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A new relativistic model for the hydrogen atom

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Abstract. A new theory for the description of relativistic particles of spin $\frac{1}{2}$ interacting with an external electromagnetic field is used to formulate a model of the hydrogen atom. The energy spectrum predicted by this model is in agreement with the spectrum obtained from the Dirac model when radiative corrections have been added. Our model, thus, predicts a Lamb shift. Energy levels are expressed in terms of the usual quantum numbers n, l, j, m and contrary to the Dirac model l is a 'good' quantum number in our model.

1. Introduction

The present paper is devoted to a study of a relativistic model of the hydrogen atom, considered as a particle of spin $\frac{1}{2}$ and electric charge e in an external electromagnetic field described by the Coulomb potential. The model is based on the theory presented in [1], and before giving the detailed definition of our model, we will shortly review the necessary properties of the general theory.

The spin $\frac{1}{2}$ particle is assumed to possess a continuous superselection rule [2] associated to the time-like unit four-vector n^μ, $\mu = 1, 2, 3, 4$ with $n^4 > 0$ and such that

$$g_{\mu\nu}n^\mu n^\nu = -c^2, \quad (g_{\mu\nu} = 1, 1, 1, -c^2).$$

It is thus described by a family of Hilbert spaces H_n. Each of which is isomorphic to $\mathbb{C}^2 \otimes L^2(\mathbb{R}^4, d^4x)$, the space of two valued functions

$$\psi(x) = \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \end{bmatrix}, \quad x \in \mathbb{R}^4$$

with the scalar product

$$<\psi, \varphi> = \int_{\mathbb{R}^4} d^4x \psi^\dagger(x)\varphi(x) = \int_{\mathbb{R}^4} d^4x \sum_{i=1}^{2} \psi_i^*(x)\varphi_i(x).$$

Accordingly, a state of the particle is described by a given time-like unit four-vector n^μ and a unit vector ψ_n of the corresponding H_n.

The superselection rule n^μ is closely related to our interpretation of the spin $\frac{1}{2}$ in the relativistic case. In fact, our spin observables are characterized by four 2×2

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matrices W_n^μ with $\mu = 1, 2, 3, 4$. For $n^\mu = n_0^\mu = (0, 0, 0, 1)$ they are given by

$$W_{n_0}^\mu = (\tfrac{1}{2}\boldsymbol{\sigma}, 0) \tag{1}$$

where $\boldsymbol{\sigma}$ denotes the Pauli matrices. And for any n^μ we define W_n^μ by

$$W_n^\mu = L(n)^\mu_\nu W_{n_0}^\nu \tag{2}$$

where $L(n)^\mu_\gamma$ denotes a boost, i.e. $L(n)^\mu_\nu n_0^\nu = n^\mu$.

The physical interpretation is as follows. Let us consider a space-like unit four-vector s^μ, i.e. $g_{\mu\nu}s^\mu s^\nu = 1$ and such that $g_{\mu\gamma}s^\mu n^\gamma = 0$. The observable $s_\mu W_n^\mu$ then corresponds to a measurement of the spin with a Stern–Gerlach apparatus whose time direction is given by n^μ and for which the (space) direction of the magnetic field is given by s^μ. This defines completely the state of the spin.

There exists a position observable in space-time $q^\mu = (\mathbf{q}, t)$ and a momentum-energy observable $p^\mu = (\mathbf{p}, E/c^2)$. The position observable is given by the four contravariant self-adjoint operators:

$$(q^\mu\psi)_n(x) = x^\mu\psi_n(x) \tag{3}$$

and the momentum-energy observable by the four contravariant self-adjoint operators:

$$(p^\mu\psi)_n(x) = -i\hbar g^{\mu\nu}\partial_\nu\psi_n(x). \tag{4}$$

∂_ν denotes the partial derivative relatively to x^ν.

The evolution of a particle is parametrized by a Lorentz invariant parameter τ, the historical time, and is governed by the Schrödinger equation

$$i\hbar\, \partial_\tau\psi_n = (K\psi)_n$$

where the operator K is a Lorentz invariant and self-adjoint operator. Moreover the evolution of n^μ is by assumption such that n^μ tends to be parallel to the mean value of p^μ [1].

For an electron (or positron) of charge e and mass M, interacting with an external electromagnetic field $A_\mu(x) = (\mathbf{A}(x), -V(x))$ we have proposed the following operator of evolution K.

$$\begin{aligned} K = {} & \frac{1}{2M} g_{\mu\nu}(p^\mu - eA^\mu(q))(p^\nu - eA^\nu(q)) \\ & - \frac{g_1\mu_0}{Mc^2}(p^\mu - eA^\mu(q))\tilde{F}_{\mu\nu}(q)W_n^\nu \\ & + \frac{g_2^2\mu_0^2}{8Mc^2}F_{\mu\nu}(q)n^\nu F^\mu{}_\rho(q)n^\rho \\ & - \frac{g_3\mu_0}{c^2}n^\mu\tilde{F}_{\mu\nu}(q)W_n^\nu \end{aligned} \tag{5}$$

where $F_{\mu\nu}(x) = \partial_\mu A_\nu(x) - \partial_\nu A_\mu(x)$ and $F_{\mu\nu}(x) = \frac{1}{2}\varepsilon_{\mu\nu\rho\lambda}\tilde{F}^{\rho\lambda}(x)$. We denote by μ_0 the Bohr magneton $e\hbar/2M$ and g_1, g_2, g_3 are dimensionless phenomenological constants. In fact we have shown in [1] that $g = g_1 + g_3$ is naturally interpreted as the g-factor of the anomalous magnetic moment.

2. The hydrogen atom

In the model of hydrogen atom the electron interacts with an external electromagnetic field described by the Coulomb potential:

$$A_\mu(x) = (\mathbf{o}, -V(x)) = \left(\mathbf{o}, \frac{e}{4\pi\varepsilon_0}\frac{1}{r}\right), \quad r = |\mathbf{x}| \tag{6}$$

where ε_0 denotes the vacuum dielectric constant.

The spectrum of the atom is identified with values of $E - Mc^2$ obtained by determining, for $n = n_0$, the solutions of the eigenvalue equations

$$K_{n_0}\psi = -\tfrac{1}{2}Mc^2\psi \tag{7}$$

and

$$p^4\psi = \frac{E}{c^2}\psi. \tag{8}$$

For the given choice (6) of $A_\mu(x)$ we have:

$$(F_{23}(x), F_{31}(x), F_{12}(x)) = \tilde{F}^{14}(x), \tilde{F}^{24}(x), \tilde{F}^{34}(x)) \equiv \boldsymbol{B}(x) = 0$$

and

$$(F_{14}(x), F_{24}(x), F_{34}(x)) = (\tilde{F}^{23}(x), \tilde{F}^{31}(x), \tilde{F}^{12}(x)) \equiv \mathbf{E}(x) = \frac{-e}{4\pi\varepsilon_0}\frac{\mathbf{x}}{r^3}.$$

Thus for $n = n_0$ we obtain the following evolution operator

$$K_{n_0} = \frac{1}{2M}\left[\mathbf{p}^2 - c^2\left(p^4 - \frac{e}{c^2}V(q)\right)^2\right] + \frac{g_1\mu_0}{2Mc^2}(\mathbf{p} \wedge \mathbf{E}(q))\boldsymbol{\sigma} + \frac{g_2^2\mu_0^2}{8Mc^4}\mathbf{E}^2(q). \tag{9}$$

Since K_{n_0} does not depend explicitly on q^4 we have $[K_{n_0}, p^4] = 0$ and the solutions of the eigenvalue equations (7) and (8) are of the form

$$\psi(x) = \exp(-iEt/\hbar)\varphi(\mathbf{x}) \tag{10}$$

where $\varphi(\mathbf{x})$ themselves are in $\mathbb{C}^2 \otimes L^2(\mathbb{R}^3, d^3x)$ and are solutions of the following eigenvalue equation

$$\left[\frac{-\hbar^2}{2M}\Delta - \frac{1}{2Mc^2}\left(E + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)^2 - \frac{g_1\mu_0}{2Mc^2}\frac{e}{4\pi\varepsilon_0}\mathbf{p} \wedge \frac{\mathbf{x}}{r^3}\cdot\boldsymbol{\sigma} + \frac{g_2^2\mu_0^2}{8Mc^4}\frac{e^2}{(4\pi\varepsilon_0)^2}\frac{1}{r^4}\right]\varphi(\mathbf{x}) = -\frac{1}{2}Mc^2\varphi(\mathbf{x}) \tag{11}$$

which has been obtained from (9). Since K_{n_0} and p^4 are rotation invariant they commute with the total angular momentum operators $\boldsymbol{J} = \boldsymbol{L} + \hbar\boldsymbol{\sigma}/2$ where $\boldsymbol{L} = \mathbf{q} \wedge \mathbf{p}$ is orbital angular momentum. Moreover it is evident that the operator $\boldsymbol{L}^2$ also commutes with K_{n_0} and p^4. Consequently we can determine solutions of (11) which also are eigenvectors for $\boldsymbol{L}^2$, $\boldsymbol{J}^2$ and $\boldsymbol{J}_3$

$$\begin{aligned} \boldsymbol{L}^2\varphi(\mathbf{x}) &= l(l+1)\hbar^2\varphi(\mathbf{x}) \\ \boldsymbol{J}^2\varphi(\mathbf{x}) &= j(j+1)\hbar^2\varphi(\mathbf{x}) \\ J_3\varphi(\mathbf{x}) &= m\hbar\varphi(\mathbf{x}). \end{aligned} \tag{12}$$

Thus, on the contrary to the Dirac model, the orbital angular momentum l is here a 'good' quantum number.

In view of the interpretation we point out that according to the symmetries of the solutions we have:

$$\int_{\mathbb{R}^3} d^3x\varphi^+(\mathbf{x})\mathbf{p}\varphi(\mathbf{x}) = 0.$$

This means that the corresponding wave packet around the mass shell, built up from the solutions of (10) and (11), represents a particle moving in space-time along the time axis. Thus the condition $n = n_0$ is clearly in agreement with the equations of evolution proposed in [1].

Because of (12) the solutions of (11) can be expressed by

$$\varphi(r, \theta, \varphi) = R(r)Y^m_{j,l}(\theta, \varphi) \tag{13}$$

in spherical coordinates, i.e. [3]

$$Y^m_{j,l}(\theta, \varphi) = (2l+1)^{-1/2}\begin{bmatrix} (l \mp m + \frac{1}{2})^{1/2}\, Y_l^{m-1/2}(\theta, \varphi) \\ \pm(l \pm m + \frac{1}{2})^{1/2}\, Y_l^{m+1/2}(\theta, \varphi) \end{bmatrix}$$

for respectively $l = j \pm 1/2$. ($Y_l^{m\pm 1/2}$ denotes the spherical harmonics.)
Now

$$\boldsymbol{L\sigma}\, Y^m_{j,l}(\theta, \varphi) = c(j, l)\hbar Y^m_{j,l}(\theta, \varphi) \tag{14}$$

for $c(j, l) = -l - 1$ or l according to whether $l = j + 1/2$ or $j - 1/2$. Moreover

$$\frac{-\hbar^2}{2M}\Delta = \frac{-\hbar^2}{2M}\frac{1}{r^2}\partial_r r^2\,\partial_r + \frac{1}{2Mr^2}\boldsymbol{L}^2 \tag{15}$$

in spherical coordinates. (13) is therefore a solution of (11) if the function $R(r)$ verifies the following differential equation:

$$\begin{aligned} \Bigg[\frac{-\hbar^2}{2M}\frac{1}{r^2}d_r r^2\, d_r + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2} - \frac{1}{2Mc^2}\left(E + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)^2 + \frac{g_1\mu_0}{2Mc^2}\frac{e}{4\pi\varepsilon_0}\frac{c(j, l)}{r^3} \\ + \frac{g_2^2\mu_0^2}{8Mc^4}\frac{e^2}{(4\pi\varepsilon_0)^2}\frac{1}{r^4}\Bigg]R(r) = -\frac{Mc^2}{2}R(r) \end{aligned} \tag{16}$$

obtained by replacing (13) in (11) and taking account of (12), (14) and (15).

We will put this equation in a more convenient form. For this purpose we introduce the fine structure constant $\alpha = e^2/4\pi\varepsilon_0\hbar c$ and the Bohr radius $a_0 = 4\pi\varepsilon_0\hbar^2/Me^2$. Since $\mu_0 = e\hbar/2M$ we obtain:

$$\left[\frac{-\hbar^2}{2M}\frac{1}{r^2}d_r r^2 d_r + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2} - \alpha^2 E\frac{a_0}{r} - \alpha^4\frac{Mc^2}{2}\frac{a_0^2}{r^2} + \alpha^4\frac{g_1 Mc^2}{4}c(j,l)\frac{a_0^3}{r^3} + \alpha^6\frac{g_2^2 Mc^2}{32}\frac{a_0^4}{r^4}\right]R(r) = \frac{E^2 - M^2c^4}{2Mc^2}R(r). \tag{17}$$

Thus finally the energy spectrum will be determined by the values of $E - Mc^2$ for which the solutions $R(r)$ of the radial equation (17) are in $L^2(\mathbb{R}_+, r^2\,dr)$.

The radial equation (17) formally looks like the corresponding one in the non-relativistic case where the particle interacts with the singular potential:

$$-\alpha^2 E\frac{a_0}{r} - \alpha^4\frac{Mc^2}{2}\frac{a_0^2}{r^2} + \alpha^4\frac{g_1 Mc^2}{4}c(j,l)\frac{a_0^3}{r^3} + \alpha^6\frac{g_2^2 Mc^2}{32}\frac{a_0^4}{r^4}.$$

Since E is of order Mc^2 we note that terms in r^{-2}, r^{-3} and r^{-4} are just perturbations.

Moreover one can show that exact solutions of (17) in $L^2(\mathbb{R}_+, r^2\,dr)$ behave like

$$R(r) = \exp(-r_0/r)0(r^{(g_1/g_2)c(j,l)}), \quad r_0 = \frac{\alpha^2 g_2}{4}a_0 \tag{18}$$

for $r \to 0$. Actually only terms in r^{-3} and r^{-4} are relevant for the nature of the singularity and thus (18) is in agreement with the results given by W. M. Frank, D. J. Land and R. M. Spector for a potential of the form $gr^{-4} + f_1 r^{-3} + f_2 r^{-2}$ where g, f_1 and f_2 are constants and $g > 0$ [4].

Accordingly solutions of (17) look like the corresponding one in the non-relativistic Schrödinger model except near the origin i.e. in the region where r is smaller or of order r_0 noting that $r_0 \ll a_0$ is much smaller than the mean value of r.

An important point is the comparison of our radial equation with the corresponding one for the large component wave function in the model of hydrogen atom derived from the Dirac equation. As a matter of fact we have shown in [1] that a free particle with $n = n_0$ in a state being an eigenstate of $K_0 = g_{\mu\gamma}p^\mu p^\gamma/2M$ with eigenvalue $-Mc^2/2$ can be identified with the corresponding large component of the Dirac theory when $\mathbf{p}^2$ is smaller than M^2c^2.

In the Dirac model of hydrogen atom [5] the energy spectrum is obtained by determining eigenstates $\psi_D(\mathbf{x})$ of the Dirac hamiltonian H_D

$$H_D = c\boldsymbol{\alpha}\mathbf{p} + eV(\mathbf{x}) + Mc^2\beta$$

with

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix} \quad \text{and} \quad \beta = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix}$$

for eigenvalue E, which are also eigenstates of J^2, J_3 and $\beta\pi$, where the operator π is defined by

$$\pi\psi_D(\mathbf{x}) = \psi_D(-\mathbf{x}).$$

In spherical coordinates such a solution is a four-spinor of the following form

$$\psi_D(r,\theta,\varphi) = \begin{bmatrix} u(r)Y^m_{j,l}(\theta,\varphi) \\ v(r)Y^m_{j,l'}(\theta,\varphi) \end{bmatrix}$$

where respectively $l' = j \mp 1/2$ for $l = j \pm 1/2$. Corresponding eigenvalue of $\beta\pi$ is $(-1)^l$.

The radial functions $u(r)$ and $v(r)$ are solution of the following first order differential system

$$ic\hbar\left(\frac{1}{r}d_r r - \frac{1 + c(j,l)}{r}\right)u(r) + (E + Mc^2 - eV(r))v(r) = 0$$

$$ic\hbar\left(\frac{1}{r}d_r r + \frac{1 + c(j,l)}{r}\right)v(r) + (E - Mc^2 - eV(r))u(r) = 0.$$

For positive energy solutions the large component is $u(r)Y^m_{j,l}(\theta,\varphi)$ and we have to compare the second order differential equation for $u(r)$ obtained by eliminating $v(r)$ in the previous system,

$$\left[\frac{-\hbar^2}{2M}\frac{1}{r^2}d_r r^2 d_r + \frac{\hbar^2}{2M}\frac{l(l+1) - \alpha^2}{r^2} - \alpha^2 E\frac{a_0}{r} + \frac{2Mc^2}{E + Mc^2(1 + \alpha^2 a_0/r)}\frac{\alpha^4 Mc^2}{4}\frac{a_0^3}{r^2}\left(\frac{c(j,l)}{r} - d_r\right)\right]u(r) = \frac{E^2 - M^2c^4}{2Mc^2}u(r) \tag{19}$$

with the corresponding one (17) for $R(r)$. Actually the comparison is meaningful only in the region where $\mathbf{p}^2 \ll M^2c^2$, i.e. in the region where electromagnetic field is not strong. In fact it is more convenient to compare the Dirac radial equation (19) with the one obtained from (17) by putting, in view of (18),

$$\tilde{R}(r) = \exp(r_0/r)R(r). \tag{20}$$

We then obtain

$$\left[\frac{-\hbar^2}{2M}\frac{1}{r^2}d_r r^2 d_r + \frac{\hbar^2}{2M}\frac{l(l+1) - \alpha^2}{r^2} - \alpha^2 E\frac{a_0}{r} + \frac{\alpha^4 Mc^2}{4}\frac{a_0^3}{r^2}\left(g_1\frac{c(j,l)}{r} - g_2 d_r\right)\right]\tilde{R}(r) = \frac{E^2 - M^2c^4}{2Mc^2}\tilde{R}(r). \tag{21}$$

For g_1 and g_2 equal to 1 this equation looks like (19) except for a factor $2Mc^2/(E + Mc^2(1 + \alpha^2 a_0/r))$ in the last two terms. Actually this factor is very close to 1 if $r \gg \alpha^2 a_0$ i.e. also greater than r_0. Then except in the region where electromagnetic field is strong our radial equation (21) for $g_1 = g_2 = 1$ gives rise to solutions very close to the corresponding ones of the Dirac model.

The spectrum has been evaluated in part 3 and the following results have been obtained. For $l = j \pm 1/2 \neq 0$

$$E - Mc^2 = -Mc^2\left[\frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4}\left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \pm \frac{n(g_1 - 1)}{2(j + \frac{1}{2})(j + \frac{1}{2} \pm \frac{1}{2})}\right) + 0(\alpha^6)\right] \tag{22}$$

where the principal quantum number n takes integer values such that $n \geq l + 1$.

For $l = j - \frac{1}{2} = 0$

$$E - Mc^2 = -Mc^2\left[\frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4}\left(n - \frac{3}{4} - n(g_2 - 1)\right) + 0(\alpha^6)\right] \tag{23}$$

and we note that for $g_1 = g_2 = 1$ these expansions coincide with the corresponding one from the Dirac model [5], i.e.:

$$E - Mc^2 = -Mc^2\left[\frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right) + 0(\alpha^6)\right]. \tag{24}$$

For g_1 and g_2 not equal to 1 expansions (22) and (23) differ from (24) by energy shift

$$\mp Mc^2\frac{\alpha^4}{4n^3}\frac{g_1 - 1}{(j+\frac{1}{2})(j+\frac{1}{2}\pm\frac{1}{2})} \quad \text{for} \quad l = j \pm \tfrac{1}{2} \neq 0 \tag{25}$$

and

$$Mc^2\frac{\alpha^4}{2n^3}(g_2 - 1) \quad \text{for } l = 0. \tag{26}$$

Such terms remove the degeneracy relatively to l in the Dirac spectrum and give rise to the Lamb shift.

Usually the Lamb shift is obtained as radiative corrections to the Dirac results. The correcting energy shift terms obtained by such a procedure are [6] for $l = j \pm \frac{1}{2} \neq 0$

$$Mc^2\frac{\alpha^4}{4n^3}\frac{\alpha}{\pi}\left(\frac{16}{3}\log\frac{R_y}{K_0(n, l)} \mp \frac{1}{(j+\frac{1}{2})(j+\frac{1}{2}\mp\frac{1}{2})}\right) \tag{27}$$

and for $l = 0$

$$Mc^2\frac{\alpha^4}{2n^3}\frac{8\alpha}{3\pi}\left(2\log\frac{1}{\alpha} + \log\frac{R_y}{K_0(n, 0)} + \frac{19}{30}\right). \tag{28}$$

For a definition of $K_0(n, l)$ and R_y we refer to [6]. Actually to compare these results with the corresponding ones (25) and (26) given by our model, we need only to know that for $l \neq 0$ the ratio $K_0(n, l)/R_y$ is very close to unity for any n (about) 0.95–0.97). For $l = 0$ this ratio is about 19.8 for $n = 1$ and varies slowly with n to 15.7 for $n = 4$ and it is not much smaller for $n = \infty$.

These radiative corrections are in very good agreement with the results of measurement performed on the $^2S_{1/2}$ and $^2P_{1/2}$ states, moreover there is also confirmation for S states of various n.

A comparison shows that the energy shift (25) and (26) depends on the principal quantum number n in the same way as (27) and (28) if we neglect the dependance of $K_0(n, l)/R_y$ on n which in any way is weak. In fact, we obtain a good numerical agreement by putting in (25) and (26) g_1 about 1.0015 and g_2 about 1.048.

Note that the experimental determination of the Lamb shift is indirect, it is extrapolated from the splitting of the Zeeman effect for different magnetic fields [7]. Since in our model, the dominating terms for the Zeeman effect, are the usual ones (with $g_1 + g_3 = g$), the interpretation of that experiment is the same.

To conclude we note that to obtain complete agreement with experimental results we must put in (15) and (17) instead of M, the free electron mass, the corresponding reduced mass and thus to take account of the non-infinite proton mass. In our theory such a modification can be understood in a completely covariant way [8], [9].

3. Evaluation of the energy spectrum

Our aim is now to evaluate the eigenvalues of the energy spectrum. More precisely we expect to determine the first terms of the power expansion in α^2 of these eigenvalues until term in α^4. To do this we use a perturbation method based on the observation that the radial wave function in our model is not so different (except near to the origin) from the usual ones obtained in the non-relativistic Schrödinger model of hydrogen atom.

At first we consider the case $l \neq 0$ for which the standard perturbation method can be directly applied. Let us consider the following eigenvalue equation:

$$\left[\frac{-\hbar^2}{2M}\frac{1}{r^2}d_r r^2 d_r + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2} - \alpha^2 Mc^2\frac{a_0}{r}\right]R(r) = \frac{E^2 - M^2c^4}{2Mc^2}R(r) \tag{29}$$

whose formal analogy with the radial equation of the Schrödinger hydrogen atom is obvious.

Then the solutions in $L^2(\mathbb{R}_+, r^2\,dr)$ of this equation are just the usual radial wave functions $R_{n,l}(r)$ [10] in the non-relativistic hydrogen atom. The corresponding eigenvalues are

$$\frac{E^2 - M^2c^4}{2Mc^2} = -Mc^2\frac{\alpha^2}{2n^2} \tag{30}$$

where n is any positive integer such that $n \geq l + 1$.

We evaluate the spectrum by considering (17) as a perturbation of the previous eigenvalue equation. The perturbation terms are thus:

$$-\alpha^2(E - Mc^2)\frac{a_0}{r} - \alpha^4\frac{Mc^2}{2}\frac{a_0^2}{r^2} + \alpha^4\frac{g_1 Mc^2}{4}c(j, l)\frac{a_0^3}{r^3} + \alpha^6\frac{g_2^2 Mc^2}{32}\frac{a_0^4}{r^4} = W$$

and the standard perturbation lead us to write (at first order)

$$\frac{E^2 - M^2c^4}{2Mc^2} = -Mc^2\frac{\alpha^2}{2n^2} + \int_0^\infty r^2\,dr R_{n,l}^*(r) W R_{n,l}(r).$$

In other respects we have [11]:

$$\int_0^\infty r^2\,dr\left(\frac{a_0}{r}\right)^k |R_{n,l}(r)|^2 = \begin{cases} 1/n^2 & \text{for } k = 1 \\ 1/(l+\frac{1}{2})n^3 & \text{for } k = 2 \\ 1/l(l+\frac{1}{2})(l+1)n^3 & \text{for } k = 3 \text{ and } l \neq 0 \\ \text{exists} & \text{for } k = 4 \text{ and } l \neq 0 \end{cases} \tag{31}$$

the term in r^{-4} in W which contributes to the spectrum by a term in α^6 can be neglected. Finally by virtue to the previous formula we obtain the relation

$$\frac{E^2 - M^2c^4}{2Mc^2} = -Mc^2\frac{\alpha^2}{2n^2} - (E - Mc^2)\frac{\alpha^2}{n^2} - \frac{Mc^2}{2}\frac{\alpha^4}{(l+\frac{1}{2})n^3} + \frac{g_1 Mc^2}{4}c(j, l)\frac{\alpha^4}{l(l+\frac{1}{2})(l+1)n^3}$$

that gives

$$E - Mc^2 = -Mc^2\left[\frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4}\left(\frac{n}{l+\frac{1}{2}} + \frac{g_1}{2}\frac{nc(j,l)}{l(l+\frac{1}{2})(l+1)} - \frac{3}{4}\right) + 0(\alpha^6)\right]$$

or

$$E - Mc^2 = -Mc^2\left[\frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right.\right.$$

$$\left.\left.\pm \frac{n}{2}\frac{g_1 - 1}{(j+\frac{1}{2})(j+\frac{1}{2}\pm\frac{1}{2})}\right) + 0(\alpha^6)\right], \quad \text{if } l = j \pm \tfrac{1}{2}. \tag{32}$$

We consider now the case $l = 0$. Obviously the standard perturbation method is not applicable in this case and must be modified. Actually we must consider the differential equation (21) for $\tilde{R}(r)$ defined by $R(r) = \exp(-r_0/r)\tilde{R}(r)$, where we have $l = 0$ and $c(j = \frac{1}{2}, l = 0) = 0$, i.e.

$$\left[\frac{-\hbar^2}{2M}\frac{1}{r^2}d_r r^2 d_r - \alpha^2 E\frac{a_0}{r} - \alpha^4\frac{Mc^2}{2}\frac{a_0^2}{r^2} - \alpha^4\frac{g_2 Mc^2}{4}\frac{a_0^3}{r^2}d_r\right]\tilde{R}(r)$$

$$= \frac{E^2 - M^2c^4}{2Mc^2}\tilde{R}(r). \tag{33}$$

In view of (18) for $l = 0$ and the definition of $\tilde{R}(r)$, $\tilde{R}(r)$ is in $L^2(\mathbb{R}_+, r^2\,dr)$ if $R(r)$ is too and conversely. Then the spectrum is also given by this value of $E - Mc^2$ such that there exists a solution of the previous Equation (33) which is in $L^2(\mathbb{R}_+, r^2\,dr)$.

As a consequence we can consider (33) as a perturbation of (29) for $l = 0$, the perturbation terms being

$$-\alpha^2(E - Mc^2)\frac{a_0}{r} - \alpha^4\frac{Mc^2}{2}\frac{a_0^2}{r^2} - \alpha^4\frac{g_2 Mc^2}{4}\frac{a_0^3}{r^2}d_r = W$$

and write as a first order perturbation

$$\frac{E^2 - M^2c^4}{2Mc^2} = -Mc^2\frac{\alpha^2}{2n^2} + \int_0^\infty r^2\,dr R^*_{n,0}(r) W R_{n,0}(r).$$

n is any positive integer.

Except terms given in (31) we have to calculate, in this expression, the term

$$\int_0^\infty R^*_{n0}(r)\frac{a_0^3}{r^2}\frac{d\,R_{n0}(r)}{dr}r^2\,dr.$$

Since $R_{nl}(r)$ are real functions and since $R_{nl}(r) \to 0$ as $r \to \infty$ it can be also written

$$\int_0^\infty \frac{a_0^3}{2}\frac{d}{dr}R_{n0}^2(r)\,dr = -\frac{a_0^3}{2}R_{n0}^2(0) = -\frac{2}{n^3}.$$

Finally we have the relation

$$\frac{E^2 - M^2c^4}{2Mc^2} = -Mc^2\frac{\alpha^2}{2n^2} - (E - Mc^2)\frac{\alpha^2}{n^2} - Mc^2\frac{\alpha^4}{n^3} + g_2 Mc^2\frac{\alpha^4}{2n^3}$$

that gives

$$E - Mc^2 = -Mc^2\left[\frac{\alpha^2}{2n^2} + \frac{\alpha^4}{2n^4}\left(n - \frac{3}{4} - n(g_2 - 1)\right) + 0(\alpha^6)\right]. \tag{34}$$

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