



GROUND STATE AND RELATIVISTIC ENERGIES OF OPEN- AND CLOSED-SHELL ATOMS ($Z = 2 - 38$) OVER INTEGER AND NONINTEGER n -SLATER TYPE ORBITALS

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Abstract

Hartree-Fock Roothaan (HFR) calculations for ground states of the neutral atoms from He to Sr have been performed using integer and noninteger Slater type orbitals (n - and ni -STOs). In addition, we calculated three largest relativistic corrections which are the relativistic kinetic energy correction, the Darwin term and spin-orbit interaction using n -STOs as perturbation. It has been seen that $1s$ electrons are responsible for almost 80-90% of the total relativistic kinetic energy and the Darwin corrections. Besides, it has been

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observed that while the total relativistic energy corrections for small atoms change between 0 and -1 au, the magnitude of the corrections increases rapidly when going through the bigger atoms. The results show that the kinetic energy correction and Darwin correction terms may not be neglected in an accurate calculation even for small atoms. Our results are in accord with the other results found in the literature.

1. Introduction

The effect computation of multicenter molecular integrals appearing in the determination of various properties of atom and molecules in HFR approximation strongly depends on the conformation of the basis function. Two type's basis functions are generally used in the multicenter molecular integrals. One of them is the Gaussian type orbitals (GTOs) which are widely used in molecular calculations, because multicenter molecular integrals can be evaluated easily over GTOs. But, GTOs do not represent the correct behaviour of the wave function especially at the nuclei and at large distances from the nuclei. The other one is Slater type orbitals (STOs). For problems in which the long part of the wave function or its behaviour in the neighbourhood of the nuclei is important, it is desirable to use STOs which describe the physical situation more accurately than GTOs. Although the use of STOs is rather difficult and tedious especially in the calculation of multicenter integrals, the use of STOs in molecular calculation has attracted great attention from several authors for three decade [1-11].

Traditionally, the principle quantum number n is assumed to be a positive integer in calculation of multicenter integrals. However, it is well-known that STOs with noninteger quantum numbers (ni -STOs) provide a more flexible basis for atomic calculations than STOs with integer quantum numbers (n -STOs), and also the energies calculated by use of ni -STOs lead to better atomic energies than those obtained by n -STOs [12-15]. The fundamental difficulty occurring in the use of ni -STOs is that the multicenter integrals cannot be calculated accurately and efficiently over ni -STOs. Recently, some authors calculated the molecular integrals and physical

parameters of atoms and molecules over *ni*-STOs with several methods [16-21]. Koga et al. [16], and later Guseinov and Mamedov [19] calculated two-electron integrals using hypergeometric functions ${}_2F_1(a, b, c, x)$ over *n*-STOs and *ni*-STOs. Afterwards, Gümüş and Özdoğan [20] employed the same functions for the calculation of ground state energies of some closed-shell atoms using both *n*-STOs and *ni*-STOs. However, it is still not clear that which method is the best in terms of speed and accuracy.

In a previous work [22], one of the authors has calculated the orbital and ground state energies of some open- and closed-shell atoms over *n*-STOs and *ni*-STOs. In order to increase the efficiency of these calculations, the atomic two-electron integrals were expressed in terms of incomplete beta function. In the present study, we have improved our previous study so as to include the three most important relativistic correction terms, also the range of the atoms, for which the calculations are performed, is extended to include all neutral atoms up to Sr. We first discuss the unperturbed Hamiltonian, and next discuss the following three largest relativistic corrections which are the relativistic kinetic energy correction, the Darwin term and spin-orbit interaction. Then we present the methods for numerical calculations, and discuss the result obtained for the ground states of neutral atoms in the range from He to Sr. Atomic units (au) will be used throughout study.

2. Theory

Using the unperturbed Hamiltonian, an *N*-electron system containing at most one open-shell is defined by a restricted determinant wave function, and the expectation value of the total energy is given by

$$E = 2 \sum_k h_k + \sum_{kl} (2J_{kl} - K_{kl}) + f \left[2 \sum_m h_m + f \sum_{mn} (2aJ_{mn} - bK_{mn}) + 2 \sum_{km} (2J_{km} - K_{km}) \right], \quad (1)$$

where the indices *k*, *l* refer to the closed-shell orbitals and *m*, *n* to the open-

shell orbitals. a , b and f are numerical constants which depend on particular open-shell problem, details are given in [25]. The h_k in the first sum refer to the energy expectation value for a single electron in the state k , where the energy consists of the kinetic energy of the electron and its potential energy in the coulomb field of the nucleus. In the following double sum, the quantities J_{kl} represent the coulomb interaction energies between the charge densities of the electrons in states k and l . This interaction includes both electrons of like spin and those of opposite spin. The last terms K_{kl} are expressions for the exchange interaction, which acts only between electrons having the same spin direction. One-electron spatial orbitals ϕ_p , which are constructed the Slater determinant, may be expressed as linear combinations of STOs, indicated χ_k , called *basis functions*,

$$\phi_p = \sum_k c_{pk} \chi_k(\zeta_k, \vec{r}), \quad (2)$$

where $k = nlm$ are quantum numbers of basis functions, c_{pk} are expansion coefficients and ζ_k are the screening constants. The general form of the normalized complex STO is given by

$$\chi_{nlm}(\zeta, \vec{r}) = [(2\zeta)^{2n+1}/\Gamma(2n+1)]^{1/2} r^{n-1} e^{-\zeta r} Y_{lm}(\theta\phi), \quad (3)$$

where $\Gamma(z)$ denotes the gamma function [24]. $Y_{lm}(\theta\phi)$ is well known complex spherical harmonic in Condon-Shortley phase convention.

There are two types of integrals appearing in the solution of the HFR equations for atoms. One of them is one-electron integrals, and the other is two-electron integrals. Nuclear attraction and kinetic energy integrals are one-electron integrals, and are defined by the following expressions in terms of the atomic orbital respectively,

$$V = \int \phi_i^* \frac{-Z}{r} \phi_i d^3r \quad (4)$$

and

$$T = \int \phi_i^* \frac{-\nabla^2}{2} \phi_i d^3r, \quad (5)$$

where Z denotes the nuclear charge and i indicates the quantum numbers of one-electron spatial orbitals. These integrals can be easily expressed in terms of overlap integrals as in [22]. Coulomb and exchange integrals which are two-electron integrals are also needed in the HFR analysis of atoms. However, both of them have the same form except for the indices of the basis orbital. Coulomb integral is defined as follows:

$$\begin{aligned} J_C &= \int \phi_i^*(r_1) \phi_j^*(r_2) \frac{1}{r_{12}} \phi_i(r_1) \phi_j(r_2) d^3r_1 d^3r_2 \\ &= \sum_{k_i k'_i} \sum_{k_j k'_j} c_{ki}^* c_{k'i} c_{kj}^* c_{k'j} A_{n_i n'_i}^{n_j n'_j} \sum_{L=\max\{|l_i-l'_i|, |l_j-l'_j|\}}^{\min\{l_i+l'_i, l_j+l'_j\}} \frac{1}{2L+1} \\ &\quad \times \langle l_i m_i | l'_i m'_i | L m_i - m'_i \rangle \\ &\quad \times \langle l'_j m'_j | l_j m_j | L m'_j - m_j \rangle R_{n_i+n'_i, n_j+n'_j}^L \\ &\quad \times (\zeta_i + \zeta'_i + \zeta_j + \zeta'_j) \delta_{|m_i-m'_i|, |m'_j-m_j|}, \end{aligned} \quad (6)$$

in which k labels the STOs with quantum numbers $n_i l_i m_i$, $A_{n_i n'_i}^{n_j n'_j}$ is the combination of normalization constants of the STOs and $\langle lm | l'm' | LM \rangle$ with $|l-l'| \leq L \leq l+l'$, $L \geq |m-m'|$ are gaunt coefficients as defined in [25].

The integral $R_{N_1 N_2}^L(z_1, z_2)$ in equation (6) has the general form

$$R_{N_1 N_2}^L(z_1, z_2) = \int_0^\infty \int_0^\infty r_1^{N_1} r_2^{N_2} e^{-z_1 r_1} e^{-z_2 r_2} \frac{r_1^L}{r_1^{L+1}} dr_1 dr_2. \quad (7)$$

In calculation with n -STOs, the integral $R_{N_1 N_2}^L(z_1, z_2)$ can easily be calculated in terms of the binomial coefficients as follows:

$$\begin{aligned}
& R_{N_1 N_2}^L(z_1, z_2) \\
&= (2\zeta_1)^{n_1+1/2} (2\zeta_1')^{n_1'+1/2} (2\zeta_2)^{n_2+1/2} (2\zeta_2')^{n_2'+1/2} \\
&\quad \times \left[\frac{F_{2n_1}(2N_1)F_{2n_2}(2N_2)}{F_{N_1+N_2-1}(2N_1-2N_2-2)} \times \frac{F_{2N_1}(2N_1+2N_2-2)}{(2N_2)(2N_2-1)} \right]^{1/2} \\
&\quad \times \left\{ \frac{1}{F_{N_1+L}(N_1+N_2-1)z_1^{N_1+L+1}z_2^{N_2-L}} - \frac{1}{F_{N_1+L}(N_1+N_2-1)} \right. \\
&\quad \times \frac{1}{z_1^{N_1+L+1}} \sum_{p=0}^{N_1+L} \frac{z_1^p}{(z_1+z_2)^{N_2-L+p}} \\
&\quad \left. + \frac{1}{F_{N_2+L}(N_1+N_2-1)z_1^{N_1-L}} \sum_{q=0}^{N_1-L-1} \frac{z_1^q F_q(N_2+L+q)}{(z_1+z_2)^{N_2+L+q+1}} \right\}, \quad (8)
\end{aligned}$$

where $F_s(k) = k!/(k-s)!s!$ are the binomial coefficients. In the case of ni -STOs, making a simple change of variable in the integral $R_{N_1 N_2}^L(z_1, z_2)$, it can easily be defined in terms of the incomplete beta function by

$$\begin{aligned}
R_{N_1 N_2}^L(z_1, z_2) &= \frac{\Gamma(N_1+L+1)\Gamma(N_2-L)}{z_1^{N_1+L+1}z_2^{N_2-L}} \\
&\quad - \frac{\Gamma(N_1+L+1)\Gamma(N_2-L)}{z_1^{N_1+L+1}z_2^{N_2-L}} B_{(q)^{-1}}(N_2-L, N_1+L+1) \\
&\quad + \frac{\Gamma(N_2+L+1)\Gamma(N_1-L)}{z_2^{N_2+L+1}z_1^{N_1-L}} B_{(q)^{-1}}(N_2+L+1, N_1-L), \quad (9)
\end{aligned}$$

in which $q = (z_1 + z_2)/z_2$ and the term $B_{(q)^{-1}}(m, n)$ is the incomplete beta function given in [26] by

$$B_{(q)^{-1}}(m, n) = \frac{\Gamma(m+n)}{\Gamma(m)} \sum_{k=0}^{\infty} \frac{(-1)^k}{q^{(m+k)}(m+k)\Gamma(n-k)\Gamma(k+1)}. \quad (10)$$

3. Relativistic Corrections

It has been assumed that a nonrelativistic calculation should give results accurate sufficiently in application of quantum mechanical methods. This assumption is very rarely checked, and in the few cases which an approximate relativistic calculation has performed, the results show that for many systems, the preceding assumption is not verified. In the present study, the interest is focused on the shifts in the total ground state energies which are caused by relativistic effects. To include relativistic effects in a rigorous way, the Dirac equation needs to be solved for many-electron system, which is difficult and time consuming. Many authors calculated the relativistic corrections, for especially small atoms, with different wave functions by using different methods [27-32]. Recently, due to the huge advance in computer technology, the relativistic corrections have also been calculated for some large atoms by several authors [33-42].

Dirac equation may be approximated in two component forms for many-electron systems in atomic unit as following [43]:

$$\left(\sum_{i=1}^N \left[-\frac{\nabla^2}{2} - \frac{Z}{r_i} + \sum_{i \neq j} \frac{1}{r_{ij}} + \frac{p_i^4}{8c^2} + \frac{\vec{\nabla} \cdot \vec{\epsilon}_{ef}}{8c^2} + \frac{\vec{\sigma} \cdot (\vec{\epsilon}_{ef} \times \vec{p}_i)}{4c^2} \right] \right) \Psi = E\Psi, \quad (11)$$

where $\vec{\epsilon}_{ef}$ is the effective electric field at \vec{r}_i , position of the i th electron, induced by the nuclei and all other electrons, and \vec{p}_i is the linear momentum of the electron. The first three terms make up the unperturbed Schrödinger Hamiltonian whose eigenvalues were mentioned above and the last three terms may be calculated perturbatively since they are relatively small in magnitude than unperturbed eigenvalue. The fourth term in equation (11) is due to the relativistic correction to the kinetic energy and its eigenvalue is given by

$$\langle E^{P4} \rangle = \frac{1}{8c^2} \left\langle \sum_{i=1}^N p_i^4 \right\rangle. \quad (12)$$

This term is called the *mass-velocity term* because it rises from the relativistic variation of mass with velocity. We calculated this correction term with method given in [32, 44]. The expectation value of the term $\langle p^4 \rangle$ can be easily expressed in terms of overlap integrals as follows:

$$\begin{aligned} \langle p^4 \rangle &= \int \phi_i^* p^4 \phi_i d^3r \\ &= \sum_k \sum_{k'} c_{ik}^* c_{ik'} \left\{ \left(\frac{\zeta_i^2 (n_i + n'_i)}{\zeta_i + \zeta'_i} - 2\zeta_i n_i + \frac{(\zeta_i + \zeta'_i)[n_i(n_i - 1) - l_i(l_i + 1)]}{n_i + n'_i - 1} \right) \right. \\ &\quad \times \frac{\zeta_i'^2 (\zeta_i + \zeta'_i)}{n_i + n'_i} \times S_{n_i l_i m_i}^{n'_i l'_i m'_i}(\zeta_i, \zeta'_i) \\ &\quad + \left(\frac{-\zeta_i^2 (n_i + n'_i - 1)}{\zeta_i + \zeta'_i} + 2\zeta_i n_i - \frac{(\zeta_i + \zeta'_i)[n_i(n_i - 1) - l_i(l_i + 1)]}{n_i + n'_i - 2} \right) \\ &\quad \times \frac{(2\zeta_i')^2 n'_i}{\sqrt{2n'_i(2n'_i - 1)}} \times \frac{(\zeta_i + \zeta'_i)}{n_i + n'_i - 1} S_{n_i l_i m_i}^{n'_i - 1 l'_i m'_i}(\zeta_i, \zeta'_i) \\ &\quad + \left(\frac{\zeta_i^2 (n_i + n'_i - 2)}{\zeta_i + \zeta'_i} - 2\zeta_i n_i + \frac{(\zeta_i + \zeta'_i)[n_i(n_i - 1) - l_i(l_i + 1)]}{n_i + n'_i - 3} \right) \\ &\quad \times \left. \frac{(2\zeta_i')^2 [n'_i(n'_i - 1) - l'_i(l'_i + 1)]}{\sqrt{2n'_i(2n'_i - 1)(2n'_i - 2)(2n'_i - 3)}} \frac{(\zeta_i + \zeta'_i)}{n_i + n'_i - 2} S_{n_i l_i m_i}^{n'_i - 2 l'_i m'_i}(\zeta_i, \zeta'_i) \right\}, \quad (13) \end{aligned}$$

in which $S_{nlm}^{n'l'm'}$ are overlap integrals and given in [22]. The fifth term in equation (11) involving with the divergence of the effective electric field is the Darwin term. It may be thought of as arising from a relativistically-induced electric moment of the electron, or from the relativistic non-localizability of the electron and its eigenvalue is calculated as follows:

$$\langle E^D \rangle = \frac{1}{8c^2} \left\langle Z \sum_{i=1}^N \delta(\vec{r}_i) - \sum_{i \neq j}^N \delta(\vec{r}_{ij}) \right\rangle, \quad (14)$$

which the first term defines probability of finding the electron on the nucleus, so this term yields the Darwin correction for only s -atomic orbital. For an electron in i th s -atomic orbital, this term is given by

$$\begin{aligned} \langle \delta(\vec{r}) \rangle &= \int \phi_i^* \delta(\vec{r}) \phi_i d^3r \\ &= \sum_k \sum_{k'} c_{ik}^* c_{ik'} \frac{1}{8c^2} \chi_k(0) \chi_{k'}(0), \end{aligned} \quad (15)$$

where k, k' label the STOs. The second term in equation (14) corresponds to shifting probability density of electron from center. For the case with electron 1 in i th atomic orbital and electron 2 in j th atomic orbital, we may express the eigenvalue of this term using Laplace operator [45] by

$$\begin{aligned} \langle \delta(\vec{r}_1 - \vec{r}_2) \rangle &= \int \phi_i^*(r_1) \phi_j^*(r_2) \delta(\vec{r}_1 - \vec{r}_2) \phi_i(r_1) \phi_j(r_2) d^3r_1 d^3r_2 \\ &= \sum_{k_i k_i'} \sum_{k_j k_j'} c_{ki}^* c_{k'i} c_{kj}^* c_{k'j} \sum_{L=\max\{|l_i-l_i'|, |l_j-l_j'|\}}^{\min\{l_i+l_i', l_j+l_j'\}} \langle l_i m_i | l_i' m_i' | L m_i - m' \rangle \\ &\quad \times \langle l_j' m_j' | l_j m_j | L m_j' - m_j \rangle \\ &\quad \times \frac{(n_i + n_i', n_j + n_j')!}{(\zeta_i + \zeta_i' + \zeta_j + \zeta_j')^{n_i+n_i'+n_j+n_j'-1}} \delta_{|m_i-m_i'|, |m_j'-m_j|}. \end{aligned} \quad (16)$$

The last term in equation (11) is the spin-orbit interaction, and the spin-orbit splitting energy for the atomic orbital with n, l, j is expressed by

$$\langle E^{SL} \rangle = \frac{1}{4c^2} \sum_i \left\langle \frac{1}{r_i} \frac{dV(r_i)}{dr_i} \vec{l}_i \cdot \vec{s}_i \right\rangle, \quad (17)$$

where $V(r_i)$ is the potential energy of i th electron which is in the field of the

nucleus and spherically averaged field of the $N - 1$ electrons, and \vec{l}_i and \vec{s}_i are, respectively, the total orbital and spin angular momentum of the atom.

$\left\langle \frac{1}{r_i} \frac{dV(r_i)}{dr_i} \right\rangle$ is known as the spin-orbit coupling constant of i th orbital, and it is given as

$$\begin{aligned}
 \left\langle \frac{1}{r_i} \frac{dV(r_i)}{dr_i} \right\rangle &= \int \phi_i^* \frac{1}{r_i} \frac{dV(r_i)}{dr_i} \phi_i d^3r \\
 &= N_{n_i n'_i} \sum_{k_i} \sum_{k'_i} c_{ki}^* c_{k'i} \left\{ \frac{(n_i + n'_i - 3)!}{(\zeta_i + \zeta'_i)^{n_i + n'_i - 2}} \right. \\
 &\quad - \sum_{\substack{p=1 \\ p \neq i}}^N \sum_{k_p} \sum_{k'_p} c_{kp}^* c_{k'p} \frac{(n_p + n'_p)! N_{n_p n'_p}}{(\zeta_p + \zeta'_p)^{n_p + n'_p + 1}} \\
 &\quad \times \left[\frac{(n_i + n'_i - 3)!}{(\zeta_i + \zeta'_i)^{n_i + n'_i - 2}} - \sum_{t=0}^{n_p + n'_p} \frac{(\zeta_p + \zeta'_p)^t}{t!} \right. \\
 &\quad \left. \left. \times \frac{(n_i + n'_i + t - 3)!}{(\zeta_p + \zeta'_p + \zeta_i + \zeta'_i)^{n_i + n'_i + t - 2}} \right] \right\} \delta_{l_i l'_i} \delta_{m_i m'_i}, \quad (18)
 \end{aligned}$$

where $N_{n_i n'_i}$ is the normalization coefficient.

4. Results and Discussion

We have calculated ground state energies of open- and closed-shell atoms in the range from He to Sr over n -STOs and ni -STOs. Also, we have calculated three largest relativistic corrections, i.e., the kinetic energy correction, the Darwin term and the spin-orbit interaction. The ground state wave functions for both n -STOs and ni -STOs were provided to us by Prof. Thakkar through private communication [46]. The calculation of one- and two-electron integrals for ni -STOs is extremely time consuming for large atoms having a number of basis functions. Therefore, it is very important that

the algorithms for calculation of these integrals be fast and accurate. In the present study, evaluation of the ground state energies of open- and closed-shell atoms was realized by using equation (8) for n -STOs and equation (9) for ni -STOs to calculate the radial part of two-electron integrals given by equation (6). The gaunt coefficients in equation (6) were evaluated by the method described in [47], and in order to speed up, the calculations over n -STOs, the radial integral given by equation (8) was evaluated with a similar approach. In calculations over ni -STOs, we have expressed in terms of incomplete beta function $B_q(m, n)$ the incomplete gamma functions $\gamma(a, x)$ and $\Gamma(a, x)$. Our calculations have indicated that the convergence behaviour of incomplete beta function is superior to incomplete gamma functions and hypergeometric functions.

It is clear from the series description of incomplete beta function given by equation (10) that the convergence is worst for $q = 1$, even for this worst case including 75 terms were enough to obtain a relative precision of 10^{-7} , and in most cases with $q > 1$ less than 15 terms were enough to obtain relative precision of 10^{-15} . We have listed in Table 1 the nonrelativistic ground state energies of atoms in the range $2 \leq Z \leq 38$ for n -STOs and ni -STOs. This table contains the results found in the literature as well for comparison. For all the atoms included in this study, the ground state energies are very close to the exact results with a relative error on the order of 10^{-7} . In order to verify our calculations, we have calculated the atomic virial coefficient which differs from the exact value of (-2) only after 7th or 8th digit. This indicates that our results are sufficiently accurate for the ground state energy of atoms.

We have calculated the three largest relativistic corrections which are relativistic kinetic energy correction $\langle E^{P^4} \rangle$, the Darwin term $\langle E^D \rangle$ and spin-orbit interaction $\langle E^{LS} \rangle$, coming from being perturbation term to the ground state energy. We have listed in Table 2 the results obtained for the relativistic kinetic energy corrections and the Darwin terms from He to Sr. It

can be seen in the first column in Table 2 that the total kinetic energy corrections increase from -0.000703 au for the atom He to a value of -165.2138 au for the atom Sr. They correspond to $2.45 \times 10^{-2}\%$ and 5.2% when they are compared with the total ground state energies of -2.861813849 au for He and -3176.367226 au for Sr, respectively. It is shown that the relativistic kinetic energy correction has increased rapidly when going to the larger atoms. Note that even for the atom Sr ($Z = 38$), the relativistic kinetic energy correction is about 5.2% of the total ground state energy 3176.367226 au, and it may not be neglected in an accurate calculation. Similar to the trend in the total energy correction, the relativistic effect in each individual orbital increases as the atom becomes larger. The major effect of the relativistic kinetic correction causes the wave function to shrink in the region near the nuclear where the wave function has large gradient. The most contribution to the kinematic correction comes from two $1s$ electrons. Consider Fe ($Z = 26$) atom for example, 83.8% of the correction comes from two $1s$ electrons and 9.77% from the $2s$ electrons. The contribution of the $3s$ and $4s$ electrons is 1.4% and $6.4 \times 10^{-2}\%$, respectively. The $2p$, $3p$ and $3d$ electrons are contributed 4.24% , $6.3 \times 10^{-1}\%$ and $8 \times 10^{-2}\%$, respectively. As most of the wave functions stay away from the nuclear regions, the contributions of p - and d -orbitals are relatively small in comparison with s orbitals. The Darwin correction listed in the second column in Table 2 increases from 0.00569 au for He to 120.391943 au for Sr, which are amount to $1.99 \times 10^{-2}\%$ and 3.79% of the corresponding total ground state energies, respectively. Take P ($Z = 15$) atom, for example, the magnitude of the Darwin correction is approximately 1.25% of the total ground state energy. The Darwin correction deals with the Laplacian of the effective potentials. For the positive nuclear charge, since only the s orbitals are non-vanishing in the nuclear regions, it does not contribute to p orbitals. The contribution of the negative electron charges is of opposite sign and effects all the states including the p -orbitals. Since the

electron charges are spread over the atomic range, this effect is much smaller. For the atom P ($Z = 15$), for example, the contribution of two $1s$ electrons is 91.84%. The $2s$ and $3s$ electrons contribute 6.68% and 0.5%, respectively. The total contribution of $2p$ and $3p$ electrons is 0.98%.

While the positive Darwin affects are higher the grounds state energies, the negative relativistic kinetic energy corrections caused by shrinkage of the wave functions are lower the ground state energies. Our results for the total Darwin corrections in small atoms are in good agreement with ones obtained by Jeng and Hsue. However, there is a small discrepancy seems to increase by increasing atomic number Z . The cause of this discrepancy is due to one-electron delta function operator in calculation of Darwin term, because the approximate wave functions are usually designed to perform accurately the common properties of the real wave functions. Although the wave functions are sufficient in determination of the various physical properties as energy and momentum, they are insufficient to calculate the characteristic properties such as amplitude, which is restricted to the narrow region.

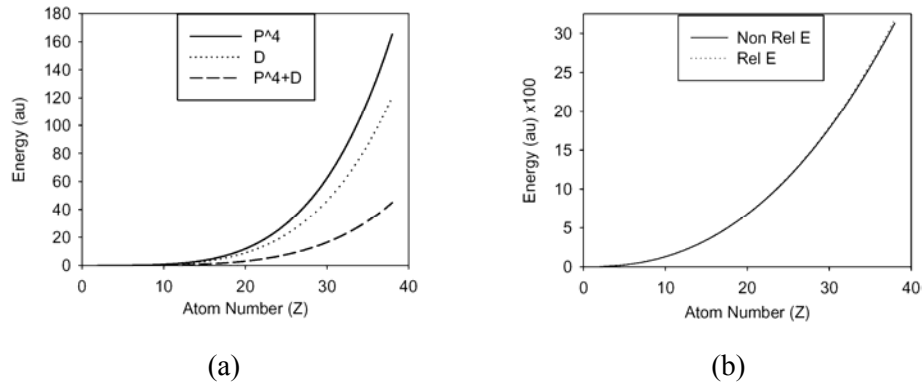


Figure 1. (a) The ground state relativistic correction energies of atoms. Solid lines are kinetic energy correction, dot line is Darwin term, and dash line is kinetic energy correction plus Darwin term. (b) The total grounds state energies of atoms. Solid lines are nonrelativistic the total ground state energy and dot line is relativistic the total ground state energy.

Table 1. Ground state energy of atoms over n-STOs and ni-STOs in au

Atom	E^a	E_{EXACT}^c	E(n-STOs)	E(ni-STOs)	Atom	E^a	E_{EXACT}^c	E(n-STOs)	E(ni-STOs)
He	-2.8601	-2.861679995	-2.861679849	-2.854208514	Sc	-759.0536	-759.7357178	-759.7355584	-759.4835135
Li	-7.3704	-7.432726927	-7.432725232	-7.425838490	Ti	-847.6741	-848.4059967	-848.4058749	-848.1138460
Be	-14.4966	-14.57302316	-14.57302092	-14.56425241	V	-942.0990	-942.8843374	-942.8841272	-942.5376537
B	-24.4097	-24.52906072	-24.5290590	-24.51556063	Cr	-1042.4768	-1043.356376	-1043.355959	-1042.828348
C	-37.5095	-37.68861895	-37.68861869	-37.66414641	Mn	-1148.9172	-1149.866251	-1149.866038	-1149.362794
N	-54.1287	-54.40093419	-54.40092402	-54.35609468	Fe	-1261.5853	-1262.443665	-1262.443269	-1261.811353
O	-74.5979	-74.80939845	-74.80938446	-74.71952794	Co	-1380.6083	-1381.414553	-1381.414171	-1380.631813
F	-99.2466	-99.40934933	-99.40933417	-99.25256304	Ni	-1506.1223	-1506.870908	-1506.870352	-1505.910049
Ne	-128.4043	-128.5470980	-128.5470888	-128.2987516	Cu	-1638.3566	-1638.963742	-1638.962932	-1637.485730
Na	-161.6240	-161.8589116	-161.8588612	-161.6286041	Zn	-1777.1668	-1777.848116	-1777.847506	-1776.445366
Mg	-199.3402	-199.6146363	-199.6145591	-199.3907874	Ga	-1922.4595	-1923.261009	-1923.260461	-1921.928593
Al	-241.5332	-241.8767072	-241.8766962	-241.6717629	Ge	-2074.4416	-2075.359733	-2075.359277	-2074.070828
Si	-288.4346	-288.8543624	-288.8543570	-288.6525907	As	-2233.1912	-2234.238654	-2234.238243	-2232.978576
P	-340.2024	-340.7187808	-340.7187426	-340.5166634	Se	-2398.7902	-2399.867611	-2399.866972	-2398.625718
S	-396.9931	-397.5048958	-397.5048207	-397.2965967	Br	-2571.3226	-2572.441332	-2572.440581	-2571.210112
Cl	-458.9629	-459.4820721	-459.4819666	-459.2645151	Kr	-2750.8731	-2752.054977	-2752.054232	-2750.828585
Ar	-526.2672	-526.8175126	-526.8174568	-526.5877033	Rb	-2937.0787	-2938.357453	-2938.356607	-2937.146402
K	-598.5363	-599.1647865	-599.1646404	-598.9407617	Sr	-3130.2127	-3131.545686	-3131.545326	-3130.345228
Ca	-676.0950	-676.7581857	-676.7580379	-676.5356738	-	-	-	-	-

^a: [40]^c: [48]^d: [16]

Table 2. Relativistic corrections and relativistic total ground state energy of atoms in au

Atom	Eq.(13)	Eq.(15)	Eqs.(13+15)	RelE ^a	RelE ^b	RelE
He	-0.000703 -0.0007 ^a	0.000569 0.0006 ^a	-0.000134 -0.0001 ^a	-2.8601	-2.861640	-2.861813849
Li	-0.004141 -0.0041 ^a	0.003326 0.0033 ^a	-0.000815 -0.0008 ^a	-7.3705	-	-7.433540232
Be	-0.014349 -0.0142 ^a	0.011466 0.0113 ^a	-0.002883 -0.0029 ^a	-14.4974	-14.575816	-14.57590392
B	-0.036821 -0.0364 ^a	0.029294 0.0290 ^a	-0.007527 -0.0074 ^a	-24.4129	-	-24.53658595
C	-0.078938 -0.0781 ^a	0.062543 0.0619 ^a	-0.016395 -0.0162 ^a	-37.5184	-	-37.70501369
N	-0.149865 -0.1484 ^a	0.118252 0.1170 ^a	-0.031613 -0.0314 ^a	-54.1479	-	-54.43253702
O	-0.260793 -0.2584 ^a	0.204943 0.2028 ^a	-0.05585 -0.0556 ^a	-74.6344	-	-74.86523446
F	-0.424505 -0.4208 ^a	0.332233 0.3287 ^a	-0.092272 -0.0921 ^a	-99.3101	-	-99.50160617
Ne	-0.655819 -0.6505 ^a	0.508147 0.5058 ^a	-0.147672 -0.1477 ^a	-128.5064	-128.69101	-128.6947608
Na	-0.975759 -0.9684 ^a	0.757132 0.7495 ^a	-0.218627 -0.2189 ^a	-161.7857	-	-162.0774882
Mg	-1.403857 -1.3942 ^a	1.084465 1.0742 ^a	-0.319392 -0.32 ^a	-199.5839	-199.93446	-199.9339511
Al	-1.960389 -1.9475 ^a	1.508099 1.4943 ^a	-0.45229 -0.4532 ^a	-241.8875	-	-242.3289862
Si	-2.669265 -2.6526 ^a	2.045482 2.0275 ^a	-0.623783 -0.6251 ^a	-288.9350	-289.44891	-289.47814
P	-3.556503 -3.5356 ^a	2.715416 2.6925 ^a	-0.841087 -0.8431 ^a	-340.8894	-	-341.5598296
S	-4.650489 -4.6244 ^a	3.538373 3.5094 ^a	-1.112116 -1.115 ^a	-397.9157	-	-398.6169367
Cl	-5.983821 -5.9494 ^a	4.537187 4.4998 ^a	-1.446634 -1.4496 ^a	-460.1779	-	-460.9286006
Ar	-7.584471 -7.5428 ^a	5.732543 5.6867 ^a	-1.851928 -1.8561 ^a	-527.8405	-528.68176	-528.6693848
K	-9.493081 -9.4460 ^a	7.152417 7.0999 ^a	-2.340664 -2.3461 ^a	-600.5474	-	-601.5053044
Ca	-11.75049 -11.6954 ^a	8.827269 8.7650 ^a	-2.923221 -2.9304 ^a	-678.6326	-679.70875	-679.6812589
Sc	-14.37908 -14.3150 ^a	10.77741 10.7020 ^a	-3.60167 -3.613 ^a	-762.2121	-	-763.3372284

Ti	-17.42544 -17.3516 ^a	13.03139 12.9432 ^a	-4.39405 -4.4084 ^a	-851.5621	-	-852.7999249
V	-20.93297 -20.8483 ^a	15.62175 15.5193 ^a	-5.31122 -5.329 ^a	-946.8378	-	-948.1953472
Cr	-24.93114 -24.8310 ^a	18.57270 18.4519 ^a	-6.35844 -6.3791 ^a	-1048.1914	-1049.6731	-1049.714399
Mn	-29.51226 -29.4022 ^a	21.94091 21.8048 ^a	-7.57135 -7.5974 ^a	-1155.7717	-	-1157.437388
Fe	-34.68222 -34.5551 ^a	25.73911 25.5823 ^a	-8.94311 -8.9728 ^a	-1269.7314	-	-1271.386379
Co	-40.50466 -40.3591 ^a	30.01028 29.8308 ^a	-10.49438 -10.5283 ^a	-1390.2226	-	-1391.908551
Ni	-47.03333 -46.8672 ^a	34.79246 34.5879 ^a	-12.24087 -12.2793 ^a	-1517.3973	-	-1519.111222
Cu	-54.21971 -54.0990 ^a	40.07225 39.8730 ^a	-14.14746 -14.226 ^a	-1651.4824	-	-1653.110392
Zn	-62.35381 -62.2186 ^a	46.00891 45.7856 ^a	-16.3449 -16.433 ^a	-1792.4091	-1794.6082	-1794.192406
Ga	-71.37705 -71.2129 ^a	52.58072 52.3242 ^a	-18.79633 -18.8887 ^a	-1790.0714	-	-1942.056791
Ge	-81.35203 -81.1601 ^a	59.83303 59.5419 ^a	-21.519 -21.6182 ^a	-2094.7034	-2097.4618	-2096.878277
As	-92.34659 -92.1261 ^a	67.81200 67.4842 ^a	-24.53459 -24.6419 ^a	-2256.3961	-	-2258.772833
Se	-104.4293 -104.1789 ^a	76.56539 76.1981 ^a	-27.86391 -27.9808 ^a	-2425.2588	-	-2427.730882
Br	-117.6707 -117.3890 ^a	86.04135 85.7318 ^a	-31.62935 -31.6572 ^a	-2601.3991	-	-2604.069931
Kr	-132.1439 -131.8292 ^a	96.58995 96.1354 ^a	-35.55395 -35.6938 ^a	-2784.9273	-2788.8555	-2787.608182
Rb	-148.0269 -147.5940 ^a	108.0204 107.476 ^a	-40.0065 -40.1178 ^a	-2975.5191	-	-2978.363107
Sr	-165.2138 -164.7560 ^a	120.3919 119.80 ^a	-44.8219 -44.9526 ^a	-3173.4689	-3178.0743	-3176.367226

^a: [40], ^b: [42]

Table 3. Spin-orbit splitting and the coupling coefficients for p -orbitals from B to Sr in au

Atom	$2p$ -splitting	$2p$ -coupling	$3p$ -splitting	$3p$ -coupling	$4p$ -splitting	$4p$ -coupling
B	0.000124	0.000041				
C	0.000339	0.000113				
N	0.000746	0.000249				
O	0.001399	0.000466				
F	0.002427	0.000809				
Ne	0.003946	0.001315				
Na	0.006941	0.002314				
Mg	0.011161	0.003720				
Al	0.016747	0.005582	0.000515	0.000172		
Si	0.024534	0.008178	0.001056	0.000352		
P	0.034728	0.011576	0.001837	0.000612		
S	0.047754	0.015918	0.002881	0.000960		
Cl	0.064061	0.021354	0.004294	0.001431		
Ar	0.084329	0.028124	0.006053	0.002019		
K	0.108936	0.036312	0.009288	0.003096		
Ca	0.138610	0.046203	0.013433	0.004478		
Sc	0.174028	0.058009	0.017831	0.005944		
Ti	0.215820	0.071940	0.023014	0.007671		
V	0.264674	0.088225	0.029131	0.009710		
Cr	0.321772	0.107257	0.035593	0.011864		
Mn	0.386589	0.128863	0.044573	0.014858		
Fe	0.461268	0.153756	0.054348	0.018116		
Co	0.546221	0.182074	0.065499	0.021833		
Ni	0.642350	0.214117	0.078204	0.026068		
Cu	0.751467	0.250489	0.091465	0.030488		
Zn	0.871901	0.290634	0.108780	0.036260		
Ga	1.007199	0.335733	0.129370	0.043123	0.003436	0.001145
Ge	1.157534	0.385845	0.153005	0.051002	0.005901	0.001967
As	1.324109	0.441370	0.180071	0.060024	0.008834	0.002945
Se	1.508081	0.502694	0.210721	0.070240	0.012160	0.004053
Br	1.710603	0.570201	0.245257	0.081752	0.016210	0.005403
Kr	1.932902	0.644301	0.284235	0.094745	0.020710	0.006903
Rb	2.176090	0.725363	0.327080	0.109027	0.028769	0.009590
Sr	2.441714	0.813905	0.375194	0.125065	0.038116	0.012705

In the third column of Table 2, we have listed the total relativistic corrections including the relativistic kinetic energy plus the Darwin correction from -0.000134 au for He to -44.9526 au for Sr. While total relativistic corrections for small atoms various between 0 and -1 au, these corrections have increased rapidly when going through the bigger atom. The

corresponding relativistic corrected ground state energy values in the literature are listed in fourth and fifth columns in Table 2 for comparison. In the fourth column, Jeng and Hsue [40] calculated the relativistic corrected energies by the local density approximation method (LDA) by employing *B*-spline basis. They took into account two correction terms which are the relativistic kinetic energy correction and the Darwin correction, in calculation of the relativistic corrected energies. In fifth column, Macedo et al. [42] calculated directly the ground state energies from relativistic Hamiltonian of the closed-shell atoms from He to Barium over Gaussian basis sets by the generator coordinate Dirac-Fock (GCDF) method. Our results calculated by *ab-initio* method over *n*-STOs for the relativistic corrected energies from He to Sr are listed in the last column in this table. As can be shown from the table that our results obtained from He to Sr atoms are better than ones calculated by Jeng and Hsue [40]. Furthermore, while our results are better than ones calculated by Macedo et al. [42] for small atoms, there is a small discrepancy with ones of larger atoms. This situation may explain that we have not taken into account the other relativistic terms which have important effects for especially larger atoms. When going to larger atoms, these effects are lower the negative total energy values of atoms. We have shown the total ground state correction terms in Figure 1(a) and the total ground state nonrelativistic and relativistic energies in Figure 1(b). It can be shown clearly from Figure 1(a) that the order of magnitude of the kinetic energy corrections and the Darwin corrections are almost the same in small atoms and they remove each other, but the relativistic kinetic energy correction is larger than the Darwin term for larger atoms. This results show that the terms of the kinetic energy corrections and Darwin terms may not be neglected in accurate calculation even for small atoms. In addition, we may see in Figure 1(b) that the total nonrelativistic and relativistic ground state energies have increased exponentially with respect to atomic number.

We have listed the results obtained for spin-orbit energies and coupling constants of *p*-orbitals in Table 3. As can be seen in the table, the magnitude of spin-orbit splitting grows rapidly as the atomic number *Z* increases. Take the dominate 2p splitting, the splitting increases from 1.24×10^{-4} au for B to

2.441714 au for Sr. As seen in this table, the inner orbitals, $l \neq 0$, have larger energy splittings whose wave functions lie nearer to the origin as equation (17) contains the expectation value of r^{-1} . Take the Si ($Z = 14$) atom, the energy 0.001056 au in the $3p$ -orbitals is only 4.3% of the $2p$ splitting energy 0.024534 au. The splitting energy of $2p$ orbital corresponds to $8.48 \times 10^{-3}\%$ merely when compared with the total ground state energy of 289.47814 au. The spin-orbit splitting energy for Si has been measured and calculated in various works. Hayes and Brown [49] measured a value of 0.65 ± 0.05 eV (0.023887 au) for this energy with the experiments on the absorption of molecules. For the energy, Siegbahn et al. [50] and Kelfve et al. [51] obtained various results which are over the range of $0.6 \sim 0.7$ eV at various experiments. This energy was calculated to be 0.7 eV (0.025724 au) with perturbation treatments on The Hartree-Fock Slater wave functions by Herman and Skillman [52]. In this study, we have calculated 0.024534 au for spin-orbit splitting energy of $2p$ in Si. The result is in good agreement with the above mentioned experimental values and with other results found in literature.

Works are in progress for the calculation of relativistic corrections for several excited states of the finite and infinite Quantum Dots with spherical confining potential, which their nonrelativistic ground state energies and wave functions were obtained with combining the Genetic algorithm and HFR method.

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