Sturm-Liouville analysis of Rydberg atoms

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Abstract

While it is clear that both Schrödinger's equation and Dirac's equations are highly accurate, after about 100 years, it is not clear why. Both of these theories seem to violate classical electromagnetics (EM) (i.e., Ohn's law), since they are built on energy principles rather than electric and magnetic fields. Here we delve into this question, by providing a classical (i.e., EM based) derivation for the Hydrogen atom, one of the most important and obvious successes of quantum mechanics (QM). The problem with QM is not that it fails, rather that it succeeds, without obvious basis. The problem is that one cannot understand the basic principles, and it seems to be in contradiction with any any principles of a physical theory. Based on the Rydberg series, we determine the reflection coefficient, and thus the radiation impedance seen by the electron, in a radial coordinate centered on the proton. Since the electron and proton both have spin 1/2, their magnetic fields must attractively align, accounting for the near field vector potential, and complementing the far field attraction due to their opposite signs. As the electron and proton approach each other, due to their far-field potential attraction, the magnetic near field would further be attractive at close range, due to the magnetic dipoles of the two "particles," causing them to merge with neutral net magnetic moment and neutral charge, giving a highly stable hydrogen atom. However given a sufficiently strong distorting field, this highly symmetric state could be disturbed, leading to photon radiation, constrained by the radial eigen states.

Introduction

Like every tuned resonant circuits, atoms have well defined resonant frequencies, aka eigen-modes. Figure 1 shows the observed radiation spectra for Hydrogen. From the very beginning, it was clear there is a pattern to these spectral lines. In 1880 Rydberg easily fit a formula that quantifies the observed eigen spectral lines of hydrogen, in terms of the reciprocal of the radiated wavelengths

$$\frac{1}{\lambda_{nm}} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \qquad \frac{f_{nm}}{c_o R} = \frac{1}{n^2} - \frac{1}{m^2}, \tag{1}$$

all based on these simple observations. Here $R = 1.097 \times 10^7$ [m^{-1}], $c_o = 3 \times 10^5$ [m/s] is the speed of light, f_{ml} are the dimensionless *Rydberg integer frequencies* with $n, l \in \mathbb{N}$ are positive integers, where n labels the series, and $m > n$ describes the transition, from orbit n to orbit m, as described in the caption of Fig. 2.

In 1909 Rutherford demonstrated that the atom consisted of a dense core (the proton) surrounded by electrons. This view was supported by the spectrum of the atom, which allows for a radiation spectrum caused by electrons jumping from one energy level to another. It was then noted by Bohr in 1913 and others that the wavelengths of hydrogen, as described by Eq. 1, are consistent with Fig. 3, where the reciprocal wavelength [m^{-1}] is given by Eq. 1, having frequencies $f_{nm} = c/\lambda_{nm}$ [Hz]. The challenge of the 1920s was to explain these intuitive and simple models of hydrogen. This gave rise to the birth of quantum mechanics, the history of which is nicely summarized in Condon and Morse (1929).

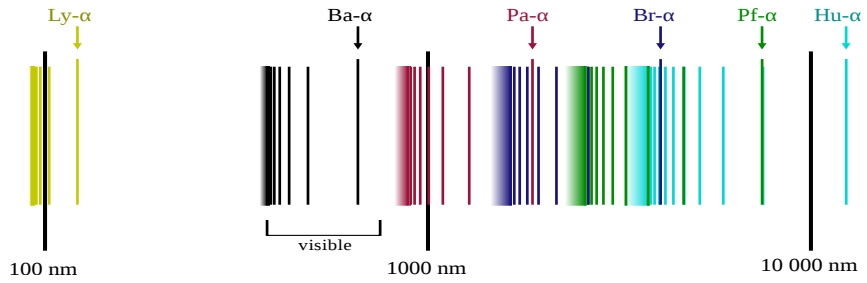

Figure 1: *Diagram of the wavelength spectrum of hydrogen for the Lyman, Balmer and Paschen series, as a function of each lines wavelength. The notation "La-α' indicates the longest wavelength $\lambda_{11} = 122$ [nm] (i.e., lowest frequency of 2.46 [GHz]) for the Lyman series. Citation: fig:HydrogenSpectrum*

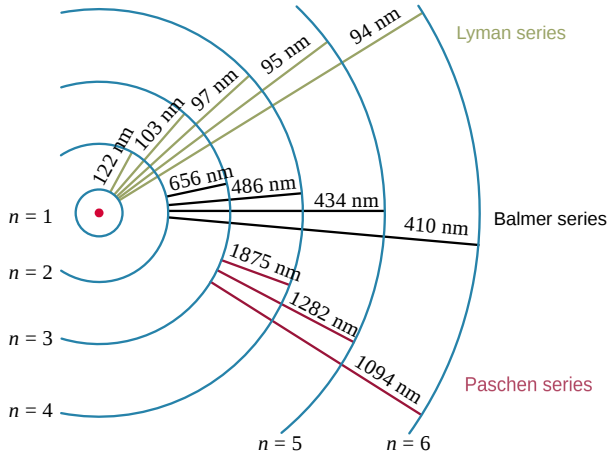

Figure 2: *This diagram defines hydrogen's allowed electron transitions, defining the Lyman (n=1), Balmer (n=2) and Paschen (n=3) series. The numbers represent the wavelengths λ [nm] of the photons having frequencies $f_{nm} = c_o/\lambda_{nm}$, following an electron transition from level n to m. Figure citation: fig:HydrogenTransitions*

It was clear from the days of Bohr that the Rydberg formula did not follow the typical rules of eigen spectra, so much so that Arnold Sommerfeld made a specific point it (Sommerfeld, 1949, p. 201):

> The lines of this spectrum cumulate at the limit given by the Rydberg constant R. The adjoining *continuum* lies in the near ultraviolet range. Both the discrete and the continuous spectrum are given by the Schrödinger equation. This equation reduces to a simple mathematical formula the enigma of the spectral lines, with their finite accumulation point, the behavior of which differs so fundamentally from that of all mechanical systems.

Objective: The objective of this report is to demonstrate that one can define a classical Sturm-Liouville model of the *enigmatic* Rydberg atom, by the use of the Webster Horn equation

$$\frac{1}{A(r)}\frac{\partial}{\partial r}A(r)\frac{\partial}{\partial r}\psi(r,t) = \frac{1}{c_o^2}\frac{\partial^2}{\partial t^2}\psi(r,t), \tag{2}$$

which is a 1 dimensional wave equation for the electric potential $\psi(r,t)$ propagating in a wave-guide having area $A(r)$ as a function of the range, where r is the *range* variable (the axis of wave propagation).

We shall show that given the Rydberg spectrum (Eq. 1), one may accurately estimate the electric reflectance $\Gamma(s)$ looking out from the origin (i.e., the proton location, as indicated by the small red dot in Fig. 2). The

radiation impedance $Z_{\text{rad}}(s)$ seen by the proton is related to the reflectance $\Gamma(s)$ by the relation

$$Z_{\text{rad}}(s) = r_o \frac{1+\Gamma(s)}{1-\Gamma(s)}. \tag{3}$$

This formula is the basis of the *Smith chart* used in both physics and engineering studies. It follows that once $\Gamma(s)$ is known (i.e., evaluated given Eq. 1), the radiation impedance may be computed. It has been shown that the area function $A(r)$ may be found given the radiation impedance (Sondhi and Gopinath, 1971; Youla, 1964).

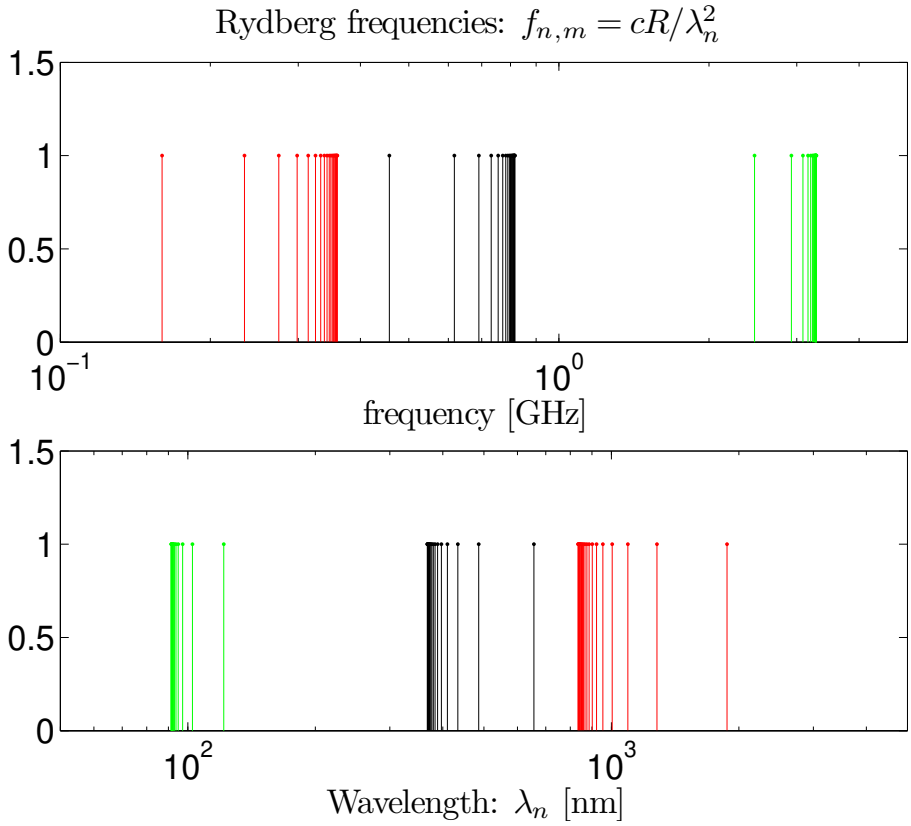

Figure 3: *Rydberg frequencies in [GHz] and the corresponding wavelengths, computed from the Rydberg formula* $\lambda_{nm}^{-1} = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$, *where integer* n *defines the series (Lyman:* $n = 1$ *, Balmer:* $n = 2$ *, Paschen:* $n = 3$*, etc.) and integer* $m > n$ *defines the outer transition line (See Fig. 2). For example,* $\lambda_{1,2} = 102$ *[nm] (*$n = 1$ *and* $m = 2$*), in agreement with Figs. 2 and 1. fig:RydbergFormula*

1 Methods

The basic idea behind the method is to use Eq. 3, by noting that the poles of the impedance are determined by the roots denominator of Z_{rad}. Specifically if s_p is an impedance pole, then it must satisfy $\Gamma(s_p) \approx 1$. Since except for losses due to radiation, the atom is loss-less, thus $|\Gamma(s)| = 1$. Namely it must be of the form

$$\Gamma(s) = e^{-\jmath 2\pi\phi(f)}, \tag{4}$$

where the *phase mode function* $\phi(f) \in \mathbb{R}$ and $s = \sigma + \omega\jmath$ is the complex Laplace radian frequency, with $\omega = 2\pi f$ [Hz]. Since we know the eigen-mode frequencies, which obey $\phi(f_{n_o,m}) = 2\pi n$, we may find $\phi(f)$,

as follows: For a given series index n_o, and given the eigen-frequencies f_m, we seek the phase mode function $\phi_{n_o}(f)$ that maps the eigen-frequencies to their mode index m, i.e.,

$$\phi_{n_o}(f_m) = m.$$

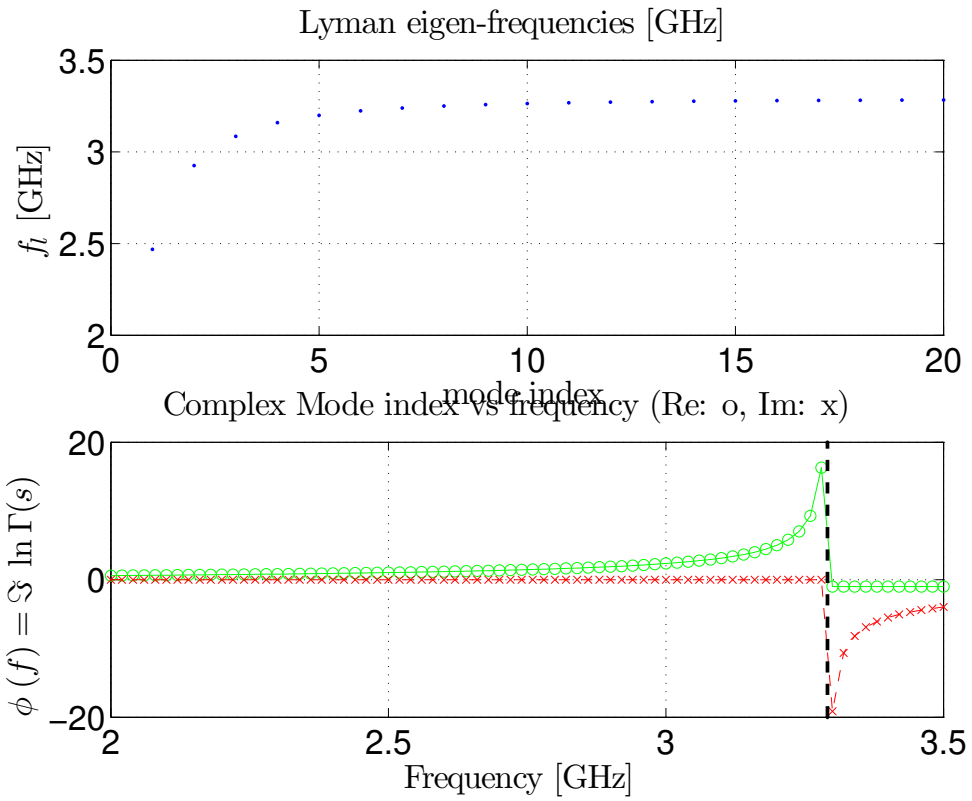

Figure 4: *The top panel is a plot of Eq. 1, showing how the eigen-mode frequencies f_l depend on the eigen-number index l. As the mode number increases, the frequency reach an asymptote at $c_o R \approx 3.29$ [GHz], with a wavelength limit near $1/R \approx 91.2$ [nm]. The lower panel shows the inverse mapping from frequency to the mode index number $\phi(f)$. This figure is for the Lyman series ($n = 1$ and $m = 1, \cdots, 20$). The inverse of this relationship is $l = \phi^{-1}(f_l)$ may be derived from Eq. 1, which provides the pole frequencies required to satisfy Eq. 3. Note that for frequencies greater than c_o/R the phase switches from real purely real to imaginary, accounting for the free electrons that must exist above the upper accumulation frequency (i.e., 3.29 [GHz] for this example).* fig:EigenFreqs

One may solve Eq. 1 for m, for the case of the Lyman series ($n_o = 1$), by the use of the following identity for the Rydberg eigen-frequencies f_{nm}, which follow directly from Eq. 1, with $m = n_o + l$ (with $n_o, m, l \in \mathbb{N}$)

$$\begin{aligned} f_{nm} = \frac{c_o}{\lambda_{nm}} &= c_o R \left(\frac{1}{n_o^2} - \frac{1}{(n_o + l)^2} \right) \\ &= \frac{c_o R}{n_o^2} \left(1 - \frac{1}{(1 + l/n_o)^2} \right) \end{aligned} \tag{5}$$

Note that as $l \to \infty$, $f_{n_o,l} \to = c_o R/n_o^2$, which is Sommerfeld's *finite accumulation point* [Hz] $f_{n_o,\infty}$ for the Lyman series ($n_o = 1$).

The above equation may be solved for the mode number $l/n < 1$ as a function of mode frequency

$$
\begin{aligned}
n^2 \frac{f_{nl}}{c_o R} &= 1 - \frac{1}{(1+l/n)^2} && \text{Starting from Eq. 5} \\
\frac{1}{(1+l/n)^2} &= 1 - n^2 \frac{f_{nl}}{c_o R} && \text{Solving for } l/n \\
(1+l/n)^2 &= \frac{1}{1 - n^2 \frac{f_{nl}}{c_o R}} \\
\frac{l}{n} &= \pm \frac{1}{\sqrt{1 - n^2 \frac{f_{nl}}{c_o R}}} - 1 && \phi(f_{nl}) = l = m - n_o \in \mathbb{N}. \qquad (6)
\end{aligned}
$$

as summarized in the lower panel of Fig. 4.

1.1 Group delay

Given the reflectance phase $2\pi\phi(f)$ one may define the group delay as $\tau(f) = -\partial\phi(f)/\partial f$ which is physically interpreted as the frequency dependent delay from the proton to the radius of the electron's orbit. Thus this delay is given by

$$\tau(f) = n \frac{\partial}{\partial f} \left(1 - \frac{n^2}{c_o R}\, f\right)^{-1/2} = \frac{n^3}{2 c_o R} \left(1 - \frac{n^2}{c_o R}\, f\right)^{-3/2}$$

which is constant for low frequencies and then rises to ∞ as frequency approaches the Rydberg frequency ($f \to c_o R/n^2$).

2 Discussion

The Rydberg frequencies f_{nl} ($n = 1, l = 1, \cdots, \infty$) has poles in the radiation impedance (Eq. 3) when $\phi_l(f_{nl}) \in \mathbb{N}$. Working backwards from the Rydberg formula (Eq. 4), we have solved for $\phi(f_{nl})$ indicating where this condition is valid (Eq. 6). Since the reflectance and the impedance must be causal complex analytic functions of Laplace frequency s, we must replace the discrete frequency f_{nl} with s

$$\jmath 2\pi f_{nl} \to s = \sigma + \omega\jmath,$$

thereby forcing $l(s)$ to be a complex analytic function of s. Then the poles of the radiation impedance must satisfy

$$\Gamma(s_{nl}) = e^{\jmath 2\pi l(f_{nl})} = 1,$$

resulting in eigen-frequencies at f_{nl}.

The next step in this analysis is determine the area function $A(r)$ given Z_{rad} (Eq. 3). To do this one must solve an integral equation for $A(r)$, as discussed by Sondhi and Gopinath (1971); Youla (1964).

Perhaps this could be done using a analytic representation for the area function

$$A(r) = \sum_k a_k r^k.$$

2.1 The exponential horn

A relevant and motivational example is the solution of the exponential horn, having area function $A(r) = A_o e^{2mr}$. This case is interesting becuse it has a closed form solution, which seems relevant, and perhaps even related to that of the hydrogen atom.

Assuming that $\varrho(r,t) \leftrightarrow \mathcal{P}(r,\omega)$ are a Fourier transform pair, with $A(r) = A_o e^{2mr}$, Eq. 2 reduces to

$$\frac{\partial^2 \mathcal{P}(r,\omega)}{\partial r^2} + 2m\frac{\partial \mathcal{P}(r,\omega)}{\partial r} = \kappa^2 \mathcal{P}(r,\omega) \leftrightarrow \frac{1}{c_o^2}\frac{\partial^2 \varrho}{\partial t^2} \tag{7}$$

with $\kappa(s) = s/c_o$.

Exercise: Show that Eq. 7 follows from Eq. 2. **Sol:** Starting from Eq. 2 with area $A(r) = A_o e^{2mr}$

$$\frac{1}{\cancel{A_o} e^{2mr}}\frac{\partial}{\partial r}\left(\cancel{A_o} e^{2mr}\frac{\partial \varrho}{\partial r}\right) = \frac{1}{c_o^2}\frac{\partial^2 \varrho}{\partial t^2}$$

$$\varrho_{rr}(r,t) + 2m\varrho_r(r,t) = \frac{1}{c_o^2}\frac{\partial^2 \varrho}{\partial t^2} \leftrightarrow \kappa^2 \mathcal{P}(r,\omega)$$

which is the time domain version of Eq. 7.

Since this equation is 2d order in time with constant coefficients, it has two closed form solutions

$$\begin{aligned}\mathcal{P}^{\pm}(r) &= \mathcal{P}_o^{\pm}(\omega)\, e^{-mr} e^{\mp\sqrt{m^2+\kappa^2}\, r} \\ &= \mathcal{P}_o^{\pm}(\omega)\, e^{-mr} e^{\mp j\frac{r}{c_o}\sqrt{\omega^2-\omega_c^2}},\end{aligned}$$

with $\omega_c = mc_o$. The two wave amplitudes $\mathcal{P}_0^{\pm}(\omega)$ must be determined from the boundary conditions.

Exercise: Shown that $\mathcal{P}^{\pm}(r,\omega)$ satisfy Eq. 7. **Sol:** Taking partials wrt r,

$$\begin{aligned}\partial_r \mathcal{P}^{\pm}(r,\omega) &= \left(-m \mp \sqrt{m^2+\kappa^2}\right)\mathcal{P}^{\pm}(r,\omega) \\ \partial_{rr} \mathcal{P}^{\pm}(r,\omega) &= \left(-m \mp \sqrt{m^2+\kappa^2}\right)^2 \mathcal{P}^{\pm}(r,\omega) \\ &= \left(2m^2+\kappa^2 \pm 2m\sqrt{m^2+\kappa^2}\right)\mathcal{P}^{\pm}(r,\omega)\end{aligned}$$

Thus Eq. 7 reduces to

$$\left(2m^2+\kappa^2 \pm 2m\sqrt{m^2+\kappa^2}\right) + 2m\left(-m \mp \sqrt{m^2+\kappa^2}\right) = \kappa^2,$$

which is an identity.

Next consider the Fourier series (or Fourier transform) of the area function

$$A(r) = \sum_k a_k e^{2m_k r}.$$

It follows from the linearity of the wave equation that the general solution of Eq. 7 is

$$\mathcal{P}^{\pm}(r,\omega) = \sum_k a_k^{\pm}(\omega)\, e^{-m_k r}\, e^{\mp\sqrt{m_k^2+\kappa^2}\, r}.$$

5 Here we have combined $\mathcal{P}^{\pm}(\omega)$ and a_k as coefficients $a_k^{\pm}(\omega)$.

3 Relations between Sturm-Liouville and Quantum Mechanics

If we compare the Schrödinger equation (SE) for hydrogen with the corresponding Sturm-Liouville equation we can begin to appreciate their differences. The QM equation for hydrogen is

$$\begin{aligned} \imath\hbar\frac{\partial}{\partial t}\psi(x,t) &= -\frac{\hbar^2}{2m_o}\nabla_r^2\psi(x,t) + V(r)\psi(x,t) \\ &= -\frac{\hbar^2}{2m_o}\ \frac{1}{r^2}\frac{\partial}{\partial r}r^2\psi(x,t) + V(r)\ \psi(x,t) \qquad (8) \\ &= -\frac{\hbar^2}{2m_o}\left[\frac{2}{r}\frac{\partial}{\partial r}\psi(x,t) + \frac{\partial^2}{\partial r^2}\psi(x,t)\right] + V(r)\ \psi(x,t) \qquad (9) \end{aligned}$$

whereas the Horn equation is given by Eq. 2.

There are several obvious and disturbing differences between these two equations: *First* the SE is, of course, first order in time. Diffusion equations have no delay, thus cannot have traditional eigen modes, which result from standing waves in a wave equation, due to boundary conditions. *Second* the EM horn equation is of Sturm-Liouville (SL) form, which is a true wave equation (vs. the SE, which is a diffusion equation). The obvious question arises: Is there a potential V that would allow these two formulations to be equivalent. If so, then this would provide an explanation as to why the SE is successful in explaining the properties of Rydberg atoms.

To explore this possibility we may expand the two differential equations, and directly compare them. Expanding Eq. 2 gives

$$\begin{aligned} \frac{1}{c_o^2}\frac{\partial^2}{\partial t^2}\psi(r,t) &= \frac{1}{A(r)}\frac{\partial}{\partial r}A(r)\frac{\partial}{\partial r}\psi(r,t) \qquad (10) \\ &= \frac{\partial^2}{\partial r^2}\psi(r,t) + \frac{1}{A(r)}\frac{\partial A(r)}{\partial r}\psi(r,t) \qquad (11) \end{aligned}$$

Between these two equations we may remove ψ''

$$\imath\hbar\frac{\partial}{\partial t}\psi(x,t) = -\frac{\hbar^2}{2m_o}\left[\frac{2}{r}\frac{\partial}{\partial r}\psi(x,t) + \frac{1}{c_o^2}\frac{\partial^2}{\partial t^2}\psi(r,t) - \frac{1}{A(r)}\frac{\partial A(r)}{\partial r}\psi(r,t)\right] + V(r)\ \psi(x,t). \qquad (12)$$

It seems that this may isolate the time and spatial parts (as in separation of variables).

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