DEVELOPMENT OF NEW SPECTROSCOPIES FROM THE ECE FERMION EQUATION

by

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ABSTRACT

The hamiltonian structure of the ECE fermion equation is used with a well known but hitherto unused Pauli algebra to produce novel results including the magnetizability of the hydrogenic orbitals, and novel spin orbit terms. All of these results should produce observable new spectroscopies. If these spectroscopies are not observed experimentally quantum mechanics would become self inconsistent at a fundamental level. The way in which these results translate into particle collision theory is illustrated by an example.

Keywords: ECE theory, ECE fermion equation, novel use fo Pauli algebra, magnetizabilities of the hydrogenic orbitals, novel spin orbit coupling spectroscopies.

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1. INTRODUCTION

In recent papers of this series {1 - 10} a well known {11} Pauli algebra has been incorporated into the ECE fermion equation to produce several novel spectroscopies, each of which should be observable experimentally. The same type of theory can be used in particle collisions and scattering, and in low energy nuclear reactors. In Section 2 of this paper the novel use of Pauli algebra with the fermion equation is used to produce several more classes of results from each relevant hamiltonian. The energy expectation values for the hydrogenic orbitals are given in Section 3 using computer algebra. The first type of hamiltonian developed with this method produces the magnetizability of each hydrogenic orbital considered, giving a range of novel results. The way in which the theory translates into particle collision theory is exemplified. Three classes of new spin orbit hamiltonian are identified by applying this method to the usual spin orbit hamiltonian with novel application of Pauli algebra. The energy expectation values from each class are evaluated in Section 3 by computer algebra for the hydrogenic orbitals. These energy expectation values should be observable experimentally, otherwise quantum mechanics becomes internally self inconsistent. This methodology will be developed in several ways in future papers.

2. EVALUATION OF THE HAMILTONIANS

The complete hamiltonian being considered systematically term by term is:

$$H\phi = \left(mc^2 + e\phi + \frac{1}{2m}\underline{\sigma}\cdot\left(\underline{p} - e\underline{A}\right)\left(1 + \frac{e\phi}{2mc^2}\right)\underline{\sigma}\cdot\left(\underline{p} - e\underline{A}\right)\right)\phi \quad -(1)$$

in a semi classical theory where the electromagnetic field interacts with the hydrogen atom. The charge on an electron of a given orbital is -e, its mass is m, and for each polarization index of ECE theory the scalar and vector potentials of the electromagnetic field are respectively ϕ and $\underline{A}$. The SU(2) basis is used with the Pauli matrices $\underline{\sigma}$ as basis elements. The linear orbital momentum of an electron is p and the wavefunction is denoted ψ. In deriving this hamiltonian a non relativistic approximation is used:

$$E \sim mc^2 \quad -(2)$$

and it is assumed that

$$e\phi << mc^2 . \quad -(3)$$

Some terms of the hamiltonian (1) have been developed in immediately preceding papers using the well known {11} Pauli algebra:

$$\underline{\sigma} \cdot \underline{p} = \frac{\underline{\sigma} \cdot \underline{r}}{r^2} \left(\underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{L} \right) \quad -(4)$$

where $\underline{r}$ is the position vector of the electron of an H atom orbital, and $\underline{L}$ is its angular momentum:

$$\underline{L} = \underline{r} \times \underline{p} . \quad -(5)$$

The spin angular momentum operator is defined as usual:

$$\underline{S} = \frac{1}{2} \hbar \underline{\sigma} . \quad -(6)$$

We first consider the term:

$$H_1 \psi = \frac{1}{2m} \underline{\sigma} \cdot \underline{p} \, \underline{\sigma} \cdot \underline{p} \, \psi \quad -(7)$$

which is the kinetic energy of the electron in the SU(2) basis. From Eqs. (4) and (7):

$$\underline{\sigma}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{p} = \frac{1}{r^2}\left(\underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{L}\right)\left(\underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{L}\right)$$

$$= \frac{1}{r^2}\left(\underline{r}\cdot\underline{p}\,\underline{r}\cdot\underline{p} + i\left(\underline{r}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{L} + \underline{\sigma}\cdot\underline{L}\,\underline{r}\cdot\underline{p}\right) - L^2 - i\underline{\sigma}\cdot\underline{L}\times\underline{L}\right) \quad -(8)$$

This classical equation is quantized using {1 - 11}:

$$\underline{r}\cdot\underline{p}\,\phi = \frac{\hbar}{i}\, r\frac{\partial\phi}{\partial r} \quad -(9)$$

$$L^2\phi = \hbar^2 l(l+1)\phi \quad -(10)$$

$$\underline{L}\times\underline{L}\,\phi = i\hbar\phi \quad -(11)$$

$$\underline{S}\cdot\underline{L}\,\phi = \frac{\hbar^2}{2}\left(j(j+1) - l(l+1) - s(s+1)\right)\phi \quad -(12)$$

Therefore:

$$\underline{r}\cdot\underline{p}\left(\underline{r}\cdot\underline{p}\,\phi\right) = \frac{\hbar}{i}\, r\left(\frac{\partial}{\partial r}\left(\left(\frac{\hbar}{i}\, r\frac{\partial}{\partial r}\right)\phi\right)\right) \quad -(13)$$

using the Leibnitz Theorem:

$$\underline{r}\cdot\underline{p}\left(\underline{r}\cdot\underline{p}\,\phi\right) = -\hbar^2 r\left(\left(\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)\right)\phi + \frac{\partial r}{\partial r}\frac{\partial\phi}{\partial r}\right)$$

$$= -\hbar^2\left(2r\frac{\partial\phi}{\partial r} + r^2\frac{\partial^2\phi}{\partial r^2}\right)$$

$$= -\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right). \quad -(14)$$

Now use:

$$\frac{\partial}{\partial r}\left(\underline{\sigma}\cdot\underline{L}\,\phi\right) = \underline{\sigma}\cdot\underline{L}\,\frac{\partial\phi}{\partial r}, \quad -(15)$$

$$\underline{p} = -i\hbar\underline{\nabla} \quad -(16)$$

to find that Eq. (7) is:

$$-\frac{\hbar^2}{2m}\nabla^2\phi = \frac{1}{2m}\Big(-\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right) - \frac{\ell(\ell+1)}{r^2}\phi + \frac{\hbar}{r}\left(\frac{\partial}{\partial r}\left(\underline{\sigma}\cdot\underline{L}\phi\right) + \underline{\sigma}\cdot\underline{L}\frac{\partial\phi}{\partial r}\right) + \hbar\frac{\underline{\sigma}\cdot\underline{L}}{r^2}\phi \qquad -(17)$$

in which:

$$\underline{\sigma}\cdot\underline{L}\phi = \frac{2}{\hbar}\underline{S}\cdot\underline{L}\phi = \hbar\big(j(j+1)-\ell(\ell+1)-s(s+1)\big)\phi \qquad -(18)$$

Therefore the hamiltonian H_1 can be expressed as

$$H_1\phi = -\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+\ell(\ell+1)\phi\right)+\frac{1}{2m}\left(\frac{2}{r}\underline{S}\cdot\underline{L}\left(2\frac{\partial\phi}{\partial r}+\frac{\phi}{r}\right)\right) \qquad -(19)$$

The laplacian in spherical polar coordinates is:

$$\nabla^2\phi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right)+\frac{1}{r^2\sin\theta}\frac{\partial^2\phi}{\partial\phi^2} \qquad -(20)$$

and the spherical harmonics are defined {11} as:

$$L^2 Y_\ell^m = \ell(\ell+1)\hbar^2 Y_\ell^m \qquad -(21)$$

Therefore if:

$$\phi = Y_\ell^m \qquad -(22)$$

the first combination of terms in Eq. (19) is the laplacian term. The overall result is therefore:

$$-\frac{\hbar^2}{2m}\underline{\sigma}\cdot\underline{\nabla}\,\underline{\sigma}\cdot\underline{\nabla}\phi = -\frac{\hbar^2}{2m}\nabla^2\phi + \frac{1}{m}\left(\frac{\underline{S}\cdot\underline{L}}{r}\left(2\frac{\partial\phi}{\partial r}+\frac{\phi}{r}\right)\right) \quad -(23)$$

where

$$\phi = Y_\ell^m . \quad -(24)$$

The spherical harmonics are part of the hydrogenic wavefunctions and Eq. (23) is expressed in spherical polar coordinates. It can be written as:

$$-\frac{\hbar^2}{2m}\underline{\sigma}\cdot\underline{\nabla}\,\underline{\sigma}\cdot\underline{\nabla}\phi = -\frac{\hbar^2}{2m}\nabla^2\phi + \frac{\hbar^2}{2mr}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\left(2\frac{\partial\phi}{\partial r}+\frac{\phi}{r}\right) \quad -(24)$$

giving two novel classes of energy expectation values:

$$E_1 = \frac{\hbar^2}{m}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\int\phi^*\frac{1}{r}\frac{\partial\phi}{\partial r}\,d\tau \quad -(25)$$

and:

$$E_2 = \frac{\hbar^2}{2m}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\int\phi^*\frac{1}{r^2}\phi\,d\tau . \quad -(26)$$

A more rigorous development for the hydrogen atom would use the hamiltonian:

$$H_2\phi = \left(e\phi + \frac{1}{2m}\underline{\sigma}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{p}\right)\phi \quad -(27)$$

in a non relativistic approximation. The usual Schroedinger hamiltonian in the H atom is:

$$H_2 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad -(28)$$

where the interaction between the electron and proton is given by the Coulomb potential in which ϵ_0 is the S. I. permittivity in vacuo. Eq. (28) gives the well known hydrogenic wavefunctions instead of the spherical harmonics. Eq. (23) is therefore extended to:

$$H_4\psi = -\frac{\hbar^2}{2m}\nabla^2\psi - \frac{e^2}{4\pi\epsilon_0 r}\psi + \frac{1}{m}\left(\frac{\underline{S}\cdot\underline{L}}{r}\left(2\frac{\partial\psi}{\partial r} + \frac{\psi}{r}\right)\right) \quad -(29)$$

which has to be solved numerically

The next term to be developed using Eq. (4) is the term quadratic in the potential:

$$H_5\psi = \frac{e^2}{2m}\underline{\sigma}\cdot\underline{A}\;\underline{\sigma}\cdot\underline{A}\,\psi. \quad -(30)$$

Now note that:

$$\underline{\sigma}\cdot\underline{A} = \frac{\underline{\sigma}\cdot\underline{r}}{r^2}\left(\underline{r}\cdot\underline{A} + i\,\underline{\sigma}\cdot\underline{r}\times\underline{A}\right) \quad -(31)$$

$$\left(\underline{\sigma}\cdot\underline{A}\right)^* = \frac{\underline{\sigma}\cdot\underline{r}}{r^2}\left(\underline{r}\cdot\underline{A} - i\,\underline{\sigma}\cdot\underline{r}\times\underline{A}\right). \quad -(32)$$

For a uniform magnetic field:

$$\underline{A} = \frac{1}{2}\underline{B}\times\underline{r} \quad -(33)$$

and

$$\underline{r}\cdot\underline{A} = 0. \quad -(34)$$

So:

$$\left(\underline{\sigma}\cdot\underline{A}\right)\left(\underline{\sigma}\cdot\underline{A}\right)^* = \frac{1}{r^2}\underline{\sigma}\cdot\underline{r}\times\underline{A}\;\underline{\sigma}\cdot\underline{r}\times\underline{A}$$

$$= \frac{1}{r^2}\left(\underline{r}\cdot\underline{r}\;\underline{A}\cdot\underline{A} - \underline{r}\cdot\underline{A}\;\underline{A}\cdot\underline{r}\right) = A^2 \quad -(35)$$

Therefore the hamiltonian (30) can be developed for real $\underline{A}$ as:

$$H_5\phi = \frac{e^2}{2m}\,\underline{\sigma}\cdot\underline{A}\,\underline{\sigma}\cdot\underline{A}\,\phi = \frac{e^2}{2m}\,\underline{\sigma}\cdot\underline{A}\left(\underline{\sigma}\cdot\underline{A}\right)^*\phi$$

$$= \frac{e^2A^2}{2m}\,\phi \quad -(36)$$

From Eqs. (33) and (35):

$$\frac{1}{r^2}\,\underline{r}\times\underline{A}\cdot\underline{r}\times\underline{A} = \frac{1}{4r^2}\,\underline{r}\times(\underline{B}\times\underline{r})\cdot\underline{r}\times(\underline{B}\times\underline{r})$$

$$= \frac{1}{4r^2}\left(r^2\underline{B}\times\underline{r}\cdot\underline{B}\times\underline{r} - \underline{r}\cdot\underline{A}\,\underline{A}\cdot\underline{r}\right) \quad -(37)$$

$$= \frac{1}{4}\left(B^2r^2 - (\underline{r}\cdot\underline{B})(\underline{r}\cdot\underline{B})\right)$$

Therefore

$$H_5\phi = \frac{e^2}{8m}\left(B^2r^2 - (\underline{r}\cdot\underline{B})(\underline{r}\cdot\underline{B})\right)\phi \quad -(38)$$

which is quadratic in the magnetic flux density $\underline{B}$. For simplicity of argument assume that:

$$\underline{B} = B_Z\,\underline{k} \quad -(39)$$

then:

$$H_5\phi = \frac{e^2B_Z^2}{8m}\left(r^2 - Z^2\right)\phi = \frac{e^2B_Z^2}{8m}\,r^2\left(1-\cos^2\theta\right)\phi \quad -(40)$$

in spherical polar coordinates. The expectation values of energy are:

$$E_5 = \frac{e^2B_Z^2}{8m}\int \phi^*\,r^2\left(1-\cos^2\theta\right)\phi\,d\tau \quad -(41)$$

where the volume element in spherical polar coordinates is:

$$d\tau = r^2\sin\theta\,dr\,d\theta\,d\phi \quad -(42)$$

Therefore:

$$E_5 = \frac{e^2 B_Z^2}{8m} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \psi^* r^4 \left(1-\cos^2\theta\right) \sin\theta \, \psi \, dr \, d\theta \, d\phi \quad -(43)$$

and the magnetizability of the hydrogenic orbital is:

$$\chi = \frac{e^2}{8m} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \psi^* r^4 \left(1-\cos^2\theta\right) \sin\theta \, \psi \, dr \, d\theta \, d\phi \quad -(44)$$

The energy:

$$E = \chi B^2 \quad -(45)$$

can be used in second order perturbation theory in a novel way.

This type of theory can be translated as follows into particle collision theory.

Consider conservation of energy and momentum in the collision process:

$$E + E_1 = E' + E'' \quad -(46)$$

$$\underline{p} + \underline{p}_1 = \underline{p}' + \underline{p}'' . \quad -(47)$$

So the translation occurs as follows:

$$\underline{p}_1 \equiv e\underline{A} \; ; \quad E_1 \equiv e\phi . \quad -(48)$$

Consider now the kinetic energy hamiltonian:

$$H_6 \psi = \frac{1}{2m} \underline{\sigma} \cdot \underline{p}_1 \, \underline{\sigma} \cdot \underline{p}_1 \, \psi \quad -(49)$$

and let:

$$\underline{p}_1 = \frac{1}{2} \underline{B} \times \underline{r} \quad -(50)$$

in analogy with:

$$\underline{A} = \frac{1}{2}\underline{\beta} \times \underline{r} \quad -(51)$$

Therefore $\underline{\beta}$ is the gravitomagnetic field of the ECE engineering model {1 - 10}. The angular momentum associated with $\underline{p}_1$ is:

$$\underline{L}_1 = \underline{r} \times \underline{p}_1 = \frac{1}{2}\left(r^2\underline{\beta} - \underline{r}\,(\underline{r}\cdot\underline{\beta})\right). \quad -(52)$$

Note that:

$$\underline{r}\cdot\underline{p}_1 = \frac{1}{2}\underline{r}\cdot\underline{\beta}\times\underline{r} = \frac{1}{2}\underline{\beta}\cdot\underline{r}\times\underline{r} = 0. \quad -(53)$$

The Z axis angular momentum in spherical polar coordinates is:

$$L_{1Z} = \frac{1}{2} r^2 \beta_Z \left(1 - \cos^2\theta\right) \quad -(54)$$

so:

$$\beta_Z = m_1 \frac{d\theta}{dt} = m_1\,\omega \quad -(55)$$

where m_1 is the mass of the particle with momentum $\underline{p}_1$. Here:

$$\omega = \frac{d\theta}{dt} \quad -(56)$$

is the angular velocity of particle 1, the particle with momentum $\underline{p}_1$.

From Eq. (49):

$$H_6\psi = \frac{1}{8m}\left(\beta^2 r^2 - (\underline{r}\cdot\underline{\beta})(\underline{r}\cdot\underline{\beta})\right)\psi \quad -(57)$$

and if:

$$\underline{\beta} = \beta_Z\,\underline{k} \quad -(58)$$

the hamiltonian is:

$$H_6 \phi = \frac{m_1^2 \omega^2 r^2}{m} \left(1 - \cos^2 \theta\right) \phi \quad - (59)$$

whose energy expectation values are:

$$E_6 = \frac{m_1^2 \omega^2}{8m} \int \phi^* \left(1 - \cos^2 \theta\right) r^2 \phi \, d\tau \quad - (60)$$

If ϕ are the hydrogenic wavefunctions then E_6 are the energy levels of an H atom interacting with a particle of momentum $\underline{p}_1$ and angular momentum L_1 given by Eq. (52).

The conventional spin orbit term of the hamiltonian (1) is {1 - 11}:

$$H_7 \phi = \frac{c^2 \, \underline{\sigma} \cdot \underline{p} \; \underline{\sigma} \cdot \underline{p}}{E - e\phi + mc^2} \phi \quad - (61)$$

where the Coulomb potential:

$$\phi = - \frac{e}{4\pi \epsilon_0 r} \quad - (62)$$

is used to describe the attraction between the electron and proton of the H atom. In the non relativistic approximation:

$$E \sim mc^2 \quad - (63)$$

Eq. (61) becomes:

$$H_7 \phi = \frac{1}{2m} \underline{\sigma} \cdot \underline{p} \left(1 + \frac{e\phi}{2mc^2}\right) \underline{\sigma} \cdot \underline{p} \, \phi \quad - (64)$$

and the spin orbit hamiltonian becomes:

$$H_8 \phi = \frac{e}{4m^2 c^2} \underline{\sigma} \cdot \underline{p} \, \phi \, \underline{\sigma} \cdot \underline{p} \, \phi \quad - (65)$$

Now use Eq. (4) in Eq. (65) to find the novel hamiltonian:

$$H_8 \psi = \frac{e}{4m^2c^2}\left(\underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{L}\right)\frac{\phi}{r^2}\left(\underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{L}\right)\psi \quad -(66)$$

which gives several new spectroscopies.

The first class of novel spectroscopy is based on:

$$H_9 \psi = \frac{e}{4m^2c^2}\,\underline{r}\cdot\underline{p}\left(\frac{\phi}{r^2}\,\underline{r}\cdot\underline{p}\,\psi\right) \quad -(67)$$

where

$$\underline{r}\cdot\underline{p}\,\psi = -i\hbar r\frac{\partial \psi}{\partial r} \quad -(68)$$

in the operator representation {11}. So:

$$H_9 \psi = -\frac{ie\hbar r}{4m^2c^2}\frac{\partial}{\partial r}\left(\frac{\phi}{r^2}\,\underline{r}\cdot\underline{p}\,\psi\right) \quad -(69)$$

Now use:

$$\underline{\sigma}\cdot\underline{r}\;\underline{\sigma}\cdot\underline{p} = \underline{r}\cdot\underline{p} + i\underline{\sigma}\cdot\underline{L} \quad -(70)$$

so:

$$\underline{r}\cdot\underline{p} = \underline{\sigma}\cdot\underline{r}\;\underline{\sigma}\cdot\underline{p} - i\underline{\sigma}\cdot\underline{L} \quad -(71)$$

Therefore the real part of H_9 in Eq. (69) is:

$$\text{Real } H_9\psi = -\frac{e\hbar r}{4m^2c^2}\frac{\partial}{\partial r}\left(\frac{\phi}{r^2}\,\underline{\sigma}\cdot\underline{L}\,\psi\right) \quad -(72)$$

$$= -\frac{e\hbar^2 r}{4m^2c^2}\left(j(j+1) - l(l+1) - s(s+1)\right)\frac{\partial}{\partial r}\left(\frac{\phi}{r^2}\psi\right)$$

Using Eq. (62) gives:

$$H_q \psi = \frac{e^2\hbar^2}{16 m^2 c^2 \pi \epsilon_0}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\frac{1}{r^3}\left(3\psi - r\frac{\partial\psi}{\partial r}\right) \quad -(73)$$

which gives energy expectation values:

$$E_{q1} = \frac{3e^2\hbar^2}{16\pi\epsilon_0 m^2 c^2}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\int \frac{\psi^*\psi}{r^3}\, d\tau \quad -(74)$$

and

$$E_{q2} = \frac{-e^2\hbar^2}{16\pi\epsilon_0 m^2 c^2}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\int \frac{\psi^*\psi}{r^2}\, d\tau \quad -(75)$$

According to the Born interpretation of quantum mechanics these expectation values are observable. If they turn out to be unobservable quantum mechanics would have developed a deep internal self inconsistency.

The hydrogenic wavefunction is { 11 }:

$$\psi = R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi) \quad -(76)$$

so an integral such as (74) is:

$$E_{q1} = \frac{3e^2\hbar^2}{16\pi\epsilon_0 m^2 c^2}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\int_0^\infty \frac{R_{n\ell}^2}{r}\, dr \int_0^{2\pi}\int_0^{\pi} Y Y^* \sin\theta\, d\theta\, d\phi \quad -(77)$$

in which:

$$\left\langle \frac{1}{r^3}\right\rangle = \int_0^\infty \frac{R_{n\ell}^2}{r}\, dr = \left(\frac{Z}{a_0}\right)^3\left(n^3\ell\left(\ell+\frac{1}{2}\right)(\ell+1)\right)^{-1} \quad -(78)$$

where:

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad -(79)$$

is the Bohr radius {1 - 11}. Here n is the main quantum number, l is the angular momentum quantum number. These analytical results are confirmed numerically in Section 3. It is seen that the energy E_{91} diverges to infinity for S orbitals but is otherwise finite.

The main spin orbit hamiltonian (66) can be split into the following four hamiltonians, each of which gives a novel spectroscopy in general:

$$H_{10}\psi = \frac{e}{4m^2c^2}\underline{r}\cdot\underline{p}\left(\frac{\phi}{r^2}\underline{r}\cdot\underline{p}\psi\right) \quad -(80)$$

$$H_{11}\psi = \frac{ie}{4m^2c^2}\underline{\sigma}\cdot\underline{L}\left(\frac{\phi}{r^2}\underline{r}\cdot\underline{p}\psi\right) \quad -(81)$$

$$H_{12}\psi = \frac{ie}{4m^2e^2}\underline{r}\cdot\underline{p}\left(\frac{\phi}{r^2}\underline{\sigma}\cdot\underline{L}\psi\right) \quad -(82)$$

$$H_{13}\psi = -\frac{e}{4m^2c^2}\underline{\sigma}\cdot\underline{L}\left(\frac{\phi}{r^2}\underline{\sigma}\cdot\underline{L}\psi\right) \quad -(83)$$

In the remainder of this Section these are evaluated systematically, and their hydrogenic energy expectation values computed in Section 3. The first class to be considered is:

$$H_{11}\psi = \frac{ie}{4m^2c^2}\frac{\phi}{r^2}\underline{r}\cdot\underline{p}\,\underline{\sigma}\cdot\underline{L}\psi \quad -(84)$$

where:

$$\underline{S} = \frac{1}{2}\hbar\underline{\sigma} \quad -(85)$$

Therefore:

$$H_{11}\psi = \frac{ie\hbar}{4m^2c^2}\left(j(j+1) - l(l+1) - s(s+1)\right)\frac{\phi}{r^2}\underline{r}\cdot\underline{p}\psi \quad -(86)$$

where:

$$\underline{S}\cdot\underline{L}\,\psi = \frac{\hbar^2}{2}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\psi \quad -(87)$$

$$\phi = -\frac{e}{4\pi\epsilon_0 r} \quad -(88)$$

and:

$$\underline{r}\cdot\underline{p}\,\psi = -i\hbar r\frac{\partial\psi}{\partial r}. \quad -(89)$$

Therefore this class of hamiltonian is:

$$H_{11}\psi = -\frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\frac{1}{r^2}\frac{\partial\psi}{\partial r} \quad -(90)$$

Using the Coulombic potential (88) gives:

$$H_{12}\psi = \frac{e\hbar}{4m^2c^2}\underline{\sigma}\cdot\underline{L}\,\frac{\phi}{r}\frac{\partial\psi}{\partial r} \quad -(91)$$

whose hydrogenic energy expectation values are:

$$E_{11} = -\frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(j(j+1)-\ell(\ell+1)-s(s+1)\right)\int\frac{\psi^*}{r^2}\frac{\partial\psi}{\partial r}\,d\tau \quad -(92)$$

where:

$$\psi = R_{n\ell}(r)\,Y_{\ell m_\ell}(\theta,\phi) \quad -(93)$$

and:

$$d\tau = r^2\sin\theta\,dr\,d\theta\,d\phi. \quad -(94)$$

The second class to be considered is:

$$H_{13}\psi = -\frac{e}{4m^2c^2}\frac{\phi}{r^2}\,\underline{\sigma}\cdot\underline{L}\;\underline{\sigma}\cdot\underline{L}\,\psi \qquad -(95)$$

$$= -\frac{e}{4m^2c^2}\frac{\phi}{r^2}\left(L^2 + i\,\underline{\sigma}\cdot\underline{L}\times\underline{L}\right)\psi$$

Using the operator representation (11) gives the hamiltonian:

$$H_{13}\psi = \frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2r^3}\left(2l(l+1) - j(j+1) + s(s+1)\right)\psi \qquad -(96)$$

whose observable energy expectation values are:

$$E_{13} = \frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(2l(l+1) - j(j+1) + s(s+1)\right)\int\frac{\psi^*\psi}{r^3}\,d\tau \qquad -(97)$$

These are evaluated by computer algebra in Section 3.

The third class derives from:

$$H_{12}\psi = i\frac{e}{4m^2c^2}\,\underline{r}\cdot\underline{p}\left(\frac{\phi}{r^2}\,\underline{\sigma}\cdot\underline{L}\,\psi\right) \qquad -(98)$$

using again the operator representation (9). So:

$$H_{12}\psi = \frac{3e^2\hbar^2}{16\pi\epsilon_0 m^2c^2r^3}\left(j(j+1) - l(l+1) - s(s+1)\right)\psi \qquad -(99)$$

The fourth class derives from:

$$H_{10}\psi = \frac{e}{4m^2c^2}\,\underline{r}\cdot\underline{p}\left(\frac{\phi}{r^2}\,\underline{r}\cdot\underline{p}\,\psi\right) \qquad -(100)$$

in which the operator representation (9) is used twice, so that:

$$H_{10}\phi = -\frac{ie\hbar}{4m^2c^2}\, r\frac{\partial}{\partial r}\left(\frac{\phi}{r^2}\left(-i\hbar r\frac{\partial\phi}{\partial r}\right)\right)$$

$$= -\frac{e\hbar^2}{4m^2c^2}\, r\frac{\partial}{\partial r}\left(\frac{\phi}{r}\frac{\partial\phi}{\partial r}\right) \quad -(101)$$

Now note that $\partial\phi/\partial r$ is a function of r, so the Leibnitz Theorem applies as follows:

$$H_{10}\phi = -\frac{e\hbar^2}{4m^2c^2}\, r\left(\left(\frac{\partial}{\partial r}\left(\frac{\phi}{r}\right)\right)\frac{\partial\phi}{\partial r} + \frac{\phi}{r}\frac{\partial^2\phi}{\partial r^2}\right) \quad -(102)$$

Therefore this class of hamiltonian is:

$$H_{10}\phi = -\frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(\frac{2}{r^2}\frac{\partial\phi}{\partial r} - \frac{1}{r}\frac{\partial^2\phi}{\partial r^2}\right) \quad -(103)$$

whose observable energy expectation values are:

$$E_{10} = -\frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\int\psi^*\left(\frac{2}{r^2}\frac{\partial\psi}{\partial r} - \frac{1}{r}\frac{\partial^2\psi}{\partial r^2}\right)d\tau \quad -(104)$$

These are evaluated by computer algebra for the hydrogenic orbitals in Section 3.

The fifth class derives from:

$$H_{14}\phi = \frac{ie}{4m^2c^2}\,\underline{\sigma}\cdot\underline{L}\left(\frac{\phi}{r^2}\,\underline{r}\cdot\underline{p}\,\phi\right) \quad -(105)$$

in which the functional representation is used:

$$\underline{r}\cdot\underline{p} = \underline{\sigma}\cdot\underline{r}\;\underline{\sigma}\cdot\underline{p} - i\,\underline{\sigma}\cdot\underline{L} \quad -(106)$$

rather than the operator representation (9). This method gives:

$$\text{Real}\, H_{14}\phi = \frac{e}{4m^2c^2}\,\underline{\sigma}\cdot\underline{L}\left(\frac{\phi}{r^2}\,\underline{\sigma}\cdot\underline{L}\,\phi\right) \quad -(107)$$

which is the same as Eq. (95) except for a sign change. The sixth and final class considered here derives from:

$$H_{15}\phi = \frac{ie}{4m^2c^2}\,\underline{r}\cdot\underline{p}\left(\frac{\phi}{r^2}\,\underline{\sigma}\cdot\underline{L}\,\phi\right) \quad -(108)$$

in which the functional representation (106) is used. This method gives the same result as Eq. (84).

The three distinct types of spin orbit hamiltonian to emerge are as follows. Class I is:

$$H_{\underline{I}}\phi = \frac{-e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(\frac{2}{r^2}\frac{\partial\phi}{\partial r} - \frac{1}{r}\frac{\partial^2\phi}{\partial r^2}\right) \quad -(109)$$

Class II is:

$$H_{\underline{II}}\phi = \frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(j(j+1) - l(l+1) - s(s+1)\right)\left(3\phi - r\frac{\partial\phi}{\partial r}\right) \quad -(110)$$

and Class III is:

$$H_{\underline{III}}\phi = \frac{e^2\hbar^2}{16\pi\epsilon_0 m^2c^2}\left(2l(l+1) - j(j+1) + s(s+1)\right)\phi \quad -(111)$$

The observable hydrogenic energy eigenvalues of these classes are evaluated by computer algebra in Section 3, analysed and tabulated.

3. EVALUATION OF ENERGY EXPECTATION VALUES

Section by co author Horst Eckardt

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Development of new spectroscopies from the ECE fermion equation

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3 Evaluation of energy expectation values

In this section the expectation values of energies defined in section 2 are evaluated by computer algebra. Basis are the analytically given Hydrogen-like wave functions as used in papers 250 and 251. In general, integration of expectation values of r^n give results in factors

$$\langle r^n \rangle \propto \left(\frac{a_0}{Z} \right)^n \tag{112}$$

where n can be a positive or negative integer. a_0 is the Bohr radius and Z is the ordinal number of the Hydrogen-like orbital. Normally the latter should be set to 1 because no multi-particle interactions are contained in this simple analytical form of wave functions. The constant factors of the energy eigenvalues have been compiled in the following list, extended by their numerical values in electron Volts (eV). To obtain the full energy expectation values, the results

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listed in the tables have to be multiplied by these values.

$$E_1 = \frac{\hbar^2}{m}\,\frac{Z^2}{a_0^2} = 1074.26\,Z^2 \tag{113}$$

$$E_2 = \frac{\hbar^2}{2m}\,\frac{Z^2}{a_0^2} = 537.131\,Z^2 \tag{114}$$

$$E_5 = \frac{e^2\,B_Z^2}{8\,m}\,\frac{a_0^2}{Z^2} = 6.15650\,10^{-11}\,\frac{B_Z^2}{Z^2} \tag{115}$$

$$E_6 = \frac{{m_1}^2\,\omega^2}{8\,m}\,\frac{a_0^2}{Z^2} = 2.39835 \cdot 10^{27}\frac{m_1^2\omega^2}{Z^2} \tag{116}$$

$$E_{91} = \frac{3\,\hbar^2\,e^2}{16\,\pi\,\epsilon_0\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = 0.0429045\,Z^3 \tag{117}$$

$$E_{92} = -\frac{\hbar^2\,e^2}{16\,\pi\,\epsilon_0\,m^2\,c^2}\,\frac{Z^2}{a_0^2} = -0.0143015\,Z^3 \tag{118}$$

$$E_{10} = -\frac{\hbar^2\,e^2}{16\,\pi\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = -0.0143015\,Z^3 \tag{119}$$

$$E_{11} = -\frac{\hbar^2\,e^2}{16\,\pi\,\epsilon_0\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = -0.0143015\,Z^3 \tag{120}$$

$$E_{13} = \frac{\hbar^2\,e^2}{16\,\pi\,\epsilon_0\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = 0.0143015\,Z^3 \tag{121}$$

$$E_I = -\frac{\hbar^2\,e^2}{16\,\pi\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = -0.0143015\,Z^3 \tag{122}$$

$$E_{II} = \frac{\hbar^2\,e^2}{16\,\pi\,\epsilon_0\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = 0.0143015\,Z^3 \tag{123}$$

$$E_{III} = \frac{\hbar^2\,e^2}{16\,\pi\,\epsilon_0\,m^2\,c^2}\,\frac{Z^3}{a_0^3} = 0.0143015\,Z^3 \tag{124}$$

It can be seen that E_1 and E_2 give remarkable energies up to the keV range. These are reduced by a factor of 10 to 100 (see the following tables), but compared to the orbital energies these splittings are huge. The energies of the other energies come to lie in the range of $1/100\ eV$, leading to minor corrections of spectra as expected. Nevertheless they should be observable by sensitive spectrometers.

The energy eigenvalues have been grouped to three tables. In the first table, those depending only on non-relativistic quantum numbers $n,\ l,\ m_l$ are listed. In the second table, those with the common factor

$$F_j := j(j+1) - l(l+1) - s(s+1) \tag{125}$$

are shown and in the third table those with

$$F_j := 2\ l(l+1) - j(j+1) + s(s+1). \tag{126}$$

Thus the effect of F_j can be seen, in particular where this factor forces the energy eigenvalues to zero. In Table 1 the integrals for E_5 and E_6 are identical, however their effects are quite different. E_5 leads to a tiny correction of the Zeeman effect quadratic in the magnetic field, producing a magnetizability of orbitals (Eq.(44)), whereas E_6 is a correction due to mechanical rotations (Eq.(60)). E_{10}

n	l	m_l	$E_5\|E_6$ $[\frac{a_0^2}{Z^2}]$	$E_{10}\|E_I$ $[\frac{Z^3}{a_0^3}]$
1	0	0	2	-5
2	0	0	28	$-\frac{9}{16}$
2	1	0	12	$\frac{1}{48}$
2	1	±1	24	$\frac{1}{48}$
3	0	0	138	$-\frac{13}{81}$
3	1	0	72	$\frac{1}{81}$
3	1	±1	144	$\frac{1}{81}$
3	2	0 1	60	$\frac{1}{405}$
3	2	±1	72	$\frac{1}{405}$
3	2	±2	108	$\frac{1}{405}$

Table 1: Energies E_5, E_6, E_{10} and E_I.

and E_I (from Eq.(109)) have the same factors, leading to similar corrections. These are particlularly significant for the $1s$ orbital.

From the first table with relativistic quantum numbers (Table 2) it can be seen that E_{92} gives no spectral corrections at all. The integral (Eq.(75)) vanishes for all orbitals. E_{91} and E_{II} are not defined for s-like orbitals. As can be seen from Eq.(110), the first term of the integral produces an expectation value of $1/r^3$ which diverges for s states. The second term is identical to E_{92} and gives no contribution. E_1 and E_2 give only contributions for $l \neq 0$.

The energy expectation values of E_{13} and E_{III} are identical as can be seen from Eqs.(121,124) and Table 3. The integrands are the same as for E_{91}, leading to diverging integrals for s-like states.

n	l	m_l	j	s	m_s	m_j	F_j	E_1 $[\frac{Z^2}{a_0^2}]$	E_2 $[\frac{Z^2}{a_0^2}]$	E_{91} $[\frac{Z^3}{a_0^3}]$	E_{92} $[\frac{Z^3}{a_0^3}]$	E_{II} $[\frac{Z^3}{a_0^3}]$
1	0	0	1/2	1/2	-1/2	-1/2	0	0	0	—	0	—
1	0	0	1/2	1/2	1/2	1/2	0	0	0	—	0	—
2	0	0	1/2	1/2	-1/2	-1/2	0	0	0	—	0	—
2	0	0	1/2	1/2	1/2	1/2	0	0	0	—	0	—
2	1	-1	3/2	1/2	-1/2	-3/2	1	$-\frac{1}{24}$	$\frac{1}{12}$	$\frac{1}{24}$	0	$\frac{1}{8}$
2	1	-1	3/2	1/2	1/2	-1/2	1	$-\frac{1}{24}$	$\frac{1}{12}$	$\frac{1}{24}$	0	$\frac{1}{8}$
2	1	0	1/2	1/2	-1/2	-1/2	-1	$\frac{1}{24}$	$-\frac{1}{12}$	$-\frac{1}{24}$	0	$-\frac{1}{8}$
2	1	0	3/2	1/2	1/2	1/2	1	$-\frac{1}{24}$	$\frac{1}{12}$	$\frac{1}{24}$	0	$\frac{1}{8}$
2	1	1	1/2	1/2	-1/2	1/2	-1	$\frac{1}{24}$	$-\frac{1}{12}$	$-\frac{1}{24}$	0	$-\frac{1}{8}$
2	1	1	3/2	1/2	1/2	3/2	1	$-\frac{1}{24}$	$\frac{1}{12}$	$\frac{1}{24}$	0	$\frac{1}{8}$
3	0	0	1/2	1/2	-1/2	-1/2	0	0	0	—	0	—
3	0	0	1/2	1/2	1/2	1/2	0	0	0	—	0	—
3	1	-1	3/2	1/2	-1/2	-3/2	1	$-\frac{1}{81}$	$\frac{2}{81}$	$\frac{1}{81}$	0	$\frac{1}{27}$
3	1	-1	3/2	1/2	1/2	-1/2	1	$-\frac{1}{81}$	$\frac{2}{81}$	$\frac{1}{81}$	0	$\frac{1}{27}$
3	1	0	1/2	1/2	-1/2	-1/2	-1	$\frac{1}{81}$	$-\frac{2}{81}$	$-\frac{1}{81}$	0	$-\frac{1}{27}$
3	1	0	3/2	1/2	1/2	1/2	1	$-\frac{1}{81}$	$\frac{2}{81}$	$\frac{1}{81}$	0	$\frac{1}{27}$
3	1	1	1/2	1/2	-1/2	1/2	-1	$\frac{1}{81}$	$-\frac{2}{81}$	$-\frac{1}{81}$	0	$-\frac{1}{27}$
3	1	1	5/2	1/2	1/2	3/2	1	$-\frac{1}{81}$	$\frac{2}{81}$	$\frac{1}{81}$	0	$\frac{1}{27}$
3	2	-2	5/2	1/2	-1/2	-5/2	2	$-\frac{2}{135}$	$\frac{4}{135}$	$\frac{2}{405}$	0	$\frac{2}{135}$
3	2	-2	5/2	1/2	1/2	-3/2	2	$-\frac{2}{135}$	$\frac{4}{135}$	$\frac{2}{405}$	0	$\frac{2}{135}$
3	2	-1	3/2	1/2	-1/2	-3/2	-2	$\frac{2}{135}$	$-\frac{4}{135}$	$-\frac{2}{405}$	0	$-\frac{2}{135}$
3	2	-1	5/2	1/2	1/2	-1/2	2	$-\frac{2}{135}$	$\frac{4}{135}$	$\frac{2}{405}$	0	$\frac{2}{135}$
3	2	0	3/2	1/2	-1/2	-1/2	-2	$\frac{2}{135}$	$-\frac{4}{135}$	$-\frac{2}{405}$	0	$-\frac{2}{135}$
3	2	0	5/2	1/2	1/2	1/2	2	$-\frac{2}{135}$	$\frac{4}{135}$	$\frac{2}{405}$	0	$\frac{2}{135}$
3	2	1	3/2	1/2	-1/2	1/2	-2	$\frac{2}{135}$	$-\frac{4}{135}$	$-\frac{2}{405}$	0	$-\frac{2}{135}$
3	2	1	5/2	1/2	1/2	3/2	2	$-\frac{2}{135}$	$\frac{4}{135}$	$\frac{2}{405}$	0	$\frac{2}{135}$
3	2	2	3/2	1/2	-1/2	3/2	-2	$\frac{2}{135}$	$-\frac{4}{135}$	$-\frac{2}{405}$	0	$-\frac{2}{135}$
3	2	2	5/2	1/2	1/2	5/2	2	$-\frac{2}{135}$	$\frac{4}{135}$	$\frac{2}{405}$	0	$\frac{2}{135}$

Table 2: Energies E_1, E_2, E_{91}, E_{92} and E_{II} with $F_j = j(j+1) - l(l+1) - s(s+1)$.

n	l	m_l	j	s	m_s	m_j	F_j	$E_{13}\|E_{III}$ $[\frac{Z^3}{a_0^3}]$
1	0	0	1/2	1/2	-1/2	-1/2	0	—
1	0	0	1/2	1/2	1/2	-1/2	0	—
2	0	0	1/2	1/2	-1/2	-1/2	0	—
2	0	0	1/2	1/2	1/2	-1/2	0	—
2	1	-1	3/2	1/2	-1/2	-3/2	1	$\frac{1}{24}$
2	1	-1	3/2	1/2	1/2	-1/2	1	$\frac{1}{24}$
2	1	0	1/2	1/2	-1/2	-1/2	3	$\frac{1}{8}$
2	1	0	3/2	1/2	1/2	1/2	1	$\frac{1}{24}$
2	1	1	1/2	1/2	-1/2	1/2	3	$\frac{1}{8}$
2	1	1	3/2	1/2	1/2	3/2	1	$\frac{1}{24}$
3	0	0	1/2	1/2	-1/2	-1/2	0	—
3	0	0	1/2	1/2	1/2	-1/2	0	—
3	1	-1	3/2	1/2	-1/2	-3/2	1	$\frac{1}{81}$
3	1	-1	3/2	1/2	1/2	-1/2	1	$\frac{1}{81}$
3	1	0	1/2	1/2	-1/2	-1/2	3	$\frac{1}{27}$
3	1	0	3/2	1/2	1/2	1/2	1	$\frac{1}{81}$
3	1	1	1/2	1/2	-1/2	3/2	3	$\frac{1}{27}$
3	1	1	5/2	1/2	1/2	-5/2	1	$\frac{1}{81}$
3	2	-2	5/2	1/2	-1/2	-5/2	2	$\frac{4}{405}$
3	2	-2	5/2	1/2	1/2	-3/2	2	$\frac{4}{405}$
3	2	-1	3/2	1/2	-1/2	-3/2	2	$\frac{8}{405}$
3	2	-1	5/2	1/2	1/2	-1/2	2	$\frac{4}{405}$
3	2	0	3/2	1/2	-1/2	-1/2	2	$\frac{8}{405}$
3	2	0	5/2	1/2	1/2	1/2	2	$\frac{4}{405}$
3	2	1	3/2	1/2	-1/2	1/2	2	$\frac{8}{405}$
3	2	1	5/2	1/2	1/2	3/2	2	$\frac{4}{405}$
3	2	2	3/2	1/2	-1/2	3/2	2	$\frac{8}{405}$
3	2	2	5/2	1/2	1/2	5/2	2	$\frac{4}{405}$

Table 3: Energies E_{13} and E_{III} with $F_j = 2\ l(l+1) - j(j+1) + s(s+1)$.