of the amplitude of ψ on x through $1/\sqrt{p}$ is the generalization of a result already noticed in the cases of the falling particle and the harmonic oscillator (Secs. **14** and **15**). It makes ψ^2 vary as $1/p$, which gives just the classical estimate of the relative probability of being found in various parts of the orbit.

But this approximation contains no hint of quantization. That step is made when the behavior at the turning points x_1

and x_2 is considered more closely. The approximation is obviously not valid here. An approximation that is good in the neighborhood of each turning point can be gotten by writing $(x - x_1)V'(x_1)$ for $V(x)$ in this neighborhood. This is equivalent to treating the particle like a freely falling particle in the neighborhood of the turning point. For $V'(x_1)$ and $V'(x_2)$, write $-k_1$ and k_2, respectively, where k_1 and k_2 are positive. Then, in the neighborhood of $x = x_1$, one has (from equation (14.2))

$$\psi \sim \sqrt{x - x_1}\, J_{1/3}\left[\left(\frac{x - x_1}{a_1}\right)^{3/2}\right],$$

in which $a_1 = \sqrt[3]{\dfrac{9h^2}{32\pi^2\mu k_1}}$ and in the neighborhood of $x = x_2$, similarly,

$$\psi \sim \sqrt{x_2 - x}\, J_{1/3}\left[\left(\frac{x_2 - x}{a_2}\right)^{3/2}\right].$$

These solutions die off rapidly to zero for $x < x_1$ or $x > x_2$, respectively. Moreover, they are finite at $x = x_1$ and $x = x_2$. In case, therefore, matters can be so arranged that the approximation valid inside of $x_1 < x < x_2$ joins on continuously with these functions for the two turning-point neighborhoods, an approximate solution will have been found that is finite everywhere. The smooth joining of these functions introduces the quantization.

For values of $(x - x_1)$, large compared to a_1, the asymptotic expansion

$$\psi \sim \frac{1}{\sqrt[4]{x - x_1}} \cos\left[\left(\frac{x - x_1}{a_1}\right)^{3/2} - \frac{5\pi}{12}\right]$$

can be used. In the same neighborhood the approximation valid inside of $x_1 < x < x_2$, can be written

$$\frac{1}{\sqrt{p}} \cos\left(\frac{2\pi}{h}\int_{x_1}^{x} p\,dx + C\right),$$

because of the ambiguous sign in the exponential function. For x near x_1 (but not too near) p can be replaced by $\sqrt{2\mu k_1}\,\sqrt{x - x_1}$ and for the argument of the cosine function,

$$\frac{2\pi}{h}\int_{x_1}^{x} p\,dx = \frac{4\pi\sqrt{2\mu k_1}}{3h}(x - x_1)^{3/2} \text{ is obtained,}$$

so that the two expressions will join on smoothly if C is set equal to $-\frac{5\pi}{12}$. This choice of C obviously implies no restriction on W. We have now to adjust matters so that there is a smooth joining of the two functions near the other turning point. Near $x = x_2$ the argument of the cosine function becomes

$$\left(\frac{2\pi}{h}\int_{x_1}^{x_2} pdx - \frac{2\pi}{h}\int_{x}^{x_2} pdx - \frac{5\pi}{12}\right).$$

A repetition of the preceding steps shows that the latter two terms here suffice to make the function vary with x in the same way as does the Bessel function form at this turning point, provided that the cosine factors are in phase. Since the sign of the two functions being joined together does not matter, the phase relations will be favorable if

$$\frac{2\pi}{h}\int_{x_1}^{x_2} pdx = m\pi,$$

where m is an integer.

This corresponds to

$$\int pdx = mh$$

where the integration is extended over a complete period of the motion. In other words, the requirement that the approximation in the central range fit on smoothly with both of the turning-point approximations requires that the allowed energy levels be chosen, approximately, according to the old rule of Bohr and Sommerfeld.

Approximate treatments of the wave equation along the lines of this section have been given by Kramers, Wentzel, and Brillouin.[1]

39. Several Degrees of Freedom.—Similar relations hold in the case of problems having more than one degree of freedom, although it is not easy to carry through the details of the approximations in which the quantization is effected by considering the special behavior at the turning points. The development of the approximate form of solution valid away from the turning points is interesting in this case, and brings out some important relations between the laws of classical mechanics and of geometrical optics. For simplicity, it will be supposed that the

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[1] Kramers, *Zeits. für Phys.*, **39**, 829 (1926), Wentzel, *Zeits. für Phys.*, **38**, 518 (1926), Brillouin, *Jour. de Physique*, **7**, 353 (1926).

problem is that of one particle moving in the field of force described by the potential energy function $V(x, y, z)$, so that the wave equation is

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}(W - V)\psi = 0,$$

The substitution,

$$\psi = e^{\frac{2\pi i}{h}S(x, y, z)},$$

supposing S developed in powers of h, is

$$S = S_0 + \frac{h}{2\pi}S_1 + \left(\frac{h}{2\pi}\right)^2 S_2 + \cdot \cdot \cdot$$

where S_0, S_1, S_2, etc. are functions of position, leads to these equations for determining the first two of the successive approximations,

$$(\text{grad } S_0)^2 = 2\mu[W - V(x, y, z)]$$
$$2 \text{ grad } S_0 \cdot \text{grad } S_1 - i\Delta S_0 = 0.$$

The first equation, that for S_0, is just the Hamilton-Jacobi equation of the same problem when treated according to the classical mechanics, *i.e.*,

$$\frac{1}{2\mu}\left[\left(\frac{\partial S}{\partial x}\right)^2 + \left(\frac{\partial S}{\partial y}\right)^2 + \left(\frac{\partial S}{\partial z}\right)^2\right] + V(x, y, z) = W.$$

In classical mechanics the momentum vector p is related to S by the formula

$$p = \text{grad } S,$$

so that all of the possible directions of motion cut perpendicularly across the family of surfaces,

$$S(x, y, z) = \text{constant}.$$

These connections point the way to a fundamental analogy between mechanics and optics. The surfaces, $S(x, y, z) =$ constant, play the rôle of the wave fronts in wave propagation, and the orbital paths, everywhere normal to these surfaces, play the rôle of the light rays. Looked at from this point of view, the mathematical theory of a dynamical problem is closely related to that of the propagation of waves in an inhomogeneous medium. This relation is just an approximate one, for it is S_0 and not S

that satisfies the Hamilton-Jacobi equation of classical mechanics. If the universal constant h is thought of as variable, then $S \rightarrow S_0$ as $h \rightarrow 0$, the connection becomes increasingly accurate as $h \rightarrow 0$. Another way of putting the same result, recalling that h measures the de Broglie wave length, is to say that the connection of the new wave function with the old becomes increasingly precise as the wave length tends to zero.

Now in optics the existence of a finite wave length is just what gives rise to diffraction effects or deviations from the laws of geometrical optics. In the same sense it is to be recognized that in quantum mechanics it is the existence of a finite value of the de Broglie wave length which gives rise to phenomena deviating from those of the classical mechanics.[1]

The approximate form used here is only valid well inside the limits of the classical motion, *.e.*, $W - V(x) > 0$. Here, as in the one-degree-of-freedom problem, special consideration of phenomena at turning points is needed in order to preserve the finiteness of ψ and this, in turn, brings in the quantization of the energy levels.

The reader will find it of interest to show that the equation for S_1 gives the variation of the amplitude of the ψ function with position equal to $1/\sqrt{p}$ just as in the case of one degree of freedom. It is also instructive to examine the current density expression of Sec. **10** in its relation to the approximate solution used in this paragraph.

40. Perturbation Theory.—A most important kind of approximation method is that by which the solution of a wave equation can be found, approximately, from the known solution of a similar problem. This method, known as the "perturbation theory," is of considerable importance in quantum mechanics.[2]

In applying the perturbation theory to a particular problem, some other problem, for which the solution is known and which has a potential energy function as much like the given one as possible, is decided upon. This substitute problem whose solution is known is referred to as the "unperturbed" problem. The difference between the potential energy functions of the actual problem and the substitute is then regarded as the "perturbation" and an attempt is then made to alter the solution of the substitute

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[1] The subject matter of this section has been considered in more detail by VAN VLECK, *Proc.* Nat. Acad. Sci., **14**, 178 (1928).

[2] SCHRÖDINGER, *Ann. der Phys.*, **80**, 437 (1926).

problem in such a way that it gives, fairly well, the solution of the actual problem.

The method is, of course, most successful when it is possible to choose, as the "unperturbed" starting point, a problem which is very much like that of the actual problem. Thus for the theory of the Stark effect in hydrogen, the applied electric fields are always very small compared to the force with which the nucleus attracts the electron. Therefore, if one chooses for the unperturbed system the hydrogen atom in no field, the effect of the field can then be taken into account easily by the perturbation theory. On the other hand, in trying to get at the normal state of helium, the repulsion of the two electrons might first be neglected to get a starting problem of known solution. But now the perturbation is quite a large one since the repulsive force between the two electrons is of the same order of magnitude as the attraction of either one to the nucleus. In such a case, the perturbation method is not so accurate.

Suppose the problem is one for which the potential energy function contains a parameter α, as well as depending on the coordinates, $x_1x_2 \cdots x_f$. In what follows, dependence on all the x's and on α will be symbolized by writing $V(x, \alpha)$ for the potential energy. Then the wave equation is

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}[(W - V(x, \alpha)]\psi = 0.$$

The boundary-value problem associated with this equation determines energy levels which depend on the value of the parameter α. Let n stand, shortly, for all the integers which label a particular state, then the energy levels and characteristic functions will be denoted by $W(n, \alpha)$ and $\psi(n, \alpha, x)$.

If one assumes that these are continuous functions of the parameter, at least in the neighborhood of α_0, then they can be expanded in power series,

$$\begin{aligned} W(n, \alpha) &= W_0(n, \alpha_0) + (\alpha - \alpha_0)W_1(n, \alpha_0) \\ &\qquad + (\alpha - \alpha_0)^2 W_2(n, \alpha_0) + \cdots \\ \psi(n, \alpha, x) &= \psi_0(n, \alpha_0, x) + (\alpha - \alpha_0)\psi_1(n, \alpha_0, x) \\ &\qquad + (\alpha - \alpha_0)^2\psi_2(n, \alpha_0, x) + \cdots \end{aligned}$$

The problem of the perturbation theory is to find expressions for the W_1, W_2, etc. and the ψ_1, ψ_2, etc. in terms of the potential energy function and the $\psi_0(n, \alpha_0, x)$. The importance of being able to do this lies in the fact that the problem may be soluble by exact methods for some particular value of α, and not for the neighboring values. Then the perturbation theory enables one to find the energy levels and characteristic functions for values of α in the neighborhood of this particular value.

To evaluate the coefficients, $W_1, W_2, \cdots \psi_1, \psi_2, \cdots$ etc., one needs first to expand the potential energy function in powers of $(\alpha - \alpha_0)$, say

$$V(x, \alpha) = V_0(x, \alpha_0) + (\alpha - \alpha_0)V_1(x, \alpha_0) + (\alpha - \alpha_0)^2V_2(x, \alpha_0) + \cdots,$$

where, of course, the functions V_1, V_2, etc. are known, since V is known. One substitutes this expansion and the assumed expansions for W and ψ in the wave equation and arranges by powers of $(\alpha - \alpha_0)$. If the wave equation is to be satisfied identically in α, the coefficient of each power must vanish. This process gives the following series of equations

$$\begin{aligned} \Delta\psi_0 + \frac{8\pi^2\mu}{h^2}(W_0 - V_0)\psi_0 &= 0, \qquad (40.1a)\\ \Delta\psi_1 + \frac{8\pi^2\mu}{h^2}(W_0 - V_0)\psi_1 &= -\frac{8\pi^2\mu}{h^2}(W_1 - V_1)\psi_0\\ \Delta\psi_k + \frac{8\pi^2\mu}{h^2}(W_0 - V_0)\psi_k &= -\frac{8\pi^2\mu}{h^2}\sum_{i=0}^{k-1}(W_{k-i} - V_{k-i})\psi_i. \end{aligned}$$

The first of these is satisfied by the definition of W_0 and ψ_0. The others are all inhomogenous equations, since their right-hand members are known functions if the equations are considered successively in the order written down.

The second equation of (40.1a) can be written

$$\left[\Delta - \frac{8\pi^2\mu}{h^2}V_0\right]\psi_1(n\alpha_0x) + \frac{8\pi^2\mu}{h^2}W_0(n\alpha_0)\psi_1(n\alpha_0x) = -\frac{8\pi^2\mu}{h^2}[W_1(n\alpha_0) - V_1]\psi_0(n\alpha_0x). \qquad (40.1b)$$

Since the known functions $\psi_0(n\alpha_0x)$ are an orthogonal set, like the functions ${}^{\sin}_{\cos}(nx)$, the unknown function $\psi_1(n\alpha_0x)$ can always be expressed by a series

$$\psi_1(n\alpha_0x) = \sum_{\tau=1}^{\infty} A^1{}_{n\tau}\psi_0(\tau\alpha_0x), \qquad (40.2)$$

similarly to the expansion in a Fourier series. The coefficients $A^1_{n\tau}$ are to be determined. Substituting this series for ψ_1 in equation (40.1*b*), and using the first equation,

$$\left[\Delta - \frac{8\pi^2\mu}{h^2}V_0\right]\psi_0(\tau\alpha_0 x) = -\frac{8\pi^2\mu}{h^2}W_0(\tau\alpha_0)\psi_0(\tau\alpha_0 x),$$

we obtain,

$$\sum_{\tau=1}^{\infty}A^1_{n\tau}[W_0(n\alpha_0) - W_0(\tau\alpha_0)]\psi_0(\tau\alpha_0 x) + W_1(n\alpha_0)\psi_0(n\alpha_0 x)$$
$$= V_1\psi_0(n\alpha_0 x). \quad (40.3)$$

Now multiply the whole equation by $\bar{\psi}_0(n\alpha_0 x)$ and integrate over all space. Since the ψ_0's are normalized and are orthogonal, the integrals $\int\psi_0(\tau\alpha_0 x)\bar{\psi}(n\alpha_0 x)dx$ in the sum are all zero except when $\tau = n$. But here the factor $[W_0(n\alpha_0) - W_0(\tau\alpha_0)]$ is zero, so that the integral of the whole sum is zero, and

$$W_1\int\psi_0(n\alpha_0 x)\bar{\psi}_0(n\alpha_0 x)dx\cdot = \int V_1\psi_0(n\alpha_0 x)\bar{\psi}_0(n\alpha_0 x)dx,$$

which determines

$$W_1 = \int V_1\psi_0^2 dx, \text{ or } \int V_1\psi_0\bar{\psi}_0 dx, \quad (40.4a)$$

if the wave function is complex. Thus the linear correction to any energy level is simply equal to the average value of the linear term in the potential energy function weighted according to the value of the squared characteristic function at each place. This theorem is the quantum mechanical analogue of a similar result in classical mechanics: *The alteration of the energy of a quantum state in the first approximation is equal to the average of the perturbation potential taken over the undisturbed orbit.*

In a similar way, the same method allows the determination of any W_k in terms of the corresponding V_k and the ψ_k's of the same set of quantum numbers, n, but of lower order,

$$W_k = \int V_k\psi_0^2 dx + \sum_{i=0}^{k-1}\int(V_{k-i} - W_{k-i})\psi_i\bar{\psi}_0 dx. \quad (40.4b)$$

The problem of finding the energy levels to any degree of approximation is thus completely referred back to that of finding the various approximations to the characteristic functions.

To determine these, equation (40.3) is multiplied by $\bar{\psi}_0(m, \alpha_0, x)$ where $m \neq n$.

The resulting equation reduces to

$$A^1{}_{nm}[W_0(n,\ \alpha_0) - W_0(m,\ \alpha_0)] = \int V_1\psi_0(n,\ \alpha_0 x)\bar{\psi}_0(m,\ \alpha_0,\ x)dx. \tag{40.5a}$$

Except in case $W_0(n,\ \alpha_0) = W_0(m,\ \alpha_0)$, this equation gives a definite result for $A^1{}_{nm}$ when $n \neq m$. The equality of the energy levels, giving a zero coefficient for $A^1{}_{nm}$ always arises for $m = n$, a case which receives attention in this section. But there is an important class of mechanical problems in which there are several wave functions associated with the same energy level, so that the zero coefficient appearing for $m \neq n$ can occur. Such systems are said to be "degenerate." The perturbation theory for them will be considered in Sec. **46.**

The same procedure is used for the higher approximations to ψ. In general, let ψ_k be expanded in the series

$$\psi_k(n,\ \alpha_0,\ x) = \sum_{m=1}^{\infty} A^k{}_{nm}\psi_0(m,\ \alpha_0,\ x).$$

Proceeding exactly as before, in the equation for ψ_k, the formula, $A^k{}_{nm}[W_0(n,\ \alpha_0) - W_0(m,\ \alpha_0)]$

$$= \sum_{i=0}^{k-1} \int (V_{k-i} - W_{k-i})\psi_i(n,\ \alpha,\ x)\bar{\psi}_0(m,\ \alpha,\ x)dx \tag{40.5b}$$

is obtained, which again gives a determinate result for

$$W_0(n,\ \alpha_0) \neq W_0(m,\ \alpha_0).$$

For the case $m = n$, the preceding formulas become indeterminate. This means that the equations will be solved no matter what the values of the $A^k{}_{nn}$, but, if the ψ are to be normalized for every value of α, these $A^k{}_{nn}$ become determined. To summarize,

$$\psi(n\alpha,\ x) = \sum_m \left(\sum_k (\alpha - \alpha_0)^k A^k{}_{nm} \right) \psi_0(m, \alpha_0, x)$$

with the convention that $A^0{}_{nm} = \delta_{nm}$. Hence, the normalizing integral becomes

$$1 = \sum_k (\alpha - \alpha_0)^k \left(\sum_m \sum_{i=0}^{k} A^i{}_{nm} A_{nm}{}^{k-i} \right).$$

Equating powers of $(\alpha - \alpha_0)^k$ on both sides the series of equations

$$1 = \sum_m (A^0{}_{nm})^2 = 1$$
$$0 = \sum_m A^0{}_{nm}A^1{}_{nm} = A^1{}_{nn}$$
$$0 = \sum_m [A^0{}_{nm}A^2{}_{nm} + (A^1{}_{nm})^2] \text{ results, } i.e., A^2{}_{nn} = -\sum_m (A^1{}_{nm})^2 \text{ etc.,} \tag{40.6}$$

which serve to determine all of the $A^k{}_{nn}$.

With this, the formal problem is completely solved since expressions for the coefficients of all powers of $(\alpha - \alpha_0)$, in the expansions both of W and of ψ, have been given explicitly in terms of known quantities. When the assertion was made that the equations for the A_{km} determine all of these, except for $m = n$, the assumption was tacitly made, of course, that all the different states have unequal values of the energy. This is not always the case. Systems in which several distinct states (having different characteristic functions) have the same energy levels are called "degenerate systems," as in the old quantum theory. The special features of the perturbation theory for them gives rise to some of the most important results of quantum mechanics. Consideration of degenerate systems is reserved for Sec. **46.**

From the practical point of view, there has been such a piling of infinite series on infinite series that it has not, thus far, proved feasible to apply it in any important cases beyond the terms in W_2 and ψ_1. For most cases, fortunately, these are sufficient; in fact, in many cases, even the linear terms are sufficient. From the theoretical point of view, there seems to have been thus far no investigation of the range of values of $(\alpha - \alpha_0)$ over which the process converges.

41. A Simple Example.—It is perhaps worth while to work through an example in which the $V(x, \alpha_0)$ is such that the solution can be found for all values of α by exact methods. Suppose there is just one coordinate x, then such an example is provided by what one might call the Stark effect of the harmonic oscillator. For a harmonic oscillator, the potential energy function is $\frac{1}{2}kx^2$. Now, if a constant force of amount $k\alpha$ urges the particle toward positive x, the potential energy function becomes

$$\begin{aligned} V(x, \alpha) &= \tfrac{1}{2}kx^2 - k\alpha x \\ &= \frac{1}{2}k(x - \alpha)^2 - \frac{k}{2}(\alpha)^2. \end{aligned}$$

From this it is clear that the effect of the field is to lower the value of the potential energy minimum by the amount $\frac{k}{2}(\alpha)^2$ and to shift the coordinate of the minimum from $x = 0$ to $x = \alpha$. It is evident from the results of Sec. **15**, the solution for any value of α will be

$$\psi(n, \alpha, x) = N(n)\cdot e^{-\frac{(x-\alpha)^2}{2a^2}} H_n\left(\frac{x-\alpha}{a}\right), \tag{41.1}$$

and,

$$W(n, \alpha, x) = \left(n + \frac{1}{2}\right)h\omega - \frac{k}{2}\alpha^2,$$

where $N(n)$ is written for the normalizing factor.

Suppose $\alpha_0 = 0$. Recognizing that the expansion in powers of α could be obtained as a Maclaurin's expansion of ψ and W, if these are known for all α

$$W_1 = 0; \quad W_2 = -1; \quad W_3, W_4, \cdots = 0 \text{ is obtained}$$

and,

$$\psi_1(n, 0, x) = \frac{1}{a}\left\{\sqrt{\frac{n+1}{2}}\psi(n+1, 0, x) - \sqrt{\frac{n}{2}}\psi(n-1, 0, x)\right\}, \tag{41.2}$$

making use of the recursion properties of the H_n, as given in Sec. **15.** Therefore, the next derivative is,

$$\frac{\partial^2\psi}{\partial\alpha^2} = \frac{1}{2a^2}[\sqrt{(n+1)(n+2)}\psi(n+2) - (2n+1)\psi(n) + \sqrt{n(n-1)}\psi(n-2)].$$

These results, obtained by expanding the exact solution for all values of α, are now to be compared with the result of applying the perturbation theory to the problem. Here $V_1(x) = -kx$ and all the other $V_i(x)$ vanish. The term linear in the α in the nth energy level is, by the application of the method of the preceding section,

$$W_1(n) = -\int_{-\infty}^{+\infty} kx\psi^2(n, x)\,dx,$$
$$= 0$$

since ψ^2 is an even function and kx is odd, making the integrand odd. For ψ_1, by the perturbation theory, the $A^1{}_{nm}$ are next to be computed.

These are,

$$A^1{}_{nm}(n - m)h\omega = -\int kx\psi(n)\psi(m)dx.$$

The integrals on the right-hand side were calculated in Sec. **15.** Using the results there found,

$$A^1_{n,(n+1)} \cdot h\omega = ka\sqrt{\frac{n+1}{2}}$$

$$A^1_{n,(n-1)} \cdot h\omega = -ka\sqrt{\frac{n}{2}},$$

while all the others vanish.

Therefore one has

$$\psi_1(n, x) = \frac{1}{a}\left\{\sqrt{\frac{n+1}{2}}\psi_0(n+1, x) - \sqrt{\frac{n}{2}}\psi_0(n-1, x)\right\}$$

because of the relation between a and ω. This is recognized as being exactly the result given by the expansion of the exact solution, as given in equation (41.2).

Now, if the perturbation theory for W_2 is applied, the result is

$$W_2 = -\int kx\psi_1(n, x)\psi_0(n, x)dx,$$

which, when evaluated by the methods used already, leads to

$$W_2 = -1$$

which is in agreement with the result found by the direct solution.

To this degree of approximation then the perturbation theory reproduces completely the results of the direct solution.

42. Stark Effect in Hydrogen: Energies.—Let it be supposed that a uniform electric field of intensity E acts in the direction of the positive z axis, then the force on an electron is eE, in the direction of negative z and the potential energy term for this force is $+eEz$. Under these circumstances, the wave equation for the motion of an electron under the combined influence of a Coulomb force toward the origin and this uniform field is

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}\left(W + \frac{Ze^2}{r} - eEz\right)\psi = 0. \qquad (42.1)$$

Using the parabolic coordinates of Sec. **27**, the term representing the action of the field becomes, simply,

$$+eEz = +eE \cdot \tfrac{1}{2}(\xi - n).$$

According to the perturbation theory, the first-order alteration of the energy levels is found simply by averaging the perturbation term over space when it is weighted with the squared wave function. Hence, for the perturbation term, use is made of equation (27.5). The averaged energy,

$$\Delta W = \frac{eE}{8} N^2 \int_0^{2\pi}\int_0^{\infty}\int_0^{\infty} (\xi - \eta)\left(\frac{\xi\eta}{n^2a^2}\right)^m e^{-\frac{\xi+\eta}{na}}\left[L^m{}_{k_1+m}\left(\frac{\xi}{na}\right)\right]^2$$

$$\cdot\left[L^m{}_{k_2+m}\left(\frac{\eta}{na}\right)\right]^2 (\xi + \eta)d\phi d\xi d\eta$$

$$= \frac{eEna}{2}\left\{\frac{k_1!}{2n[(k_1 + m)!]^3}\int_0^{\infty} x^{m+2}e^{-x}[L^m{}_{k_1+m}(x)]^2dx\right.$$

$$\left. - \frac{k_2!}{2n[(k_1 + m)!]^3}\int_0^{\infty} y^{m+2}e^{-y}[L^m{}_{k_2+m}(y)]^2dy\right\}$$

$$= \frac{3}{2}eEna(k_1 - k_2), \quad (42.2)$$

by successive applications of equation (20.6). Since na is of the order of magnitude of the size of the orbit, the term $naeE$ is of the order of the difference in potential energy of an electron between two positions whose distance in the field is about equal to the size of the atom. The factor $(k_1 - k_2)$, in this result, expresses the effect of orientation of the orbit. A little consideration will show that those states for which $k_1 > k_2$ have greater weight on the $+z$ side of the origin. Since the force on the electron due to the field is in the $-z$ direction such orbits will have positive energy in the field in accordance with the result just derived. The expression for the alteration of the energy levels just found is identical with the one derived by Epstein, in 1916, as one of the first applications of the Bohr-Sommerfeld quantization rules after the appearance of Bohr's theory of the hydrogen atom. Its success in giving the effect of the electric field in splitting up the lines of the Balmer series as observed experimentally is therefore well-known.[1] The details of the Stark effect patterns for several lines will be considered in the next section in connection with the question of the relative intensities of the component lines.

There remains but one point in connection with the foregoing formula for the energy levels which touches on the degeneracy of the hydrogen-atom problem. In the discussion which has gone before, there has appeared no reason why we should use the unperturbed solution in parabolic coordinates instead of spherical polar coordinates. Evidently, one could also purely formally compute the mean of z weighted with respect to ψ^2 where ψ is a spherical polar form for the wave function. Such a procedure does not give the correct answer, and the special development of

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[1] Pauling and Goudsmit, Sec. **20**.

the perturbation theory for degenerate systems given in Sec. **46,** shows why. It is, therefore, to be borne in mind that the preceding discussion of the Stark effect is incomplete because it did not show which was the correct coordinate system in which to apply the perturbation theory.

43. Stark Effect in Hydrogen: Intensities.—The application of an electric field to a hydrogen atom not only alters the energy levels in accordance with the results just found but it also influences the wave function associated with each state. Just as the alteration in the energy levels is small for the fields used in experiments on the Stark effect, so also is the alteration in the wave functions small. In computing the relative intensities of the different components into which a line is split by the field, it is convenient, therefore, to neglect the alteration of the wave function produced by the field, using the unperturbed wave functions.

The calculation of the relative intensities of the lines in the Stark effect proceeds, therefore, along the same lines as the radiation intensity calculations which were made in the last chapter. Parabolic coordinates have to be used here as in the preceding section, which brings in integrals of the sort that have been considered in Sec. **36,** involving products of Laguerre polynomials of different arguments. Since the calculations, themselves, present no new features, this section will be given over to a comparison of the theoretical results with those found experimentally. What is also interesting is a comparison with the more uncertain theoretical predictions which Kramers was able to make by using the quantized orbits and Bohr's correspondence principle.

In the table the transitions are labelled by giving the quantum numbers k_1, k_2, $m + 1$ for the initial and final states:

Transition	Displacement	Experimental intensities	Correspondence principle	Quantum mechanics
111 011	2	1.0	0.21	729
102 002	3	1.1	0.26	2,304
‖201 101	4	1.2	0.71	1,681
201 011	8	. . .	0	1
Hα		3.3	1.18	4,715

Transition	Displacement	Experimental intensities	Correspondence principle	Quantum mechanics
003 002	0	2.6	2.0	4,608
111 002	0	....	0.07	882
⊥ 102 101	1	1.0	0.95	1,936
102 011	5	....	0	16
201 002	6	....	0.003	18
		3.6	3.023	
112 002	0	1.4	0	0
211 101	2	1.2	0.0004	9
?	4	1.0		
Hβ∥ 211 011	6	4.8	0.0210	81
202 002	8	9.1	0.03	384
301 101	10	11.5	0.075	361
?	(12)	1.0		
301 011	14	....	0	1
		30.0	0.1264	836
?	0	1.4		
112 011	2	3.3	0.014	72
103 002	4	12.6	0.036	384
Hβ 211 002	4	....	0.004	72
202 101	6	9.7	0.074	294
?	8	1.3		
202 011	10	1.1	0	6
301 002	12	1.0	0.0004	8
		30.4	0.1284	836
221 011	2	1.6	0.0011	15,625
212 002	5	1.5	0.0005	19,200
311 101	8	1.0	0.0016	1,521
Hγ∥ 311 011	12	2.0	0.0055	16,641
302 002	15	7.2	0.0086	115,200
401 101	18	10.8	0.0188	131,769
401 011	22	1.0	0	729
		25.1	0.0361	300,685
113 002	0	7.2	0.0041	115,200
221 002	0	....	0.0009	26,450
212 101	3	3.2	0.0032	46,128
212 011	7	1.2	0.0020	5,808
Hγ ⊥ 203 002	10	4.3	0.0072	76,800
311 002	10	....	0.0006	11,250
302 101	13	6.1	0.0877	83,232
302 011	17	1.1	0	2,592
401 002	20	1.0	0.0002	4,050
		24.1	0.1059	300,685
222 002	0	....	0	0
321 101	4	1.9	0.0001	8
321 011	8	1.2	0.0007	32
312 002	12	1.5	0.0004	72
Hδ∥ 411 101	16	1.2	0.0003	18
411 011	20	1.1	0.0020	18
402 002	24	2.8	0.0036	180
501 101	28	7.2	0.0063	242
501 011	32	1 (?)	0	2
		17.9	0.0134	572
222 011	2	1.3	0.0008	36
213 002	6	3.2	0.0013	162
321 002	6	....	0.0003	36
312 101	10	2.1	0.0011	98
Hδ ⊥ 312 011	14	1.0	0.0005	2
303 002	18	2.0	0.0024	90
411 002	18	....	0.0002	9
402 101	22	2.4	0.0050	125
402 011	26	1.3	0	5
501 002	30	1 (?)	0.00004	9
		14.3	0.01164	572

In the table data are given only for the components for which $k_1 \geq k_2$ because theory and experiment are in agreement concerning the complete symmetry of the pattern around the undisplaced line.

The table shows that either theory gives the main features of the pattern quite well although the fit in either case is not all that might be expected.

In favor of the quantum mechanics, as against the correspondence principle, estimates is that the former is a definite rule while the latter is not, and also that the former gives equality of the total intensities of the parallel and perpendicularly polarized components of each line. It has also to be borne in mind that the calculations here are based on the use of the unperturbed wave functions. It is possible that the use of the perturbed forms (that is, to the first order of approximation) would improve the agreement. But such calculations would be extremely laborious. On the other hand, the experimental difficulties in the measurement of the intensities are numerous, so that the data may not be very accurate in some cases.

Since the above was written, Foster and Chalk have published (*Proc. Roy. Soc.* **A123**, 108 (1929)) an account of their accurate measurements of relative intensities of the different Stark effect components. The results show excellent agreement with the theoretical predictions of quantum mechanics. Pauling and Goudsmit in their Sec. **20a**, show graphically this agreement.

The point is sometimes made in favor of quantum mechanics that on the old theory it was necessary to exclude, arbitrarily, the orbits corresponding to zero for the quantum number in the φ coordinate, whereas in the wave theory this is not necessary. But such an exclusion was really no different nor more arbitrary than the one which made the lowest allowed value of the total angular momentum be one instead of zero, to avoid collision between the electron and the nucleus.

44. Simple Zeeman Effect: Larmor Theorem.—By the Zeeman effect is understood the action of a magnetic field in splitting spectral lines into several components. This phenomenon has been much investigated since its discovery by P. Zeeman in the closing years of the nineteenth century. A theoretical explanation of some special instances of the effect by Lorentz, in terms of the then new electron theory, was so successful that for many years it was one of the strong supports of the electron theory.

But the general phenomenon is quite complicated and has to be explained, as is now understood, by means of models taking into account the magnetic property of the electron itself. The theory of the simple triplet, first treated by Lorentz, remains simple in the quantum mechanics. This theory is the subject of the present section.[1]

According to Lorentz' early result, each line should be split into a triplet when the emitting substance is placed in a magnetic field. The central undisplaced line is polarized in the direction of the magnetic field. The two displaced lines are displaced by equal amounts on each side of the undisplaced line, the amounts being proportional to the strength of the field. One of them exhibits right-handed circular polarization while the other shows left-handed polarization.

To treat the simple triplet by the quantum mechanics, it is assumed that a particle of mass μ and charge e, moving under the influence of a field of force given by the potential energy function $V(r, z)$ is being dealt with. It is supposed that this potential energy is independent of φ where φ is the angular coordinate in a system of cylindrical coordinates having the direction of the magnetic field for its axis. It will be further supposed that the magnetic field is constant in direction and magnitude over the space occupied by the motion of the particle, in which case, if its magnitude is H, the associated vector potential is

$$\boldsymbol{A} = \tfrac{1}{2} r H \boldsymbol{\varphi},$$

where $\boldsymbol{\varphi}$ signifies a unit vector in the direction of increasing φ. From Sec. **9**, we obtain for the wave equation of the particle under the combined action of the forces arising from $V(r, z)$ and the magnetic field,

$$\Delta\psi - \frac{4\pi i e}{hc}\boldsymbol{A}\cdot\operatorname{grad}\psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0 \tag{44.1}$$

Making use of well-known expressions for the gradient and the Laplace operator in cylindrical coordinates, this is,

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{\partial^2\psi}{\partial z^2} - \frac{2\pi i e H}{hc}\frac{\partial\psi}{\partial\varphi} + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0. \tag{44.2}$$

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[1] This problem was first treated by a somewhat different method by Epstein, *Proc.* Nat. Acad. Sci., **12,** 629 (1926).

In these equations, terms proportional to the square of the magnetic field strength have been neglected. Therefore, although the solution to be obtained is an exact one for this equation, it represents only an approximate solution of the problem.

In this equation, φ is a cyclical coordinate (Sec. **23**) so that one may make the substitution,

$$\psi = F(r, z)e^{im\varphi},$$

finding as the equation for F,

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial F}{\partial r}\right) + \frac{\partial^2 F}{\partial z^2} - \frac{m^2}{r^2}F + \frac{8\pi^2\mu}{h^2}\left[E + \frac{eHhm}{4\pi\mu c} - V\right]\cdot F = 0. \tag{44.3}$$

This equation is noteworthy in that it differs only from that in which the magnetic field is zero by a term which adds to the energy parameter. The energy levels in the magnetic field are, therefore, the same as those without the field except for this additive term. If E_0 is an energy level, corresponding to the same system in the absence of a magnetic field, then the energy levels in the presence of a magnetic field are given by,

$$E = E_0 - m\cdot\frac{h}{2\pi}\cdot\frac{eH}{2\mu c}. \tag{44.4}$$

Clearly the characteristic functions are the same for the atom in the magnetic field as in the case of the same system not in a magnetic field. Moreover, since the characteristic functions depend on m only through the $e^{im\varphi}$ factor, the selection principle for m is the same as it is in any central-force field problem (Sec. **16**). In the section on this subject it has already been seen that the polarization of the light associated with various changes in m is the same as that of the classical Lorentz theory, in agreement with experiment.

The formula for the alteration of the energy levels in the magnetic field is the same as that given by the old quantum theory and is, therefore, in agreement with experiment.[1]

Problems

1. The phase angular velocity of the characteristic functions in the φ-coordinate is

$$U = \frac{2\pi}{mh}\left(E_0 - \frac{mh}{2\pi}\frac{eH}{2\mu c}\right).$$

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[1] PAULING and GOUDSMIT, Sec. **17**.

From this expression compute the group velocity, using the ideas of Sec. **5**, and show that this group velocity is exactly equal to the classical velocity of orbital precession according to the Larmor theorem, *i.e.*, to $eH/2\mu c$.

2. Obtain the results for the simple Zeeman effect by ignoring the fact that φ remains separable even in the presence of the magnetic field, and applying the perturbation theory to the problem.

It is instructive to apply the formulas of Sec. **10** to the calculation of the current density associated with the motion of the particle in a magnetic field. In making the calculation it will be supposed that the factor $F(r, z)$ is wholly real.

The current expression,

$$\mathbf{i} = \frac{e}{2\mu}\left[\frac{h}{2\pi i}(\bar{\psi} \text{ grad } \psi - \psi \text{ grad } \bar{\psi}) - \frac{1}{c}A\rho\right],$$

gives

$$\mathbf{i} = \frac{e}{\mu}F^2(r, z)\left[\frac{mh}{2\pi}\frac{1}{r} - \frac{eH}{2c}r\right]\boldsymbol{\phi}.$$

The first part of this expression can be interpreted as the current arising from the orbital motion of the particle. Classically, the integral of angular momentum tells that the velocity at any point from the axis is inversely proportional to the distance from the axis, and it is here found that that is the way in which this term varies with r, except for the factor $F^2(r, z)$ which tells the distribution in space of the motion. The second term, on the other hand, corresponds to the current arising from the classical Larmor precession of the classical motion. It is clear that this term of the current distribution is exactly that which would arise from the rotation of the charge density distribution $F^2(r, z)$, like a rigid body, with the angular velocity $\frac{eH}{2\mu c}$.

The permanent current (*i.e.*, the first part, that independent of H) is accompanied by a magnetic moment in the direction of the magnetic field, the magnitude of which is

$$m \cdot \frac{eh}{4\pi\mu c}.$$

This expression as was seen in Sec. **32** agrees exactly with that of the old quantum theory in giving integral multiples of the Bohr magneton.

Computing similarly the magnetic moment arising from the induced currents represented by the Larmor precession, one finds this to be dependent on the characteristic function $F(r, z)$ according to the formula,

$$\frac{e^2H}{4\mu c^2}\int_0^{\infty} F^2(r, z)r^2rdrdz.$$

Problem

3. Observe that the integral in this formula can be interpreted as the quantum mechanical analogue of the mean square distance of the moving charge from the axis of coordinates, and thus that the formula is the complete analogue of the classical one for the induced magnetic moment which lies at the basis of the Langevin electronic theory of diamagnetism.

These results for the amount of the permanent magnetic moment and the induced magnetic moment find their application in the theory of the para- and diamagnetic properties of gases.

45. Normal State of Helium.—The problem of the helium atom requires the solution of the wave equation for two electrons under the influence of a nucleus and subject to their mutual repulsion. In the usual notation this becomes

$$\Delta_1\psi + \Delta_2\psi + \frac{8\pi^2\mu}{h^2}\left(W + \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}\right)\psi = 0. \qquad (45.1)$$

For helium $Z = 2$ but it is well to leave the problem general in order that the equation may be used for the stripped atoms, Li II, Be III, B IV etc. This equation has not been solved by finite methods. No transformation of coordinates is known which separates the variables and it is, therefore, necessary to discuss the equation in substantially the form given.

The difficulty has its origin in the potential energy term e^2/r_{12} which represents the interaction of the two electrons. If it were absent neither electron would be affected by the presence of the other and so each would behave in a hydrogen-like way in its relation to the nucleus. It is, therefore, natural to attempt to get some information from the equation by regarding this term in the potential energy function as a perturbation, since the problem is rigorously solved in case this term is absent. The physical problem thus presented is, of course, a purely fictitious one. We suppose that the perturbation term e^2/r_{12} is multiplied by a parameter α. The equation with $\alpha = 0$ is that for a fictitious helium atom in which the electrons do not repel each other. The true helium atom is given by the value $\alpha = 1$.

One then attempts to apply the perturbation theory to get from $\alpha = 0$ to $\alpha = 1$. What can be done in this way by a direct application of the Schrödinger method is severely limited by the fact that e^2/r_{12} is not small in its effects. The first order term of the theory, therefore, cannot be expected to be accurate and it has not hitherto been feasible to carry this method to the higher approximations.

If $\alpha = 0$, as already mentioned, each electron will have a hydrogen-like relation to the nucleus. This suggests that it will be advantageous to use the same change of units for W and for lengths as was used in equation (19.2*a*) for hydrogen,

$$W = \frac{2\pi^2\mu e^4 Z^2}{h^2}E;\ x = \frac{h^2}{8\pi^2\mu e^2 Z}x',\ \text{etc.}$$

The wave equation then becomes,

$$\Delta_1\psi + \Delta_2\psi + \left(\frac{E}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Zr_{12}}\right)\psi = 0, \qquad (45.2a)$$

where the primes on coordinates will be dropped, as, from now on, the lengths are all measured in the new units. This transformation brings out clearly the fact that the nuclear repulsion becomes relatively less important in the total value of the energy as one goes to larger values of Z. The appearance of a new letter in the equations can be avoided by regarding $1/Z$ as the perturbation parameter.

In proceeding now to the discussion of the normal state, the usual interpretation of this as being a state in which both electrons move in an orbit which has the hydrogen-like quantum numbers, $n = 1$, $l = 0$, $m = 0$, is retained. For $1/Z = 0$ the unperturbed ψ function of the problem is, therefore,

$$\psi_{100}(r_1)\cdot\psi_{100}(r_2) \qquad (45.2b)$$

where $\psi_{100}(r)$ is the normalized function for the normal state of hydrogen. The first order perturbation E_1 is, therefore, given by

$$E_1 = \int \frac{1}{r_{12}}\psi^2{}_{100}(r_1)\cdot\psi^2{}_{100}(r_2)dx_1dy_1dz_1dx_2dy_2dz_2$$

the integration extending from $-\infty$ to $+\infty$ for each of the six variables. The value of the integral turns out to be

$$E_1 = \tfrac{5}{4},$$

and, since $E_0 = -2$ for the unperturbed state, the first approximation to the total energy of the ground state of helium-like atoms is

$$W = -2RhZ^2 + \tfrac{5}{4}RhZ.$$

Subtracting the value of the energy of the ion which has accurately the hydrogen-like value $-RhZ^2$, the first order value for the ionization potential turns out to be

$$I = Rh(Z^2 - \tfrac{5}{4}Z). \tag{45.3}$$

For $Z = 2$ this amounts to $1.50Rh$. The experimental value is $1.818Rh$, so this calculation is 18 per cent below the true value.[1] The fact that the ionization potential comes out too low is readily understood. The presence of either electron tends partially to screen the other from the field of the nucleus and make it move in a larger orbit. This, in turn, makes the interaction energy smaller and hence would make the ionization potential greater.

The foregoing calculation serves merely to show that the perturbation theory works in the right direction. The unperturbed state from which we started had an ionization potential of $4Rh$, a value which is 120 per cent too large. From such a bad start it is fair to say that the first-order perturbation has done well in coming so close to the true value. To compute the second-order perturbation by this method would call for the evaluation of a large number of integrals of the interaction term multiplied by hydrogen-like ψ functions and has not been carried out.

Instead, another method of computing the lowest energy level has been carried out with results which justify the conviction that the lowest characteristic value of the wave equation for helium will agree precisely with the experimental value. This has been done by consideration of the calculus of variations rule with which the wave equation is equivalent. In Sec. **3** this rule was stated. The kinetic energy as a function of q and p, say $T(q, p)$, is taken and $\frac{h}{2\pi}\frac{\partial\psi}{\partial q}$ written for each p. The problem is then to find a function $\psi(q)$ which is normalized,

$$\int\psi^2(q)dq = 1,$$

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[1] Unsöld, Ann der Phys., **82**, 355 (1927).

where the integration is over the volume element of the configuration space and which renders the integral

$$W = \int \left[T\left(q, \frac{h}{2\pi}\frac{\partial\psi}{\partial q}\right) + V\psi^2 \right] dq \tag{43.4}$$

a minimum. Born has shown that the value of this integral is that of the energy of the normal state so that the expression is the analogue of the representation of the energy of the electromagnetic field as a volume integral of the energy density throughout the field.

This affords another means of finding the energy levels in that one seeks directly to find a function which will minimize the integral. A method of doing this was developed by Ritz, in 1908, and used by him to develop the theory of the natural oscillations of a square plate, a problem in elasticity theory whose differential equation has not been solved. The method has been applied to the helium problem by Kellner and by Hylleraas, whose results will now be presented.[1] The details of the method must be omitted.

The general idea is simple enough. A guess is made concerning the general type of ψ function which will minimize the integral and which is a form containing several adjustable parameters. Substituting such a trial form in the integral to be minimized, one finds an expression for the integral which depends on the parameters occurring in the trial form for ψ. It is then an ordinary calculus problem to choose the values of the parameters such that they make the integral a minimum. This gives the minimum of the integral from among all the family of functions represented in the trial form. If the trial form happened to contain among itself that one of all normalized functions which was the true minimizing function then the problem is solved at this step. But as this will not be apt to be the case, the next step is to add another function with another parameter to the trial function and seek the value of this parameter which makes the integral a minimum. The calculations involved become quite laborious in a complicated case like that of the normal state of helium.

From this sketch one sees that a good deal depends on how wisely one chooses the trial function. If bad guesses are made

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[1] Ritz, *Jour. für Math.*, **135,** 1 (1908), Kellner, *Zeits. für Phys.*, **44,** 91 (1927), Hylleraas, *Zeits. für Phys.*, **48,** 469 (1928).

the trial form will differ greatly from the true ψ and will give a bad value of the energy. It is in regard to the choice of the trial functions and also the number of adjustable parameters employed that the work of Kellner and of Hylleraas differs. Kellner carries the calculations through four successive approximations and finds the following values:

Degree of approximation	I	II	III	IV
Ionization potential (volts)	22.904	23.226	23.255	23.750
Error per cent on 24.5 volts	6.5	5.3	4.9	2.9

Hylleraas uses somewhat different trial functions and carries out eleven successive approximations. The values he obtains are

Degree of approximation	I	II	III	IV	V	VI
Ionization potential (R = 1)	1.500	1.6888	1.7444	1.7552	1.7558	1.7560
Error per cent (on 1.8070)	17	6.5	3.46	2.87	2.84	2.82

Degree of approximation	VII	VIII	IX	X	XI
Ionization potential (R = 1)	1.7568	1.7920	1.7944	1.7960	1.7984
Error per cent	2.78	0.83	0.70	0.61	0.48

One observes that the final value agrees within $\frac{1}{2}$ per cent with the observed value for which Hylleraas uses Lyman's 198,298 cm^{-1} together with the value 109,737 cm^{-1} for the Rydberg constant. The workings of the method are indicated by the fact that the convergence toward the true value is very slow through IV, V, VI, and VII. With VIII, a different class of trial function was introduced allowing for a dependence of the ψ function on the cosine of the angle between the radius vectors of the two electrons. This speeded up the convergence considerably.

Still another method of approximate calculation of the normal state has been developed by Slater with a resulting theoretical value for the ionization potential which is not quite so close to the experimental as are the higher approximations of Hylleraas.[1] It therefore appears probable that this lowest characteristic value of Schrödinger's equation really represents the experimental value accurately.

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[1] SLATER, *Proc.* Nat. Acad. Sci., **13,** 423 (1927); *Phys. Rev.,* **32,** 349 (1928.)

DEGENERATE SYSTEMS

A mechanical system is said to be degenerate if there are several distinct wave functions corresponding to the same energy level. It is better to speak of a particular level as degenerate or non-degenerate, for there are mechanical systems in which some states are degenerate and others are not. One of the most important examples of a degenerate system is furnished by the whole class of central-force problems. It will be recalled that in these the energy level is independent of the quantum number m. If $l = 0$ there is only one possible value of m, namely, $m = 0$, and so such a state is not degenerate. But, in general, the number of values of m associated with a particular value of l is $2l + 1$ so the states for which l is not zero are degenerate.

All central-force field problems are therefore degenerate in this way, corresponding to the obvious physical fact that the energy of a state must be independent of its orientation in space. The Coulomb law of central force gives rise to still another kind of degeneracy, however, in that the energy levels are also independent of the quantum number l, whereas for other laws than the Coulomb law the energy depends on l as well as n.

In quantum mechanics an important case of degeneracy is that known as equivalence degeneracy and which arises whenever a mechanical system has two or more dynamically equivalent parts. For example, one may consider two hydrogen atoms situated at a great distance apart in space so that their interaction can be neglected. If the two atoms are regarded, in thought, as making up one mechanical system, then it is evident that energy levels of the combined system are simply the sums of any pair of levels for the two atoms. A level which corresponds to the first atom being in state a, and the second in state b, has the same energy, however, as that in which the first atom is in state b and the second in state a. This comes about because the two separate parts of which the complete system s composed are exactly alike and so have the same set of energy levels. Such states are therefore doubly degenerate since there are two different wave functions corresponding to the same energy level. This type of degeneracy is evidently of great importance for atomic physics since our standpoint is that all atoms are built of two kinds of dynamically equivalent units, protons and electrons.

We now consider the necessary extensions of the perturbation theory to cover the case of degenerate systems together with their application to the influence of equivalence degeneracy on the spectra of atoms having more than one electron.

46. Perturbation Theory.—In the perturbation theory as developed in Sec. **40** it was necessary to exclude the case in which there were several different characteristic functions associated with the same energy level, *i.e.*, the case of degenerate systems. In determining $\psi_1(n, x)$ in Sec. **40** it was assumed that $\psi_1(n, x)$ could be expanded in a series of the functions $\psi_0(m, x)$ and equation (40.51) was found for the coefficients,

$$A^1_{nm}[W_0(n, \alpha_0) - W_0(m, \alpha_0)] = \int V_1\psi_0(n, x, \alpha_0)\psi_0(m, x, \alpha_0)dx.$$

If now $W_0(m, \alpha_0)$ and $W_0(n, \alpha_0)$ are equal, *i.e.*, if m and n are the quantum designations of two states belonging to the same degenerate energy level, then the equation gives infinity for A^1_{nm} if the right-hand side is not equal to zero, or an indeterminate ratio if it is equal to zero. The present problem is that of considering this situation more closely in order to find the correct way of applying the perturbation theory to degenerate systems. An infinite value of an A^1_{nm} violates the basic assumption that as $(\alpha - \alpha_0)$ tends to zero the function $\psi(n, \alpha, x)$ tends continuously to $\psi(n, \alpha_0, x)$.

A clue to the solution of this problem is furnished by considering the special case of the central-force field problems. Any central-force problem has complete spherical symmetry in its Hamiltonian function. The spherical polar coordinates with which we usually handle such a problem artificially introduce a preferred direction in space into the problem. The different wave functions corresponding to the degeneracy in m differ in their relation to this artificially introduced spacial direction. But this particular direction in space can have no special significance for the problem; one might have used coordinates having a different polar axis, with equal correctness. This shows that there is no absolute significance to the wave functions in regard to a particular polar coordinate system, so long as the problem has complete spherical symmetry. From the properties of spherical harmonics it is known that any harmonic in regard to one coordinate system, θ_2, φ_2, can be expressed as a linear combination of the harmonics of the same order referred to another coordinate system θ_1, φ_1, that is,

$$P_{lm}(\theta_2) \cdot e^{im\varphi_2} = \sum_{j=-l}^{+l} A_j e^{ij\varphi_1} P_{lj}(\theta_1).$$

Here the A_j are constants whose values depend on the angle between the polar axes of the two coordinate systems. Inasmuch as one polar axis is as good as another, this suggests that the wave functions for a degenerate state are somewhat indeterminate. It appears that any set of orthogonal functions associated with the degenerate level may be used, rather than just the particular one that appears when the problem is solved in a particular coordinate system.

If now a perturbation acts which does not itself possess central symmetry, it seems natural to suppose that the indeterminateness associated with the central symmetry will be in part removed. For now there is a preferred direction in space, determined by the perturbation, and the perturbed wave functions will have a definite situation in space relative to this preferred direction. As the strength of the perturbation tends to zero, the wave functions will approach some definite form of the degenerate wave functions. Clearly, this definite limiting form might not be one of the forms which is being used as a basic solution, $\psi_0(n, \alpha_0, x)$, of the unperturbed problem. Instead, it may be some linear combination of the $\psi_0(n, \alpha_0, x)$ involving all the different values of n associated with the same degenerate energy level.

The necessary generalization of the theory is obtained by supposing that the limiting torm of $\psi(n, \alpha, x)$ as $\alpha \rightarrow \alpha_0$, is not one of the particular forms $\psi_0(n, \alpha_0, x)$ but is some linear combination of all of the forms associated with the degenerate energy level. It is convenient to choose the parameter α in such a way that $\alpha = 0$ corresponds to the unperturbed problem and, further, to express the degeneracy of the problem by writing the unperturbed wave functions and characteristic values as

$$\psi_0(n, m, x) \text{ and } W_0(n).$$

That is, the quantum numbers fall into two groups, one symbolized by n, on which the unperturbed energy levels depend, and the other symbolized by m, of which the values of the unperturbed energies are independent. The wave equation to be solved is

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}(W - V - \alpha V_1)\psi = 0.$$

As in Sec. **40,** development in powers of α is assumed

$$\begin{aligned} \psi(n, p, x) &= \psi^0(n, p, x) + \alpha\psi_1(n, p, x) + \cdots \\ W(n, p) &= W_0(n) + \alpha W_1(n, p) + \cdots \end{aligned}$$

This development is more general than the corresponding one for non-degenerate systems in it is supposed that the limiting form, $\psi^0(n, p, x)$ is a linear transformation of the initially given $\psi_0(n, m, x)$,

$$\psi^0(n, p, x) = \sum_m C_{pm}\psi_0(n, m, x) \tag{46.1}$$

where the C_{pm} are to be determined. Substituting these forms in the wave equation,

$$\Delta\psi^0 + \frac{8\pi^2\mu}{h^2}[W_0(n) - V]\psi^0 = 0$$

$$\Delta\psi_1 + \frac{8\pi^2\mu}{h^2}[W_0(n) - V]\psi_1 = \frac{8\pi^2\mu}{h^2}(V_1 - W_1)\psi^0.$$

The first of these is satisfied, since ψ^0 is a linear combination of the solutions of the unperturbed equation. To solve the second, it is assumed that ψ_1 can be developed in terms of the unperturbed $\psi_0(n, m, x)$,

$$\psi_1(n, p, x) = \sum_{n'm'} A^{np}{}_{n'm'}\psi_0(n', m', x).$$

Substituting this assumption in the equation to be satisfied by ψ_1, the result is

$$\sum_{n'm'} A^{np}{}_{n'm'}[W_0(n) - W_0(n')]\psi_0(n'm'x) = (V_1 - W_1)\psi^0.$$

This equation can now be multiplied through by $\psi_0(n', m', x)$ and integrated over the whole range of all the coordinates. Because of the normal and orthogonal property of the $\psi_0(n'm'x)$, this gives for all n' and m',

$$A^{np}{}_{n'm'}[W_0(n) - W_0(n')] = \int(V_1 - W_1)\psi^0(n, p, x)\cdot\psi_0(n'm'x)dx. \tag{46.2a}$$

A set of equations for the C_{pm} and W_1 is now found by considering from all of these, the ones for which $n' = n$. These become

$$\int(V_1 - W_1)\psi^0(n, p, x)\psi_0(n, m', x)dx = 0 \text{ (for all } m')$$

and can be written in the form

$$\sum_m (W_{m'm} - \delta_{mm'}W_1)C_{pm} = 0 \quad m' = 1, 2 \cdot \cdot \cdot , \tag{46.2b}$$

where

$$W_{m'm} = \int V_1\psi_0(n, m', x)\psi_0(n, m, x)dx.$$

They are thus a set of linear homogeneous equations for the unknown quantities, $C_{p1}C_{p2}C_{p3} \cdots$ The condition that such a set of equations have a solution which does not vanish identically is that the determinant of the coefficients vanish. Equating the determinant to zero, therefore, an equation for W_1 in terms of the known quantities $W_{m'n'}$ is found,

$$\begin{vmatrix} W_{11} - W_1 & W_{12} & W_{13} & \cdots \\ W_{21} & W_{22} - W_1 & W_{23} & \cdots \\ W_{31} & \cdots\cdot & \cdots & \cdots \\ \cdots\cdots & & \cdots & \cdots \end{vmatrix} = 0. \quad (46.2c)$$

The order of this determinant is the same as the order of degeneracy of the nth state and, therefore, the equation for W_1 may have as many roots as the order of degeneracy of the state in question. An algebraic equation of this type is known as a secular equation, and appears in classical mechanics in the theory of normal coordinates of vibrating systems. It is known that the roots are necessarily real if $W_{mm'} = W_{m'm}$ and, as this is the case here, one is assured that values of W cannot come out complex. There is, however, the possibility that several of the roots may be equal. Physically, this means that the degeneracy of the state is not completely removed by the perturbation.

The allowed values of W_1, having been determined from this equation, may be numbered as $W_1(n, 1)$, $W_2(n, 2) \cdots$ To *each* of them corresponds a solution of the equations for the ratios of the C's. A set of C's is obtained corresponding to a limiting form for ψ associated with each of the perturbed energy levels. An important property of the C's is that they give rise to an orthogonal transformation: from the original orthogonality of the functions $\psi_0(n, m, x)$ for different m, may concluded the orthogonality of the $\psi^0(n, p, x)$ for different p. Since the equations determine only the ratios of the C's, a factor is left free by means of which the $\psi^0(n, p, x)$ may be normalized.

With the several values of $W_1(n, p)$ and the $\psi^0(n, p, x)$ already determined, the question of determining the $\psi_1(n, p, x)$ may be next considered. The equations for the $A^{np}_{n'm'}$ serve to determine all of these quantities except for $n' = n$, which have already been used to find W_1 and the C's; and which leave the A^{np}_{nm} indeterminate. As in the simpler case of non-degenerate systems these are fixed by the requirement that the perturbed ψ be normalized. It can be easily seen that this requires that all of the A^{np}_{nm} vanish.

The complete formula for $\psi(n, p, x)$ to the first power in α is, therefore,

$$\psi(n, p, x) = \sum_m C_{pm}\left[\left(\psi_0(n, m, x) + \alpha\sum_{n'm'}\frac{\int V_1\psi_0(n, m, x)\psi_0(n', m', x)dx}{W_0(n) - W_0(n')}\right)\right]. \qquad (46.3)$$

The summation inside the parenthesis extends over all states for which the denominator does not vanish.

There are cases in which the perturbation does not affect the degeneracy in the first-order calculation, *i.e.*, in which $W_1(n, p) = 0$ for all p. Such a case is that of the physical pendulum (Sec. **25**) when this is regarded as the perturbation of the free rotator with fixed axis by the potential energy term, $eEa \cos \theta$. In such cases an extension of the method is necessary, but this will not be developed here. This has been done by Van Vleck.[1]

47. Stark Effect.—In Sec. **42,** the problem of the Stark effect in hydrogen was treated by using the solution of the unperturbed problem in parabolic coordinates as the starting point for the application of the perturbation theory. The discussion there given was incomplete, in that it did not take account of the degeneracy of the unperturbed hydrogen atom.

In the equation for W_1, given in the preceding section, a great simplification occurs if the $\psi_0(n, m, x)$ and the perturbation function $V_1(x)$ happen to be such that $W_{mm'} = 0$ if $m \neq m'$. Then the determinant reduces to the continued product of its diagonal elements and the roots are obviously equal to the $W_{mm'}$ for all m. In this simple case all but one of a given set of C_{pm} vanish, and so the linear combination $\psi^0(n, p, x)$ of the $\psi_0(n, m, x)$, associated with the level $W_1 = W_{mm}$, is simply $\psi_0(n, m, x)$. This means that the particular set of basic solutions with which one started was just the one appropriate to the form of perturbation being considered and so the appropriate linear transformation of the basic solutions is simply the identical transformation which leaves them unaltered. In such a case the special machinery for handling degenerate systems is not really called into play, and the discussion goes ahead as if the starting system had not been degenerate.

That is the reason why it was possible to do the Stark effect in parabolic coordinates without mention of the degeneracy

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[1] Van Vleck, *Phys. Rev.* **33,** 467 (1929).

of its states; it is simply that the wave functions, found on solving the problem in parabolic coordinates, are themselves the limiting forms of the perturbed wave functions as the electric field tends to zero. The verification of this statement consists in showing that the $W_{mm'}$ really do vanish for $m \neq m'$ when the parabolic coordinate forms for $\psi_0(n, m, x)$ are used and the perturbation is due to a uniform electric field. This will be left as an exercise for the reader.

When the same problem is treated in spherical polar coordinates, however, the wave functions so found are not the limiting forms and the methods of the preceding section are really operative. The detailed calculation of the problem is given by Schrödinger and will not be reproduced here as it is somewhat lengthy. The hydrogen energy level whose principal quantum number in n has n^2 different wave functions, so that the equation for W_1 is of n^2 degree when dealing with perturbation of a state of principal quantum number n. Although a great many of the $W_{mm'}$ vanish, the equation for W_1 is, nevertheless, quite complicated. Since the correct solution is known, from the discussion for parabolic coordinates, it is possible to verify that the known values of W_1 satisfy the equation for W_1 and thus avoid the discussion of the equation.

It will be observed that the electric-field perturbation of the hydrogen atom does not fully remove the degeneracy. The energy levels of a non-degenerate problem of three degrees of freedom depend on all three of the quantum numbers which specify the wave functions. But the hydrogen energy levels when perturbed by an electric field remain independent of the quantum number associated with the angle φ. The degeneracy can be completely removed by supposing the atom to be acted on by parallel electric and magnetic fields. If this problem is handled with parabolic coordinates, it will be found that the magnetic action will work out as in Sec. **44**, while leaving the other equations unaltered. In this case, therefore, the Stark and Zeeman effects are simply additive. The case in which combined electric and magnetic fields act on the hydrogen atom obliquely to one another has not been published, except for a determination of the energy levels by matrix methods.

In case a charged particle moves in a field of central force which deviates appreciably from the Coulomb law, the energy levels will depend on l as well as n. The application of a perturbing uniform electric field to such a system thus is not influenced by a degeneracy in l and so is somewhat different from the Stark effect of hydrogen. Such a problem is not separable in parabolic coordinates and so must be handled in spherical coordinates. The only degeneracy is that in m, the quantum number associated with φ, which is not removed by the electric field, since the value of the perturbing potential is independent of φ. The alteration of the energy levels will therefore be dependent on $\int_0^\pi \cos\theta[P_{lm}(\theta)]^2 \sin\theta d\theta$ which vanishes, as the integrand is odd in $\cos x$. This gives at once the important result that the first-order Stark effect for non-Coulomb central-force problems is zero.

This result was also found on classical mechanics where it had a simple interpretation. For non-Coulomb forces the orbits precess rapidly, that is, the line of apsides turns rapidly. This has, as a consequence, the result that the moving particle is as much (to the first order) on one side of the center of force as another, so its average energy in the perturbing field vanishes. In the Coulomb field, the orbits do not precess and so it is possible for them to take up various positions relative to the electric field in which the average perturbing energy is not zero.

48. Two-electron Atoms.—The simplest example of the phenomenon of equivalence degeneracy in atomic spectra presents itself in the spectrum of helium-like atoms. For the normal state, considered in Sec. **45**, this does not come into play. In this section the method of applying perturbation theory to the calculation of the excited states is considered.[1]

With the same choice of units as in Sec. **45** equation (45.2a) for two electrons in a Coulomb field of a nuclear charge $-Ze$ and interacting with a Coulomb repulsion is

$$\Delta_1\psi + \Delta_2\psi + \left[\frac{E}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Zr_{12}}\right]\psi = 0.$$

This shows that for Z large the repulsion of the electrons is small compared to the interaction of each of them with the nucleus. We, therefore, choose $1/Z$ as the parameter of the perturbation theory.

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[1] HEISENBERG, *Zeits für Phys.*, **39**, 499 (1926) first considered this problem. The account here follows more closely the work of Unsöld.

For $1/Z = 0$ the equation is separable into two hydrogen-like equations and the solution for ψ and W takes on the form,

$$\begin{gathered}\psi = \psi_H(n_a l_a m_a r_1\theta_1\varphi_1)\cdot\psi_H(n_b l_b m_b r_2\theta_2\varphi_2) \\ E(n_a, n_b) = E(n_a) + E(n_b).\end{gathered} \tag{48.1}$$

It is observed that the energy levels are degenerate (in addition to the degeneracy of the Coulomb central-force problem) in that the energy of the state having the wave function,

$$\psi_H(n_a l_a m_a r_2\theta_2\varphi_2)\cdot\psi_H(n_b l_b m_b r_1\theta_1\varphi_1),$$

is the same as the other form just written. Therefore, we have to follow the methods of Sec. **46** and suppose that the initial functions, ψ^0 are

$$\psi^0(p) = C_{p1}\psi_H(n_a r_1)\psi_H(n_b r_2) + C_{p2}\psi_H(n_b r_1)\psi_H(n_a r_2) \tag{48.2}$$

as in equation (46.1) where p takes on the two values 1 and 2. In this equation $\psi^0(p)$ ought, logically, to be written as

$$\psi^0(n_a n_b l_a\ l_b\ m_a\ m_b\ p\ r_1\theta_1\varphi_1 r_2\theta_2\varphi_2),$$

but probably no confusion will arise from the omission of a few of the subscripts. One has then to determine the C's and W_1 by the methods of Sec. **46.** This leads to the following equations for the c's,

$$\left.\begin{aligned}(E_{11} - E_1)C_{p1} + E_{12}C_{p2} \qquad &= 0 \\ E_{21}C_{p1} \qquad + (E_{22} - E_1)C_{p2} &= 0\end{aligned}\right\} p = 1 \text{ or } 2,$$

in which

$$\begin{gathered}E_{11} = \int\frac{1}{r'_{12}}\psi_H{}^2(n_a, r_1)\psi_H{}^2(n_b r_2)dV;\ E_{22} = \int\frac{1}{r'_{12}}\psi_H{}^2(n_b r_1)\psi_H{}^2(n_a r_2)\,dV \\ E_{12} = E_{21} = \int\frac{1}{r'_{12}}\psi_H(n_a r_1)\psi_H(n_b r_1)\psi_H(n_a r_2)\psi_H(n_b r_2)dV.\end{gathered} \tag{48.3}$$

Because of the symmetry of the problem with regard to the two electrons, $E_{11} = E_{22}$. Therefore, the two values of E_1, found by equating the determinant of the coefficients to zero, are

$$E_{11} \pm E_{12}.$$

Associated with the upper sign, the values of the C's are

$$C_{11} = C_{12},$$

and, with the lower sign,

$$C_{21} = -C_{22}.$$

This means that in the limit, as the interaction tends to zero, the limiting form of the ψ functions for two electrons is not a function which corresponds to the first electron being in state a and the second in state b. On the contrary, each limiting form corresponds to each electron's having an equal probability of being in each of the two states, a and b. One of the two wave functions is symmetric in the two electrons (the one with energy $E_{11} + E_{12}$) in the sense that interchanging the coordinates of the two electrons does not alter the function. The other is anti-symmetric, since an interchange of the electron coordinates alters the sign of the wave function. The actual value of the C's is $\pm\frac{1}{\sqrt{2}}$ in order that the resulting forms shall be normalized.

This very important property of the solution for two dynamically equivalent particles was discovered by Heisenberg and designated as a "resonance phenomenon," because the secular equation resembles that which governs the normal coordinates in classical mechanics when two similar simple harmonic oscillators (resonators) are loosely coupled. As the phenomenon is not exactly one of resonance in quantum mechanics, the term will not be used here. Instead, it will be described as *equivalence degeneracy.* This name too has disadvantages, the main one being that the problem is not degenerate when the interactions are not neglected. It is only degenerate because one starts to solve the problem by neglecting the interaction.

The property of the solution of presenting a symmetric and an anti-symmetric solution has also been called by some the "exchange" ("Austausch") phenomenon. The implication here is that the motion can be thought of as a continual exchange of place by the two electrons. For a time, according to this view, electron 1 is in state a, while electron 2 is in state b. Then the two electrons exchange places and electron 2 is in state a while electron 1 is in state b. This exchange is thought of as taking place in such a way that in the mean, each electron is equally likely to be in either state. Another way of making this view somewhat more precise, is to take at $t = 0$ that linear combination of functions which represents the certain knowledge that electron 1 is in state a and electron 2 is in b.

This will be

$$\frac{1}{\sqrt{2}}e^{\frac{2\pi i(W_0+W_{11})t}{h}}\left[\psi^0(1)e^{\frac{2\pi iW_{12}t}{h}}+\psi^0(2)e^{-\frac{2\pi iW_{12}t}{h}}\right].$$

Putting $t = 0$ and using the values just found for the C's it is found that this reduces to

$$\psi_H(n_ar_1)\psi_H(n_ar_2),$$

as it should. As time goes on, because of the difference in the time factor associated with $\psi^0(1)$ and $\psi^0(2)$, the two get out of phase, which means that there will be a certain probability that electron 1 will have gone over into state b and electron 2 into state a, that is, that an exchange of place has occurred. At precisely the time $t = h/4W_{12}$, the two forms will be in opposite phase so that their sum represents the certainty that electron 1 is in b and electron 2 is in a. After the same period of time the reverse exchange will have taken place with certainty, and electron 1 will again be in a and electron 2 will be in b, as at $t = 0$. The rate at which this exchange takes place is governed by the extent of the interaction. It is to be emphasized that such an exchange of place is not a quantum jump associated with radiation. On the contrary, it is a consequence of the fact that there is no stationary state which corresponds to one electron's remaining in one state and the other in another. If the period of the exchange is of the order of magnitude of time intervals of our direct experience (a second or more), then the "exchange" point of view of this paragraph is quite a helpful one. But in atoms like helium, the exchange frequency is of the same order as the frequencies involved in the emission of visible light. When the exchange is this rapid, it is of little value to hold in mind the picture of the electrons trading places.

Returning to the question of the energy levels of helium-like atoms, it is seen that numerical values depend on the evaluation of the integrals for W_{11} and W_{12}. The general evaluation of these has not been affected. The important ones for the interpretation of spectra are those in which one state is the normal state ($n_a = 1$, $l_a = 0$, $m_a = 0$).

49. Empirics of the Helium-like Spectra.—Before considering further the quantum mechanical interpretation of the spectrum of helium-like atoms (He, Li^+, Be^{++}, B^{+++}, C^{++++} etc.) it is of importance to present a brief statement of the facts to be explained.[1] The spectrum of neutral helium has long been fully analyzed into term values. The terms are found to group themselves into series which can be designated as S, P, D, on the basis of the way they combine to give the observed lines.

The remarkable feature of the spectrum consists in the fact that there are two series of each kind, *i.e.*, the term values may be said to constitute two whole systems of terms, where by system is understood a set of series of S, P, D terms which combine with each other. The two systems are distinct from each other in that spectral lines, corresponding to jumps between terms of two systems, are so improbable that for a long time they were believed not to occur at all. While such transitions have been observed, they are so weak that the two systems may be said to be non-combining.

The two systems are further distinguished by their multiplicity. All of the terms of one of the systems are single, as are the S terms of both systems. But the terms of the other system are quite obviously double, so that the earlier analyses report helium as having a system of doublet and a system of singlet terms. Later work with high resolving power has shown that the doublet terms are in reality triplets, one of the components of the apparent doublet being itself a very close doublet. The singlet system of terms is known as "par-helium" and the triplet system as "ortho-helium."

Each series of terms can be represented by a formula of the Rydberg-Ritz type,

$$\nu = \frac{R}{\left(n + \delta_1 + \frac{\delta_2}{n^2}\right)^2}, \tag{49.1}$$

where δ_1 and δ_2 are constants within a given series and n takes on integer values from some empirically assigned least value to infinity. In the modern spectroscopic notation a term is designated by a capital letter S, P, or D, preceded by a superscript to indicate the multiplicity, and an integer indicating the value of n in the series formula to which that term corresponds, *e.g.*, 5^3P is the term with $n = 5$ in the P series of the ortho-term system. The spectra of the ionized atoms $\mathrm{Li}^+, \mathrm{Be}^{++} \ldots$ have not been analyzed so completely as He, principally because they lie in the extreme ultra-violet, but all the experimental results fall

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[1] See also Pauling and Goudsmit, Sec. **22.**

in with the scheme for He if one writes $(Z - 1)^2$ as a factor in the numerator of the above series formula, Z being the atomic number of the atom in question. The empirical values of δ_1 and δ_2 for each series also show a dependence on Z. Between the empirical analysis of the terms into series and the final solution of the problem from the quantum mechanical standpoint, there stands a system of rules and approximate theoretical arguments by means of which the states are assigned quantum numbers. This semi-empirical theory has been of great value to working spectroscopists. On this theory of term systematics, each electron in the atom is assigned four quantum numbers. Three of them are the numbers n, l, and m, which correspond to the orbits in a central-force field of the nucleus. The fourth is denoted by s. It characterizes the magnetic moment of the electron itself and is capable of assuming only two values. The extension of quantum mechanics to include the theory of the electron spin requires rather fundamental changes in the equations on which the present treatment is based and is omitted from consideration until Chap. VI. The term theory is largely based on arguments of the possible modes of coupling of the vectors of angular momentum of the several electrons. Each electron has an orbital angular momentum whose amount is $\sqrt{l(l+1)}\frac{h}{2\pi}$ and a spin angular momentum of $\frac{1}{2}\frac{h}{2\pi}$.

The different kinds of terms in an atomic spectrum can then be concisely described by means of arguments concerning the couplings. It is outside the scope of this book to go into the development of the term theory from its beginnings in empiricism and analogy with the Bohr orbits. In this section the discussion will be restricted to a statement of the coupled-vector description of the different terms of the 2-electron spectra.

The two electrons have quantum numbers n_1, l_1, m_1, s_1 and n_2, l_2, m_2, s_2. Both systems of helium-like terms are built out of the manifold of terms obtained by setting

$$n_1 = 1,\ l_1 = 0,\ m_1 = 0,\ s_1 = \tfrac{1}{2}.$$

The spin angular momentum of the second electron can then orient itself in two ways relative to the spin of the first. It can orient itself oppositely so the resultant spin momentum of the two electrons is $(s_1 - s_2) = 0$, or it can be parallel to the first giving a resultant spin of unity, $(s_1 + s_2) = 1$. For resultant s one uses the designation S.

While in more complicated spectra one next has to consider the coupling of l_1 and l_2, here there are no possibilities of coupling since $l_1 = 0$. Resultant l is denoted by L. On this interpretation the resultant l gives the nature of the term as S, P, D, or F according to the scheme,

Series designation	· · ·	S, P, D, F · · ·
L = resultant l value	· · ·	$0,\ 1,\ 2,\ 3$ · · ·

Next is considered the terms that can arise from different quantized orientations of the resultant spin with the resultant orbital angular momentum. If the resultant s is zero, as it can be in 2-electron systems, then there is but one way of coupling resultant s and resultant l. Therefore, the whole system of terms for which the S is zero, but for different L and different n_2, is a system of singlet terms. This system of terms is the one which is identified with the singlet or par system in helium-like spectra. When the S is one, however, and L is not zero, the possible values of the resultant of S and L, which is known as J, are $J = L + 1$, L, and $L - 1$. If the energy of the state, therefore, depends somewhat on the relative orientation of the vectors represented by S and L, this will make the system of terms for which $S = 1$ be a triplet system, except for the S terms of this system which are single because $L = 0$ for them. (One has to guard against confusion in the two uses of S, one to label the series for which $L = 0$, and the other as the numerical value of the resultant s.)

The manifold of term values represented in the observed spectrum of helium is therefore given by this mode of assignment of quantum numbers to the electrons. As the quantum mechanics of electron spin is being postponed, it is important to consider the way in which the electron's own s vector enters the coupling argument. A little consideration shows that the spin has two somewhat distinct effects. One of these is to give rise to two distinct term systems, one for $S = 0$ and one for $S = 1$. The other is to make one of the term systems (that for $S = 1$) be a system of triplets instead of a system of singlets. Without the special theory of the electron spin the quantum mechanics is capable, as was seen in Sec. **48**, of giving the two distinct term systems but both are systems of single terms.

The effect of introduction of the extension of the theory which includes electron spin will be to cause a splitting of the terms of one of these systems into triplets while leaving the others single.

In adapting the treatment of Sec. **48** to the helium spectrum quantum numbers are assigned to the electrons just as in the coupled-vector theory. All of the terms of the spectrum are included in the manifold obtained by setting $n_a = 1$, $l_a = 0$, $m_a = 0$ and $n_b = n$, $l_b = L$, while m_b remains free to express the degeneracy due to spherical symmetry of the undisturbed atom. The system of terms associated with the symmetrical wave functions will be identified with the ortho or triplet system and that associated with the antisymmetric wave functions with the par or singlet system.

50. Helium-like Spectra: S Terms.—The n^1S and n^3S terms of the helium atoms are to be found by putting $n_a = 1$, $l_a = 0$, $m_a = 0$, and $n_b = n$, $l_b = 0$ and $m_b = 0$ in the formulas of Sec. **48**, and evaluating the integrals which occur there. The calculation of the integrals for $n = 2$, 3, and 4 has been carried out by Unsöld. For $n = 1$ there is no degeneracy and hence but one state. This is the normal state and is counted with the singlet system for reasons which will appear later.

The values of the integrals E_{11} and E_{12} for these states are found to be

$$E_{11} = \left(\frac{2}{n^2} - a\right) \text{ and } E_{12} = b, \tag{50.1}$$

where the a and b have the values,

	$2S$	$3S$	$4S$
a	0.0802	0.0232	0.00973
b	0.0439	0.0115	0.00468

The energies of these terms, to the first order in $1/Z$, which is here the perturbation parameter, are therefore

$$W = -RhZ^2\left[1 + \frac{1}{n^2} + \frac{1}{Z}\left(a \pm b - \frac{2}{n^2}\right) + \cdots\right] \tag{50.2}$$

the + sign giving the ortho-term and the − sign the par-term. This formula when compared directly with experiment for helium ($Z = 2$) naturally does not give a very good agreement because the higher powers of $1/Z$ in the development are not small. The agreement should improve as one considers term values for larger values of Z, but the data here are lacking. This theoretical energy expression is for the total energy of the atom measured from double ionization. As the energy for the removal of the second electron is simply RhZ^2, the energy of the state, reckoned in the usual way from the energy of the singly charged ion in its normal state is given by omitting the 1 in the bracket of this expression. For purposes of comparison with the experimental term values, it is better to write the term value, reckoned from the unexcited state of the singly charged ion in the Rydberg form of equation (49.1),

$$-\frac{W}{h} = \frac{R(Z-1)^2}{(n-\delta)^2}.$$

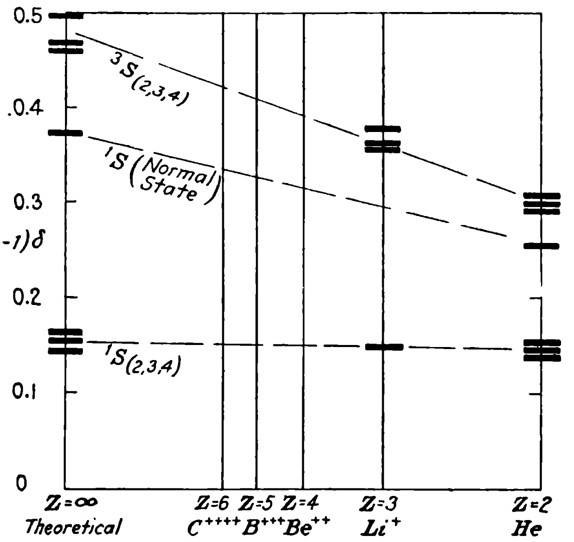

FIG. 15.—Comparison of theoretical and experimental values of δ for ^1S and ^3S terms of helium-like atoms.

This expression agrees with the first order calculation as far as terms in Z^2 and Z, which is the degree of approximation of the present calculation, if one takes

$$(Z-1)\cdot\delta = \frac{n^3}{2}(a \pm b). \tag{50.3}$$

The theoretical values are the limiting values as $Z \to \infty$ and have to be compared with the observed values for helium ($Z = 2$) and Li^+ ($Z = 3$). This is done in Fig. 15.[1] The theoretical value for the normal state is from the simple first-order calculation given in Sec. **45**. This mode of comparison of the results of the theoretical calculation with the data makes it appear that the theory is capable of giving good agreement when higher approximations are considered, but leaves a good deal to be desired.

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[1] These data are from UNSÖLD's Table 2, p. 367.

Heisenberg has given similar approximate calculations of the δ's for the P, D, and F terms which are in fairly good agreement with the term values. For these the reader is referred to the original paper.[1]

In conclusion it may be said that the most striking result of the quantum mechanical treatment is the automatic way in which the perturbation theory provides the two term systems, one of which has a symmetric and the other an antisymmetric wave function.

Subsequently, the theory of equivalence degeneracy has been extended so that at present there is a fairly complete account of the systematics of the energy levels of higher atoms built directly on the equivalence degeneracy for all the electrons in the atom. These developments, however, call for the use of the electron spin and results of the theory of finite groups and so are beyond the scope of this volume.[2]

In case there are κ equivalent particles, and the interactions are neglected, then the ψ function for the ith particle alone may be written as

$$\psi_\alpha(x_i)$$

where α is written for the quantum numbers labelling that state. Consider now κ sets of quantum numbers which may be designated by the indices 1 to κ. Then a starting form for application of the perturbation theory is

$$\psi = \psi_1(x_1)\cdot\psi_2(x_2)\psi_3(x_3) \cdot \cdot \cdot \psi_\kappa(x_\kappa).$$

But the ψ function which results from this when any permutation of the electrons is made will be one which has the same energy. Since there are $\kappa!$ such permutations the problem with κ electrons is $\kappa!$-fold degenerate. In the special case $\kappa = 2$, illustrated by helium, the degeneracy is two-fold as we have just seen.

Therefore, while the methods of Sec. **46** are applicable in principal for any value of κ, they rapidly become inapplicable in practice as κ increases, the equation for the determination of the first-order perturbed energies, for instance, involving a determinant of $\kappa!$ rows and columns. In the discussion of the symmetry properties of the more complicated cases involving larger numbers of particles, the theory of groups has proven especially useful.

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[1] HEISENBERG, *Zeits. für Phys.*, **39**, 499 (1926).

[2] The principal references to these developments are: WIGNER, *Zeits. für Phys.* **43**, 624 (1927) and **45**, 601 (1927); HUND, *Zeits. für Phys.* **43**, 788 (1927); HEISENBERG, *Zeits. für Phys.* **41**, 239 (1927); NEUMANN and WIGNER, *Zeits. für Phys.* **47**, 203 (1928).

CHAPTER V

DIATOMIC MOLECULES

When the potential energy function for the wave equation is due, not to a single nucleus and its surrounding electrons, but to several nuclei and their surrounding electrons, the problem of determining the resulting allowed energy levels becomes much more complicated. The nuclei have motions relative to each other, and the electron configurations and corresponding electronic energies are thereby continually changing as the nuclei change.

This chapter will confine itself to a discussion of the simplest case, that of two nuclei, since this case only has been systematically investigated.

It will be shown that the general wave equation for such a diatomic molecule can be separated into two equations, one considering the nuclei as fixed in space and concerned only with the electronic energies as a function of the nuclear separation as a parameter; and the other concerned only with the nuclear energies, using as a "potential energy function" the sum of the electronic energies and the nuclear potential energy.

The nuclear wave equation is discussed, the allowed energies of rotational and vibrational motion are obtained, and the probabilities of transition from one level to another are considered.

The electronic equation is treated for the two simplest molecules, the hydrogen molecular ion and the hydrogen molecule. The general properties of the electronic energies are then discussed.

51. The General Equation.—The diatomic molecule is made up of two nuclei of charges Z_1e and Z_2e, and masses M_1 and M_2, respectively, and of N electrons. The six coordinates of the nuclei may be chosen so that three of them refer to the position in space of the nuclear center of gravity (which can be considered as very nearly coinciding with the molecular center of gravity); another coordinate c is the nuclear separation, and the other two are angles ϑ and φ, giving the orientation of the nuclear axis with respect to some axis fixed in space. Since the energy of translation of the molecule as a whole, corresponding to changes in the first three coordinates, cannot be radiated when the molecule is undisturbed, these three coordinates can be neglected in setting up the wave equation.

The coordinates of each electron can be given with reference to the positions of the nuclei. Thus, if r_1 be the distance from the first nucleus, and r_2 the distance from the second, a suitable coordinate system for the electrons will be the orthogonal elliptic set

$$\xi = \frac{(r_1 + r_2)}{c}; \; \eta = \frac{(r_1 - r_2)}{c}, \tag{51.1}$$

and the orientation angle about the nuclear axis, ϕ. Since there are several electrons, there will be several sets of coordinates, $\xi_1, \eta_1, \phi_1, \xi_2, \eta_2, \phi_2,$ —, etc.

Then the general wave equation for the whole molecule can be obtained by the method outlined in Chap. I, and is,[1]

$$-\frac{h^2}{8\pi^2\mu}\sum_{s=1}^{N}\Delta_s\Psi - \frac{h^2}{8\pi^2\mu}\left(\frac{\mu}{M}\right)\Delta_c\Psi + V(\xi_s, \eta_s, \phi_s, c)\Psi - W\Psi = 0, \tag{51.2}$$

where Δ_c is the Laplacian for the spherical coordinates c, ϑ and φ; $M = M_1M_2/(M_1 + M_2)$ is the average nuclear mass introduced when the nuclear coordinates were changed to c, ϑ, and φ; and V is the potential energy, a sum of the electronic potential energy $V_e(\xi_s, \eta_s, \phi_s)$ and of the nuclear energy of repulsion $E_n = Z_1Z_2e^2/r$, and is independent of ϑ and φ. The first term represents the kinetic energies of the electrons, and contains their energy of motion with respect to the nuclear axis plus the energy of motion they possess due to the fact that the nuclear axis is rotating. Rigorously, there should appear in the equation cross-products involving mixed partial derivatives with regard to electronic and nuclear coordinates. These are of importance in problems involving the distortion of electronic multiplets due to the rotation of the molecule, but will be disregarded here. It will be seen later that the nuclear energy of rotation is of the order of $(\mu/M)^2$ times that of the electrons with respect to the nuclei, and, therefore, the electronic energy due to this rotation would

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[1] This treatment is given in a more general form, suitable for polyatomic molecules by BORN and OPPENHEIMER, *Ann. der Phys.*, **84**, 457 (1927).

be of the order of $(\mu/M)^3$ times their kinetic energy relative to the nuclei. Since in the following, only terms involving the small quantity μ/M to the zero and first powers are going to be considered, this change in electronic kinetic energy due to nuclear rotation can be neglected. In this case, Δ_s is the Laplacian in the elliptical coordinates ξ_s, η_s, and ϕ_s.

For simplicity in handling, the operator, $\left[-\frac{h^2}{8\pi^2\mu}\sum_{s=1}^{N}\Delta_s + V\right]$, will be called H_0 and the operator, $-\frac{h^2}{8\pi^2\mu}\Delta_c$, will be called H_1. The small quantity μ/M will be called α.

Then the equation (51.2) can be written

$$(H_0 + \alpha H_1 - W)\Psi = 0. \qquad (51.3)$$

As a first approximation α will be considered as zero. Then the equation is one concerned only with the electronic motions, and is

$$(H_0 - E)\psi = 0. \qquad (51.4)$$

This means that in this approximation the heavy nuclei are considered as fixed, and the molecular energy as due only to the electronic motions. Since c enters only as a parameter, the allowed energies E_σ of this equation are functions of c, and the allowed wave functions ψ_σ are functions of the ξ's, η's, ϕ's, and of c.

This energy E_σ, where σ indicates the ensemble of electronic quantum numbers, is the sum of the nuclear repulsion energy E_n, and the "electronic energy" E_e. Indeed, since E_n behaves as an additive constant in equation (51.4), this equation could be written

$$[(H_0 - E_n) - E_e]\psi = 0, \qquad (51.4a)$$

where E_n is removed from the operator H_0, and the resulting equation solved to find E_e. The total energy E_σ as a function of c, must have a minimum value $E_\sigma{}^0$ in order that the molecule be stable. The value of c, where E_σ becomes a minimum, can be called c_0.

It is expected now that there will exist solutions such that ψ has appreciable values only for values of c in the neighborhood of c_0 corresponding to the classical small oscillations around such a position of stable equilibrium. Then c can be set equal to $c_0 + \rho$ and E_σ can be considered as made up of a constant

$E_\sigma{}^0$ independent of ρ, plus a small quantity $E_\sigma{}''$, which is a function of ρ. To emphasize that this quantity is small, we shall let it equal $\alpha E_\sigma{}^1$, and then

$$E_\sigma = E_\sigma{}^0 + \alpha E_\sigma{}^1. \tag{51.5a}$$

The operator H_0 also depends on c, and can similarly be expanded about c_0,

$$H_0 = H_0{}^0 + \alpha H_0{}^1, \tag{51.5b}$$

where $H_0{}^0$ is the operator with c_0 substituted for c and $\alpha H_0{}^1$ is the difference between this operator and the one with $c_0 + \rho$ substituted for c. $H_0{}^0$ is therefore independent of ρ.

Likewise, the wave function ψ_σ can be expanded,

$$\psi_\sigma = \psi_\sigma{}^0 + \alpha\psi_\sigma{}^1. \tag{51.5c}$$

The function $\psi_\sigma{}^1$ can be expressed as a linear function of all the $\psi_\sigma{}^0$'s, as in equation (40.2),

$$\psi_\sigma{}^1 = \sum_\tau A_{\tau\sigma}\psi_\tau{}^0, \tag{51.6a}$$

where the A's are functions of ρ but independent of the ξ's, η's and ϕ's. Multiplying both sides by $\bar{\psi}_\tau{}^0$, and integrating with respect to the electronic coordinates over all space, since the integral of $\psi_\tau{}^0\bar{\psi}_\sigma{}^0$ equals unity, one obtains

$$A_{\tau\sigma} = \int\int \cdot\cdot\cdot \int\int \bar{\psi}_\tau{}^0\psi_\sigma{}^1 d\xi_1 \cdot\cdot\cdot d\phi_N. \tag{51.6b}$$

Making all these substitutions in the first approximate equation (51.4), there results

$$(H_0{}^0 - E_\sigma{}^0)\psi_\sigma{}^0 + \alpha(H_0{}^0 - E_\sigma{}^0)\psi_\sigma{}^1 + \alpha(H_0{}^1 - E_\sigma{}^1)\psi_\sigma{}^0 \\ + \alpha^2(H_0{}^1 - E_\sigma{}^1)\psi_\sigma{}^1 = 0.$$

Since α enters as a parameter, we can set the coefficients of its various powers equal to zero in turn.

$$(H_0{}^0 - E_\sigma{}^0)\psi_\sigma{}^0 = 0. \tag{51.7a}$$

This, of course, follows directly from equation (51.4) when c is set equal to c_0.

The next coefficient,

$$(H_0{}^0 - E_\sigma{}^0)\psi_\sigma{}^1 + (H_0{}^1 - E_\sigma{}^1)\psi_\sigma{}^0 = 0, \tag{51.7b}$$

gives some of the properties of $H_0{}^1$ and $E_\sigma{}^1$. From equations (51.6a) and (51.7a),

$$H_0{}^0\psi_\sigma{}^1 = \sum_\tau A_{\tau\sigma}H_0{}^0\psi_\tau{}^0 = \sum_\tau A_{\tau\sigma}E_\tau{}^0\psi_\tau{}^0.$$

Substitute this in (51.7*b*), multiply by $\bar{\psi}_\tau^0$, and integrate. Then the first term disappears, and

$$\iint \cdots \iint \bar{\psi}_\sigma^0 H_0^1 \psi_\sigma^0 d\xi_1 \cdots d\phi_N - E_\sigma^1 = 0. \qquad (51.8a)$$

With this property of the integral of H_0^1 developed, it is possible to consider the complete equation (51.3), $(H_0 + \alpha H_1 - W)\Psi = 0$. When H_1 is introduced the character of the solution is changed. W must be independent of both electronic and nuclear coordinates, and Ψ must be dependent on all the coordinates. Since we have seen that the effect of the nuclear motion is small compared to that of the electronic motion, it is reasonable to expect that Ψ and W cannot be much different from ψ and $E\sigma^0$. It will be assumed that

$$\begin{aligned} \Psi_{\sigma n} &= \chi_{\sigma n}(\rho, \vartheta, \varphi) \cdot \psi_\sigma(\xi_s, \eta_s, \phi_s, \rho) \\ &= \chi_{\sigma n}(\psi_\sigma^0 + \alpha\psi_\sigma^1), \end{aligned} \qquad (51.8b)$$

and that

$$W_{\sigma n} = E_\sigma^0 + \alpha W^1_{\sigma n}. \qquad (51.8c)$$

These assumptions are sanctioned by the fact that they can be made to satisfy equation (51.3). For if all the substitutions be made, (51.3) becomes

$$\begin{aligned} (H_0^0 - E_\sigma^0)\chi_{\sigma n}\psi_\sigma^0 &+ \alpha(H_0^0 - E_\sigma^0)\psi_\sigma^1\chi_{\sigma n} \\ &+ \alpha(H_0' + H_1 - W'_{\sigma n})\chi_{\sigma n}\psi_\sigma^0 \\ &\qquad + \alpha^2(H_0^1 + H_1 - W'_{\sigma n})\chi_{\sigma n}\psi_\sigma^1 = 0. \end{aligned}$$

Equating coefficients of α,

$$\chi_{\sigma n}(H_0^0 - E_\sigma^0)\psi_\sigma^0 = 0,$$

$\chi_{\sigma n}$ can be put ahead of the operator H_0^0 since it is not a function of the electronic coordinates, and hence behaves as a constant to H_0^0. This last equation is the same as (51.7*a*).

The next coefficient is

$$\chi_{\sigma n}(H_0^0 - E_\sigma^0)\psi_\sigma^1 + (H_\sigma^1 + H_1 - W^1_{\sigma n})\chi_{\sigma n}\psi_\sigma^0 = 0. \qquad (51.8d)$$

Multiply by $\bar{\psi}_\sigma^0$ and integrate. As in the reduction of (51.7*b*), the first term becomes

$$\chi_{\sigma n}A_{\sigma\sigma}(E_\sigma^0 - E_\sigma^0) = 0,$$

so that

$$\iint \cdots \iint \bar{\psi}_\sigma^0 (H_\sigma^1 + H_1 - W^1_{\sigma n})\chi_{\sigma n}\psi_\sigma^0 d\xi_1 \cdots d\phi_N = 0.$$

Since H_1, $W'_{\sigma n}$, and $\chi_{\sigma n}$ are independent of the electronic coordinates, they can be removed from the integral sign, and

$$\chi_{\sigma n}\iint \cdots \iint \bar{\psi}_\sigma^0 H_0^1 \psi_\sigma^0 d\xi_1 \cdots d\phi_N + (H_1 - W^1_{\sigma n})\chi_{\sigma n} = 0,$$

but from equation (51.8a) the first term is simply $E_\sigma{}^1\chi_{\sigma n}$, so that the final equation for nuclear motion is $(H_1 + E_\sigma{}^1 - W^1{}_{\sigma n})\ \chi_{\sigma n} = 0$. From (49.8$c$) and (49.5$a$),

$$\alpha(E_\sigma{}^1 - W^1{}_{\sigma n}) = E_\sigma - W_{\sigma n},$$

so that

$$(\alpha H_1 + E_\sigma - W_{\sigma n})\chi_{on} = 0;$$

or, remembering the definition of α and H_1, the equation can be set into the form,

$$\Delta_c\chi + \frac{8\pi^2 M}{h^2}[W - E_\sigma(c)]\chi = 0. \tag{51.9}$$

This states that the potential energy used in this equation for nuclear motion is the combination E_σ of the electronic energies and of the nuclear energy of repulsion.

This rather complicated argument seems necessary to prove what appears probable without proof. For from the classical standpoint, the heavy nuclei move so slowly that the electrons have gone through many cycles of motion before the nuclei have gone through one cycle. Therefore, when considering the electrons the nuclei can be considered as standing still, and when considering the nuclei, the only effect of the electronic motion is to introduce the electronic energy as an additional potential energy.

52. Nuclear Motion.—The equation (51.9) for nuclear motions will be considered first. The first question is that of the form of the potential energy function $E_\sigma(c)$. If the energy for infinite nuclear separation ($c = \infty$) is considered as zero, then for the molecule to be stable, E_σ must have a minimum value $-D$ at $c = c_0$, and for small values of c, the energy must be large, positive, and made up almost entirely of the nuclear repulsion energy $Z_1Z_2e^2/c$. Later in this chapter approximate functions will be calculated for E_σ for two simple cases, by consideration of the electronic equation (51.4). It is possible, however, to assume various functional forms for $E_\sigma(c)$, and to calculate the resulting energy levels. An approximate form for the true E_σ for any molecule can then be obtained if these calculated energy levels can be made to fit the experimentally determined levels.

Equation (51.9) has been separated in polar coordinates in Sec. **16.** It was found there that,

$$\chi = \Phi(\varphi).\Theta(\vartheta)\cdot R(c)/c,$$

where

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$$

and

$$\Theta = \sqrt{\frac{2}{(2j+1)} \frac{(j+m)!}{(j-m)!}} \sin^m\vartheta \cdot P_j^m(\cos\vartheta);$$

j and m are integers and R satisfies the equation,

$$\frac{d^2R}{dc^2} + \frac{8\pi^2M}{h^2}\left[W - E_\sigma(c) - \frac{h^2}{8\pi^2M}\frac{j(j+1)}{c^2}\right]R = 0. \quad (52.1)$$

This gives the equation for the vibratory motion of the nuclei, and its solution will give the vibrational energy levels.

The simplest assumption to make as to the form of E_σ is that it is a parabola about c_0; *i.e.*,

$$E_\sigma = -D + \frac{(2\pi\omega_0)^2M}{2}\rho^2 \qquad (52.2a)$$

where $\rho = c - c_0$ as before. If we are primarily interested in the pure vibration spectrum, j can be set equal to zero, and the equation is then

$$\frac{d^2R}{d\rho^2} + \frac{8\pi^2M}{h^2}\left[W + D - \frac{(2\pi\omega_0)^2M}{2}\rho^2\right]R = 0.$$

This is the equation of a particle vibrating in simple harmonic motion about an equilibrium distance c_0 The classical frequency of vibration would be ω_0 which is the reason the coefficient of ρ^2 was chosen as it was. This problem is treated in Sec. **15**, and it was found there that the allowed energy levels were

$$W_n + D = h\omega_0(n + \tfrac{1}{2}) \qquad (52.2b)$$

where n is an integer.

This assumption of a form for the potential energy function is too simple. In the first place, E_σ does not approach a finite value as c tends to infinity, and does not approach infinity as c tends to zero. Also, the spacing between consecutive energy levels, ΔW_n, has the same value, $h\omega_0$, for any value of n It is an empirical fact that the spacing between the vibrational levels of a great many diatomic molecules is given by the rule,

$$\Delta W_n = h\omega_0 - 2h\omega_0x(n + \tfrac{1}{2}); \qquad (52.3a)$$

that is,

$$W_n = -D + h\omega_0(n + \tfrac{1}{2}) - h\omega_0x\,(n + \tfrac{1}{2})^2, \qquad (52.3b)$$

where x is some constant. This formula holds so well for many molecules for a large range of n that it can often be used for determining the energy of molecular dissociation. For when ΔW becomes zero, the molecule has the greatest vibrational energy it can have, and any more energy would dissociate it. Therefore, when $h\omega_0 = 2h\omega_0 x\left(n + \frac{1}{2}\right)$ or $\left(n + \frac{1}{2}\right) = \frac{1}{2x}$ then W must equal zero.

This means that,

$$0 = D - h\omega_0 \frac{1}{2x} + h\omega_0 x\left(\frac{1}{2x}\right)^2,$$

or

$$D = \frac{h\omega_0}{4x} = \frac{h(\omega_0)^2}{4(\omega_0 x)} \tag{52.3c}$$

The values of the dissociation energies D calculated in this way from experimentally determined values of (ω_0) and $(\omega_0 x)$ are usually within 2 or 3 per cent of the experimentally determined value of D.[1]

In a few cases, (for CuH, SiN, etc.), terms in powers of $(n + \frac{1}{2})$ higher than the first must be added in equation (52.3*a*). In all save these special cases the higher terms can be neglected. The coefficient $h\omega_0 x$ cannot be neglected, however, for any set of levels, and so assumption (52.2*a*) cannot be a good approximation to the true potential energy function.

It is possible to let

$$E_\sigma = -D + \frac{(2\pi\omega_0)^2 M}{2}[\rho^2 + k_3'\rho^3 + k_4'\rho^4 + \cdots] \tag{52.4a}$$

and to calculate the perturbation on the levels given by (52.2*b*) due to these small additional terms.[2]

This gives a general formula

$$W_n = -D + h\omega_0[(n + \tfrac{1}{2}) + a_2'(n + \tfrac{1}{2})^2 + a_3'(n + \tfrac{1}{2})^3 + \cdots]$$

where a_2', a_3', etc. are functions of k_3', k_4', etc. But this method of correcting the form of E_σ is not very satisfactory, for E_σ still does not stay finite at $c = \sigma$ or become infinite at $c = 0$.

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[1] BIRGE and SPONER, *Phys. Rev.*, **28,** 259 (1926).

[2] FUES, *Ann. der Phys.*, **80,** 367 (1926).

Suppose a formula,

$$E_\sigma = -D + (2\pi\omega_0)^2 M\left[\frac{c_0^{\,2}}{2} - \frac{c_0^{\,3}}{c} + \frac{c_0^{\,4}}{2c^2}\right], \tag{52.4b}$$

be chosen. This becomes $+\infty$ when $c = 0$ and remains finite when $c = 0$, and therefore corresponds to the general requirements for E_σ. The coefficients were so chosen that the minimum value of E_σ comes at $c = c_0$, and the classical frequency of small vibrations about c_0 is ω_0.

The equation for R becomes

$$R'' - \frac{j(j+1)}{c^2}R + \frac{8\pi^2 M}{h^2}\left[\left(W + D - \frac{(2\pi\omega_0)^2 M c_0^{\,2}}{2}\right) + \frac{(2\pi\omega_0)^2 M c_0^{\,3}}{c} - \frac{(2\pi\omega_0)^2 M c_0^{\,4}}{2c^2}\right]R = 0.$$

If the substitutions,

$$\left(W + D - \frac{(2\pi\omega_0)^2 M c_0^{\,2}}{2}\right) = -\frac{32\pi^6\omega_0^{\,4} M^3 c_0^{\,6}}{\sigma^2 h^2};$$

$$c = \frac{\sigma h^2}{32\pi^4\omega_0^{\,2} M^2 c_0^{\,3}}x; \qquad b = \frac{16\pi^4\omega_0^{\,2} M^2 c_0^{\,4}}{h^2}$$

are made, this equation becomes

$$R'' + \left[-\frac{1}{4} + \frac{\sigma}{x} - \frac{b + j(j+1)}{x^2}\right]R = 0.$$

This equation is the same as equation (21.4). Since it was shown in Sec. **21** that

$$\sigma = n + \tfrac{1}{2} + \sqrt{b + (j + \tfrac{1}{2})^2},$$

then the energy

$$\begin{aligned} W &= -D + \frac{(2\pi\omega_0)^2 M c_0^{\,2}}{2} - \frac{32\pi^6\omega_0^{\,4} M^3 c_0^{\,6}}{h^2[n + \frac{1}{2} + \sqrt{b + (j + \frac{1}{2})^2}]^2} \\ &= -D + h\omega_0(n + \tfrac{1}{2}) - \frac{3h^2(n + \frac{1}{2})^2}{8\pi^2 M c_0^{\,2}} + \cdots \\ &\qquad + \frac{h^2(j + \frac{1}{2})^2}{8\pi^2 M c_0^{\,2}} \cdots \end{aligned}$$

if both $(n + \frac{1}{2})$ and $(j + \frac{1}{2})$ are considered small compared to b.

This formula includes both rotational and vibrational energies. The coefficient of $(n + \frac{1}{2})^2$ is wrong, however, for it does not turn out, in general, that the $h\omega_0 x$ of equation (52.3*a*) is equal to $3h^2/8\pi^2Mc_0^2$. It is possible to correct this term to fit the empirical facts by making the potential energy function,

$$E_\sigma = -D + (2\pi\omega_0)^2M\left[\frac{c_0^2}{2} - \frac{c_0^3}{c} + \frac{c_0^4}{c^2}\right] + k_3\rho^3 + k_4\rho^4 + \cdots$$

where, as before, $\rho = (c - c_0)$. If the change in the energy values due to these terms in ρ be calculated by means of the method of perturbations it will be found that they correspond to

$$\begin{aligned} W = -D + h\omega_0(n + \tfrac{1}{2}) + a_2(n + \tfrac{1}{2})^2 + \cdots \\ + \frac{h^2(j + \frac{1}{2})^2}{8\pi^2Mc_0^2} - b_2(j + 1)^4 + \cdots, \qquad (52.4c) \end{aligned}$$

where the a's and b's are functions of the k's.

As for the rotational energies, the formula developed by Kratzer on the old quantum theory for both rotational and vibrational levels is

$$\begin{aligned} W = -D + h\omega_0\left(n + \frac{1}{2}\right) - \frac{h^2\omega_0^2}{4D}\left(n + \frac{1}{2}\right)^2 + \cdots \\ + \frac{h^2j(j + 1)}{8\pi^2Mc_0^2} - \frac{h^4j^2(j + 1)^2}{128\pi^6M^3c_0^6\omega_0^2} + \cdots \\ - \frac{h^3\omega_0(n + \frac{1}{2})j(j + 1)}{16\pi^2DMc_0^2} + \cdots \qquad (52.5) \end{aligned}$$

where $j(j + 1)$ and $(n + \frac{1}{2})$ have been substituted for j^2 and n in the original formula. This formula has been verified by experiment for a great many cases. For most purposes, the additional terms in higher powers of $(n + \frac{1}{2})$ and $j(j + 1)$ are negligible.

It can be seen that equation (52.4c) corresponds to the Kratzer formula except for the term in $(n + \frac{1}{2})j(j + 1)$.

It would be much more satisfactory, however, to find some potential energy function which would give equation (52.3a) exactly, and give equation (52.5) to the first approximation when the small quantity $\dfrac{h^2}{2\pi^2M}\dfrac{j(j + 1)}{c^2}$ is added as a perturbing energy.

It will be noticed that the allowed levels obtained in equation (22.4) are of just the form of equation (52.3a). The potential energy giving these levels is

$$E_\sigma = -2De^{-a\rho} + De^{-2a\rho}. \qquad (52.6a)$$

This form of the potential energy function satisfies the requirements that E_σ be zero for $c = \infty$ and, that its one minimum point be $-D$ at $c = c_0$. E_σ does not rise to infinity at $c = 0$, but for the values of a corresponding to actual molecules E_σ becomes so large (between $100D$ and $10{,}000D$) that its effect is nearly the same as if it were infinity. This gives allowed energy levels,

$$W_n = -D + h\omega_0\left(n + \frac{1}{2}\right) - \frac{h^2\omega_0{}^2}{4D}\left(n + \frac{1}{2}\right)^2 \qquad (52.6b)$$

when $j = 0$.

The analyses of molecular band spectra give empirical values of ω_0 and $\omega_0 x$ in wave numbers, and values of c_0 in Angstrom units for various electronic levels of diatomic molecules. From these data the potential energy of the levels of the molecules for various values of nuclear separation can be obtained from the formula,[1]

$$E_\sigma = A + De^{-2a(c-c_0)} - 2De^{-a(c-c_0)}, \qquad (52.6c)$$

where A is the potential energy of the dissociated molecule in the particular electronic state,

$$D = \omega_0{}^2/4\omega_0 x$$

where D is in wave numbers if ω_0 and $\omega_0 x$ are given in wave numbers, and

$$a = \sqrt{\frac{8\pi^2 M\omega_0 x}{h}} = 0.2454\sqrt{M\omega_0 x},$$

if c_0 is given in Angstrom units, and

$$M = \frac{M_1 M_2}{(M_1 + M_2)}$$

is in terms of oxygen = 16.

Typical curves for E_σ are given for the oxygen molecule in Fig. 16.

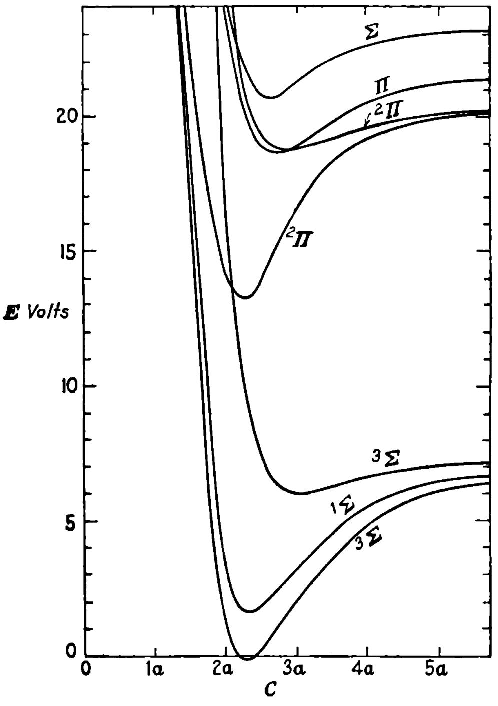

FIG. 16.—Potential energy curves of the oxygen molecule and molecular ion, calculated by means of equation (52.6c).

When the rotational quantum number j is different from zero, the potential energy E_σ in equation (52.6a) is increased by an amount $E_j = j(j + 1)h^2/8\pi^2\mu c^2$. Inasmuch as this increase only affects the wave function to an appreciable extent

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[1] MORSE, *Phys. Rev.*, **34**, 57 (1929).

in the region near $c = c_0$ (where $W > E_\sigma$), it can be expanded about this point,

$$E_j = \frac{h^2 j(j+1)}{8\pi^2\mu c_0^2}\left[1 - 2\frac{\rho}{c_0} + 3\frac{\rho^2}{c_0^2} - \cdots\right].$$

In the range where E_j has any appreciable effect, ρ is small compared to c_0, and since $\frac{h^2 j(j+1)}{8\pi^2\mu c_0^2}$ (which can be called B), is small compared to E for the usual values of j, this expansion can be added to the expansion for E, giving for the first two terms,

$$E_\sigma + E_j = -D + B - \frac{B^2}{Da^2c_0^2} + a^2(D - B)\left(\rho - \frac{B}{c_0a^2D}\right)^2,$$

plus terms in higher powers of ρ.

These two terms can be considered as the first two terms of the expansion of

$$E_\sigma + E_j = \left(D - B + \frac{B^2}{Da^2c_0^2}\right)e^{-2a\left(\rho - \frac{B}{c_0a^2D}\right)} \\ -2\left(D - B + \frac{B^2}{Da^2c_0^2}\right)e^{-a\left(\rho - \frac{B}{c_0a^2D}\right)},$$

indicating that to the first approximation D has decreased to $\left(D - B + \frac{B^2}{Da^2c_0^2}\right)$ and that c_0 has increased to $\left(c_0 + \frac{B}{c_0a^2D}\right)$. The resultant energy levels will be, to the first approximation,

$$\begin{aligned} W_{nj} &= -D + B + \frac{ah}{2\pi}\sqrt{\frac{2D - 2B}{\mu}}\left(n + \frac{1}{2}\right) \\ &\qquad - \frac{a^2h^2(n + \frac{1}{2})^2}{8\pi^2\mu} - \frac{B^2}{Da^2c_0^2} \\ &= -D + h\omega_0\left(n + \frac{1}{2}\right)\left[1 - \frac{h\omega_0}{4D}\left(n + \frac{1}{2}\right) - \frac{h^2(j+1)j}{16\pi^2D\mu c_0^2}\right] \\ &\qquad + \frac{h^2j(j+1)}{8\pi^2\mu c_0^2}\left[1 - \frac{h^2j(j+1)}{16\pi^4\mu^2c_0^4\omega_0^2}\right]. \end{aligned} \tag{52.7}$$

This agrees with the general Kratzer formula given in equation (52.5).

53. Vibration Transition Intensities.—For vibration transitions unaccompanied by an electron transition, the vibration quantum number could only change by one unit if the oscillations were accurately governed by the harmonic law. Since they are not, although the deviation is not great for the first few levels, this breaks down the harmonic oscillator selection rule of Sec. **31**, with the result that infra-red bands are observed corresponding to changes of the vibration quantum number greater than one unit.

It would be a simple matter to give a theoretical calculation of the relative intensity of such bands in terms of the deviation of the force law from that of the harmonic oscillator. From the spacing of the vibrational levels themselves, the force law or $V(c)$ for the molecule and in turn from this could be inferred, by using the perturbation theory to find approximate wave functions, approximate values for the various transition probabilities. This has not been done apparently because there are virtually no empirical data on relative intensities of the vibration bands with which to compare the theory.

Since this was written such a study has been made by Dennison[1] based on recent experimental work by Meyer and Levin and theoretical work by Colby. It is found that the ratio of the intensity of the 0 → 2 absorption band to that of the 0 → 1 band in HCl gas is experimentally 0.017. The ratio obtained by the correspondence principle and the old quantum theory is 0.039; whereas that obtained by the quantum mechanics, using the law of force given in equation (52.4*a*), and calculating by perturbation theory, is 0.0197. Dunham has made a calculation using the law of force given in equation (52.6*a*), and obtains a ratio of 0.0161. The fact that this last ratio is closer to the experimental value again shows that expression (52.6*a*) expresses the potential energy function better than the other form.

The question of the relative intensities of the different bands of an electronic band system is much more interesting in that it can be treated approximately by simple classical mechanical considerations which have an easily understood relation to the quantum mechanical treatment of the same question. The problem is, what are the relative probabilities of various nuclear motions taking place when a given electronic transition occurs in the molecule? As in previous sections, the electronic motion is approximately separable from the nuclear motion which, in turn, is governed by a potential energy curve characteristic of each electronic state. The characteristic feature of the molecular theory is that the nuclei are so massive that their relative motion is affected only by the average of the rapidly fluctuating forces

[1] MEYER AND LEVIN, *Phys. Rev.*, **34**, 52 (1929); DUNHAM, *Phys. Rev.*, **34**, 438 (1929).

exerted on them by the electrons. When, therefore, the electron jumps, with the emission of a quantum of radiation, the momentum changes involved are so small that it is natural to suppose that, during the transition, the nuclear motion is not affected. That is to say, the nuclei have the same velocity and momentum the instant after the transition as they have before. On this assumption, that the nuclear separation and momentum is not affected by the transition, a value for the energy of vibration in the final state in terms of the two potential energy curves and of the initial vibratory motion can be found. Then if it be further assumed that the electron transition is just as likely to happen at one time as another, independently of the phase of the vibratory motion, a complete theory of the relative probability of transition to the various final vibrational energies is had. The picture is evidently too classical, for it gives probability of transition to a continuum of vibrational energy values instead of just to the allowed levels. The quantum nature of matter has then to be introduced by supposing that each quantum level will actually get the amount assigned to the continuum extending on either side of itself halfway to the next adjacent allowed levels.

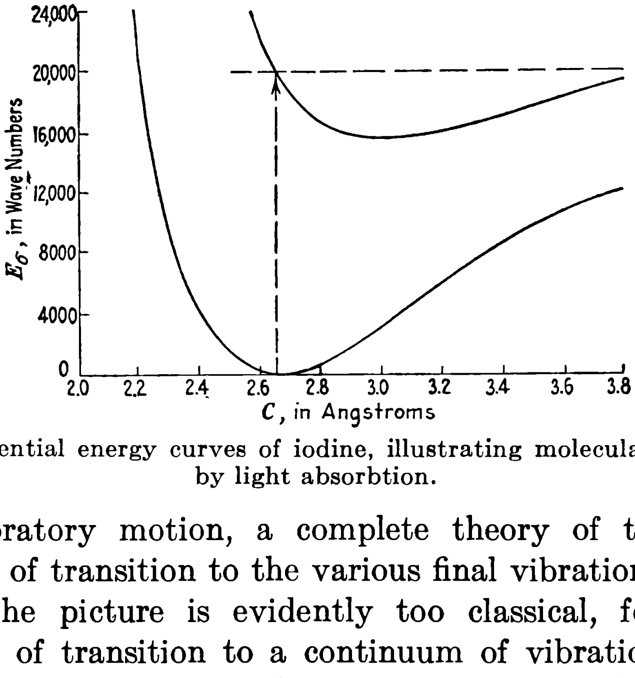

FIG. 17.—Potential energy curves of iodine, illustrating molecular dissociation by light absorbtion.

This picture was first advanced by Franck[1] as a mechanism whereby molecules could be dissociated directly by the absorption of light. Experiments of Dymond showed that this was happening in iodine vapor. Franck pointed out that if the two potential energy curves were related as in Fig. 17 (owing to incomplete analysis of the bands the curves were not known at that time),

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[1] FRANCK, *Trans., Far. Soc.*, **21**, Part 3 (1925).

then for the reasons just given a non-vibrating molecule for which the nuclear separation would correspond to the minimum of the normal state curve would most probably absorb light which would not call for an alteration of nuclear separation during the transition. This is to the energy which is obtained by drawing a line vertically upward from the minimum of the lower curve to where it intersects the upper curve. For iodine, the figure shows that this corresponds to just enough energy to effect dissociation of the molecule. The molecule starts to oscillate with the amplitude appropriate to the new amount of vibrational energy. But as this exceeds the dissociation energy, the result is direct dissociation. Empirically, what happens is that iodine absorbs, from the zero vibration level of its normal state, energy which may raise it to anything from the last twenty vibration levels up to amounts somewhat in excess of the dissociation limit.

With chlorine and bromine, the upper curve lies even more to the right of the lower curve, relatively, so by these arguments one would predict that the strongest absorption would correspond to energy more than sufficient to cause dissociation. This is observed experimentally. What is found is a broad band of continuous absorption which corresponds to dissociation which leaves the constituent atoms flying apart with residual kinetic energy left over at infinite separation. Thus these views are in the main correct, although they give no understanding of why the continuous absorption band has the breadth which it has.

Applied to systems of bands, the picture gives a good semi-quantitative account of the facts.[1] Referring to Fig. 18 suppose that the molecule is initially in the upper electronic state vibrating with an amount of energy represented by the horizontal line through A. At the instant it is at A it is moving with kinetic energy measured by AB so, if the electron transition takes place at this instant, it will most probably find itself with the energy given by a horizontal line through D where CD is equal to AB. In this way, a most probable final vibrational energy is correlated to each phase of the initial vibrational motion. Consideration of the relationships involved makes it evident that if the two curves are precisely of the same shape and situated with their minima at the same nuclear separation, then there will be no tendency for the vibrational energy to be changed by the electron tran-

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[1] Condon, *Phys. Rev.*, **28**, 1192 (1926); **32**, 858 (1928).

sition. Such a case is offered by the known band system of silicon nitride. On the other hand, if the curves are quite different in shape, or, if they are similar but not situated one above the other, large changes in vibrational energy, even to dissociation as with the halogens, may occur. In general, it works out that for each value of the initial vibrational quantum number there are two groups of values of the final vibrational quantum number which are most favored. For one of these the change, $n' - n''$, is positive, and for the other it is negative.

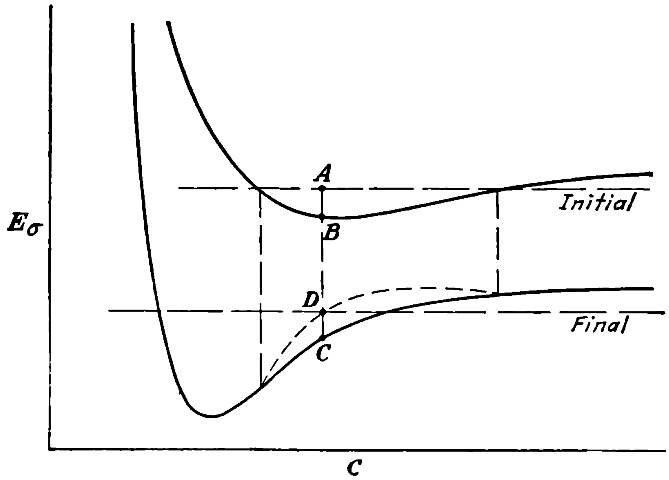

Fig. 18.—Potential energy curves illustrating transition probabilities for electronic bands.

A correlation of the intensity distribution in the band system with the structure of the bands is had, therefore, since this too is determined by the potential energy curves. Since the original publication of this interpretation, in 1926, it has been tested on a large number of band systems and in every case agrees with the facts in a way that is as satisfactory as can be expected from such a classical argument.

When the same question is approached from the standpoint of the quantum mechanics, at first sight quite a different picture is obtained. According to the methods of Chap. III, the matrix component of the electric moment of the molecule corresponding to the transition in question must be computed. We denote the electronic coordinates collectively by x, and the nuclear separation by c, and the electronic and vibrational quantum numbers, respectively, by σ and n. The wave function, according to equation (51.8b) will be approximately of the form,

$$\psi_\sigma(x) \cdot \chi_{\sigma n}(c),$$

and the electric moment will be a linear function of x and c, $M(x, c)$, therefore, the integral which measures the transition probability for $\sigma' \rightarrow \sigma''$ and $n' \rightarrow n''$ is approximately,

$$M(n'n'') = \int M(x, c)\psi_{\sigma'}(x)\psi_{\sigma''}(x) \cdot \chi_{\sigma' n'}(c)\chi_{\sigma'' n''}(c)dxdc.$$

If the same electronic transition is always dealt with, that is, the same band system, the integration over the electronic coordinates may be supposed to be carried out giving

$$M(n'n'') = \int M_{\sigma'\sigma''}(c)\chi_{\sigma' n'}(c)\chi_{\sigma'' n''}(c)dc,$$

where $M_{\sigma'\sigma''}(c)$ is the result of integrating $M(x, c)$ with the two electronic factors of the wave function over the electron coordinates. $M_{\sigma'\sigma''}(c)$ is thus an effective electric moment of the molecule for the electron jump in question. Without great error, it can probably be regarded as essentially constant for the range of c in which the radial factors $\chi(c)$ are appreciably different from zero.

That this formula is in the main consistent with the qualitative classical ideas just presented can now be seen, simply because of the known relation of the wave functions to the range of the classical motion. Thus, if there is a large change in the nuclear separation for zero vibration between the two electronic states, the $0 \rightarrow 0$ band will be relatively weak, for in the integrand of $M(0, 0)$ the two wave functions will each have very small values where the other is appreciable and so the whole integral will have a relatively small value. An essential difference between the two ways of looking at the phenomenon, and one which favors the wave mechanical method, is that it does give an understanding of the amount of deviation from Franck's ideas which is to be expected. In the case just considered, for example, no matter how large the change in moment of inertia, the integral will not vanish completely. Thus, the part of the principle which says that those transitions calling for least change in the nuclear separation are most probable is here a consequence of the fact that the wave function tends rapidly to zero outside of the range of the corresponding classical motion.

The principle that the nuclear momentum tends also to be unaltered in the transition also follows from the quantum mechanical formula. In the simplest instance suppose there is little or no change in the moment of inertia during the electron transition. Then there is no question of the integrals vanishing because of the factors not both having appreciable values at any part of the range of integration. Now, however, the integral for a transition $0 \rightarrow n''$ where n'' is large will be small because the $\chi_{\sigma''n''}(c)$ will be rapidly oscillatory in the essential part of the range of integration so the integrand tends to be as much positive as negative. Of course the oscillatory character of the second factor is the quantum mechanical expression of the fact that the nuclei have relative momentum. Here too the quantum mechanical formula only shows a trend in favor of small alterations in the nuclear momentum rather than a definite requirement of no change.

While the quantum mechanical formula thus gives results agreeing in the main with the classical picture, it is better in that it shows an unsharpness in the strict application of the ideas which corresponds to the observed facts in the band intensity distribution. On reexamining the classical view of the matter, one sees why it is that this leads to an over-precise prediction of the transitions. It is simply that the argument made use essentially of a precise correlation between the instantaneous values of the position and momentum of the nuclei, a thing which is contrary to the quantum mechanics. It has been shown (Sec. 7) that the wave picture does not allow the use of such arguments unless an inaccuracy in the predictions of an amount governed by $\Delta p \cdot \Delta x > h$ is contemplated. A closer consideration of the behavior of the matrix component integral shows that the difference between its predictions and those of the classical view may be said to have their origin in just this fundamental difference between classical and quantum mechanics.

54. Hydrogen Molecular Ion.—From what we have seen so far, it is clear that the molecular potential energy function $E_\sigma(c)$ is the function which determines the molecular properties. By means of equation (52.6*c*) it is possible to compute this function if the structure of the molecular band spectrum is known. It should be possible to compute E_σ theoretically, however, by means of equation (51.4), but mathematical difficulties prevent any such calculation except for the case of a diatomic molecule with 1 or, at the most, 2 electrons.

The rest of this chapter will be devoted to a discussion of the calculation of the potential energy functions $E_\sigma(c)$ for the two simplest molecules, the hydrogen molecular ion H_2^+ and the neutral hydrogen molecule H_2. These will be calculated by means of equation (51.4), $(H_0 - E)\psi = 0$.

It is possible, as was mentioned before, to separate the constant term $E_r = \dfrac{Z_1 Z_2 e^2}{c}$ from H_0 and to calculate E_e by the equation,

$$-\frac{h^2}{8\pi^2\mu}\sum_{s=1}^{N}\Delta_s\psi + V_e(\xi_s, \eta_s, \phi_s, c)\psi = E_e\psi,$$

where V_e is the potential energy of the electrons alone.

Then

$$E_\sigma = E_r + E_e.$$

For the molecule $H_2{}^+$, $Z_1 = Z_2 = 1$, $M_1 = M_2 = 2M$ and there is only 1 electron. In this case, the above equation becomes,

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}\left[E_e + \frac{e^2}{r_1} + \frac{e^2}{r_2}\right]\psi = 0. \tag{54.1a}$$

The elliptic coordinates $\xi = \dfrac{(r_1 + r_2)}{c}$, $\eta = \dfrac{(r_1 - r_2)}{c}$ and ϕ are used, and the Laplacian in these coordinates can be calculated by the general method given in Chap. I. When this is done the equation becomes,

$$\begin{aligned}\frac{\partial}{\partial\xi}\left[(\xi^2 - 1)\frac{\partial\psi}{\partial\xi}\right] + \frac{\partial}{\partial\eta}\left[(1 - \eta^2)\frac{\partial\psi}{\partial\eta}\right]& \\ + \left[\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2}\right]\frac{\partial^2\psi}{\partial\phi^2}& \\ + \frac{2\pi^2\mu c^2}{h^2}\left[E_e(\xi^2 - \eta^2) + \frac{4e^2}{c}\xi\right]\psi &= 0.\end{aligned}$$

This equation can be separated, and the usual assumption is made, that

$$\psi = \Phi(\phi)\cdot\Xi(\xi)\cdot H(\eta).$$

Since ϕ is a cyclic coordinate,

$$\Phi = \frac{1}{\sqrt{2\pi}}e^{i\lambda\phi}$$

where λ is an integer.

The equations for the other two factors are

$$\left.\begin{aligned} &\frac{d}{d\xi}\left[(\xi^2-1)\frac{d\Xi}{d\xi}\right] - \frac{\lambda^2\Xi}{\xi^2-1} \\ &\qquad + \frac{2\pi^2\mu c^2}{h^2}\left[E_e\xi^2 + \frac{4e^2}{c}\xi + K\right]\Xi = 0 \\ &\frac{d}{d\eta}\left[(1-\eta^2)\frac{dH}{d\eta}\right] - \frac{\lambda^2 H}{1-\eta^2} + \frac{2\pi^2\mu c^2}{h^2}[E_e\eta^2 - K]H = 0, \end{aligned}\right\} \tag{54.1b}$$

where K is the arbitrary constant introduced when the equations were separated. Since $\frac{8\pi^2\mu e^2 c}{h^2} = \frac{2c}{a}$ where a is again the radius of the first Bohr orbit of hydrogen, and $-\frac{2\pi^2\mu c^2 E_e}{h^2} = \frac{E_e}{4a^2R}c^2$ where R is the energy of the lowest state of the hydrogen atom, the equations become,

$$\begin{aligned} &(\xi^2-1)\Xi'' + 2\xi\Xi' \\ &\qquad + \left(A + \frac{2c}{a}\xi - \frac{E_e}{4a^2R}c^2\xi^2 - \frac{\lambda^2}{\xi^2-1}\right)\Xi = 0 \\ &(1-\eta^2)H'' - 2\eta H' - \left(A - \frac{E_e}{4a^2R}c^2\eta^2 + \frac{\lambda^2}{1-\eta^2}\right)H = 0 \end{aligned} \tag{54.2}$$

where

$$A = \frac{8\pi^2\mu K}{h^2}.$$

The solutions of these, simultaneously, will fix the allowed values of E_e and A for which Ξ and H will be finite, continuous, and single valued over the ranges $+1 \leqslant \xi \leqslant \infty$ and $-1 \leqslant \eta \leqslant +1$.

No exact solution of these equations has been devised as yet. Several attempts have been made, however, to obtain an approximate solution.

For instance, when the value of E_e for the lowest possible electronic state only is sought, m becomes zero, and since it has been shown that the wave function for a lowest state has no nodal surfaces, therefore Ξ and H will not be zero within the intervals for ξ and η the functions,

$$X = -\frac{1}{\Xi}\frac{d\Xi}{d\xi}; \qquad Y = -\frac{1}{H}\frac{dH}{d\eta}$$

will have no infinite values in the ranges of ξ and η.

Then

$$\frac{dX}{d\xi} = \frac{1}{\Xi^2}\left(\frac{d\Xi}{d\xi}\right)^2 - \frac{1}{\Xi}\frac{d^2\Xi}{d\xi^2}$$

$$= X^2 + \frac{\left[A + \left(\frac{2c}{a} - 2X\right)\xi - \frac{E_e c^2 \xi^2}{4a^2 R}\right]}{(\xi^2 - 1)}$$

from equation (54.1*b*).

Similarly,

$$\frac{dY}{\mathrm{d}\eta} = Y^2 - \frac{\left[A - 2Y\eta - \frac{E_e c^2 \eta^2}{4\partial^2 R}\right]}{(1 - \eta^2)}.$$

These equations are in a form for numerical integration.[1] $Y(\eta)$ should be $-Y(-\eta)$, since $H(\eta) = H(-\eta)$, so that the series,

$$Y(\eta) = b_1\eta + b_3\eta^3 + b_5\eta^5 + \cdots,$$

can be taken to express Y for a certain range of values of η, say from $-\frac{1}{2}$ to $+\frac{1}{2}$. When this series is substituted in the equation above, there arise certain equations relating $A, 2c/a$, and $E_ec^2/4a^2R$ with the b's, so that the value of Y is known when values of A, E_e, c, and η are assumed. However, when η is nearly unity, it can be represented as $1 + \delta$ where δ is essentially negative.

Then

$$Y(1 + \delta) = Y(1) + c_1\delta + c_2\delta^2 + c_3\delta^3 + \cdots$$

can express Y for the range of values from $\eta = 1$ to $\eta = \frac{1}{2}$. This can also be substituted in the equation for Y, and the b's can be found in terms of A and E_e. Since Y must be finite over the whole range of η, the first series must be finite over the range $0 \leqslant \eta \leqslant \frac{1}{2}$, and the second over the range $0 \geqslant \delta \geqslant -\frac{1}{2}$. Presumably, this will be true for certain ranges of values of A and E_e. Moreover, the numerical value of Y determined by the first series for $\eta = \frac{1}{2}$ must equal the value of Y determined by the second series for $\delta = -\frac{1}{2}$ and for the same assumed values of A and E_e for a given value of c. This imposes a restriction on the possible pairs of values of A and E_e, *i.e.*, for given assumed values of A and c there will be only one value of E_e which will make the series join at $\eta = \frac{1}{2}$.

These allowed values of E_e are calculated for various values of A for a given value of c, and the relationship is plotted.

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[1] Burrau, Kgl. Danske., Vid. Selskob., **7**, 14 (1927).

A similar pair of series is set up for X, in terms of $\epsilon = \xi - 1$, and $\zeta = \frac{1}{\xi}$, and by making the two series join at $\epsilon = 1$, another relation between E_e and A for a given c can be calculated. But this relation is not the same as the one obtained from the series for Y, and there will only be one pair of values of A and E_e for any given c which will satisfy both requirements.

By this means, numerical values for E_e can be obtained for various values of c, and these represent the allowed energy values for the lowest electronic level as a function of the nuclear separation c. This curve is plotted in Fig. 19 as is also the potential energy function. $E_\sigma = E_e + \frac{e^2}{c}$. The values of E_σ for several values of $S = \frac{c}{a}$ are given in the table in this section, in the column marked E_σ, Burrau.

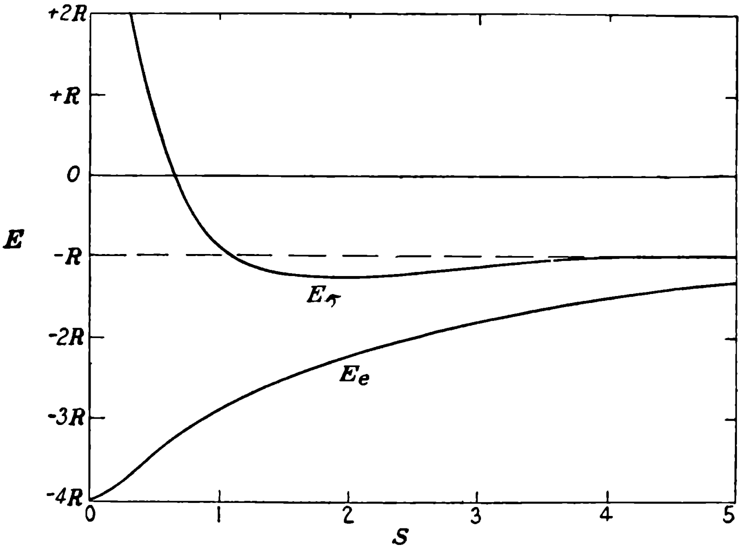

FIG. 19.—Electronic and potential energies of the lowest electronic state of the hydrogen molecular ion. R here equals minus the R in text.

It is to be noticed that although E_σ becomes infinite at $c = 0$, E_e is finite throughout the whole range of c. This is not surprising, for at $c = \infty$ the system (called the separated atoms) must be a hydrogen atom in its normal state infinitely separated from a proton. Since the proton has zero energy by itself, then E_e at $c = \infty$ must equal R, the energy of a normal hydrogen atom. For $c = 0$ the system (called the united atom) is that of an electron about a single nucleus of charge $2e$ (*i.e.*, that of a helium ion) and, therefore, $E_e = 4R$. The calculated curve shows a smooth line connecting these two limiting values.

This result for the limiting values of c can be shown in a better way. When $c \to 0$, the elliptical coordinates, ξ, η, and ϕ, degenerate into spherical coordinates r, θ, and ϕ, where $c\xi = 2r$ and $n = \cos\theta$.

Equations (54.2) become

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\Xi_0}{dr}\right] + \left[-\frac{E_{e0}}{a^2R} + \frac{4}{ar} + \frac{A}{r^2}\right]\Xi_0 = 0$$

$$\sin\theta\frac{d}{d\theta}\left[\sin\theta\frac{dH_0}{d\theta}\right] + [\lambda^2 - A\sin^2\theta]H_0 = 0. \qquad (54.3a)$$

These equations are similar to those for the hydrogen atom, and the solution is,

$$\psi_0 = \Phi_0\Xi_0 H_0 = N_0 e^{i\lambda\phi}\cdot\sin^\lambda\theta\cdot P_l^\lambda(\cos\theta)\cdot e^{-\frac{2r}{n_0a}}\cdot$$

$$\left(\frac{4r}{n_0a}\right)^l\cdot L_{n_0+l}^{2l+1}\left(\frac{4r}{n_0a}\right), \qquad (54.3b)$$

the allowed energy levels being,

$$E_{e0} = \frac{4R}{{n_0}^2} \qquad (n_0 = 1\ 2,3\cdots) \qquad (54.3c)$$

n_0 is the sum $n_r + n_\theta + \lambda + 1$ and $l = n_\theta + \lambda$ where n_r, n_θ, and λ are quantum numbers indicating the number of nodal surfaces in the coordinates r, θ, and ϕ, respectively (see Sec. **28**).

When $c = \infty$, the wave function is effectively zero except near one or the other nuclei. In other words, the only range of the variables in the differential equation which are of interest are for values of ξ very near unity and for values of η very near $+1$ or -1. In this case, $\xi - 1$ is the variable and ξ alone can be considered unity.

This gives the equations,

$$\frac{d^2\Xi_\infty}{d(\xi-1)^2} + \frac{1}{(\xi-1)}\frac{d\Xi_\infty}{d(\xi-1)} +$$

$$\left[-\frac{c^2E_{e\infty}}{4a^2R} + \frac{c(1-\beta)}{a(\xi-1)} - \frac{\lambda^2}{4(\xi-1)^2}\right]\Xi_\infty = 0, \qquad (59.4a)$$

and

$$\frac{d^2H_\infty'}{d(1+\eta)^2} + \frac{1}{(\eta+1)}\frac{dH_\infty'}{d(1+\eta)} + \left[-\frac{c^2E_{e\infty}}{4a^2R} + \frac{c(1+\beta)}{a(1+\eta)} - \frac{\lambda^2}{4(1+\eta)^2}\right]H'_\infty = 0,$$

or

$$\frac{d^2H_\infty''}{d(1-\eta)^2} + \frac{1}{(1-\eta)}\frac{dH_\infty''}{d(1-\eta)} + \left[-\frac{c^2E_{e\infty}}{4a^2R} + \frac{c(1+\beta)}{a(1-\eta)} - \frac{\lambda^2}{4(1-\eta)^2}\right]H_\infty'' = 0,$$

depending on whether the wave function is effective at the one nucleus or the other. Since the nuclei are exactly similar, it is just as probable that the electron be about one as the other, the complete wave function must be,

$$\begin{aligned}\psi_\infty &= \frac{1}{\sqrt{2}}[\psi_\infty' \pm \psi_\infty''] \\ &= N_\infty e^{i\lambda\phi}\cdot e^{-\frac{c\xi}{n_\infty a}}\cdot\left[\frac{2c(\xi-1)}{n_\infty a}\right]^{\frac{\lambda}{2}}\cdot L^{\lambda}_{n_x+\lambda}\left[\frac{2c(\xi-1)}{n_\infty a}\right] \\ &\quad\cdot\left\{e^{-\frac{c\eta}{n_\infty a}}\cdot\left[\frac{2c(1+\eta)}{n_\infty a}\right]^{\frac{\lambda}{2}}\cdot L^{\lambda}_{n_y+\lambda}\left[\frac{2c(1+\eta)}{n_\infty a}\right]\right. \\ &\quad\left.\pm e^{+\frac{c\eta}{n_\infty a}}\cdot\left[\frac{2c(1-\eta)}{n_\infty a}\right]^{\frac{\lambda}{2}}\cdot L^{\lambda}_{n_y+\lambda}\left[\frac{2c(1-\eta)}{n_\infty a}\right]\right\}\end{aligned} \tag{54.4b}$$

where $n_\infty = n_x + n_y + \lambda + 1$. These latter quantum numbers represent the number of nodal surfaces near each nucleus in the ξ, η, and ϕ coordinates, respectively.

The energy for $c = \infty$ is

$$E_{e\infty} = \frac{R}{n_\infty{}^2}. \tag{54.4c}$$

The energy E_e for intermediate values of c must be represented by a set of continuous curves connecting the set of E_{eo}'s and $E_{e\infty}$'s.

The oscillatory properties of the wave function considered in Sec. **28** can be applied here to determine which E_{eo} goes to which $E_{e\infty}$. For since the general equation (54.1a) is separable in elliptic coordinates, then the nodal surfaces will be in these coordinates. The total number of nodal surfaces in ξ, n_ξ, the number in η, n_η, and the number in ϕ, λ will remain unchanged as c is changed slowly. Therefore, n_ξ will equal n_r when $c = 0$ and will equal n_x when $c = \infty$ and will have the same value throughout. Also, n_η will equal n_θ but, in general, it will not equal n_y. For n_y represents the number of nodal surfaces in η near one nucleus, whereas n_η is the total number of these surfaces in the system. Therefore, when the symmetric factor $(H_\infty' + H_\infty'')$ is used $n_\eta = 2n_y$, and when the antisymmetric factor $(H_\infty' - H_\infty'')$ is used $n_\eta = 2n_y + 1$, for the antisymmetry introduces on extra nodal surface midway between the nuclei. Therefore, when $c = \infty$ the quantum numbers are n_x, n_y, and λ, the energy will be

$$E_{e\infty} = \frac{R}{(n_x + n_y + \lambda + 1)^2},$$

and as c is brought adiabatically to zero, this energy will become

$$E_{eo} = \frac{4R}{n_x + 2n_y + \lambda + 1)^2}$$

or

$$\frac{4R}{(n_x + 2n_y + \lambda + 2)^2}$$

according as the wave function is symmetric or antisymmetric in the H factor.

The quantum numbers used here are related to the various angular velocity vectors dealt with by band spectroscopists. The number $l = n_\eta + \lambda$ represents the total orbital angular momentum of the electron, and λ represents the projection of l on the nuclear axis. The number representing the electronic spin s which is not considered here, has the projection χ on the nuclear axis, and the vector sum of l and s, j, has the projection ω. The question of the "coupling" between l, s and the nuclear rotation will not be treated here.

The energy levels E_σ for a single electron are labelled first by the number representing n, then by a Roman letter (in the order, s, p, d, f, g . . .) representing l, and by a Greek letter (in the order σ, π, δ, ϕ, γ . . .) representing λ. Levels in systems of more than 1 electron are labelled, analogously, to the atomic levels Σ_J, where $r(= 2s + 1)$ is the "multiplicity," Σ (in the order Σ, Π, Δ, Φ, ,Γ . . .) represents the value of Λ, the sum of the λ's, and J is the sum of the j's.

The above discussion suggests another method of obtaining the value of E_e for any c which will be more powerful than the method outlined previously, since it will give a simple expression for the wave function as well, and will be applicable to other levels beside the lowest.[1]

The energy of the lowest state will be obtained as an example of the method.

A glance at the expressions for ψ_0 and ψ_∞ for $n = 1$, will show that both functions can be represented by the expression,

$$\psi = Be^{-\frac{S\alpha\xi}{2}}\left(e^{-\frac{S\beta\eta}{2}} + e^{+\frac{S\beta\eta}{2}}\right), \tag{54.4}$$

where B, α, and β are functions of c whose values for various values of c are to be found. $S = c/a$, the nuclear separation in units of a.

In Sec. **45** it was shown that the Schrödinger equation can be solved by the Ritz method by transforming it into the integral of equation (45.4),

$$J = \iiint\left[T\left(q, \frac{h}{2\pi}\frac{\partial\psi}{\partial q}\right) + V_e\psi^2\right]dv$$
$$= \iiint\left[\frac{h^2}{8\pi^2\mu}\text{ grad }\psi\cdot\text{grad }\psi + V_e\psi^2\right]dv,$$

where dv is the volume element. This integral has a stationary value, where $\delta J = 0$, and the value of J at this stationary point is the allowed value of E_e.

By Green's theorem it is possible to show that

$$J = \iiint\bar{\psi}\left[-\frac{h^2}{8\pi^2\mu}\Delta\psi + V_e\psi\right]dv + \iint\bar{\psi}\text{ grad }\psi\cdot dS.$$

The surface integral disappears at the boundary as for equation (12.1), and therefore,

$$J = \int\int\int\bar{\psi}H\psi dv$$

where H is the operator $\left[-\frac{h^2}{8\pi^2\mu}\Delta + V_e\right]$, as before.

Now if the form, equation (54.4), chosen for ψ is correct, then the values of B, α and β which make J a minimum for a given c will give at once the correct wave function and the allowed energy. If the form chosen is not quite correct, then the wave

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[1] Guillemin and Zener, *Proc.* Nat. Acad. Sci., **15**, 314 (1929).

function and energy so determined will be approximately equal to the true ψ and E_e.

The operator H is applied to the ψ chosen in equation (54.4), this is multiplied by ψ and the quantity is integrated, whence

$$J = \frac{f_1 + \left(S\alpha - 4S - \frac{4}{\alpha} + 1\right)\cdot f_2 - \frac{2}{3}(S\beta)^2}{\frac{1}{\beta^2}f_2 + \left(\frac{S}{\alpha} + \frac{1}{\alpha^2}\right)\cdot f_2 + \frac{2}{3}S^2} + \frac{2}{S}$$

where

$$f_1 = e^{S\beta}\left(1 - \frac{1}{S\beta}\right) + e^{-S\beta}\left(1 + \frac{1}{S\beta}\right)$$

and

$$f_2 = \frac{1}{S\beta}(e^{S\beta} - e^{-S\beta}) + 2$$

Then by graphical methods the values of α and β were found which make $\partial J/\partial\alpha = \partial J/\partial\rho = 0$ for an assumed value of S. The values of α, β and $E_\sigma = E_e + e^2/c$ are given in the table. The values of $E\sigma$ are given in the column marked E_σ (Ritz) and the column E_σ (Burrau) gives the values obtained by the preceding special method. The close agreement shows that both methods probably give good approximations to the true E_σ.

S	α	β	E_σ (Burrau)	E_σ (Ritz)	E_σ (pert)
0	2.00	1.00	$-\infty$	$-\infty$	$-\infty$
1.0	1.50	0.99	0.896	0.903	0.770
1.3			1.110	1.112	0.914
1.6			1.186	1.191	0.990
1.8	....	....	1.198	1.203	1.018
2.0	1.36	0.92	1.204	1.205	1.036
2.2			1.200	1.199	1.042
2.4			1.192	1.192	1.044
2.95	....	....	1.158	1.155	1.035
3.00	1.22	0.89	.....	1.154	1.033
4.00	1.14	0.88	.....	1.092	1.006
∞	1.00	1.00	1.000	1.000	1.000

S in terms of a as a unit, E in terms of R as a unit.

Presumably the Ritz method could be used for the other electronic states of $H_2{}^+$, but so far no attempt has been made to do so.

It is possible, however, to obtain the values of E_e for the higher states by the usual perturbation methods discussed in Chap. IV.[1]

There are two methods of approach. First, the unperturbed state can be considered as that of the united atom ($c = 0$), and the perturbing energy can be taken as the difference between the resulting centrally symmetric field and the field resulting when the two nuclei are slightly separated,

$$V_1 = \frac{2e^2}{r} - \frac{e^2}{r_1} - \frac{e^2}{r_2}$$

$$= \begin{cases} \dfrac{2e^2}{r}P_0 - \displaystyle\sum_{\alpha=1}^{\infty}\frac{2e^2c^{2\alpha}}{r^{2\alpha+1}}P_{2\alpha}(\cos\theta) & (r > c/2) \\ \dfrac{2e^2}{r}P_0 - \displaystyle\sum_{\alpha=1}^{\infty}\frac{2e^2r^{2\alpha}}{c^{2\alpha+1}}P_{2\alpha}(\cos\theta) & (r < c/2) \end{cases}$$

when expanded into a series of Legendre polynomials.

The energy of perturbation, as before

$$W^{nlm}_{nl'm} = \int \psi(nl\lambda)\bar{\psi}(nl'\lambda)V_1 dv$$

where ψ is that given in equation (54.3*b*).

The complete potential energy function,

$$E_\sigma'(n_\xi, n_\eta, \lambda) = \frac{4R}{(n_\xi + n_\eta + \lambda + 1)^2} + \frac{e^2}{c} + W'(n_\xi, n_\eta, \lambda),$$

where the last term is one of the roots of the equation,

$$|W^{nl\lambda}_{nl'\lambda} - W'\delta^l{}_{l'}| = 0$$

as given in equation (46.2*c*).

This method is only accurate for small values of c. The other method is to consider the separated nuclei ($c = \infty$) as the unperturbed state, and the perturbing energy as the effect of the other nucleus on the electron. This is,

$$V_2 = \begin{cases} -\dfrac{e^2}{r_2} \text{ for the part of } \psi \text{ representing the electron about the first nucleus.} \\ -\dfrac{e^2}{r_1} \text{ for the part of } \psi \text{ representing the electron about the second nucleus.} \end{cases}$$

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[1] MORSE and STUECKELBERG, *Phys. Rev.*, **33**, 932, (1929).

The energy is calculated similarly to that above, with the wave function as that given in equation (54.3*b*).

The potential energy function is,

$$E_\sigma''(n_x, n_y, \lambda) = \frac{R}{(n_x + n_y + \lambda + 1)^2} + \frac{e^2}{c} + W''(n_x, n_y, \lambda),$$

where the values of E_σ calculated by means of this method are only accurate for large values of c. The curves for $E\sigma'$ and for E_σ'' can be plotted, and joined by a smooth curve.

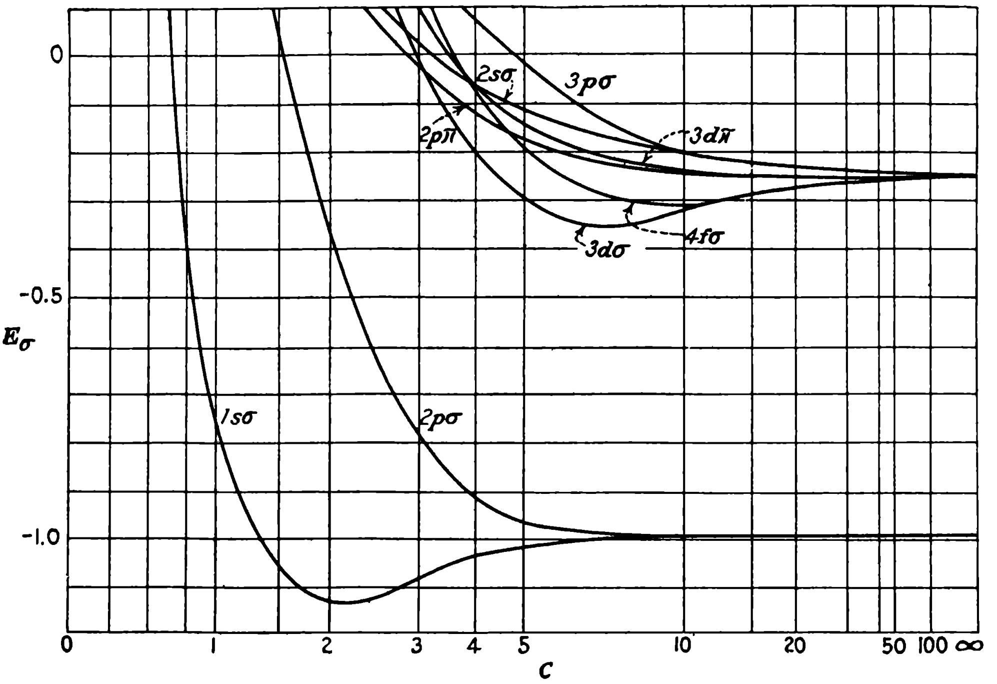

FIG. 20.—Potential energy curves for the hydrogen molecular ion, calculated by perturbation methods. The ordinate is in terms of minus R.

The values calculated by this method for the lowest electronic state are given in the table in the column headed E_σ(pert.), and the curves for E_σ for the first eight electronic states are given in Fig. 20. It will be noticed that the majority of the curves have no minima, representing cases where the molecule will dissociate. Such curves do not give a vibrational or rotational spectrum, and so were not considered in the section on nuclear motion. They have physical reality, however, for certain continuous absorption spectra have been explained by attributing them to a transition from a stable level to an unstable level, with subsequent molecular dissociation.

This last method, although perhaps more straightforward than the others, does not give as satisfactory results, for the accuracy of approximation decreases as c recedes from its limiting values, zero and infinity, and at values near the usual value of c_0 (where the values of E_σ are most interesting) the accuracy is poorest. Also, it is extremely difficult to calculate the second or higher terms in the approximation series for E_σ. It does, however, give an idea of the behavior of E_σ for the excited electronic states, where no calculation has been made by the other methods.

55. The Hydrogen Molecule.—The next simplest diatomic molecule is that having two electrons and two protons.

The general equation is given by

$$\Delta_1\psi + \Delta_2\psi + \frac{8\pi^2 M}{h^2}\left[E + \frac{e^2}{c(\xi_1 + \eta_1)} + \frac{e^2}{c(\xi_1 - \eta_1)} + \right.$$
$$\left. \frac{e^2}{c(\xi_2 + \eta_2)} + \frac{e^2}{c(\xi_2 - \eta_2)} - \frac{e^2}{r_{12}}\right]\psi = 0 \quad (55.1)$$

where Δ_1, ξ_1, η_1, ϕ_1 refer to the first electron, Δ_2, ξ_2, η_2, ϕ_2 refer to the second, and r_{12} is the distance between the two electrons. The term e^2/r_{12} is the interaction and is the same as for the helium atom.

When $c = 0$ the united atom is a helium atom, with its energy values and the wave functions as discussed in Sec. **48.** If the interaction term be neglected this wave function is, as in equation (48.2),

$$\Psi_0 = \frac{1}{\sqrt{2}}[\psi_{01}(n_0 l\lambda)\psi_{02}(n_0' l'\lambda') \pm \psi_{01}(n'_0 l'\lambda')\psi_{02}(n_0 l\lambda)] \quad (55.2a)$$

where the ψ's are those for the helium ion given in equation (54.3*b*). The subscript unity indicates that the wave function is for electron 1, and is in the coordinates ξ_1, η_1, ϕ_1, while subscript two indicates that ψ is for the second electron.

When $c = \infty$ the separated atoms are either two neutral hydrogen atoms (homopolar separation) or one proton and a negative hydrogen atomic ion H^- (polar separation) and the wave functions, when the interaction term is neglected,

$$\Psi_\infty = \tfrac{1}{2}\{[\psi_{\infty 1}'(n_\infty n_x\lambda)\cdot\psi_{\infty 2}''(n'_\infty n'_x\lambda') \pm \psi_{\infty 1}'(n_\infty' n_x'\lambda')\psi_{\infty 2}''(n_\infty n_x\lambda)]$$
$$\pm [\psi_{\infty 1}''(n_\infty n_x\lambda)\cdot\psi_{02}'(n_\infty' n_x'\lambda') \pm \psi_{\infty 1}''(n_\infty' n_x'\lambda')\cdot\psi_{\infty 2}'(n_\infty n_x\lambda)]\},$$

or

$$= \tfrac{1}{2}\{[\psi_{\infty 1}'(n_\infty n_x\lambda)\psi_{\infty 2}'(n_\infty' n_x'\lambda') \pm \psi_{\infty 1}'(n_\infty' n_x'\lambda')\psi_{\infty 2}(n_\infty n_x\lambda)] \pm$$
$$[\psi_{\infty 1}''(n_\infty n_x\lambda)\,.\,\psi_{\infty 2}''(n_\infty' n_x'\lambda') \pm$$
$$\psi_{\infty 1}''(n_\infty' n_x'\lambda')\psi_{\infty 2}''(n_\infty n_x\lambda)]\}, \quad (55.2b)$$

where the ψ's are obtained from equation (54.4*b*). This case illustrates the two different types of symmetry. The symmetry dealt with in the H_2^+ problem is in the nuclei (*i.e.*, if the primes are interchanged for double primes in the above equation, Ψ is symmetric in the nuclei if it keeps the same sign and antisymmetric in the nuclei if it changes sign). The symmetry dealt with in the case of helium is in the electrons (*i.e.*, if the subscripts 1 and 2 are interchanged above, Ψ is symmetric in the electrons if it keeps the same sign and antisymmetric in the electrons if it changes sign).

The problem of obtaining the electronic energies can be attacked by the last two methods used in the section on H_2^+. The lowest level of homopolar H_2 can be assumed to be of the form,[1]

$$\Psi = Ce^{-S\alpha(\xi_1+\xi_2)}[e^{-S\alpha(\eta_1-\eta_2)} + e^{+S\alpha(\eta_1-\eta_2)}], \qquad (55.3)$$

similar to that assumed in equation (54.4). The Ritz method can then be applied to this wave function to obtain the best value of α and therefore of the energy E.

Only the minimum value of E_σ has been obtained. This value is $2.278R$, with a normal nuclear separation $S_0 = 1.23$, corresponding to $\alpha = 1.166$.

The second method of attack is by the usual perturbation theory,[2] using as unperturbed wave functions those given in equations (55.2*a*) or (55.2*b*), and as perturbation in the first case the electronic interaction plus the change in potential energy due to separation of the nuclei; and in the second case, the interaction plus the change in energy due to the approach of the nuclei. These methods of obtaining E_σ are even more inaccurate than the similar methods for H_2^+, for at the values of c near the average c_0, both perturbations are large, and it cannot be expected that the first term in the approximation series for the perturbation energy will be anything more than indicative.

The first case, for small values of c, has not been calculated. The second case, for large values of c, has been calculated for some of the lower symmetric and antisymmetric states of the homopolar molecule. For the lowest state, the wave function is,

$$\Psi = Ce^{-S(\xi_1+\xi_2)}[e^{-S(\eta_1-\eta_2)} + e^{S(\eta_1-\eta_2)}]$$

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[1] WANG, *Phys. Rev.*, **31,** 579 (1928).

[2] HEITLER and LONDON, *Zeits. für Phys.*, **44,** 455 (1927).

and the perturbing potential energy is,

$$V_2 = \frac{e^2}{r_{12}} - \frac{2e^2}{c(\xi_1 - \eta_1)} - \frac{2e^2}{c(\xi_2 + \eta_2)},$$

for the part of Ψ representing the first electron about the first nucleus and the second about the second; and

$$V_2 = \frac{e^2}{r_{12}} - \frac{2e^2}{c(\xi_1 + \eta_1)} - \frac{2e^2}{c(\xi_2 - \eta_2)}$$

for the part of Ψ representing the first electron about the second nucleus and the second about the first.

The calculation of higher levels is similar.[1]

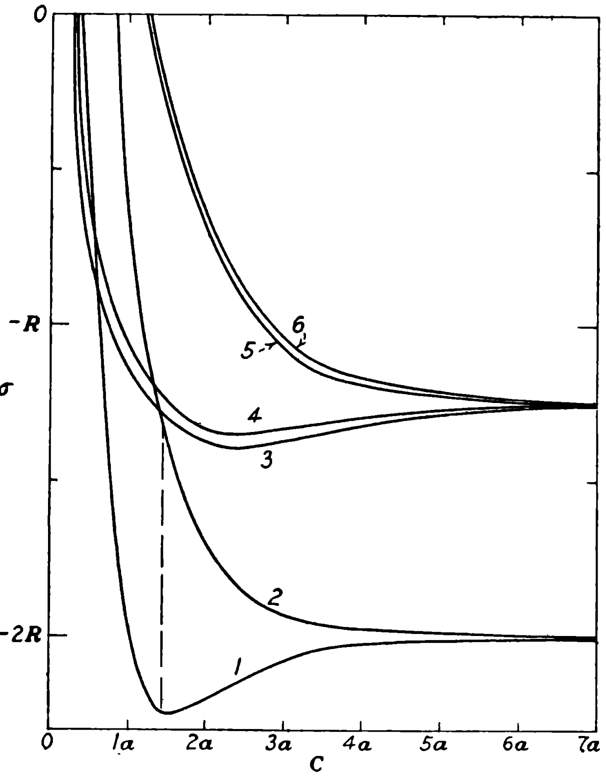

FIG. 21.—Potential energy curves for the hydrogen molecule, calculated by perturbation methods. R here equals minus the R in the text.

The curves for several states are shown in Fig. 21. The value of the minimum $E_\sigma{}^0$ for the lower curve is $2.24R$ with a value of S_0 as 1.30 in fairly good agreement with the values computed by means of the Ritz method.

The experimental values for this level are $E_\sigma{}^0 = 2.32R$, and $S_0 = 1.23$, which are somewhat nearer those calculated by the Ritz method than those calculated by the usual perturbation methods. It is surprising, however, that this latter method

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[1] KEMBLE and ZENER, *Phys. Rev.*, **33**, 512 (1929).

should give results as well in accord with experiment as it seems to do.

No calculations have been made for more complex systems, and any discussion of the behavior of such molecules would seem to be necessarily confined to an empirical determination of their potential energy curves, as discussed in Sec. **50**, or else to a qualitative analysis of the types of coupling and of multiplet separation, as in atomic spectra, which is beyond the scope of this work.

56. Continuous Spectrum of Molecular Hydrogen.—Besides the many band systems which are known to be emitted by the neutral hydrogen molecule, an outstanding feature of its spectrum is the continuous radiation which is emitted by it extending from the red part of the visible spectrum to the far ultra-violet. The molecular process involved here was originally interpreted along the lines of Sec. **53** by supposing that it arose in transitions from some excited states of the molecule to the normal state with simultaneous dissociation of the molecule.

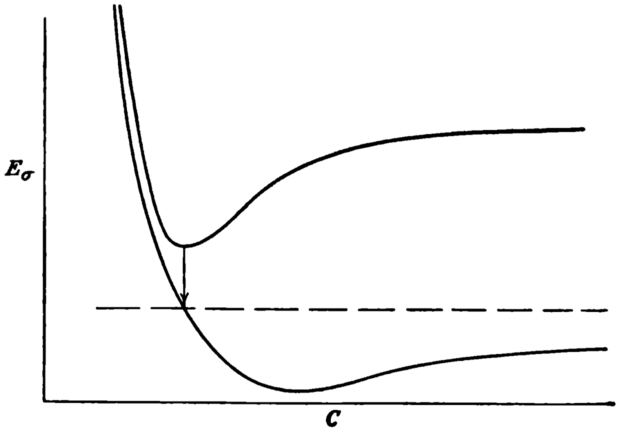

Fig. 22.—Potential energy curves illustrating Blackett and Franck's explanation of continuous molecular spectrum of hydrogen.

For this to happen it would be necessary for one of the excited states to have the minimum of its potential energy curve over the steep part of the normal state potential energy curve as in Fig. 22, in order that transitions from it into the continuous spectrum above dissociation would occur. Such an interpretation was proposed by Blackett and Franck before the molecular spectrum had been worked out. But with the subsequent analysis of the bands, it became apparent that in molecular hydrogen all of the excited states have moments of inertia which are considerably larger than that of the normal state, therefore this explanation is unsatisfactory.

Winans and Stueckelberg[1] saw a satisfactory way out by making use of the purely repulsive potential energy curve

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[1] Winans and Stueckelberg, *Proc.* Nat. Acad. Sci., **14,** 871 (1928). Condon and Smyth, *Proc.* Nat. Acad. Sci., **14,** 871 (1928).

corresponding to the antisymmetrical mode of coming together of two hydrogen atoms in the normal state as discussed in Sec. **55.** Transitions from any of the excited states of the molecule to the electronic state of the molecule represented by this repulsive curve would plainly lead to a direct dissociation of the molecule, and, because the curve comes up so steeply under the minima of those for the various excited states, one has a good probability for transitions to occur to a large range of final energy values giving rise to the extraordinarily great frequency range of the observed continuous spectrum. The continuous spectrum may thus be regarded as one or more band systems whose initial states are various excited states of the molecule and whose final state is represented by the electronic state which gives a pure repulsion of the two atoms.

This view of the continuous spectrum seems to be wholly satisfactory and affords at the same time definite evidence for the physical reality of this mode of interaction of two hydrogen atoms. It appears that some experiments of Hughes and Skellett on the direct dissociation of the hydrogen molecule by electron impact are also to be interpreted as transitions involving the repulsive $1^3\Sigma$ state of the molecule. It was found that impacting electrons whose voltages were less than 11.5 would not dissociate molecular hydrogen even though the heat of dissociation of the molecule is but 4.4 volts. The failure to dissociate at 4.4 volts is to be understood by the fact that the impacting electron cannot communicate the necessary relative momentum to the nuclei directly. But at about 11.5 volts, dissociation began to occur although this is definitely lower than the lowest of the excited states of the molecule known from band spectra. This effect is evidently to be understood as involving transitions from the ground state to the repulsive state caused by the electron impact. Because of the considerations of Sec. **53** this will happen most favorably when the energy change is such as to require virtually no instantaneous alteration in the nuclear separation. Reference to Fig. 21 shows that the distance of the repulsive curve (2) above the minimum of the ground state curve (1) agrees well with the critical voltage at which dissociation was first observed to occur. The distance in question is $0.86R = 11.6$ volts.

CHAPTER VI

GENERAL FORMULATION OF THE THEORY

In the preceding chapters enough has been given of the direct application of the Schrödinger wave equation to give an idea of its fruitfulness in dealing with various problems of atomic physics. It is now desirable to return to a consideration of the fundamental ideas involved, leading to the more generalized form of the theory which is due to Dirac, Jordan, and others.

The essential part of what has gone before may be readily summed up as follows: In treating a dynamical system one starts with a Hamiltonian function which is taken over from the classical theory. From this one builds a wave equation and inquires after solutions of it which are everywhere finite continuous and single valued. The values of the energy parameter for which such solutions exist are taken as the allowed values of the energy. For each allowed value W there is then a function $\psi(W, x)$ whose square can be interpreted as the probability that x lies between x and $x + dx$ when the system is known to be in a state of energy W. Approaching the general formulation of the theory one is led to the desire to be able to answer generally questions of this type, referring to any pair of dynamical variables rather than simply to the probability connecting position and energy value. For example, the general theory should tell what is the probability that various components of momentum lie between certain values when the energy is known.

In seeking an answer to such questions, Dirac and Jordan were led to a formulation of the laws of quantum mechanics which contain the Schrödinger equation as a special case. These more general methods have already shown themselves to be of great value in a variety of applications not handled by the simple wave mechanical methods.

57. Probability Amplitudes.—An essential characteristic of what has preceded has been the fact that although it is $\psi_W(x)$ which is found as the solution of a linear differential equation, and which appears throughout the calculations, it is $\psi_W(x)\bar{\psi}_W(x)dx$ which is interpreted as the probability that x lies between

x and $x + dx$ when the energy has the value W. This is analogous to the situation in the wave theory of light where the field vectors $\boldsymbol{E}$ and $\boldsymbol{H}$ of Maxwell's equations are calculated and then the intensity of light is computed from certain quadratic expressions in them like the energy density $\frac{1}{8\pi}(\boldsymbol{E}^2 + \boldsymbol{H}^2)$ and the Poynting vector $\frac{c}{4\pi}(\boldsymbol{E} \times \boldsymbol{H})$. One may expect that this will be the case in the general theory of quantum mechanics and is thus led to postulate that:

Any two dynamical quantities F_1, F_2 *have associated with them a function* $\varphi(x, y; F_1F_2)$ *such that* $\varphi\bar{\varphi}\,dx$ *gives the probability, if* F_2 *is known to have the value* y, *that* F_1 *have the value between* x *and* $x + dx$.

The Schrödinger function, $\psi_W(x)$, is evidently a special case of this for the case in which F_2 is the energy and F_1 is the ensemble of spatial coordinates specifying the configuration of the system. The function $\varphi(xy; F_1F_2)$ will be called the probability amplitude for F_1F_2.

Another postulate, which is made concerning the probability amplitudes, is the law of combination of them which is expressed in the following equation,

$$\varphi(x, z; F_1F_3) = \int \varphi(x, y; F_1F_2)\varphi(y, z; F_2F_3)dy. \qquad (57.1)$$

This postulate is suggested by the fact that in optics amplitudes and not intensities are superposed when dealing with coherent radiation. This postulate, it is to be observed, marks a sharp break with the ordinary laws of combination of probabilities in the case of independent events. There, one would say that if $W(y, z, F_2F_3)dy$ gives the probability that F_2 lie between y and $y + dy$ when $F_3 = z$ and if $W(x, y, F_1F_2)$ gives the probability that F_1 lie between x and $x + dx$ when F_2 has the value y then the probability that F_1 have the value x when F_3 has the value z and F_2 has the value y is the product of the two probabilities. Finally, the whole probability connecting F_1 and F_3 would be obtained by adding the separate products over all possible values of the intermediate quantity F_2. That leads to a formula of the type of equation (57.1) except that it would contain the probabilities themselves rather than the probability amplitudes.

One has now to build up a general theory[1] governing the calculation of these amplitudes in order to be able to compute the answer to any question which may arise concerning the probabilities. It is to be emphasized that the probabilities take the place of the strict functional relations of classical mechanics. In classical mechanics, one sought an exact expression for each coordinate and momentum as a function of the time and the various constants of integration, such as the energy, the angular momentum and others. The quantum mechanics does not attempt this but seeks instead to provide explanations of the results of experiments in the field of atomic physics solely in terms of the various probability functions.

58. Physical Quantities as Operators.—It has been seen that the Schrödinger equation can be written in the form

$$H(p, q)\psi = W\psi,$$

in which $H(p, q)$ is the classical Hamiltonian function made into a differential operator. The equation may be considered then as the statement that the operator representing the energy must, when acting on the appropriate function give a constant multiple of the function on which it operates. This is a result which one naturally seeks to embody in the theory in a more general form. Thus one is led to postulate that an operator may be associated with every physical quantity. Suppose, for the moment, that the physical quantity is F, and that this same letter stands for the operator representing the physical quantity. Then one may expect that quite generally the allowed values of F will be the numbers f such that

$$F\psi = f\psi$$

where F is the operator and f is simply a number.

Looking more closely at the matter it is seen that this equation is not as general as is needed in that the $\psi(W, x)$ occurring in the wave equation of Schrödinger is a particular probability amplitude, namely $\varphi(x, W; q, H)$, *i.e.*, the amplitude that the coordinate q have a value between x and $x + dx$ when the

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[1] The notation of this section is that of Hilbert, von Neuman, and Nordheim, *Math. Ann.*, **98**, 1 (1927). This paper contains a clear presentation of the transformation theory. Other important references are Jordon, *Zeits. für Phys.*, **40**, 809 (1927); Jordon, *Zeits. für Phys.*, **44**, 1 (1927); Dirac, *Proc.* Roy. Soc., **113A**, 621 (1927); London, *Zeits. für Phys.*, **40**, 193 (1927); Weyl, H., "Gruppentheorie und Quantenmechanik," Leipzig, 1928.

energy has the value W. Thus, the equation just written for F can be expected to yield the corresponding amplitude with F playing the rôle of H, *i.e.*,

$$F\varphi(x, f;\, q, F) = f\varphi(x, F;\, q, F) \qquad (58.1)$$

is the equation for the determination of the probability amplitude and the allowed values of F if the operator corresponding to F is known. There remain then two important questions to be answered: Given a dynamical quantity, how is it known what operator is to be associated with it? And, how is the foregoing equation to be generalized so as to provide a means of determining the probability amplitudes for other combinations than merely those connecting the configuration q and any physical quantity?

Before passing to the discussion of these questions some light may be thrown on them by considering the way in which the operator for $H(p, q)$ is formed from the classical expression for the Hamiltonian function. It will be recalled that this could be done simply by leaving each q in the function and replacing each p by the operation $\frac{h}{2\pi i}\frac{\partial}{\partial q}$, using the q that is associated with the particular p. Since a product like pq in the Hamiltonian became different, as an operator, from qp it was necessary first to be sure that all the products were written in the proper order before replacing the p by $\frac{h}{2\pi i}\frac{\partial}{\partial q}$. Ignoring, for a while, the question of how one is to know the proper order, it is seen that this rule contains two parts:

(*a*) The operator corresponding to a coordinate q is simply the process of multiplication by the value of q.

(*b*) The operator corresponding to a momentum p is that of multiplying by $h/2\pi i$ and differentiating with regard to the canonically conjugate coordinate q.

This suggests that this may be a general rule for finding the operator associated with F, if F is given as the corresponding classical expression in terms of the p's and q's. This supposition may be readily tested in some simple cases. First, suppose F is simply a coordinate q. One supposes the allowed values of the coordinates are known just as was done in dealing with the Schrödinger equation. The equation for $\varphi(x, f;\, q, F)$ becomes then simply

$$x\varphi = f\varphi,$$

which says that $\varphi = 0$ for $x \neq f$. In other words, if F and q are the same dynamical variable, then there is zero probability that q take the value x when F is known to equal f and $x \neq f$. On the other hand, if $x = f$ the φ does not vanish. This is as it should be, the example being quite trivial. Next, suppose that the physical quantity F is really p. Then the equation for $\varphi(x, f; q, p)$ becomes

$$\frac{h}{2\pi i}\frac{\partial}{\partial x}\varphi = f\varphi$$

whence

$$\varphi = e^{\frac{2\pi i f x}{h}}$$

Therefore, $\varphi\bar{\varphi} = 1$, which amounts to the statement that if p is known to have the value f then all values of q are equally likely, which is in accord with the elementary discussion of Sec. **7**. In this example, if all values of x are allowed, then plainly all values of f are allowed. But, if x is an angular coordinate such that physical states given by adding an integral multiple of 2π are indistinguishable, then it is natural to suppose that φ must have this period. This means that

$$f = \frac{nh}{2\pi} \qquad n = \text{an integer,}$$

so the allowed values of p, the angular momentum, become integral multiples of $h/2\pi$. This result is of course one of the earliest quantization rules known to quantum theory.

It would appear then that the tentative rule could be laid down that if F is given in terms of its classical expression in terms of p, q one has to replace q by x and p by $\frac{h}{2\pi i}\frac{\partial}{\partial x}$ in order to find the operator appropriate to finding the allowed values of f and the probability amplitude $\varphi(x, f; q, F)$. The rule is incomplete in that it is not yet known what order of factors should occur in products like pq.

Considering the second question concerning the generalization of the Schrödinger equation so as to provide a means of finding the amplitude connecting any pair of dynamical variables, it is seen that this must necessarily imply different modes of associating operators with physical quantities. In finding $\varphi(x, f; q, F)$ in the case that F was really q, it was necessary to have φ vanish unless $x = f$. This came about in virtue of the fact that the operation multiplication by x represented the quantity q. Quite generally one must have the result that $\varphi(x, f; G, F)$ must vanish unless $x = f$, if G and F are really the same physical quantities. If one then adheres to the equation

$$F\varphi(x, f; G, F) = f\varphi(x, f; G, F)$$

as the equation for φ where G is any physical quantity and not merely the coordinate q, it is evident that the operator for F must be built up on a scheme such that, according to that same scheme, the operator for G would be simply the operation of multiplication by x. One, therefore, has to know how to associate different operators with the same physical quantity when different probability amplitudes are being sought. Before considering this question further, it will, however, be desirable to study some general properties of the operators which present themselves in quantum mechanics.

59. Outline of Operator Calculus.[1]—By an operator will be understood *any rule whereby a function is changed into another function.* The operator may be symbolized by a letter as T and the function by φ. If the result of operating on φ by the operation T is ψ, it is written formally as

$$\psi = T\varphi.$$

The operators occurring in quantum theory, and at the same time those which have been most studied by mathematicians, are the linear or distributive operators. These are such as have the properties that

$$T(\varphi_1 + \varphi_2) = T\varphi_1 + T\varphi_2,$$

and

$$T(c\varphi) = cT\varphi, \tag{59.1}$$

where c is a constant. Examples of linear operators are (a) multiplication by the independent variable, (b) differentiation by the independent variable. An example of a non-linear operator is "taking the reciprocal of." For then

$$T(\varphi_1 + \varphi_2) = \frac{1}{\varphi_1 + \varphi_2}$$

whereas

$$T\varphi_1 + T\varphi_2 = \frac{1}{\varphi_1} + \frac{1}{\varphi_2},$$

and these are not the same.

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[1] For the material of this section see PINCHERLE, *Encyc. Math. Wiss.* II A 11.

One can now proceed to define an algebra of linear operators. The operator that is the sum of T and S is defined by the equation

$$(T + S)\varphi = T\varphi + S\varphi.$$

The operator that is the product of a constant c and T is defined by

$$(cT)\varphi = c(T\varphi)$$

and the product TS of two operators is defined by

$$(TS)\varphi = T(S\varphi),$$

that is, one applies T to the result of operating on φ with S. In general, multiplication is not commutative, *i.e.*, $TS \neq ST$. A simple example of this which is of great importance for quantum theory is case of the two linear operators just cited,

T: multiplication by x
S: differentiation by x,

for which

$$TS\varphi = x\varphi'(x), \qquad ST\varphi = \varphi + x\varphi'(x),$$

so that

$$(ST - TS)\varphi = \varphi.$$

The simplest of all operations (as all humans know) is that of doing nothing. This is called the "identical operator" and is denoted by 1. Applied to any function it leaves the function unaltered,

$$1\varphi = \varphi.$$

Hence in the particular example just considered, the law of commutation of T and S is

$$ST - TS = 1.$$

If to an operator T, there exists another operator S, such that

$$TS = ST = 1,$$

then S is said to be the reciprocal of T and is written T^{-1}. Conversely, T is the reciprocal of S. For the reciprocal of a product one has

$$(TS)^{-1} = S^{-1}T^{-1},$$

the reversed order of factors being needed in order that

$$(TS)^{-1}(TS) = S^{-1}T^{-1}TS = 1$$

by the associative law of multiplication.

Evidently, linear operators form a very general class of operators. One has next to consider the problem of the analytic representation of the operators. Evidently, any finite rational polynomial in the two operations multiplication by x and differentiation by x is a linear operator. Infinite series of these operations may also present themselves in the representation of operations which are simply stated in words. Thus, if D is the differentiation operation, and E is the operation defined by

$$E\varphi(x) = \varphi(x+1),$$

the connection between E and D becomes an operator statement of Taylor's Theorem:

$$E = 1 + D + \frac{D^2}{2!} + \frac{D^3}{3!} + \cdot \cdot \cdot = e^D.$$

E is an operation much studied in the calculus of finite differences. A very general class of linear operators is obtained by considering

$$T\varphi(x) = \int_{-\infty}^{\infty} t(y, x)\varphi(x)dx. \tag{59.2}$$

Such a rule for computing $T\varphi(x)$ from $\varphi(x)$ is said to be an integral representation of T and the function $t(y, x)$ is said to be the kernel of T. Evidently, there is a linear operator T corresponding to every function of two variables $t(y, x)$. Of course, those $t(y, x)$ for which the integral does not converge are naturally excluded.

It is desirable to have an integral representation for every operator but this leads in the case of the very simplest operators to forms for $t(y, x)$ which are quite outside the range of those considered by mathematicians. Thus, to represent the identical operator in this way formally, the kernel $t(y, x)$ must be such a function that it is zero for $y \neq x$ and infinite at $y = x$ in such a way that its integral from $x < y$ to $x > y$ will equal unity. Such a function may be regarded as the limit of a continuous function, *i.e.*,

$$\delta(y, x) = \delta(y - x) = \lim_{a \to 0} \frac{1}{\sqrt{\pi a}} e^{-\left(\frac{y-x}{a}\right)^2}.$$

Similarly the operation D (differentiation), when given an integral representation, may be readily seen to have as a kernel a function that is even more strikingly discontinuous. Such points, however, need cause no difficulty as the complication arises in practice only when one seeks to give an integral representation to all operators.

If the kernels of two operators are known, the kernel of the product is easily obtained. One has

$$\begin{aligned} TS\varphi(x) &= \int t(z, y) \int s(y, x)\varphi(x)dxdy \\ &= \int \left(\int t(z, y)s(y, x)dy\right)\varphi(x)dx \qquad (59.3) \end{aligned}$$

from which it is evident that the kernel of the product must be

$$\int t(z, y)s(y, x)dy.$$

From this result it is seen that the kernel of an operator and the kernel of its reciprocal must be orthogonal functions. Let $t_{-1}(y, x)$ be the kernel of T^{-1}, then, since $TT^{-1} = 1$, one has

$$\int t(z, y)t_{-1}(y, x)dy = \delta(z - x),$$

where $\delta(z - x)$ is the discontinuous kernel of the identical operator.

An interesting property of the kernel $t(y, x)$ of T is that it is the function which results from operating on the unit kernel $\delta(x - y)$ with the operator T, for one has

$$T\delta(x - z) = \int t(y, x)\delta(x - z)dx = t(y, z).$$

In relations of this type it will be observed that the particular letters which represent the independent variables are continually being changed. This makes no essential difference in the operator, since what is essential is the mode of dependence of a function on its independent variable and not the letter which stands for that variable.

Dirac avoids this change of letter by using the same letter with different numbers of primes attached to indicate different values of the same dynamical quantity. This is a convenient notation when working with the quantum mechanical equations.

The connection of operator calculus with the quantum mechanics is now made by assuming that the probability amplitudes of Sec. **57** are to be identified with the kernels of certain operators. There are thus two types of operators occurring in the theory. One is that of the operators which represent physical quantities, and the other those whose kernels are the probability amplitudes.

60. Relation to Linear Transformations.[1]—A clearer insight into the workings of operator calculus may be obtained by considering the algebraic theory of linear transformations of n

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[1] PASCAL, Repertorium der höheren Math. Vol. 1, Chap. 2, Leipzig, 1910.

variables. These are connected with the theory of matrices of n rows and n columns. The mathematical methods involved are a product of the nineteenth century and their usual application is to analytic geometry and to vector and tensor analysis. For application to quantum mechanics an extension of matrix algebra is needed to cover the case of linear transformations in infinitely many variables, as will be seen later.

When an operator T acting on a function is given in terms of its kernel, the equation

$$\psi(y) = \int t(y, x)\alpha(x)dx,$$

is evidently analogous to the linear transformation,

$$\psi_y = \sum_{x=1}^{n} t_{xy}\alpha_x.$$

The difference consists in the fact that in the former the variables take on an infinity of values, whereas in the latter, they take on but n discrete values. Such linear transformations in n discrete variables bear an important relation to the geometry of n dimensional space. Consideration of these relations is very fruitful in suggesting the direction in which to look for the general expression of the laws of quantum mechanics.

A given linear transformation is characterized by the array of n^2 coefficients, t_{yx}. Such an ordered array of coefficients is called a "matrix." An algebra of such quantities may now be built by defining the fundamental operations for matrices. Just as T symbolizes the operator whose kernel is $t(y, x)$, so T can here stand for the matrix of n^2 quantities t_{yx}.

If two matrices, T and S, have the elements t_{yx} and s_{yx}, the sum $(T + S)$ is defined to be the matrix whose elements are the sums of the corresponding elements of T and S, that is, $t_{yx} + s_{yx}$.

The quantities φ_x can be regarded as the coordinates of a point φ in a certain coordinate system, and the ψ_y as the coordinates of another point ψ in the same coordinate system. The coordinates of a point are also the components of its position vector relative to the origin so that the linear transformation makes the position vector of ψ be a linear vector function of that of φ. Another quite different application of a linear transformation is that by means of which a new coordinate system is introduced. Then, if the φ_x are the coordinates of a point in the old system, the coordinates of the same point in the new coordinate system, ψ_y, will be related to the φ_x in the old system by a linear transformation.

In passing from the language of linear transformations to that of operators it will be seen that these two types of linear transformation correspond to the two types of operators. The operators representing physical quantities are analogous to those which make one point a linear vector function of another, while the operators whose kernels are the probability amplitudes are the ones by which a change of coordinate system is effected.

The law of combination of linear transformations is the same for both interpretations. If one has the further transformation,

$$\chi_z = \sum_{y=1}^{n} s_{zy}\psi_y,$$

then the relation between χ_z and φ_x is evidently,

$$\begin{aligned}\chi_z &= \sum_y \sum_x s_{zy} t_{yx} \varphi_x \\ &= \sum_x u_{zx}\varphi_x,\end{aligned}$$

where u_{zx} is defined by

$$u_{zx} = \sum_y s_{zy} t_{yx}.$$

In other words, χ_z and φ_x are connected by a linear transformation· The law whereby the matrix u_{zx} is formed from the matrices s_{zy} and t_{yx} is evidently analogous to the law of combining operator kernels as defined in the preceding section. The matrix u_{zx} is defined to be the product, ST.

Evidently a symbolic algebra can be built for operations with the matrices of linear transformations just as was done with operators. As in the case of operators, in general, multiplication is not commutative. The matrix of the identical transformation δ is the one for which δ_{yx} is zero if $y \neq x$ and equal to one for $y = x$.

The reciprocal of a matrix A is defined as the one which satisfies the equation

$$AZ = \delta.$$

In the case of linear transformations it is evident that Z is the inverse transformation which "undoes" A.

Thus,

$$\psi_y = \sum_x a_{yx}\varphi_x,$$

and

$$\varphi_x = \sum_y z_{xy}\psi_y.$$

Therefore, the problem of finding the matrix z_{xy} in terms of a_{yx} is simply that of solving the first set of linear equations for the φ_x in terms of ψ_y. This is a problem of elementary algebra and leads to the result

$$z_{xy} = \frac{1}{|A|}\frac{\partial|A|}{\partial a_{yx}}$$

in which $|A|$ is the determinant of the matrix a_{yx}.

Considering now the two types of transformations occurring, one naturally seeks the answer to the question: If A is the transformation connecting the point ψ to the point φ, *i.e.*,

$$\psi = A\varphi \quad \text{or} \quad \psi_y = \sum_x a_{yx}\varphi_x,$$

and if one introduces a new coordinate system by the transformation T, so that the coordinates of φ and ψ in the new system are given by

$$\varphi_y' = \sum_x t_{yx}\varphi_x \qquad \psi_y' = \sum_x t_{yx}\psi_x,$$

what is the matrix expressing the connection between ψ and φ in the new system? *i.e.*, writing

$$\psi' = A'\varphi' \quad \text{or} \quad \psi_y' = \sum_x a'_{yx}\varphi_x',$$

what is the relation between A', T, and A?

This question can be answered by the following self-explanatory calculations:

$$\psi_y' = \sum_x t_{yx}\psi_x = \sum_{xz} t_{yx}a_{xz}\varphi_z = \sum_{xzu} t_{yx}a_{xz}t_{zu}^{-1}\varphi_u'$$

in which t_{zu}^{-1} is written for the matrix of the inverse transformation to T. But the last expression is what would be written

$$\sum_u a'_{yu}\varphi_u'$$

by the definition of a'_{yu}. Therefore,

$$a'_{yu} = \sum_{xz} t_{yx}a_{xz}t_{zu}^{-1},$$

or, symbolically,

$$A' = TAT^{-1}.$$

The properties of a given functional relation between two vectors that is described by A can best be summarized by finding those vectors which A leaves unaltered in direction. This calls for consideration of the equation,

$$A\varphi = a\varphi,$$

which in this form is seen to be the analogue of the equations for probability amplitudes which were set up in **Sec. 57.**

Written in terms of components this is

$$\sum_x a_{yx}\varphi_x - a\varphi_y = 0 \qquad (y = 1, 2, \cdots n).$$

This is a set of homogeneous linear equations for the n unknown components of φ. The condition that they have non-vanishing solutions is simply that the determinant of the coefficients vanish. That is,

$$\begin{vmatrix} a_{11} - a & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} - a & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} - a \end{vmatrix} = 0$$

This is an equation of the nth degree which will, in general, have n roots. Corresponding to each of these roots, there will be a solution for the components of a vector which has the property demanded. These n values of a are known as the characteristic values of A.

If the characteristic values and the characteristic vectors associated with them are determined, it is natural to inquire, what form will A assume if a new coordinate system is introduced having these characteristic vectors as axes? Let the characteristic values be numbered by the subscript u, *i.e.*, a_u $(u = 1 \cdots n)$. Then the components of a characteristic vector associated with a_u may be called φ_{xu} (*i.e.*, φ_{xu} is the xth component of the uth characteristic vector).

Any transformation t_{yx} will change the components of φ_{xu} into φ'_{yu} by

$$\varphi'_{yu} = \sum_x t_{yx}\varphi_{xu}.$$

But if t_{yx} is to be so chosen that the u^{th} axis lies along φ_u, one must have $\varphi'_{yu} = 1$ or 0 according as $u = y$ or $u \neq y$. Evidently, now the n^2 quantities φ_{xu} may be regarded as forming a matrix in which case the preceding equation merely expresses the fact that t_{yx} must be the inverse of the transformation whose matrix is φ_{xu}. In other words,

$$t_{yx}^{-1} = \varphi_{yx}.$$

From this the form of A in the new coordinate system follows at once.

It is

$$a'_{yu} = \sum_{xz} t_{yx}a_{xz}t_{zu}^{-1} = \sum_{x} t_{yx}a_u\varphi_{xu} = a_u\delta_{yu}.$$

In other words, in the new coordinate system the matrix corresponding to the operator A takes on the simple diagonal form in which the characteristic values occupy places on the diagonal where $y = u$ and all the other elements are zero.

The axes of this coordinate system are known as the principal axes of the matrix A.

The problem of finding the principal axes of a matrix is of considerable importance in classical physics, at least in the case $n = 3$. For example, in a small deformation of an elastic body, the point whose coordinates are initially $(\varphi_1, \varphi_2, \varphi_3)$ will be displaced to the point (ψ_1, ψ_2, ψ_3) where ψ and φ are connected by a linear vector functional relation. The principal axes of the deformation are the directions in which the strain is a pure expansion or compression. By such a deformation, the points initially on a sphere about the origin are made to lie on an ellipsoid. Hence, the problem is closely related to the purely geometrical one of finding the principal axes of an ellipsoid.

It is important to know what restriction on the transformations of coordinates is placed by requiring that the length of the vector remain invariant, that is, unchanged in value, by the transformation. The length of a vector is a particular quadratic form of its components,

$$L^2 = \sum_{x} \varphi_x^2.$$

For $L^{2\prime}$, in the new system, one has

$$L^{2\prime} = \sum_{x} \varphi_x'^2 = \sum_{x} (t_{xu}\varphi_u)(t_{xv}\varphi_v) = L^2.$$

In order that this agree with L for any vector φ one must have

$$\sum_x t_{xu}t_{xv} = \delta_{uv}.$$

As it stands this is not a matrix multiplication, since the sum is taken over the first index in both factors. $\tilde{T}$ is defined, therefore, as the matrix which is obtained from T by interchanging rows and columns. This is called the transposed T.

As

$$t_{xu} = \tilde{t}_{ux}$$

so the preceding requirement is

$$\sum_x \tilde{t}_{ux}t_{xv} = \delta_{uv}.$$

In other words, the transposed T is equal to the reciprocal of T if the lengths of all vectors are to be preserved.

$$\tilde{T} = T^{-1}.$$

For quantum mechanics a slight generalization of the preceding is of importance. One needs to know what transformations leave

$$\sum_x \bar{\varphi}_x\varphi_x$$

unchanged in value.

One has

$$\sum_x \varphi_x{}'\bar{\varphi}_x{}' = \sum_{xuv}(t_{xu}\varphi_u)(\bar{t}_{xv}\bar{\varphi}_v).$$

Hence, since this must be an identity in φ_x

$$\sum_x t_{xu}\bar{t}_{xv} = \delta_{uv}.$$

Introducing the notation $\bar{T}$ for the matrix whose elements are the conjugate complex quantities to the elements of T, this is

$$\tilde{T}\bar{T} = 1$$

or

$$\tilde{T} = (\bar{T})^{-1}.$$

Transformations of coordinates which leave the length of φ invariant are called orthogonal. Those which leave $\sum_x \varphi_x\bar{\varphi}_x$ invariant are called unitary. Their importance for quantum mechanics lies in the fact that the expression $\sum_x \varphi_x \varphi_x$ becomes the total probability which must be set equal to unity and must remain equal to unity for any change of coordinate system.

The matrices A which change one vector into another in the same coordinate system are the analogues of the operators which represent physical quantities. For these it is desirable to know what restriction will insure that their characteristic values are real, since in the general formulation of quantum mechanics, the characteristic values of an operator are the allowed values which the corresponding physical quantity may assume. The question was investigated by Hermite who found that the characteristic values are real if the matrix of A satisfies the requirement,

$$a_{ik} = \bar{a}_{ki},$$

or, in matrix notation,

$$\tilde{A} = \bar{A}.$$

Matrices satisfying this condition are said to be Hermitian, since they were much investigated by Hermite.

One may now show that the Hermitian character of a matrix is preserved when new coordinates are introduced by means of a unitary transformation. To do this these rules are needed,

$$\bar{A} = \bar{\tilde{A}}; \quad \overline{A^{-1}} = (\bar{A})^{-1}; \quad (\widetilde{A^{-1}}) = (\tilde{A})^{-1},$$

for any matrix.

For the product of any two matrices A and B,

$$(\widetilde{AB}) = \tilde{B}\tilde{A} \text{ but } \overline{AB} = \overline{A}\,\overline{B}.$$

By the law of transformation,

$$A' = TAT^{-1}$$

and, therefore,

$$\bar{A}' = \bar{T}\bar{A}\bar{T}^{-1};$$

also,

$$\tilde{A}' = \widetilde{TAT^{-1}} = \widetilde{T^{-1}}\tilde{A}\tilde{T}.$$

But if A is Hermitian and T is unitary, by the definitions of these properties, $\tilde{A} = \bar{A}$ and $\widetilde{T^{-1}} = \bar{T}$ and $\tilde{T} = \bar{T}^{-1}$ so that

$$\tilde{A}' = \overline{A'},$$

which proves that the transformed matrix is Hermitian.

It is important to know that the result of successively applying two unitary transformations is equivalent to another unitary transformation. This is evident, for if $\sum_x \varphi_x \bar{\varphi}_x$ is altered by neither of them, it will not be altered by the successive application of both. Formally, however, if S and T are the two transformations, one has to prove that $\widetilde{ST} \cdot \overline{ST}$ is equal to unity. One has $ST = \tilde{T}\tilde{S}$ whereas $\overline{ST} = \bar{S}\bar{T}$ so

$$\widetilde{ST}\,\overline{ST} = \tilde{T}\tilde{S}\bar{S}\bar{T} = \tilde{T}\bar{T} = 1.$$

Hence, the combined transformation is unitary.

61. Extension to Function Space.—The results of the preceding section, so long as they are restricted to matrices of n rows and columns with n finite, belong to the subject of algebra. Their generalization to $n \rightarrow \infty$, including both the case in which the values of x become an infinite denumerable set as all integers, and where the values become a non-denumerable set, as all real values of x from $-\infty$ to $+\infty$, constitutes a problem of analysis. The finite algebraic theory is a product of nineteenth century mathematicians—Cayley, Frobenius, and Hermite being the principal contributors. The extension to infinitely many variables is a product of the twentieth century—Hilbert's is the principal name in this development, a name which has occupied a central place in analysis in the last three decades.

One of the most important tasks of physicists in the present century has been the development of quantum mechanics. It is interesting to observe that the mathematical developments which are now being used in quantum theory were being made independently of the quantum theory and now suddenly find themselves of central importance for physics. The mathematicians have been in the habit of restricting the types of infinite matrices which they have studied to a class somewhat too narrow for the needs of quantum mechanics. The union of quantum theory and the mathematics of infinite matrices is therefore bound to have a stimulating effect on the latter as has so often happened in the closely interwoven histories of mathematics and physics.

The formal generalization of the work of the preceding section to provide an analysis for quantum mechanics, when one ignores completely the important questions of convergence of series, is easily carried out. This standpoint will now be adopted as valuable heuristically but with no implication that the mathematical questions arising are not of the greatest importance.

Evidently, all of the work of the preceding section can be generalized formally by merely writing operators for matrices when infinitely many variables present themselves. If this be done it is seen at once that the Schrödinger equation,

$$H\psi = W\psi,$$

where H is an operator is the formal equivalent of the problem of finding the characteristic values of the operator H. The functions $\psi(W, x)$ which occur are then closely related to the transformation which makes the operator H take on the simple form of a diagonal matrix with the characteristic values occupying the places on the diagonal.

If one seeks to retain the very helpful geometrical idea of transformation of coordinates in a space of n dimensions in the limit as n tends to infinity, one is led to the important conception of function space. This viewpoint has already been introduced in Sec. **12.** Function space is a "space" of infinitely many dimensions in which each value of x labels a separate and distinct coordinate axis. In this space a function $\psi(x)$ is a point or a position vector. The linear operators representing physical quantities are then relations between vectors in function space.

The allowed values of a physical quantity are the characteristic values of its operator. The probability amplitudes are related to the transformation by means of which one sets up a new coordinate system in function space. The state of a dynamical system is described by some vector in function space say, $\varphi(x)$. This vector will be regarded as normalized in the Hermitian sense so

$$\int_{-\infty}^{+\infty} \varphi(x)\bar{\varphi}(x)dx = 1.$$

The probability that the coordinate x of the system lies between x and $x + dx$ is given by $\varphi(x)\bar{\varphi}(x)dx$ so the normalization expresses the fact that the coordinate certainly has some value. The state vector is here given in the form suitable for telling what are the probabilities of the coordinate having different values.

If now one wants to know what are the probabilities of the various allowed values of the energy, one must introduce a new coordinate system in function space such that its axes are the principal axes of the energy operator. The transformation to these axes is just what is given by the Schrödinger functions, as will now be seen by paralleling the discussion of the preceding section.

$$H\psi = W\psi$$

will have for each allowed value of W a solution $\psi(x, W)$. From the present standpoint this solution is the vector in function-space corresponding to the energy value W. In the new system of coordinates the state vector will be given by

$$\varphi'(W) = \int t(W, x)\varphi(x)dx.$$

The transformation operator's kernel is now given in analogy with the preceding section by

$$t^{-1}(W, x) = \psi(W, x).$$

Since, however, the transformation operators are unitary,

$$\tilde{T}\bar{T} = 1,$$

it follows that

$$t(W, x) = \bar{\psi}(W, x).$$

Therefore, the state vector in the new system is given by

$$\varphi'(W) = \int_{-\infty}^{+\infty} \varphi(x)\bar{\psi}(W, x)dx.$$

Just as $\varphi(x)\bar{\varphi}(x)dx$ gave the probability that x had the value between x and $x + dx$ so now $\varphi(W)\bar{\varphi}(W)dW$ gives the probability that W has the value between W and $W + dW$ in the state in question. Because the transformation is unitary, one is assured that

$$\int \varphi'(W)\bar{\varphi}'(W)dW = 1,$$

as it should be.

What has just been said for the energy is true for any other physical quantity characteristic of the system. To find the probability of its values in a state of the system one must refer the vector characterizing that state to a coordinate system in function space determined by the principal axes of the operator representing that physical quantity. Then the components of the state vector along the different principal axes multiplied by their complex conjugates give the probabilities of each value for the state in question.

A special case is afforded by the probability amplitudes themselves. Suppose that the state vector is given by $\psi(W_1, x)$ where this is a particular one of the Schrödinger functions. Then the state vector in the energy coordinate system is

$$\varphi'(W) = \int_{-\infty}^{+\infty} \psi(W_1, x)\bar{\psi}(W, x)dx.$$

This is equal to zero unless $W = W_1$ in which case it is equal to one, by the known orthogonality properties of the ψ which in the general theory are a consequence of the fact that $\psi(W, x)$ is the kernel of a unitary transformation. Thus $\psi(W_1, x)$ describes a state in which the energy value is known with certainty, in accord with the definition of probability amplitude in Sec. **57.**

Finally, it is of interest to examine the interpretation of the result of applying the operator corresponding to a physical quantity to the state vector. This has the simplest interpretation in the coordinate system given by the principal axes in question. For example, if the physical quantity is the energy and the state vector is $\varphi'(W)$, then the result of operating on it with the energy operator is $W\varphi'(W)$. If one takes the scalar product of this with the original vector $\varphi'(W)$, in the sense of Sec. **12,** one obtains the mean value, or the expected value of the energy for the state in question,

$$\int\bar{\varphi}'(W)W\varphi'(W)dW = W_m,$$

since the $\varphi'\bar{\varphi}'$ in the integrand gives the probability of each value of W for the state in question.

62. The Indetermination Principle.—It has already been seen (Chap. I) that the probability interpretation of the de Broglie waves leads to the result that certain physical quantities are not simultaneously observable with unlimited precision. This question takes on an especially interesting form in terms of the present formulation of quantum mechanics.

In order to be able to say that the system is in a given state, characterized by having the values of two different physical quantities, A and B, precisely known, the state vector must be such that it lies simultaneously along a principal axis of A and of B. This follows from the result of the preceding section in which it was seen that for a state in which A is known to have the value a, the state vector lies along the principal axis in the A coordinate system which is labelled by the value a.

The equivalent mathematical question is therefore: under what conditions do two operators have the same principal axes? If some, but not all, of the principal axes of the two operators were parallel, this would correspond to two physical quantities so related that the system could exist in a state such that certain values of A and certain values of B could be simultaneously precisely known, but not all of them. An example of this is afforded by considering the case of the angular momentum operator (Sec. **64**). The investigation of the question is best considered by supposing that the coordinate system determined by the principal axes of A has already been introduced. In this system, B will generally be an operator whose kernel will be denoted by $b(a'a'')$. But, if its principal axes are to coincide with those of A, it must be a diagonal matrix in the A coordinate system, that is,

$$b(a'a'') = b(a')\delta(a' - a'').$$

If this is the case, the combined operation BA will be the same as AB for, since A is represented by $a'\delta(a' - a'')$, each product will be

$$a'b(a')\delta(a' - a'').$$

Therefore, two operators which have the same principal axes commute with each other. Conversely, if the two operators commute they must have the same principal axes. In the A coordinate system one has

$$BA - AB = b(a'a''')a'''\delta(a''' - a'') - a'\delta(a' - a''')b(a'''a'') = b(a'a'')(a'' - a').$$

If this is to vanish, it requires that $b(a'a'') = 0$ for $a'' \neq a'$, that is B, is diagonal when A is diagonal.

The most important special case of two physical quantities which do not commute are a spatial coordinate and the associated momentum. In the ordinary function space coordinate system in which the spatial coordinate is referred to its principal axes, the conjugate momentum p is represented by the operator, $\frac{h}{2\pi i}\frac{\partial}{\partial x}$, which does not commute with x, as was seen in Sec. **59.** In Sec. **58** the allowed values of p were found to be all real values and the wave functions $\psi(p, x) = e^{\frac{2\pi ipx}{h}}$.

If the state vector $\varphi(x)$ is taken to be

$$\varphi(x) = \frac{1}{\sqrt{a\sqrt{\pi}}} e^{-\frac{1}{2}\left(\frac{x-x_0}{a}\right)^2 + \frac{2\pi i p_0 x}{h}},$$

this represents a case in which x is known to have a value x_0 with an uncertainty which may be said to be measured by a. To find the state vector in form for determination of the probabilities of various values of the momentum one must transform it by the relation,

$$\begin{aligned} \varphi(p) &= \frac{1}{\sqrt{a\sqrt{\pi}}} \int_{-\infty}^{+\infty} e^{-\frac{1}{2a^2}(x-x_0)^2 + \frac{2\pi i}{h} p_0 x} \, e^{-\frac{2\pi i}{h} p x} dx \\ &= \frac{1}{\sqrt{a\sqrt{\pi}}} e^{-\frac{2\pi i}{h}(p-p_0)x_0} \int_{-\infty}^{+\infty} e^{-\frac{x^2}{2a^2} - \frac{2\pi i}{h}(p-p_0)x} dx \\ &= \frac{1}{\sqrt{a\sqrt{\pi}}} e^{-\left(\frac{2\pi a}{h}\right)^2 (p-p_0)^2 - \frac{2\pi i}{h}(p-p_0)x_0}. \end{aligned} \tag{62.1}$$

This, therefore, represents a state in which p has the mean value p_0 with an uncertainty amounting to $\frac{1}{\sqrt{2}} \frac{h}{2\pi a}$. From this it follows that the order of magnitude of the product of the uncertainties is $h/2\pi$.

63. Momentum-energy Amplitudes.—As a further illustration of the application of the methods of the transformation theory, one may consider the direct determination of the amplitudes connecting momentum and energy.[1] The basic relation between the operators for p and q in any function space coordinate system is

$$pq - qp = \frac{h}{2\pi i}.$$

In finding the transformation from the system in which q is diagonal to one in which the energy is diagonal (*i.e.*, is referred to its principal axes) one satisfies this by making q be the operation of multiplication by x while p is $\frac{h}{2\pi i} \frac{\partial}{\partial x}$. In transforming from the principal axes of p to those of the energy, p is necessarily the operation of multiplying by the value of p. This requires for q the operation $-\frac{h}{2\pi i} \frac{\partial}{\partial p}$ in order that the invariant relation between p and q be satisfied.

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[1] CONDON, *Jour.* Franklin Inst., **207**, 467 (1929); PODOLSKY and PAULING, *Phys. Rev.*, **34**, 109 (1929).

Therefore, one can make an operator out of the Hamiltonian function $H(p, q)$ of the type $H\left(p, -\frac{h}{2\pi i}\frac{\partial}{\partial p}\right)$ in which case, the equation for the allowed energy levels and the transformation functions $\psi(W, p)$, is

$$H\left(p, -\frac{h}{2\pi i}\frac{\partial}{\partial p}\right)\psi(W, p) = W\psi(W, p). \qquad (63.1)$$

By the general theory, $\psi(W, p)\psi(W, p)\, dp$ gives the probability that p have a value between p and $p + dp$ when W has the value W. In some cases, this leads to a simpler equation than the ordinary Schrödinger equation. In the case of the harmonic oscillator, because the Hamiltonian is simply the sum of squares of p and q, the equation for $\psi(W, p)$ is of the same form as that for $\psi(W, q)$ so that the $\psi(W, p)$ are also Hermitian polynomials exactly as in Sec. **15.**

64. Angular Momentum.—Because of the great importance of central-force problems for atomic theory, it is important to consider the operators corresponding to angular momentum. If the momentum of a particle is $\boldsymbol{p}$ when at position $\boldsymbol{r}$ relative to the origin, its angular momentum $\boldsymbol{M}$, about the origin is

$$\boldsymbol{M} = \boldsymbol{r} \times \boldsymbol{p}$$

or

$$M_x = yp_z - zp_y.$$

Therefore, the operator corresponding to the transformation from $\boldsymbol{r}$ diagonal to $\boldsymbol{M}$ diagonal is

$$\boldsymbol{M} = \frac{h}{2\pi i}\boldsymbol{r} \times \text{grad}$$

so the equation for determination of the allowed value of the angular momentum becomes

$$\boldsymbol{r} \times \text{grad}\, \psi = \frac{2\pi i}{h}\boldsymbol{M}\psi.$$

Letting $\frac{2\pi}{h}\boldsymbol{M} = \boldsymbol{m}$ this becomes,

$$\begin{aligned} y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y} &= im_x\psi \\ z\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial z} &= im_y\psi \\ x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x} &= im_z\psi. \end{aligned} \qquad (64.1)$$

It is easy to see, however, that there are no values of m_x, m_y, m_z, (except 0, 0, 0) for which these three simultaneous equations can be solved. In other words, it is impossible to refer all three components of angular momentum to their principal axes, simultaneously. In accordance with Sec. **62** this means that all three components of angular momentum are not simultaneously observable. This result follows most directly from the observation that the operators M_x, M_y, M_z do not commute with each other. Computing the products M_xM_y from the forms for M_x, M_y, M_z, just given, one readily establishes the relation,

$$M_xM_y - M_yM_x = M_z\left(\frac{h}{2\pi i}\right), \tag{64.2}$$

and two more given by cyclical permutation of the indices x, y, and z.

The knowledge of a definite numerical value for one of them therefore precludes the possibility of knowing precise numerical values for the other two. Fixing attention on m_z one recognizes, as in Sec. **44,** that $x\dfrac{\partial}{\partial y} - y\dfrac{\partial}{\partial x}$ is $\dfrac{\partial}{\partial \varphi}$ where φ is the azimuth angle of a polar coordinate system having the z axis for its polar axis. Since the configuration of the system has period 2π in φ, m_z must be an integer and, therefore,

$$\psi(m_z, x, y, z) = F(r, z)e^{im_z\varphi},$$

where $F(r, z)$ is an arbitrary function of its arguments.

The operator corresponding to $(M_x^2 + M_y^2 + M_z^2) = M^2$ which gives the square of the resultant angular momentum is easily computed from the forms for the components.

The result is

$$M^2 = \left(\frac{h}{2\pi}\right)^2\left\{(\boldsymbol{r}\cdot\nabla)^2 + (\boldsymbol{r}\cdot\nabla) - r^2\Delta\right\}, \tag{64.31}$$

in which

$$\boldsymbol{r}\cdot\nabla = x\frac{\partial}{\partial x} + y\frac{\partial}{\partial y} + z\frac{\partial}{\partial z}.$$

Expressed in spherical polar coordinates $\boldsymbol{r}\cdot\nabla$ becomes $r\dfrac{\partial}{\partial r}$ so the operator M^2 is simply

$$M^2 = -\left(\frac{h}{2\pi}\right)^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right)\right]. \tag{64.32}$$

Since M^2 contains no differentiation with respect to r, one sees that the transformation function from spatial coordinates to values of M^2 can be multiplied by an arbitrary function of r. The equation for the transformation function is, therefore,

$$-\left(\frac{h}{2\pi}\right)^2\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right]\psi=\beta\psi, \quad (64.33)$$

where β is an allowed value of M^2. This, however, is just the equation for the spherical harmonics as studied in another connection in Sec. **16.**

Therefore, the allowed values of M^2 are

$$l(l+1)\left(\frac{h}{2\pi}\right)^2. \quad (64.4)$$

Angular momentum has the peculiar property in quantum mechanics of being a vector quantity of which one can know the value of the squared resultant and of one component simultaneously (since $M_zM^2 - M^2M_z = 0$) although one cannot know the values at once of all three components. The fact that one can know simultaneously M^2 and M_z is also reflected in the fact that the spherical harmonics which are the transformation functions for M^2 contain $e^{im_z\varphi}$, the transformation function for M_z, as a factor.

65. Pauli's Theory of Electron Spin.[1]—At about the same time that the principles of the quantum mechanics were being worked out, it was discovered by Goudsmit and Uhlenbeck that the systematics of atomic spectra could be greatly clarified by the assumption that the electron is spinning about an axis so that it possesses both angular momentum and magnetic moment. From the spectral interpretations to which this view is applied it is learned that it must be assumed that the angular momentum has the value $h/4\pi$ (half the usual unit!) while the magnetic moment is that of a Bohr magneton. The problem of treating this spin property of the electron in terms of quantum mechanics thus presents itself.

Naturally, one would first try simply to treat the electron as a little rigid body introducing, say, Eulerian angles to specify its orientation. Then, adopting certain hypotheses concerning its moment of inertia it would be natural to introduce these extra

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[1] PAULI, *Zeits. für Phys.*, **43,** 601 (1927). For a general discussion, see GOUDSMIT and PAULING, Chap. IV.

coordinates into the Schrödinger equation. This program fails in two important ways. In the first place, the hypothesis of single-valued ψ functions leads at once to values of the angular momentum which are integral multiples of $h/2\pi$, instead of the value $h/4\pi$. In the second place, it gives all integral multiples of $h/2\pi$ whereas empirical results demand that the spin angular momentum have but one value. Pauli was thus led to handle the spin as an application of the general transformation theory with results which have given a rather satisfactory account of the electron spin.

To describe the electron, four coordinates are used. Three are the spatial coordinates of position of the electron's "center" as usual. The fourth is taken as the component of the angular momentum in some particular direction, as the z direction. This component, s_z, is a dynamical quantity which can only take on two values, $+\frac{h}{4\pi}$ and $-\frac{h}{4\pi}$. Choosing for this section $h/4\pi$ as the unit of angular momentum, this means that the operator for s_z referred to its principal axes must be the matrix

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The Schrödinger wave function will depend on the four coordinates x, y, z, s_z and W such that $\psi(x, y, z, s_z, W)\bar{\psi}(x, y, z, s_z, W)dxdydz$ gives the probability that the electron be in the volume element around x, y, z and have the spin component s_z when it is known to be in the state of energy W. Since, however, s_z takes on only the two discrete values $+1$ and -1 it is perhaps more convenient to regard $\psi(x, y, z, +1, W)$ as one wave function $\psi_1(x, W)$ and $\psi(x, y, z, -1, W)$ as another wave function $\psi_2(x, W)$. The operation s_z becomes then just a linear transformation of the two ψ functions,

$$s_z\psi = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} \psi_1 \\ -\psi_2 \end{pmatrix}.$$

The normalization has to be such that

$$\int[\psi_1(x, W)\bar{\psi}_1(x, W) + \psi_2\bar{\psi}_2]dx = 1$$

to express the fact that the electron is certainly somewhere, and with its spin pointing in either of the two possible ways.

The next question to be answered is, what are the operators corresponding to the other two components of the spin angular momentum s_x and s_y? Of course, the spin characteristic of the electron differs in many respects from the angular momentum of translatory motion. Nevertheless, it is natural to seek to keep the analogy with ordinary angular momentum as close as possible. This suggests seeking two-rowed and two-columned matrices for s_x and s_y being guided by the requirement that they obey the same rules of commutation as equations (64.2) for the operators which represent angular momentum. Putting $l = \frac{1}{2}$ and remembering that $h/4\pi$ has been taken as unit, this requirement is

$$\begin{aligned} s_x{}^2 + s_y{}^2 + s_z{}^2 &= 3 \\ s_x s_y - s_y s_x &= -2is_z \\ s_y s_z - s_z s_y &= -2is_x \\ s_z s_y - s_x s_z &= -2is_y. \end{aligned}$$

Since the matrix form for s_z is known, it is now easy to write down forms for s_x and s_y with unknown quantities as the elements, determining them from these requirements. In this way one finds that the operators for the spin components are

$$s_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad s_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}, \quad s_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \qquad (65.1)$$

The remainder of the theory is concerned with the effect of spin on the energy levels. For this one needs to know how the Hamiltonian function depends on the spin components. Reasoning from the classical behavior of a magnet in an electromagnetic field, one expects that there will be two contributions to the Hamiltonian. One of these will arise from the direct interaction of the magnet with the magnetic field. If the magnetic moment is μ $(=eh/4\pi mc)$ this is

$$\mu(H_x s_x + H_y s_y + H_z s_z), \qquad (65.21)$$

where H_x, H_y, H_z are the components of the magnetic field. The other contribution will arise from the fact that the electron is usually moving in an electric field. Relative to axes moving with the electron's translatory motion, the electric field will be in part a magnetic field which will also interact with the magnetic moment of the electron to give a contribution to the energy. The calculation of the expression for this second contribution is a rather complicated problem in electrodynamics and will be omitted.

The result is

$$\frac{1}{4}\left(\frac{h}{2\pi}\right)^2 \frac{Ze^2}{mc^2}\frac{1}{r^3}\frac{1}{i}(k_x s_x + k_y s_y + k_z s_z) \qquad (65.22)$$

where k_x, k_y and k_z are related to the operators associated with the orbital angular momentum,

$$k_x = y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}.$$

The derivation of the expression for the interaction of the spin with the translatory motion is due to Thomas and to Frenkel.

The effect of this interaction on the energy levels is of the same order of magnitude as the relativity fine structure of the hydrogen levels. A detailed presentation of the fine-structure theory will be omitted but the main facts may be stated briefly. Before the new quantum mechanics, Sommerfeld worked out the modification in energy of the elliptical orbits due to the relativistic variation of the mass of the electron with its velocity. So far as energy levels were concerned Sommerfeld's theory agreed completely with the observed fine structure. But the selection rules governing the fine structure seemed to be somewhat different from those given by the theory. With the advent of the electron-spin hypothesis of Goudsmit and Uhlenbeck, still working by classical mechanical methods, the azimuthal quantum number was changed to half-integral values. This alone would spoil the agreement of the theory for energy levels. But, remarkably enough, the energy contributed by the interaction of the spin with the orbital motion was of just the correct amount to restore agreement as regards energy levels. The new interpretation of the levels carries with it an alteration in the selection rules which improves the agreement between predicted intensities in the fine structure and the observed intensities.

Schrödinger and others have given a relativistic form of the wave equation.[1] This, when applied to the hydrogen-atom problem, gives wrong values for the energy levels. The discrepancy is removed in the quantum mechanics by taking into account the effect of the spin by the method of Pauli's theory. That the new equations, involving two ψ functions, give the correct energy levels, was first worked out by Darwin[2] who discovered

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[1] Schrödinger, *Ann. der Phys.*, **81**, 132 (1926); Fock, *Zeits. für Phys.*, **39**, 226 (1926); Klein, *Zeits. für Phys.*, **41**, 407 (1927).

[2] Darwin, *Proc.* Roy. Soc. **116A**, 227 (1927).

them by a semi-empirical method. Darwin set himself the problem: Required to set up two simultaneous wave equations for two ψ functions such that they will give the fine structure energy levels correctly. Working backwards, in this way he arrived at the same equations as are given directly by the Pauli theory.

It is not quite true to say that the Pauli-Darwin equations give the correct energy levels for they fail for the $S(l = 0)$ levels For all others the fine structure is correctly given. This defect has been removed and, at the same time, the whole relativity-spin theory of the electron has been given a new and extremely important development by the work of Dirac.[1] Dirac's theory of the electron is, however, outside the scope of this book. Although representing a considerable advance Dirac's theory is still beset with difficulties so that much more remains to be done before a good understanding of this problem is reached.

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[1] Dirac, *Proc.* Roy. Soc.; Darwin, *Proc.* Roy. Soc., **118A,** 654 (1928); Gordon, *Zeits. für Phys.*, **48,** 11, (1929).

CHAPTER VII

APERIODIC PHENOMENA

The physical applications of quantum mechanics which have been thus far presented have been largely concerned with the determination of the stationary states of atomic systems. Such applications can be based almost entirely on the Schrödinger wave equation from which the dependence on the time has been eliminated Consideration of collision phenomena and the more detailed treatment of the interaction of radiation and matter calls for a study of the equation of Sec. **8**,

$$-\frac{h}{2\pi i}\frac{\partial\varphi}{\partial t} = H\varphi,$$

in which H is the Hamiltonian energy operator, and φ is the state vector in function space regarded as a function of the spatial coordinates of the mechanical system. This equation will be assumed to govern variation in time of the state vector of the mechanical system. Some properties of the equation will now be considered from the standpoint of the preceding chapter before proceeding to the study of aperiodic phenomena.

66. Variation of State in Time.—In accordance with the ideas of Chap. VI, the state of a mechanical system can be described by the function $\varphi(x_1 \ldots x_n)$, where $x_1 \ldots x_n$ are the spatial coordinates of the system and $\varphi\bar{\varphi}dV$ gives the probability that the configuration is specified by a volume dV of the configuration space around the values of $x_1 \ldots x_n$ occurring as arguments in $\varphi\bar{\varphi}$. The variation of the state in time will now be supposed governed by the fundamental equation,

$$-\frac{h}{2\pi i}\frac{\partial\varphi}{\partial t} = H\varphi. \tag{66.1}$$

The result of operating on φ with H can be expressed in terms of the expansion of φ in terms of the wave functions of the problem.

It will be supposed that $\varphi(x)$ can be expanded in a series of the wave functions $\psi(W, x)$,

$$\varphi(x) = \sum_W c(W)\psi(W, x). \tag{66.2a}$$

In the language of Sec. **61,** this means that $\varphi(x)$ can be referred to the coordinates in function space which are determined by the principal axes of H. Referred to these coordinates one has

$$H\varphi(x) = \sum_W c(W)H\psi(W, x) = \sum_W Wc(W)\psi(W, x).$$

Hence, the equation for the variation of $c(W)$ with the time is

$$\sum_W \left\{ \frac{h}{2\pi i}\frac{\partial c(W)}{\partial t} + Wc(W) \right\} \psi(W, x) = 0.$$

Multiplying through by $\bar{\psi}(W, x)$, for any W, and integrating over configuration space this yields,

$$\frac{h}{2\pi i}\dot{c}(W) + Wc(W) = 0, \tag{66.2b}$$

from which the result is obtained that

$$c(W) = c_0(W)e^{-\frac{2\pi i Wt}{h}}, \tag{66.2c}$$

where $c_0(W)$ is written for the initial value of $c(W)$.

From the preceding chapter one has that $c(W)\bar{c}(W)$ gives the probability that the system be in the state of energy W. From the result just obtained for the dependence of $c(W)$ on the time, it is seen that $c(W)\bar{c}(W)$ is independent of the time. This establishes the theorem that the relative probabilities of being in the different energy states are independent of the time.

Consider now any physical quantity whose operator A commutes with the Hamiltonian operator H. By Sec. **62** the transformation to principal axes of A will be equivalent to that for H, which means that H and A can be observed simultaneously with unlimited precision. In this case, every $\psi(W, x)$ can be labelled as associated with an allowed value, a, of A, *i.e.*,

$$A\psi(W, a, x) = a\psi(W, a, x)$$

is satisfied by the Schrödinger wave function. The state vector $\varphi(x)$ may now be referred to the values of a, *i.e.*,

$$\varphi(x) = \sum_a d(a)\psi(W, a, x).$$

Hence the equation for the variation of $d(a)$ with the time is

$$\sum_a \left\{ -\frac{h}{2\pi i}\dot{d}(a) + W \right\} \psi(W, a, x) = 0,$$

the solution being,

$$d(a) = d_0(a)e^{-\frac{2\pi i Wt}{h}}. \tag{66.3}$$

In other words, the probabilities for the various values of A remain constant in time if A commutes with H.

An important special example of this is afforded by the central-force field problems. For a particle which moves in a central field of potential energy, the Hamiltonian function is

$$H = \frac{1}{2\mu}p^2 + V(r).$$

Because of the symmetry of H, this Hamiltonian commutes with M^2, the operator for the square of the resulting angular momentum and M_z, the operator for the component of the angular momentum along the z axis. This statement can be readily verified by using the forms for M^2 and M_z from Sec. **64.** Therefore, a state of the system that is stationary in time, in the sense that its probability is independent of the time, can be labelled by simultaneous values of W, M^2, and M_z. This is essentially what is done in Sec. **16** where the problem is considered from the elementary point of view. The quantum number m there labelled the value of M_z in the stationary state, while l labelled the value of M^2, according to the relations,

$$\text{value of } M_z = m\frac{h}{2\pi},$$
$$\text{value of } M^2 = l(l+1)\frac{h^2}{4\pi^2},$$

which were developed in Sec. **64.**

If A does not commute with H then the value of the probability of a particular value of A is not independent of the time. Suppose that at $t = 0$ the value of A is known to be some particular value which may be denoted by a'. Then the state vector at $t = 0$ must be given by $\chi(a', x)$ where

$$A\chi(a', x) = a'\chi(a', x).$$

At any other time the state vector may be denoted by $\varphi(x)$. Each of the characteristic functions for H can be expanded in terms of those for A, *i.e.*,

$$\psi(W, x) = \sum_a t(W, a)\chi(a, x).$$

At any time $\varphi(x)$ is given by $\Sigma c(W)\psi(W, x)$ so one has

$$\varphi(x) = \Sigma c(W)\psi(W, x) = \sum_a [\sum_W c(W)t(W, a)]\chi(a, x).$$

The coefficient of $\chi\ (a, x)$ at any time gives the probability that the quantity A have the value a. It can be called $d(a)$. Since the dependence of $c(w)$ on the time is known, one has also an expression for the dependence of $d(a)$ on time,

$$d(a) = \sum_W c(W)t(W, a).$$

The initial condition, that at $t = 0$, the value of a is known to be a' determines the initial values of the $c(W)$.

One has

$$\chi(a', x) = \sum_W t^{-1}(a', W)\psi(W, x),$$

so the initial values of the $c(W)$ are $t^{-1}(a', W)$, the coefficients of the expansion of $\chi(a', x)$ in terms of $\psi(W, x)$. The complete solution for $d(a)$ is therefore,

$$d(a) = \sum_W t^{-1}(a', W)t(W, a)e^{-\frac{2\pi i W t}{h}}. \tag{66.4}$$

67. The Free Particle.—In Sec. **62**, the state vector which represents a particle whose position is known to be $x_0 \pm a$ and whose momentum is known to be $p_0 \pm \frac{h}{2\pi a}$, were written down. We have now to consider how this state vector will depend on the time. It is to be expected, of course, that after the lapse of time t the particle will be located at the position $\left(x_0 + \frac{p_0}{m}t\right)$ in the mean, but with a somewhat increased uncertainty in its position owing to the uncertainty in its speed. The classical way of compounding probable errors would lead one to suppose that the uncertainty in position after time t would be,

$$\sqrt{a^2 + \frac{h^2}{4\pi^2 a^2 m^2}t^2}.$$

The expectation is then that, in this case, the state vector will depend on the time in such a way that $\psi\bar{\psi}$ remains a Gauss error curve whose maximum moves with a uniform velocity p_0/m but which becomes broader, corresponding to the increased uncertainty of position.

That this is the case was shown by Kennard and by Darwin.[1] The question will now be considered from the standpoint of the preceding section. For a free particle, the Hamiltonian is simply

$$H = \frac{1}{2m}p^2,$$

so that H commutes with p. The allowed values of p are all values from $-\infty$ to $+\infty$ so all values of W from 0 to $+\infty$ are allowed. Since H and p commute, the relation between the numerical values W and p is simply

$$W = \frac{1}{2m}p^2.$$

By the preceding section the wave function of energy W depends on the time through a factor $e^{-\frac{2\pi i Wt}{h}}$ which means here that the component of the state vector corresponding to momentum p has the time factor $e^{-\frac{\pi i p^2 t}{mh}}$. Using the expression (62.1) for $\varphi(p)$ found in Sec. **62**, and multiplying it by this time factor one has

$$\varphi(p, t) = e^{-\left(\frac{2\pi a}{h}\right)^2(p-p_0)^2+\frac{2\pi i}{h}(p-p_0)x_0-\frac{\pi i p^2 t}{mh}}. \qquad (67.1)$$

To find $\varphi(x, t)$, in order to know the probabilities for various positions of the electron, one writes

$$\varphi(x, t) = \int_{-\infty}^{+\infty} exp\left\{-\frac{2\pi i}{h}px - \left(\frac{2\pi a}{h}\right)^2(p - p_0)^2 + \frac{2\pi i}{h}(p - p_0)x_0 - \frac{2\pi i}{h}\frac{p^2 t}{2m}\right\}dp.$$

Carrying out the integration, one finds for $\varphi\bar{\varphi}$ except for the normalizing factor,

$$\varphi\bar{\varphi} = e^{-\frac{(x-x_0-p_0t/m)^2}{\sigma^2}} \qquad (67.2)$$

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[1] Kennard, *Zeits. für Phys.*, **44,** 326 (1927); Darwin, *Proc. Roy. Soc.* **117A,** 258 (1927).

where

$$\begin{aligned}\sigma^2 &= a^2 + \left(\frac{ht}{4\pi ma}\right)^2 \\ &= (\Delta x)^2 + \left(t\frac{\Delta p}{m}\right)^2.\end{aligned}$$

Here Δx and Δp are the associated uncertainties in position and momentum as they were found in Sec. **62.** This verifies the expectation from elementary considerations that the maximum probability should move with the velocity corresponding to the mean momentum, while the distribution curve became broader because of the uncertainty in the velocity. The example serves as a useful check on the correctness of the equation for the time dependence of φ.

Darwin has considered some other interesting examples of the motion of such wave packets where forces act on the particle. Thus, in the case of a uniform force field which is of such strength as to cause a uniform acceleration g, he finds the probability of being between x and $x + dx$ to be given by

$$exp\left\{-\frac{\left(x - x_0 - \frac{p_0 t}{m} - \frac{1}{2}gt^2\right)^2}{a^2 + \left(\frac{ht}{4\pi ma}\right)^2}\right\}. \qquad (67.3)$$

In other words, the place of maximum probability moves down the field with uniform acceleration in exactly the same way as a particle moves classically under the same circumstances. The packet grows in extent at the same rate as before corresponding to the uncertainty principle estimate. He has also worked out the behavior of an electron in a uniform magnetic field according to this method.

Schrödinger[1] was originally of the opinion that the packet of waves could be interpreted as giving the actual charge density of the moving particle instead of the probability of its being at a certain place. Evidently, if this were to be a satisfactory interpretation, it would be necessary for the packet to remain of approximately constant dimensions as it moved about from place to place. He, at first, thought that this was the case. He constructed from the ψ functions for the harmonic oscillator a

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[1] Schrödinger, *Ann. der Phys.*, **79**, 500 (1926).

packet which oscillated with simple harmonic motion[1] and, although it underwent periodic fluctuations in extent, it did not grow in extent with time as in the cases just considered. This particular case is, therefore, a misleading one. The reason that it is exceptional is connected with the fact that the classical motions associated with different energies in the harmonic oscillator all have the same frequency. Therefore, even though there is some uncertainty in the energy necessary to fix the coordinate in a fairly definite part of a large oscillation, the equivalent classical particles moving in the orbits of the various energies involved will never get very far out of step with each other. Another such exceptional case is that of electrons under no force except that arising from a magnetic field, and is connected with the fact that the Larmor precession frequency is independent of the electron's speed.

Debye[2] has given an approximate discussion of the behavior of the packet in problems of one degree of freedom for any forces and finds that the maximum moves according to classical laws. The question has also been handled by Ehrenfest and by Ruark.[3]

68. One-dimensional Collisions.—The term, one-dimensional collision, will be adopted to denote cases of motion of a particle with one degree of freedom on which the force vanishes except in a limited range of the coordinate. The cases which arise are of considerable interest in that they present some important revisions of ideas from classical mechanics.

Let the coordinate be denoted by x and the potential energy $V(x)$ be such that it is zero for $x > x_0$ and for $x < 0$. If $V(x) < 0$ in the range $0 < x < x_0$, then the possibility of quantized energy levels, $W < 0$ corresponding to classical motions restricted to this range presents itself. These discrete levels will not be considered further.

Figure 23 illustrates a possible $V(x)$ which is sufficiently general to bring out the important cases. Consider first the case of a particle coming from negative x with energy W_1, greater than the absolute maximum of $V(x)$. According to classical mechanics $W - V(x)$ is the kinetic energy, which in this case remains positive throughout the range of x. The velocity never vanishes,

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[1] Schrödinger, *Naturwiss*, **14**, 644 (1926).

[2] Debye, *Phys. Zeits.*, **28**, 170 (1927).

[3] Ehrenfest, *Zeits. für Phys.*, **45**, 455 (1927); Ruark, *Phys. Rev.*, **32**, 1133 (1928) (abstract).

therefore, and the particle is certain to pass through the region where forces act on it and escape to $x = +\infty$. For the case of W_2, however, a particle coming from the left is reduced to zero speed where $W_2 - V(x) = 0$ and then reverses its direction of motion and returns to $x = -\infty$. For W_2 there are two types of motion, one representing an approach from and recession to $-\infty$, the other an approach from and recession to $+\infty$. Similarly, for W_3 which is greater than zero but less than the secondary maximum of $V(x)$ there are three types of motion. Two are in the infinite stretches of x to the left and right which give aperiodic motions, while the third is periodic and confined to the region between the two "hills" of $V(x)$. Finally to negative energies, as W_4, only the periodic motion corresponds.

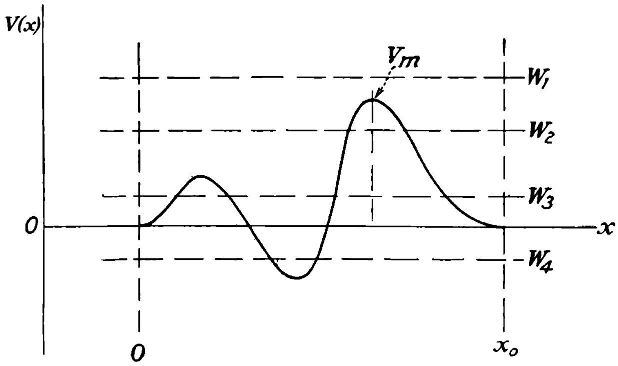

FIG. 23.—Energy levels of a possible potential energy function.

This situation will now be studied from the quantum mechanical standpoint. The results to be found are similar to the classical ones but show very striking differences. Considering always what happens to particles coming from the left it will be found that for W much larger than V_m (the absolute maximum of $V(x)$) the probability that the particle moves off to the right approaches certainty. But there is always a finite probability of returning to the left even in the case of $W > V_m$, which is in sharp contradiction to classical mechanics. Similarly, in the range W_2 it will be found that there is always a certain probability that the particle will move off to the right having passed through the region forbidden by classical mechanics where the potential energy exceeds the total energy. This probability, however, becomes rapidly small for values of W much less than V_m. The first main result is therefore that the value V_m for W no longer is a critical one for which there is an abrupt change in the character of the motion. Instead, there is a steady change in the probabilities of reflection or transmission as this value is passed.

Similarly, in the range characterized by W_3 it will be seen that there are no longer three sharply differentiated types of motion. Instead, the stationary state corresponding to each energy level will correspond either to a right-to-left motion or a left-to-right motion. There is one trace, however, of the old quantized periodic motions in the present theory. Whenever the energy almost corresponds to one of the allowed levels on the old theory, it will be found that a particle coming from the left has a certain probability of getting into the region belonging to the periodic motion, remaining there for some time and then escaping to infinity either to the right or to the left.

To establish the assertions just made it is better to consider a particular form for $V(x)$ for which the Schrödinger equation can be solved rigorously. Their truth in the more general case can be obtained by an appeal to methods of approximation. For this purpose the form in which $V(x)$ is constant except for discontinuities is well suited. In a region where $V(x)$ is constant and equal to V the equation for ψ becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}(W - V)\psi = 0$$

which has the solution,

$$\psi(W, x) = Ae^{ikx} + Be^{-ikx} \tag{68.1}$$

with

$$k = \frac{2\pi}{h}\sqrt{2\mu(W - V)}.$$

To find the solution for a $V(x)$ consisting of various constant values of V connected by abrupt discontinuities, it is natural to piece together such forms by requiring that both ψ and $d\psi/dx$ be continuous at the discontinuity in V.

To obtain the particular solution corresponding to a source of particles at $x = -\infty$, one observes that for $x \rightarrow +\infty$ it must correspond to a pure left-to-right flow. That is, one must require that $\psi(W, x)$ take on the form ce^{ik_0x} for x large, and positive where $k_0 = \frac{2\pi}{h}\sqrt{2\mu W}$.

As an illustration, consider the case in which $V(x) = 0$ except in the range $0 < x < a$ where it equals V. For $x > a$ one has $\psi(W, x) = e^{ik_0 x}$ so at $x = a$ the values of ψ and $d\psi/dx$ are e^{ik_0a} and

$ik_0e^{ik_0x}$, respectively. In the range $0 < x < a$, one has $\psi(W, x)$ given by (68.1) with A and B determined so that

$$\begin{aligned} Ae^{ika} + Be^{-ika} &= e^{ik_0a} \\ k(Ae^{ika} - Be^{-ika}) &= k_0e^{ik_0a} \end{aligned}$$

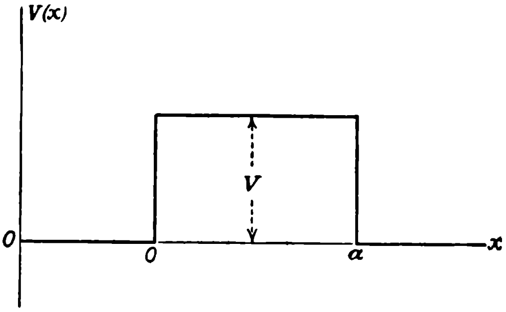

FIG. 24.—A simple form of $V(x)$ illustrating collision phenomena.

whence the values of A and B are

$$\begin{aligned} A &= \frac{1}{2}\left(1 + \frac{k_0}{k}\right)e^{i(k_0-k)a} \\ B &= \frac{1}{2}\left(1 - \frac{k_0}{k}\right)e^{i(k_0+k)a}. \end{aligned} \tag{68.2}$$

Similarly in the range $x < 0$, $\psi(W, x)$ will be given by

$$\psi(W, x) = Ce^{ik_0x} + De^{-ik_0x},$$

with C and D determined so that ψ and $d\psi/dx$ are continuous at $x = 0$. This leads directly to

$$\begin{aligned} C &= \frac{1}{2}\left[\left(1 + \frac{k}{k_0}\right)A + \left(1 - \frac{k}{k_0}\right)B\right] \\ D &= \frac{1}{2}\left[\left(1 - \frac{k}{k_0}\right)A + \left(1 + \frac{k}{k_0}\right)B\right]. \end{aligned} \tag{68.3}$$

Using the current density expression of Sec. **10**, it is found that this solution for ψ corresponds to an incident beam of intensity $C\bar{C}$, a reflected beam of $D\bar{D}$, and a transmitted beam of unit intensity. The fraction transmitted is therefore $1/C\bar{C}$ and the fraction reflected is $D\bar{D}/C\bar{C}$. Considering the case $W > V$, k is a real quantity so

$$\begin{aligned} C\bar{C} = \frac{1}{16}\biggl[&\left(1 + \frac{k}{k_0}\right)^2\left(1 + \frac{k_0}{k}\right)^2 + \left(1 - \frac{k}{k_0}\right)^2\left(1 - \frac{k_0}{k}\right)^2 \\ &+ 2\left(1 + \frac{k}{k_0}\right)\left(1 - \frac{k}{k_0}\right)\left(1 + \frac{k_0}{k}\right)\left(1 - \frac{k_0}{k}\right)\cos 2ka\biggr]. \end{aligned} \tag{68.4}$$

For $W \to \infty$, $k \to k_0$ so $C\bar{C} \to 1$, that is, for large energy the probability of transmission approaches certainty. As W increases from V to ∞, the probability of transmission increases. The cosine term has a coefficient which is essentially negative so the transmission probability is increased whenever $ka = n\pi$, that is, whenever an integral number of half de Broglie wave lengths is contained in the distance a.

Similarly, if $W < V$, then k becomes pure imaginary and the formula for $C\bar{C}$ is (on writing now ik for k),

$$C\bar{C} = \frac{1}{2} + \frac{1}{8}\left[\left(\frac{k_0}{k} - \frac{k}{k_0}\right)^2 + \left(1 + \frac{k_0^2}{k^2}\right)\left(1 + \frac{k^2}{k_0^2}\right)\cosh 2ka\right]. \qquad (68.5)$$

If $W < V$, there is a finite probability of transmission which approaches zero as ka becomes large, because of the hyperbolic cosine term. If V and a are not very large, however, it is impossible for ka to become very large; in other words, the barrier does not have a great stopping effect on the particles.

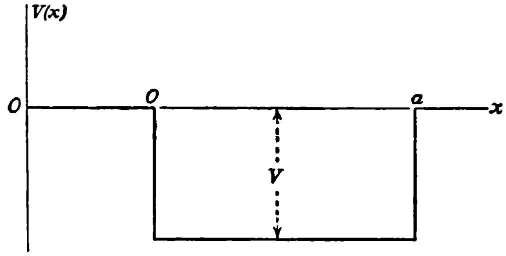

FIG. 25.—A simple form of $V(x)$ illustrating collision phenomena.

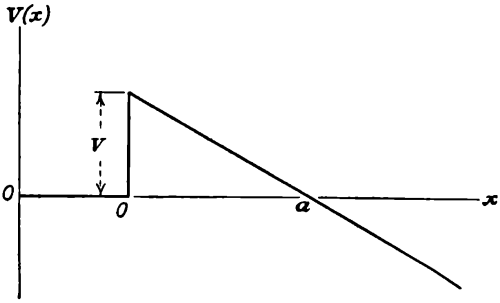

FIG. 26.—A simple form of $V(x)$ illustrating the behavior of electrons at the surface of a metal.

This same investigation applies for $V < 0$ and $W > 0$. In this case the particles have some probability of reflection although by classical mechanics they would certainly move always in the same direction. In this case $W > V$ so the first of the two formulas just given is applicable.

Another form of curve which can be handled by this method is shown in the figure. Here the analytical work is more complicated because on the portion to the right of the origin Bessel's functions of order one-third must be used (Sec. **13**). This form was used by Fowler and Nordheim[1] to give a theory of the pulling of electrons out of metals with high electric fields. For this purpose, they idealized the metal by regarding it as a region

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[1] FOWLER and NORDHEIM, *Proc.* Roy. Soc. **119A,** 1 (1928).

in which no forces act on the electrons except at the surface where there is an abrupt discontinuity in the potential energy corresponding to the work of removing an electron from the metal. If no electric field is applied outside the metal, the potential energy curve is horizontal outside, but if a uniform field acts, the curve is of the type shown so there is a small probability that an electron, colliding with the metal surface from the inside, will escape through it in violation of the laws of classical mechanics. This view of the phenomenon has been subsequently made more precise and appears to contain all the elements necessary for an explanation of the known experimental results.

The preceding calculation will serve to show the nature of the general theory. For an arbitrary $V(x)$ this method is not applicable. In this case an approximation method is needed.[1] One has to solve

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}(W - V(x))\psi = 0,$$

for the particular solution which approaches e^{ikx} for $x \to +\infty$. Approximately, the solution may be written as

$$\psi = \psi_1 + \psi_2 + \psi_3 + \cdots \tag{68.6}$$

if

$$\frac{8\pi^2\mu}{h^2}V(x) = U(x),$$

and

$$\begin{aligned} \psi_1'' + k^2\psi_1 &= 0 \\ \psi_2'' + k^2\psi_2 &= U(x)\psi_1 \end{aligned}$$

determining $\psi_2, \psi_3 \ldots$ so that they vanish for $x \to +\infty$. This gives

$$\psi_2 = \frac{i}{2\kappa}\left\{e^{ikx}\int_x^\infty U(x)dx - e^{-ikx}\int_x^\infty U(x)e^{2ikx}dx\right\} \tag{68.7}$$

and similar but more complicated formulas for $\psi_3 \ldots$

It is instructive to consider simply the approximation given by $\psi_1 + \psi_2$. This, for $x \to -\infty$, becomes

$$\psi \to \left(1 + i\frac{U_0}{2k}\right)e^{ikx} - \frac{i}{2k}U_{2k}e^{-ikx} \tag{68.8}$$

in which

$$U_0 = \int_{-\infty}^{+\infty} U(x)dx \quad \text{and} \quad U_{2k} = \int_{-\infty}^{+\infty} U(x)e^{2ikx}\,dx.$$

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[1] BORN, *Zeits. für Phys.*, **38**, 803 (1926).

The intensity of the incident beam is, therefore,

$$1 + \left(\frac{U_0}{2k}\right)^2,$$

while that of the transmitted beam is 1. On the other hand, the intensity of the reflected beam is $(U_{2k}/2k)^2$ so one sees that in this approximation the number of particles is not conserved. That the infinite series for ψ converges may be proven under the assumption that $\int_{-\infty}^{+\infty} |U(x)|dx$ is bounded.

69. Radioactive Disintegration.—By far, the most important application of the ideas of the preceding section is to the theory of the ejection of α-particles from the nuclei of the radioactive atoms. This application was worked out independently by Gurney and Condon and by Gamow and has subsequently been discussed by a number of others.[1] Little is known concerning the forces which bind together the constituents of the atomic nucleus, but from the α-particle scattering experiments of Rutherford it is known that the force is quite accurately given by the Coulomb law down to distances of the order of 10^{-11} to 10^{-12} centimeters. At small distances attractive forces must predominate, however, in order to hold the α-particle into the nucleus.

For a working picture we may consider one α-particle as moving in a central-force field due to the action on it of the rest of the nucleus. For simplicity, one may restrict the discussion to the states for which $l = 0$ so that in accordance with Sec. **16** the equation for $R(r)$, where $\psi = \frac{1}{r}R(r)$, becomes

$$R''(r) + \frac{8\pi^2\mu}{h^2}(W - V(r))R = 0. \tag{69.1}$$

$R(0)$ must equal zero and $R(\infty)$ must be finite. Since for $r \gg 10^{-12}$ *cm*, $V(r)$ obeys the Coulomb law but for smaller values attractive forces outweigh the Coulomb repulsion, the $V(r)$ must be of the type shown in Fig. 27.

Two types of energy levels now present themselves, $W_1 > 0$ and $W_2 < 0$. The latter correspond to absolutely stable orbits, and

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[1] GURNEY and CONDON, *Phys. Rev.*, **33,** 127 (1929); GAMOW, *Zeits. für Phys.*, **51,** 204 (1928); **52,** 510 (1928); GAMOW and HOUTERMANS, *Zeits. für Phys.*, **52,** 496 (1928); KUDAR, *Zeits. für Phys.*, **53,** 61 (1929); **53,** 95 (1929); **53,** 134 (1929); VON LAUE, *Zeits. für Phys.*, **52,** 726 (1928); Discussion of Royal Society, *Proc. Roy. Soc.*, **A123,** 373 (1929).

would give stable nuclei. The former call for closer consideration. According to classical mechanics for $W < V_m$ there would be two types of motion possible, one an aperiodic motion extending from infinity to the larger value of r for which $W = V(r)$, the other a periodic motion confined to the interior of the nucleus. This result has to be modified considerably.

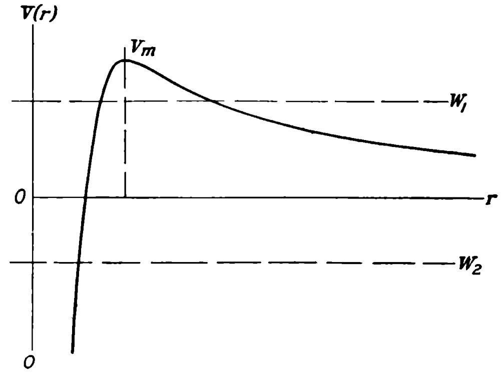

Fig. 27.—An assumed form of nuclear potential function.

Since for W positive both of the fundamental solutions of equation (69.1) remain finite for $r \rightarrow \infty$, every value of W is an allowed energy level. But the $\psi(W, x)$ associated with different levels are very different. In the two regions where $W > V(r)$, the $\psi(W, x)$ will have an oscillatory character, whereas in the region where $W < V(r)$, it will behave roughly like the exponential function of a real argument. In general, $\psi(W, x)$ will start from the value 0 at $x = 0$ and perform a few oscillations in the inner part. In the region where $W < V(r)$ it will behave roughly like an exponential function which means that it will generally increase very rapidly in amplitude until the other region where $W > V(r)$ is reached where it will again assume an oscillatory character but with the greatly augmented amplitude. Certain energy levels will be exceptional in that the amplitude will *decrease* exponentially in the $W < V(r)$ range so that the amplitude of the outer oscillations is very small compared to that inside. These statements are readily verified rigorously if the $V(r)$ curve is square as in Fig. 28, otherwise, they can be proved by an appeal to the approximate method of integrating the wave equation which was used in Sec. **38**.

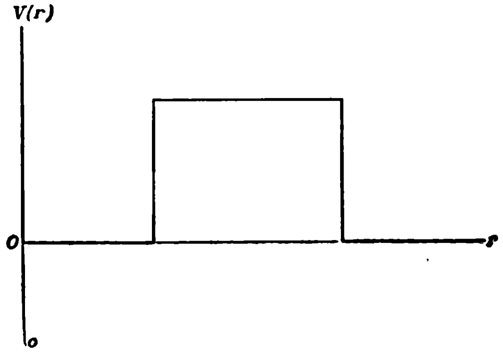

Fig. 28.—A simple potential function illustrating radioactive decay.

The interpretation is now as follows: These wave functions represent aperiodic motions in which the particle comes from infinity and recedes to infinity. For most energy levels $\psi(W, x)$ is small inside compared to its value outside the critical region. For these it is highly probable that the particle will be simply reflected back by the nucleus with very little chance of penetration into it. But for certain almost discrete energy levels, the situation is just reversed. For these the particles come from infinity, almost certainly penetrate to the inside of the nucleus, and remain there a long time before escaping again to infinity. This follows from the fact that the amplitude of ψ is very large inside compared to the amplitude outside and so the probability of being in a given range of r inside is much greater than that outside.

These considerations afford the clue to a simple calculation of the mean time which the particle will remain inside the nucleus before escaping. Suppose that $\psi(W, x)$ approaches asymptotically to the value sin kr for $r \rightarrow \infty$ while in the portion inside the nucleus the mean amplitude of its oscillations is Ψ. When the particle is far away from the nucleus, its speed is approximately $\sqrt{2W/\mu}$. The time in which it is in unit length far out from the nucleus is $2\sqrt{\mu/2W}$, since it traverses the length twice, once coming in and once going out in an aperiodic motion. If the size of the inner part of the nucleus is a, the mean time spent inside the nucleus T must be approximately

$$T = 2a\sqrt{\mu/2W}\Psi^2,$$

since tne probability of being in unit length inside to that outside stands in the ratio of Ψ^2.

The value of Ψ can be estimated by the approximate method of Sec. **38** with the result

$$\Psi = exp\frac{2\pi}{h}\int\sqrt{2\mu(V - W)}dr \tag{69.1}$$

where the integration is extended over the range in which $V(r) > W$. The mean duration of the α-particle inside the nucleus thus becomes of the order

$$T = 2a\sqrt{\mu/2W}\, exp\frac{4\pi}{h}\int\sqrt{2\mu(V - W)}dr. \tag{69.2}$$

It has been shown that the substitution of a reasonable form for $V(r)$ of the type of Fig. 27 where outside it is of appropriate Coulomb type and where the maximum value of V occurs near

3×10^{-12} centimeters, together with the observed values of W for emitted α-particles, in this formula gives the correct order of magnitude of the mean life T. Moreover, as it is natural to suppose that the $V(r)$ curves are somewhat similar for all radioactive atoms, this formula contains a relation between the mean life T, and the energy W of the emitted α-particle. This relation appears to agree quantitatively quite well with the empirical relation between W and T discovered by Geiger and Nuttall. The picture of the disintegration process here employed is undoubtedly too much simplified to give an accurate picture of the phenomenon but as any understanding of it had been hitherto lacking this must be looked upon as an important advance on the question of the structure of the nucleus.

The discussion just given proceeds on an argument from a single stationary state or energy level. Approaching the same problem from the wave packet standpoint of Sec. **67**, one would have to superpose the $\psi(W, x)$ for various values of W in such a way that at $t = 0$ they interfered destructively outside of the nucleus. Then, as time goes on, since the different constituent wave functions in the packet oscillate with different frequencies, the waves will no longer interfere outside the nucleus. This means that there is a certain probability of being outside the nucleus which grows with time. From the rate of growth of the wave function outside or its rate of diminution inside, an estimate of T could be gotten. A detailed analysis from this standpoint has not thus far been given.

The property of quantum mechanics, whereby particles may escape from a classical periodic motion to an aperiodic motion of equal energy, was first noticed by Oppenheimer.[1] He applied it to the case of hydrogen atoms in an electric field as in the Stark effect. It appears, from arguments similar to those just given for the nucleus, that the electron will not remain indefinitely in a region close to the hydrogen-atom nucleus if the atom is in a field. Instead, there is a certain probability that the electron will escape from the atom to be accelerated away by the field.

This means that it is possible to ionize atoms solely by the application of high fields, without any indirect action like the formation of ions by collision.

70. Scattering of Electrons by Atoms.—The case in which a particle is free to move in three dimensions and is acted on by no

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[1] OPPENHEIMER, *Phys. Rev.*, **31**, 66 (1928)

forces except when it is near the origin, is one of considerable importance. The treatment of such cases is due to Born.[1] An important special case is that of the scattering of α-particles by atomic nuclei, a phenomenon studied experimentally by Rutherford and his co-workers and which originally led to the model of the nuclear atom in which the positive electricity is confined to an extremely small nucleus.

If no forces acted on the particle, the wave equation could be solved by an infinite plane wave of appropriate wave length and moving in an arbitrary direction. This would correspond to a stream of particles moving in the direction of the normal to the wave front. If forces act while the particle is near the origin, then a solution of the wave equation which is asymptotically equal to e^{+ikz} as $z \to -\infty$, will represent an incident beam of particles from this particular direction. Such a solution will for large values of r in each direction take on an asymptotic value e^{ikr} multiplied by a function of the direction. The square of this function then measures the probability of scattering in that particular direction.

Approximate values for the scattered-wave amplitudes may be found by a method of solving the wave equation which is the three-dimensional analogue of that given in Sec. **68.** In case one is dealing with the scattering of electrons by an atom or molecule it is necessary to know the Hamiltonian operator of the atom. If, now, the coordinates of the electron to be scattered are denoted by x, y, z and if ξ denote the ensemble of the coordinates of the particles in the scattering atom, then the potential energy of interaction between the atom and the electron may be written $V(x, y, z, \xi)$. The Schrödinger equation governing the problem is then

$$-\frac{h^2}{8\pi^2\mu}\Delta\psi + H\psi + V\psi = W\psi. \tag{70.1}$$

If $V = 0$ there is no interaction and the equation can be solved by writing

$$\psi_1 = e^{i\mathbf{k}\cdot\mathbf{r}}u(\xi, E), \tag{70.2a}$$

which corresponds to the particle moving freely in the direction given by $\mathbf{k}$ while the atom is in the state of energy E.

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[1] BORN, *Zeits. für Phys.*, **38,** 803 (1926) and the excellent report by WENTZEL, *Phys. Zeits.*, **29,** 321 (1928).

To take the interaction into account we proceed as in Sec. **68,** writing

$$\psi = \psi_1 + \psi_2 + \cdots,$$

using for ψ_1, the form just given and demanding of ψ_2, ψ_3 etc. that they vanish as $\boldsymbol{k}\cdot\boldsymbol{r} \to +\infty$. This will give a solution in which unit intensity has passed by the atom unaffected. $\psi_2, \psi_3 \ldots$ mav now be determined by the equations

$$-\frac{h^2}{8\pi^2\mu}\Delta\psi_2 + H\psi_2 - W\psi_2 = V\psi_1 \tag{70.2b}$$

with the boundary condition that $\psi_2, \psi_3 \ldots$ vanish for $r \to \infty$. For W in this case one has

$$W = E + \frac{1}{2\mu}\left(\frac{hk}{2\pi}\right)^2. \tag{70.2c}$$

To find ψ_2 one assumes that it can be developed in a series of the wave functions of the atom each multiplied by a function of the electron coordinate,

$$\psi_2 = \sum_{E'} f(x, E')U(\xi, E'). \tag{70.3a}$$

Substituting in the differential equation for ψ_2 and making use of the orthogonality property of the atomic wave functions, one finds for $f(x, E)$ the equation,

$$\Delta f(x, E) + \alpha^2 f = \Phi(x), \tag{70.3b}$$

in which

$$\alpha^2 = \frac{8\pi^2\mu}{h^2}(E - E') + k^2,$$

and

$$\Phi(x) = \frac{8\pi^2\mu}{h^2}\int V(x, \xi)e^{-ik.r}U(\xi, E)\bar{U}(\xi, E')d\xi.$$

This equation for $f(x, E)$ is of the type already considered in electromagnetic theory and which leads to formulas for radiation from oscillating charges as given in Sec. **30.**

One finds for $f(x, E)$ the formula

$$f(x, E') = -\frac{1}{4\pi}\int dx'\Phi(x')\frac{e^{-i\alpha|r'-r|}}{|r' - r|}, \tag{70.4a}$$

the integration extending over all values of $dx'dy'dz'$. Thus, the problem of finding the first approximation is solved. Since $V(x)$ is essentially zero, except in the neighborhood of the origin, the same is true of $\Phi(x)$. Therefore, an asymptotic form for $f(x, E')$ valid for large distances from the origin may be taken in the form,

$$f(x, E') \rightarrow f(\boldsymbol{s}, E')\frac{e^{i\alpha r}}{r}, \tag{70.4b}$$

where $\boldsymbol{s}$ is a unit vector indicating the direction away from the origin in which the asymptotic value is taken.

To summarize, the form of ψ_2 which is valid for large distances of the electron from the atom is given by

$$\psi_2 = \sum_{E'} f(\boldsymbol{s}, E')\frac{e^{i\alpha r}}{r}U(\xi, E') \tag{70.5}$$

in which

$$f(\boldsymbol{s}, E') = -\frac{2\pi\mu}{h^2}\int d\xi dx' V e^{-i(\boldsymbol{k}.\boldsymbol{r}+\alpha\boldsymbol{s}.\boldsymbol{r})}U(\xi, E)\bar{U}(\xi, E').$$

The details of the development of the formulas will be omitted here as they parallel quite closely those for the corresponding classical radiation problem.

Although this first approximation cannot be expected to represent the facts very accurately it nevertheless shows the main features of the collision of an electron with an atom. The terms in ψ_2 represent electrons which move out radially from the atom with translational energy connected with the constant α. This is the case if α is real; if α is imaginary, the waves die out too rapidly to be observed at large distances. Associated with this outward stream of electrons there appears a certain probability that the atom now appears in the state of energy E' instead of E. On examining the formula for α, it is seen that the final energy of the scattered electron beam is just equal to the original energy diminished by the increase of the atom. One is therefore dealing here with the quantum mechanical description of the critical potential experiments of Franck and Hertz.

In particular, the term in ψ_2 for which $E' = E$ corresponds to the scattering of the incident particles without change in the state of the atom, the so-called elastic impacts. Collisions of the second kind are those in which the particle collides with an atom in the excited state and is scattered with increase in kinetic energy. These can happen if E is not the lowest state of the atom and are represented by the terms for which $E' < E$.

The theory of this section is connected with a very important group of experiments devised to measure the excitation function of atoms, that is, the probability that an atom be excited by an electron in a definite way, as a function of the velocity of the impacting electron. These experiments have usually been concerned with the total probability independently of the angle through which the electron is scattered. It is also connected with the theory of the abnormally long free paths of electrons moving in gases as studied by Ramsauer and by Brode. Although much has been written on the subject from the standpoint of the collision theory, a satisfactory account of the phenomenon from the theoretical side is still lacking.

At about the same time that Born developed the collision theory for quantum mechanics, Dymond reported some experiments on the distribution in angle of the electrons scattered by helium without appreciable loss in energy.[1] The striking feature of the results was that the electrons were scattered strongly in certain rather closely defined directions, which was highly suggestive of the diffraction of light by small particles. Since the wave theory of electrons was just then having many successes, it was assumed on all sides that these results were an evidence of the diffraction of electron waves by the atom.

Subsequently, however, it has turned out that these results were spurious.[2] Instead, the distribution in angle shows but a single maximum in the forward direction. This is in actual agreement with the approximate theory, as the collision theory does not give any distinct diffraction maxima at least in the first approximation.

The only angular scattering problem of importance for which the solution has thus far been given rigorously is that of the scattering of particles in a Coulomb field of force.[3] The application is to the scattering of α-particles by atomic nuclei, a phenomenon studied experimentally by Rutherford and which originally led to the nuclear model of the atom. The mathematical details are rather complicated and lead finally to the same result

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[1] DYMOND, *Phys. Rev.*, **29**, 433 (1927).

[2] HARNWELL, *Proc. Nat. Acad. Sci.*, **14**, 564 (1928); DYMOND and WATSON, *Proc.* Roy. Soc., **A122**, 571 (1929).

[3] TEMPLE, *Proc.* Roy. Soc., **A121**, 673 (1928); MOTT, *Proc.* Roy. Soc., **A118**, 542 (1928); WENTZEL, *Zeits. für Phys.*, **40**, 590 (1927); OPPENHEIMER, *Zeits. für Phys.*, **43**, 413 (1927).

as given by classical mechanics. At one time it was suggested that the wave mechanical formula might depart from the classical Coulomb scattering in the same way as do the experiments. These deviations have usually been attributed to the finite size of the scattering nucleus, a view which is probably the correct one since the quantum mechanical scattering agrees rigorously with the classical formula for the Coulomb law.

In the case of the scattering of electrons by atoms only approximate evaluations of the integrals of the first approximation of Born's theory have been given. It is rather hard to know how well these results express the results which would be given by exact solutions, and as moreover the experimental data with which formulas could be compared are meager, the topic will not be discussed here in greater detail. Oppenheimer[1] has pointed out the necessity of allowing for the equivalence of the electrons when an electron is scattered by an atom containing electrons, for it may not be the same electron coming out as the one sent in.

71. Scattering by Crystals.—Probably the most direct evidence we have for the wave theory of the electron is afforded by the experiments of Davisson and Germer in which the scattering of a beam of electrons by a single crystal of nickel is studied. Since the de Broglie wave length of electrons having an energy of the order of 100 electron volts, is about the same as the lattice space in crystals one would expect, independently of a detailed theory, the scattering to be governed by interference laws analogous to those which govern the scattering of X-rays by crystals. That this is the case for electrons was first discovered by Davisson and Germer and subsequently by many other investigators. Thomson studied the angular scattering of electrons which have penetrated thin sheets of polycrystalline material and found diffraction rings, the experiment being analogous to the powder method of Debye and Scherrer in X-rays. The first experiments of Davisson and Germer were concerned with the back scattering of electrons striking a single crystal at normal incidence, and were analogous to the Laue space-lattice diffraction of X-rays. Later, they employed also an arrangement which was the analogue of the Bragg reflection method.

Corresponding to the recent experiments of Doan and Rearden in which X-rays are diffracted by a ruled grating, Rupp has studied the diffraction effects of an electron beam incident on a

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[1] OPPENHEIMER, *Phys. Rev.*, **32**, 361 (1928).

ruled grating. Kikuchi has studied the diffraction of electrons which penetrate thin sheets of mica and has obtained most beautiful photographs of the diffraction patterns. Further studies by the powder method have been made by Ponte with the conclusion that the study of electron diffraction should prove just as powerful a tool for the investigation of crystal structure as has that of X-rays.

On the theoretical side, it may be noted that the probable existence of such effects was pointed out by Elsasser shortly after the appearance of de Broglie's thesis and before the development of the quantum mechanics. Shortly after the work of Davisson and Germer, brief theoretical papers relating the effect to quantum mechanics were published by Zwicky and by Eckart.

The most thorough-going theoretical treatment is that given by Bethe. He represents the potential energy of an electron in the crystal lattice as a triple Fourier series whose fundamental periods are the dimensions of the unit cell of the crystal lattice. Corresponding to such a potential energy function, it is possible to find by an approximation method ψ functions which determine the scattering.[1]

72. Variation of Constants.—There is another mode of treating small perturbations of an atomic system which is frequently quite useful. It is known as the variation of constants. Suppose that the solution of the unperturbed equation

$$H\psi = W\psi$$

is known. If the Hamiltonian for the disturbed system is $(H + \lambda H_1)$, the energy levels are, of course, changed, and the original ψ functions no longer correspond to stationary states of the system. Nevertheless, it is possible to expand the state vector in terms of the undisturbed ψ functions at any given instant. At $t = 0$ suppose then the state of the system is given by $\varphi(x)$ where

$$\varphi(x) = \sum_W c(W)\psi(W, x), \tag{72.1}$$

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[1] Davisson and Germer, *Phys. Rev.*, **30,** 705 (1927); Thomson, G. P., *Proc.* Roy. Soc., **117A,** 600 (1927); Rose, D. C., *Phil. Mag.*, **6,** 712 (1928); Davisson and Germer, *Proc.* Nat. Acad. Sci., **14,** 317 (1928); Eckart, *Proc.* Nat. Acad. Sci., **13,** 519 (1927); Zwicky, *Proc.* Nat. Acad. Sci., **13,** 518 (1927); Bethe, *Ann. der Phys.*, **87,** 55 (1928); Kikuchi, *Proc.* Imp. Acad., Tokyo, **4,** 271, 354 (1928); Ponte, *Comp. Rend.*, **188,** 244, 909 (1929).

where the summation is over the undisturbed energy levels W. Because the $\psi(W, x)$ are not solutions of the problem with the complete Hamiltonian, the $c(W)$ will not vary with the time in the simple way of Sec. **66**; instead, the equation for the time variation becomes

$$\sum_W \left\{ +\frac{h}{2\pi i}\dot{c}(W) + Wc(W) \right\} \psi(W, x) + \lambda c(W) H_1 \psi(W, x) = 0. \tag{72.2}$$

which reduces to the usual equation for the c's for $\lambda = 0$. Multiplying by $\bar{\psi}(W', x)$ and integrating, one has

$$\frac{h}{2\pi i}\dot{c}(W') + W'c(W') + \lambda \sum_W c(W) \int \bar{\psi}(W', x) H_1 \psi(W, x) dx = 0. \tag{72.3a}$$

Consider now the special case in which at $t = 0$ all the c's are zero except some particular one $c(W)$ which equals unity. Then, for a small lapse of time around $t = 0$, one may write

$$\frac{h}{2\pi i}\dot{c}(W) + \left[W + \lambda \int \bar{\psi}(W, x) H_1 \psi(W, x) dx \right] c(W) = 0. \tag{72.3b}$$

In other words, the $c(W)$ will vary with the time in the same way as if it corresponded to a stationary state of energy given by the bracketed coefficient of $c(W)$. This agrees exactly with the formula for the first-order variation of the energy level by the perturbation as found in Sec. **40.**

Thus, in a first approximation each $c(W')$ contains a time factor which depends on the perturbed energy level. If one now writes W for the perturbed value of the energy and puts

$$c(W) = d(W) e^{-\frac{2\pi i W t}{h}}, \tag{72.4a}$$

the time variation of $d(W)$ is given by

$$\dot{d}(W') + \lambda \frac{2\pi i}{h} \sum_W d(W) e^{\frac{2\pi i}{h}(W' - W)t} \int \bar{\psi}(W') H_1 \psi(W) dx = 0, \tag{72.4b}$$

so that the d's are constants if $\lambda = 0$. These equations may be solved approximately by successive approximations, if at $t = 0$, $d(W) = 1$ and all others vanish.

One has then

$$\dot{d}(W') + \lambda\frac{2\pi i}{h} e^{\frac{2\pi i}{h}(W' - W)t}\int\bar{\psi}(W')H_1\psi(W)dx = 0$$

so

$$d(W') = \lambda\frac{e^{\frac{2\pi i}{h}(W' - W)t} - 1}{W' - W}\int\bar{\psi}(W')H_1\psi(W)dx. \qquad (72.5)$$

This formula is especially important in the limiting case of resonance where one is concerned with the interaction of two states of equal energy levels. In this case one has a linear increase of $d(W')$ with the time,

$$d(W') = \lambda\frac{2\pi i\, t}{h}\int\bar{\psi}(W')H_1\psi(W)dx.$$

This linear increase with the time is of course connected with the resonance phenomenon as studied in Sec. **48.**

73. Interaction of Radiation and Matter.—The various phenomena connected with the interaction of radiation and matter constitute an important part of quantum theory. Strictly speaking, they are not so much problems of quantum mechanics as of quantum electrodynamics. One holds to the Maxwellian view of the electromagnetic nature of light because of its successes, but at the same time recognizes that fundamental changes are needed to account for the phenomena of light quanta. The solution of this problem must necessarily call for a modification of the laws of electrodynamics, just as modification of classical mechanical laws has been necessary to account for the quantum behavior of mechanical systems. At the present time, very little progress has been made on the formulation of quantum electrodynamics.

For the purpose of giving provisional theories of the interaction, radiation has been handled in two different ways in the quantum theory.[1] In one of these light of frequency, ν traveling in the x direction and polarized with the electric vector in the z direction is treated as being synonymous with the electromagnetic field given by the potentials,

$$\varphi = 0, \quad A_x = 0, \quad A_y = 0, \quad A_z = a\cos 2\pi\nu\left(t - \frac{x}{c}\right), \qquad (73.1)$$

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[1] Slater, *Proc.* Nat. Acad. Sci., **13, 7,** 104 (1927); Born, *Zeits. für Phys.*, **40,** 167 (1926); Dirac, *Proc.* Roy. Soc.,**114A,** 243 (1927).

where φ is the electrostatic potential and A the vector potential. The Hamiltonian function for an atom in such a radiation field is then to be obtained by considering that the field of the radiation acts on each of the charges in the atom according to the equation (9.1) for the Hamiltonian of a charge in an electromagnetic field. This method is capable of giving a good account of the absorption and induced emission of light by atoms, of the photoelectric effect, the Compton effect, and of dispersion and of the so-called Raman scattering of light.

The other method calls for treating the radiation as contained in an enclosure with reflecting walls. In such a case the electromagnetic field of the radiation may be analyzed into standing waves whose form and frequency depend on the shape and size of the enclosure. The variation of the amplitude of each type of standing wave with the time, since it is simple harmonic, must satisfy an equation of motion like the classical equation of motion of a harmonic oscillator. The state of the radiation field is therefore to be described by giving the amplitude of each standing wave at a particular time. Each amplitude thus plays the rôle of a coordinate. It is natural to suppose that these coordinates must be subject to the laws of quantum mechanics, in other words, that the state of the field is to be regulated by an equation of the type of equation (66.1) where H is the Hamiltonian function of the radiation field and φ is a function of the amplitudes of each of the standing waves. This procedure was adopted by Dirac. He regarded the interaction of matter and radiation as the interaction of the atom with the system of infinitely many degrees of freedom whose coordinates are the amplitudes of the standing electromagnetic waves in the enclosure. It turns out that this method gives the probabilities of emission of both the spontaneous and induced type, required in Einstein's theory of the Planck radiation law (Sec. **37**). It also provides an alternative theory of dispersion and light scattering.

The second method appears to be nearer the truth than the first in that it provides a place for the spontaneous emission. The first method seems to give the same results as the second with regard to the absorption and induced emission. Moreover, it is much simpler to handle analytically and is therefore suited to the discussion of most questions concerning interaction.

For simplicity let it be supposed that the atom has but one electron, of charge e and mass μ and that this electron moves in a field of potential energy, $V(x, y, z)$. Then the equation for the dependence of φ on the time is

$$-\frac{h}{2\pi i}\frac{\partial\varphi}{\partial t} = \frac{1}{2\mu}\left(p - \frac{e}{c}A\right)^2\varphi + V\varphi. \tag{73.2}$$

In this, if φ is sought as a function of x, y, z then p_x must be interpreted as $\frac{h}{2\pi i}\frac{\partial}{\partial x}$ and similarly for p_y and p_z. In what follows it will be supposed that the A is simply that of the plane wave (equation (73.1)), that A^2 can be neglected, and that the wave functions and energy levels of the atom for $A = 0$ are known to be $\psi(W, x)$ and W. Then one may regard the action of the term in A as a perturbation.

Let the value of φ at time t be expanded in terms of the undisturbed $\psi(W, x)$ as follows:

$$\varphi(x, y, z, t) = \sum_W c(W, t)e^{-\frac{2\pi i Wt}{h}}\cdot\psi(W, x). \tag{73.3}$$

By Sec. **66** the c's would be constants if A were zero. When A is not zero, but is small, they may be expected to vary slowly. Making use of the value of A from equation (73.1) one has therefore the following equation for the time variation of $c(W)$, by the method of Sec. **72,**

$$\dot{c}(W, t) = \frac{ea}{\mu c}\sum_{W'}\alpha(W, W')c(W'), \tag{73.4}$$

where

$$\alpha(W, W') = \int\bar{\psi}(W)\cos 2\pi\nu\left(t - \frac{x}{c}\right)e^{\frac{2\pi i}{h}(W - W')t}\frac{\partial}{\partial z}\psi(W')dxdydz.$$

Using the exponential form for the cosine term, it is seen that $\alpha(W, W')$ is the sum of two integrals,

$$\tfrac{1}{2}\beta(W, W')e^{\frac{2\pi i}{h}(W - W' + h\nu)t}$$

and

$$\tfrac{1}{2}\gamma(W, W')e^{\frac{2\pi i}{h}(W - W'h\nu)t},$$

where

$$\beta(W, W') = \int\bar{\psi}(W)e^{-\frac{2\pi i\nu x}{c}}\frac{\partial}{\partial z}\psi(W')dxdydz$$

and

$$\gamma(W, W') = \int\bar{\psi}(W)e^{+\frac{2\pi i\nu x}{c}}\frac{\partial}{\partial z}\psi(W')dxdydz.$$

From the form of the equation for $c(W, t)$ it is evident that $c(W, t)$ can show a secular change with the time if one of these integrals is actually independent of the time. Let $c_0(W')$ denote the initial value of each of the coefficients. Then an approximate integration gives

$$c(W, t) = \frac{ea}{\mu c}\sum_{W'} c_0(W') \int_0^t \alpha(W_1 W')dt. \tag{73.5}$$

$c(W, t)$ changes linearly with the time, therefore, if there is a value W' such that

$$W - W' + h\nu = 0 \tag{73.6}$$

or

$$W - W' - h\nu = 0.$$

This corresponds to the Bohr frequency condition for emission and absorption of light. Since ν is essentially positive, the first equation can be fulfilled for values of W' greater than W; this term corresponds therefore to the emission transitions downward from W' to W induced by the light. Similarly, the second equation can be satisfied by values of W' less than W, so this term corresponds to the upward absorption transitions induced by the light.

Suppose now that initially the atom is in a particular state of energy W' so that all c_0 but one are zero and that one is equal to 1, that W is higher than W', and that the second of equations (73.6) is satisfied. Then for the secular increase in $c(W, t)$ one has,

$$c(W, t) = \frac{eat}{2\mu c}\gamma(W, W').$$

The probability that an atom be in the state of energy W at time t is, therefore,

$$c(W, t)\bar{c}(W, t) = \frac{e^2a^2}{4\mu^2c^2}\gamma\gamma t^2 \tag{73.7}$$

which increases with the square of the time.

Finally, to connect this result with the theory of radiation, it is necessary to take account of the fact that one deals, in natural radiation, with a large number of wave trains of finite length. As the phases of the separate trains are distributed at random, this increase with t^2 occurs only during the time that one wave train is passing over the atom. There is thus an average transition probability for each wave train. The total transition probability is then this average value multiplied by the number of separate wave trains. As this number increases proportionally with the time it turns out that in natural radiation the transition probability increases linearly with the time as ordinarily assumed.

The preceding argument shows that Einstein's absorption coefficient is measured by $\gamma(W, W')\bar{\gamma}(W, W')$. The inverse process to that of absorption of $h\nu$ from the beam moving in the x direction by an atom in state W' causing a transition to state W is the induced transition from state W to state W' with emission of $h\nu$ into the beam. By an argument similar to the one just given it is seen that this is measured by $\beta(W'\ W,)\bar{\beta}(W', W)$ which can be readily shown to be equal to $\gamma(W, W')\bar{\gamma}(W, W')$. Hence, the equality of the corresponding probability coefficients for absorption and induced emission.

There remains now the examination of the value of $\gamma(W, W')$ and the investigation of its relation to the integrals over wave functions which were used in Chap. III as the basis of a theory of radiation intensities. If the wave length c/ν is large compared to the size of the atom, then the factor $e^{+2\pi i\nu x/c}$ will be sensibly constant over the range of integration and may be set equal to unity. By an integration by parts one may show that

$$\int \bar{\psi}(W)\frac{\partial}{\partial z}\psi(W')dxdydz = -\int \frac{\partial\bar{\psi}(W)}{\partial z}\psi(W')dxdydz,$$

and, therefore,

$$2\gamma(W, W') = \int\left(\bar{\psi}(W)\frac{\partial\psi(W')}{\partial z} - \psi(W')\frac{\partial\bar{\psi}(W)}{\partial z}\right)dxdydz.$$

One recognizes that the integrand is proportional to the z component of the part of the current density expression which arises from the states of energy W and W'.

By the results of Sec. **10** one has

$$\frac{h}{4\pi\mu i}\text{div}\ (\bar{\Psi}\ \text{grad}\ \Psi - \Psi\ \text{grad}\ \bar{\Psi}) + \frac{\partial\Psi\bar{\Psi}}{\partial t} = 0$$

and, therefore,

$$\frac{h}{4\pi\mu i}\text{div}\ [\bar{\psi}(W)\ \text{grad}\ \psi(W') - \psi(W')\ \text{grad}\ \bar{\psi}(W)] + \frac{2\pi i}{h}(W - W')\bar{\psi}(W)\psi(W') = 0.$$

Moreover by an easy transformation, based on the equation of continuity,

$$\int i_z dxdydz = -\int z \operatorname{div} i dxdydx = \int z \frac{\partial \rho}{\partial t} dxdydz.$$

Therefore,

$$2\gamma(W, W') = -\mu\left(\frac{2\pi}{h}\right)^2 (W - W') \int z\bar{\psi}(W)\psi(W')dxdydz, \tag{73.8}$$

so that $\gamma(W, W')$ is seen to be proportional to the integral which was used in Chap. III from a more elementary standpoint for calculating radiation intensities.

The approximation in which $e^{2\pi i\nu x/c}$ is replaced by unity cannot always be made. It can easily happen that the wave length of the radiation is not large compared with the size of the atom as in the case of x-rays. Roughly speaking, it can be said that such an approximation can be made in cases where the momentum of the light quantum is small compared to the momentum of the electrons in the atom.

INDEX