Theory of ZPE for Lamb Shift on Hydrogen Fine Structure

Thomas Li

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1 Introduction

The theoretical understanding of hydrogen spectrum has been vital to the whole physics field since the beginning of quantum era. The famous Bohr model serves as one of the pioneers to quantize a hydrogen atom with corresponding discrete energy levels, i.e., n=1,2,3,..., which is later known as the principle quantum number. However, experimental results - hydrogen spectroscopy shows there are more finer split levels in addition to n's. Some later efforts in the last century attempting to theorize these levels succeeded well, for example, gross structure, fine structure, and hyperfine structure.

However, by the time when Dirac fine structure and Hyperfine structure were beautifully studied, there were still some disagreement on the Hydrogen spectrum. One of them is the splitting between certain s and p levels, e.g., $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$. The former theories predict them to be degenerate but there is $\sim 1000MHz$ splitting between these levels. In 1947 this phenomenon was explained by Hans Bethe that Zero Point Energy (ZPE) is the major culprit behind this. This work mainly follows the original theory [1] and performs a detailed derivation for ZPE correction on the Dirac fine structure using time-independent non-degenerate perturbation theory based on Centmetre-Gram-Second (CGS)-Gaussian units.

2 Formulation

Since ZPE is considered small perturbations compared to Coulomb interaction, it suffices to limit our time-independent perturbation theory to first order. Let $|n, l, m\rangle$ be the atom state given by quantum numbers n (principle quantum number), l(orbital quantum number), and m(magnetic quantum number). Let a superscript of (1) indicate the first-order correction, we have the ZPE correction as

$$\Delta\varepsilon_n^{(1)} = \langle nlm| \hat{V}_I |nlm\rangle , \tag{1}$$

where $\hat{V}_I$ is the perturbing potential.

2.1 Preliminary expression for $\hat{V}_I$

First we tackle on $\hat{V}_I$. The familiar Coulombic potential energy between electron and proton in Hydrogen atom is,

$$V = \frac{-e^2}{4\pi\epsilon_o r},$$

where r represents here the electron's standard orbit. In Gaussian units, this is

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

Suppose that ZPE produces small fluctuations around this orbit by some Δr. Now the change in potential produced by this small change in ΔV becomes

$$\Delta V = V(r + \Delta r) - V(r) = [V(x + \Delta x, y + \Delta y, z + \Delta z] - V(x, y, z).$$

Recall Taylor's series of three variables writes

$$\begin{aligned}
&f(x+\Delta x, y+\Delta y, z+\Delta z) = f(x,y,z) \\
&+ [f_x(x,y,z)\Delta x + f_y(x,y,z)\Delta y + f_z(x,y,z)\Delta z] \\
&+ \frac{1}{2!}\Big[(\Delta x)^2 f_{xx}(x,y,z) + (\Delta y)^2 f_{yy}(x,y,z) + (\Delta z)^2 f_{zz}(x,y,z) \\
&+ 2\Delta x\Delta y f_{xy}(x,y,z) + 2\Delta y\Delta z f_{yz}(x,y,z) + 2\Delta x\Delta z f_{xz}(x,y,z)\Big] \\
&+ \cdots,
\end{aligned}$$

in which the dots indicate the higher order terms. Apply this identity, we have,

$$\begin{aligned}
\Delta V = &\Big[\cancel{V(x,y,z)} + \Delta x\frac{\partial V}{\partial x}\Big|_{x=\Delta x} + \Delta y\frac{\partial V}{\partial y}\Big|_{y=\Delta y} + \Delta z\frac{\partial V}{\partial z}\Big|_{z=\Delta z} \\
&+ \frac{1}{2!}(\Delta x)^2\frac{\partial^2 V}{\partial x^2}\Big|_{x=\Delta x} + \frac{1}{2!}(\Delta y)^2\frac{\partial^2 V}{\partial y^2}\Big|_{y=\Delta y} + \frac{1}{2!}(\Delta z)^2\frac{\partial^2 V}{\partial z^2}\Big|_{z=\Delta z} \\
&+ \cdots\Big] - \cancel{V(x,y,z)}.
\end{aligned}$$

Since fluctuations are isotropic (direction independent), we have,

$$\begin{aligned}
\langle\Delta x\rangle = \langle\Delta y\rangle = \langle\Delta z\rangle = 0 \\
\text{and } \left\langle(\Delta x)^2\right\rangle = \left\langle(\Delta x)^2\right\rangle = \left\langle(\Delta y)^2\right\rangle = \frac{\left\langle(\Delta r)^2\right\rangle}{3},
\end{aligned}$$

where $\langle\rangle$ is supposed to indicate time average. Hence, average change in potential is,

$$\begin{aligned}
\langle\Delta V\rangle = &\cancelto{0}{\langle\Delta x\rangle\frac{\partial V}{\partial x}\Big|_{x=\Delta x}} + \cancelto{0}{\langle\Delta y\rangle\frac{\partial V}{\partial y}\Big|_{y=\Delta y}} + \cancelto{0}{\langle\Delta z\rangle\frac{\partial V}{\partial z}\Big|_{z=\Delta z}} \\
&+ \frac{1}{2!}\frac{\left\langle(\Delta r)^2\right\rangle}{3}\frac{\partial^2 V}{\partial x^2}\Big|_{x=\Delta x} + \frac{1}{2!}\frac{\left\langle(\Delta r)^2\right\rangle}{3}\frac{\partial^2 V}{\partial y^2}\Big|_{y=\Delta y} + \frac{1}{2!}\frac{\left\langle(\Delta r)^2\right\rangle}{3}\frac{\partial^2 V}{\partial z^2}\Big|_{z=\Delta z} \\
&+ \cdots \\
= &\frac{1}{6}\left\langle(\Delta r)^2\right\rangle\left(\frac{\partial^2 V}{\partial x^2}\Big|_{x=\Delta x} + \frac{\partial^2 V}{\partial y^2}\Big|_{y=\Delta y} + \frac{\partial^2 V}{\partial z^2}\Big|_{z=\Delta z}\right) + \cdots.
\end{aligned}$$

Since third order terms of Δx, Δy, and Δz are too small to make significant difference, we neglect but the first two orders and have

$$\langle\Delta V\rangle \cong \frac{1}{6}\left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2}\right) = \left\langle(\Delta r)^2\right\rangle\nabla^2 V(x,y,z) = \left\langle(\Delta r)^2\right\rangle\nabla^2 V(r),$$

where, $\nabla^2 := \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Laplacian.

Making use of the familiar identity from E& M: $\nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(\mathbf{r})$, we have

$$\nabla^2 V(r) = \nabla^2\left(\frac{-e^2}{r}\right) = -e^2\nabla^2\left(\frac{1}{r}\right) = -e^2\left(-4\pi\delta(\mathbf{r})\right) = 4\pi e^2\delta(\mathbf{r}),$$

where $\delta(\mathbf{r})$ is the Dirac delta function defined at $r = 0$.

Define $\hat{V}_I \equiv \langle\Delta V\rangle$, we get

$$\hat{V}_I \equiv \langle\Delta V\rangle = \frac{4\pi e^2}{6}\delta(\mathbf{r})\left\langle(\Delta r)^2\right\rangle = \frac{2\pi e^2}{3}\delta(\mathbf{r})\left\langle(\Delta r)^2\right\rangle. \tag{2}$$

This $\langle\Delta V\rangle$ serves as the perturbing potential. We can plug this $\hat{V}_I$ into *eq.*(1) and the next step is to find a proper expression for $\left\langle(\Delta r)^2\right\rangle$.

2.2 The $\left\langle(\Delta r)^2\right\rangle$ Term

Since, as assumed, the electrons perturbed by the fluctuating fields are not in the relativity regime. Let Δr_ν be its position; we have the general equation of motion as

$$\frac{md^2}{dt^2}(\Delta r_\nu) = eE_\nu(t),$$

where E_ν is the fluctuating field with frequency ranging from ν to $\nu + d\nu$, m is mass of electron, and e is charge of electron. For a given harmonic component of E_ν the solution of above equation

can be worked with ease. Now we have

$$\begin{aligned} E_\nu(t) &= E_\nu \frac{1}{2} e^{i2\pi\nu t} \\ m\frac{d^2}{dt^2}(\Delta r_\nu) &= eE_\nu \frac{1}{2} e^{i2\pi\nu t} \\ \frac{d^2(\Delta r_\nu)}{dt^2} &= \frac{eE_\nu}{2m} e^{i2\pi\nu t}. \end{aligned}$$

For a more explicit expression we now calculate in terms of the real part of the field. Integrating the above equation the first time,

$$\begin{aligned} \int \frac{d^2(\Delta r_\nu)}{dt^2} dt &= \frac{eE_\nu}{m} \int \cos(2\pi\nu t) dt \\ \frac{d(\Delta r_\nu)}{dt} &= \frac{eE_\nu}{2\pi\nu m} \sin(2\pi\nu t); \end{aligned}$$

and second time,

$$\begin{aligned} \int \frac{d(\Delta r_\nu)}{dt} dt &= -\frac{eE_\nu}{2\pi\nu m} \int \sin(2\pi\nu t) dt \\ \Delta r_\nu &= -\frac{eE_\nu}{(4\pi^2\nu^2)m} \cos(2\pi\nu t), \end{aligned}$$

in which we have taken constants of integrations to be zero.

To proceed towards $\langle (\Delta r)^2 \rangle$, we have,

$$(\Delta r_\nu)^2 = \frac{e^2 E_\nu^2}{(16\pi^4\nu^4)m^2} \cos^2(2\pi\nu t).$$

The time average of $(\Delta r_\nu)^2$ then is

$$\langle (\Delta r_\nu)^2 \rangle = \frac{e^2 E_\nu^2}{(16\pi^4\nu^4)m^2} \langle \cos^2(2\pi\nu t) \rangle .$$

Since a squared sinusoidal function is still periodic, it suffices to calculate the average value of over just one cycle to represent the fast-oscillating value variations over a longer time stretch. To do so, let T be the time period of oscillation related to ν through:

$$\begin{aligned} \nu T &= 1 \\ T &= \frac{1}{\nu}, \end{aligned}$$

following which we get,

$$\begin{aligned} \langle \cos^2(2\pi\nu t) \rangle &= \frac{1}{T} \int_0^T \cos^2(2\pi\nu t) dt \\ &= \frac{1}{T} \int_0^T \left(\frac{1 + \cos(4\pi\nu t)}{2} \right) dt \\ &= \frac{1}{2T} \left(T - \frac{sin(4\pi\nu t)}{4\pi\nu} \Big|_0^T \right) \\ &= \frac{1}{2} - \frac{1}{8\pi\nu} \left(\cancelto{0}{sin(4\pi)} - 0 \right) \\ &= \frac{1}{2}. \end{aligned}$$

In fact, this result came out with no surprise since one can expect any real function in the form of $\cos^2(\theta)$ as such averaging to the same as the mean value of one cycle, i.e., $\frac{1}{2}$, over merely a few cycles. A more visually intuitive illustration is given in Fig.2 below.

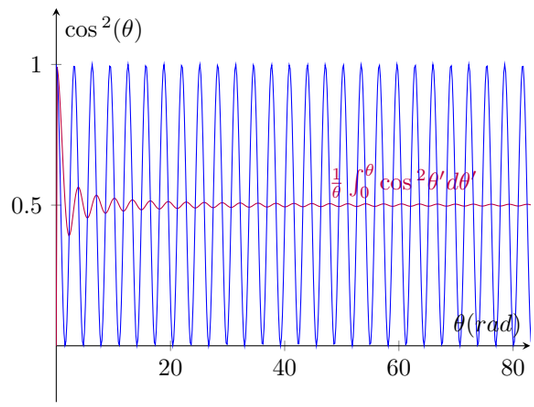

Figure 2. Plot of $\cos^2\theta$ (blue) with an added red function representing the average value of the function between from 0 to θ. The latter is given by $\frac{1}{\theta}\int_0^\theta \cos^2\theta' d\theta' = \frac{\sin(2\theta)+2\theta}{4\theta}$. One can easily observe that the time average gets steady around $\frac{1}{2}$ after only a few cycles.

Now, we have

$$\left\langle (\Delta r_\nu)^2 \right\rangle = \frac{e^2 E_\nu^2}{16\pi^4\nu^4 m^2}(\frac{1}{2}) = \frac{e^2 E_\nu^2}{32\pi^4\nu^4 m^2}. \tag{3}$$

Next, we proceed to find E_ν in terms of fundamental constants like $m, e, \hbar, c$, etc. The energy stored in EM field by ZPE modes lying between ω and $\omega + d\omega$ is [2],

$$\frac{1}{8\pi}\int_v \left(E_\nu^2 + B_\nu^2\right) dV = \frac{1}{2}h\nu g(\nu)d\nu,$$

where the constant outside the integral on the LHS is consistent with the Gaussian units, $\frac{1}{2}h\nu$ is the ZPE energy for single mode, $g(\nu)$ stands for the density of states in ν space for light, and $d\nu$ is considered between ν and $\nu + d\nu$.

In phase space, the density of states in terms of ν is,

$$\begin{aligned} f(\nu)d\nu &= \prod_i \int_{q_i} \cdots \int_{p_i} \cdots 2dq_i dp_i \\ &= 2V 4\pi p^2 dp \\ &= \frac{8\pi V h^3 \nu^2}{c_o^3} d\nu, \end{aligned}$$

where the integral goes over all position space (q), with V denoting the volume, and momentum space (p), for which $q = h\nu/c_o$, with c_o being the speed of light in vacuum and h is the Plank constant. The two in the integrand denotes the degeneracy of transverse modes of light. To convert the phase space results to numbers per $d\nu$, we divide the phase space density by h^N, where N denotes the dimension and is 3 in this case. The derivation of this relation is provided in [3]. Name the number density as $g(\nu)$ and we have

$$g(\nu)d\nu = \frac{8\pi\nu^2 V}{c_o^3} d\nu.$$

Taking E_ν and perform volume integral, we have,

$$\begin{aligned} \frac{1}{8\pi} E_\nu^2 \cancel{V} &= \frac{h\nu}{2}\frac{8\pi\nu^2 \cancel{V}}{c_o^3} d\nu \\ E_\nu^2 &= \frac{32\pi^2 h\nu^3}{c_o^3} d\nu. \end{aligned}$$

Plug (3) into above,

$$\left\langle (\Delta r_\nu)^2 \right\rangle = \frac{\cancel{32} e^2 \cancel{\pi^2} h\cancel{\nu^3}}{\cancel{32}\pi^{\cancel{2}} \nu^{\cancel{4}} m^2 c_o^3} d\nu = \frac{he^2}{\pi^2 m^2 c_o^3}\frac{d\nu}{\nu}. \tag{4}$$

This is the desired result for $\left\langle (\Delta r_\nu)^2 \right\rangle$.

2.3 Final Derivation for $\Delta\varepsilon_n^{(1)}$

Combining (4) and (2), we have,

$$\hat{V}_I = \frac{2\cancel{\pi}e^2\delta(r)}{3}\frac{he^2}{\cancel{\pi^2}m^2c_o^3}\frac{d\nu}{\nu} = \frac{2he^4\delta(r)}{3\pi m^2c_o^3}\frac{d\nu}{\nu}. \tag{5}$$

Now that we are armed with this perturbing potential, first-order energy correction for Hydrogen atom becomes

$$\Delta\varepsilon_n^{(1)} = \langle nlm|\,\hat{V}_I\,|nlm\rangle = \langle nlm|\,\frac{2he^4\delta(r)}{3\pi m^2c_o^3}\frac{d\nu}{\nu}\,|nlm\rangle\,.$$

Recall that the completeness relation for continual states in position space is

$$\hat{\mathbb{1}} = \int d^3\mathbf{x}\,|\mathbf{x}\rangle\,\langle\mathbf{x}|\,, \text{for } \mathbf{x} = (r,\theta,\phi).$$

Note that this is an identity matrix and can be plugged into our latest $\Delta\varepsilon$ expression in which the implicit spatial part can be solved easily as $\langle\mathbf{x}|nlm\rangle = \Psi_{nlm}(r_o,\theta_o,\phi_o)$, where, instead of a general indication of a function's independent variables, the (r_o,θ_o,ϕ_o) is the coordinates of the state $|\mathbf{x}\rangle$. This gives

$$\begin{aligned}
\Delta\varepsilon_n^{(1)} &= \frac{2he^4}{3\pi m^2c_o^3}\frac{d\nu}{\nu}\int\langle nlm|\mathbf{x}\rangle\,\langle\mathbf{x}|\,\delta(\mathbf{r})\,|nlm\rangle\,d^3\mathbf{x}\\
&= \frac{2he^4}{3\pi m^2c_o^3}\frac{d\nu}{\nu}\int\left|\Psi_{nlm}(r,\theta,\phi)\right|^2\delta(\mathbf{r})d^3\mathbf{x}\\
&= \frac{2he^4}{3\pi m^2c_o^3}\frac{d\nu}{\nu}\left|\Psi_{nlm}(0,\theta,\phi)\right|^2.
\end{aligned}$$

The values of θ and ϕ have no significance when r vanishes.

To find corresponding atomic quantum numbers such that they give non-vanishing values to this $\Delta\varepsilon$, recall that all atomic states excluding s have a node (in terms of the probability distribution of an electron in the orbit to be found) at origin. The dumbbell-shaped P orbitals is no exception, for which the $\left|\Psi_{nlm}(0,\theta,\phi)\right|^2$term would vanish, and so would $\Delta\varepsilon_n^{(1)}$ for P. This implies that there would be no ZPE energy shift for the state $2^2P_{\frac{1}{2}}$, which is of our exemplary interest. For the spherically symmetric s orbitals, ($l=0$, and thus $m=0$), $\left|\Psi_{nlm}(0,\theta,\phi)\right|^2$ has a non-trivial value. Now our $2^2P_{\frac{1}{2}}$ and $2^2S_{\frac{1}{2}}$ non-degeneracy puzzle reduces to finding the ZPE perturbed energy for $2^2S_{\frac{1}{2}}$ only, which would account for their energy gap. For S state, we have,

$$\left|\Psi_{n00}(0,\theta,\phi)\right|^2 = \frac{1}{\pi n^3a_0^3},$$

which leads to

$$\begin{aligned}
\Delta\varepsilon_n^{(1)} &= \frac{2he^4}{3\pi m^2c_o^3}\frac{d\nu}{\nu}\left|\Psi_{n00}(0,\theta,\phi)\right|^2\\
&= \frac{2he^4}{3\pi m^2c_o^3}\frac{d\nu}{\nu}\frac{1}{\pi n^3a_0^3}\\
&= \frac{2he^4}{3\pi^2n^3m^2c_o^3a_o^3}\frac{d\nu}{\nu}.
\end{aligned}$$

The next step is to find a proper domain to perform an integration over ν. Since at low frequencies, the atom does not effectively respond to the field, we take the electron's orbit frequency $\nu_o = \frac{e^2}{\hbar a_0^3n^3}$ as the lower limit. For the higher limit, since the electron's motion is not taken relativistically, it must obey the limit $v < c_o$, from which we have,

$$\begin{aligned}
\frac{p}{m} &< c_o\\
\hbar k &< mc_o\\
k &< \frac{mc_o}{\hbar}\\
\frac{2\pi\nu}{c_o} &< \frac{mc_o}{\hbar}\\
\nu &< \frac{mc_o^2}{h}.
\end{aligned}$$

Taking $\nu_f = \frac{mc_o^2}{h}$ as the upper limit (a careful justification of the limits can be found in part VI and VII in [1]), we now have the energy shift over all proper ZPE frequencies for s orbits as

$$\begin{aligned}\Delta\varepsilon_n^{(1)} &= \frac{2he^4}{3\pi^2 n^3 m^2 c_o^3 a_o^3}\int_{\nu_o}^{\nu_f}\frac{d\nu}{\nu} \\ &= \frac{2he^4}{3\pi^2 n^3 m^2 c_o^3 a_o^3}\ln\left(\frac{mc_o^2\hbar a_o^3 n^3}{he^2}\right) \\ &= \frac{2he^4}{3\pi^2 n^3 m^2 c_o^3 a_o^3}\ln\left(\frac{mc_o^2 a_o^3 n^3}{2\pi e^2}\right).\end{aligned}$$

To verify if this calculation indeed match the energy splittings of interest, we perform a final calculation on the energy (in terms of frequency on spectrum) gap between $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$, which is equivalent to $\Delta\varepsilon_n^{(1)}$ for $n = 2$ as demonstrated previously, and have

$$\Delta f_{2^2S_{\frac{1}{2}}\to 2^2P_{\frac{1}{2}}} = \frac{\Delta E_{2^2S_{\frac{1}{2}}\to 2^2P_{\frac{1}{2}}}}{h} = \frac{\Delta\varepsilon_{(2)}^{(1)}}{h} = \frac{e^4}{12\pi^2 m^2 c_o^3 a_o^3}\ln\left(\frac{4mc_o^2 a_o^3}{\pi e^2}\right). \tag{6}$$

In Gaussian units, we have, $c_o = 2.998 * 10^{10} cm/s$, $a_o = 5.292 * 10^{-9} cm$, $m = 9.109 * 10^{-28} g$, and $e = 4.803 * 10^{-10} Fr (1Fr = 1cm^{3/2} g^{1/2} s^{-1})$. Plugging them into above, we have

$$\Delta f_{2^2S_{\frac{1}{2}}\to 2^2P_{\frac{1}{2}}} = -3.801 * 10^9 Hz \sim 1000 MHz,$$

where the negative sign means the energy is shifted downwards (goes lower). This result is consistent with the experimental observation and we conclude that the theory of vacuum fluctuation of EM field hiterto best accounts for the Lamb shift.

3 References

[1] T.A. Welton, *Phys. Rev.*, **74** (1948) (1157)

[2] C. Gerry and P. Knight, *Introductory Quantum Optics*, (Cambridge, Cambridge University Press, 2005)

[3] R. Pathria and P. Beale, *Statistical Mechanics*, 3rd edition (Burlington, Elsevier, 2011)