Abstract

We make use of the Dirac equation to provide a relativistic calculation of the binding energy of a hydrogen-like atom confined within a penetrable spherical barrier. We take the potential to be Coulombic within the barrier and constant outside the barrier. The derived energy values are compared with the energy values obtained from a non-relativistic calculation based on the Schrödinger equation, where significant differences are found for small values of the barrier radius. In addition, we show that without the introduction of the principle quantum number \( n \), all energy states of the confined atom, determined by a single quantum number \( k \), transfer into the known energy states of the free atom as the radius of the barrier becomes large.

1 Introduction

The effect of confinement on the energy levels of an atom has been studied by multiple authors, probably first by Michels and deBoer \([1]\), and then followed by Sommerfeld and Welker who computed the confinement radius at which the binding energy becomes zero. \([2]\) These and more recent authors provided non-relativistic treatments of the problem based on the Schrödinger equation. See in particular Refs. 3-7, the last of which provides additional sources. The intent here is to provide a model for confined relativistic hydrogen-like atoms, investigate the effects of confinement on the relativistic energy levels, and compare the energies of a confined relativistic hydrogen atom with the energies of a confined non-relativistic hydrogen atom (based on the Schrödinger equation).

The fields of nano-structures and semi-conductor quantum dots have stimulated renewed interest in the problem we consider as a consequence of the need to take account of the effect on atoms from confining boundaries. Because confinement of the atom can cause the energy of its electrons to become relativistic, a relativistic treatment of the problem seems required. But, at present, we are unaware of a previous relativistic treatment.
2 Theory

To provide a description of a compressed hydrogen-like atom based on the Dirac equation we assume the wave function of the electron to satisfy the Dirac equation in the form

\[ [-i\hbar c\gamma_0 \vec{\gamma} \cdot \nabla + \gamma_0 mc^2 + V(r)]\psi(r) = E\psi(r), \quad (1) \]

where \( \gamma_0 \) and \( \gamma \) represent Dirac \( \gamma \)-matrices, and \( m \) and \( E \) are the rest mass and total energy of the electron respectively. The solution of Eq. (1) can in general be represented as a four element column matrix dependent on the spherical coordinates, \( r, \theta \) and \( \phi \) of the coordinate vector \( r \) as

\[ \psi(r) = \frac{1}{r} \begin{pmatrix} G(r)\Omega_{j\ell m_j}(\theta,\phi) \\ iF(r)\Omega_{j'\ell' m'}(\theta,\phi) \end{pmatrix}, \quad (2) \]

where \( \Omega_{j\ell m_j}(\theta,\phi) \) is a two-row spherical spinor and the quantum numbers \( \ell \) and \( \ell' \) characterize the upper and lower components of the Dirac matrix.

The interest is in the radial coordinate dependence of \( \psi \), expressed through the radial functions \( G(r) \) and \( F(r) \), which the Dirac equation connects through the coupled equations

\[ \left[ \frac{d}{dr} - k \frac{r}{r} \right] F(r) + \frac{1}{\hbar c}[E - mc^2 - V(r)]G(r) = 0, \quad (3.a) \]

\[ \left[ \frac{d}{dr} + k \frac{r}{r} \right] G(r) - \frac{1}{\hbar c}[E + mc^2 - V(r)]F(r) = 0, \quad (3.b) \]

where the quantum number \( k \) has the two possible values \( k = \pm (j + \frac{1}{2}) \), with \( j = l \pm \frac{1}{2} \).

Here, for values of the radial coordinate \( r \) less than a certain "radius of confinement" \( R \), the central potential \( V(r) \) is assumed to have the usual Coulomb form

\[ V(r) = -Ze^2/r \quad (r < R), \quad (4) \]

while, for values of \( r > R \), we simulate confinement of the electron by equating \( V(r) \) to a constant (barrier potential), denoted \( W \)

\[ V(r) = W \quad (r > R). \quad (5) \]

2.1 Solution of the Dirac equation for \( r < R \)

It is useful to introduce the dimensionless coordinate \( \rho \equiv 2qr \) into Eqs. (3), where we have \( q \equiv \sqrt{(mc^2)^2 - E^2}/\hbar c \). Solutions of the equations for \( F(\rho) \) and \( G(\rho) \) that are finite at the origin can be shown to be expressible in terms of confluent hypergeometric functions of the first kind \[8\].

\[ G(\rho) = A\sqrt{mc^2 + E\rho^2}e^{-\rho} \left[ \begin{pmatrix} 1F_1(\gamma - \frac{Z\alpha E}{\hbar c}, 1) + 1, 2\gamma + 1, \rho) + \\
\left( \frac{k - Z\alpha mc^2/\hbar c}{\frac{Z\alpha E}{\hbar c} - \gamma} \right) \right] \begin{pmatrix} 1F_1(\gamma - \frac{Z\alpha E}{\hbar c}, 2\gamma + 1, \rho) \end{pmatrix}, \quad (6.a) \]
\[ F(\rho) = A \sqrt{mc^2 - E}\rho e^{-\frac{\rho}{2\gamma}} \left[ _1F_1\left(\gamma - \frac{Z\alpha E}{\bar{hc}}, 1, 2\gamma + 1, \rho\right) - \left(\frac{k - Z\alpha mc^2/\bar{hc}}{Z\alpha E/\bar{hc} - \gamma}\right) _1F_1\left(\gamma - \frac{Z\alpha E}{\bar{hc}}, 2\gamma + 1, \rho\right) \right], \quad (6.b) \]

where the function \(_1F_1\) has the series representation
\[ _1F_1(a, b; \rho) = 1 + \frac{a}{b} \rho + \frac{1}{2!} \frac{a(a+1)}{b(b+1)} \rho^2 + ... \quad (7) \]

Here \(A\) represents a normalization constant, and we use the notation
\[ \alpha \equiv \frac{e^2}{\bar{hc}} \quad (8.a) \]
\[ \gamma \equiv \sqrt{\gamma^2} = \sqrt{k^2-(\alpha Z)^2}. \quad (8.b) \]

### 2.2 Solution of the Dirac equation for \( r > R \)

We simulate a barrier at \( r = R \) by equating the potential \( V \) to the constant value \( W \) for \( r > R \). Introduction of this potential into Eqs. (3) converts the equations for the radial functions \( G \) and \( F \) into the forms
\[ \frac{dG}{d\rho} + \frac{k}{\rho} G - \frac{\eta_1}{2q} F = 0, \quad (9) \]
\[ \frac{dF}{d\rho} - \frac{k}{\rho} F - \frac{\eta_2}{2q} G = 0, \quad (10) \]

where
\[ \eta_1 \equiv \left( \frac{mc^2 + E - W}{\bar{hc}} \right), \quad \eta_2 \equiv \left( \frac{mc^2 - E + W}{\bar{hc}} \right). \quad (11) \]

Differentiating Eq. (9) with respect to \( \rho \) produces the second order equation for \( G \),
\[ \frac{d^2G}{d\rho^2} + k \frac{dG}{d\rho} - \frac{k}{\rho^2} G - \frac{\eta_1}{2q} \frac{dF}{d\rho} = 0. \quad (12) \]

Solving Eq. (9) for \( F(\rho) \) and using it in Eq. (10) results in an equation for \( \frac{dF}{d\rho} \) in terms of \( G \)
\[ \frac{dF}{d\rho} = \frac{k}{\rho} \frac{dG}{d\rho} \left( \frac{G}{\rho} + \frac{k}{\rho} G \right) + \frac{\eta_2}{2q} G, \quad (13) \]

the use of which in Eq. (12) gives a second order equation for \( G \) that reduces after cancellations to the form
\[ \frac{d^2G}{d\rho^2} = \frac{k(k+1)}{\rho^2} G + \frac{\eta_1 \eta_2}{(2q)^2} G. \quad (14) \]
In order to solve this second order differential equation, it helps to introduce the variable substitution \( G(\rho) = \rho \hat{G}(\rho) \) and to let \( \nu = \frac{\sqrt{\eta_1 \eta_2}}{2q} \) in order to produce a new second order differential equation of the form

\[
\rho^2 \frac{d^2 \hat{G}}{d\rho^2} + 2\rho \frac{d\hat{G}}{d\rho} - [\nu^2 \rho^2 + k(k+1)]\hat{G} = 0, \quad (15)
\]

the general solution of which is expressible as

\[
\hat{G}(\rho) = c_1 \frac{I_i(\nu \rho)}{\sqrt{\rho}} + c_2 \frac{K_i(\nu \rho)}{\sqrt{\rho}}, \quad i = \frac{1}{2} \sqrt{(2k+1)^2}. \quad (16)
\]

In Eq. (16) above, \( I_i \) and \( K_i \) are the modified Bessel functions of the first and second kind of order \( i \) respectively. Here, for solutions of Eq. (15) for which \( E < mc^2 \) and \( W < 2mc^2 \), \( \nu \) will remain real and the arguments of the Bessel functions will remain real. Multiplying Eq. (16) by \( \rho \) we obtain an equation for \( G \),

\[
G(\rho) = c_1 \sqrt{\rho} I_i(\nu \rho) + c_2 \sqrt{\rho} K_i(\nu \rho). \quad (17)
\]

\( I_i(x) \) increases exponentially as \( x \) increases while \( K_i(x) \) decreases exponentially as \( x \) increases. Therefore the requirement that \( G \) and \( F \) remain finite for all \( r > R \) requires that \( c_1 = 0 \), which reduces Eq. (17) to

\[
G(\rho) = c_2 \sqrt{\rho} K_i(\nu \rho). \quad (18)
\]

From Eq. (9), we see that

\[
F(\rho) = 2q \left( \frac{dG}{d\rho} + \frac{k}{\rho} G \right). \quad (19)
\]

To obtain \( \frac{dG}{d\rho} \), we make use of the following recurrence relations from Ref. 9, namely

\[
K_{i-1} - K_{i+1} = \frac{-2i}{x} K_i, \quad (20.a)
\]

\[
K_{i-1} + K_{i+1} = -2 \frac{dK_i}{dx}, \quad (20.b)
\]

where the \( i \) in the numerator on the right hand side of Eq. (20.a) refers to the subscript \( i \). Adding Eq. (20.a) to Eq. (20.b) results in an equation that can be used to determine \( \frac{dG}{d\rho} \),

\[
\frac{dG}{d\rho} = c_2 \left( \frac{1}{\sqrt{\rho}} K_i(\nu \rho) \left( \frac{1}{2} - i \right) - \nu \sqrt{\rho} K_{i-1}(\nu \rho) \right). \quad (21)
\]

Combining Eq. (21) above with equation Eq. (18) results in an equation for \( F \):

\[
F(\rho) = c_2 \sqrt{\rho} \left[ \frac{q}{\eta_1 \rho} K_i(\nu \rho) (1 - \sqrt{(2k+1)^2 + 2k}) - \sqrt{\eta_1 \eta_2} K_{i-1}(\nu \rho) \right], \quad (22)
\]

where here \( i = \frac{1}{2} \sqrt{(2k+1)^2}, \nu = \frac{\sqrt{\eta_1 \eta_2}}{2q} \), and \( F(\rho) \) decreases exponentially as \( \rho \) approaches infinity as required.
2.3 Boundary condition at \( r = R \)

The continuity of \( \psi(r) \) required at \( r = R \) results in the simultaneous equations

\[
G_{r<R}(R) = G_{r>R}(R), \tag{23.a}
\]

\[
F_{r<R}(R) = F_{r>R}(R). \tag{23.b}
\]

After division of Eq. (23.b) by Eq. (23.a), the two equations are conveniently combined into the "matching equation" [10]

\[
\frac{F_{r<R}(R)}{G_{r<R}(R)} = \frac{F_{r>R}(R)}{G_{r>R}(R)}, \tag{24}
\]

independent of the normalization constants \( c_2 \) and \( A \). Use of Eqs. (18) and (22) expresses the right hand side of Eq. (24) in the form

\[
1 - \frac{\sqrt{(2k+1)^2 + 2k}}{2\eta_1 R} - \sqrt{\frac{\eta_2}{\eta_1}} \frac{K_{-i-1}(\sqrt{\eta_1 \eta_2} R)}{K_{i}(\sqrt{\eta_1 \eta_2} R)}. \tag{25}
\]

Meanwhile, the left hand side of Eq. (24) can be evaluated by the use of Eqs. (6.a) and (6.b), in the form

\[
\sqrt{mc^2 - E} \times \\
\frac{1}{mc^2 + E} \left[ \begin{array}{c}
1F_1(\gamma - \frac{ZeE}{\hbar c} + 1, 2\gamma + 1, 2qR) - \left( \frac{k - Z\alpha mc^2/\hbar c}{\frac{Z\alpha E}{\hbar c} - \gamma} \right) 1F_1(\gamma - \frac{ZeE}{\hbar c}, 2\gamma + 1, 2qR)
\end{array} \right]
\]

\[
\left[ \begin{array}{c}
1F_1(\gamma - \frac{ZeE}{\hbar c} + 1, 2\gamma + 1, 2qR) + \left( \frac{k - Z\alpha mc^2/\hbar c}{\frac{Z\alpha E}{\hbar c} - \gamma} \right) 1F_1(\gamma - \frac{ZeE}{\hbar c}, 2\gamma + 1, 2qR)
\end{array} \right]. \tag{26}
\]

Eq. (24) reduces the computation of the energy of the electron to the solution of an equation for a single unknown, \( E \), with parameters \( W, k, \) and \( R \).

3 Results

Whereas the equations here can be used to compute the relativistic effects of confinement on the energy levels of any hydrogen-like atom, the data presented will be restricted to a comparison of the non-relativistic and relativistic energies of the hydrogen atom. In addition, to avoid imaginary arguments in the Bessel functions, we restrict total energy \( E \) to be less than \( mc^2 \) and \( W \) to be less than \( 2mc^2 \), while also requiring \( W \) to be larger than \( E \) (which is necessary for the electron to be confined). Restricting \( E \) to be less than \( mc^2 \) also helps us to avoid imaginary elements in Eq. (26) (or the left hand side of Eq. (24)).

Solutions for the binding energy values of the confined atom, which come from solving Eq. (24), requires a numerical method that avoids taking derivatives. This is because the unknown \( E \) exists in the first parameter of the hypergeometric functions, and derivatives with respect to their parameters necessitate further approximation. This in turn would produce less accurate results for energy. The obvious go-to method that does not require
taking derivatives is the Bisection method \[11\], which is what we will employ to help solve for \( E \). To check the accuracy of the numerical analysis we also make use of Brent’s method \[12\], which similarly does not warrant derivatives.

In the case of an unconfined H-atom, the requirement that the solution of the Dirac equation in a coulomb field converges makes it necessary that the first parameter in the confluent hypergeometric function be a negative integer, resulting in a description of the state of the atom in terms of a quantum number \( n \). Here, in the case of the confined atom, no such condition is necessary because of the finite value of \( R \). Therefore, the state of the electron in this model is distinguished only by the integer \( k = \pm (j + \frac{1}{2}) \), connected to the angular momentum quantum number \( j \).

In order to perform a discernible comparison with the non-relativistic model from Ref. 4, we must convey our results using the same language as the non-relativistic theory. Solving for energy using the Dirac equation gives you the total energy, whereas solving for energy using the Schrodinger equation gives you the binding energy. It is noted in Ref. 8 that you can obtain the binding energy from the total energy by subtracting \( mc^2 \) from \( E \). We therefore introduce the energy variable \( E_{\text{bind}} = E - mc^2 \) along with the barrier height parameter \( V_0 = W - mc^2 \) (after solving for \( E \) in Eq. (24)), which will be used for comparing the relativistic model based on Eq. (24) with the non-relativistic model from Ref. 4.

| \( R \) (\( a_0 \)) | \( E_{\text{bind}} \) (Nonrel eV) | \( E_{\text{bind}} \) (Rel eV) |
|---|---|---|
| 2.04918 | -11.882607 | -4.2807435 |
| 2.51487 | -12.824073 | -9.243599 |
| 3.15412 | -13.336981 | -11.978529 |
| 3.45203 | -13.443100 | -12.568924 |
| 4.08889 | -13.550580 | -13.210255 |
| 4.87924 | -13.591395 | -13.488761 |
| 5.77827 | -13.602279 | -13.577845 |

Table 1: Comparison of relativistic (\( k = -1 \)) and non-relativistic hydrogen ground state binding energies. The confining radii \( R \), in multiples of the Bohr radius, was taken from Ref. 4 and used in Eq. (24) to produce relativistic energies. Both sets of energies were also computed by setting \( V_0 = 0 \).

Table 1 compares relativistic binding energies derived from Eq. (24) by use of the Bisection method with non-relativistic binding energies from Ref. 4. To check the accuracy of the relativistic results in Table 1, Table 2 compares energy values obtained using Brent’s method to energy values obtained using the Bisection method, where each set of energy values were computed using the same domain of \( R \) values. The essentially identical energies given by the two methods serve as a check on the precision of the relativistic results in Table 1 as well as the results that will follow.

All energies in Table 1 are plotted in Figure 1(a) as a function of the confining radius \( R \) in units of \( a_0 \). As the radius of confinement increases, the plot shows that the energies approach the value \(-13.6eV\) associated with the \( 1s_{1/2} \) state (\( 1s \) state in the non-relativistic context) in the free atom. It is significant that the relativistic and non-relativistic energy values are in close agreement for relatively weak confinement, corresponding to \( R \) values
$R (a_0)$ | $E_{\text{bind}}$ (eV)-Bisection | $E_{\text{bind}}$ (eV)-Brent’s
---|---|---
1.84 | -0.20305021 | -0.20305008
2.14 | -5.60050384 | -5.60050372
2.44 | -8.69302215 | -8.69302181
2.74 | -10.5382419 | -10.5382415
3.04 | -11.6702382 | -11.6702385
3.34 | -12.3777199 | -12.3777201
3.64 | -12.8251123 | -12.8251127
3.94 | -13.1098944 | -13.1098948
4.24 | -13.2916421 | -13.2916418
4.54 | -13.4075874 | -13.4075873
4.84 | -13.4813634 | -13.4813634
5.14 | -13.5281127 | -13.5281131
5.44 | -13.5575839 | -13.5575841

Table 2: Ground state ($k = -1$) binding energy versus confinement radius in units of Bohr radii with the barrier height $V_0 = 0$ using Bisection and Brent’s method. Both sets of energies are for relativistic hydrogen, derived from Eq. (24).

greater than about 4.5 Bohr radii. However, for $R$ values approaching 2 Bohr radii, the energy values derived from Eq. (24) are significantly higher than the non-relativistic values (by a factor approaching 3).

![Figure 1](image_url)

Figure 1: Binding energy (eV) versus confinement radius ($a_0$) with $V_0 = 0$. (a) The relativistic curve represents the $1s_{1/2}$ state with $k = -1$ while the non-relativistic curve represents the $1s$ state from Ref. 4. (b) More $k = -1$ relativistic states appear as $R$ becomes large.

When the barrier wall is very close to the nucleus, the electron can only be in its ground state. Conversely, when the barrier is moved further from the nucleus, the volume of the atom accommodates states of the electron with larger orbits, associated with higher values of the quantum numbers $n$ and $\ell$ in the free atom. In particular, Figure 1(b) graphs the binding energies of additional solutions of Eq. (24) found for $k = -1$ and larger values.
of the confining radius \( R \). The graph shows that as \( R \) increases, the computed energy values asymptotically approach the binding energies of the free atom \cite{8} corresponding to the electron states \( 2s_{1/2}, 3s_{1/2}, \) and \( 4s_{1/2} \), which all have \( \ell = 0 \).

Figure 2: Relativistic binding energy (eV) versus confinement radius \((a_0)\) with \( V_0 = 0 \). (a) For \( k = +1 \), the \( 2p_{1/2}, 3p_{1/2}, \) and \( 4p_{1/2} \) states appear as \( R \) becomes large. (b) For \( k = -2 \), the \( 2p_{3/2}, 3p_{3/2}, \) and \( 4p_{3/2} \) states appear as \( R \) becomes large.

It is noteworthy that these energy values are determined only by the quantum number \( k \) and the position of the barrier wall restricting the electron to specific states. Figure 2(a) shows a set of solutions of Eq. (24) for \( k = +1 \), with the the same domain of \( R \) values as in Figure 1(b). Here, as \( R \) increases the energy values approach the binding energies of the free atom \cite{8} corresponding to the electron states \( 2p_{1/2}, 3p_{1/2}, \) and \( 4p_{1/2} \), all of which have \( \ell = 1 \) and \( j = \ell - \frac{1}{2} \). Figure 2(b), with \( k = -2 \), displays the same behavior as Figures 1(b) and 2(a) with the same domain of confining radii. The energies in this graph also asymptotically approach the free atom values \cite{8} corresponding to the electron states \( 2p_{3/2}, 3p_{3/2}, \) and \( 4p_{3/2} \) as \( R \) becomes large, with \( \ell = 1 \) and \( j = \ell + \frac{1}{2} \).

4 Conclusion

We compare the binding energy values of the confined hydrogen atom obtained from Dirac theory with the binding energy values obtained from a non-relativistic calculation based on the Schrödinger equation from Ref. 4. The differences between the energy values of the compressed atom derived from the relativistic and non-relativistic calculations make evident the necessity for a relativistic treatment of a tightly confined atom. It is a consequence of the uncertainty principle that a reduction in the uncertainty in position of the atomic electron causes an increase in the uncertainty in the momentum of the electron and a consequent increase in the electron’s momentum. This increase in the momentum of the electron causes an increase in the energy of the electron, which can cause the energy to become relativistic. We show, in addition, the unexpected result that, without introduction of the principle
quantum number \( n \), the energy states of the confined atom, determined by a single quantum number \( k \), evolve into the known states of the free atom as the radius of the barrier becomes large.

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