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# Relativistic Density Functional Theory Method: Applications to Autoionization States of Atoms

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## Abstract

A brief introductory information about the accurate atomic calculations using Density Functional Theory has been reviewed. How relativistic effects can be considered in atomic calculations through the density functional theory has been discussed. Some sample calculation results for the autoionization states of the neutral and cationic atoms have been presented.

## 1. Introduction

The Newtonian assumption that the probe (light or photon) does not interact with the object of measurement is not valid in the microscopic world, because of uncertainty principle. Quantum mechanics was invented to overcome the difficulties introduced by the uncertainty principle. This is what leads to a probabilistic picture in quantum mechanics. The fundamental equation in quantum mechanics, the Schrödinger equation,  $H\psi = E\psi$ , is obtained by inserting the operators for the position and energy in the classical Hamiltonian energy expression;  $p_\alpha \rightarrow -i\hbar \frac{\partial}{\partial \alpha}$ ,  $\alpha = x, y, z$ ;  $E \rightarrow i\hbar \frac{\partial}{\partial t}$ . The Hamiltonian for a particle is given in classically, by

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V \quad (1)$$

substituting the appropriate operators for the momenta and energy we get the time-dependent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial \psi}{\partial x^2} + \frac{\partial \psi}{\partial y^2} + \frac{\partial \psi}{\partial z^2} \right) + V\psi = i\hbar \frac{\partial \psi}{\partial t} \quad (2)$$

If  $\psi$  does not depend on time, then the energy  $E$  is a constant of the system, then we obtain the time-independent Schrödinger equation:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial \psi}{\partial x^2} + \frac{\partial \psi}{\partial y^2} + \frac{\partial \psi}{\partial z^2} \right) + V\psi = E\psi \quad (3)$$

All quantum mechanical expressions, operators, and equations can be obtained from their classical expressions by simply replacing the appropriate operators. Both time-dependent and time-independent Schrödinger equations cannot be relativistic, since they were derived with the assumption that the kinetic energy is given by

$$T = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \quad (4)$$

However, in relativistic quantum mechanics the kinetic energy is no longer given by this expression, since the mass of a particle is a variable of the speed. The relativistic kinetic energy operator is different from

the nonrelativistic quantum mechanical kinetic energy term. The potential energy term is also different in relativistic picture. The Schrödinger equation is not Lorentz-invariant. Any physically acceptable relativistic wave equation must treat the spatial (space) and temporal (time) coordinates on equal footing, and must be Lorentz-invariant [1].

## 2. The Klein–Gordon Equation

In 1926 several physicists proposed such equations to treat relativistic quantum-mechanical problems. The energy of a free particle is given by

$$E = \sqrt{p^2 c^2 + m_0^2 c^4} \quad (5)$$

Substituting  $\mathbf{p} \rightarrow -i\hbar\nabla$ , and  $E \rightarrow i\hbar\frac{\partial}{\partial t}$  and then operating on a wavefunction  $\psi(x, y, z, t)$ , we obtain

$$i\hbar\frac{\partial\psi}{\partial t} = \sqrt{-\hbar^2 c^2 \nabla^2 + m_0^2 c^4} \psi \quad (6)$$

This form has some difficulties in solutions, the presence of a square-root term with the Laplacian operator poses some problems. A logical starting point is to use the square of the relativistic energy expression,

$$E^2 = p^2 c^2 + m_0^2 c^4 \quad (7)$$

This was done by Klein and Gordon [2], independently among several others, and hence came to be known as the Klein–Gordon equation [3,4],

$$-\hbar^2 \frac{\partial^2 \psi}{\partial t^2} = (-\hbar^2 c^2 \nabla^2 + m_0^2 c^4) \psi \quad (8)$$

This equation can be expressed in a more convenient form by the introduction of the operator

$$\square = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} - \frac{\partial^2}{\partial z^2} \quad (9)$$

The wave equation then can be written as

$$(\hbar^2 \square + m_0^2 c^2) \psi(x, y, z, t) = 0 \quad (10)$$

or, in relativistic units ( $\hbar = 1, c = 1$ )

$$(\square + m_0^2) \psi(x, y, z, t) = 0 \quad (11)$$

This equation is known as the Klein–Gordon equation for a free particle in the absence of any electromagnetic field. The solution of this equation yields a relativistic scalar wavefunction for a free particle. Klein–Gordon equation is Lorentz-invariant. For a free particle the solution is in plane-wave form (if  $\psi$  depends only on  $x$  and  $t$ ):

$$\psi(x, t) = e^{\frac{i}{\hbar}(p_0 t - \mathbf{p} \cdot \mathbf{x})} \quad (12)$$

$$cp_0 = E = \mp \sqrt{c^2 p^2 + m_0^2 c^4} \quad (13)$$

The Klein–Gordon equation for a charged particle moving in a static Coulomb field, represented by the wave function

$$\psi(\mathbf{r}, t) = u(\mathbf{r}) e^{-iEt} \quad (14)$$

is in the form

$$\nabla^2 u = [m_0^2 - (E - e\varphi)^2] u \quad (15)$$

Taking

$$u(\mathbf{r}) = R(r) Y_{lm}(\theta, \phi) \quad , \quad e\varphi(r) = -\frac{Ze^2}{4\pi r} \quad , \quad \alpha = \frac{e^2}{4\pi} \approx \frac{1}{137} \quad (16)$$

$$\frac{1}{\lambda} = Ze\alpha \quad , \quad \rho = \frac{r}{\lambda} \quad , \quad E = (m_0^2 - E^2)\lambda^2 > 0$$

the differential equation becomes

$$\left[ \frac{d^2}{d\rho^2} + \frac{2}{\rho} \frac{d}{d\rho} - \epsilon + \frac{Z}{\rho} - \frac{l(l+1) - Z^2\alpha^2}{\rho^2} \right] U(\rho) = 0 \quad (17)$$

where  $U(\rho) = R(r)$ . The energy expression becomes

$$E = m_0 \left\{ 1 + \frac{Z^2\alpha^2}{\left[ n_r + \frac{1}{2} + \sqrt{\left( l + \frac{1}{2} \right)^2 - Z^2\alpha^2} \right]^2} \right\}^{-1/2} \quad (18)$$

The Klein–Gordon equation for the Coulomb field requires that

$$(Z\alpha)^2 \leq \left( l + \frac{1}{2} \right)^2 \quad (19)$$

This means for the minimum value of  $Z$ , which occurs when  $l = 0$ ,

$$Z > \frac{1}{2\alpha} \quad \text{or} \quad Z > 69. \quad (20)$$

That is if  $Z > 69$ , the energy eigenvalue can become complex for the  $s$  orbitals, and thus the solution of the Klein–Gordon equation suggests that an atom cannot exist with  $Z > 69$ , as this would lead to complex energy eigenvalues. Therefore, it is clear that the Klein–Gordon equation does not yield satisfactory results for an electron in a Coulomb field. The problem is that an electron is a spin 1/2 particle; one must treat the angular momentum as a four–vector. Thus, the wave function of any spin particle, in general, cannot be described by a simple scalar wave function, one needs to seek a vectorial solution for the wave function in relativistic quantum mechanics of any particle possessing spin.

### 3. The Dirac Equation

Dirac in 1928 proposed a relativistic quantum–mechanical equation, now well known as the Dirac equation. Dirac proposed a first–order differential equation in both temporal and spatial coordinates. Dirac assumed that the relativistic wave function  $\psi$  consists of  $n$  components for a general positive integer  $n$ ; subsequently, it will be established that  $n$  is 4 [1]. Thus  $\psi$  is treated as a  $n$ –dimensional column vector with components  $\psi_1, \psi_2, \dots, \psi_n$ . The general first–order differential equation in both spatial and temporal coordinates looks like:

$$\frac{1}{c} \frac{\partial \psi_l}{\partial t} + \sum_{k=1}^3 \sum_{i=1}^n \alpha_{li}^k \frac{\partial \psi_i}{\partial x^k} + \frac{im_0c}{\hbar} \sum_{i=1}^n \beta_{li} \psi_i = 0 \quad (21)$$

where  $l = 1, 2, \dots, n$ .  $\alpha$  and  $\beta$  are dimensionless constants.

The Dirac equation is obtained once  $n$  and the matrices  $\alpha$  and  $\beta$  are determined. This is accomplished by stipulating that (a) the continuity equation for the charge density current be satisfied and (b) the free–particle solution satisfies the free–particle Klein–Gordon equation. The matrices  $\alpha$  and  $\beta$  are constructed as follows:

$$\alpha^k = \begin{bmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{bmatrix} \quad , \quad \beta = \begin{bmatrix} I & 0 \\ 0 & I \end{bmatrix} \quad (22)$$

where

$$I = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad , \quad \sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad , \quad \sigma_2 = \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \quad , \quad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (23)$$

$\sigma_k$  are Pauli matrices.

The Dirac equation for a free particle in the absence of any external field takes the form [1]

$$\frac{1}{c} \frac{\partial \psi}{\partial t} + (\alpha \cdot \nabla) \psi + \frac{im_0c}{\hbar} \beta \psi = 0 \quad (24)$$

or (considering  $\mathbf{p} \rightarrow -i\hbar\nabla$ ,  $E \rightarrow i\hbar\frac{\partial}{\partial t}$ )

$$[c(\boldsymbol{\alpha} \cdot \mathbf{p}) + \beta m_0 c^2]\psi = E\psi \quad (25)$$

Therefore, we derive the Dirac Hamiltonian for a free particle in the absence of any external field as

$$H = c(\boldsymbol{\alpha} \cdot \mathbf{p}) + \beta m_0 c^2 \quad (26)$$

The Dirac equation, as well as the Dirac Hamiltonian, is a  $4 \times 4$  matrix equation. Consequently, the wavefunction is also a column vector of length 4. This four-component wave function is called a **spinor**. Using the relations  $\gamma_k = -i\beta\alpha_k$ ,  $k = 1, 2, 3$ , and  $\gamma_4 = \beta$ , Dirac equation can be simplified further, (in relativistic units, that is  $\hbar = 1$ ,  $c = 1$ )

$$(\gamma_\mu \frac{\partial}{\partial x_\mu} + m_0)\psi = 0 \quad , \quad \mu = 1, 2, 3, 4 \quad (27)$$

The explicit form of the four equations in terms of spinors:

$$\left(\frac{\partial}{\partial t} + im_0\right)\psi_1 + \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\psi_4 + \frac{\partial}{\partial z}\psi_3 = 0 \quad (28)$$

$$\left(\frac{\partial}{\partial t} + im_0\right)\psi_2 + \left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\psi_3 - \frac{\partial}{\partial z}\psi_4 = 0 \quad (29)$$

$$\left(\frac{\partial}{\partial t} - im_0\right)\psi_3 + \left(\frac{\partial}{\partial x} - i\frac{\partial}{\partial y}\right)\psi_2 + \frac{\partial}{\partial z}\psi_1 = 0 \quad (30)$$

$$\left(\frac{\partial}{\partial t} - im_0\right)\psi_4 + \left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\psi_1 - \frac{\partial}{\partial z}\psi_2 = 0 \quad (31)$$

For free electron we seek a plane-wave solution for each component. Thus the following form for the components is taken:

$$\psi_\mu = A_\mu e^{i(\mathbf{p}\cdot\mathbf{r} - Et)} \quad (32)$$

The expression for energy,  $E$ , takes the following form:

$$[E^2 - m_0^2 - (p_1^2 + p_2^2 + p_3^2)]^2 = 0 \quad (33)$$

or

$$E_\mp = \mp \sqrt{p_1^2 + p_2^2 + p_3^2 + m_0^2} \quad (34)$$

The Dirac equation for a charged particle in an electromagnetic field is given as

$$(\gamma_\mu \Pi_\mu - im_0)\psi = 0 \quad (35)$$

This equation explicitly splits into the following four equations in terms of the four components,

$$\left(-i\frac{\partial}{\partial t} - e\varphi + m_0\right)\psi_1 + \Pi_- \psi_4 + \Pi_3 \psi_3 = 0 \quad (36)$$

$$\left(-i\frac{\partial}{\partial t} - e\varphi + m_0\right)\psi_2 + \Pi_+ \psi_3 - \Pi_3 \psi_4 = 0 \quad (37)$$

$$\left(-i\frac{\partial}{\partial t} - e\varphi + m_0\right)\psi_3 + \Pi_- \psi_2 + \Pi_3 \psi_1 = 0 \quad (38)$$

$$\left(-i\frac{\partial}{\partial t} - e\varphi + m_0\right)\psi_4 + \Pi_+ \psi_1 - \Pi_3 \psi_2 = 0 \quad (39)$$

where

$$\Pi_\mp = \Pi_1 \mp i\Pi_2 \quad (40)$$

$$\Pi_k = -i\frac{\partial}{\partial x_k} + eA_k \quad (k = 1, 2, 3) \quad (\text{spatial conjugate}) \quad (41)$$

$$\Pi_4 = -\frac{\partial}{\partial t} + ie\varphi \quad (\text{temporal conjugate}) \quad (42)$$

## 4. The Dirac Equation for the Hydrogen Atom

The Dirac equation for the hydrogen atom becomes a special case of the general Dirac equation for a charged particle in an electromagnetic field [1,3]. In the case of hydrogen atom we have  $\mathbf{A} = 0$ ,  $\varphi(r) = \frac{Ze}{4\pi r}$ . The appropriate relativistic momenta operators for the hydrogen atom are given by

$$\Pi_{\mp} = p_{\mp} = -i \left( \frac{\partial}{\partial x} \mp i \frac{\partial}{\partial y} \right) \quad , \quad \Pi_3 = p_3 = -i \frac{\partial}{\partial z} \quad (43)$$

For bound electronic states, we have

$$E = \omega + m_0 = \omega + E_0 \quad (44)$$

where  $\omega < 0$  for bound states.

The four differential equations for the components of the spinor reduce to following equations:

$$-\left(E + \frac{Ze^2}{4\pi r} - E_0\right)\phi_1 + p_- \phi_4 + p_3 \phi_3 = 0 \quad (45)$$

$$-\left(E + \frac{Ze^2}{4\pi r} - E_0\right)\phi_2 + p_+ \phi_3 - p_3 \phi_4 = 0 \quad (46)$$

$$-\left(E + \frac{Ze^2}{4\pi r} + E_0\right)\phi_3 + p_- \phi_2 + p_3 \phi_1 = 0 \quad (47)$$

$$-\left(E + \frac{Ze^2}{4\pi r} + E_0\right)\phi_4 + p_+ \phi_1 - p_3 \phi_2 = 0 \quad (48)$$

For the hydrogen atom, which possesses a single electron, two cases arise for a given orbital angular-momentum quantum number. Only  $j$  is a good quantum number in the relativistic quantum picture, and for a given  $l$  there are two possible  $j$  values:

$$j = l + \frac{1}{2} \quad (\text{case I}) \quad , \quad j = l - \frac{1}{2} \quad (\text{case II}) \quad (49)$$

in both cases we have the condition  $-j \leq m \leq j$ .

For case I,  $j = l + \frac{1}{2}$ , the components  $\phi_1$  and  $\phi_2$  have to be chosen, because these are the large components for the hydrogen atom in stationary states,  $\phi_3$  and  $\phi_4$  are small components and these correspond to positive energy states. These conditions yield the first two components as

$$\phi_1(r, \theta, \phi) = g(r) \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} Y_{l, m-\frac{1}{2}}(\theta, \phi) \quad (50)$$

$$\phi_2(r, \theta, \phi) = -g(r) \sqrt{\frac{l-m+\frac{1}{2}}{2l+1}} Y_{l, m+\frac{1}{2}}(\theta, \phi) \quad (51)$$

where  $g(r)$  is a radial function, which is yet to be determined by solving the Dirac equation. Inserting  $\phi_1$  and  $\phi_2$  in the last two equations one gets two equations which depend only on  $\phi_3$  and  $\phi_4$ . We therefore seek the following forms for the third and fourth components:

$$\phi_3(r, \theta, \phi) = -if(r) \sqrt{\frac{l-m+\frac{3}{2}}{2l+3}} Y_{l+1, m-\frac{1}{2}}(\theta, \phi) \quad (52)$$

$$\phi_4(r, \theta, \phi) = -if(r) \sqrt{\frac{l+m+\frac{3}{2}}{2l+3}} Y_{l+1, m+\frac{1}{2}}(\theta, \phi) \quad (53)$$

where the function  $f(r)$  is yet to be determined. The relation between  $f(r)$  and  $g(r)$  can be found substituting the spinor components into the four differential equations, then we obtain the following two differential equations:

$$(E + \frac{Ze^2}{4\pi r} + E_0)f(r) = \frac{dg}{dr} + (l+1)\frac{g}{r} \quad (54)$$

$$(E + \frac{Ze^2}{4\pi r} - E_0)g(r) = -\frac{df}{dr} + (l-1)\frac{f}{r} \quad (55)$$

It is convenient to express these differential equations in terms of a new quantum number, called the relativistic quantum number  $\kappa$ , defined as follows:

$$\kappa = \begin{cases} -(j + \frac{1}{2}) = -(l+1) & \text{if } j = l + \frac{1}{2} \\ +(j + \frac{1}{2}) = l & \text{if } j = l - \frac{1}{2} \end{cases} \quad (56)$$

In terms of the relativistic quantum numbers, the radial differential equations become:

$$\frac{df}{dr} + (1 - \kappa)\frac{f}{r} + (E + \frac{Ze^2}{4\pi r} - E_0)g(r) = 0 \quad (57)$$

$$\frac{dg}{dr} + (1 + \kappa)\frac{g}{r} - (E + \frac{Ze^2}{4\pi r} + E_0)f(r) = 0 \quad (58)$$

The relativistic quantum number  $\kappa$  introduced above can take both positive and negative integral values, but  $\kappa$  cannot be zero. For each nonzero  $\kappa$ , there are  $2|\kappa|$  eigenfunctions with the magnetic quantum number  $m$  varying as

$$m = -(|\kappa| - \frac{1}{2}), -(|\kappa| - \frac{3}{2}), \dots, |\kappa| - \frac{3}{2}, |\kappa| - \frac{1}{2} \quad (59)$$

The radial functions  $f(r)$  and  $g(r)$  can be obtained by solving the two coupled differential equations. We introduce functions  $F$  and  $G$  as  $F(r) = rf(r)$ ,  $G(r) = rg(r)$ . Substituting these back into the differential equations we obtain

$$\frac{dF}{dr} - \kappa\frac{F}{r} = [m_0(1 - \epsilon) - \frac{\beta}{r}]G \quad (60)$$

$$\frac{dG}{dr} + \kappa\frac{G}{r} = [m_0(1 + \epsilon) + \frac{\beta}{r}]F \quad (61)$$

where the dimensionless constants are defined as

$$\epsilon = \frac{E}{m_0}, \quad \alpha = \frac{e^2}{4\pi} \sim \frac{1}{137}, \quad \beta = Z\alpha \quad (62)$$

We introduce another dimensionless variable parameter  $\rho$  as

$$\rho = 2m_0\sqrt{1 - \epsilon^2}r \quad (63)$$

and introduce the functions  $u$  and  $v$ , defined as

$$F(\rho) = \sqrt{1 - \epsilon}e^{-\frac{1}{2}\rho}\rho^\gamma(u - v) \quad (64)$$

$$G(\rho) = \sqrt{1 + \epsilon}e^{-\frac{1}{2}\rho}\rho^\gamma(u + v) \quad (65)$$

where  $\gamma$  is a constant yet to be determined. To employ the power-series method to the coupled differential equations, we take

$$u = \sum_{s=0}^{\infty} a_s \rho^s, \quad v = \sum_{s=0}^{\infty} b_s \rho^s \quad (66)$$

On substituting these power series for  $u$  and  $v$  in the coupled differential equations we get the determinant of the coefficient matrix for nontrivial solutions:

$$\begin{vmatrix} \gamma + \frac{\beta\epsilon}{\sqrt{1-\epsilon^2}} & \kappa + \frac{\beta}{\sqrt{1-\epsilon^2}} \\ \kappa - \frac{\beta}{\sqrt{1-\epsilon^2}} & \gamma - \frac{\beta\epsilon}{\sqrt{1-\epsilon^2}} \end{vmatrix} = 0 \quad (67)$$

From this determinant we obtain two solutions for  $\gamma$ :

$$\gamma = \mp \sqrt{\kappa^2 - \beta^2} = \mp \sqrt{\kappa^2 - Z^2 \alpha^2} \quad (68)$$

The negative root is not physical, we use the positive root as solution. To obtain the functions  $u$  and  $v$ , we eliminate  $b_s$  from the two equations. This yields

$$a_s = \frac{s + \gamma - (\beta\epsilon/\sqrt{1-\epsilon^2})}{(s + \gamma)^2 - \gamma^2} a_{s-1} \quad (69)$$

The power series must terminate for some value of  $s = n'$ :  $a_{n'} = 0$  ( $n' =$  positive integer),  $a_{n'-1} \neq 0$ . This yields

$$n' = \frac{\beta\epsilon}{\sqrt{1-\epsilon^2}} - \gamma \quad (70)$$

Another positive quantum number  $n$  is introduced as follows:

$$n = n' + |\kappa| \quad \text{or} \quad n = n' + j + \frac{1}{2} \quad (71)$$

The energy levels then can be obtained as

$$\frac{\beta^2 \epsilon^2}{1 - \epsilon^2} = (n' + \sqrt{\kappa^2 - Z^2 \alpha^2})^2 \quad (72)$$

or

$$\epsilon = \left\{ \sqrt{1 + \left[ \frac{Z\alpha}{n - j - \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - Z^2 \alpha^2}} \right]^2} \right\}^{-1} \quad (73)$$

The energy depends only on  $n$  and  $j$ . The power factor  $\gamma$  becomes imaginary if  $Z > 137$ , as seen below:

$$\gamma = \sqrt{\kappa^2 - Z^2 \alpha^2} \quad \text{since} \quad \kappa^2 \geq 1 \quad Z^2 \alpha^2 \leq 1 \quad , \quad Z \leq \frac{1}{\alpha} \quad \text{or} \quad Z \leq 137. \quad (74)$$

That is, the Dirac solution for the hydrogen atom implies that atoms with  $Z > 137$  cannot exist. This result is an outcome of the point charge nucleus assumed in deriving the Coulomb potential.

Here we note some interesting analogies between the Dirac radial functions and the nonrelativistic Schrödinger radial functions. In the case of the Dirac radial wave functions, we have the apparent principle quantum number  $N$  instead of the Schrödinger principle quantum number  $n$ . The relativistic quantum number  $\kappa$  replaces the nonrelativistic  $l$  quantum number. In the nonrelativistic limit, that is

$$Lt = c \rightarrow \infty, \quad \alpha = \frac{e^2}{\hbar c} \rightarrow 0 \quad (75)$$

Therefore, the Dirac wave function should reduce to the Schrödinger wave function for the hydrogen atom, if we set  $\alpha$  to zero in the Dirac wave function. Neglecting the fine-structure constant leads to  $N = n$ ,  $\epsilon = 1$ ,  $|\kappa| = l$ . The function  $f(r)$  vanishes, the four-component Dirac spinor wave function results in a simple single-component wave function in the nonrelativistic limit. The explicit form of the first few low-lying energy levels are in the following form (here we take  $m_0 c = E_0$ ):

$$1S_{\frac{1}{2}} \text{ state: } n = 1, l = 0, j = \frac{1}{2}, \kappa = -1 : E = \frac{E_0}{\sqrt{1 + [(Z\alpha)^2/\sqrt{1 - (Z\alpha)^2}]}} \quad (76)$$

$$2S_{\frac{1}{2}} \text{ state: } n = 2, l = 0, j = \frac{1}{2}, \kappa = -1 : E = \frac{E_0}{\sqrt{1 + [(Z\alpha)^2/(1 + \sqrt{1 - (Z\alpha)^2})]}} \quad (77)$$



$$2P_{\frac{1}{2}} \text{ state: } n = 2, l = 1, j = \frac{1}{2}, \kappa = 1 : E = \frac{E_0}{\sqrt{1 + [(Z\alpha)^2/(1 + \sqrt{1 - (Z\alpha)^2})]}} \quad (78)$$

$$2P_{\frac{3}{2}} \text{ state: } n = 2, l = 1, j = \frac{3}{2}, \kappa = -2 : E = \frac{E_0}{\sqrt{1 + [(Z\alpha)^2/\sqrt{4 - (Z\alpha)^2}]}} \quad (79)$$

For  $n = 2$ , the energies of the  $2S_{\frac{1}{2}}$  and  $2P_{\frac{1}{2}}$  energy levels within the Dirac theory are degenerate. The difference between the  $2P_{\frac{1}{2}}$  and  $2P_{\frac{3}{2}}$  states is the spin-orbit splitting of the  ${}^2P$  state of the hydrogen atom. In nonrelativistic Schrödinger theory there is no difference between the energies of these two states. The Dirac theory thus includes the spin-orbit coupling. In the Schrödinger theory, there are  $n^2$  linearly independent eigenstates for a given principle quantum number  $n$ ; in Dirac's theory, we have  $2n^2$  eigenstates, since for each electron we have two possible spins.

## 5. Breit Equations for Two-Electron Problem

The relativistic Hamiltonian for the two-electron problem can be written in terms of the one-electron Dirac Hamiltonian for each electron, and an interaction term for the two electrons.

$$H = H_1 + H_2 + H_{12} \quad (80)$$

$$H_i = c\alpha_i \cdot (\mathbf{p}_i + e\mathbf{A}_i) + \beta_i m_0 c^2 - e\varphi(r_i) \quad (81)$$

Non-relativistically, the  $H_{12}$  term corresponds to the electron-electron repulsion term. However, relativistically, this is not an acceptable two-electron term, since the Coulombic repulsion term of the form  $H_{12} = \frac{e^2}{r_{12}}$  is not Lorentz-invariant.

Derivation of a fully covariant form for the two-electron system involves quantum-electrodynamic treatment of the problem. A fully covariant derivation of the relativistic two-electron problem leads to an equation called the Bethe-Salpeter equation, which is Lorentz-invariant. A somewhat approximate treatment, by way of truncation of an expansion, leads to the Breit equation for the two-electron problem [3]:

$$\left\{ H_1 + H_2 + \frac{e^2}{r_{12}} - \frac{e^2}{2r_{12}} \left[ \alpha_1 \cdot \alpha_2 + \frac{(\alpha_1 \cdot \mathbf{r}_{12})(\alpha_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right] \right\} \Psi = E\Psi \quad (82)$$

where  $H_i$  are the one-electron Dirac Hamiltonians of the form

$$H_i = c\alpha_i \cdot (\mathbf{p}_i + e\mathbf{A}_i) + \beta_i m_0 c^2 - e\varphi(r_i) \quad (83)$$

where  $\alpha_i$  and  $\beta_i$  are the Dirac matrices for the  $i$ th electron. The Breit equation is not Lorentz-invariant because it is correct only to order  $\alpha^4$ . The exact Hamiltonian contains terms involving higher orders of the fine-structure constant.

The two-electron relativistic spinor wave function is somewhat more complex in that it has 16 components. A typical 16-component two-electron spinor can be written in a four-component representation as follows:

$$\Psi = \begin{bmatrix} \psi_{++} \\ \psi_{+-} \\ \psi_{-+} \\ \psi_{--} \end{bmatrix} \quad (84)$$

where  $\psi_{++}$  is a four-component spinor, for which both electrons have positive energies, and so on for the other components. A somewhat extended form of the approximate two-electron Hamiltonian, which includes terms up to  $\mathcal{O}(\alpha^4)$ , is called the Breit-Pauli Hamiltonian [3,4]. The various terms in the Breit-Pauli two-electron Hamiltonian can be arranged and interpreted as follows:

$$H = H_0 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 \quad (85)$$

$$H_0 = \frac{1}{2}(p_1^2 + p_2^2) - eV \quad (86)$$

$$H_1 = -\frac{1}{8m^3c^3}(p_1^4 + p_2^4) \quad (87)$$

$$H_2 = -\frac{e^2}{2m^2c^2} \left[ \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{r_{12}} + \frac{(\mathbf{r}_{12} \cdot \mathbf{p}_1)(\mathbf{r}_{12} \cdot \mathbf{p}_2)}{r_{12}^3} \right] \quad (88)$$

$$H_3 = \frac{\mu}{mc} \left\{ \left[ \mathbf{E}_1 \times \mathbf{p}_1 + \frac{2e}{r_{12}^3}(\mathbf{r}_{12} \times \mathbf{p}_1) \right] \cdot \mathbf{s}_1 + \left[ \mathbf{E}_2 \times \mathbf{p}_2 + \frac{2e}{r_{12}^3}(\mathbf{r}_{12} \times \mathbf{p}_2) \right] \cdot \mathbf{s}_2 \right\} \quad (89)$$

$$H_4 = \frac{ie\hbar}{4m^2c^2}(\mathbf{p}_1 \cdot \mathbf{E}_1 + \mathbf{p}_2 \cdot \mathbf{E}_2) \quad (90)$$

$$H_5 = 4\mu^4 \left\{ -\frac{8\pi}{3}(\mathbf{s}_1 \cdot \mathbf{s}_2)\delta^3(r_{12}) + \frac{1}{r_{12}^3} \left[ \mathbf{s}_1 \cdot \mathbf{s}_2 - 3\frac{(\mathbf{s}_1 \cdot \mathbf{r}_{12})(\mathbf{s}_2 \cdot \mathbf{r}_{12})}{r_{12}^2} \right] \right\} \quad (91)$$

$$H_6 = 2\mu(\mathbf{B}_1 \cdot \mathbf{s}_1 + \mathbf{B}_2 \cdot \mathbf{s}_2) + \frac{e}{mc}(\mathbf{A}_1 \cdot \mathbf{p}_1 + \mathbf{A}_2 \cdot \mathbf{p}_2) \quad (92)$$

where

$$V = \frac{Ze}{r_1} + \frac{Ze}{r_2} - \frac{e}{r_{12}} + \varphi_1(r_1) + \varphi_2(r_2) \quad (93)$$

$$\mathbf{p}_1 = -i\hbar\nabla_1, \quad \mathbf{p}_2 = -i\hbar\nabla_2, \quad \mu = \frac{e\hbar}{2mc}, \quad s_i = \frac{1}{2}\sigma_i \quad (94)$$

$$\mathbf{E}_1 = -\nabla_1 V, \quad \mathbf{E}_2 = -\nabla_2 V \quad (95)$$

In these expressions,  $\varphi_1(r_1)$  and  $\varphi_2(r_2)$  are the scalar external potentials due to electrons 1 and 2, while  $\mathbf{A}_1$  and  $\mathbf{A}_2$  are the external vector potentials due to electrons 1 and 2, respectively. The terms in the Breit–Pauli Hamiltonian are interpreted as follows:

$H_0$  is the non-relativistic Schrödinger Hamiltonian for the two-electron system.

$H_1$  is the mass-velocity term attributed to relativistic correction arising from the variation of the mass of the electron with its speed.

$H_2$  is the relativistic retardation due to the electromagnetic field generated by an electron.

$H_3$  is the spin-orbit coupling term. This corresponds to the interaction between the spin magnetic moment and the orbital magnetic moment of the electron.

$H_4$  is called the Darwin correction term, it is a relativistic correction in Dirac's theory, it arises from the smearing of the charge of the electron due to its relativistic motion.

$H_5$  arises from the interaction of the spin magnetic moments of two electrons, and constitutes a dipole-dipole interaction between the two spin magnetic moments, and a Fermi-contact type interaction.

$H_6$  is an interaction term with the external electromagnetic field.

## 6. Breit–Pauli Approximation to the Multielectron Problem

The Breit–Pauli Hamiltonian for the two-electron problem expressed above can be generalized for a multielectron problem. The multielectron Breit–Pauli Hamiltonian is written as

$$H = H_0 + H_1 + H_2 + H_3 + H_4 + H_5 + H_6 \quad (96)$$

$$H_0 = \sum_i \left( \frac{p_i^2}{2m_0} - \frac{Ze^2}{r_i} \right) + \sum_{i<j} \frac{e^2}{r_{ij}} \quad (97)$$

$$H_1 = -\frac{1}{8m_0^3c^3} \sum_i p_i^4 \quad (98)$$

$$H_2 = -\frac{e^2}{2m_0^2c^2} \sum_{i<j} \left[ \frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}} + \frac{(\mathbf{r}_{ij} \cdot \mathbf{p}_i)(\mathbf{r}_{ij} \cdot \mathbf{p}_j)}{r_{ij}^3} \right] \quad (99)$$

$$H_3 = \frac{\mu}{m_0c} \sum_i \mathbf{s}_i \cdot \left[ \mathbf{E}_i \times \mathbf{p}_i + \sum_{i<j} \frac{2e}{r_{ij}^3} (\mathbf{r}_{ij} \times \mathbf{p}_j) \right] \quad (100)$$

$$H_4 = \frac{ie\hbar}{(2m_0c)^2} \sum_i (\mathbf{p}_i \cdot \mathbf{E}_i) \quad (101)$$

$$H_5 = 4\mu^2 \left\{ \sum_{i<j} \left[ \frac{\mathbf{s}_i \cdot \mathbf{s}_j}{r_{ij}^3} - 3 \frac{(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{8\pi}{3} (\mathbf{s}_i \cdot \mathbf{s}_j) \delta^3(r_{ij}) \right] \right\} \quad (102)$$

$$H_6 = 2\mu \sum_i \mathbf{B}_i \cdot \mathbf{s}_i + \frac{e}{m_0c} \sum_i \mathbf{A}_i \cdot \mathbf{p}_i \quad (103)$$

$$\mu = \frac{e\hbar}{2m_0c}, \quad \mathbf{E}_i = \nabla_i V, \quad V = -Ze^2 \sum_i \frac{1}{r_i} + e^2 \sum_{i<j} \frac{1}{r_{ij}} \quad (104)$$

in these equations  $\mathbf{p}_i$  is given by  $\mathbf{p}_i = -i\nabla_i$  (without the  $\hbar$  term).

The Breit–Pauli Hamiltonian given above, as well as the Breit interaction term, are not Lorentz–invariant, since they are approximations to a fully covariant multielectron relativistic wave equation. Methods have been developed for fully covariant representation of the interaction between two relativistic electrons using quantum–electrodynamic methods. The formulation by Bethe and Salpeter is one such equation [3]. However, it is not a popular choice for practical solutions to heavy atoms, because of the numerical complexities it leads to in practical applications.

## 7. Relativistic Hamiltonians for Multielectron Systems

The Dirac Hamiltonian for a multielectron atom can be written as

$$H_D = \sum_i h_D(i) + \sum_{i<j} \frac{1}{r_{ij}} \quad (105)$$

where  $h_D(i)$  is the one–electron Dirac Hamiltonian

$$h_D(i) = (\alpha_i \cdot \mathbf{p}_i + \beta_i c^2 - \frac{Z}{r_i}) \quad (106)$$

This Hamiltonian ignores the two–electron relativistic Breit interaction. Introduction of the Breit interaction as a perturbation shows that it is very small in the valence region, and more important for the properties of core electrons.

Since the one–particle Dirac Hamiltonian involves  $4 \times 4$  matrices instead of scalar functions, the solution of the Dirac equation is a vector of four components (a four–component spinor), which takes the form

$$\psi_{nkm} = \frac{1}{r} \begin{bmatrix} P_{nk}(r) & \chi_{km}(\theta, \phi) \\ iQ_{nk}(r) & \chi_{-km}(\theta, \phi) \end{bmatrix} \quad (107)$$

where

$$\chi_{km}(\theta, \phi) = \sum_{\sigma=\mp\frac{1}{2}} C(l\frac{1}{2}j; m-\sigma, \sigma) Y_{\lambda}^{m-\sigma}(\theta, \phi) \Phi_{\frac{1}{2}}^{\sigma} \quad (108)$$

where  $Y_{\lambda}^{m-\sigma}$  is a spherical harmonic, and

$$\Phi_{\frac{1}{2}}^{\frac{1}{2}} = \alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \Phi_{\frac{1}{2}}^{-\frac{1}{2}} = \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (109)$$

are the Pauli two-component spinors,  $C(l\frac{1}{2}j; m-\sigma, \sigma)$  are the Clebsch–Gordon coefficients,  $k$  is the relativistic quantum number,

$$k = \begin{cases} j + \frac{1}{2} & \text{if } j = l - \frac{1}{2} \\ -(j - \frac{1}{2}) & \text{if } j = l + \frac{1}{2} \end{cases} \quad (110)$$

and  $\lambda$  is defined as

$$\lambda = \begin{cases} k & \text{if } j = l - \frac{1}{2} \\ -(k + 1) & \text{if } j = l + \frac{1}{2} \end{cases} \quad (111)$$

The  $Q_{nk}$  and  $P_{nk}$  are the small and large components, respectively. They satisfy the coupled differential equations for a central force field:

$$\frac{dP_{nk}}{dr} + \frac{kP_{nk}}{r} \left( \frac{2}{\alpha} + \alpha[v(r) - \epsilon_{nk}] \right) Q_{nk} = 0 \quad (112)$$

$$\frac{dQ_{nk}}{dr} - \frac{kQ_{nk}}{r} + \alpha[v(r) - \epsilon_{nk}] P_{nk} = 0 \quad (113)$$

Desclaux [5] numerical Dirac–Fock implementation in a computer is widely used to generate relativistic all–electron wave functions for almost any atom in the periodic table. Detailed information about and the derivations of the above equations may be found in [6].

## 8. Relativistic Quantum Numbers for Atomic Configurations

For the electron configuration  $nl$  the possible angular momentum vectors are  $\mathbf{l}$ ,  $\mathbf{s}$ , and  $\mathbf{j}$ , where  $\mathbf{j} = \mathbf{l} + \mathbf{s}$ ,  $s = 1/2$  for electron, therefore  $j = l + 1/2$  or  $j = l - 1/2$ . The relativistic quantum number,  $\kappa$ , takes the values

$$\kappa = l \text{ for } j = l - \frac{1}{2} \quad \text{and} \quad \kappa = -l - 1 \text{ for } j = l + \frac{1}{2}$$

Principle quantum number,  $n$ , can be related to  $\kappa$  as

$$n = n' + |\kappa| = n' + j + \frac{1}{2}, \quad n = 1, 2, 3, \dots, \quad \kappa = \mp(j + \frac{1}{2}) = \mp 1, \mp 2, \mp 3, \dots$$

$n' = n - j - \frac{1}{2} = n - |\kappa|$  is called as the radial quantum number. The values of the quantum numbers for some of the electronic configurations are given in Tables 1 and 2.

**Table 1.** Values of quantum numbers for the electron configurations  $nl$ .

$nl$	$n$	$l$	$j$	$n'$	$\kappa$	$nl$	$n$	$l$	$j$	$n'$	$\kappa$	$nl$	$n$	$l$	$j$	$n'$	$\kappa$
1s	1	0	1/2	0	-1	3p	3	1	1/2	2	1	4p	4	1	1/2	3	1
2s	2	0	1/2	1	-1		3	1	3/2	1	-2		4	1	3/2	2	-2
2p	2	1	1/2	1	1	3d	3	2	3/2	1	2	4d	4	2	3/2	2	2
		2	3/2	0	-2		3	2	5/2	0	-3		4	2	5/2	1	-3
3s	3	0	1/2	2	-1	4s	4	0	1/2	3	-1	4f	4	3	5/2	1	3
													4	3	7/2	0	-4

**Table 2.** Values of quantum numbers for the electron configurations  $nl^q$ . Oc represents the occupancy (number of electrons).

$nl$	$n$	$\kappa$	Oc	$nl$	$n$	$\kappa$	Oc	$nl$	$n$	$\kappa$	Oc	$nl$	$n$	$\kappa$	Oc
ns	n	-1	1.0	np <sup>4</sup>	n	-2	2.0	nd <sup>2</sup>	n	-3	1.0	nd <sup>6</sup>	n	-3	3.0
ns <sup>2</sup>	n	-1	2.0		n	1	2.0		n	2	1.0		n	2	3.0
np	n	-2	1.0	np <sup>5</sup>	n	-2	3.0	nd <sup>3</sup>	n	-3	2.0	nd <sup>7</sup>	n	-3	4.0
	n	1	0.0		n	1	2.0		n	2	1.0		n	2	3.0
np <sup>2</sup>	n	-2	1.0	np <sup>6</sup>	n	-2	4.0	nd <sup>4</sup>	n	-3	2.0	nd <sup>8</sup>	n	-3	4.0
	n	1	1.0		n	1	2.0		n	2	2.0		n	2	4.0
np <sup>3</sup>	n	-2	2.0	nd	n	-3	1.0	nd <sup>5</sup>	n	-3	3.0	nd <sup>9</sup>	n	-3	5.0
	n	1	1.0		n	2	0.0		n	2	2.0		n	2	4.0
												nd <sup>10</sup>	n	-3	6.0
													n	2	4.0

## 9. Applications to Atoms

In this section we present some results of relativistic calculations based on the single-particle Dirac equation in which we applied an approximate time-independent RDFT to the low-lying autoionization (AI) states of neutral atoms and positive ions [7]. The calculations require a computational effort similar to ground-state DFT calculations. The method of calculation is based on the self-consistent solution of  $N$  one-particle Dirac equations (Kohn-Sham orbital equations) of the form (in Rydberg atomic units)

$$[-ic\alpha \cdot \nabla + (\beta - 1)\frac{1}{2}c^2 + v_{eff}^\sigma]\psi_{\sigma,i} = \epsilon_{\sigma,i}\psi_{\sigma,i} \quad (114)$$

where

$$v_{eff}^\sigma(\mathbf{r}) = v(\mathbf{r}) + 2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}^\sigma(\mathbf{r}) \quad (115)$$

In these equations  $\sigma$  is a quantum number that labels the solutions according to their spin state. The wave functions  $\psi$  are four-vectors, but can be described by two radial functions only. The spin dependent charge density  $\rho_\sigma(\mathbf{r})$  is obtained self-consistently, and defined as

$$\rho_\sigma(\mathbf{r}) = \sum_i^{N_\sigma} |\psi_{i,\sigma}(\mathbf{r})|^2 \quad \text{and} \quad \rho = \sum_\sigma \rho_\sigma \quad (116)$$

$v(\mathbf{r})$  is the Coulomb potential between electron and nucleus, and  $v_{xc}^\sigma(\mathbf{r})$  is the exchange-correlation potential. The total energy of the atom consists of the kinetic energy of the electrons, the electron-nucleus Coulomb potential energy, and the exchange-correlation energy of the electrons. The total energy can be determined from the self-consistent resultant charge density as

$$E[\rho] = \sum_{\sigma,i} \epsilon_{\sigma,i} - \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho_\sigma] - \sum_\sigma \int v_{xc}^\sigma(\mathbf{r})\rho_\sigma(\mathbf{r}) d\mathbf{r} \quad (117)$$

The local-spin-density approximation has been used for the exchange-correlation energy in the form due to Von Barth and Hedin and parameterized by Janak [7]

$$v_{xc}^\sigma(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho_\sigma(\mathbf{r})} \quad (118)$$

where the functional  $E_{xc}[\rho]$  is defined as

$$E_{xc}[\rho] = \sum_\sigma \int \rho_\sigma(\mathbf{r}) \epsilon_{xc}^\sigma(\rho(\mathbf{r})) d\mathbf{r} \quad (119)$$

As is normally done in this approach, the spin states are defined by the large components only. We divide the electrons in two groups, labeled by  $\sigma$ . If we use the potential for  $\sigma = +1$  we solve the Dirac equations and choose the large component to be spin up. Similarly, for  $\sigma = -1$  we choose spin down. The small components will have a mixture of both spins, but the effects of this spin mixing are small compared to with the energy differences we are trying to obtain. In the calculations each occupied orbital is defined by an occupation number; we consider integral occupation of states. Some of the results of the calculations are given in Table 3 for comparison.

**Table 3.** Comparison of calculated AI energies with experimental values and other calculations for some neutral atoms and positive ions. Energies are in eV and with respect to the ground state of the corresponding system [7].

Atom(state)	RDFT	Expt.	Other calc.	Atom(state)	RDFT	Expt.	Other calc.
He( $2s^2$ )	56.54	57.64	57.85	Li <sup>+</sup> ( $2s^2$ )	71.70	70.62	70.58
Li( $1s2s^2$ )	55.69	56.35	56.32	B <sup>2+</sup> ( $1s2s^2$ )	191.05	193±0.5	192.70
F( $1s^22s2p^6$ )	18.34	20.99	20.68	O <sup>5+</sup> ( $1s2s^2$ )	547.49	551±1.5	551.45
Ne( $2s2p^63p$ )	41.75	45.55	46.25	F <sup>6+</sup> ( $1s2s^2$ )	707.27	711±1.0	710.31
Al( $2s3p3d$ )	8.22	8.43	8.03	F <sup>6+</sup> ( $1s2s2p$ )	708.48	716±2.0	714.07

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