Spin-dependent localized Hartree-Fock density-functional approach for the accurate treatment of inner-shell excitation of close-shell atoms

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Abstract

We present a spin-dependent localized Hartree-Fock (SLHF) density-functional approach for the treatment of the inner-shell excited-state calculation of atomic systems. In this approach, the electron spin-orbitals in an electronic configuration are obtained first by solving Kohn-Sham (KS) equation with SLHF exchange potential. Then a single-Slater-determinant energy of the electronic configuration is calculated by using these electron spin-orbitals. Finally, a multiplet energy of an inner-shell excited state is evaluated from the single-Slater-determinant energies of the electronic configurations involved 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 close-shell atomic systems: Be, B\textsuperscript{+}, Ne, and Mg. The correlation effect is taken into account by incorporating the correlation potentials and energy functionals of Perdew and Wang’s (PW) or Lee, Yang, and Parr’s (LYP) into calculation. The calculated results with the PW and LYP energy functionals are in overall good agreement with each other and also with available experimental and other \textit{ab initio} theoretical data. In addition, we present some new results for highly excited inner-shell states.

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I. INTRODUCTION

Density functional theory (DFT)\textsuperscript{1,2} has been widely applied to many areas in theoretical physics and chemistry as a powerful \textit{ab initio} approach for the calculation of ground-state properties of many-electron systems due to its computational simplicity and efficiency\textsuperscript{3,4}. The basic equation of DFT is Kohn-Sham (KS) equation\textsuperscript{2} and the key part in KS equation is exchange-correlation (XC) potential\textsuperscript{5}.

DFT with a traditional XC potential obtained from uniform electron gas, such as local density approximation (LDA)\textsuperscript{3,4} and generalized gradient approximation (GGA)\textsuperscript{6,7,8,9}, is a ground-state approach. Because of incomplete cancellation of spurious self-interactions in the conventional DFT using LDA or GGA\textsuperscript{6,7,8,9} and the inherent degeneracy (due to the use of spin and angular-momentum independent local potentials), the differences of the KS energy eigenvalues of unoccupied and occupied orbitals are not 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 KS equation with a high-quality XC potential\textsuperscript{10}. A number of theoretical methods have been developed by adopting this point of view\textsuperscript{11}. In particular, density work-functional approach (WF)\textsuperscript{12,13,14,15}, open-shell localized Hartree-Fock (LHF) density-functional approach\textsuperscript{16,17,18,19}, and multireference LHF density-functional approach\textsuperscript{20,21}, etc., have been successfully used to calculate excited-state properties of atomic and molecular systems.

Recently, an exchange (X)-only LHF density-functional theory has been proposed and successfully applied to ground-state calculations of atomic and molecular systems\textsuperscript{10}. In this X-only DFT, the exchange potential in the KS equation is a LHF exchange potential derived under the assumption that X-only KS determinant is equal to the Hartree-Fock (HF) determinant. We have recently extended this approach to excited states of atomic and molecular systems by assuming that the X-only KS determinant is also equal to the HF determinant for excited states\textsuperscript{22}. Based on this postulate we have developed a spin-dependent localized Hartree-Fock (SLHF) density-functional approach for excited-state calculation of atomic and molecular systems\textsuperscript{22}. In this approach, the exchange potential in the KS equation is an exact nonvariational SLHF exchange potential constructed for both the ground and excited states. The SLHF potential is an analogue of the LHF potential. It is self-interaction free and exhibits the correct long-range behavior. Further, the SLHF potential requires the use of only the occupied orbitals and is dependent of the orbital symmetry of the state. This approach associating with Slater’s diagonal sum rule\textsuperscript{23} has been successfully used to calculate singly, doubly, and triply excited states of valence electrons of He- and Li-like ions\textsuperscript{22} with accurate results.

In this paper, we extend the SLHF density-functional approach to inner-shell excited states of atomic systems. We compute the total and excitation energies of inner-shell excited states of close-shell atomic systems: Be, B\textsuperscript{+}, Ne and Mg. In the calculation, the correlation potentials and energy functionals proposed by Perdew and Wang (PW)\textsuperscript{8} and by Lee, Yang, and Parr (LYP)\textsuperscript{8} are used to take into account the electron correlation effect. We will show that the calculated results are in overall good agreement with available theoretical and experimental data, demonstrating that the SLHF density-functional approach can provide a simple and computationally efficient approach for the accurate calculation of inner-shell excited states of close-shell atomic systems within DFT.
Finally, we also present some new results for the highly excited inner-shell states for the first time.

II. THEORETICAL METHOD

The SLHF density-functional approach has been discussed in Ref. 22 in detail and is outlined in this section for convenience.

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

\[
H_{\sigma}(r) \psi_{i\sigma} (r) = \varepsilon_{i\sigma} \psi_{i\sigma} (r),
\]

where,

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

is the KS Hamiltonian and

\[
V_{\sigma}^{\text{eff}}(r) = V_{\text{ext}}(r) + V_{H}(r) + V_{\text{xc}\sigma}(r),
\]

is the local effective potential. In Eq. (3), \( V_{\text{ext}}(r) \) is the external potential, \( V_{H}(r) \) is Hartree potential (classical Coulomb electrostatic potential between electrons), and \( V_{\text{xc}\sigma}(r) \) is the XC potential.

For a given atomic system, the external potential \( V_{\text{ext}}(r) \) is known exactly. The Hartree potential \( V_{H}(r) \) is given by

\[
V_{H}(r) = \int \frac{\rho(r')}{|r-r'|} dr',
\]

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

\[
\rho_{\sigma}(r) = \sum_{i=1}^{N_{\sigma}} w_{i\sigma} |\psi_{i\sigma}(r)|^2.
\]

Here \( N_{\sigma} \) is the number of electrons with spin \( \sigma \) and \( w_{i\sigma} \) is the occupied number of electrons in the spin-orbital \( \psi_{i\sigma}(r) \).

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

\[
V_{\text{SLHF}}^{x\sigma}(r) = V_{x\sigma}^{S}(r) + V_{x\sigma}^{C}(r),
\]

where,

\[
V_{x\sigma}^{S}(r) = -\frac{1}{\rho_{\sigma}(r)} \sum_{i,j=1}^{N_{\sigma}} \gamma_{ij}^{\sigma}(r) \int \frac{\gamma_{ij}^{\sigma}(r')}{|r-r'|} dr',
\]

is the Slater potential 23 and

\[
V_{x\sigma}^{C}(r) = \frac{1}{\rho_{\sigma}(r)} \sum_{i,j=1}^{N_{\sigma}} \gamma_{ij}^{\sigma}(r) Q_{ij}^{\sigma},
\]

is a correction to Slater potential. In Eqs. (7) and (8) \( \gamma_{ij}^{\sigma}(r) \) and \( Q_{ij}^{\sigma} \) are defined by

\[
\gamma_{ij}^{\sigma}(r) = \psi_{i\sigma}(r) \overline{\psi_{j\sigma}}(r),
\]

and

\[
Q_{ij}^{\sigma} = \langle \psi_{j\sigma}| V_{\text{SLHF}}^{x\sigma} - V_{\text{NL}}^{x\sigma} | \psi_{i\sigma} \rangle,
\]

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

The SLHF exchange potential determined by Eqs. (6)–(10) has two arbitrary additive constants. The physical orbitals can only be obtained by the use of appropriate constants in the exchange potential 10. To settle down the constants so as to pick up the physical orbitals, it is required that the highest-occupied-orbital \( N_{\sigma} \) of each spin \( \sigma \) does not contribute to the correction term \( V_{x\sigma}^{C}(r) \). In this case, the correction term \( V_{x\sigma}^{C}(r) \) decays exponentially, the SLHF exchange potential behaves asymptotically as Slater potential and thus approaches to \(-1/r \) at long range 10.

In atomic systems, an electron spin-orbital is characterized by three quantum numbers \( n, l, \) and \( \sigma \), where \( n \) and \( l \) are the principal quantum number and orbital angular momentum quantum number of the electron, respectively. In the spherical coordinates, the spin-orbital \( \psi_{i\sigma}(r) \) of an electron with quantum numbers \( n, l, \) and \( \sigma \) can be expressed by

\[
\psi_{i\sigma}(r) = \frac{R_{n\ell\sigma}(r)}{r} Y_{\ell m}(\theta, \phi),
\]

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

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

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

\[
v_{\sigma}^{\text{eff}}(r) = v_{\text{ext}}(r) + v_{H}(r) + v_{\text{SLHF}}^{x\sigma}(r) + v_{\text{corr}}(r).
\]

In Eq. (13), \( v_{\text{ext}}(r), v_{H}(r), v_{\text{SLHF}}^{x\sigma}(r), \) and \( v_{\text{corr}}(r) \) 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

\[
v_{\text{ext}}(r) = -\frac{Z}{r}.
\]
In central-field approach, the radial Hartree potential is calculated from

$$v_H(r) = 4\pi \int \frac{1}{r} \rho(r') r'^2 dr', \quad (15)$$

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 $\beta$) is the spherically averaged spin-dependent electron density given by

$$\rho_\sigma(r) = \frac{1}{4\pi} \int \rho_\sigma(r) d\Omega = \frac{1}{4\pi} \sum_{n l m} w_{n l \sigma} \left( \frac{R_{n l \sigma}}{r} \right)^2. \quad (16)$$

Here the symbol $\nu_\sigma$ stands for a set of quantum numbers for summation and the sum is performed over all the occupied spin-orbitals with spin $\sigma$. 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, the error is negligible compared to the order of calculated multiplet splitting [11].

The radial SLHF exchange potential is given by

$$v_{x\sigma}^{\text{SLHF}}(r) = v_{x\sigma}^S(r) + v_{x\sigma}^C(r), \quad (17)$$

where,

$$v_{x\sigma}^S(r) = -\frac{1}{4\pi \rho_\sigma(r)} \sum_{n l m n' l' m'} \sum_{\nu_\sigma} \sum_{\nu'_\sigma} s^\sigma_{n l m, n' l' m'}(r), \quad (18)$$

is the radial Slater potential and

$$v_{x\sigma}^C(r) = \frac{1}{4\pi \rho_\sigma(r)} \sum_{n l m n' l' m'} \sum_{\nu_\sigma} \sum_{\nu'_\sigma} c^\sigma_{n l m, n' l' m'}(r). \quad (19)$$

is a correction to the radial Slater potential. The matrix elements $s^\sigma_{n l m, n' l' m'}(r)$ and $c^\sigma_{n l m, n' l' m'}(r)$ in Eq. (19) are given in Ref. [22].

To calculate electron spin-orbital, the Legendre generalized pseudospectral (LGPS) method [24] is used to discretize the radial KS equation [11]. This method associated with an appropriate mapping technique can overcome difficulties due to singularity at $r = 0$ and long-tail at large $r$ of Coulomb interaction and thus provides a very effective and efficient numerical algorithm for high-precision solution of 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 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

$$E_k = \frac{\beta}{2} \sum_{\sigma = \alpha} \sum_{n l} w_{n l \sigma} \int R_{n l \sigma}(r) \left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} \right) R_{n l \sigma}(r) dr \quad (20)$$

$$E_{ext} = 4\pi \int v_{ext}(r) \rho(r) r^2 dr, \quad (21)$$

$$E_H = \frac{1}{2} \sum_\Pi \eta_{lm, l' m'} F^k_{n l \sigma, n' l' \sigma'}, \quad (22)$$

and

$$E_x = -\frac{1}{2} \sum_{\Pi} \lambda_{lm, l' m'} G^k_{n l \sigma, n' l' \sigma'} \delta_{\sigma \sigma'}, \quad (23)$$

where, $\Pi$ represents a collection of all the quantum numbers involved, the matrix elements $\eta^k_{lm, l' m'}$, $F^k_{n l \sigma, n' l' \sigma'}$, and $G^k_{n l \sigma, n' l' \sigma'}$ are given in Ref. [22].

For a multiplet state that can be described completely 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 [23]. According to this rule, a sum over single-Slater-determinant energy $E(D_i)$ of determinant $D_i$ from an electron configuration equals to a weighted sum over multiplet energy $E(M_j)$ of multiplet state $M_j$ involved in the same electron configuration, namely,

$$\sum_i E(D_i) = \sum_j d_j E(M_j), \quad (24)$$

where, the weight $d_j$ is the times that the multiplet state $M_j$ appears in all the single Slater determinants. Similar procedures have been employed in recent excited-state calculations [14, 15, 23].

III. RESULTS AND DISCUSSION

The procedure described in the preceding section is extended to calculate the total energies ($E$) and excitation energies ($\Delta E$) of inner-shell excited states of closed-shell atomic systems: Be, B⁺, Ne, and Mg. In the calculations, the correlation effect, which is characterized by the correlation potential $v_{c\sigma}(r)$ and correlation energy $E_c$, is taken into account through the correlation potentials and energy functionals of Perdew and Wang (PW) [8] and of Lee, Yang, and Parr (LYP) [8], respectively. The results obtained with these two correlation energy functionals are listed in columns PW and LYP in the following tables, respectively. For simplicity, henceforward we use an abbreviation $(nl)^{-1} (nl')$ to represent an electronic configuration for an electron in inner-shell $(nl)$ being excited to sub-shell $(nl')$, unless otherwise specified. For instance, an abbreviation $1s^{-1}2p$ represents an electronic configuration of inner-shell excitation $1s2s^22p$ of Be.
A. Be

In TABLE I we present the total energies and excitation energies from our calculations for inner-shell excited states 1s\(^{-1}\)np \(^{1,3}\)P \((n = 2 \sim 8)\) of Be. For comparison we also list in this table the theoretical results of density work-functional approach (WF) \([26]\), saddle-point complex-rotation approximation (SPCR) \([27, 28]\), and R-matrix method in the close-coupling approximation (RMCC) \([29]\) and experimental results (Exp.) \([30, 31, 32, 33]\). For the total energies, the maximum relative discrepancies of our PW and LYP results are 0.10% and 0.25% to the WF results, and 0.27% and 0.39% to the SPCR results. For excitation energies, the maximum relative deviations of our PW and LYP results to the experimental results are 0.37% and 0.90%, respectively, while the maximum relative discrepancies of the WF, SPCR, and RMCC results to the experimental results are 0.41%, 0.05%, and 0.14%, respectively. This demonstrates that both the total energies and excitation energies from our calculations agree well with the experimental and other theoretical results. On the other hands, due to overestimation of LYP energy functional to correlation energies of atomic systems with smaller Z \([8, 22]\), the LYP results are a little bit worse than the PW results. It is also shown that our PW results for excitation energy are a little bit better than the WF results.

B. B\(^{+}\)

To explore the feasibility of the approach to inner-shell excitation of atomic ions, we also apply the procedure to inner-shell excited-state calculation of B\(^{+}\). The total energies and excitation energies of inner-shell excited states 1s\(^{-1}\)np \(^{1,3}\)P \((n = 2 \sim 8)\) are given in TABLE III along with theoretical results of Dirac-Fock method (DF) \([34]\) and available experimental results \([34]\). For excitation energies, the relative deviations of our PW and LYP results are less than 0.32% and 0.64% to the DF results, and less than 0.29% and 0.60% to the experimental results. This demonstrates again that our results are in good agreement with both the experimental and other theoretical results, and the PW results are a little bit more accurate than the LYP results for this atomic ion having smaller Z.

C. Ne

We present in TABLE III and TABLE IV the total energies and excitation energies from our calculations for inner-shell excited states 1s\(^{-1}\)ns \(^{1,3}\)S \((n = 3 \sim 8)\) and 1s\(^{-1}\)np \(^{1,3}\)P \((n = 3 \sim 8)\) of Ne, respectively. We also present in TABLE IV the total energy of inner-shell excited state 1s2s\(^2\)2p\(^2\) \(^2\)S of Ne\(^{+}\) and ionization energy of an inner-shell 1s electron of Ne. For comparison we also show in these tables the theoretical results of density work-functional approach (WF) \([26]\), configuration-interaction model (CI) \([35]\), and Hartree-Fock method (HF) \([36]\), and experimental results (Exp.) \([37, 38, 39, 40, 41, 42, 43, 44]\). For the total energies of excited states 1s\(^{-1}\)ns \(^{1,3}\)S \((n = 3 \sim 8)\) given in TABLE III the relative deviations of our PW and LYP results to the WF results are not more than 0.03% and 0.02%, respectively. This demonstrates that the PW energy functional has almost the same precision as the LYP energy functional in calculation of total energies of these inner-shell excited states. For excitation energies, the relative discrepancies of our PW and LYP results to the experimental result are less than 0.13% and 0.02%, respectively. This indicates that the LYP results for the excitation energy are better than the PW results. Since the total energies from calculation with PW energy functional are very close to those with LYP energy functional, the larger discrepancy of the PW results for excitation energy mainly comes from the ground-state energy, which is -128.8952 (a.u.) from the calculation with PW energy functional. This value is different from that with LYP energy functional -128.9331 (a.u.) \([22]\) and that obtained from Hartree-Fock energy plus correlation energy -128.937 (a.u.). In addition, the maximum relative discrepancies of the excitation energies from WF calculation and CI calculation are 0.08% and 0.03% to the experimental results, respectively. This illustrates that our LYP results are very close to the CI results and better than the WF results.

For the total energies of inner-shell excited states 1s\(^{-1}\)np \(^{1,3}\)P \((n = 3 \sim 8)\) given in TABLE IV the relative deviations of our PW and LYP results to the WF results are not more than 0.02% and 0.02%, respectively. This implies that the PW energy functional has the same precision as the LYP energy functional in the total energy calculation of these states. For the excitation energies, the maximum relative discrepancies of our PW and LYP results to the experimental results are 0.14% and 0.02%, while the maximum relative deviations of the WF and CI results to the experimental results are 0.07% and 0.02%, respectively. This demonstrates that the LYP results for excitation energy are a little bit more accurate than the PW results for these inner-shell excited states. It is also shown that the LYP results are again very close to the CI results and a little bit better than the WF results.

D. Mg

For Mg, we have computed the total energies and excitation energies for inner-shell excited states 2p\(^{-1}\)ns \(^{1,3}\)P \((n = 4 \sim 8)\), 2s\(^{-1}\)np \(^{1,3}\)P \((n = 3 \sim 8)\), 2s\(^{-1}\)ns \(^{1,3}\)S \((n = 4 \sim 8)\), 1s\(^{-1}\)np \(^{1,3}\)P \((n = 3 \sim 8)\), and 1s\(^{-1}\)ns \(^{1,3}\)S \((n = 4 \sim 8)\). The results are shown in TABLE V to TABLE IX respectively. For comparison, the theoretical results from configuration-interaction calculation with improved and optimized orbitals (CHIOO) \([17]\) and exper-
### TABLE I: Total energies (E) and excitation energies (ΔE) of inner-shell excited states 1s⁻¹np ¹³P (n = 2 ~ 8) of Be. The ground state energies obtained from calculation with PW and LYP correlation potentials and energy functionals are −14.6575 (a.u.) and −14.6886 (a.u.), respectively. Here 1 a.u. = 27.2116 eV is used.

| States          | Present work | LYP⁺ | PW | Other theory | LYP⁺ | PW | SPCR⁺ | RMCC | JSCK⁺ | JNT⁺ | RHF⁺ |
|-----------------|--------------|------|----|--------------|------|----|-------|------|-------|------|------|
| 1s⁻¹2p ³P       | 0.54  2.56   | 0.4362 | 0.4628 | 0.4654 | 114.4221 | 115.1794 | 114.4304 | 114.2  |
| ¹P              | 0.5417 | 0.4163 | 0.4146 | 0.4209 | 115.5350 | 115.7119 | 115.7420 | 115.513 | 115.66 | 115.49 |
| 1s⁻¹3p ³P       | 0.5843 | 0.4173 | 0.4942 | 121.7229 | 122.4059 | 121.7395 |
| ¹P              | 0.5879 | 0.4171 | 0.4882 | 0.2073 | 122.8481 | 122.9430 | 121.9028 | 121.420 | 121.42 | 121.4 |
| 1s⁻¹4p ³P       | 0.6140 | 0.1290 | 0.1504 | 122.9012 | 123.5309 | 122.9314 |
| ¹P              | 0.6132 | 0.1276 | 0.1480 | 0.1662 | 122.9502 | 123.5690 | 122.9967 | 122.537 | 122.63 | 122.5 |
| 1s⁻¹5p ³P       | 0.6239 | 0.1123 | 0.1331 | 123.3665 | 123.9848 | 124.4021 |
| ¹P              | 0.6229 | 0.1116 | 0.1319 | 0.1495 | 123.3937 | 124.0044 | 123.4348 | 122.992 | 123.08 | 122.96 |
| 1s⁻¹6p ³P       | 0.6152 | 0.1039 | 0.1042 | 123.6033 | 123.2125 |
| ¹P              | 0.6146 | 0.1035 | 0.1042 | 123.6196 | 123.2240 |
| 1s⁻¹7p ³P       | 0.6102 | 0.1009 | 0.1098 | 123.7393 | 123.3431 |
| ¹P              | 0.6098 | 0.0998 | 123.7502 | 123.3508 |
| 1s⁻¹8p ³P       | 0.6070 | 0.0961 | 123.8264 | 124.4250 |
| ¹P              | 0.6068 | 0.0959 | 123.8318 | 124.4299 |

PW results, LYP results, SPCR⁺, and RMCC.

### TABLE II: Total energies (E) and excitation energies (ΔE) of inner-shell excited states 1s⁻¹np ¹³P (n = 2 ~ 8) of B⁺. The ground state energies obtained from calculation with PW and LYP correlation potentials and energy functionals are −24.3284 (a.u.) and −24.3432 (a.u.), respectively.

| States          | Present work | LYP⁺ | PW | Other theory | LYP⁺ | PW | SPCR⁺ | RMCC | JSCK⁺ | JNT⁺ | RHF⁺ |
|-----------------|--------------|------|----|--------------|------|----|-------|------|-------|------|------|
| 1s⁻¹2p ³P       | 0.7559 | 0.2412 | 192.4546 | 193.2571 | 192.460 |
| ¹P              | 0.7837 | 0.1977 | 194.4187 | 194.4417 | 194.394 |
| 1s⁻¹3p ³P       | 1.6568 | 1.5858 | 210.3876 | 211.0921 | 209.850 |
| ¹P              | 1.6561 | 1.5799 | 210.6797 | 211.2534 | 210.125 |
| 1s⁻¹4p ³P       | 1.6550 | 1.4444 | 214.2478 | 214.9409 | 213.611 |
| ¹P              | 1.6509 | 1.4422 | 214.3599 | 214.9983 | 213.715 |
| 1s⁻¹5p ³P       | 1.6395 | 1.3851 | 215.8549 | 216.5545 | 215.189 |
| ¹P              | 1.6393 | 1.3841 | 215.9099 | 216.5796 | 215.237 |
| 1s⁻¹6p ³P       | 1.6354 | 1.3546 | 216.6860 | 217.3845 | 215.999 |
| ¹P              | 1.6342 | 1.3541 | 216.7170 | 217.3970 | 216.028 |
| 1s⁻¹7p ³P       | 1.6347 | 1.3368 | 217.1684 | 217.8672 |
| ¹P              | 1.6346 | 1.3365 | 217.1886 | 217.8745 |
| 1s⁻¹8p ³P       | 1.6336 | 1.3256 | 217.4803 | 218.1725 |
| ¹P              | 1.6335 | 1.3254 | 217.4895 | 218.1767 |

PW results, LYP results, SPCR⁺, and RMCC.

### TABLE III: Total energies (E) and excitation energies (ΔE) of inner-shell excited states 1s⁻¹ns ¹³S (n = 3 ~ 8) of Ne. The ground state energies obtained from calculations with PW and LYP correlation potentials and energy functionals are −128.9852 (a.u.) and −128.9331 (a.u.), respectively.

| States          | Present work | Other theory | LYP⁺ | PW | SPCR⁺ | RMCC | JSCK⁺ | JNT⁺ | RHF⁺ |
|-----------------|--------------|--------------|------|----|-------|------|-------|------|------|
| 1s⁻¹3s ³S       | 0.97143 | 0.97145 | 97.1729 | 864.9920 | 864.8826 | 864.9197 |
| ¹S              | 0.97137 | 0.97141 | 97.1631 | 864.1601 | 865.1112 | 864.6583 | 865.37 | 865.1 | 865.32 |
| 1s⁻¹4s ³S       | 0.97035 | 0.97034 | 867.0081 | 868.0038 |
| ¹S              | 0.97031 | 0.97036 | 867.0516 | 868.0636 | 868.21 |
| 1s⁻¹5s ³S       | 0.96999 | 0.97008 | 867.9208 | 868.9290 |
| ¹S              | 0.96993 | 0.97000 | 867.9382 | 868.9507 | 869.06 |
| 1s⁻¹6s ³S       | 0.96985 | 0.96983 | 868.3189 | 869.3235 |
| ¹S              | 0.96985 | 0.96985 | 868.3276 | 869.3344 | 869.44 |
| 1s⁻¹7s ³S       | 0.96977 | 0.96978 | 868.5279 | 869.5276 |
| ¹S              | 0.96974 | 0.96976 | 868.5328 | 869.5331 |
| 1s⁻¹8s ³S       | 0.96973 | 0.96974 | 868.6522 | 869.6474 |
| ¹S              | 0.96972 | 0.96973 | 868.6555 | 869.6501 |

PW results, LYP results, SPCR⁺, and RMCC.
For inner-shell excitation of Mg, the excited states involving in excitation of a 2p electron, 2p⁻¹ns⁻¹³P, are the only ones that experimental excitation energies are available, as shown in TABLE IV. For these states, the excitation energies from our calculation are in good agreement with the experimental results. The relative deviations of our PW and LYP results to the CIIOO results are not more than 0.38% and 0.36%, respectively. Thus the PW energy functional has the same precision as the LYP energy functional in the excitation energy calculation of these inner-shell excited states. Apart from an excited state 2p⁻¹4s⁻¹³P our results also agree well with the CIIOO results. The maximum relative discrepancies of our PW and LYP results to the CIIOO results are 0.58% and 0.60%, respectively. The larger discrepancies of our results to the CIIOO results for the state 2p⁻¹4s⁻¹³P are caused by the fact that the excitation energy from the CIIOO calculation is too small. It is shown from TABLE V that the CIIOO result is much smaller than the experimental data while our excitation energies are very close to the experimental results.

For inner-shell excited states relevant to excitation of a 2s electron, the excitation energies from our calculations with both PW and LYP energy functionals are larger than the CIIOO results, as shown in TABLE VIII and TABLE IX, our PW and LYP results are smaller and larger than the CIIOO results, respectively. For excited states 1s⁻¹np⁻¹³P the relative deviations of our PW and LYP results to the CIIOO results are less than 0.02% and 0.08%, respectively. For excited states 1s⁻¹ns⁻¹³S, apart from a state 1s⁻¹4s⁻¹³S, the relative discrepancies of our PW and LYP results to the CIIOO results are not more than 0.04% and 0.03%, respectively. For the state 1s⁻¹4s⁻¹³S our LYP result is larger than the CIIOO result by 0.11%.

### IV. Conclusions

In summary, the procedure we have developed for excited-state calculation based on SLHF density functional approach and Slater’s diagonal sum rule has been extended to the treatment of inner-shell excited states of atomic systems. In this procedure, electron spin-orbitals in an electronic configuration are obtained first by solving the KS equation with the exact SLHF exchange potential. Then a single-Slater-determinant energy of the electronic configuration is calculated by using these electron spin-orbitals. Finally, a multiplet energy of an excited state is evaluated from the single-Slater-determinant energies of the electronic configurations involved in terms of Slater’s diagonal sum rule. In this procedure, the key part is the SLHF exchange potential. This potential qualifies for inner-shell excited-state calculation because it provides a potential with free self-interaction, correct long-range behavior, and symmetry dependence of atomic state. We have applied this procedure to the calculations of total energies and excitation energies of inner-shell excited states of close-shell atomic systems: Be, B⁺, Ne, and Mg. In the calculation, the generalized pseudospectral...
method with nonuniform grids is used for optimal discretization of the spatial coordinates, allowing accurate and efficient treatment of the KS equation and the spin-orbital energies for both the ground and excited states. The correlation effect is taken care of by incorporating the PW and LYP correlation potentials and energy functionals into calculation. The results from our calculations with LYP and PW energy functionals are in overall good agreement with each other and also with the available more sophisticated ab initio theoretical results and experimental data. The maximum relative discrepancy of our calculated excitation energies to the available experimental results is not more than 0.90%, demonstrating that the SLHF density-functional approach is capable of providing a powerful and computationally efficient scheme for accurate inner-shell excited-state calculation of close-shell atomic systems within DFT. Extension of the SLHF density-functional approach to open-shell atomic systems

| States       | $-E$ (a.u.) | $\Delta E$ (eV) | Present work | PW       | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
|--------------|-------------|-----------------|--------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|------|
| $2p^{-1}4s^2 3p^1$ | 196.64182 196.6721 92.5785 92.5820 | 91.72 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $2s^{-1}3p^1 1p$ | 196.64182 196.6721 92.5785 92.5820 | 91.72 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $2s^{-1}4p^1 3p$ | 196.4612 196.5181 96.8256 96.7718 | 96.18 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $2s^{-1}5p^1 3p$ | 196.4679 196.4871 97.7574 97.6164 | 97.11 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $2s^{-1}6p^1 3p$ | 196.4275 196.4865 97.6777 97.6317 | 97.66 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $2s^{-1}7p^1 3p$ | 196.4313 196.4738 98.1403 97.9775 | 97.66 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $2s^{-1}8p^1 3p$ | 196.4065 196.4669 98.3411 98.1721 | 97.66 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |

TABLE VIII: Total energies ($E$) and excitation energies ($\Delta E$) of inner-shell excited states $1s^{-1}np\ 1P$ ($n = 3 \sim 8$) of Mg.

| States       | $-E$ (a.u.) | $\Delta E$ (eV) | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
|--------------|-------------|-----------------|--------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|------|
| $1s^{-1}4p^1 3p$ | 152.1281 152.1433 1304.2275 1304.2822 | 1303.25 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $1s^{-1}4p$ | 152.1207 152.1353 1303.4275 1304.5002 | 1304.50 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $1s^{-1}5p$ | 151.9659 151.9839 1307.6412 1307.6912 | 1308.01 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $1s^{-1}5p^1 3p$ | 151.9314 151.9536 1308.5256 1308.4853 | 1308.01 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $1s^{-1}6p^1 3p$ | 151.9121 151.9401 1308.9139 1308.8019 | 1308.01 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
| $1s^{-1}7p^1 3p$ | 151.9073 151.9290 1309.2344 1310.1145 | 1308.01 | Present work | PW $\alpha$ | PW $\alpha'$ | PW $\alpha''$ | LYP $\alpha$ | LYP $\alpha'$ | LYP $\alpha''$ | Other theory | Exp. |
is in progress.

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