Direct Derivation of a Reduced Dirac Equation for Two-Body Hydrogenlike Atoms

Gil Raviv (ugraviv@gmail.com)

Abstract

In contrast to the non-relativistic Schrodinger equation, there is no true two-body formulation using the relativistic Dirac equation for the case of a hydrogenlike atom. Instead, the relativistic Dirac equation treats the atom as a single particle in a Coulomb field asserted by a static nucleus of infinite mass located at its core, which fails to take into account the nuclear mass and recoil. A new simple and elegant approach is presented that allows for the formulation of a true two-body relativistic equation, as well as for the reduction of the formula into an equivalent one-body equation with a readily known solution.

A special and important case of a two-body system is the case of two particles of mass m and M interacting via a potential $V(\vec{r}_1 - \vec{r}_2)$ that depends on the relative coordinate $\vec{r} = \vec{r}_1 - \vec{r}_2$, rather than on their individual positions $\vec{r}_1$ and $\vec{r}_2$. It is well established that in the case of the non-relativistic Schrodinger equation, the problem of two mutually interacting particles can be formulated and easily transformed into a problem of a single particle of reduced mass $\mu = \frac{mM}{m+M}$ and position $\vec{r}$ when viewing the particles within the inertial frame where their center of momentum (CM) is at rest [1]. In the relativistic approach, however, a simple extension of the Schrodinger equation for a two-body hydrogenlike system is not yet available. Instead, the relativistic Dirac equation treats the atom as a single particle of mass m and charge -e in a Coulomb field asserted by a static nucleus of infinite mass and charge Ze located at its core, providing the following energy solutions [2,3,4]:

Equation 1

$$E_{n,j} = mc^2(f(n,j) - 1), \text{ with } f(n,j) = \left[1 + \frac{(Z\alpha)^2}{\left(\sqrt{\left(j+\frac{1}{2}\right)^2 - (Z\alpha)^2} + n - j - \frac{1}{2}\right)^2}\right]^{-\frac{1}{2}}$$

where α is the fine-structure constant, n is the principal quantum number and j is the total angular momentum of the state.

Consequently, unlike the non-relativistic Schrodinger equation, the relativistic theory fails to take into account the mass of the nucleus, and thus provides the same energy levels for the hydrogen atom as for the deuterium atom, contrary to experimental results. In addition, measurements of various hydrogenlike atoms reveal that the measured energy levels associated with photons emitted or absorbed in transition between various atomic energy levels are smaller than the values predicted by the one-body Dirac equation by almost precisely a factor of $\frac{1}{1+m/M}$ [2,3]. Since the electron motion in the case of a hydrogen atom is essentially non-relativistic, several articles have suggested to resolve these shortcomings by substituting the reduced mass μ in place of the mass m in equation 1 [2,3,5]. However, theoretical derivation that supports such a substitution has never been obtained. Therefore, while the relativistic Dirac equation provides the correct description of the atom's fine structure, it does not provide the proper mass dependence for a nucleus of finite mass. This problem has been sidestepped in QED by forming a new effective Hamiltonian $H = H_0 + V_C$, where $H_0 = \frac{{p_m}^2}{2m} + \frac{{p_M}^2}{2M} - \frac{Ze^2}{4\pi r}$ is the original Schrodinger

Hamiltonian and where V_C is a correction potential that includes the first order relativistic correction terms[1]. Thus, in essence, the finite nuclear mass problem was sidestepped by retreating back to the non-relativistic Schrodinger equation, where the need to replace the mass m by the reduced mass μ has been established on solid theoretical grounds, and by reinforcing the Hamiltonian.

The goal of this article is to generalize and apply the Dirac equation to hydrogenlike atoms, while taking into account both the finite masses of their nuclei as well as the full effect of nuclear recoil.

To begin, a well-known relativistic equation often used for analyzing collisions between two interacting particles of mass m and M provides[2]

Equation 2

$$W^2 = m^2c^4 + M^2c^4 + 2E_{m,restM}\,Mc^2$$

where W is the energy of the two-body system when viewed in the CM inertial frame, and where $E_{m,restM}$ is the energy of the particle of mass m when viewed in the inertial frame in which the particle of mass M is momentarily at rest. Consequently,

Equation 3

$$E_{m,restM} = \frac{W^2 - (m^2c^4 + M^2c^4)}{2Mc^2}$$

Note that since the CM is an inertial frame, and since the two particles are interacting only with each other, conservation of energy dictates that W is a constant of motion. Due to nuclear recoil, in order to constantly view the particle of mass m from an inertial frame where the nucleus is at rest, a periodic change of reference frame is required. However, as W is a constant of motion, equation 3 dictates that $E_{m,restM}$ must also be a constant of motion in spite of the periodic change of frame.

Our goal is to formulate an equation in which the energy levels W of the two-body system can be calculated. Since $E_{m,restM}$ is the energy of a single particle in a momentarily static Coulomb field, it can be described by the following one-body Dirac equation [4]:

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[1] Note that aside from first order relativistic corrections, which are naturally provided by the Dirac equation, the potential V_c is also comprised of additional terms that aim to resolve more subtle discrepancies with the observed spectrums of atoms, such as hyperfine structure, the Lamb shift, radiative-recoil effects, as well as corrections due to the strong and the weak interactions [3,4,5].

[2] Equation 2 can be proven as follows: The four-momentum vectors of the particles of mass m and M in the frame where the particle of mass M is momentarily at rest are $P_{m,restM} = \left(E_{m,restM}, p_{mrestM,x}, p_{mrestM,y}, p_{mrestM,z}\right)$ and $P_{M,restM} = (Mc^2, 0,0,0)$, while in the inertial frame CM, $P_{Mc} = \left(E_{Mc}, p_{c,x}, p_{c,y}, p_{c,z}\right)$ and $P_{mc} = \left(E_{mc}, -p_{c,x}, -p_{c,y}, -p_{c,z}\right)$. Conservation of energy in the CM inertial frame dictates that the total energy W= $E_{Mc} + E_{mc}$ must be conserved. Adding the two four-momentum vectors within the CM frame yields $P_c = P_{mc} + P_{Mc} = (W, 0,0,0)$, and thus, $P_c^{\,2} = W^2 = (P_{mc} + P_{Mc})^2 = P_{mc}{}^2 + 2P_{mc} \cdot P_{Mc} + P_{Mc}{}^2$. It is given that $P_{mc}{}^2 = m^2c^4$ and $P_{Mc}{}^2 = M^2c^4$. Since $P_{mc} \cdot P_{Mc}$ is Lorenz invariant, it can be calculated in the inertial frame where particle M is momentarily at rest, where $P_{m,restM}\,P_{M,restM} = E_{m,restM}\,Mc^2$. Therefore $W^2 = m^2c^4 + M^2c^4 + 2E_{m,restM}\,Mc^2$.

Equation 4

$$\begin{pmatrix} -\frac{\left(E_{m,restM} + eA_0 - mc^2\right)}{c} & \vec{\sigma}\cdot\left(\vec{\mathrm{p}} + \frac{\mathrm{e}}{\mathrm{c}}\vec{\mathrm{A}}\right) \\ -\vec{\sigma}\cdot\left(\vec{\mathrm{p}} + \frac{\mathrm{e}}{\mathrm{c}}\vec{\mathrm{A}}\right) & \frac{\left(E_{m,restM} + eA_0 + mc^2\right)}{c} \end{pmatrix}\begin{pmatrix}\Psi_{\mathrm{mA}} \\ \Psi_{\mathrm{mB}}\end{pmatrix} = 0$$

In equation 4, $\vec{\mathrm{p}} = \frac{\hbar}{i}\nabla_{\mathrm{r}}$ is the momentum operator of the particle of mass m and $\vec{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ provides the Pauli matrices collected into a vector. Furthermore, $\left(A_0, \vec{\mathrm{A}}\right)$ denotes the 4-potential of the electromagnetic field asserted by the nucleus on the particle of mass m when viewed within the frame where the particle of mass M is momentarily at rest, while Ψ_{mA} and Ψ_{mB} are the two component spinors of that particle. Substituting the energy $E_{m,restM}$ from equation 3 into equation 4 yields

Equation 5

$$\begin{pmatrix} -\frac{\left(\frac{W^2 - (m^2c^4 + M^2c^4)}{2Mc^2} + eA_0 - mc^2\right)}{c} & \vec{\sigma}\cdot\left(\vec{\mathrm{p}} + \frac{\mathrm{e}}{\mathrm{c}}\vec{\mathrm{A}}\right) \\ -\vec{\sigma}\cdot\left(\vec{\mathrm{p}} + \frac{\mathrm{e}}{\mathrm{c}}\vec{\mathrm{A}}\right) & \frac{\left(\frac{W^2 - (m^2c^4 + M^2c^4)}{2Mc^2} + eA_0 + mc^2\right)}{c} \end{pmatrix}\begin{pmatrix}\Psi_{\mathrm{mA}} \\ \Psi_{\mathrm{mB}}\end{pmatrix} = 0$$

Thus, combining equation 3 with equation 4 produced an equation from which, in principle, the energy levels W of the two-body system within the CM frame of reference can be calculated via a single-particle Dirac equation. Consequently, a relativistic equation for the two-body system of finite mass can be formulated and reduced to a one-body equation that takes into account the masses of both particles.

Further note that equation 4 is identical to the equation initially used to solve the spectrum of the hydrogen atom for the case of a nucleus with infinite mass and with charge Ze . The same equation was shown at the non-relativistic limit to reduce to equation 1 given above. Substituting the energy $E_{m,restM} = E_{n,j} + mc^2$ from equation 1 into equation 2 provides

Equation 6

$$W^2 = m^2c^4 + M^2c^4 + 2Mmc^4\big(f(n,j)\big) = (m+M)^2c^4 + 2Mmc^4(f(n,j) - 1)$$

or

Equation 7

$$W = \pm(m+M)c^2\left(1 + \frac{2Mmc^4(f(n,j) - 1)}{(m+M)^2c^4}\right)^{1/2}$$

where positive values of W represent the energy levels of hydrogenlike atoms, while negative values of W indicate the energy levels of anti-hydrogenlike atoms. For simplicity, and without loss of generality, the minus sign will be dropped and only the special case of an actual hydrogen atom will be discussed.

In the case of the hydrogen atom, $\left|E_{n,j}\right| = |mc^2(f(n,j) - 1)| \leq 13.6\ ev$ (the ground level energy), thus defining $x = \frac{2Mmc^4(f(n,j)-1)}{(m+M)^2c^4}$ and using the relations $\frac{M}{m+M} < 1$ and $(m+M)c^2 \approx 9.385 * 10^8 ev$ leads to

$|x| \leq \frac{27.2ev*\frac{M}{(m+M)}}{(m+M)c^2} < \frac{27.2ev}{9.385*10^8 ev} < 3*10^{-8}$

and to

Equation 8

$W = (m+M)c^2(1+x)^{1/2}$

Defining the function $g(x) = \sqrt{1+x}$, the Taylor expansion around $x = 0$ provides

$$g(x) = \sum_{n=0}^{\infty} \frac{g^{(n)}(0)}{n!} x^n$$

where $g^{(0)}(0) = 1$, $g^{(1)}(0) = \left[\frac{1}{2}(1+x)^{-1/2}\right]_{x=0} = \frac{1}{2}$, $g^{(2)}(0) = \left[-\frac{1}{4}(1+x)^{-3/2}\right]_{x=0} = -\frac{1}{4}$, $g^{(3)}(0) = \left[\frac{3}{8}(1+x)^{-5/2}\right]_{x=0} = \frac{3}{8}$ and $g^{(n)}(0) = (-1)^{n+1}\left|\frac{2n-3}{2^n}\right|$ for any integer $n \geq 1$.

Therefore, $g(x) = 1 + \sum_{n=1}^{\infty}(-1)^{n+1}a_n$, where $a_n = \left|\frac{2n-3}{2^n}\right| x^n$

The series $\{a_n\}$ converges monotonically to 0 for all $0 < x < 1$. Thus according to the Leibniz test for alternating series, the series $1 + \sum_{n=1}^{\infty}(-1)^{n+1}a_n$ is convergent and its tail, starting with the $m+1$ term, is bounded by

$$\left|\left(1 + \sum_{n=1}^{\infty}(-1)^{n+1}a_n\right) - \left(1 + \sum_{n=1}^{m}(-1)^{n+1}a_n\right)\right| \leq |a_m|$$

Consequently, the Taylor series of $[1+x]^{1/2}$ is convergent, and the absolute value of the ratio between its tail starting at the $m = 2$ term divided by a_1 is bounded by

$$\left|\frac{(1 + \sum_{n=1}^{\infty}(-1)^{n+1}a_n) - (1 + \sum_{n=1}^{2}(-1)^{n+1}a_n)}{a_1}\right| \leq \left|\frac{a_2}{a_1}\right| = \left|\frac{-\frac{1}{8}x^2}{\frac{1}{2}x}\right| < 7.5*10^{-9}$$

Note that the first term of the expansion ($= 1$) was not included in the denominator, as we are only interested in the spectrum energies and not in the rest mass of the hydrogen atom.

Therefore, replacing the term $(1+x)^{1/2}$ in equation 8 by the term $1 + 0.5x$ will result in negligible error. Thus,

Equation 9

$$W_{n,j} = (m+M)c^2\left(1 + \frac{2Mmc^4(f(n,j)-1)}{(m+M)^2c^4}\right)^{1/2} = \left((m+M)c^2 + \frac{Mm}{(M+m)}c^2(f(n,j)-1)\right)$$
$$= (m+M)c^2 + \mu c^2(f(n,j)-1)$$

Defining $W_{n,j}^{NR}$ and $E_{n,j}^{NR}$ as the non-relativistic energy levels of the hydrogen atom when calculated for the cases of finite and infinite nuclear mass respectively will lead to

$$W_{n,j}^{NR} = W_{n,j} - (m+M)c^2 = \mu c^2(f(n,j)-1) = \frac{M}{M+m}mc^2(f(n,j)-1) = \frac{1}{1+m/M}E_{n,j}^{NR}$$

Note that the equality $W_{n,j}^{NR} = \frac{1}{1+m/M} E_{n,j}^{NR}$ is in complete agreement with the experimental results referenced above, while $W_{n,j}^{NR} = \mu c^2(f(n,j) - 1)$ confirms, from the theoretical point of view, the suggested substitution of the reduced mass μ in place of the mass m in the hydrogenlike energy equation $E_{n,j} = mc^2(f(n,j) - 1)$.[3]

In summary, as demonstrated by equation 5, we were able to formulate a true two-body Dirac equation that transforms into an equivalent one-body particle equation for both relativistic and non-relativistic cases. This equation was solved for the case of the nearly non-relativistic hydrogenlike atom, and was shown to provide the expected solution of $W_{n,j}^{NR} = \mu c^2(f(n,j) - 1)$.

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[3] Note, however, that there is no reason to assume that the mass m should also simply be replaced by the reduced mass μ in higher-order corrections such as those associated with the hyperfine structure, radiative-recoil effects, or corrections due to the strong and the weak interactions. As stated in Eides et al., the dependence of these corrections on the masses of all of the constituents is expected to be more complicated [3].