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Spin-dependent localized Hartree-Fock density-functional calculation of singly, doubly, and triply excited and Rydberg states of He- and Li-like ions

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A spin-dependent density-functional approach for the calculation of highly and multiply excited state of atomic system is proposed based on the localized Hartree-Fock density-functional method and Slater's diagonal sum rule. In this approach, electron spin orbitals in an electronic configuration are obtained first by solving the Kohn-Sham equation with an exact nonvariational spin-dependent localized Hartree-Fock 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. This approach has been applied to the calculation of singly, doubly, and especially triply excited Rydberg states of He- and Li-like ions. The total energies obtained from the calculation with an exchange-only (X-only) potential are surprisingly close to those of Hartree-Fock method and the total energies from the calculation with exchange-correlation potential are in overall agreement with available theoretical and experimental data. The presented procedure provides a simple and computationally efficient scheme for the accurate calculation of highly and multiply excited Rydberg states of an atomic system within density-functional theory.

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I. INTRODUCTION

Density-functional theory (DFT) [1,2] has been widely applied to many areas in theoretical physics and chemistry [3,4] as a powerful *ab initio* approach of calculating the ground-state properties of many-electron systems due to its computational simplicity in dealing with systems having a large number of electrons. The basis of DFT is the Hohenberg and Kohn (HK) theorem [1] and the Kohn-Sham (KS) equation [2]. The most important and troublesome part in DFT is the exchange-correlation (XC) potential because it determines not only calculation accuracy but also the usefulness of a DFT calculation [5].

In a traditional approximation, such as the local density approximation (LDA) [3,4] and the generalized gradient approximation (GGA) [6–8], the XC potential is obtained by using uniform electron gas. Because of the incomplete cancellation of spurious self-interactions [9], the approximate XC potential falls off too fast and thus exhibits some incorrect asymptotic behaviors [10]. As a result, no Rydberg series and only a few bound unoccupied states can be available from a calculation with this kind of XC potential. In addition, the traditional XC potential has an inherent degeneracy due to its independence of symmetries such as orbital angular momentum and spin of the state considered and thus the calculated energies for different symmetries may have the same value. Therefore, the KS equation with traditional XC potential cannot be directly applied to the calculation of excited-state energy, especially highly excited-state energy.

In fact, DFT itself is a ground-state theory. KS eigenvalue differences of unoccupied and occupied orbitals are not rigorously defined as excitation energies. One needs to go beyond the standard DFT, for example, using a time-dependent DFT approach [11–13] to calculate excitation energy. However, KS eigenvalues can serve as good zero-order excited-state energies provided that they are gained by solving the KS equation with a high-quality XC potential [14]. A number of theoretical methods have been developed by adopting this point of view (see a recent review article [15] for more approaches), in which the work-function- (WF-) based exchange potential approach [16–19], the open-shell localized Hartree-Fock (LHF) density-functional approach [20,21], and the multireference LHF density-functional approach [22,23] have drawn more attention because of their successful applications to the calculations of atomic and molecular excited states.

However, almost all the calculations using the time-dependent DFT approach, open-shell LHF approach, and multireference LHF approach so far are performed for lower singly excited states. Although better results from calculations of the WF method were reported for both singly and doubly excited states of atomic systems [18,19], one needs the rotational component of the field in computation, which, in general, is very hard to calculate. In the atomic case, it may be neglected in comparison with the irrotational component, but in the molecular case, it cannot be ignored due to the departure of electronic structure from spherical symmetry [15]. Even for the atomic case, WF calculation often encounters a self-consistent convergence problem for high-lying Rydberg excited states [19]. Therefore, an effective, simple, and easy-to-be-applied density-functional method for the calculation of highly and multiply excited states remains to be explored.

In this paper, we present a spin-dependent density-functional approach for the calculation of highly and multiply excited states of atomic systems based on the LHF density-functional method [14,24] and Slater's diagonal sum rule [25]. In this approach, the exchange potential used is an exact nonvariational spin-dependent localized Hartree-Fock (SLHF) exchange potential constructed by extending the ground-state LHF exchange potential to excited states, electron spin orbitals in an electronic configuration are obtained by solving KS equation with the SLHF exchange potential, a single-Slater-determinant energy of the electronic configuration is calculated by using these electron spin orbitals, and 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. The SLHF exchange potential is free of Coulomb self-interactions, dependent on symmetries of the state under consideration, requires occupied orbitals only, and exhibits correct long-range behaviors; it can be used to calculate the spin orbitals and density for each individual excited state and thus is promising for the calculation of highly and multiply excited states of atomic system. We have applied this procedure to the calculations of singly, doubly, and especially triply excited states of He- and Li-like ions. Due to the singularity at the origin and long-range nature of the Coulomb potential, we use the generalized pseudospectral (GPS) method [26] to discretize spatial coordinates and optimize solution of the KS equation so as to obtain accurate eigenvalues and density functionals. The total energies obtained from the calculation with an exchange-only (X-only) potential (X-only calculation) are found to be surprisingly close to those of the Hartree-Fock (HF) method and the total energies from the calculation with the XC potential (XC calculation) are in overall agreement with available theoretical and experimental data.

II. THEORETICAL METHOD

A. Spin-dependent localized Hartree-Fock density-functional method

In spin-dependent DFT, the spin-dependent electron density $\rho_\sigma(\mathbf{r})$ is defined by

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

where σ is the electron spin, equal to α and β for spin-up and spin-down, N_σ is the number of electrons with spin σ, $\varphi_{i\sigma}(\mathbf{r})$ is the ith spin orbital with spin σ, and $w_{i\sigma}$ is the occupied number of electrons in the spin orbital $\varphi_{i\sigma}(\mathbf{r})$. The electron spin orbital $\varphi_{i\sigma}(\mathbf{r})$ is determined by the KS equation

$$H_\sigma(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma}\varphi_{i\sigma}(\mathbf{r}), \tag{2}$$

with the KS Hamiltonian $H_\sigma(\mathbf{r})$ given by

$$H_\sigma(\mathbf{r}) = -\tfrac{1}{2}\nabla^2 + V_\sigma^{\text{eff}}(\mathbf{r}), \tag{3}$$

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

$$V_\sigma^{\text{eff}}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc\sigma}(\mathbf{r}), \tag{4}$$

where $V_{ext}(\mathbf{r})$ 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 XC potential. The external potential is known accurately for a given atomic system. The Hartree potential can be calculated exactly by

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}', \tag{5}$$

where $\rho(\mathbf{r})=\rho_\alpha(\mathbf{r})+\rho_\beta(\mathbf{r})$ is the total electron density. Thus finding a suitable XC potential is the key to the calculation of both the ground state and excited states. The XC potential can be divided into the exchange potential $V_{x\sigma}(\mathbf{r})$ and the correlation potential $V_{c\sigma}(\mathbf{r})$.

Recently, the X-only LHF density-functional method has been proposed and successfully applied to the ground-state calculation of atomic and molecular systems [14,24]. In that method, electron orbitals are calculated by solving the KS equation with the LHF exchange potential as its exchange potential. The LHF exchange potential is derived under the assumption that the X-only KS determinant is equal to the HF determinant. This potential is free of Coulomb self-interactions, requires only occupied orbitals, and exhibits correct long-range behaviors. The exchange potential in the Krieger, Li, and Iafrate (KLI) procedure [27,28], an approximation of the exact exchange (EEX) optimized effective potential (OEP) [29], is an approximation to the LHF exchange potential.

In this paper, we extend the LHF exchange potential to the excited-state calculation of the atomic system by assuming that the electron spin orbitals of excited states are determined by the KS equation of a noninteracting system and the X-only KS determinant of the noninteracting system equals the HF determinant of the interacting system for the excited states. Based on this postulate, following a similar procedure used in Ref. [14], we obtain the spin-dependent localized Hartree-Fock (SLHF) exchange potential

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

where the first term $V_{x\sigma}^{\text{S}}(\mathbf{r})$ is the Slater potential [25] and the second term $V_{x\sigma}^{\text{C}}(\mathbf{r})$ is a correction to the Slater potential. Both of them are determined by occupied KS spin orbitals and are calculated by

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

and

$$V_{x\sigma}^{\text{C}}(\mathbf{r}) = \frac{1}{\rho_\sigma(\mathbf{r})}\sum_{i,j=1}^{N_\sigma}\gamma_{ij}^\sigma(\mathbf{r})Q_{ij}^\sigma, \tag{8}$$

where $\gamma_{ij}^\sigma(\mathbf{r})$ and Q_{ij}^σ are defined by

$$\gamma_{ij}^\sigma(\mathbf{r}) = \varphi_{i\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}), \tag{9}$$

and

$$Q_{ij}^\sigma = \langle\varphi_{j\sigma}|V_{x\sigma}^{\text{SLHF}} - V_{x\sigma}^{\text{NL}}|\varphi_{i\sigma}\rangle. \tag{10}$$

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, $\langle\varphi_{j\sigma}|V_{x\sigma}^{\text{SLHF}}|\varphi_{i\sigma}\rangle$ and $\langle\varphi_{j\sigma}|V_{x\sigma}^{\text{NL}}|\varphi_{i\sigma}\rangle$ are symmetric matrix elements calculated by

$$\langle \varphi_{j\sigma}|V_{x\sigma}^{\mathrm{SLHF}}|\varphi_{i\sigma}\rangle = \int \gamma_{ij}^{\sigma}(\mathbf{r}')V_{x\sigma}^{\mathrm{SLHF}}(\mathbf{r}')d\mathbf{r}' \tag{11}$$

and

$$\langle \varphi_{j\sigma}|V_{x\sigma}^{\mathrm{NL}}|\varphi_{i\sigma}\rangle = -\sum_{k=1}^{N_\sigma}\int\int \frac{\gamma_{ik}^{\sigma}(\mathbf{r})\gamma_{kj}^{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \tag{12}$$

In the spin-dependent DFT, the exchange interaction only occurs among electrons with the same spin. In Eq. (6), when $V_{x\sigma}^{\mathrm{C}}(\mathbf{r})=0$, the SLHF exchange potential is reduced to the Slater potential of the HF method [25]. Because $V_{x\sigma}^{\mathrm{C}}(\mathbf{r})$ depends on $V_{x\sigma}^{\mathrm{SLHF}}$, the SLHF exchange potential $V_{x\sigma}^{\mathrm{SLHF}}(\mathbf{r})$ has to be computed in a self-consistent manner. In Eq. (8), if the terms with $i\neq j$ are neglected, the SLHF exchange potential reduces to the KLI exchange potential [27,28].

For the spin-dependent DFT, SLHF exchange potentials determined by Eqs. (6)–(12) have two arbitrary additive constants. The physical orbitals can only be obtained by the use of appropriate constants in the exchange potential. To settle down the constants so as to pick up the physical orbitals, we demand the highest occupied orbital N_σ of each spin σ to satisfy [14]

$$\langle \varphi_{N_\sigma\sigma}|V_{x\sigma}^{\mathrm{SLHF}} - V_{x\sigma}^{\mathrm{NL}}|\varphi_{N_\sigma\sigma}\rangle = 0. \tag{13}$$

This condition indicates that the highest occupied orbital does not contribute to the correction term $V_{x\sigma}^{\mathrm{C}}(\mathbf{r})$. In this case, the correction term $V_{x\sigma}^{\mathrm{C}}(\mathbf{r})$ decays exponentially, the SLHF exchange potential behaves asymptotically as the Slater potential, and thus approaches to $-1/r$ at long range [14]. Moreover, the SLHF exchange potential depends only on the occupied orbitals and thus contains detailed information of the electronic configuration considered.

It should be noted that the SLHF exchange potential above is an extension of the ground-state LHF exchange potential although they are very similar to each other [14]. Since the SLHF formalism is not derived from a variational principle for energy, the variational restriction on the ground state being the lowest state of a given space-spin symmetry is not applicable here. Thus the calculation of spin orbitals for excited states by solving the KS equation (2) with the SLHF exchange potential is not subject to a variational bound for energy. Furthermore, unlike the WF method, the SLHF method guarantees the existence of a local effective potential for both the ground state and excited states [14,20]. Because of the nonvariational nature of the SLHF exchange potential, the KS equation (2) is no longer a variational equation and thus the problem of variational collapse to the ground state is avoided in our approach. This is a considerable advantage since, for a variational calculation of excited-state energy, to satisfy the wave function orthogonality (to prevent variational collapse) can be a task of formidable complexity [19].

Calculation of the total energy should include the correlation effect. This effect is taken into account via correlation energy in the DFT calculation. Although quite a few approaches have been developed for this purpose, the second-order gradient correlation potential and energy functional proposed by Lee, Yang, and Parr (LYP) [7] have been shown to provide an excellent representation of actual correlation energy and will be incorporated into our calculation to estimate the correlation effect.

B. Central-field approach of atomic system

To demonstrate the feasibility of the approach developed above, we apply it to the excited-state calculation of atomic system. To specify the spin-dependent property, an electron spin orbital is signified by three quantum numbers n, l, and σ, where n and l are the principal quantum number and orbital angular momentum quantum number of the electron, respectively. In spherical coordinates, a spin orbital $\varphi_{i\sigma}(\mathbf{r})$ of the electron with quantum numbers n, l, and σ can be expressed by

$$\varphi_{i\sigma}(\mathbf{r}) = \frac{R_{nl\sigma}(r)}{r}Y_{lm}(\theta,\phi), \tag{14}$$

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 electron density is evaluated by substituting Eq. (14) into Eq. (1). For the atomic system investigated in this work, the system is described by a spherically averaged electron density given by

$$\rho_\sigma(r) = \frac{1}{4\pi}\int \rho_\sigma(\mathbf{r})d\Omega = \frac{1}{4\pi}\sum_{nl}^{\nu_\sigma} w_{nl\sigma}\left[\frac{R_{nl\sigma}}{r}\right]^2, \tag{15}$$

where the symbol ν_σ stands for a set of quantum numbers for summation and the sum is performed over all the occupied spin-orbitals with spin σ. The electron density obtained in this way is accurate for spherically symmetric (close-shell) states, but approximate for nonspherically symmetric (open-shell) states. When this kind of electron density is used to evaluate the energy of a nonspherically symmetric state, it may induce an error. However, the error is negligible compared to the order of the calculated multiplet splitting [15].

Substituting Eq. (14) into Eq. (2), multiplying the equation by $Y_{lm}^{*}(\theta,\phi)$, integrating the equation over angles, and averaging the equation over m, finally, we obtain the radial KS equation for the radial spin orbital $R_{nl\sigma}(r)$,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v_\sigma^{\mathrm{eff}}(r)\right]R_{nl\sigma} = \varepsilon_{nl\sigma}R_{nl\sigma}, \tag{16}$$

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

$$\begin{aligned} v_\sigma^{\mathrm{eff}}(r) &= \frac{1}{2l+1}\sum_{m=-l}^{l}\int Y_{lm}^{*}(\theta,\phi)V_\sigma^{\mathrm{eff}}(\mathbf{r})Y_{lm}(\theta,\phi)d\Omega \\ &= v_{ext}(r) + v_H(r) + v_{x\sigma}^{\mathrm{SLHF}}(r) + v_{c\sigma}^{\mathrm{LYP}}(r). \end{aligned} \tag{17}$$

Here, $v_{ext}(r)$, $v_H(r)$, $v_{x\sigma}^{\mathrm{SLHF}}(r)$, and $v_{c\sigma}^{\mathrm{LYP}}(r)$ are the radial external potential, radial Hartree potential, radial SLHF exchange potential, and radial LYP correlation potential [7], respectively.

In an atomic system, the external potential is the Coulomb potential between the electron and the nucleus. For the atom with a nuclear charge Z, the radial external potential is given by

$$v_{ext}(r) = -\frac{Z}{r}. \tag{18}$$

To calculate the radial Hartree potential, by applying the multipole expansion of $1/|\mathbf{r}-\mathbf{r}'|$, the orthonormality of spherical harmonics, and the spherical-harmonic expansion of two spherical harmonics to Eq. (5), we obtain [30]

$$v_H(r) = 4\pi \int \frac{1}{r_>}\rho(r')r'^2 dr', \tag{19}$$

where $r_>$ is the larger of r and r', and $\rho(r)=\rho_\alpha(r)+\rho_\beta(r)$ is the spherically averaged total electron density.

Similarly, from Eqs. (6)–(12), we obtain the radial SLHF exchange potential

$$v_{x\sigma}^{\mathrm{SLHF}}(r) = v_{x\sigma}^{\mathrm{S}}(r) + v_{x\sigma}^{\mathrm{C}}(r), \tag{20}$$

where the radial Slater potential is given by

$$v_{x\sigma}^{\mathrm{S}}(r) = -\frac{1}{4\pi\rho_\sigma(r)}\sum_{nlm}^{\nu_\sigma}\sum_{n'l'm'}^{\nu_\sigma} s_{nlm,n'l'm'}^{\sigma}(r), \tag{21}$$

and the radial correction is given by

$$v_{x\sigma}^{\mathrm{C}}(r) = \frac{1}{4\pi\rho_\sigma(r)}\sum_{nlm}^{\nu_\sigma}\sum_{n'l'm'}^{\nu_\sigma} c_{nlm,n'l'm'}^{\sigma}(r). \tag{22}$$

In Eqs. (21) and (22),

$$s_{nlm,n'l'm'}^{\sigma}(r) = p_{nl\sigma,n'l'\sigma}(r)\sum_k \lambda_{lm,l'm'}^{k} q_{nl\sigma,n'l'\sigma}^{k}(r), \tag{23}$$

$$c_{nlm,n'l'm'}^{\sigma}(r) = p_{nl\sigma,n'l'\sigma}(r)\,\delta_{ll'}\,\delta_{mm'}\,\mu_{nl,n'l'}^{\sigma m'}, \tag{24}$$

$$p_{nl\sigma,n'l'\sigma'}(r) = \frac{R_{nl\sigma}(r)R_{n'l'\sigma'}(r)}{r^2}, \tag{25}$$

$$q_{nl\sigma,n'l'\sigma'}^{k}(r) = \int \frac{r_<^k}{r_>^{k+1}} p_{nl\sigma,n'l'\sigma'}(r')r'^2 dr', \tag{26}$$

$$\lambda_{lm,l'm'}^{k} = (-1)^{m'-m}\langle lmkm'-m|l'm'\rangle\langle l'm'km-m'|lm\rangle \times\langle l0k0|l'0\rangle\langle l'0k0|l0\rangle, \tag{27}$$

and

$$\mu_{nl,n'l'}^{\sigma m'} = \sum_{n_0l_0m_0}^{\nu_\sigma}\int p_{nl\sigma,n_0l_0\sigma}(r')\left[v_{x\sigma}^{\mathrm{SLHF}}(r')\,\delta_{n'n_0}\,\delta_{l'l_0} + \sum_k \lambda_{l_0m_0,l'm'}^{k} q_{n_0l_0\sigma,n'l'\sigma}^{k}(r')\right]r'^2 dr'. \tag{28}$$

In Eq. (27), the symbol $\langle\cdots|\cdots\rangle$ is the Clebsch-Gordan coefficient. According to the property of the Clebsch-Gordan coefficient, $k=|l-l'|, |l-l'|+1,\ldots,l+l'$ and $l+l'+k=$even.

C. Generalized pseudospectral method and optimal solution of the KS equation

In order to solve the radial KS equation, we use the generalized pseudospectral (GPS) method [26] to discretize Eq. (16). The GPS method is a kind of collocation-cardinal function method. The basic idea of this method is to approximate an exact function $f(x)$ defined on the interval $[-1,1]$ by an Nth-order polynomial $f_N(x)$ constructed by a cardinal function $g_j(x)$,

$$f(x) \simeq f_N(x) \equiv \sum_{j=0}^{N} f(x_j)g_j(x), \tag{29}$$

and ensure the approximation to be exact at the collocation point x_i, namely $f_N(x_i)\equiv f(x_i)$. This requires that the cardinal function satisfies $g_j(x_i)=\delta_{ij}$.

In the Legendre generalized pseudospectral (LGPS) method used in this work, the cardinal function $g_j(x)$ is constructed by the Nth-order Legendre polynomial $P_N(x)$ and its first derivative $\dot{P}_N(x)$

$$g_j(x) = -\frac{1}{N(N+1)P_N(x_j)}\frac{(1-x^2)\dot{P}_N(x)}{x-x_j}. \tag{30}$$

The collocation points, x_0 $(=-1)$, x_1, $x_2,\ldots,x_N$ $(=1)$, are determined by the roots of the first derivative of the Nth-order Legendre polynomial with respect to x, namely, $\dot{P}_N(x_i)=0$.

For the electronic structure calculation involving Coulomb interaction, the potential has a singularity at $r=0$ and long tail at large r. These problems can be overcome by using the LGPS method associated with an appropriate mapping technique. In this procedure, the singularity problem can be taken considerate care of by the nonuniform collocation points of the LGPS method and the long-tail problem can be suppressed efficiently by mapping the semi-infinite domain $r\in[0,\infty]$ into the finite domain $x\in[-1,1]$ with a mapping function $r=r(x)$. The mapping function is taken to be a nonlinear function given by [26]

$$r(x) = L\frac{1+x}{1-x+x_m}, \tag{31}$$

where L is a mapping parameter used to optimize calculation by adjusting distribution of the collocation points and $x_m=2L/r_{\max}$, where $r_{\max}$ is the maximum r. This method provides a very effective and efficient numerical algorithm for a high-precision solution of the Schrödinger equation and the KS equation. It has been successfully applied to the calculation of eigenvalues and eigenfunctions of atomic and molecular systems for the study of electronic structure [10,18], multiphoton processes in strong fields [31,32], and Rydberg atom spectroscopy and dynamics [33].

Making use of the mapping function (31) in the KS equation (16), we obtain a differential equation for the transformed radial wave function defined on $x\in[-1,1]$, $f(x)=R_{nl\sigma}(r(x))/\sqrt{\dot{r}(x)}$, where $\dot{r}(x)$ is the first derivative of r with respect to x. Applying the LGPS method to the new differential equation, considering boundary conditions, and following the symmetrization procedure [26], we finally achieve a symmetric matrix eigenvalue equation

$$\sum_{j=1}^{N-1}\left[-\frac{1}{2}D_{ij}+u_i\delta_{ij}\right]\chi_j=\varepsilon_{nl\sigma}\chi_i, \tag{32}$$

where

$$\chi_i=\frac{\sqrt{\dot{r}_i}}{P_N(x_i)}R_{nl\sigma}(r_i), \tag{33}$$

$$u_i=\frac{l(l+1)}{2r_i^2}+v_\sigma^{\mathrm{eff}}(r_i), \tag{34}$$

$$D_{ij}=\begin{cases}-\dfrac{2}{\dot{r}_i(x_i-x_j)^2\dot{r}_j}, & i\neq j,\\[2ex] -\dfrac{N(N+1)}{3\dot{r}_i^2(1-x_i^2)}, & i=j,\end{cases} \tag{35}$$

and $\chi_i=\chi(x_i)$, $u_i=u(x_i)$, $r_i=r(x_i)$, and $\dot{r}_i=\dot{r}(x_i)$. Solving the matrix eigenvalue equation (32), one can obtain the spin orbitals and orbital energies.

D. Multiplet excited-state energy

For a particular electron configuration, Eq. (32) is solved self-consistently to obtain a set of spin orbitals. Using these spin orbitals, a single Slater determinant for a specific electronic state is constructed and its total energy calculated. The total energy is a sum of noninteracting kinetic energy E_k, external-field energy E_{ext}, Hartree energy E_H, exchange energy E_x, and correlation energy E_c. They are evaluated by

$$\begin{aligned}E_k&=\sum_{\sigma=\alpha}^{\beta}\sum_{i=1}^{N_\sigma}w_{i\sigma}\int\varphi_{i\sigma}(\mathbf{r})\left(-\frac{\nabla^2}{2}\right)\varphi_{i\sigma}(\mathbf{r})d\mathbf{r}\\ &=\sum_{\sigma=\alpha}^{\beta}\sum_{nl}^{\nu_\sigma}w_{nl\sigma}\int R_{nl\sigma}(r)\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}\right)R_{nl\sigma}(r)dr,\end{aligned} \tag{36}$$

$$E_{ext}=\int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}=4\pi\int v_{ext}(r)\rho(r)r^2dr, \tag{37}$$

$$E_H=\frac{1}{2}\int V_H(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}=\frac{1}{2}\sum_{\Pi}\eta^k_{lm,l'm'}F^k_{nl\sigma,n'l'\sigma'}, \tag{38}$$

$$E_x=\frac{1}{2}\sum_{\sigma=\alpha}^{\beta}\int V^{\mathrm{S}}_{x\sigma}(\mathbf{r})\rho_\sigma(\mathbf{r})d\mathbf{r}=-\frac{1}{2}\sum_{\Pi}\lambda^k_{lm,l'm'}G^k_{nl\sigma,n'l'\sigma'}\delta_{\sigma\sigma'}, \tag{39}$$

and E_c is computed by using the LYP approximation [7]. In Eqs. (38) and (39),

$$\sum_{\Pi}=\sum_{\sigma,\sigma'=\alpha}^{\beta}\sum_{nlm}^{\nu_\sigma}\sum_{n'l'm'}^{\nu_{\sigma'}}\sum_{k}, \tag{40}$$

$$\eta^k_{lm,l'm'}=\langle lmk0|lm\rangle\langle l'm'k0|l'm'\rangle\langle l0k0|l0\rangle\langle l'0k0|l'0\rangle, \tag{41}$$

$$F^k_{nl\sigma,n'l'\sigma'}=\int p_{nl\sigma,nl\sigma}(r)q^k_{n'l'\sigma',n'l'\sigma'}(r)r^2dr, \tag{42}$$

and

$$G^k_{nl\sigma,n'l'\sigma'}=\int p_{nl\sigma,n'l'\sigma'}(r)q^k_{nl\sigma,n'l'\sigma'}(r)r^2dr, \tag{43}$$

where $k=0,\ 2,\ldots,2\times\min(l,l')$ due to the Clebsch-Gordan coefficient.

From Eqs. (27) and (41)–(43), if $n'l'm'\sigma'=nlm\sigma$, the terms of E_H in Eq. (38) completely cancel those of E_x in Eq. (39). This illustrates that the X-only calculation presented here is free of self-interaction.

The procedure above can only be used to calculate the energy value for a single Slater determinant. For a multiplet state that can be described completely by a single Slater determinant, this energy is just the multiplet energy. 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 [25]. According to this rule, the sum of the single-Slater-determinant energy $E(D_i)$ of determinant D_i from an electron configuration is equal to the weighted sum of the multiplet energy $E(M_j)$ of the multiplet state M_j involved in the electron configuration, namely,

$$\sum_i E(D_i)=\sum_j d_jE(M_j), \tag{44}$$

where the weight d_j is the times that the multiplet state M_j appears in all the single Slater determinants.

To show how to use this method, let us consider a two-electron configuration p^2. For this configuration, there are 15 different states and thus 15 determinants corresponding to various values of Σm_l and Σm_s. Of those, there are three determinants with $(m_{l_1}m_{s_1};m_{l_2}m_{s_2})=(1\alpha;-1\beta)$, $(-1\alpha;1\beta)$, and $(0\alpha;0\beta)$ that correspond to a particular set of $\Sigma m_l=0$ and $\Sigma m_s=0$, which are denoted by D_1, D_2, and D_3, respectively. On the other hand, there are three multiplet states ${}^1D$, ${}^3P$, and ${}^1S$ that are involved in this particular set, and each emerges once. According to Eq. (44) we have

$$E(D_1)+E(D_2)+E(D_3)=E\left({}^1D\right)+E\left({}^3P\right)+E\left({}^1S\right). \tag{45}$$

The energy terms on the left-hand side are computed by using the single Slater determinants, while the energies $E({}^1D)$ and $E({}^3P)$ on the right-hand side can also be determined by the single Slater determinants. Thus $E({}^1S)$ is calculated from Eq. (45). Similar procedures have been employed in recent excited-state calculations [18,19,34].

III. RESULTS AND DISCUSSION

A. The ground-state energy

We first calculate the total ground-state energies for the neutral atoms of $Z\leqslant 18$ using the procedure introduced in the

TABLE I. Negative values of the total ground-state energies (a.u.) for neutral atoms of $Z \leqslant 18$.

	X-only			XC	
Atoms	SLHF[a]	HF[b]	OEP[c]	SLHF[a]	HFC[d]
He	2.8617	2.8617		2.9074	2.904
Li	7.4325	7.4327	7.4325	7.4872	7.479
Be	14.5726	14.5730	14.5724	14.6686	14.667
B	24.5284	24.5291	24.5283	24.6586	24.654
C	37.6886	37.6886	37.6889	37.8522	37.845
N	54.4029	54.4009	54.4034	54.5977	54.590
O	74.8115	74.8094	74.8121	75.0798	75.067
F	99.4085	99.4093	99.4092	99.7393	99.731
Ne	128.5455	128.5471	128.5454	128.9331	128.937
Na	161.8565	161.8589	161.8566	162.2687	162.257
Mg	199.6112	199.6146	199.6116	200.0744	200.059
Al	241.8728	241.8767	241.8733	242.3726	242.356
Si	288.8501	288.8544	288.8507	289.3853	289.374
P	340.7140	340.7188	340.7150	341.2835	341.272
S	397.5018	397.5049	397.5016	398.1388	398.139
Cl	459.4770	459.4821	459.4776	460.1750	460.196
Ar	526.8118	526.8175	526.8122	527.5658	527.604

[a] Current results.
[b] Reference [35].
[c] Reference [28].
[d] References [39,40].

preceding section. Special attention is paid to the nonsymmetric states of atoms with open shells. In Table I, we present the total ground-state energies obtained from X-only calculation together with those of the HF method [35] and the optimized effective potential (OEP) method [28] for comparison. Although the spherically averaged electronic density is used in the calculation, the present SLHF results are in excellent agreement with HF values even for the nonsymmetric states of the open-shell atoms. The maximum deviation to HF results in energy is about 0.0037%. It occurs at a highly nonsymmetric state of N, where the OEP energy also has the maximum deviation with respect to the HF value. The discrepancies of SLHF energies to OEP results are less than 0.0009%, a negligibly small number. Thus SLHF has practically the same accuracy as OEP and is very close to HF.

To examine and appraise the SLHF exchange potential we give, in Table II, the exchange energies for the ground states of neutral atoms of $Z \leqslant 18$. We also list in this table the results of the HF method [6] and Becke's gradient-corrected density-functional exchange-energy approximation (BX) [36]. The overall agreement of our calculated exchange energies with the results of HF and BX is quite good. This indicates that the SLHF exchange potential has behaviors as good as those of the HF method.

Orbital energy is a measurement of the basic properties of electron orbital. The highest-occupied-orbital energy is even essential since it is related to the ionization potential in independent particle calculation such as the DFT calculation.

TABLE II. Negative values of the exchange energies (a.u.) for the ground states of neutral atoms of $Z \leqslant 18$.

Atoms	SLHF[a]	HF[b]	BX[c]
He	1.026	1.026	1.025
Li	1.779	1.781	1.775
Be	2.663	2.667	2.658
B	3.744	3.744	3.728
C	5.048	5.045	5.032
N	6.599	6.596	6.589
O	8.181	8.174	8.169
F	10.005	10.00	10.02
Ne	12.112	12.11	12.14
Na	14.023	14.02	14.03
Mg	15.986	15.99	16.00
Al	18.058	18.07	18.06
Si	20.262	20.28	20.27
P	22.618	22.64	22.62
S	24.983	25.00	24.98
Cl	27.490	27.51	27.49
Ar	30.155	30.19	30.15

[a] Current results.
[b] Reference [6].
[c] Reference [36].

TABLE III. Negative values of the highest-occupied-orbital energies (a.u.) for neutral atoms of $Z \leqslant 18$.

Atoms	SLHF[a]	HF[b]	OEP[c]	Expt.[d]
He	0.9179	0.9180		0.904
Li	0.1963	0.1963	0.1963	0.198
Be	0.3091	0.3093	0.3093	0.343
B	0.3074	0.3099	0.3097	0.305
C	0.4250	0.4333	0.4353	0.414
N	0.5707	0.5676	0.5712	0.534
O	0.5200	0.6319	0.5077	0.501
F	0.6578	0.7300	0.6735	0.640
Ne	0.8495	0.8504	0.8507	0.793
Na	0.1821	0.1821	0.1821	0.189
Mg	0.2526	0.2531	0.2531	0.281
Al	0.2141	0.2100		0.217
Si	0.2894	0.2971		0.300
P	0.3911	0.3917		0.385
S	0.3719	0.4374		0.381
Cl	0.4629	0.5064		0.477
Ar	0.5902	0.5910	0.5908	0.579

[a] Current results.
[b] Reference [35].
[c] Reference [27].
[d] References [37,38].

In Table III, we present the highest-occupied-orbital energies obtained from the X-only SLHF calculation for the ground states of atoms with $Z \leqslant 18$ along with experimental ionization potentials [37,38], HF results [35], and the results from spin-dependent OEP [27]. It is shown that our results are very close to OEP results. Compared to the experimental results, our results are even more accurate than HF results.

One of the most touchy effects in the DFT calculation is the correlation effect. This effect is considered through the correlation energy. So far, all the correlation functionals used in the DFT calculation are developed for the ground state. In this work, we choose the widely used LYP correlation energy functional [7] to estimate the electron correlation effect. In Table I, we present the total ground-state energies from the XC calculation for atoms with $Z \leqslant 18$. For comparison, we also list in Table I the total energies that are obtained from the sum of HF energies [39] and correlation energies [40] (HFC). It is shown that inclusion of the correlation effect does lead to a significant improvement in the ground-state energies compared to the HFC results. For the total energy, our results agree very well with HFC results. For larger atoms ($Z > 8$), deviations of our results to HFC results are less than 0.008%. For smaller atoms ($Z \leqslant 8$), our total energies are a little bit more negative than HFC results. The maximum discrepancy is about 0.12%. The larger deviations for the smaller atoms are caused by the overestimated correlation energies computed with LYP correlation energy functional [7].

B. Singly excited state

The main purpose of this paper is to develop a procedure for the excited-state calculation of an atomic system, particularly for multiply excited states such as triply excited states. Before performing a multiply excited-state calculation, we would like to report some results for singly and doubly excited states of atomic systems so as to calibrate the accuracy of the approach presented in this paper.

As has been shown above, the total ground-state energies from an X-only calculation are quite accurate and comparable to HF results. Since the SLHF exchange potential is free of self-interactions, dependent on symmetries of electronic state, and has good long-range behaviors, it is expected to work well in the excited-state calculation of atomic system. In Table IV, we list the total energies from the XC calculation for singly excited states $1sns\,{}^3S$ and ${}^1S$ ($n=1-16$) of He together with the total energies of the complex rotation approach (CRA) [41] and the WF method (WF-I) [18]. According to the LYP correlation energy functional [7], the spin-dependent correlation interaction only occurs between electrons with different spins. For the triplet S states in Table IV, correlation energies are zero and total energies from the X-only calculation are the same as those from the XC calculation. This may tempt one to conclude that the correlation energies for these states are underestimated by the LYP approximation, particularly for low excited states where the correlation interaction is expected to be larger than highly excited states. However, for the $1s2s\,{}^3S$ state, our result, 2.173 90 a.u., is only 0.06% higher than the CRA result, 2.175 23 a.u., and 0.07% higher than the WF-I result, 2.175 45 a.u., indicating that our calculation is accurate and the correlation interaction in the triplet S states is indeed small and plays an insignificant role. For the $1s2s\,{}^1S$ state, the deviation of our result with respect to the CRA result is 0.06%, illustrating that the calculation for triplet S states is as precise as that for singlet S states. For a highly excited Rydberg state with large n, the agreement of our results with those of a more sophisticated CRA calculation becomes excellent for both multiplet states. This signifies that the SLHF exchange potential has very similar asymptotic long-range behaviors to that of CRA because the electronic structure of the highly excited Rydberg state is dominated by the asymptotic long-range Coulomb potential arising from exchange potential. For low excited states with small n, our results are slightly higher than those of CRA because of an underestimation of correlation energy. In all cases for both multiplet states, the deviations are less than 0.07%. This demonstrates that the calculation with the SLHF exchange potential for singly excited states is comparable to the more sophisticated *ab initio* calculation.

TABLE IV. Negative values of the total energies (a.u.) for singly excited states of He. The SLHF results are obtained from the XC calculation.

	${}^3S$			${}^1S$	
Configuration	SLHF[a]	CRA[b]	WF-I[c]	SLHF[a]	CRA[b]
$1s2s$	2.17390	2.17523	2.17545	2.14471	2.14597
$1s3s$	2.06827	2.06869	2.06890	2.06226	2.06127
$1s4s$	2.03631	2.03651	2.03671	2.03423	2.03359
$1s5s$	2.02250	2.02262	2.02264	2.02157	2.02118
$1s6s$	2.01530	2.01538	2.01539	2.01482	2.01456
$1s7s$	2.01108	2.01113	2.01115	2.01080	2.01063
$1s8s$	2.00839	2.00843	2.00845	2.00821	2.00809
$1s9s$	2.00657	2.00660	2.00660	2.00646	2.00637
$1s10s$	2.00529	2.00531	2.00531	2.00521	2.00514
$1s11s$	2.00435	2.00431	2.00431	2.00429	2.00424
$1s12s$	2.00364	2.00365	2.00365	2.00359	2.00355
$1s13s$	2.00309	2.00310	2.00310	2.00306	2.00302
$1s14s$	2.00265	2.00266	2.00266	2.00263	2.00260
$1s15s$	2.00230	2.00231	2.00231	2.00228	2.00226
$1s16s$	2.00202	——	2.00203	2.00200	2.00199

[a] Current results.
[b] Reference [41].
[c] Reference [18].

It should be mentioned that many quantum mechanical calculations confront a self-consistent convergence problem for highly excited states with large n [42]. Even the WF method often encounters the same problem [19]. However, in our calculation, the advantages of the LGPS procedure over the Coulomb potential enable us to obtain converged results for all states by using the same number of grid points. It is straightforward to extend the calculation to even higher states, reflecting the effectiveness of the SLHF exchange potential for the excited-state calculation.

TABLE V. Negative values of the total energies (a.u.) obtained from the XC calculation for singly excited states of He-like ions.

	Z							
States	3	4	5	6	7	8	9	10
$1s2s\,^3S$	5.1089	9.2951	14.7317	21.4185	29.3554	38.5423	48.9792	60.6662
	5.1043[a]	9.2886[a]	14.7240[a]	21.4100[a]				
$1s2s\,^1S$	5.0463	9.1969	14.5959	21.2437	29.1406	38.2867	48.6826	60.3278
	5.0422[a]	9.1813[a]	14.5710[a]	21.2115[a]				
$1s2p\,^3P$	5.0241	9.1708	14.5686	21.2170	29.1157	38.2645	48.6634	60.3124
	5.0210[a]	9.1647[a]	14.5605[a]	21.2075[a]				
$1s2p\,^1P$	5.0138	9.1394	14.5118	21.1321	29.0013	38.1196	48.4873	60.1045
	4.9809[a]	9.0886[a]	14.4478[a]	21.0587[a]				

[a]TDM results [43].

To check the feasibility of the SLHF exchange potential for atomic ions, we also apply it to the calculation of He-like ions ($Z=3-10$). The total energies obtained from the XC calculation are shown in Table V together with the results of the truncated diagonalization method (TDM) [43]. It is shown that for all the data in the table, our results are close to the results of TDM. The deviations for the triplet *S* and *P* states (where the correlation energies are zero) are less than 0.09%, while for the singlet *S* and *P* states, the discrepancies are no more than 0.66% though a little bit larger. It demonstrates that the SLHF exchange potential together with the LYP correlation potential is reasonably accurate for the calculation of atomic ions. On the other hand, for all the data in the table, our results are a little bit more negative than those of TDM. This again hints that the LYP energy functional is overestimated to the correlation energies for smaller atoms as has already been pointed out in the calculations of neutral atoms.

TABLE VI. Negative values of the total energies (a.u.) for singly excited states of Li.

	X-only		XC		Others
States	SLHF[a]	WF-I[b]	SLHF[a]	WF-I[b]	CIH[c]
$1s^2 3s\,^2S$	7.31003	7.30966 7.31021[d]	7.35953	7.35773	7.35410
$1s^2 4s\,^2S$	7.27478	7.27466	7.32316	7.31978	7.31853
$1s^2 5s\,^2S$	7.25991	7.25996	7.30785	7.30466	7.30355
$1s^2 6s\,^2S$	7.25227		7.30000		
$1s^2 7s\,^2S$	7.24783		7.29546		
$1s^2 8s\,^2S$	7.24502		7.29259		
$1s^2 9s\,^2S$	7.24313		7.29067		
$1s^2 10s\,^2S$	7.24180		7.28932		
$1s^2 2p\,^2P$	7.36474	7.36486 7.36507[d]	7.41683	7.41204	7.41016
$1s^2 3p\,^2P$	7.29296	7.29295 7.29319[d]	7.34236	7.33862	7.33716
$1s^2 4p\,^2P$	7.26804	7.26859	7.31646	7.31262	7.31190
$1s^2 5p\,^2P$	7.25658	7.25756	7.30457	7.30053	7.30030
$1s^2 6p\,^2P$	7.25038		7.29816		
$1s^2 7p\,^2P$	7.24665		7.29432		
$1s^2 8p\,^2P$	7.24424		7.29184		
$1s^2 9p\,^2P$	7.24258		7.29013		
$1s^2 10p\,^2P$	7.24140		7.28893		

[a]Current results.
[b]Reference [18].
[c]Reference [45].
[d]HF results [44].

TABLE VII. Negative values of the total energies (a.u.) for doubly excited states $ns^2\,^1S$ ($n=2-20$) of He.

	X-only		XC		
States	SLHF[a]	WF-II[b]	SLHF[a]	WF-II[b]	WF-I[c]
$2s^2\,^1S$	0.71968	0.7197	0.73473	0.7333	0.76637
$3s^2\,^1S$	0.31996	0.3200	0.33061	0.3265	0.34578
$4s^2\,^1S$	0.17995	0.1800	0.18814	0.1838	0.19659
$5s^2\,^1S$	0.11511	0.1152	0.12129	0.1177	0.12754
$6s^2\,^1S$	0.07991	0.0800	0.08460	0.0818	0.08808
$7s^2\,^1S$	0.05869	0.0588	0.06234	0.0601	0.06524
$8s^2\,^1S$	0.04492		0.04783		0.04855
$9s^2\,^1S$	0.03548		0.03784		0.03889
$10s^2\,^1S$	0.02873		0.03068		0.03084
$11s^2\,^1S$	0.02374		0.02538		0.02503
$12s^2\,^1S$	0.01994		0.02134		0.02121
$13s^2\,^1S$	0.01698		0.01819		0.01811
$14s^2\,^1S$	0.01464		0.01569		0.01555
$15s^2\,^1S$	0.01275		0.01367		0.01348
$16s^2\,^1S$	0.01120		0.01202		0.01176
$17s^2\,^1S$	0.00992		0.01064		0.01132
$18s^2\,^1S$	0.00885		0.00949		
$19s^2\,^1S$	0.00794		0.00852		
$20s^2\,^1S$	0.00716		0.00769		

[a]Current results.
[b]Reference [19].
[c]Reference [18].

TABLE VIII. Negative values of the total energies (a.u.) for doubly excited states $n'snp\ ^3P$ $(n'=2–3, n=n'–10)$ of He.

States	X-only WF-II[b]	XC		Other results	
		SLHF[a]	WF-I[c]	CCR[d]	RMSP[e]
$2s2p\ ^3P$	0.7537	0.75354	0.76770 0.7682[b]	0.76049	0.76086
$2s3p\ ^3P$	0.5713	0.57193	0.58253 0.5804[b]	0.58467	0.58476
$2s4p\ ^3P$		0.53757	0.54558	0.54284	0.54281
$2s5p\ ^3P$		0.52295	0.53121	0.52571	0.52475
$2s6p\ ^3P$		0.51553	0.52367	0.51711	
$2s7p\ ^3P$		0.51119	0.51924	0.51219	
$2s8p\ ^3P$		0.50847		0.50910	
$2s9p\ ^3P$		0.50663			
$2s10p\ ^3P$		0.50533			
$3s3p\ ^3P$	0.3417	0.34167	0.34918 0.3486[b]	0.35038	0.35082
$3s4p\ ^3P$		0.27156	0.27365	0.27948	0.27980
$3s5p\ ^3P$		0.24826		0.25516	0.25509
$3s6p\ ^3P$		0.23939		0.24338	0.24274
$3s7p\ ^3P$		0.23442		0.23688	
$3s8p\ ^3P$		0.23133			
$3s9p\ ^3P$		0.22929			
$3s10p\ ^3P$		0.22787			

[a] Current results.
[b] WF-II results [19].
[c] WF-I results [18].
[d] Reference [47].
[e] Reference [48].

TABLE IX. Negative values of the total energies (a.u.) for doubly excited states $n'snp\ ^1P$ $(n'=1–2, n=n'–10)$ of He.

States	X-only SLHF[a]	XC SLHF[a]	Other theory	Expt. results[e]
$2s2p\ ^1P$	0.65039 0.6456[b]	0.69699 0.6588[b]	0.69275[c]	
$2s3p\ ^1P$	0.56650	0.57407	0.56384[c]	
$2s4p\ ^1P$	0.53568	0.53860	0.53418[c]	
$2s5p\ ^1P$	0.52225	0.52349		
$2s6p\ ^1P$	0.51519	0.51587		
$2s7p\ ^1P$	0.51104	0.51134		
$2s8p\ ^1P$	0.50836	0.50852		
$2s9p\ ^1P$	0.50656	0.50665		
$2s10p\ ^1P$	0.50528	0.50533		
$3s3p\ ^1P$	0.29101	0.33001	0.33566[d]	0.33330
$3s4p\ ^1P$	0.26380	0.27009	0.27110[d]	0.27014
$3s5p\ ^1P$	0.24730	0.25019	0.25058[d]	0.25020
$3s6p\ ^1P$	0.23897	0.24053	0.24074[d]	0.24060
$3s7p\ ^1P$	0.23417	0.23510	0.23574[d]	0.23530
$3s8p\ ^1P$	0.23119	0.23178	0.23260[d]	0.23184
$3s9p\ ^1P$	0.22919	0.22956		
$3s10p\ ^1P$	0.22780	0.22807		

[a] Current results.
[b] WF-II results [19].
[c] RMSP results [48].
[d] FF results [49].
[e] Experimental results [50].

In Table VI, we present the total energies obtained from both the X-only calculation and the XC calculation for singly excited states $1s^2ns\ ^2S$ $(n=3–10)$ and $1s^2np\ ^2P$ $(n=2–10)$ of Li. For comparison, we also list the total energies of the WF method (WF-I) [18], the HF method [44], and the configuration-interaction Hylleraas method (CIH) [45]. The deviations of X-only results to HF results are 0.0025%, 0.0045%, and 0.0032% for $1s^23s\ ^2S$, $1s^22p\ ^2P$, and $1s^23p\ ^2P$, respectively. This illustrates that our X-only calculation is quite accurate, almost as accurate as the HF method. The deviations of X-only results to WF-I results range from 0.0051% to 0.0007% for $1s^2ns\ ^2S$ $(n=3–5)$ states and from 0.0135% to 0.0001% for $1s^2np\ ^2P$ $(n=2–5)$ states. For the total energies obtained from the XC calculation, our results are only a little bit more negative than the WF results and CIH results due to the overestimation to the correlation energies by the LYP correlation energy functional. Nevertheless, the maximum discrepancy of our results to the CIH results is no more than 0.0738% for $1s^2ns\ ^2S$ $(n=3–5)$ states and 0.0900% for $1s^2np\ ^2P$ $(n=2–5)$ states, demonstrating the accuracy of our calculation.

C. Doubly excited state

The calculation of doubly excited state is more challenging. For doubly excited states, the results of the HF method are rare. To check the applicability and calibrate the accuracy of the SLHF exchange potential in the doubly excited-state calculation, we will compare our X-only results with other X-only DFT results available in the literature. In Tables VII–X, we present the total energies obtained from both the X-only calculation and the XC calculation for doubly excited states $ns^2\ ^1S$ $(n=2–20)$, $n'snp\ ^3P$ $(n'=2–3,\ n=n'–10)$, $n'snp\ ^1P$ $(n'=2–3,\ n=n'–10)$, and $np^2\ ^1D$ $(n=2–20)$, of He, respectively. In these tables, we also list the available experimental results and other theoretical results for comparison.

In Table VII, we report the total energies for doubly excited Rydberg states $ns^2\ ^1S$ $(n'=2–20)$. For the X-only calculation, our results are in very good agreement with those of the WF method (WF-II) [19]. For the XC calculation, our results are a little bit more negative than those of WF-II and less negative than those from another WF calculation (WF-I) [18]. Obviously, the deviations are caused by correlation energies since the correlation energy functionals used in these calculations are different from one another. A Wigner-type parametrized correlation energy functional [46] was used in the WF-II, a spin-independent LYP correlation energy functional was used in the WF-I, and a spin-dependent LYP cor-

TABLE X. Negative values of the total energies (a.u.) for doubly excited states $np^2\,{}^1D$ $(n=2-20)$ of He.

	X-only		XC		
States	SLHF[a]	WF-II[b]	SLHF[a]	WF-II[b]	WF-I[c]
$2p^2\,{}^1D$	0.66868	0.6679	0.69626	0.6823	0.69272
$3p^2\,{}^1D$	0.30934	0.3091	0.32360	0.3160	0.31540
$4p^2\,{}^1D$	0.17606	0.1760	0.18565	0.1800	0.18095
$5p^2\,{}^1D$	0.11326	0.1132	0.12005	0.1158	0.11610
$6p^2\,{}^1D$	0.07886	0.0788	0.08386	0.0807	0.08115
$7p^2\,{}^1D$	0.05803	0.0580	0.06183	0.0593	0.05980
$8p^2\,{}^1D$	0.04447		0.04745		0.04565
$9p^2\,{}^1D$	0.03516		0.03756		0.03604
$10p^2\,{}^1D$	0.02849		0.03046		0.02920
$11p^2\,{}^1D$	0.02356		0.02520		0.02414
$12p^2\,{}^1D$	0.01980		0.02119		0.02028
$13p^2\,{}^1D$	0.01687		0.01807		0.01728
$14p^2\,{}^1D$	0.01455		0.01559		0.01490
$15p^2\,{}^1D$	0.01268		0.01358		0.01297
$16p^2\,{}^1D$	0.01114		0.01194		0.01140
$17p^2\,{}^1D$	0.00987		0.01058		0.01010
$18p^2\,{}^1D$	0.00881		0.00944		
$19p^2\,{}^1D$	0.00790		0.00848		
$20p^2\,{}^1D$	0.00713		0.00765		

[a] Current results.
[b] Reference [19].
[c] Reference [18].

relation energy functional is used in our calculation. Because both the Wigner-type correlation energy functional and the LYP correlation energy functional are designed basically for the ground-state calculation, all the calculations for the excited states by using these functionals are only rough estimations to the correlation energies.

In Table VIII, we present the results of doubly excited states $n'snp\,{}^3P$ $(n'=2-3,\ n=n'-10)$ of He. As has already been mentioned, the correlation energies obtained from the LYP correlation energy functional are zero for electrons with the same spin in the spin-dependent calculation. Thus the total energies from the X-only calculation are the same as those from the XC calculation. For the X-only calculation, our results agree well with the WF-II results. For the XC calculation, our results are close to those of the WF-I, WF-II, the complex-coordinate rotation (CCR) methods [47], and the R-matrix method with saddle-point technique (RMSP) [48]. For $2snp\,{}^3P$ $(n=2-8)$ states, the deviations of our results to the results of the CCR method are less than 1.0% with an exception of state $2s3p\,{}^3P$, for which the deviation is 2.2%. For $3snp\,{}^3P$ $(n=3-7)$ states, the errors are a little bit larger, but no more than 2.8%. The larger deviations may again be induced by the underestimated (zero) correlation energies by the LYP correlation energy functional.

In Table IX we show the total energies of doubly excited states $n'snp\,{}^1P$ $(n'=2-3,\ n=n'-10)$ of He. For the X-only calculation, our result for $2s2p\,{}^1P$ is 0.74% lower than the WF-II result. For the XC calculation, our result for this state is better than the WF-II result compared to the result of the RMSP [48]. The deviations of our results to the RMSP results are less than 1.8% for states $2snp\,{}^1P$ $(n=2-4)$. For

TABLE XI. Negative values of the total energies (a.u.) for triply excited states of Li-like ions $(Z=3-10)$.

	Li			Be$^+$			B^{2+}	
States	SLHF[a]	TDM[b]	MSPCR[c]	SLHF[a]	TDM[b]	MSPCR[d]	SLHF[a]	TDM[b]
$2s2p^2\,{}^4P$	2.2209	2.2331(0.55)	2.2394(0.83)	4.4163	4.4248(0.19)	4.4361(0.45)	7.3617	7.3671(0.07)
$2s2p^2\,{}^2D$	2.1517	2.1480(0.17)	2.1582(0.30)	4.3052	4.2885(0.39)	4.3073(0.05)	7.2062	7.1792(0.38)
$2s2p^2\,{}^2S$	2.0821	2.0827(0.03)	2.0950(0.62)	4.2038	4.1853(0.44)	4.2085(0.11)	7.0731	7.0415(0.45)
$2s2p^2\,{}^2P$	2.0960	2.0675(1.38)	2.0788(0.83)	4.2184	4.1711(1.13)	4.1900(0.68)	7.0861	7.0245(0.88)
$2p^3\,{}^4S$	2.0762	2.0953(0.91)		4.2085	4.2221(0.32)		7.0910	7.1000(0.13)
$2p^3\,{}^2D$	2.0606	2.0700(0.45)	2.0790(0.89)	4.1704	4.1655(0.12)	4.1832(0.31)	7.0275	7.0108(0.24)
$2p^3\,{}^2P$	2.0159	2.0035(0.62)	2.0124(0.17)	4.1046	4.0542(1.24)	4.0755(0.71)	6.9405	6.8611(1.16)

	C^{3+}			N^{4+}	O^{5+}	F^{6+}	Ne^{7+}
States	SLHF[a]	TDM[b]	MSPCR[d]	SLHF[a]	SLHF[a]	SLHF[a]	SLHF[a]
$2s2p^2\,{}^4P$	11.0571	11.0601(0.03)	11.0777(0.19)	15.5025	20.6978	26.6432	33.3385
$2s2p^2\,{}^2D$	10.8557	10.8207(0.32)	10.8509(0.04)	15.2541	20.4017	26.2989	32.9457
$2s2p^2\,{}^2S$	10.6908	10.6494(0.39)	10.6860(0.04)	15.0574	20.1734	26.0389	32.6540
$2s2p^2\,{}^2P$	10.7010	10.6283(0.68)	10.6597(0.39)	15.0640	20.1758	26.0367	32.6469
$2p^3\,{}^4S$	10.7236	10.7289(0.05)		15.1063	20.2390	26.1218	32.7545
$2p^3\,{}^2D$	10.6329	10.6068(0.25)	10.6382(0.05)	14.9872	20.0909	25.9440	32.5468
$2p^3\,{}^2P$	10.5249	10.4195(1.01)	10.4574(0.65)	14.8582	19.9407	25.7728	32.3544

[a] Current results.
[b] Reference [43].
[c] Reference [52].
[d] Reference [51].

TABLE XII. Autoionization channel energies (eV) for the triply excited resonance states of Li-like ions.

Initial states	Final states	Li				Be$^+$			
		SLHF[a]	TDM[b]	MSPCR[c]	Expt.[d]	SLHF[a]	TDM[b]	MSPCR[e]	Expt.[d]
$2s2p^2\,^4P$	$1s2p\,^3P$	76.280	75.864(0.55)	75.879(0.53)	75.88±0.1(0.53)	129.378	128.980(0.31)	128.992(0.30)	128.9±0.2(0.37)
$2s2p^2\,^2D$	$1s2s\,^3S$	80.470	80.444(0.03)	80.349(0.15)	80.26±0.1(0.26)	135.783	136.061(0.20)	135.839(0.04)	135.8±0.2(0.01)
	$1s2s\,^1S$	78.767	78.755(0.02)	78.447(0.41)		133.111	133.140(0.02)	132.783(0.25)	132.8±0.2(0.23)
	$1s2p\,^3P$	78.163	78.178(0.02)	78.089(0.09)	78.13±0.1(0.04)	132.401	132.688(0.22)	132.514(0.09)	132.4±0.2(0.00)
	$1s2p\,^1P$	77.882	77.086(1.03)	77.153(0.94)		131.546	130.618(0.71)	130.766(0.60)	
$2s2p^2\,^2S$	$1s2s\,^3S$	82.364	82.220(0.18)	82.067(0.36)	82.06±0.1(0.37)	138.543	138.869(0.23)	138.532(0.01)	138.5±0.3(0.03)
	$1s2s\,^1S$	80.661	80.532(0.16)	80.165(0.62)	80.26±0.1(0.50)	135.870	135.948(0.06)	135.477(0.29)	135.4±0.3(0.35)
	$1s2p\,^3P$	80.057	79.955(0.13)	79.807(0.31)	*79.9±0.1(0.20)	135.160	135.496(0.25)	135.207(0.03)	
	$1s2p\,^1P$	79.776	78.862(1.16)	78.871(1.15)	*78.7±0.2(1.37)	134.306	133.426(0.66)	133.460(0.63)	
$2s2p^2\,^2P$	$1s2p\,^3P$	79.678	80.369(0.86)	80.250(0.71)	80.26±0.1(0.73)	134.763	135.884(0.82)	135.660(0.66)	135.8±0.2(0.76)
	$1s2p\,^1P$	79.398	79.278(0.15)	79.314(0.11)	79.30±0.1(0.12)	133.908	133.813(0.07)	133.913(0.00)	134.0±0.2(0.07)
$2p^3\,^2D$	$1s2p\,^3P$	80.642	80.301(0.42)	80.244(0.50)	80.26±0.1(0.48)	136.069	136.036(0.02)	135.879(0.14)	135.8±0.2(0.20)
	$1s2p\,^1P$	80.361	79.210(1.45)	79.308(1.33)	79.30±0.1(1.34)	135.214	133.965(0.93)	134.132(0.81)	134.0±0.2(0.91)
$2p^3\,^2P$	$1s2s\,^3S$	84.165	84.378(0.25)	84.315(0.18)		141.242	142.436(0.84)	142.166(0.65)	142.4±0.3(0.81)
	$1s2s\,^1S$	82.462	82.688(0.27)	82.413(0.06)		138.570	139.517(0.68)	139.110(0.39)	
	$1s2p\,^3P$	81.858	82.111(0.31)	82.055(0.24)	82.06±0.1(0.25)	137.859	139.065(0.87)	138.841(0.71)	138.8±0.2(0.68)
	$1s2p\,^1P$	81.578	81.020(0.69)	81.120(0.56)	*81.2±0.2(0.47)	137.005	136.994(0.01)	137.094(0.06)	137.0±0.3(0.00)

Initial states	Final states	B^{2+}		C^{3+}		N^{4+}	O^{5+}	F^{6+}			Ne^{7+}
		SLHF[a]	TDM[b]	SLHF[a]	TDM[b]	SLHF[a]	SLHF[a]	SLHF[a]	HSCC[f]	Expt.[g]	SLHF[a]
$2s2p^2\,^4P$	$1s2p\,^3P$	196.111	195.743(0.19)	276.467	276.126(0.12)	370.437	478.018	599.205	599.29(0.01)	599.0±0.7(0.03)	734.003
$2s2p^2\,^2D$	$1s2s\,^3S$	204.781	205.306(0.26)	287.431	288.153(0.25)	383.719	493.635	617.167	618.39(0.20)	619.1±0.8(0.31)	754.319
	$1s2s\,^1S$	201.086	201.141(0.03)	282.674	282.751(0.03)	377.874	486.679	609.096	609.35(0.04)	609.4±0.5(0.05)	745.111
	$1s2p\,^3P$	200.343	200.856(0.26)	281.948	282.642(0.25)	377.196	486.075	608.574	609.74(0.19)	609.4±0.5(0.14)	744.692
	$1s2p\,^1P$	198.797	197.791(0.51)	279.637	278.592(0.38)	374.083	482.132	603.782			739.034
$2s2p^2\,^2S$	$1s2s\,^3S$	208.403	209.053(0.31)	291.918	292.812(0.31)	389.071	499.847	624.242	625.73(0.24)	625.4±0.5(0.19)	762.257
	$1s2s\,^1S$	204.707	204.888(0.09)	287.161	287.410(0.09)	383.226	492.892	616.171	617.08(0.15)	616.7±0.5(0.09)	753.048
	$1s2p\,^3P$	203.965	204.603(0.31)	286.435	287.301(0.30)	382.549	492.288	615.649	617.47(0.29)	616.7±0.5(0.17)	752.629
	$1s2p\,^1P$	202.419	201.538(0.44)	284.124	283.251(0.31)	379.436	488.345	610.857			746.972
$2s2p^2\,^2P$	$1s2p\,^3P$	203.611	205.067(0.71)	286.157	287.877(0.60)	382.369	492.222	615.709	618.11(0.39)	619.1±0.8(0.55)	752.823
	$1s2p\,^1P$	202.065	202.000(0.03)	283.847	283.828(0.01)	379.256	488.280	610.917	611.73(0.13)	611.9±0.6(0.16)	747.165
$2p^3\,^2D$	$1s2p\,^3P$	205.205	205.439(0.11)	288.010	288.462(0.16)	384.459	494.533	618.231	619.04(0.13)	619.1±0.8(0.14)	755.546
	$1s2p\,^1P$	203.660	202.373(0.64)	285.700	284.413(0.45)	381.346	490.590	613.439	613.60(0.03)	613.6±0.6(0.03)	749.889
$2p^3\,^2P$	$1s2s\,^3S$	212.011	213.962(0.91)	296.432	299.069(0.88)	394.492	506.179	631.483			770.409
	$1s2s\,^1S$	208.316	209.799(0.71)	291.676	293.668(0.68)	388.647	499.224	623.412			761.201
	$1s2p\,^3P$	207.573	209.513(0.93)	290.949	293.559(0.89)	387.969	498.620	622.890	627.12(0.67)	627.1±0.5(0.67)	760.782
	$1s2p\,^1P$	206.027	206.446(0.20)	288.639	289.510(0.30)	384.856	494.677	618.098			755.125

[a] Current results.
[b] Reference [43].
[c] Reference [52].
[d] Experimental results [53,52].
[e] Reference [51].
[f] Reference [54].
[g] Experimental results [54].

$3snp\ ^1P$ ($n=3-8$) states, the discrepancies of our results are less than 1.7% with respect to the results of the Feshbach formalism approach (FF) [49] and less than 1.0% with respect to the experimental results [50], demonstrating the accuracy of our excited-state calculation.

In Table X, we report the total energies of doubly excited states $np^2\ ^1D$ ($n=2-10$) of He. It is shown again that X-only results are in very good agreement with those of WF-II [19] and XC results are close to those of WF-I [18].

D. Triply excited states

For the DFT calculation, triply excited states are really a trial to both the exchange potential and the correlation potential because of possible high nonsymmetric atomic structures. Even for sophisticated *ab initio* methods, it is an ordeal to accurately calculate the electronic structures of triply excited states. In this section, we present total energies and Auger electron energies from our calculation for triply excited resonance states of Li-like ions. For these resonance states and Auger processes, there are neither HF results nor DFT results to compare to. We will compare our results to other theoretical results and experimental data. To our knowledge, this is the first time that the triply excited resonance states of Li-like ions have been calculated using the DFT method.

In Table XI, we present the total energies obtained from the XC calculation for triply excited resonance states of Li-like ions ($Z=3-10$). Also given in this table are the theoretical results of the truncated diagonalization method (TDM) [43] and the multichannel saddle-point complex-rotation (MSPCR) method [51,52]. The numbers in the parentheses denote the absolute percentage deviations of our results with respect to the data followed by these numbers. It is shown that our results are in very good agreement with those of MSPCR. The absolute deviations are less than 0.95%. Apart from $2s2p^2\ ^2P$ and $2p^3\ ^2P$ states, the discrepancies of the results of the TDM are less than 0.91%. For $2s2p^2\ ^2P$ and $2p^3\ ^2P$ states, the deviations are a little bit larger, but no more than 1.38%. This demonstrates that our calculations for triply excited states are quite accurate. We noticed that for $2s2p^2\ ^2P$ and $2p^3\ ^2P$ states, our results are more negative than other theoretical results, which may be caused by the overestimations of correlation energy to these states.

One of the most important processes from the highly triply excited resonance states of Li-like ions is Auger electron emission via autoionization, leaving states of He-like ions [53,54]. The calculation of the Auger electron spectroscopy involves the total energies of the triply excited resonance states of Li-like ions given in Table XI and the total energies of the singly excited states of He-like ions listed in Table V. In Table XII, we report the calculated Auger electron energies for the triply excited resonances of Li-like ions. To examine the calculation precision for triply excited states, we also list, in Table XII, the theoretical results of the TDM [43], MSPCR [51,52], and hyperspherical close-coupling (HSCC) methods [54], as well as the experimental results [53,54]. Again, the numbers in the parentheses denote the absolute percentage deviations of our results with respect to the data followed by the numbers. It is shown that apart from the processes related to the $1s2p\ ^1P$ state in neutral Li the discrepancies of our results with respect to both the experimental results and other theoretical results are less than 0.95%. Even for the processes involved in the $1s2p\ ^1P$ state in neutral Li, the deviations are no more than 1.5%. This illustrates that our calculation of the triply excited states is quite accurate and the proposed approach with the SLHF exchange potential is efficient and effective to the multiply excited-state calculation.

In summary, based on the spin-dependent localized Hartree-Fock density functional method and Slater's diagonal sum rule, we present an approach for the calculation of highly and multiply excited states of atomic systems. In this approach, the KS exchange potential is replaced by an exact nonvariational SLHF exchange potential. The SLHF exchange potential qualifies for the calculation of the excited state because it provides a potential with free self-interaction, the correct long-range behavior, and the symmetry dependence of an atomic state. The procedure has been applied to the calculation of singly, doubly, and triply excited Rydberg states of He- and Li-like ions. The generalized pseudospectral method with nonuniform grids is used to discretize the spatial coordinates and to optimize the solutions of the KS equation to obtain accurate spin orbitals and orbital energies for both the ground state and excited states. X-only results are in very good agreement with HF results and X-only WF results, demonstrating that the proposed procedure is very accurate for the calculations of highly and multiply atomic excited states. The correlation effects are considered by incorporating the LYP correlation potential and the energy functional into calculation. The total energies from the XC calculation are close to the available sophisticated *ab initio* theoretical results and experimental data. The maximum discrepancy of our calculated energies to the available experimental results is less than 1.0%, illustrating that the SLHF exchange potential combined with the LYP correlation potential is satisfactory for the excited-state calculation of atomic systems. Thus the procedure presented in this paper provides a simple and computationally efficient scheme for the accurate calculation of highly and multiply excited Rydberg states within the DFT.

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