Inner-shell excitation of open-shell atoms: a spin-dependent localized Hartree–Fock density-functional approach

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Abstract

We present a spin-dependent localized Hartree–Fock (SLHF) density-functional approach for the treatment of inner-shell excited states of open-shell atomic systems. In this approach, the electron spin-orbitals and single-Slater-determinant energies of an electronic configuration are computed by solving the Kohn–Sham (KS) equation with SLHF exchange potential. The multiplet energy of an inner-shell excited state is evaluated from the single-Slater-determinant energies in terms of Slater’s diagonal sum rule. Based on this procedure, we perform calculations of the total and excitation energies of inner-shell excited states of open-shell atomic systems: Li, B, Ne⁺, Ne²⁺, Ne³⁺ and Na. In the calculation, the electron correlation effect is taken into account via the correlation potential and energy functional of Perdew and Wang (PW) or of Lee, Yang and Parr (LYP). The calculated results are in good agreement with the available experimental and other *ab initio* theoretical data. In addition, new results for highly excited inner-shell states are also presented.

1. Introduction

Due to its computational simplicity and efficiency, density-functional theory (DFT) [1, 2] has been widely used as a powerful *ab initio* approach for the study of many-electron quantum systems in the last several decades. Conventional DFT using traditional exchange–correlation (XC) potentials obtained from uniform electron gas, such as local density approximation (LDA) [3, 4] and generalized gradient approximation (GGA) [4–6], is a ground-state approach. Because of incomplete cancellation of spurious self-interaction energies and inherent degeneracy (due to the use of spin- and angular-momentum-independent local potentials) of the XC potential, the differences of energy eigenvalues of unoccupied and occupied orbitals obtained from the Kohn–Sham (KS) equation [2] cannot be rigorously defined as excitation energies. However, the KS energy eigenvalues can serve as good zeroth-order excited-state energies provided they are obtained by solving the KS equation with a high-quality XC potential [7, 8].

Recently, an exchange (X)-only localized Hartree–Fock (LHF) density-functional theory has been proposed and successfully applied to ground-state calculations of atomic and molecular systems [7]. In this X-only DFT, the exchange potential in the KS equation is a LHF exchange potential derived under the assumption that the X-only KS determinant is equal to the Hartree–Fock (HF) determinant. The LHF potential is self-interaction free and exhibits the correct long-range behaviour. It requires only the use of occupied orbitals and is dependent on the orbital symmetry of the state.

We have developed, as an extension of this theory, a spin-dependent localized Hartree–Fock (SLHF) density-functional approach for the excited-state calculation of atomic and molecular systems [9]. In this approach, the exchange potential in the KS equation is an exact nonvariational SLHF exchange potential obtained in a similar way as the LHF potential by assuming that for excited states the X-only KS determinant is also equal to the HF determinant [9]. The SLHF potential is an analogue of the LHF potential but for both the ground and excited states. This approach together with Slater’s diagonal sum rule [10] have been successfully used to calculate the energies of multiply excited states of valence electrons of atomic systems [9] and inner-shell excited states of close-shell atomic systems [11] with accurate results.

In this paper, we extend the SLHF density-functional approach to the calculation of total and excitation energies of inner-shell excited states of open-shell atomic systems: Li, B, Ne⁺, Ne²⁺, Ne³⁺ and Na. In the calculation, the electron correlation effect is taken into account through the correlation potential and energy functional of Perdew and Wang (PW) [12] or of Lee, Yang and Parr (LYP) [13]. The calculated results are in good agreement with the available theoretical and experimental data. We also present some new results for the highly excited inner-shell states for the first time.

2. Theoretical method

In the spin-dependent density-functional approach, a spin-orbital $\varphi_{i\sigma}(\mathbf{r})$ of the i th electron with spin σ ($\sigma = \alpha$ and β for spin-up and spin-down, respectively) and its orbital energy $\varepsilon_{i\sigma}$ are determined by the KS equation

$$H_{\sigma}(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma}\varphi_{i\sigma}(\mathbf{r}), \quad (1)$$

where $H_{\sigma}(\mathbf{r})$ is the KS Hamiltonian

$$H_{\sigma}(\mathbf{r}) = -\frac{1}{2}\nabla^2 + V_{\sigma}^{\text{eff}}(\mathbf{r}), \quad (2)$$

and $V_{\sigma}^{\text{eff}}(\mathbf{r})$ is the local effective potential given by

$$V_{\sigma}^{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc\sigma}(\mathbf{r}). \quad (3)$$

In equation (3), $V_{\text{ext}}(\mathbf{r})$ is the external potential, $V_H(\mathbf{r})$ is the Hartree potential (classical Coulomb electrostatic potential between electrons) and $V_{xc\sigma}(\mathbf{r})$ is the spin-dependent XC potential.

The external potential $V_{\text{ext}}(\mathbf{r})$ is known exactly for a given atomic system. The Hartree potential $V_H(\mathbf{r})$ is calculated from

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (4)$$

where $\rho(\mathbf{r}) = \rho_{\alpha}(\mathbf{r}) + \rho_{\beta}(\mathbf{r})$ is the total electron density and $\rho_{\sigma}(\mathbf{r})$ (for $\sigma = \alpha$ and β) is the spin-dependent electron density defined by

$$\rho_{\sigma}(\mathbf{r}) = \sum_{i=1}^{N_{\sigma}} w_{i\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2. \quad (5)$$

Here, N_σ is the total number of electrons with spin σ and $w_{i\sigma}$ is the occupied number of electrons in the spin-orbital $\varphi_{i\sigma}(\mathbf{r})$.

The XC potential can be decomposed into the exchange potential $V_{x\sigma}(\mathbf{r})$ and the correlation potential $V_{c\sigma}(\mathbf{r})$. In the SLHF density-functional approach, the exchange potential is the SLHF exchange potential $V_{x\sigma}^{\text{SLHF}}(\mathbf{r})$ given by

$$V_{x\sigma}^{\text{SLHF}}(\mathbf{r}) = V_{x\sigma}^{\text{S}}(\mathbf{r}) + V_{x\sigma}^{\text{C}}(\mathbf{r}), \quad (6)$$

where $V_{x\sigma}^{\text{S}}(\mathbf{r})$ is the Slater potential [10]

$$V_{x\sigma}^{\text{S}}(\mathbf{r}) = -\frac{1}{\rho_\sigma(\mathbf{r})} \sum_{i,j=1}^{N_\sigma} \varphi_{i\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \int \frac{\varphi_{i\sigma}(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (7)$$

and $V_{x\sigma}^{\text{C}}(\mathbf{r})$ is a correction to the Slater potential

$$V_{x\sigma}^{\text{C}}(\mathbf{r}) = \frac{1}{\rho_\sigma(\mathbf{r})} \sum_{i,j=1}^{N_\sigma} \varphi_{i\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \langle \varphi_{j\sigma} | V_{x\sigma}^{\text{SLHF}} - V_{x\sigma}^{\text{NL}} | \varphi_{i\sigma} \rangle. \quad (8)$$

Here, $V_{x\sigma}^{\text{NL}}$ is a nonlocal exchange operator of the form of the HF exchange potential but constructed from KS spin-orbitals.

The SLHF exchange potential determined by equations (6)–(8) has two arbitrary additive constants. To settle down the constants so as to pick up the physical orbitals, it is required that the highest-occupied-orbital N_σ of each spin σ does not contribute to the correction term $V_{x\sigma}^{\text{C}}(\mathbf{r})$. In this case, the correction term $V_{x\sigma}^{\text{C}}(\mathbf{r})$ decays exponentially, the SLHF exchange potential behaves asymptotically as the Slater potential and thus approaches to $-1/r$ at long range [7].

For atomic systems, an electron is characterized by three quantum numbers: the principal quantum number n , orbital angular momentum quantum number l and spin σ . In the spherical coordinates, the spin-orbital $\varphi_{i\sigma}(\mathbf{r})$ of an electron with quantum numbers n , l and σ can be expressed by

$$\varphi_{i\sigma}(\mathbf{r}) = \frac{R_{nl\sigma}(r)}{r} Y_{lm}(\theta, \phi), \quad (9)$$

where $R_{nl\sigma}(r)$ is the radial spin-orbital, $Y_{lm}(\theta, \phi)$ is the spherical harmonic, m is the azimuthal quantum number and i is a set of quantum numbers apart from spin σ of the spin-orbital. The radial spin-orbital $R_{nl\sigma}(r)$ is governed by a radial KS equation

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_\sigma^{\text{eff}}(r) \right] R_{nl\sigma} = \varepsilon_{nl\sigma} R_{nl\sigma}, \quad (10)$$

where $v_\sigma^{\text{eff}}(r)$ is the radial effective potential given by

$$v_\sigma^{\text{eff}}(r) = v_{\text{ext}}(r) + v_H(r) + v_{x\sigma}^{\text{SLHF}}(r) + v_{c\sigma}(r). \quad (11)$$

In equation (11), $v_{\text{ext}}(r)$, $v_H(r)$, $v_{x\sigma}^{\text{SLHF}}(r)$ and $v_{c\sigma}(r)$ are the radial external potential, radial Hartree potential, radial SLHF exchange potential and radial correlation potential, respectively.

For an atomic system with a nuclear charge Z , the external potential is the Coulomb potential between electron and nucleus

$$v_{\text{ext}}(r) = -\frac{Z}{r}. \quad (12)$$

In the central-field approach, the radial Hartree potential is calculated from

$$v_H(r) = 4\pi \int \frac{\rho(r')}{r_{>}} r'^2 dr', \quad (13)$$

where $r_>$ is the larger of r and r' , $\rho(r) = \rho_\alpha(r) + \rho_\beta(r)$ is the spherically averaged total electron density and $\rho_\sigma(r)$ ($\sigma = \alpha$ or β) is the spherically averaged spin-dependent electron density given by

$$\rho_\sigma(r) = \frac{1}{4\pi} \int \rho_\sigma(\mathbf{r}) d\Omega = \frac{1}{4\pi} \sum_{nl}^{v_\sigma} w_{nl\sigma} \left[\frac{R_{nl\sigma}}{r} \right]^2. \quad (14)$$

Here, the symbol v_σ stands for a set of quantum numbers for summation and the sum is performed over all the occupied spin-orbitals with spin σ . This expression is accurate for spherically symmetric (close-shell) states, but it is only an approximation for non-spherically symmetric (open-shell) states. It may induce an error when it is used to evaluate the energy of a non-spherically symmetric state. However, as will be shown, the error is negligible compared to the order of calculated multiplet splitting [14].

The radial SLHF exchange potential is given by

$$v_{x\sigma}^{\text{SLHF}}(r) = v_{x\sigma}^{\text{S}}(r) + v_{x\sigma}^{\text{C}}(r), \quad (15)$$

where $v_{x\sigma}^{\text{S}}(r)$ is the radial Slater potential

$$v_{x\sigma}^{\text{S}}(r) = -\frac{1}{4\pi\rho_\sigma(r)} \sum_{nlm}^{v_\sigma} \sum_{n'l'm'}^{v_\sigma} s_{nlm,n'l'm'}^\sigma(r), \quad (16)$$

and $v_{x\sigma}^{\text{C}}(r)$ is a correction to the radial Slater potential

$$v_{x\sigma}^{\text{C}}(r) = \frac{1}{4\pi\rho_\sigma(r)} \sum_{nlm}^{v_\sigma} \sum_{n'l'm'}^{v_\sigma} c_{nlm,n'l'm'}^\sigma(r). \quad (17)$$

The matrix elements $s_{nlm,n'l'm'}^\sigma(r)$ and $c_{nlm,n'l'm'}^\sigma(r)$ in equations (16) and (17), respectively, are given in [9].

To calculate electron spin-orbitals, the Legendre generalized pseudospectral (LGPS) method [15] is used to discretize the radial KS equation (10). This method associated with an appropriate mapping technique can overcome difficulties due to singularity at $r = 0$ and long-tail at large r of the Coulomb interaction and thus provides a very effective and efficient numerical algorithm for high-precision solution of the KS equation. Using the electron spin-orbitals of an electronic configuration, a single Slater determinant for a specific electronic state is constructed and its total energy is calculated. The total energy is a sum of non-interacting kinetic energy E_k , external-field energy E_{ext} , Hartree energy E_H , exchange energy E_x and correlation energy E_c . The values of E_k , E_{ext} , E_H and E_x are evaluated by

$$E_k = \sum_{\sigma=\alpha}^{\beta} \sum_{nl}^{v_\sigma} w_{nl\sigma} \int R_{nl\sigma}(r) \left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} \right) R_{nl\sigma}(r) dr, \quad (18)$$

$$E_{\text{ext}} = 4\pi \int v_{\text{ext}}(r) \rho(r) r^2 dr, \quad (19)$$

$$E_H = \frac{1}{2} \sum_{\Pi} \eta_{lm,l'm'}^k F_{nl\sigma,n'l'\sigma'}^k \quad (20)$$

and

$$E_x = -\frac{1}{2} \sum_{\Pi} \lambda_{lm,l'm'}^k G_{nl\sigma,n'l'\sigma'}^k \delta_{\sigma\sigma'}, \quad (21)$$

where Π represents a collection of all the quantum numbers involved, the matrix elements $\eta_{lm,l'm'}^k$, $F_{nl\sigma,n'l'\sigma'}^k$, $\lambda_{lm,l'm'}^k$ and $G_{nl\sigma,n'l'\sigma'}^k$ are given in [9].

Table 1. Total energies (E (a.u.)) and excitation energies (ΔE (eV)) of inner-shell excited states $1s2sns\ ^{2,4}S$ ($n = 2-8$) of Li. The ground-state energies obtained from calculations with the PW and LYP correlation potentials and energy functionals are -7.4837 (a.u.) and -7.4872 (a.u.), respectively. Here, 1 a.u. = 27.2116 eV is used.

States	$-E$					ΔE							
	Present work		Other theory			Present work		Other theory			Exp.		
	PW ^a	LYP ^b	WF ^c	SPCR ^d	ECI ^e	PW ^a	LYP ^b	WF ^c	ECI ^e	RRV ^f	ZBS ^g	RPR ^h	RBB ⁱ
$1s2s^2\ ^2S$	5.3940	5.3822	5.3994	5.4052		56.8641	57.2796	57.055			56.352	56.395	56.362
$1s2s3s\ ^4S$	5.2225	5.2451			5.2127	61.5317	61.0114		61.637	61.69		62.00	
$\quad\quad\quad\ ^2S$	5.2019*	5.1466*				62.0917*	63.6907*				61.995		62.012*
	5.1475 [†]	5.1418 [†]				63.5728 [†]	63.8310 [†]						63.192 [†]
$1s2s4s\ ^4S$	5.1703	5.1918				62.9513	62.4615		63.113	63.18			
$\quad\quad\quad\ ^2S$	5.1288	5.1022				64.0806	64.8999				63.17	63.16	63.292
$1s2s5s\ ^4S$	5.1508	5.1715				63.4819	63.0142			63.73			
$\quad\quad\quad\ ^2S$	5.1108	5.0855				64.5704	65.3549						63.792
$1s2s6s\ ^4S$	5.1412	5.1616				63.7432	63.2847			63.99			
$\quad\quad\quad\ ^2S$	5.1018	5.0772				64.8153	65.5810						
$1s2s7s\ ^4S$	5.1358	5.1560				63.8901	63.4370			64.33			
$\quad\quad\quad\ ^2S$	5.0966	5.0724				64.9568	65.7100						
$1s2s8s\ ^4S$	5.1324	5.1525				63.9826	63.5315						
$\quad\quad\quad\ ^2S$	5.0933	5.0695				65.0466	65.7909						

^a PW results, ^b LYP results, ^c [27], ^d [28], ^e [34, 35], ^f [40], ^g [20], ^h [22], ⁱ [25]. Here, * for $1s2s(3s)3s^2S$ and [†] for $1s2s(1s)3s^2S$.

For a multiplet state that can be completely described by a single Slater determinant, the energy is calculated directly from the single Slater determinant. For a multiplet state that cannot be represented by a single determinant, the energy can be calculated by means of Slater's diagonal sum rule [10] from the single-Slater-determinant energies [9, 11]. Similar procedures have been employed in recent excited-state calculations [16, 17].

3. Results and discussion

The procedure described in the preceding section has been applied to the inner-shell excited-state calculation of open-shell atomic systems: Li, B, Ne⁺, Ne²⁺, Ne³⁺ and Na. In the calculations, the correlation potential $v_{cor}(r)$ and the energy functional E_c are taken to be those of PW's [12] or LYP's [13]. The results obtained with these two correlation potentials and energy functionals are listed in columns PW and LYP in the following tables, respectively.

3.1. Inner-shell excitation of Li

Inner-shell excitation of Li has been the subject of extensive experimental and theoretical studies. Both experimental data [18–26] and theoretical data [27–40] are abundant. In tables 1–3, we present the total and excitation energies of our calculations for inner-shell excited states $1s2sns\ ^{2,4}S$ ($n = 2-8$), $1s2snp\ ^{2,4}P$ ($n = 2-8$) and $1s2p^2\ ^2S, ^{2,4}P$ and 2D , respectively. For comparison, we also list in these tables the representative experimental data (Exp.) [20, 22, 25] as well as the theoretical results of the density work-functional formalism (WF) [27], saddle-point complex-rotation (SPCR) [28–31], extensive configuration–interaction calculation (ECI) [34–37] and Rayleigh–Ritz variational method (RRV) [40].

For the total energies of inner-shell excited states $1s2sns\ ^{2,4}S$ ($n = 2-8$) given in table 1, the maximum relative discrepancies of our PW and LYP results are 0.10% and 0.32% to the WF results, 0.21% and 0.43% to the SPCR results and 0.19% and 0.62% to the ECI results,

Table 2. Total energies (E (a.u.)) and excitation energies (ΔE (eV)) of inner-shell excited states $1s2snp\ ^2,4P$ ($n = 2-8$) of Li.

States	$-E$					ΔE							
	Present work		Other theory			Present work		Other theory			Exp.		
	PW ^a	LYP ^b	WF ^c	SPCR ^d	ECI ^e	PW ^a	LYP ^b	WF ^c	ECI ^e	RRV ^f	ZBS ^g	RPR ^h	RBB ⁱ
$1s2s2p\ ^4P$	5.3811	5.4117	5.4114	5.3678	5.3679	57.2151	56.4777	56.728	57.413	57.47	57.385	57.41	57.432
$\ ^2P$	5.3177*	5.2854*	5.2912	5.3133*		58.9403*	59.9145*	59.999			58.912*	58.912*	58.912*
	5.2407 [†]	5.2223 [†]		5.2585 [†]		61.0356 [†]	61.6316 [†]				60.397 [†]	60.405 [†]	60.402 [†]
$1s2s3p\ ^4P$	5.1994	5.2212	5.2205		5.1873	62.1595	61.6610	61.923	61.262	61.33			
$\ ^2P$	5.1589	5.1308	5.1767	5.1841		63.2615	64.1220	63.115			62.425	62.421	62.462
$1s2s4p\ ^4P$	5.1623	5.1835				63.1690	62.6874						
$\ ^2P$	5.1232	5.0973				64.2330	65.0330						
$1s2s5p\ ^4P$	5.1470	5.1676				63.5853	63.1200						
$\ ^2P$	5.1081	5.0832				64.6439	65.4167						
$1s2s6p\ ^4P$	5.1391	5.1594				63.8003	63.3432						
$\ ^2P$	5.1003	5.0759				64.8561	65.6153						
$1s2s7p\ ^4P$	5.1345	5.1547				63.9255	63.4711						
$\ ^2P$	5.0956	5.0717				64.9840	65.7296						
$1s2s8p\ ^4P$	5.1315	5.1516				64.0071	63.5554						
$\ ^2P$	5.0928	5.0690				65.0602	65.8031						

^a PW results, ^b LYP results, ^c [27], ^d [31, 30], ^e [34, 35, 37], ^f [40], ^g [20], ^h [22] and ⁱ [25]. Here, * for $1s(2s2p\ ^3P)\ ^2P$ and [†] for $1s(2s2p\ ^1P)\ ^2P$.

Table 3. Total energies (E (a.u.)) and excitation energies (ΔE (eV)) of inner-shell doubly excited states $1s2p^2\ ^2S, ^2,4P$ and 2D of Li.

States	$-E$					ΔE							
	Present work		Other theory			Present work		Other theory			Exp.		
	PW ^a	LYP ^b	WF ^c	SPCR ^d	ECI ^e	PW ^a	LYP ^b	WF ^c	ECI ^e	RRV ^f	ZBS ^g	RPR ^h	RBB ⁱ
$1s2p^2\ ^4P$	5.2526	5.2862	5.2860	5.2453	5.2453	60.7118	59.8927	60.140	60.750	60.74		60.75	60.802
$\ ^2D$	5.2254	5.2232	5.2356	5.2342		61.4520	61.6071	61.512			61.065	61.065	61.062
$\ ^2P$	5.2382	5.1930	5.2323	5.2137	5.2137	61.1036	62.4289	61.602					
$\ ^2S$	5.1761	5.1739	5.1780			62.7935	62.9486	63.079					63.492

^a PW results, ^b LYP results, ^c [27], ^d [29, 31], ^e [34–36], ^f [40], ^g [20], ^h [22] and ⁱ [25].

respectively. It is shown that both the PW and LYP results are in good agreement with those of other complicated *ab initio* methods and the PW results are a little bit better than the LYP results. For the excitation energy of excited state $1s2s^2\ ^2S$, the relative deviations of our PW and LYP results to the experimental results are 0.91% and 1.65%, respectively, while the relative deviation of the WF results to the experimental results is 1.25%. This demonstrates that the PW result is better than both the LYP and WF results. For the excitation energies of excited states $1s2sns\ ^2S$ with $n \geq 3$, the maximum relative discrepancies of our PW and LYP results to the experimental results are 1.45% and 2.75%, respectively. For these states, our results have a little bit larger deviations but still agree with the experimental results within the DFT. For the excitation energy of excited state $1s2s3s\ ^4S$, the relative deviations of our PW and LYP results to the experimental result are 0.75% and 1.60%, respectively, while the relative discrepancies of the ECI and RRV results to the experimental result are 0.59% and 0.50%, respectively. Hence our PW result is in good agreement with both the experimental result and other theoretical results for this state. For the excitation energies of excited states $1s2sns\ ^4S$ with $n > 3$, the maximum relative deviations of our PW and LYP results to the RRV results are 0.68% and 1.39%, respectively. Our PW results are close to the RRV results. Note that for all the excitation energies considered here the PW results are better than the LYP results. As has already been demonstrated [9, 13], due to an overestimation of the LYP energy functional

to correlation energies of atomic systems with smaller Z , the LYP results are generally worse than the PW results for atomic systems with $Z \leq 8$.

For the total energies of excited states $1s2snp^{2,4}P$ ($n = 2-8$) given in table 2, the maximum relative discrepancies of our PW and LYP results are 0.56% and 0.89% to the WF results, 0.64% and 1.03% to the SPCR results and 0.25% and 0.82% to the ECI results, respectively. It is shown again that both the PW and LYP results are in good agreement with those of other complicated *ab initio* methods. For the excitation energies, the maximum relative deviations of our PW and LYP results to the experimental results are 1.35% and 2.73%, respectively, while the maximum relative discrepancies of the WF, ECI and RRV results to the experimental results are 1.85%, 0.03% and 0.07%, respectively. Thus, our PW results are better than the WF results.

For the total energies of inner-shell doubly excited states $1s2p^2\ ^2S, ^{2,4}P$ and 2D given in table 3, the maximum relative deviations of our PW and LYP results are 0.63% and 0.75% to the WF results, 0.47% and 0.78% to both the SPCR and ECI results, respectively. This indicates that our PW and LYP results agree well with those of other *ab initio* methods. For the excitation energies, the relative discrepancies of our PW and LYP results to the experimental result are not more than 1.10% and 1.50%, respectively, while the maximum relative discrepancies of the WF results to the experimental results are 1.09%. Hence our PW results are close to the WF results.

3.2. Auger transition of B

The second open-shell atom we have computed is B. In table 4, we present transition energies for Auger transitions from inner-shell excited states $1s2s^22p^2\ ^2S, ^{2,4}P$ and 2D of B to singly excited states $1s^22s2p\ ^{1,3}P$ and doubly excited states $1s^22p^2\ ^1S, ^3P$ and 1D of B^+ . For comparison, we also give in this table the available experimental results (Exp.) [25] as well as theoretical results of WF [27], perturbation Z-expansion theory (PZE) [41, 42] and perturbation Z-expansion theory with relativistic effects (RPZE) [25].

It is shown that except for the transitions $1s2s^22p^2\ ^2D \rightarrow 1s^22p^2\ ^1S$ and $1s2s^22p^2\ ^2S \rightarrow 1s^22p^2\ ^1S$, the maximum deviations of our PW and LYP results to the experimental results are 0.63% and 0.24%, respectively. Thus, our results are in good agreement with the experimental results. Furthermore, the maximum discrepancies of the WF, PZE and RPZE results to the experimental results are 0.78%, 1.21% and 0.41%, respectively. This indicates that our results are much better than the PZE results, a little bit better than the WF results, and much closer to the RPZE results. As for the transitions $1s2s^22p^2\ ^2D \rightarrow 1s^22p^2\ ^1S$ and $1s2s^22p^2\ ^2S \rightarrow 1s^22p^2\ ^1S$, the relative deviations of our PW and LYP results to the experimental results are less than 1.82% and 1.23%, respectively, while the relative deviations of the PZE and RPZE results to the experimental results are not more than 3.26% and 0.07%, respectively. This indicates again that our results are much better than the PZE results. In addition, according to our result the spectrum line with 170.7 eV being originally assigned to the transition $1s2s^22p^2\ ^2D \rightarrow 1s^22p^2\ ^1S$ may belong to the transition $1s2s^22p^2\ ^2D \rightarrow 1s^22p^2\ ^3P$.

3.3. Inner-shell excitation of Ne^+ , Ne^{2+} and Ne^{3+}

To explore the feasibility of the approach to inner-shell excitation of open-shell atomic ions, we also apply the procedure to the inner-shell excited-state calculation of positive ions Ne^+ , Ne^{2+} and Ne^{3+} . In table 5, we present the transition energies of optically allowed transitions involved in inner-shell excited states of these ions along with the theoretical results of multiconfiguration

Table 4. Transition energies (ΔE (eV)) for Auger transitions from inner-shell excited states $1s2s^22p^2\ ^2S, ^2,4P$ and 2D of B to singly excited states $1s^22s2p\ ^1,3P$ and doubly excited states $1s^22p^2\ ^1S, ^3P$ and 1D of B^+ .

Initial states	Final states	ΔE					
		Present work		Other theory			Exp.
		PW ^a	LYP ^b	WF ^c	PZE ^d	RPZE ^e	
$1s2s^22p^2\ ^4P$	$1s^22p^2\ ^3P$	168.3500	169.1008		167.4101	169.10	169.2
	$1s^22p^2\ ^1D$	167.3105	168.5612		166.7952		
	$1s^22p^2\ ^1S$	165.5064	167.2558		163.2454		
2D	$1s^22p^2\ ^3P$	170.4344	170.7805		169.3045		
	$1s^22p^2\ ^1D$	169.3949	170.2409		168.6895		
	$1s^22p^2\ ^1S$	167.5908	168.9356		165.1397	170.58	170.7
2P	$1s^22p^2\ ^3P$	170.4181	170.2883	171.5858	169.0290	170.73	170.7
	$1s^22p^2\ ^1D$	169.3786	169.7487		168.4140		
	$1s^22p^2\ ^1S$	167.5745	168.4433		164.8643		
2S	$1s^22p^2\ ^3P$	172.7828	173.1289		171.0097		
	$1s^22p^2\ ^1D$	171.7433	172.5893		170.3947		
	$1s^22p^2\ ^1S$	169.9392	171.2840		166.8450	169.13	169.2
$1s2s^22p^2\ ^4P$	$1s^22s2p\ ^3P$	176.1516	176.8376		175.7192		
	$1s^22s2p\ ^1P$	171.4249	172.9961		170.8674		
	$1s^22s2p\ ^3P$	178.2360	178.5173		177.6135		
2D	$1s^22s2p\ ^1P$	173.5093	174.6759	173.2321	172.7617	174.17	174.6
	$1s^22s2p\ ^3P$	178.2197	178.0251		177.3381		
	$1s^22s2p\ ^1P$	173.4930	174.1836	173.4062	172.4862	173.90	174.6
2P	$1s^22s2p\ ^3P$	180.5843	180.8657		179.3188		
	$1s^22s2p\ ^1P$	175.8577	177.0242		174.4669		

^a PW results, ^b LYP results, ^c [27], ^d [41, 42], ^e [25] and ^f [25].

Dirac–Fock method (MCDF) [43]. Note that the MCDF results given in this table are the weighted-averaged values of those in [43].

It is shown that the relative deviations of our PW and LYP results to the MCDF results are not more than 0.17% and 0.07% for Ne^+ , 0.16% and 0.06% for Ne^{2+} and 0.16% and 0.08% for Ne^{3+} , respectively. The satisfactory agreement of our results with the MCDF results demonstrates that the SLHF together with the PW or LYP correlation potential and energy functional are accurate for the calculation of inner-shell excited states of positive ions. It is also shown that for the atomic systems with $Z = 10$ the LYP results are more accurate than the PW results, as has already been demonstrated in our previous work [9, 11].

3.4. Inner-shell excitation of Na

Finally, we calculate the total and excitation energies of inner-shell excited states $1s2s^22p^63s(^1S)np\ ^2P$ ($n = 3-8$) and $1s2s^22p^63s(^3S)np\ ^2,4P$ ($n = 3-8$) of Na. The results are shown in table 6 together with experimental results (Exp.) [44] as well as theoretical results of the relativistic configuration interaction method (RCI) [45] and multiconfiguration Hartree–Fock method (MCHF) [46] for comparison.

For the excitation energies of excited states $1s2s^22p^63s(^1S)np\ ^2P$ with $n = 3-5$, the relative deviations of our PW and LYP results to the experimental results are less than 0.18% and 0.07%, respectively, while the maximum relative discrepancies of the RCI and MCHF

Table 5. Transition energies (ΔE (eV)) of optically allowed transitions of inner-shell excited states of Ne^+ , Ne^{2+} and Ne^{3+} .

Ions	Initial state	Final state	ΔE		
			Present work		Others
			PW ^a	LYP ^b	MCDF ^c
Ne^+	$1s^2 2s^2 2p^5 \ ^2P$	$1s 2s^2 2p^6 \ ^2S$	848.0278	848.8786	849.48
Ne^{2+}	$1s^2 2s^2 2p^4 \ ^3P$	$1s 2s^2 2p^5 \ ^3P$	853.7724	854.6535	855.16
		$\ ^1D$	855.0747	856.3277	856.14
		$\ ^1S$	850.1188	851.3728	851.19
Ne^{3+}	$1s^2 2s^2 2p^3 \ ^4S$	$1s 2s^2 2p^4 \ ^4P$	861.0411	861.8325	862.41
		$\ ^2D$	862.2075	863.0207	863.33
		$\ ^2P$	863.1715	863.6460	864.20
	$\ ^2P$	$\ ^2D$	858.5203	859.3295	859.78
		$\ ^2P$	859.4843	859.9549	860.65
		$\ ^2S$	864.5179	865.3302	865.62

^a PW results, ^b LYP results and ^c obtained from data in [43].**Table 6.** Total energies (E (a.u.)) and excitation energies (ΔE (eV)) of inner-shell excited states $1s 2s^2 2p^6 3s(^1S)np^2P$ and $1s 2s^2 2p^6 3s(^3S)np^2P$ ($n = 3-8$) of Na. The ground-state energies obtained from calculations with the PW and LYP correlation potentials and energy functionals are -162.2265 (a.u.) and -162.2687 (a.u.), respectively.

States	$-E$		ΔE				
	Present work		Present work		Other theory		Exp.
	PW ^a	LYP ^b	PW ^a	LYP ^b	RCI ^c	MCHF ^d	TLE ^e
$1s 2s^2 2p^6 3s(^1S)3p \ ^2P$	122.7947	122.7552	1073.0024	1074.1765	1074.28	1074.50	1074.95
$\ 4p \ ^2P$	122.6680	122.6708	1076.4501	1077.5222	1077.52	1077.96	1078.17
$\ 5p \ ^2P$	122.6378	122.6424	1077.2719	1078.2950	1078.27	1078.60	1078.9
$\ 6p \ ^2P$	122.6246	122.6301	1077.6311	1078.6297			
$\ 7p \ ^2P$	122.6176	122.6234	1077.8215	1078.8120			
$\ 8p \ ^2P$	122.6134	122.6195	1077.9358	1078.9182			
$1s 2s^2 2p^6 3s(^3S)3p \ ^2P$	122.7540	122.7714	1074.1099	1074.7847	1075.97	1076.04	1076.47
$\ 4p \ ^2P$	122.6858	122.6976	1075.9657	1076.7929	1077.21	1077.83	
$\ 5p \ ^2P$	122.6601	122.6705	1076.6651	1077.5304	1077.88	1078.56	
$\ 6p \ ^2P$	122.6481	122.6582	1076.9916	1077.8651			
$\ 7p \ ^2P$	122.6414	122.6517	1077.1739	1078.0420			
$\ 8p \ ^2P$	122.6374	122.6478	1077.2828	1078.1481			
$\ 3p \ ^4P$	122.8152	122.8176	1072.4445	1073.5276	1073.87		
$\ 4p \ ^4P$	122.6916	122.6983	1075.8079	1076.7739	1076.94		
$\ 5p \ ^4P$	122.6619	122.6703	1076.6161	1077.5358	1077.71		
$\ 6p \ ^4P$	122.6487	122.6580	1076.9753	1077.8705			
$\ 7p \ ^4P$	122.6418	122.6515	1077.1630	1078.0474			
$\ 8p \ ^4P$	122.6377	122.6476	1077.2746	1078.1535			

^a PW results, ^b LYP results, ^c [45], ^d [46] and ^e [44].

results to the experimental results are 0.06% and 0.04%, respectively. This indicates that both our PW and LYP results are in good agreement with the experimental results, the LYP results are better than the PW results and the LYP results are very close to the RCI and MCHF results.

It is also shown that according to our results the identification of the photoionization spectra $1s2s^22p^63s(^1S)3p^2P$ and $1s2s^22p^63s(^3S)3p^2P$ in the experiment [44] should be exchanged. This agrees well with the RCI and MCHF results.

For the excitation energy of excited state $1s2s^22p^63s(^3S)3p^2P$, the relative deviations of our PW and LYP results to the experimental results are 0.22% and 0.16%, respectively, which are a little bit larger than those of RCI and MCHF results, 0.05% and 0.04%. For the excitation energies of excited states $1s2s^22p^63s(^3S)np^2P$ with $n = 4$ and 5, the relative deviations of our PW and LYP results are not more than 0.12% and 0.04% to the RCI results and 0.18% and 0.10% to the MCHF results, respectively. Thus, the agreement of our results with the experimental and other theoretical results is good and our LYP results are closer to the RCI results.

For the excitation energies of excited states $1s2s^22p^63s(^3S)np^4P$ with $n = 3-5$, the relative deviations of our PW and LYP results to the RCI results are less than 0.13% and 0.03%, respectively. This shows again that our LYP results are in very good agreement with the RCI results. Note that for all the excited states discussed here the LYP results are better than the PW results. Thus, the LYP correlation potential and energy functional is more accurate than those of PW for the inner-shell excited-state calculation of open-shell atomic systems with large Z .

4. Conclusions

In summary, the SLHF density-functional approach together with Slater's diagonal sum rule are extended to the inner-shell excited-state calculation of open-shell atomic systems. In this procedure, the electron spin-orbitals in an electronic configuration are obtained first by solving the KS equation with the exact SLHF exchange potential. Then the single-Slater-determinant energies of the electronic configuration are calculated by using these electron spin-orbitals. And finally the multiplet energy of an excited state is evaluated from the single-Slater-determinant energies in terms of Slater's diagonal sum rule. This procedure has been used to calculate the total and excitation energies of inner-shell excited states of open-shell atomic systems: Li, B, Ne^+ , Ne^{2+} , Ne^{3+} and Na. The electron correlation effect is taken into account by incorporating the PW or LYP correlation potential and energy functional into the calculation. It is shown that the PW results are better for atomic systems with $Z \leq 8$, while the LYP results are better for atomic systems with $Z > 8$. They are in good agreement with each other and also with the available experimental as well as other *ab initio* theoretical results. Therefore, the SLHF density-functional approach provides a powerful and computationally efficient scheme for the accurate calculation of inner-shell excited states of open-shell atomic systems within DFT.

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