Bound State

John P. Wallace

Casting Analysis Corp.,
8379 Ursa Lane, Weyers Cave,
Virginia 24486 USA

Michael J. Wallace

Freeport-McMoRan, Phoenix,
Az 85050

The ground state energy of atomic hydrogen is difficult to measure precisely. This allowed theorists to bypass the role relativity plays in setting the energy levels. Rather they concentrated on lesser effects. Data for hydrogen like ions at high Z confirmed the strong role relativity plays in bonding showing how special relativity's γ takes on values less than one in the bound state. Another major omission was found dating to the 1920s on how the asymmetrical binding fields of the proton and electron must be treated before allowing the atomic hydrogen states to be solved by the standard perturbation theory.[a]

CONTENTS

I. INTRODUCTION

One electron hydrogen atom or hydrogen like ions are the simplest bound state system that can be experimentally explored as data can be taken over a wide range of binding strength of the ground state. The spherical electron density of the ground state is the easiest state to solve but not the easiest to gain precision experimental data. Most experimental studies of hydrogen seek to measure transition energies between states rather than the absolute energy of the ground state.

Bound electrostatic states limit the range of long range electrostatic fields. The truncated field supplies the bond energy. With opposite behavior, the weak force is a transformation that preserves long range fields. Leaving gravity with a weak unattenuated long range reach. There are at least five different mechanisms that can produce a bound state: 1) electrostatic, 2) magnetic, 3) strong force, 4) lower dimensional assemblies forming three dimensional baryons/mesons, and 5) gravity (Wallace and Wallace, 2025a) (Wallace and Wallace, 2025b). All except gravity convert rest mass to supply energy for the bond. Inertial mass shrinks the lab frame volume to generate gravitational attraction (Wallace and Wallace, 2024).

All five bonding mechanisms result from correctly dealing with special relativity. For a free particle $\gamma \geq 1$, but in the bound states $\gamma < 1$. The simplest bound state to deal with is atomic hydrogen since the deuterium nucleus has both the magnetic and strong force competing in forming the bond. The magnetic spin effects for the atomic hydrogen are small ($> 10^{-5} eV$) and that allows the analysis to concentrate on the role relativity plays in forming the electrostatic bound state.

II. HYDROGEN GROUND STATE HISTORY

In 1947 Polykarp Kusch and Henry Foley reported their experiment of the gyromagnetic ratio of the electron (Foley and Kusch, 1948). This work on the magnetic moment and the Lamb shift gave rise to a theory called quantum electrodynamics that was used to compute the corrections to the Dirac electron theory. Until the early 1960s P. Kusch had no public problem with quantum electrodynamics but by 1967 he had come to the conclusion it was not valid physics. The troubling experimental question was the large discrepancy in the ground state energy of hydrogen $^2\mathbf{S}_{\frac{1}{2}}$. Both the Schrödinger and Dirac equations computed values for the ground state were greater by $> .003$ eV.

We first found a failure of the Schrödinger equation in the bound state problem for the spherical flat bottom potential in three dimensions. Three bound states with angular momentum $l = 0, 1,$ & 2 were still found after the potential was forced to vanish (Wallace and Wallace, 2011). The interesting part of that result was it yielded a scale size that was the Compton scale, $r = \hbar/mc$, for a particle with mass. This was a hint that massive particles could not be mathematical points rather they must possess some finite scale size.

In the development of quantum mechanics in the 20th century the quadratic energy conservation relation, $E^2 = (mc^2)^2 + p^2c^2 = \gamma(mc^2)^2$, was not taken seriously in dealing with low energy atomic problems. It is through this relation that all the interaction potentials except gravity can be directly extracted (Wallace and Wallace, 2017). Potentials enters quantum mechanics both as a first and second order dependence in the differential equations replacing the Schrödinger and Dirac equations.

The second failure in the early development of quantum mechanics was not recognizing that longitudinal fields would represent massive particles. This came with a requirement for an independent space to generate each particle's properties that would extract a proportional volume from the laboratory frame producing gravity (Wallace and Wallace, 2024). Experimentally, these new spaces were first detected by studying longitudinal spin waves in well annealed iron (Wallace, 2009a) (Wallace, 2009b).

III. RELATIVISTIC BOUND STATE

Neither the Schrödinger (Raimes, 1961) nor the Dirac equations are derived from the relativistic conservation of energy relation. In addition is their failure to recognize that the γ of special relativity can take on values less than one for the bound state and less than zero for anti-particles. It did not help that particles were treated as mathematical points with no structure. Correcting these errors produced a better starting point yielding a pair of laboratory frame wave equation derived using the relativistic conservation of energy that replace the Schrödinger and Dirac equations (Wallace and Wallace, 2020).

$$\nabla^2\Phi - \frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2} = \frac{2m_o}{\hbar^2}\{-i\hbar\frac{\partial\Phi}{\partial t} + V(1 + \frac{V}{2m_oc^2})\Phi\}$$

$$i\hbar\frac{\partial\Phi}{\partial t} = -\frac{\hbar^2}{m_o(1+\gamma)}\nabla^2\Phi + \frac{2V}{1+\gamma}(1 + \frac{V}{2m_oc^2})\Phi \tag{1}$$

The upper equation describes the behavior of a free field, either massive and/or massless. The massless wave equation automatically integrates electromagnetism into the quantum wave equation that will describe either photons or neutrinos. This wave equation has been useful for describing the quantum basis of refraction (Wallace and Wallace, 2018).

The lower equation describes the relative dynamics of a particle, free or bound in a potential such as the hydrogen atom. By dropping the quadratic potential term and setting γ to one, the result is the Schrödinger equation that has now been properly derived as a non-relativistic approximation. The interaction potentials for the electromagnetic and strong forces are generated from the mass lost to produce the potential fields.

Applying the lower equation 1 to hydrogen atom with the Coulomb potential was originally not even considered because the point charge of the Coulomb potential is not valid. Both the electron and the proton have finite structures with a charge distributions that are not singular at the origin (Wallace and Wallace, 2015). Peter Hagelstein in looking for a problem to give his quantum mechanics class found a simple solution to the upper equation 1 using the Coulomb potential. His three dimensional spherically symmetric trial solution was $\phi(r) \sim r^s e^{-\beta r}$ that also can be used for the lower equation for the $^2\mathbf{S}_{\frac{1}{2}}$ ground state.

The trial solution for the time dependent portion of the wave function:

$$\Phi(r,t) = \phi(r)e^{-\frac{iE_{rel}t}{\hbar}} \tag{2}$$

producing.

$$E_{rel}\ \phi(r) = -\frac{\hbar^2}{m_o(1+\gamma)}\nabla^2\phi + \frac{2V}{1+\gamma}(1 + \frac{V}{2m_oc^2})\phi \tag{3}$$

Taking $\phi(r) = r^s e^{-\beta r}$ yields in 3D spherical coordinates:

$$E_{rel} \ \phi(r) =$$
$$-\frac{\hbar^2}{m_o(1+\gamma)}\{\beta^2 - \frac{2\beta(s+1)}{r} + \frac{s(s+1)}{r^2}\}\phi(r) \ + \tag{4}$$
$$\frac{2V}{1+\gamma}(1 + \frac{V}{2m_oc^2})\phi(r)$$

Applying the Coulomb potential to the two potential terms the relativistic wave equation becomes:

$$V + \frac{V^2}{2m_oc^2} = -\frac{Ze^2}{2(1+\gamma)\pi\epsilon_o r} + \frac{1}{(1+\gamma)m_oc^2}\frac{Z^2e^4}{(4\pi\epsilon_o)^2r^2} \tag{5}$$

Separating the terms in powers of r allows E_{rel}, s and β to be computed as all factors of r^m must equal zero.

$$E_{rel} + \frac{\hbar^2\beta^2}{m_o(1+\gamma)} =$$
$$\frac{1}{r}\{-\frac{2\hbar^2\beta(s+1)}{m_o(1+\gamma)} - \frac{Ze^2}{2(1+\gamma)\pi\epsilon_o}\} \ + \tag{6}$$
$$\frac{1}{r^2}\{-\frac{\hbar^2 s(s+1)}{m_o(1+\gamma)} + \frac{1}{(1+\gamma)m_oc^2}\frac{Z^2e^4}{(4\pi\epsilon_o)^2}\}$$

Solving for s and then substituting for the fine structure constant α:

$$s^2 + s = \frac{Z^2e^4}{(4\pi c\hbar\epsilon_o)^2} = \alpha^2 Z^2 \tag{7}$$

$$s = \sqrt{1 + 4Z^2\alpha^2} - 1 \tag{8}$$

For β the equation is simplified by using the Bohr radius a_o:

$$\beta = \frac{1}{s+1}\frac{m_o}{\hbar^2}\frac{Ze^2}{4\pi\epsilon_o} = \frac{Z\alpha}{\sqrt{1+4Z^2\alpha^2}}\frac{m_oc}{\hbar} = \frac{Z}{a_o\sqrt{1+4Z^2\alpha^2}} \tag{9}$$

Then the expression for the ground state energy of the $^2S_{\frac{1}{2}}$ state when the factor representing the reduce mass effect is applied where m_N is the nucleon mass. (Bethe and Salpeter, 1957).

$$E_{rel} = -\frac{m_oc^2}{(1+\gamma)}\frac{Z^2\alpha^2}{1+4Z^2\alpha^2}\frac{m_N}{m_o + m_N} \tag{10}$$

The γ dependence can be factored out by using the expression for total energy $E_t = \gamma m_o c^2$.

$$E_{rel} = E_t - m_oc^2 = m_oc^2(\gamma - 1) \tag{11}$$

Substituting into equation 10 to remove γ yields:

$$E_{rel}^2 + 2m_oc^2 E_{rel} + (m_oc^2)^2\frac{Z^2\alpha^2}{1+4Z^2\alpha^2}\frac{m_N}{m_o + m_N} = 0 \tag{12}$$

$$E_{rel} = m_oc^2\{-1 + \sqrt{1 - \frac{Z^2\alpha^2}{1+4Z^2\alpha^2}\frac{m_N}{m_o + m_N}}\} \tag{13}$$

The wave function then becomes:

$$\Phi(r,t) = Ar^{\sqrt{1+4Z^2\alpha^2}-1} \ e^{-\frac{Zr}{a_o\sqrt{1+4Z^2\alpha^2}} - i\frac{Et}{\hbar}} \tag{14}$$

The relation for energy is a function of the constants: c, $\hbar$, e, and $m_{electron}$. These values have varied over the years depending on the conventions for selecting their values. Because the expression 13 is one where a small value for the ground state energy depends on an accurate value to the total self-energy of the electron where a large number multiplies a small difference, the accuracy of these four constants becomes important. The largest uncertainty comes from Planck's constant with a variance since 1974 of $\pm.0001eV$ and $\pm.00005eV$ for the rest. These values determine the limiting accuracy of any calculation. NIST for some time has been posting calculated values of the ground state energy of hydrogen rather than experimental energies, because as they explained when questioned the theoretical numbers are more accurate. Currently they are revising their website. Even though it is possible to measure very accurate energy difference between state such as **1S-2S**, **2S-2P**, and **1S-3S** the absolute energy of the ground state are not easily determined by optical spectroscopy (Niering and et. al., 2000) (Lamb and Retherford, 1947) (Grinin, 2020). Also there has been a tendency after the 1970s to make experimental data fit the models rather than the other way around (Pickering, 1984). Because of the behavior of NIST over the past two decades we have chosen an experimental value from 1971 published by the NBS. Because of the experimental difficulty of measuring the ground state energy of hydrogen spectroscopically the favored technique is electron scattering ionization.

The ground state energies for the three different wave equations: Schrödinger, Dirac, and 1 are computed in Table I. γ in the bound state now takes on values less than one as the self-energy is reduced to supplying the field that binds the state. The change in γ can be computed using equation 11. The result is a large discrepancy between the experimental value and the results produced from the Schrödinger and Dirac equations.

Table I **H**ydrogen ground state energy from Bohr (Bohr, 1913) the Schrödinger Equation (Bethe and Salpeter, 1957) , modified Dirac equation (Gordon, 1928), and the relativistic wave ground state energy (eq. 13). The experimentally measured ground state energy is **-13.595** eV (Moore, 1971).

Bohr	**1913**
-13 eV	planetary atomic quantized model $E_{Bohr} = -\frac{R}{2}$
Schrödinger equation	**1926**
solution relativity ground state energy **-13.5983** eV deviation **-.0033** eV $\gamma = 1$	regular at origin not considered $E_{Schro.} =$ $-\frac{Z^2 m_o e^4}{2(4\pi\epsilon_o)^2\hbar^2}\frac{m_N}{m_o+m_N}$
mod. Dirac Equation	**1928**
solution relativity ground state energy **-13.5985** deviation **-.0035** eV $\gamma = 1$	singular at origin incorrectly applied $E_{Dirac} = m_o c^2\{-1$ $+\frac{1}{\sqrt{1+\frac{m_N Z^2\alpha^2}{(1-Z^2\alpha^2)(m_e+m_N)}}}\}$
Relativistic Wave Equation	**2023**
solution relativity ground state energy **-13.5956** eV deviation **-.0006** eV $\gamma = .9997339$	regular at origin correctly applied $E_{rel} = m_o c^2\{-1+$ $\sqrt{1-\frac{Z^2\alpha^2}{(1+4Z^2\alpha^2)}\frac{m_N}{m_o+m_N}}\}$

IV. Z DEPENDENCE OF GROUND STATE ENERGY FOR HYDROGEN LIKE IONS

A stronger proof of the incomplete nature of special relativity and 20th century quantum mechanics comes by considering the energy levels of K-shell electrons in heavier elements. For the high **Z** hydrogen like ions there is a strong divergence between the behavior of the ground state energy of the relativistic wave equation verse the Schrödinger and Dirac equations as shown in Figure 1. There is no single electron ionization data available at high **Z** and the best data is that of **K**-shell x-ray ionization data. Care has to be taken since NIST tables report ionization data for high **Z** that are only calculations and not experimental.

The reason the **K**-shell x-ray data is interesting is that Moseley's parabolic law for **K**-shell ionization breaks down (Condon and Shortley, 1951) in the same area where the ground state energies diverge for the three relations. This indicates electrostatic binding energy has a limit.
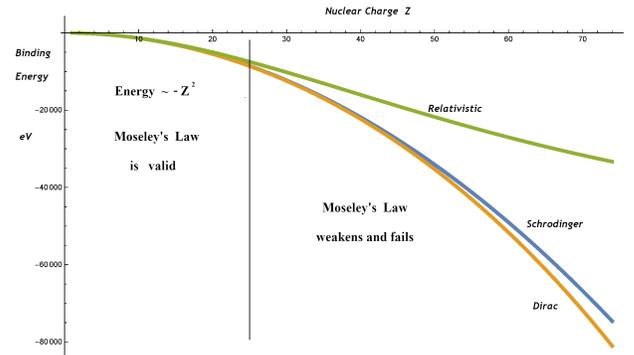

Figure 1 **Binding energy of hydrogen like ions taking Z from 1 to 74 in eV for three models.**

In the limit of infinite charge using equation 13 γ does not go to zero. The bound state energy is limited to a finite value independent of Z.

$$E_{rel} \geq m_o c^2\{\sqrt{\frac{4}{5}}-1\} = \text{-.10557}\ m_o c^2 \quad (15)$$

The ground state energies when computed from both the Schrödinger and Dirac equation continue to decrease with increasing **Z**. This limit in binding occurs for potentials generated from the self-energy of the particles themselves. That is not the case for the gravitational potential that enters the second order differential lab frame field equation in a different way (Wallace and J., 2021) (Wallace and Wallace, 2024). At high **Z** the **K**-shell electron contribution to binding is exhausted and they become a hardened inelastic shell between the nuclear charge and the outer electrons.

V. HIGHER ENERGY STATES

It is possible to extend the use of the trial solution used for the **1S** state to higher energy states. However, the results are mixed as shown in Table III. The problem is greater with those wave functions that are not a simple

Table II **Ground state binding limits for the three wave equations as a function of Z.**

Analysis	$Z \to 0$	$Z \to \infty$
Schrödinger fails at upper limit	0	$-\infty$
Dirac fails at upper limit	0	**undefined**
Relativistic predicts limit to Moseley's Law	0	$>$ .106 $m_o c^2$ Limit to Binding

power of the radial variable multiplying the exponential term. These trial solutions can be used as a starting point in a second order perturbation analysis to calculate the wave functions and state energies.

Table III **Trial Solutions for the 2S, 2P and 3D states of hydrogen. The model of supplying an exponent, s, with a factor, r^s, to be determined appears only to work where there is no complicate polynomial in, r. The 2S and 2P states are separated by a factor of 10 times greater than the experimental value of the Lamb shift. Things get worse for larger principal quantum numbers.**

1S	2S	2P	3D
$l = 0$	$l = 0$	$l = 1$	$l = 2$
$r^s e^{-\beta r}$	$r^s e^{-\beta r/2} \times \{1 - \frac{\beta r}{2}\}$	$r^{s+1} e^{-\beta r/2}$	$r^{s+2} e^{-\beta r/3}$
-13.5956 eV	-3.40256 eV	-3.40323 eV	-1.51256 eV

The question remains of why the computed energy from the relativistic wave equation for the hydrogen ground state is within the error bounds of the experimental value when a singular Coulomb potential, $\frac{1}{r}$ is being used? Neither the electron nor proton are point

charges (Wallace and Wallace, 2015) (Wallace and Wallace, 2019). The proton's charge density is more compact than that of the electron, however, it plays the dominant role in defining the central force potential field due to its greater mass. The proton's potential is better approximated by the singular Coulomb potential, but not the electron's potential. The correction to the electrostatic potential of the electron due to its structure can be computed from the electrons state function in its self-reference frame, $u^*(r)u(r)$ and is shown in Figure 2 (Wallace and Wallace, 2015).

$$V_{Coul.}(r) = -\frac{Ze^2}{4\pi\epsilon_o r} \qquad (16)$$

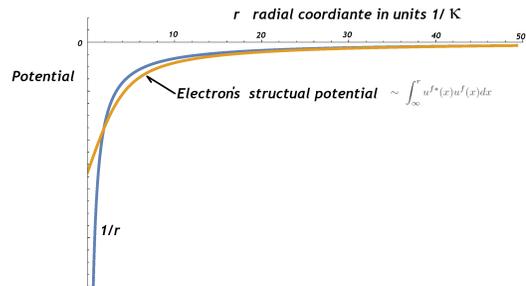$$\Delta V(r) = V_{Coul}(r) - \int_{\infty}^{r} u^{f*}(x)u^f(x)dx \qquad (17)$$

Figure 2 **The difference between the $1/r$ potential of a point charge and the electron's structural potential is significant in the electrons core region. In the plot $r = 1$ represent the electron's Compton scale of $\hbar/mc = 3.86 \times 10^{-13}m$ (Wallace and Wallace, 2015).**

The difference between of the real potential field as compared to the $1/r$ field occurs over a range of about twenty times the Compton scale for the electron. This variation will show up as a significant alteration in the bound state wave function and energy level as found in Table III. Meaning, the simple trial wave function is insufficient to establish the energies for the states $n \neq l-1$. The polynomial part of the atomic wave function are not well modeled by a single exponential parameter because of the structure of the electron density found in Figure 2. The same kind of analysis must be done for the proton as the finite charge structure of the proton's charge distribution will not be an insignificant contribution to the Lamb shift energy.

A weak point in the argument for the Dirac relativistic wave equation is the restriction of it being solely for the electron. The second point of failure is that the electron is represented as a mathematical point. Its possible to

produce a general derivation for the particle structure in its own frame of reference using a second order equation to generate a pair of solutions, for both a fermion and boson in three spatial dimensions (Wallace and Wallace, 2015). There is the restriction to a single spatial spherically symmetric free variable, r, ensuring $U(1)$ group symmetry in the particles self-reference frame. Where $u^f(r; \kappa, n, \gamma)$ one for fermion and one $u^b(r; \kappa, n, \gamma)$ for a boson are dependent on three parameter: n the dimension (1, 2, or 3), κ inverse particle scale, and γ. Dynamics is not expressed in this space, except indirectly through the relativistic parameter γ (Wallace and Wallace, 2014).

The electron's architectural description defines its static electric field, $\mathbf{E} \sim u^*(r)u(r)\hat{\mathbf{r}}$, that is dependent on two parameter: inverse scale κ and γ. In the self-reference frame where there are no internal dynamics γ is a function of the particle's environment.

The spatial expression $u^f(r)$ and $u^b(r)$ for 3D elementary massive fermion and boson in their own frame of reference, which for the fermion solution will be taken as an electron is one of the two solutions of equation 19. The lower solution being for the boson where $_1F_1$ and U are confluent hypergeometric functions (Wallace and Wallace, 2014).

$$u^f(r) = Ae^{-\kappa r}{}_1F_1\left[\frac{2}{1+i\gamma}, 2, (1+i\gamma)\kappa r\right]$$

$$u^b(r) = Ae^{-\kappa r}U\left[\frac{2}{1+i\gamma}, 2, (1+i\gamma)\kappa r\right] \tag{18}$$

The field equation that produced these solution is derived from the behavior of a longitudinal field. These solutions are coupled to the laboratory frame relativistic wave equation through the second order potential term generating pair-production of the same particle. This continual annihilation renewal process isolates the two spaces because of the statistical independence generated by the loss of a history as to which particle annihilate (Wallace and Wallace, 2014).

$$\frac{\partial^2 u(r)}{\partial r^2} + \left(\frac{n-1}{r} + \kappa\{1-i\gamma\}\right)\frac{\partial u(r)}{\partial r} - i\kappa^2\gamma u(r) = 0 \tag{19}$$

The role of γ for the bound state and its effect on structure of the particle is of interest for both bosons and fermions. The simplest way to display the effect is to plot the particle's self-reference frame density function, comparing values of γ, when both greater and less than one. The effect of an external binding potential in altering γ acts differently on fermions and bosons. This can be seen in their density function, $u^*(r)u(r)r^{n-1}$ for the three dimensional solutions. In the electron's own frame of reference, its self-reference frame, γ modifies the electron's structure. In free space for $\gamma < 1$ the electron expands, its wave function is divergent and grows,

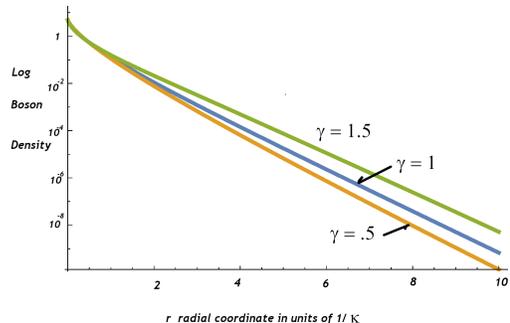inhibiting additional occupation of the same state.

Figure 3 **Origin of the Bose-Einstein condensate is seen in the shrinkage of the boson density function in the self-reference frame with an external binding potential.**

A. Ranking Corrections

The computed difference between hydrogen atom's energy states were used as an argument for the validity of quantum electrodynamics. Particularly, in defining the energy difference between the **2S** and **2P** states. This was a slight of hand argument because the relativistic correction to absolute energy of the states were at least two orders of magnitude greater and ignored.

The first problem that has to be dealt with are the potentials: There is a significant difference in structure of the electrostatic potential of the proton and the electron. They are different and have to be treated in much the same way the reduced mass for components enters into the ground state energy calculation (Born, 1969). The reduced mass correction is a ratio of self-energies. A measure of the charge distribution difference between the electron and proton is given by their relative magnetic moments, μ_e and μ_p. In the potential calculation it is the ratio of field energy that the square of the magnetic moments represents that goes into the reduced field equation 20.

$$V(r) = \frac{m_p\mu_p^2}{m_p\mu_p^2 + m_e\mu_e^2}V_p(r) + \frac{m_e\mu_e^2}{m_p\mu_p^2 + m_e\mu_e^2}V_e(r)$$

$$V(r) = .99578\,V_p(r) + .00422\,V_e(r) \tag{20}$$

This allows for the correction of **2S** state first order perturbation calculation which used the non-relativistic hydrogen wave functions and the potential that differed from the $1/r$ potential as shown in Figure 2. The calculation over estimates the contribution because it has not included the effect of the reduced relative fields.

$$\text{Reduced elec. field}: f \quad = \quad \frac{m_e \mu_e^2}{m_p \mu_p^2 + m_e \mu_e^2} = .00422$$

$$\langle 2S|\delta V_e|2S\rangle_{corr.} \quad = \quad f \quad \langle 2S|\delta V_e|2S\rangle \tag{21}$$

A similar calculation must be done for the proton because it will not be a small effect since its reduced mass scale factor is ~ 200 greater than that of the electron even though the scale size of the proton charge density is much smaller. The correction for the distributed charge of the electron makes up $\sim 70\%$ of the Lamb shift and the proton's contribution is not expected to be small and may complete the correction.
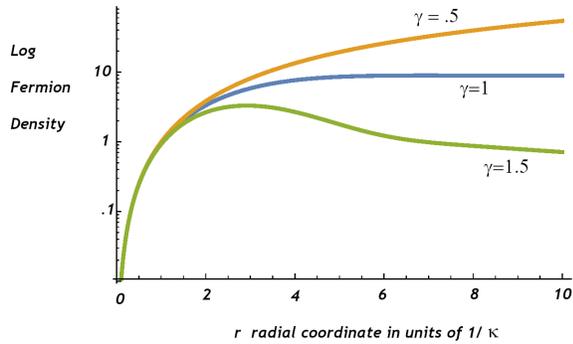

Figure 4 **Origin of fermion repulsion is seen in the density function diverging in an external binding potential.**

VI. DISCUSSION

The improved hydrogen ground state energy found with the relativistic wave equation derived from the quadratic energy conservation relation was reinforced when extended to high **Z** hydrogen like ions showing the necessity of expanding Special Relativity to values of $\gamma < 1$. Also discovered was a limit to the strength of the electrostatic bond. In addition the physical origin of quantum statistics has been exposed. Finally, a direct and physical approach to computing the much smaller Lamb shift was introduced that only requires standard perturbation theory.

VII. ACKNOWLEDGMENT

Table IV **Hydrogen energy levels and Lamb shift corrections, with energies in eV. (Wallace and Wallace, 2015) (Wallace and Wallace, 2021). The relativistic correction generated by equation 3 is a much larger correction compared to what is generated by the fact the electron's charge distribution and is not a point particle. This difference is two orders of magnitude. The charge distribution of electron is the dominate effect in generating the Lamb shift as even with the wrong non-relativistic wave functions it supplies 72% of the Lamb shift.**

function	original	corrected
1S Rel. Correction	0	3.3×10^{-3}
2S Rel. Correction	0	3.1×10^{-3}
2P Rel. Correction	0	3.6×10^{-3}
3D Rel. Correction	0	1.7×10^{-3}
$\langle 1S|\delta V|1S\rangle$	7.09822×10^{-3}	2.995×10^{-5}
$\langle 2S|\delta V|2S\rangle$	8.87307×10^{-4}	3.744×10^{-6} $.726 GHz$
$\langle 2P|\delta V|2P\rangle$	2.73322^{-8}	1.14699×10^{-10}

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