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Applications of B-Splines to the Local Density Functional Calculations for Atoms from H to Ca

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B-splines is employed to solve the Kohn-Sham equations of the local density functional theory for atoms from H to Ca in a variational self-consistent field procedure. The local-density-approximation (LDA), local-spin-density-approximation (LSD), and self-interaction-correction local-spin-density-approximation (SIC-LSD) schemes have all been considered and comparisons of the results are presented. Both the Gunnarsson-Lundqvist (GL) and Ceperley-Alder (CA) exchange-correlation energies are used. We have tried to achieve high accuracy in the numerical procedure. Comparisons of the energies show that the results of SIC-LSD are more accurate while LDA and LSD are more efficient. The results are in agreement with published results. The expectation values of different powers of *r* for each orbital which depends on the detailed behavior of the wave functions of the atoms are given. Additional corrections including relativistic effects, the reduced mass effects and the finite nuclear size corrections are also considered. The calculated results including these corrections are presented and compared with experimental data and other theoretical calculations. The comparison illustrates the ability of the B-spline applications to the density functional theory to be an efficient method and yet is capable of arriving at accurate results which can compete with results of sophisticated methods. As an additional test of the method, we have calculated the oscillator strengths of the 3s-3p and 4s-4p transition of the alkali iso-electron atoms: Na, Mg^+ and K, Ca^+. Compared with available experimental results, our results are among the best published theoretical values so far.

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I. Introduction

The density functional (DF) formalism [1, 2] has been employed extensively and successfully for the study of the ground state electronic structures in recent years. In view of its simplicity and versatility as compared with other many-body techniques, the method has established itself as one of the leading tools for calculating the ground state properties of complicated many-electron systems such as atoms, molecules, and solids. Based on the

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theorem of Hohenberg and Kohn [1] that the ground state energy attains its minimum with respect to the variation of the electron density, Kohn and Sham [2] proposed local density approximation (LDA). In this approximation, the exchange and correlation potential is approximated by a local function depending only on the total electron density. Von Barth and Hedin [3] extended the spinless Kohn-Sham theory to the spin polarized case. By studying the spin dependent exchange-correlation potential with the spin-polarized electron liquid model in the local approximation, Gunnarsson, Lundqvist, and Wilkins [4] introduced the local-spin-density approximation (LSD) as a spin-polarized generation of LDA. Perdew and Zunger [5-7] pointed out that most of the errors in the LSD energy come from the unphysical electrostatic self-interaction of the electrons especially in the localized 1s orbital. They presented the self-interaction-correction local-spin-density approximation (SIC-LSD) in which the self-interaction Coulomb and the spin-polarized exchange-correlation energy was subtracted out for each orbital. The SIC-LSD approach leads to a more tightly bound atom as a consequence of having correct asymptotic potential, and results for the total ground state energy calculated have been shown to improve systematically. To save time, a simplified SIC-LSD version by taking spherical averaging was suggested [8] and has been found to be adequate for most of the applications. In recent years, approaches based on improved description of exchange-correlation energies in reciprocal space leading to the-so-called generalized-gradient approximation (GGA) are still subjects of active research [9, 10], with promising results in quite a few cases. Many review articles introducing various approaches of DF theory [11, 12] with diverse applications [13, 14] have appeared in the literature.

In practical calculation, the most commonly used numerical method to solve the Kohn-Sham equation is by a direct integration over dense grid points. This method is time consuming and may cause problem in an accurate calculation of complicated situations because it handle the gradient term by difference between these dense grid points which tends to cause numerical instabilities by truncation errors. The problem is even more severe for higher order gradients. In this respect, B-spline method has recently been introduced in atomic structure calculations. Many basic properties of B-splines have been discussed by Carl de Boor [15] in detail. Johnson Blundell, and Sapirstein [16] used B-splines to relativistic many-body perturbation calculations. Fischer and Guo [17] performed self-consistent Hartree-Fock calculations on the ground state energy of the He atom with B-splines as basis sets. Applications of B-spline to one-electron diatomic molecules [18, 19], hydrogen atoms in strong magnetic field [20, 21], the configuration-interaction (CI) calculations for atoms [22, 23], and many other studies [24, 25] in recent years have shown that this method is convenient and successful for accurate calculation on various atomic systems. Applications of B-splines to CI and calculations based on many-body perturbation theory has been reviewed by Hansen et al. [26].

In this paper we report the application of B-splines to the study of the ground state structures of atoms form H to Ca by using variational method in spherically averaged density functional formalism. The electron density and the wave functions of the atoms are represented by the B-spline basis. The B-splines are briefly mentioned in section II. In section III, we briefly summarize the three approaches of the density functional theory: local-density-approximation (LDA), local-spin-density-approximation (LSD), and self-interaction-correction local-spin-density approximation (SIC-LSD). The Kohn-Sham eigen equations are solved in a Self-consistent-field iteration procedure until the electron density becomes stationary. The ground state structure of the many-electron system is then obtained. The results of the LDA, LSD and SIC-LSD schemes are all obtained for comparison. Detailed discussions of the calculated results are presented in section IV. In this work, the range $15 < R < 20\ (a_0)$ is used to make sure that the electron density vanishes to at least 10^{-10} for all the atoms considered. The exponential type knot sequences of order 7 are used to generate about 110 B-spline basis for an accurate representation of the electron wave functions. The self-consistent density functional iteration is terminated as the B-spline fitted electron density converges to within lo- “ . In fact, since the accuracy of exchange-correlation energy has only four digits, the basis set of B-splines may be reduced and the converge criterion may be related for time saving purpose. Based on the ground state wave functions of the atomic system, we calculated the expection values of different powers of r and compared them with other calculations for testing the reality of the resultant wave functions. In section V, we discuss various corrections including the relativistic effects, the nuclear size effects and the reduced mass effects. The corresponding detailed numerical results are presented in section VI. In section VII, we discuss the application of this method to the calculation of the oscillator strengths of alkali iso-electron atoms. Conclusions and discussions are given in section VIII.

II. B-splines

The ith B-spline basis $B_{i,k}$ of order k defined on a nondecreasing knot sequence $\{t_i\}$, $i = 1,2,\cdots$ is a positive piecewise polynomial of degree k- 1 which vanishes everywhere outside the interval $t_i \leq x < t_{i+k}$. The B-spline basis set of order k and knot sequence $\{t_i\}$ is generated by the following recursion relation [15]:

$$B_{i,k}(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(x), \tag{1}$$

with

$$B_{i,1}(x) = \begin{cases} 1, & t_i \leq x < t_{i+1} \\ 0, & \text{otherwise.} \end{cases} \tag{2}$$

An important advantage of the B-spline basis is that the knot sequence can be readily adjusted to suit the properties of the wave function in consideration. By suitably increasing the density of the knot sequence in regions where the wave function varies repidly, the B-spline basis set can represent the function accurately. We use knot sequences of order $k = 7$ defined in the atomic region with k-fold multiplicity at the endpoints $r = 0$ and $r = R$. Exponential type knot sequences have been used in this work. The electron density $n(r)$ and the radial wave function $R(r)$ of the Kohn-Sham eigen equation are represented as linear combinations of these B-splines:

$$n(r) = \sum_i a_i B_i(r), \qquad R(r) = \sum_i c_i B_i(r), \tag{3}$$

where $B_i(r)$ is the abbreviation of $B_{i,k}(r)$ and a_i, c_i are basis coefficients. An advantage of the B-spline basis is the fact that the matrix elements forms from this basis is sparse resulating in a dramatic saving on the computer storage and computation time. The nonorthogonal

B-spline basis are solved iteratively for the single-particle eigen equation by the Galerkin method and the boundary condition is automatically satisfied in our algorithm written in C language, taking into account the sparseness of the matrix elements in this basis.

III. Density functional theory

We briefly summarize here the three basic approaches : LDA, LSD, and SIC-LSD, used in this paper to obtain the ground state wave functions. Detailed description can be found, for example, in Refs. [2,4,7].

Consider an N-electron system with the nonrelativistic Hamiltonian in atomic units ($\hbar = e = m_e = 1$)

$$H = \sum_i \left(\frac{p_i^2}{2} + U(\vec{r}_i) \right) + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\vec{r}_i - \vec{r}_j|}, \tag{4}$$

where the indexes i, j run from 1 to N and $U(\vec{r}_i)$ is the external potential interacts on the electrons. The last term in the Hamiltonian is the Coulomb interactions between the electrons. In general, this rigorous N-particle Hamiltonian is too complicated to be solved exactly. In the local density approximation (LDA) [1,2], the total ground state energy E_G is represented as functional of the electron density $n(\vec{r})$:

$$E_G = T_0[n] + \int d^3r n(\vec{r}) U(\vec{r}) + \frac{1}{2} \int d^3r_1 d^3r_2 \frac{n(\vec{r}_1) n(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + E_{xc}[n]. \tag{5}$$

with

$$n(\vec{r}) = \sum_\alpha w_\alpha |\psi_\alpha(\vec{r})|^2, \tag{6}$$

where w_α is the occupation number of each orbital indicated by α. The total ground state kinetic energy $T_0[n]$ of noninteracting particles in the system may be written as

$$T_0[n] = \frac{1}{2} \sum_\alpha w_\alpha \int d^3r \vec{\nabla} \psi_\alpha^\dagger \cdot \vec{\nabla} \psi_\alpha. \tag{7}$$

The second term of the ground state energy E_G is the total interaction energies between the electrons and the external field $U(\vec{r})$ such as the nuclear potential in atoms. The third term is the Coulomb interactions among the electrons. And the last term $E_{xc}[n]$ is the total exchange-correlation energy

$$E_{xc}[n] = \int d^3r n(\vec{r}) \varepsilon_{xc}(n(\vec{r})), \tag{8}$$

where ε_{xc} denotes the exchange-correlation energy per electron. With the particle conserving constraint, the single particle eigen equation is obtained by taking the functional derivative to minimize the total ground state energy E_G with respect to the wave function $\psi_\alpha^\dagger(\vec{r})$ through the electron density $n(\vec{r})$:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\vec{r})\right\}\psi_\alpha(\vec{r}) = \lambda_\alpha\psi_\alpha(\vec{r}), \tag{9}$$

where the eigen values λ_α come from the Lagrange multipliers for the constraint and the effective single particle potential $v_{\mathrm{eff}}(\vec{r})$ is written as

$$v_{\mathrm{eff}}(\vec{r}) = U(\vec{r}) + \int d^3r\frac{n(\vec{r'})}{|\vec{r}-\vec{r'}|} + v_{xc}(\vec{r}). \tag{10}$$

Iteration procedure is then used to solve the eigen functions in a self-consistent-field manner. After the electron density becomes stationary, the resultant wave functions and the electron density are substituted into the total energy

$$E_G = \sum_\alpha w_\alpha \int d^3r\psi_\alpha^\dagger\left\{-\frac{1}{2}\nabla^2 + U(\vec{r}) + \frac{1}{2}\int d^3r\frac{n(\vec{r'})}{|\vec{r}-\vec{r'}|} + \varepsilon_{xc}(\vec{r})\right\}\psi_\alpha, \tag{11}$$

yielding the following expression

$$E_G = \sum_\alpha w_\alpha\lambda_\alpha - \frac{1}{2}\int d^3r_1d^3r_2\frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} + \int d^3rn(\vec{r})[\varepsilon_{xc}(n(\vec{r})) - v_{xc}(n(\vec{r}))], \tag{12}$$

where in practice, the ground state exchange-correlation energy ε_{xc} and the potential v_{xc} per electron are parameterized in terms of the unit charge radius r,.

In the spin-polarized LSD approach [4], the ground state energy E_G is a functional dependining on the spin density $n_\sigma(\vec{r})$

$$n(\vec{r}) = \sum_{\sigma\alpha} w_{\sigma\alpha}|\psi_{\sigma\alpha}(\vec{r})|^2 = \sum_\sigma n_\sigma(\vec{r}), \tag{13}$$

with the spin quantum number $\sigma = \uparrow, \downarrow$. The spin-dependent orbitals are the solutions of the following equation

$$\left\{-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}^\sigma(\vec{r})\right\}\psi_{\sigma\alpha}(\vec{r}) = \lambda_{\sigma\alpha}\psi_{\sigma\alpha}(\vec{r}), \tag{14}$$

where

$$v_{\mathrm{eff}}^\sigma(\vec{r}) = U(\vec{r}) \ \mathtt{t} \ \int d^3r\frac{n(\vec{r'})}{|\vec{r}-\vec{v'}|} + v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \vec{r}). \tag{15}$$

After self-consistency is achieved in the iteration, the spin-polarized total ground state energy E_G is calculated by

$$\begin{aligned} E_G = \sum_{\sigma\alpha} w_{\sigma\alpha}\lambda_{\sigma\alpha} &- \frac{1}{2}\int d^3r_1d^3r_2\frac{n(\vec{r}_1)n(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|} \\ &+ \int d^3rn(\vec{r})\varepsilon_{xc}(n_\uparrow, n_\downarrow) \\ &- \sum_\sigma \int d^3rn_\sigma(\vec{r})v_{xc}^\sigma([n_\uparrow, n_\downarrow]; \vec{r})), \end{aligned} \tag{16}$$

and the exchange-correlation potential is approximated [4] as

$$v_{xc}^{\sigma,LSD} = \mu_{xc}^{\sigma}(n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})), \tag{17}$$

where $\mu_{xc}^{\sigma}(n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r}))$ is obtained from calculations for the uniform electron gas.

The self-interaction free treatment (SIC-LSD) proposed by Perdew and Zunger [7] has been shown to perform better for the ground state structure of many-electron systems. In this approach, the basic variable for the total ground state energy functional is the spin and orbital dependent electron density $n_{\sigma\alpha}(\vec{r})$ with

$$n(\vec{r}) = \sum_{\sigma\alpha} w_{\sigma\alpha} |\psi_{\sigma\alpha}(\vec{r})|^2 = \sum_{\sigma\alpha} n_{\sigma\alpha}(\vec{r}). \tag{18}$$

The spin and orbital dependent single particle eigen equation becomes

$$\left\{-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\sigma\alpha}(\vec{r})\right\} \psi_{\sigma\alpha}(\vec{r}) = \lambda_{\sigma\alpha}^{SIC} \psi_{\sigma\alpha}(\vec{r}), \tag{19}$$

where

$$v_{\text{eff}}^{\sigma\alpha}(\vec{r}) = U(\vec{r}) + \int d^3r \frac{n(\vec{r'}) - n_{\sigma\alpha}(\vec{r'})}{|\vec{r} - \vec{r'}|} + v_{xc}^{\sigma}([n_{\uparrow}, n_{\downarrow}]; \vec{r}) - v_{xc}^{\uparrow}([n_{\sigma\alpha}, 0]; \vec{r}). \tag{20}$$

The total ground state energy functional E_G is now expressed as

$$\begin{aligned} E_G = \sum_{\sigma\alpha} w_{\sigma\alpha} \lambda_{\sigma\alpha}^{SIC} - \frac{1}{2} \sum_{\sigma\alpha} \int d^3r_1 d^3r_2 \frac{n_{\sigma\alpha}(\vec{r}_1)[n(\vec{r}_2) - n_{\sigma\alpha}(\vec{r}_2)]}{|\vec{r}_1 - \vec{r}_2|} \\ + \sum_{\sigma\alpha} \int d^3r n_{\sigma\alpha}(\vec{r})[\varepsilon_{xc}(n_{\uparrow}, n_{\downarrow}) - \varepsilon_{xc}(n_{\sigma\alpha}, 0)] \\ - \sum_{\sigma\alpha} \int d^3r n_{\sigma\alpha}(\vec{r})[v_{xc}^{\sigma}(n_{\uparrow}, n_{\downarrow}) - v_{xc}^{\uparrow}(n_{\sigma\alpha}, 0)]. \end{aligned} \tag{21}$$

Spherical averaging approximation is taken for all the three calculations in this work. We use the exchange-correlation potential proposed by Gunnarsson and Lundqvist (GL) [4] which are modeled on the spin-polarized electron liquid for all three approaches and the Monte Carlo results by Ceperley and Alder (CA) [27] for low and metallic densities which has been parameterized smoothly to the high density limit by Perdew-Zunger [7] for SIC-LSD also.

IV. Results of local density approximation to atoms from H to Ca

In this paper the eigen value equations with the B-spline basis for LDA, LSD, and SIC-LSD schemes are solved in a self-consistent manner. A relative accuracy of 10^{-10} in the self-consistency of the electron density has been maintained in this work. The resultant wave functions of the orbitals are them used to calculate the total energy and other properties of the ground state. For comparison, both the Gunnarsson-Lundqvist (GL) [4] and the Ceperley-Alder (CA) [27] parameterized electron-gas correlation energies $\epsilon_c(\uparrow, \downarrow)$ are used to calculate the effective potentials. For the LSD and SIC-LSD calculations, the spin configurations with the largest total spins for the porbitals are used in accordance with the Hund's rule. The ground state properties for atoms from H to Ca are calculated and presented in this paper.

To check our program, we list in Table I the Kohn-Sham eigenvalues for each individual orbitals as well as the total energy, and the total correlation energy for the Kr atom calculaated in both LSD and SICLSD formalisms using both GL and CA correlations. The CA results from Perdew-Zunger [7] are also included in the table for comparison. Notice that in Ref. [7] a relative accuracy of 10^{-5} in the energy is maintained. There is a good agreement between our results and those of Perdew-Zunger's [7] results for both the total exchange and the correlation energies of the ground state. There is some small difference between the total LSD correlation energy calculated with the GL and the CA result. This difference is greatly reduced in the self-interaction free SICLSD calculation. The situation is similar for the eigen energies of each individual orbitals. Note that even in such a large atom Kr, 44% of the self-interaction correction to the total energy comes from the 1s orbitals.

In Table II the total ground state energies of various atoms obtained from LSD and SICLSD are listed together for comparison. Also included in the table are the results from Perdew-Zunger [7], the Hartree-Fock(HF) [28], and the nonrelativistic experiment energies [29]. In the LSD(CA) and the SICLSD scheme, our total energies agree well with Perdew-Zunger's results up to 1 x 10^{-5} which is the accuracy maintained by Perdew-Zunger. It

TABLE I. Eigenvalues for each individual orbitals ϵ_{nl}, total energy E, and the total correlation Ec energies for Kr atom. Negative energies in a.u.

energy	LSD(CA)^a	LSD(CA)^b	LSD(GL)^b	SIC(CA)^a	SIC(CA)^b	SIC(GL)^b
ϵ_{1s}	509.9555	509.9841	509.9994	519.1722	519.2006	519.2841
ϵ_{2s}	66.2810	66.2864	66.3003	68.0560	68.0597	68.0797
ϵ_{2p}	60.0153	60.0179	60.0319	62.2901	62.2935	62.3167
ϵ_{3s}	9.3145	9.3153	9.3285	9.9025	9.9033	9.9061
ϵ_{3p}	7.0856	7.0867	7.0999	7.6813	7.6821	7.6849
ϵ_{3d}	3.0733	3.0742	3.0873	3.7216	3.7222	3.7248
ϵ_{4s}	0.8195	0.8205	0.8314	1.0202	1.0208	1.0200
ϵ_{4p}	0.3454	0.3464	0.3565	0.5127	0.5134	0.5126
E	2749.9717	2750.1315	2750.8731	2756.7667	2756.9197	2756.9050
Ec	3.2486	3.2664	4.0088	1.9573	1.9687	1.9540

a : Ref. 7.

b : This work in B-spline basis.

TABLE II. Calculated negative ground-state total energies in a.u. of atoms compared with nonrelativistic experimental results.

Atom	HF”	LSD(CA)^b	LSD(CA)^c	LSD(GL)^c	SIC(CA)^b	SIC(CA)^c	SIC(GL)^c	Expt.^{d}
H	0.5000	0.4777	0.4789	0.4920	0.4998	0.5000	0.5000	0.5000
He	2.8628	2.8334	2.8343	2.8601	2.9179	2.9193	2.9123	2.9037
Li	7.4307	7.3425	7.3427	7.3830	7.5042	7.5046	7.4976	7.4785
Be	14.5711	14.4425	14.4462	14.4966	14.6924	14.6938	14.6804	14.6667
B	24.5265	24.3464	24.3518	24.4198	24.6955	24.7003	24.6868	24.6514
N	54.3963	54.1207	54.1288	54.2431	54.7161	54.7223	54.7156	54.5838
F	99.4032	99.0982	99.1086	99.2612	99.9838	99.9953	99.9838	99.7193
Ne	128.5417	128.2147	128.2273	128.4034	129.2694	129.2825	129.2715	128.9203
Na	161.8513	161.4250	161.4406	161.6348	162.6561	162.6678	162.6562	162.2372
Mg	199.6039	199.1188	199.1327	199.3402	200.5189	200.5319	200.5140	200.0338
Al	241.8656	241.2960	241.3140	241.5397	242.8688	242.8864	242.8679	242.3249
P	340.7028	339.9715	339.9953	340.2661	341.9045	341.9231	341.9092	341.2210
AI	520.7903	525.9010	525.9378	526.2672	528.3926	528.3921	528.4078	527.5216

a : Ref. 45.
b : Ref. 7.
c : This work
d : Ref. 46.

is interesting to mention that although for a uniform electron gas the Monte Carlo results of CA are believed to be more accurate for the exchange and the correlation energy, the performance of GL is slightly better for atoms in general. This is one of the reason why GL has been more widely used in practical application of LDA to atoms, molecules and solids where the gradient of the electron densities probably also plays an important role. There is a marked reduction of this difference between CA and GL in the SICLSD scheme, and the total ground state energies of both results lie slightly lower than the experimental values but differ very little from them. In general, the spin-polarized LSD slightly improves the results of the spin-independent LDA except for the lightest atoms such as H and Li. Both the energies of HF and of LSD lie higher than the experiment data with the results of HF lie closer to the experimental values. The errors of SICLSD is comparable with the results of HF for the larger atoms, but the performance of SICLSD is much better than HF for the smaller atoms.

In the Hartree-Fock approximation, the correlation energy is conventionally defined as the difference between the experimental total energy and the HF value. In Table III, we compare calculated correlation energies from the density-functional with the conventional correlation energies. For the CA correlation energies, there is a good agreement between the Perdew-Zunger’s and our results in both the LSD and SICLSD calculations for all the listed atoms. The SICLSD correlation energies are much closer to the conventional correlation energie but overjumps by about 10%. For the GL scheme, the LSD correlation energies are worse than the CA results by 20 ~30%, while the SICLSD versions perform slightly batter than the CA ones.

TABLE III. Calculated correlation energies of atoms compared with “conventional” experimental values (negative energies in a.u.).

Atom	LSD(CA)^a	LSD(CA)^b	LSD(GL)^b	SIC(CA)^a	SIC(CA)^b	SIC(GL)^b	conv^c
H	0.022	0.022	0.035	0.000	0.000	0.000	0.000
He	0.110	0.111	0.137	0.055	0.058	0.051	0.040
Be	0.221	0.223	0.274	0.114	0.116	0.103	0.096
Ne	0.731	0.737	0.914	0.419	0.424	0.413	0.382
Mg	0.878	0.885	1.093	0.500	0.504	0.487	0.426
Ar	1.411	1.421	1.751	0.820	0.828	0.809	0.731

a : Ref. 7.
b : This work.
C : Ref. 46. (The relativistic effect were not included in the experimental values.)

TABLE IV. Binding energies of negative ions in a.u.

ion	HF”	SIC(CA)^b	SIC(CA)”	SIC(GL)^c	Expt.^{d}
H -	-0.0121	0.0257	0.0265	0.0196	0.0276
O -	-0.0198	0.0588	0.0666	0.0655	0.0537
F–	0.0500	0.1323	0.1380	0.1388	0.1250
Cl–	0.0948	0.1396	0.1472	0.1477	0.1330

a : Ref. 47,48.
b : Ref. 7.
c : This work.
d : Ref. 49.

As a severe test of the density-functional theory, calculations on the binding energies of four negative ions are listed in Table IV. The calculated binding energies of the listed four negative ions from SICLSD are in good agreement with the experiment [29] results. This is in contrast to the fact that the HF calculation does not obtain bound state for the ions H- and 0- because it does not take into consideration of correlation at all.

Listed in Table V are the maximum orbital energies for various atoms. The calculated LSD results from the CA and GL are close to each other but both eigenvalues are about 40% away from the experiment [30]. For the SICLSD scheme, both the CA and the GL

TABLE V. Outer-orgital eigenvalues ϵ_{max} with measured first ionization potentials I_1 in a.u.

Atom	-HF[a]	-LSD(CA)[b]	-LSD(CA)[c]	-LSD(GL)[c]	-SIC(CA)[b]	-SIC(CA)[c]	-SIC(GL)[c]	I_1[d]
H	0.500	0.268	0.269	0.283	0.500	0.500	0.500	0.500
Li	0.195	0.118	0.116	0.124	0.198	0.196	0.196	0.198
Na	0.184	0.114	0.113	0.121	0.187	0.189	0.189	0.187
K	0.147	0.096	0.096	0.102	0.158	0.158	0.158	0.158
N	0.566	0.305	0.307	0.322	0.548	0.548	0.551	0.533
P	0.393	0.232	0.230	0.244	0.367	0.369	0.372	0.386
Cr	0.239	0.147	0.146	0.158	0.246	0.247	0.251	0.250
Mn	0.246	0.169	0.170	0.173	0.261	0.263	0.257	0.272
He	0.919	0.570	0.570	0.582	0.948	0.948	0.944	0.904
Ne	0.849	0.496	0.498	0.510	0.842	0.842	0.841	0.794
Ar	0.592	0.382	0.382	0.393	0.581	0.579	0.578	0.581
Kr	0.526	0.345	0.346	0.357	0.514	0.513	0.513	0.514

a : Ref. 45.
b : Ref. 7.
c : This work.
d : Ref. 50.

results are very close to the experimental data. In average, the SICLSD results are better than the HF eigenvalues.

In Table VI, we list the calculated negative total ground state energies and various ground state properties for a series of atoms from H to Ga with LDA, LSD and SICLSD formalisms in both CA and GL correlation energies. The CA and GL results for each of the three schemes are very close in general. The differences between the CA and GL results for small atoms such as H are about ~ 2% and is reduced to $2 * 10^{-4}$ for larger atoms such as Ca. The total ground state energies calculated with GL [4] correlation energy are slightly better than the CA ones for most atoms in all the three schemes.

For reference, the expectation values of $\langle r \rangle$ for each orbital of atoms from H to Ca are listed in Table VII. The LSD and SIC expectation values of r for the spin up and the spin down electron in both CA and GL are very close to each other.

In this chapter, the performance of different approaches of the local density approximation are compared with each other. In general, except for atoms in the first row, the total ground state energies of LDA are very close to the LSD results. The self-interaction-correction(SIC-LSD) approach for the GL and CA exchange-correlation energies are close to each other and the results from both schemes exhibit a systematic improvement for the nonrelativistic ground state energies and lie very close to the experiments.

TABLE VI. Comparisons of the negative total ground state energies to LDA, LSD, SICLSD calculations in both GL and CA exchange-correlation potentials.

Atom	LDA(GL)	LSD(GL)	SIC(GL)	LDA(CA)	LSD(CA)	SIC(CA)
H	0.4537	0.4920	0.5000	0.4459	**0.4789**	0.5000
He	2.8601	2.8601	2.9123	2.8343	2.8343	2.9193
Li	7.3704	7.3830	7.4976	7.3341	7.3427	7.5046
Be	14.4966	14.4966	14.6803	14.4462	14.4462	14.6938
B	24.4097	24.4198	24.6868	24.3432	24.3518	24.7003
C	37.5095	37.5555	37.9187	37.4243	37.4657	37.9296
N	54.1287	54.2431	54.7156	54.0225	54.1288	54.7223
0	74.5979	74.6526	75.2432	74.4693	74.5211	75.2538
F	99.2466	99.2612	99.9838	99.0946	99.1086	99.9953
Ne	128.4034	128.4034	129.2715	128.2273	128.2273	129.2825
Na	161.6240	161.6348	162.6562	161.4334	161.4406	162.6678
Mg	199.3402	199.3402	200.5140	199.1327	199.1327	200.5319
Al	241.5332	241.5397	242.8679	241.3090	241.3140	242.8864
Si	288.4346	288.4617	289.9460	288.1920	288.2144	289.9629
P	340.2024	340.2661	341.9092	339.9398	339.9953	341.9231
S	396.9931	397.0219	398.8275	396.7093	396.7353	398.8462
Cl	458.9629	458.9703	460.9416	458.6567	458.6635	460.9616
Ar	526.2672	526.2672	528.4078	525.9378	525.9378	528.3921
K	598.5363	598.5445	600.8502	598.1915	598.1966	600.8692
Ca	676.0950	676.0950	678.5656	675.7329	675.7329	678.5894

V. Corrections from the relativistic effects, nuclear size effects, and the reduced mass effects

Refinement of the results including relativistic effects, the nuclear size effects and the reduced mass effects are considered in this section. Since all the corrections including the relativistic effects are small in comparison with the total ground state energies of the atoms, a first order perturbation treatment is adequate for atoms with $Z \leq 20$. We first consider the reduced mass and the finite nuclear size effects. The deviation of the Hamiltonian caused by the finite mass of the nuclear is

$$H^{\mu} = \frac{\mathbf{p}^2}{2\mu} - \frac{\mathbf{p}^2}{2} = \frac{\mathbf{p}^2}{2M}, \tag{22}$$

with the momentum operator

TABLE VII. The LDA(GL) expection value of r in a.u. for every state (n,l) from H to Ca.

atom	1s	2s	3s	4s	2P	3P
H	1.65924					
He	0.95581					
Li	0.58809	3.88518				
Be	0.42490	2.60216				
B	0.33225	1.95945			2.26314	
C	0.27279	1.58048			1.78098	
N	0.23137	1.32835			1.47362	
0	0.20086	1.14742			1.25956	
F	0.17746	1.01079			1.10134	
Ne	0.15893	0.90374			0.97933	
Na	0.14389	0.79109	4.03374		0.80684	
Mg	0.13144	0.70236	3.11296		0.69068	
Al	0.12095	0.63081	2.52978		0.60484	3.39278
Si	0.11201	0.57244	2.15851		0.53906	2.76952
P	0.10430	0.52396	1.89617		0.48675	2.35849
S	0.09757	0.48307	1.69782		0.44401	2.06322
Cl	0.09166	0.44812	1.54108		0.40836	1.83883
Ar	0.08642	0.41790	1.41330		0.37813	1.66148
K	0.08174	0.39139	1.27622	4.85567	0.35198	1.43665
Ca	0.07754	0.36799	1.16421	3.95550	0.32920	1.27385

$$\mathbf{p}^2 = -\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{r^2}, \tag{23}$$

and the reduced mass $\mu = Mm_e/(M$ + m,). The nuclear mass may be express in terms of the atomic weight ***A as*** $M = 1822.8885A$. The reduced mass correction of the total ground state energy is

$$\Delta^\mu = \sum_{nl} w_{nl}\langle H^\mu\rangle_{nl}, \tag{24}$$

where w_{nl} denotes the occupation number of each orbital denoted by (n,l).

We have used the point nuclear potential $V(r) = -z/r$ for the whole atomic range. Due to the finite size of the nuclear, the potential inside the uclear radius ***R*** is approximated as

$$V_{in}(r) = \frac{zr^2}{2R^3} - \frac{3z}{2R}, \tag{25}$$

where $R = 2.2677 \times 10^{-5} A^{1/3} a_0$ and a_0 is the Bohr radius. The total energy shift caused by the perturbative potential inside the nuclear region is now given by

$$\Delta^{nu} = \sum_{nl} w_{nl} \left\langle \frac{z}{r} - \frac{3z}{2R} + \frac{zr^2}{2R^3} \right\rangle_{nl} . \tag{26}$$

We next discuss the following three largest relativistic effects : the relativistic kinetic energy correction, the Darwin term correction, and the spinorbit splitting. In the spherical approximation the wave functions $R(r)$ are expressed in terms of the B-spline basis $B_i(r)$:

$$R(r) = \sum_i c_i B_i(r) , \tag{27}$$

where c_i are the linear coefficients.

Since the magnitude of the electric field potential is small, $A_0 \ll C^2$, the four-component Dirac equation equations may be approximated in atomic units in two-component form as [31],

$$\left[\frac{\mathbf{p}^2}{2} - A_0 - \frac{\mathbf{p}^4}{8c^2} + \frac{\nabla \cdot \mathbf{E}}{8c^2} + \frac{\sigma \cdot (\mathbf{E} \times \mathbf{p})}{4c^2} \right] \Psi = E\Psi, \tag{28}$$

where E denotes the nonrelativistic eigen energy. The first two terms are just the unperturbed Schrödinger Hamiltonian and the last three terms may be calculated perturbatively since they are relatively small in magnitude for smaller atoms.

The third term in Eq. (28) is due to the relativistic correction to the kinetic energy, and the energy shift for each orbital n, l is

$$\Delta^p_{nl} = -\left\langle \frac{4}{8c^2} \right\rangle_{nl} = -\frac{1}{8c^2} \langle R_{nl} | \mathbf{p}^2 \mathbf{p}^2 | R_{nl} \rangle, \tag{29}$$

where $R_{nl}(r)$ is the radial component of the wave function $\psi_{nl}(\vec{r}$. In the spherical approximation, the operator $\mathbf{p}^2$ is expressed as

$$\mathbf{p}^2 = -\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{r^2} . \tag{30}$$

Since the operator $\mathbf{p}^2$ is Hermitian and the radial wave function $R_{nl}(r)$ is real, by employing integration by parts twice, the energy shift for the orbital n, l may be written as

$$\Delta^p_{nl} = -\frac{1}{8c^2} \int r^2 dr \left[\frac{d^2 R_{nl}}{dr^2} + \frac{2}{r} \frac{dR_{nl}}{dr} - \frac{l(l+1)}{r^2} R_{nl} \right]^2 , \tag{31}$$

and the total relativistic kinetic energy correction is

$$\Delta^p_{tot} = \sum_{n,l} w_{n,l} \Delta^p_{n,l} , \tag{32}$$

where $w_{n,l}$ denotes the occupation number of the orbital $(\mathrm{n,l})$. Here an advantage of using B-splines comes out clearly. Since the B-splines are locally polynomials, high order derivatives may be easily and accurately evaluated. This is in contrast to the current numerical procedure using dense grid points where careful handling is needed to avoid numerical instabilities,

The fourth Darwin term in Eq. (28) involving with the divergence of the electric field from the charge density is calculated for each orbital n, l as

$$\Delta_{nl}^{D} = \frac{1}{8c^2}\langle \nabla \cdot \mathbf{E} \rangle_{nl} = \frac{1}{8c^2}\langle R_{nl} | \nabla^2 V_{\rm eff}(r) | R_{nl} \rangle, \tag{33}$$

where the Laplacian operator is given by

$$\nabla^2 V_{\rm eff}(r) = \frac{1}{r^2}\,\frac{d}{dr} r^2 \frac{dV_{\rm eff}}{dr}, \tag{34}$$

with the effective potential

$$V_{\rm eff}(r) = -\frac{z}{\ } + \quad \frac{n(r')}{\ } d^3r' + v_{xc}(r). \tag{35}$$

The Laplacian of the nuclear part of the effective potential resulting in a delta function yields the Darwin correction for sorbital as

$$\frac{1}{8c^2}|R_{nl}(0)|^2 . \tag{36}$$

Substituting the charge interaction term of the effective potential into the Darwin correction and employing integration by parts twice, we have

$$-\frac{1}{8c^2}\int r^2 dr R_{nl}(r) n(r) R_{nl}(r), \tag{37}$$

which is just the expectation value of the charge distribution. The last term of the effective potential may be calculated via the following formula:

$$\frac{1}{4c^2}\int dr v_{xc}(r)\left[2rR_{nl}\frac{dR_{nl}}{dr} + r^2\left(\left(\frac{dR_{nl}}{dr}\right)^2 + R_{nl}\frac{d^2R_{nl}}{dr^2}\right)\right]. \tag{38}$$

And the total Darwin correction is simply given by

$$\Delta_{tot}^{D} = \sum_{nl} w_{nl}\Delta_{nl}^{D} . \tag{39}$$

The last term in Eq. (28) is the spin-orbit interaction, and is expressed explicitly as [32]

$$\frac{\sigma \cdot (\mathbf{E} \times \mathrm{p})}{4c^2} = \frac{1}{2c^2}\frac{1}{\mathrm{T}}\frac{dV}{dr}\mathbf{S} \cdot \mathbf{L} . \tag{40}$$

The spin-orbit splitting energy for the orbital n, l, j is

$$\Delta^{LS}_{nlj} = \frac{1}{4c^2}\left\langle \frac{1}{r}\frac{dV_{\text{eff}}}{dr}\right\rangle_{nl} \begin{cases} l, & j = l + \frac{1}{2}, \\ -l - 1, & j = l - \frac{1}{2}, \end{cases} \tag{41}$$

with the Lande's interval rule

$$\left\langle \frac{1}{r}\frac{dV_{\text{eff}}(r)}{dr}\right\rangle_{nl} = \int r^2 dr R_{nl}(r)\frac{1}{r}\frac{dV_{\text{eff}}}{dr}R_{nl}(r), \tag{42}$$

and the effective potential $V_{\text{eff}}(r)$ given in Eq. (35). Substituting the first nuclear term of the effective potential into the Lande's interval rule, we have the well-known expectation value $\langle Zr^{-3}\rangle_{nl}$ for hydrogen like atoms. In the spherical approximation

$$\frac{1}{|\vec{r} - \vec{r'}|} = \frac{1}{r_>}, \qquad r_> = \max.(r, r'), \tag{43}$$

The second electronic potential term of $V_{\text{eff}}(r)$ yields

$$-\left\langle \frac{1}{r^3}\int_0^r n(s)s^2 ds\right\rangle_{nl} \tag{44}$$

which is actually caused by the screening potential of the inner shell electrons. Contribution from the last exchange-correlation term is written as

$$\int dr v_{xc}(r)\left[R^2_{nl} + 2rR_{nl}\frac{dR_{nl}}{dr}\right]. \tag{45}$$

VI. Numerical results for the corrections from reduced mass effects, finite nuclear size effects and relativistic effects

The corrections from the reduced mass effect and the finite nuclear size effects to each individual orbital and the total ground state energies are listed in Tables VIII and IX respectively. Since the reduced mass corrections are proportional to the electron kinetic energies $\langle p^2\rangle$ (Eq. (22)) of the relevant orbitals the corrections are larger for the inner shell orbitals as was shown in Table VIII. For the atom N, the magnitude of the total reduced mass correction is 200 times larger than the finite nuclear size correction. This ratio is reduced to 11 for the larger atom Ca. As the nuclear becomes larger, the attraction force between the nuclear and the electron becomes stronger, and the electronic densities near the nuclear increases rapidly, Of course, the larger nuclear size of the larger atoms has some additional contribution to this result. For the p orbitals the wave functions vanish in the nuclear region, and there is no finite size corrections as can be seen in Table IX. Notice that the magnitude of both these two corrections are negligibles in comparison with the various relativistic effects to be discussed below.

TABLE VIII. Calculated LDA(GL) reduced mass corrections in a.u.

atom	1s	2S	3S	4S	2P	3P	tot
H	0.00023						0.00023
He	0.00019						0.00038
Li	0.00028	0.00002					0.00057
Be	0.00040	0.00003					0.00087
B	0.00054	0.00005			0.00004		0.00123
C	0.00072	0.00007			0.00006		0.00170
N	0.00085	0.00009			0.00007		0.00211
O	0.00099	0.00011			0.00009		0.00254
F	0.00106	0.00012			0.00010		0.00285
Ne	0.00124	0.00014			0.00012		0.00347
Na	0.00133	0.00016	0.00001		0.00014		0.00384
Mg	0.00150	0.00019	0.00002		0.00018		0.00448
Al	0.00160	0.00022	0.00002		0.00020	0.00001	0.00489
Si	0.00179	0.00025	0.00003		0.00024	0.00002	0.00562
P	0.00187	0.00027	0.00004		0.00026	0.00003	0.00601
S	0.00206	0.00031	0.00005		0.00030	0.00003	0.00677
Cl	0.00211	0.00033	0.00005		0.00032	0.00004	0.00708
Ar	0.00210	0.00034	0.00006		0.00033	0.00004	0.00721
K	0.00240	0.00039	0.00007	0.00001	0.00038	0.00006	0.00838
Ca	0.00260	0.00043	0.00009	0.00001	0.00042	0.00007	0.00923

In Table X, we compare the calculated relativistic corrected total ground state energies of the second row atoms in the SIC-LSD approach by using the CA exchange-correlation potential with the experimental data [29] and also with the calculated results of the Dirac-Hartree-Fock (DHF) [33]. The value of the first order perturbation calculation of relativistic corrections based on the Hartree-Fock (HF) [29] and the SIC(CA) results (this work) are also listed in the table. For atoms from Na to Ar the magnitude of the difference of our total energies of SIC (CA) from the experimental data are 0.28% ~ 0.19% a.u. lower and is comparable with the more complicated DHF results which are 0.22% ~ 0.12% a.u. higher. The relativistic corrections here include both the relativistic kinetic energy corrections (P4) and the Darwin effects (Dw), and are 12.4% ~ 7.4% larger than the corresponding HF [29] results. The correlation-neglected Hartree-Fock algorithm leads to inflated atoms while the orbitals in the SIC tend to be tighter leading to a larger relativistic correction.

We list in the last column of Table XI the total negative relativistic kinetic energy corrections for the atoms from H to Ca $(Z=20)$ with SICLSD formalism using CA exchange-correlation potential. Included in the table are also the individual negative relativistic kinetic energy corrections to each orbitals. Since the deviations of the corrections between

TABLE IX. Calculated LDA(GL) finite nuclear size corrections in a.u.

atom	1s	2s	3s	4s	2p	3P	tot
H	0.00000						0.00000
He	0.00000						0.00000
Li	0.00000	0.00000					0.00000
Be	0.00000	0.00000					0.00000
B	0.00000	0.00000			0.00000		0.00000
C	0.00000	0.00000			0.00000		0.00000
N	0.00000	0.00000			0.00000		0.00001
O	0.00001	0.00000			0.00000		0.00001
F	0.00001	0.00000			0.00000		0.00002
Ne	0.00001	0.00000			0.00000		0.00003
Na	0.00002	0.00000	0.00000		0.00000		0.00005
Mg	0.00003	0.00000	0.00000		0.00000		0.00007
Al	0.00005	0.00000	0.00000		0.00000	0.00000	0.00011
Si	0.00007	0.00001	0.00000		0.00000	0.00000	0.00015
P	0.00010	0.00001	0.00000		0.00000	0.00000	0.00021
S	0.00013	0.00001	0.00000		0.00000	0.00000	0.00028
Cl	0.00017	0.00001	0.00000		0.00000	0.00000	0.00038
Ar	0.00024	0.00002	0.00000		0.00000	0.00000	0.00052
K	0.00029	0.00002	0.00000	0.00000	0.00000	0.00000	0.00064
Ca	0.00037	0.00003	0.00000	0.00000	0.00000	0.00000	0.00080

orbitals of different spin orientations are quite small, e.g., $\leq 10^{-3}$ in the largest atom Ca ($Z=20$), we list only the spin up states for reference. As can be seen in the last column the total kinetic energy corrections increases from 0.0000.3 a.u. for the smallest atom H to a value of 11.7398 a.u. for the atom Ca. Compared with the total ground state energies of 0.5 a.u. for H and 681.5841 for Ca, they correspond to 6×10^{-5} and 17.2% respectively. Note that even for the small atom Si ($Z=14$), the relativistic kinetic energy correction is about 1% of the total ground state energy, and may not be neglected in an accurate calculation. The contribution to each orbital is also listed in the table. Similar to the trend in the total energy correction, the relativistic effect in each individual orbital increases as the atom becomes larger. The major effects of the relativistic kinematic correction causes the wave function to shrink in the region near the nuclear where the wave function has large gradient. Most of the corrections come from the contributions of the inner 1s orbital which are listed in the second column. Take CA ($Z=20$) for example, 85.6% of the correction comes from the two 1s orbitals and 8.9% from the 2s orbitals while all the other electrons account for only 5.5%. The contributions of the porbitals are relatively small in comparison with the s orbitals because most of their wave functions stay away from the nuclear regions.

TABLE X. Comparison of the negative relativistic corrected total ground state energies of the second row atoms in SIC(CA) calculations with Dirac-Hartree-Fock (DHF)[b] results and the experimental data[a]. The relativistic corrections based on the SIC(CA) and the Hartree-Fock" are also compared.

atom	state	−SIC(CA)	− Exp"	−DHF[b]	-E.Rel(SIC).	−E.Rel(HF).[a]
Na	^2S	162.896	162.441	162.078	0.2285	0.20021
Mg	^1S	200.865	200.333	199.935	0.3327	0.29505
Al	^2P	243.356	242.752	242.331	0.4696	0.42062
Si	^3P	290.609	289.927	289.450	0.6460	0.58351
P	^4S	342.792	342.025	341.489	0.8691	0.79111
S	^3P	399.993	399.144	398.609	1.1469	1.05076
Cl	^2P	462.450	461.514	460.940	1.4881	1.37168
Ar	^1S	530.294	529.303	528.684	1.9022	1.76094

a : Ref. 11.
b : Ref. 9.

The corrections of the Darwin term calculated in SICLSD scheme using CA exchange-corrections potential are listed in Table XII. Again, since the difference of the magnitudes for different spins in the same orbital is rather small, we list only the spin up ones. As shown in the table, as the atom becomes larger, the energy correction increases for both individual orbital and the total atom. The total Darwin correction listed in the last column increases from 0.00002 a.u. for H to 8.745 a.u. for Ca, which amount to 4 x 10^{-5} and 1.3% of the corresponding total ground state energies respectively. For the atom Si(Z=14), the magnitude of the Darwin term is about 0.7% of the total ground state energy. The Darwin term 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 the p orbitals. The contribution of the negative electron charges is of opposite sign and affects all the states including the p orbitals. Since the electron chalges are spread over the atomic range, this effect is much smaller. This can be seen clearly in the table e.g., all the combined influences from the p orbitals of Ca(Z=20) contribute only about 0.2% of the total Darwin corrections. But the contribution from the two 1s electrons account for 91.6%. The 2s electrons contribute 7.6% and the rest 0.8% comes from all the other electrons combined together.

In Table XIII we compare the total relativistic kinetic energy (P4) and the Darwin (Dw) corrections calculated in LDA, LSD, and SICLSD schemes for atoms from He to Ca. The P4 and Dw corrections calculated in LDA by using GL exchange-correlation potential are listed in the first two columns. Listed in the second two columns are those of LSD(GL) and the corresponding values from SIC-LSD(GL) are listed in the next two columns. The two corrections calculated in SIC-LSD scheme with CA exchange-correlation potential are

TABLE XI. Negative relativistic kinetic energy correction in a.u. for spin up states in SICLSD scheme using CA exchange-correlation potentials for the atoms from H to Ca.

atom	1s	2s	3s	4s	2P	3P	tot
H	0.00003						0.00003
He	0.00035						0 00071
Li	0.00204	0.00008					0.00415
Be	0.00685	0.00034					0.01438
B	0.01736	0.00102			0.00006		0.03683
C	0.03692	0.00235			0.00017		0.07888
N	0.00965	0.00464			0.00038		0.14968
0	0.12064	0.00821			0.00071		0.26047
F	0.19557	0.01342			0.00122		0.42395
Ne	0.30096	0.02069			0.00194		0.65494
Na	0.44383	0.03272	0.00120		0.00338		0.97462
Mg	0.63244	0.04964	0.00268		0.00550		1.40253
Al	0.87574	0.07258	0.00521		0.00848	0.00039	1.95839
Si	1.18340	0.10277	0.00879		0.01250	0.00076	2.66657
P	1.56590	0.14156	0.01362		0.01779	0.00130	3.55299
S	2.03467	0.19049	0.01996		0.02460	0.00204	4.64596
Cl	2.60175	0.25115	0.02794		0.03317	0.00302	5.97566
Ar	3.27998	0.32523	0.03781		0.04379	0.00427	7.57443
K	4.08290	0.41490	0.05242	0.00310	0.05683	0.00651	9.48369
Ca	5.02506	0.52211	0.07088	0.00568	0.07260	0.00946	11.7398

listed in the final two columns. In general, the results from these four calculations LDA(GL), LSD(GL), SIC(GL), and SIC(CA) are very close to each other. For the P4 corrections, the differences between the results of LDA(GL) and LSD(GL) are about $10^{-3}\sim10^{-4}$ smaller than those of SIC(GL) and SIC(CA). But for Dw, the LDA(GL) results are 10^{-3} larger than the other three calculations in average. The SIC-LSD contains better wave functions and leads to relatively more accurate results as compared with the LDA and LSD ones. As for P4 effects, the difference between SIC and Others varies from 10^{-3} to 10^{-4}, while for Dw, they differ typically 10^{-4} only as compared with the total corrections. In the SIC-LSD calculations the difference due to the two different exchange-correlation potential GL and CA used are typically 10^{-4} for both, P4 and Dw corrections. The negative P4 effects caused by the shrinkage of the wave functions lower the ground state energies while the positive Dw ones tend to compensate it. It can be seen clearly from this table that the order of the magnitude of the Darwin effects and the kinetic energy corrections are about the same but with opposite sign. Take the SIC-LSD(CA) results of atom Ca(Z=20) for example, the

TABLE XII. Darwin term correction in a.u. spin up states in SIC-LSD scheme using CA exchange-correlation potentials for the atoms from H to Ca.

atom	1s	2s	3s	4s	2P	3P	tot
H	0.00002						0.00002
He	0.00027						0.00054
Li	0.00158	0.00005					0.00321
Be	0.00535	0.00023					0.01115
B	0.01363	0.00068			-0.00001		0.02861
C	0.02909	0.00155			-0.00002		0.06123
N	0.05501	0.00304			-0.00003		0.11599
0	0.09544	0.00535			-0.00006		0.20136
F	0.15492	0.00871			-0.00009		0.32681
Ne	0.23865	0.01340			-0.00014		0.50323
Na	0.35226	0.02112	0.00076		-0.00023		0.74612
Mg	0.50232	0.03195	0.00169		-0.00035		1.06982
Al	0.69599	0.04661	0.00327		-0.00050	-0.00002	1.48877
Si	0.94100	0.06585	0.00549		-0.00069	-0.00003	2.02059
P	1.24573	0.09054	0.00846		-0.00092	-0.00005	2.68392
S	1.61928	0.12163	0.01236		-0.00120	-0.00008	3.49910
Cl	2.07128	0.16010	0.01724		-0.00153	-0.00011	4.48756
Ar	2.61200	0.20703	0.02326		-0.00191	-0.00014	5.67224
K	3.25228	0.26375	0.03215	0.00189	-0.00236	-0.00021	7.08285
Ca	4.00372	0.33150	0.04336	0.00345	-0.00288	-0.00028	8.74511

separate P4 and Dw effects are about 1.7% (-11.73398 a.u.) and 1.28% (8.745 a.u.) as compared with the total ground state energy of 681.584 a.u.. But due to this cancellation, the net influence is only 2.995 a.u. which amounts to 0.44% of the total ground state energy. This cancellation results in relatively small net relativistic correction to the total ground state energies of small atoms.

In Table XIV the nonrelativistic total ground state energies calculated in LDA(GL), LSD(GL), SIC(GL), and SIC(CA) schemes for atoms from He to Ca are listed in the first four column and the corresponding relativistic corrected values are listed in the next four columns for comparison. The Dirac-Hartree-Fock[33] results are also listed in the last column. The relativistic corrections including the relativistic kinetic energy and the Darwin effects varies from 7.0 x 10^{-5} for He to 0.44% for Ca of the corresponding non-relativistic energies. For a typical second-row atom Si(Z=14), the relativistic effects account for 0.22% of the total energy. For atoms from Ne(Z=10) to Ca(Z=20) the relativistic energies from LDA(GL) and LSD(GL) are 0.1% higher in average than the Dirac-Hartree-Fock(DHF) results while the ones from SIC(GL, CA) are 0.1 $\sim$ 0.26% lower. It is interesting to note

TABLE XIII. Calculated relativistic kinetic energy corrections (P4) and Darwin corrections (Dw) from He to Ca in LDA, LSD, and SICLSD schemes. The CL and CA correlation energies are used. Energies in a.u..

atom	LDA GL P4	LDA GL Dw	LSD GL P4	LSD GL Dw	SIC GL P4	SIC GL Dw	SIC CA P4	SIC CA Dw
He	-0.0007	0.0006	-0.0007	0.0006	-0.0007	0.0005	-0.0007	0.0005
Li	-0.0041	0.0033	-0.0041	0.0032	-0.0042	0.0032	-0.0042	0.0032
Be	-0.0142	0.0113	-0.0142	0.0112	-0.0144	0.0112	-0.0144	0.0112
B	-0.0364	0.0290	-0.0364	0.0287	-0.0369	0.0286	-0.0368	0.0286
C	-0.0781	0.0619	-0.0780	0.0614	-0.0790	0.0613	-0.0789	0.0612
N	-0.1484	0.1170	-0.1483	0.1162	-0.1499	0.1161	-0.1497	0.1160
0	-0.2584	0.2028	-0.2583	0.2017	-0.2607	0.2015	-0.2605	0.2014
F	-0.4208	0.3287	-0.4208	0.3272	-0.4243	0.3270	-0.4240	0.3268
Ne	-0.6505	0.5058	-0.6505	0.5038	-0.6554	0.5035	-0.6549	0.5032
Na	-0.9684	0.7495	-0.9684	0.7468	-0.9753	0.7465	-0.9746	0.7461
Mg	-1.3942	1.0742	-1.3942	1.0705	-1.4033	1.0703	-1.4025	1.0698
AI	-1.9175	1.4943	-1.9475	1.4895	-1.9594	1.4894	-1.9584	1.4888
Si	-2.6526	2.0275	-2.6526	2.0214	-2.6679	2.0214	-2.6666	2.0206
P	-3.5356	2.6925	-3.5355	2.6848	-3.5546	2.6849	-3.5530	2.6839
S	-4.6244	3.5094	-4.6243	3.5011	-4.6479	3.5002	-4.6460	3.4991
Cl	-5.9494	4.4998	-5.9494	4.4889	-5.9779	4.4889	-5.9757	4.4876
Ar	-7.5428	5.6867	-7.5428	5.6757	-7.5770	5.6738	-7.5744	5.6722
K	-9.4460	7.0999	-9.4461	7.0836	-9.4867	7.0847	-9.4837	7.0829
Ca	-11.6954	8.7650	-11.6954	8.7457	-11.7433	8.7472	-11.7398	8.7451

that the difference of the relativistic energies for LDA and LSD with the DHF energies remains about a constant while for SIC the difference with the DHF energies decreases graduallly.

Presented in Table XV are the spin-orbit energy splitting for the p states according to equation (41), and the coupling coefficients calculated with

$$C_{nl}^{LS} = \frac{1}{4c^2}\left\langle \frac{1}{r}\frac{dV_{\text{eff}}}{dr}\right\rangle_{nl} , \tag{46}$$

in LDA(GL) for atoms from B to Ca. As can be seen in the table, the magnitude of the spin-orbit interaction grows rapidly as the atomic number increases. Take the dominate 2p splitting for example, it increases from 0.00012 a.u. for B to 0.13362 a.u. for Ca. Since the Lande’s interval rule in equation (42) contains the expectation value of r^{-1}, the inner

TABLE XIV. Comparison of the negative nonrelativistic total ground state energy and the relativistic corrected total energy in LDA(GL), LSD(GL), SIC-LSD(GL), and SIC-LSD(CA) schemes and the Dirac-Hartree-Fock results from He to Ca.

atom	LDA GL	LDA GL	SID GL	SIC CA	rel-LDA GL	rel-LDA GL	rel-SIC GL	rel-SIC CA	DHF[a]
He	2.8601	2.8601	2.9123	2.9193	2.8603	2.8603	2.9124	2.9195	2.8618
Li	7.3704	7.3830	7.4976	7.5046	7.3712	7.3838	7.4985	7.5055	7.4335
Be	14.4966	14.4966	14.6803	14.6938	14.4994	14.4995	14.6836	14.6971	14.5759
B	24.4097	24.4198	24.6868	24.7003	24.4171	24.4274	24.6951	24.7086	24.5366
C	37.5095	37.5555	37.9187	37.9296	37.5257	37.5721	37.9364	37.9472	37.6574
N	54.1287	54.2431	54.7156	54.7223	54.1601	54.2752	54.7493	54.7560	54.3170
0	74.5979	74.6526	75.2432	75.2538	74.6535	74.7092	75.3024	75.3129	74.8393
F	99.2466	99.2612	99.9838	99.9953	99.3387	99.3547	100.0810	100.0924	99.5023
Ne	128.4034	128.4034	129.2715	129.2825	128.5481	128.5501	129.4234	129.4342	128.6919
Na	161.6240	161.6348	162.6562	162.6678	161.8429	161.8565	162.8850	162.8963	162.0781
Mg	199.3402	199.3402	200.5140	200.5319	199.6602	199.6639	200.8471	200.8646	199.9351
Al	241.5332	211.5397	242.8679	242.8864	241.9863	241.9976	243.3379	243.3560	242.3311
Si	288.4346	288.4617	289.9460	289.9629	289.0598	289.0929	290.592s	290.6089	289.4499
P	340.2024	340.2661	341.9092	341.9231	341.0455	341.1167	342.7789	342.7922	341.4889
S	396.9931	397.0219	398.8275	398.8462	398.1081	398.1452	399.9751	399.9931	398.6087
Cl	458.9629	458.9703	460.9416	460.9616	460.4125	460.4307	462.4306	462.4497	460.9398
Ar	526.2672	526.2672	528.4078	528.3921	528.1233	528.1343	530.3111	530.2943	528.6838
K	598.5363	598.5445	600.8502	600.8692	600.8825	600.9070	603.2522	603.2700	610.5260
Ca	676.0950	676.0950	678.5656	678.5894	679.0254	679.0447	681.5617	681.5841	679.7102

a: Ref. 9.

$1 \neq 0$ orbitals whose wave functions lie nearer to the origin have larger energy splittings. For the atom Ca, the energy splitting of 0.01417 a.u. in the 3p orbitals are only 15.3% of the 2p splitting of 0.13362 a.u.. As compared with the nonrelativistic total energy of 678.589 a.u. of Ca, the energy splitting of the 2p orbitals corresponds to 0.08% only. Consider for example the spin-orbit splitting of the 2p orbitals for atom Si. This splitting has been measured and calculated in various studies. Herman and Skillman [34] calculated the 2p splitting to be 0.7 eV with perturbation treatments on the Hartree-Fock-Slater wave functions. The experiments on the absorption of molecules by Hayes and Brown's [35] obtained a value of 0.65 ± 0.05 eV. The results of Various experiments [36, 37] various over the range of 0.6 ~ 0.7 eV. In this work the calculated 2p spin-orbit splitting for Si in LDA(GL), LSD(GL), SIC(GL), and SIC(CA) are 0.02365, 0.02364, 0.02400, and 0.02398 a.u. which correspond to 0.64, 0.64, 0.65, and 0.65 eV respectively. The results in this work are in good agreement with each other and with the experimental value 0.65 eV experimental value 0.65 eV for 2p splitting of Si reported by Hayers and Brown [35].

TABLE XV. The LDA(GL) spin-orbit splittings and the coefficients in a.u. for the p orbitals of atoms from B to Ca.

atom	(split) 2P	(coef.) 2P	(split) 3P	(coef.) 3P
B	0.00012	0.00004		
C	0.00033	0.00011		
N	0.00071	0.00024		
0	0.00136	0.00045		
F	0.00235	0.00078		
Ne	0.00381	0.00127		
Na	0.00657	0.00219		
Mg	0.01057	0.00352		
Al	0.01615	0.00538	0.00064	0.00021
Si	0.02365	0.00788	0.00121	0.00040
P	0.03345	0.01115	0.00204	0.00068
S	0.04600	0.01533	0.00316	0.00105
Cl	0.06174	0.02058	0.00465	0.00155
Ar	0.08118	0.02706	0.00656	0.00219
K	0.10495	0.03498	0.00989	0.00330
Ca	0.13362	0.04454	0.01417	0.00472

VII. Oscillator strengths

The oscillator strength for the absorption transition from an initial state *i* to a final state *f* may be given in atomic unit (e.g. Ref. [38]) either by the “length” form:

$$f^l_{if} = \frac{2}{3}(E_f - E_i)|\langle\Psi_i|\sum_\alpha \vec{r}_\alpha|\Psi_f\rangle|^2\frac{1}{(2L_i+1)}, \tag{47}$$

or the “velocity” form:

$$f^v_{if} = \frac{2}{3}\frac{1}{(E_f - E_i)}|\langle\Psi_i|\sum_\alpha \nabla_\alpha|\Psi_f\rangle|^2\frac{1}{(2L_i+1)}, \tag{48}$$

where Ψ, E, and L are the total wave function the energy and the orbital angular momentum respectively and the sum on α is over all the electrons. With exact wave functions and energies the two different forms should yield the same result. The oscillator strengths depend very sensitive on the energy difference and the detail behavior of the wave functions of both the initial and the final state of the transition. Hence it provides a stringent test for various theories which can then be tested experimentally. Various factors such as electron correlations relativistic effects, core polarizations etc. have to be carefully handled in order to obtain correct oscillator strengths. For example, Theodosiou and Curtis [39, 403 concluded in their Dirac-Fock computations that the core-polarization effects are significant and must be included to obtain results in agreement with experiments. In practice, the energy difference for the two states can be obtained either from the experimental energy levels or by theoretical calculations. In general, most of the theoretical efforts are focused on an accurate determination of the transition integral or equivalently the reduced matrix elements. Table XVI depicts the calculated oscillator strengths in the " length " form by using the single configuration density functional orbital wave functions in the 3s-3p and 4s-4p transition of the Alkali iso-electron atoms: Na, Mg^+ and K, Ca^+. The results of other theoretical and experimental results are also included in the table. The speciific transition involved are listed in the first column. The next two columns are the recent Coulomb approximation (Cap) and model potential (MP) calculations by Laughlin et al. [41]. The items with * symbol in the same columns take into consideration the core polarization effects. The following three columns are the *ab initio* calculations of the single configuration Hartree-Fock (HF) [42], multiconfiguration Hartree-Fock (MCHF) [38], Dirac-Hartree-Fock [43], and the SIC(CA) results in this work. The experimental data, from various works are listed in the last column. For Na(Z=11), the experimental results [44-47] differ by about 1% and the most accurate one is 0.9489 of Refs, [46, 47]. The Hartree-Fock outcome overestimates by about 10%. The Coulomb approximation and the model potential (without core polarization consideration) results are about 2% higher. The core polarization corrected ones are very close to the best experimental value. Our SIC(CA) oscillator strength turns out to be 0.959 and is also very close to this value. The Dirac-Hartree-Fock and the much more complicated multiconfiguration Hartree-Fock calculation yields a value of 0.965 which is not too far away but is still a little bit higher. For Mg^+(Z=12), the experiments [48-50] differ by about 5% and the best value is 0.884. Again, the Hartree-Fock approach gives result that is 10% higher than the experimental data. Both the Coulomb approximations (with and without core polarization considerations) overestimate more than 3%. Our SIC(CA) result of 0.9145 is vary close to the MCHF approach of 0.913 and both values are about 1.5% higher than the experimental value. The model potential with core polarization considerations provides by far the best value of 0.9036 which lies within 0.5% of the experiment results of Mg^+. A more accurate experimental result is definitely needed here. For K(Z=19), the experimental value is 1.0017 [51, 52]. Our result of 1.03 agrees with the this results to within 3%. Only the MP calculation including the core polarization effects and the Dirac Hartree-Fock yield better results than our work. As for Ca^+(Z=20), discrepancy between differents experiments [49, 53] is about 8% and the average value is 0.98. The Coulomb approximation and the model potential calculations give worse results (1.1199, 1.0890) if the core polarization considerations are not included. Our SIC(CA) value of 1.035 ($\sim$ 5% larger), are in comparable with the results (0.9709, 0.9838) of model potentials with the core polarization considerations included. From the above comparisons, the performances of density functional approach SIC(CA) are surprisingly good. Our results are much better than the Hartree-Fock and also both the Coulomb approximations (Cap) and the model potential (MP) calculations without considering core polalizations. Only the Cap and MP calculations including core polarization effects and also the much more involved MCHF which take the electron correlations into account gives slightly better results than the density functional calculations.

TABLE XVI. The oscillator strengths of 3s-3p and 4s-4p transitions in Alkali iso-electron atoms.

Atom	Tran.	Coulomb approx.[a]	Model potential[a]	HF[b]	MCHF[c]	DHF[d]	SIC(CA)[e]	Expt.
Na	3s-3p	0.9870	0.9810	1.05	0.965	0.966	0.959229	0.98[f]
		‘0.9597	-0.9584					0.964[g]
								0.9489[h]
Mg+	3s-3p	0.9769	0.9380	0.988	0.913		0.914539	0.88’
		‘0.9320	‘0.9036					0.933
								0.884[k]
K	4s-4p	1.0627	1.0634			1.005	1.030083	1.0017’~”
		0.9696	0.9916					1.02”
Ca+	4s-4p	1.1199	1.0890				1.034950	1.02[o]
		*0.9709	‘0.9838					0.94[p]

* : including core polarization.
a : Ref. [41].
b : Ref. [42].
c : Ref. [38].
d : Ref. [43].
e : This work.
f : Ref. [44].
g : Ref. [45].
h : Ref. [46,47].
i : Ref. [48].
j : Ref. [49].
k : Ref. [50].
l : Ref. [51].
m : Ref. [52].
n : Ref. [54].
o : Ref. [49].
p : Ref. [53].

VIII. Conclusion

A successful application of the B-splines to the local density functional (LDF) calculations for atoms from H(Z=1) to Ca(Z=20) is presented in this paper. As was already demonstrated in many recent papers [15-26], the B-splines basis has been shown to be an efficient tools on obtaining accurate results on various physical problems. We have applied the B-splines to the density functional formalism LDA, its spin-polarized version LSD and the self-interaction free approach SIC-LSD which can provide reasonable energies for ions O^-, H^-, F^-, Cl^-, where Hartree-Fock either fails to obtain stable ground state or with energy far from the experimental results. The applications of B-spline method on the density functional formalisms provides a simple, efficient procedure which yields realistic results as compared with the experiment. We have checked the results of our program with existing literatures and experiments. We have maintained a numerical accuracy of 10^{-10} which is probably an over kill for LDA.

The introduction of B-spline basis provide a fast and accurate numerical tools in the complicated case such as SICLSD calculations. Using first order perturbations, it also provide an efficient handling of the additional corrections such as reduced mass effect nuclear size effect and the relativistic corrections including relativistic kinetic energy, the Darwin term corrections and also the spin-orbit interactions. The accuracy of the energies obtained for atoms from H to Ca is comparable with the results of the much more involved Dirac-Hartree-Fock method. The spin-orbit splittings of the p orbitals are in good agreement with the experimental values.

As a severe test of the wave functions we have calculated the oscillator strengths of the atoms Na Mg^+, K and Ca^+. The results of the oscillator strengths are among the best published theoretic values and are in good agreement with the experimental measurements. For larger atoms the relativistic effects grow rapidly and the first order perturbation is not an adequate approximation any more. The Dirac equation has to be employed for a serious calculation on these heavy atoms. The generalization of our algorithm to the Dirac relativistic scheme as well as the generalized gradient method will be presented in a future publication. This B-spline based DF algorithm call also be extended to diatoms, moleculars, solid, and surface systems.

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