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

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A spin-dependent localized Hartree-Fock density-functional approach is presented for the efficient and accurate treatment of inner-shell excited states of atomic systems. The approach is applied to the calculation of the total and excitation energies of inner-shell excited states of several closed-shell atomic systems: Be, B^+, Ne, and Mg. The predicted results are in overall good agreement with available experimental and other *ab initio* theoretical data. In addition, results for highly excited inner-shell states are presented.

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Recently there is considerable interest in the experimental study of the inner-shell photoionization of atoms and molecules [1,2]. The dynamics of inner-shell photoionization and the resulting relaxation of the excited atom are complicated by the collective response of all the electrons of the atomic target. Furthermore, the correlated response of the electrons in the atom couples the photoionization and relaxation processes. Thus, theoretical study of the inner-shell excited states, taking into account both exchange and correlation effects accurately, is a subject of current interest. In this paper we focus on the study of the electron structure of inner-shell excited states of closed-shell atoms by means of a spin-dependent localized Hartree-Fock (SLHF) density-functional approach [3] recently developed, along with the generalized gradient approximation (GGA) treatment of the electron correlation.

TABLE I. Total energies (E) and excitation energies (ΔE) of inner-shell excited states $1s^{-1}np\ ^{1,3}P$ ($n=2\sim 8$) of Be. The ground-state energy is −14.6575 (a.u.).

	$-E$ (a.u.)		ΔE (eV)		
States	Present work[a]	Other theory	Present work[a]	Other theory	Expt.
$1s^{-1}2p\ ^3P$	10.4526	10.4628[b]	114.4221	114.4304[b]	
		10.4654[c]			
^1P	10.4117	10.4146[b]	115.5350	115.7420[b]	115.49[d]
		10.4209[c]		115.513[c]	
$1s^{-1}3p\ ^3P$	10.1843	10.1942[b]	121.7229	121.7395[b]	
^1P	10.1797	10.1882[b]	121.8481	121.9028[b]	121.42[d]
		10.2073[c]		121.420[c]	121.4[e]
$1s^{-1}4p\ ^3P$	10.1410	10.1504[b]	122.9012	122.9314[b]	
^1P	10.1392	10.1480[b]	122.9502	122.9967[b]	122.52[d]
		10.1662[c]		122.537[c]	122.5[e]
$1s^{-1}5p\ ^3P$	10.1239	10.1331[b]	123.3665	123.4021[b]	
^1P	10.1229	10.1319[b]	123.3937	123.4348[b]	122.96[d]
		10.1495[c]		122.992[c]	123.0[e]
$1s^{-1}6p\ ^3P$	10.1152		123.6033		
^1P	10.1146	10.1412[c]	123.6196	123.219[c]	123.16[d]
$1s^{-1}7p\ ^3P$	10.1102		123.7393		
^1P	10.1098		123.7502		
$1s^{-1}8p\ ^3P$	10.1070		123.8264		
^1P	10.1068		123.8318		

[a] From PW potential.
[b] WF [14].
[c] SPCR [15,16].
[d] References [17,18].
[e] Reference [19].

The SLHF approach is based on an extension of the exchange (X)-only localized Hartree-Fock (LHF) density-functional theory (DFT) [4] to the excited states. In the original X-only LHF DFT [4], developed and successfully used for the treatment of the ground-state calculations of atomic and molecular systems, the basic equation is the Kohn-Sham (KS) equation and the exchange potential is a LHF exchange potential derived under the assumption that the X-only KS

TABLE II. Total energies (E) and excitation energies (ΔE) of inner-shell excited states $1s^{-1}np\ ^{1,3}P$ ($n=2\sim 8$) of B^+. The ground-state energy is −24.3284 (a.u.).

	$-E$ (a.u.)	ΔE (eV)		
States	Present work[a]	Present work[a]	Other theory[b]	Expt.[c]
$1s^{-1}2p\ ^3P$	17.2559	192.4546	192.460	
^1P	17.1837	194.4187	194.394	194.39
$1s^{-1}3p\ ^3P$	16.5968	210.3878	209.850	
^1P	16.5861	210.6797	210.125	210.14
$1s^{-1}4p\ ^3P$	16.4550	214.2478	213.611	
^1P	16.4509	214.3599	213.715	213.76
$1s^{-1}5p\ ^3P$	16.3959	215.8549	215.189	
^1P	16.3939	215.9099	215.237	215.30
$1s^{-1}6p\ ^3P$	16.3654	216.6860	215.999	
^1P	16.3642	216.7170	216.028	216.10
$1s^{-1}7p\ ^3P$	16.3477	217.1684		
^1P	16.3469	217.1886		
$1s^{-1}8p\ ^3P$	16.3362	217.4803		
^1P	16.3359	217.4895		

[a] Form PW potential.
[b] DF results [20].
[c] Reference [20].

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TABLE III. Total energies (E) and excitation energies (ΔE) of inner-shell excited states $1s^{-1}ns\ ^{1,3}S$ and $1s^{-1}np\ ^{1,3}P$ ($n=3\sim 8$) of Ne. The ground-state energy is -128.9331 (a.u.).

	$-E$ (a.u.)		ΔE (eV)		
States	Present work[a]	Other theory[b]	Present work[a]	Other theory	Expt.
$1s^{-1}3s\ ^3S$	97.1495	97.1729	864.8826	864.3917[b]	
^1S	97.1411	97.1631	865.1112	864.6583[b]	865.1[d]
				865.37[c]	865.32[e]
$1s^{-1}4s\ ^3S$	97.0348		868.0038		
^1S	97.0326		868.0636	868.21[c]	
$1s^{-1}5s\ ^3S$	97.0008		868.9290		
^1S	97.0000		868.9507	869.06[c]	
$1s^{-1}6s\ ^3S$	96.9863		869.3235		
^1S	96.9859		869.3344	869.44[c]	
$1s^{-1}7s\ ^3S$	96.9788		869.5276		
^1S	96.9786		869.5331		
$1s^{-1}8s\ ^3S$	96.9744		869.6474		
^1S	96.9743		869.6501		
$1s^{-1}3p\ ^3P$	97.0766	97.0982	866.8663	866.4244[b]	
^1P	97.0736	97.0950	866.9480	866.5115[b]	867.05[d]
				867.18[c]	867.12[e]
$1s^{-1}4p\ ^3P$	97.0151	97.0330	868.5398	868.1986[b]	
^1P	97.0141	97.0318	868.5671	868.2312[b]	868.68[d]
				868.70[c]	868.69[e]
$1s^{-1}5p\ ^3P$	96.9919	97.0098	869.1712	868.8299[b]	
^1P	96.9915	97.0095	869.1820	868.8462[b]	869.23[d]
				869.32[c]	869.27[e]
$1s^{-1}6p\ ^3P$	96.9814	96.9900	869.4569	869.1238[b]	
^1P	96.9812	96.9988	869.4623	869.1347[b]	869.63[d]
				869.58[c]	869.56[e]
$1s^{-1}7p\ ^3P$	96.9756		869.6147		
^1P	96.9755		869.6174	869.79[c]	869.73[e]
$1s^{-1}8p\ ^3P$	96.9721		869.7099		
^1P	96.9720		869.7127	869.87[c]	

[a] From LYP potential.
[b] WF [14].
[c] CI [21].
[d] References [22,23].
[e] References [21,24,25].

determinant is equal to the Hartree-Fock (HF) determinant. In the SLHF approach [3], we assume that the X-only KS determinant is also equal to the HF determinants for the excited states. Here the exchange potential is an exact nonvariational SLHF exchange potential. The KS energy eigenvalues obtained by solving the KS equation with this high-quality exchange potential can serve as good zeroth-order excited-state energies. The accuracy and usefulness of the SLHF approach has been demonstrated by the recent successful calculations of singly, doubly, and triply Rydberg states of the valence electrons of He- and Li-like ions [3].

In this paper, we extend the SLHF density functional approach and GGA to the treatment of atomic inner-shell excited states. Total and excitation energies of inner-shell excited states are calculated for closed-shell atomic systems: Be, B$^+$, Ne, and Mg. The results are in overall good agreement with available experimental and *ab initio* theoretical data. We also present some new results for the highly excited inner-shell states.

In the SLHF density-functional approach, an electron spin-orbital is determined by the KS equation and the exchange potential is the SLHF exchange potential [3]. For an atomic system in the spherical coordinates, the spin-orbital $\varphi_{i\sigma}(\mathbf{r})$ of the ith electron with spin σ can be expressed as $\varphi_{i\sigma}(\mathbf{r})=R_{nl\sigma}(r)Y_{lm}(\theta,\phi)/r$, where, n, l, and m are the principal quantum number, orbital angular momentum quantum number, and azimuthal quantum number of the electron, respectively, $Y_{lm}(\theta,\phi)$ is the spherical harmonic, and $R_{nl\sigma}(r)$ is the radial spin-orbital. The radial spin-orbital is governed by the radial KS equation [3]

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

where, $\varepsilon_{nl\sigma}$ is the spin-orbital energy, $v_{\mathrm{eff}}(r)=v_{\mathrm{ext}}(r)+v_H(r)+v_{x\sigma}(r)+v_{c\sigma}(r)$ is the radial effective potential, and $v_{\mathrm{ext}}(r)$, $v_H(r)$, $v_{x\sigma}(r)$, and $v_{c\sigma}(r)$ are the radial external potential, radial Hartree potential, radial SLHF exchange potential, and radial correlation potential, respectively. The radial SLHF exchange potential is given by [3]

$$v_{x\sigma}(r)=-\frac{1}{4\pi\rho_\sigma(r)}\sum_{\nu\nu'}^{\nu_\sigma\nu'_\sigma}[s^\sigma_{\nu\nu'}(r)-c^\sigma_{\nu\nu'}(r)], \tag{2}$$

where $\nu=\{nlm\}$, ν_σ stands for a set of quantum numbers of the occupied spin-orbitals with the spin σ, $s^\sigma_{\nu\nu'}(r)$ and $c^\sigma_{\nu\nu'}(r)$ are the matrix elements given in [3], and $\rho_\sigma(r)$ is the spherically averaged spin-dependent electron density given by

TABLE IV. Total energies (E) and excitation energies (ΔE) of inner-shell excited states $2p^{-1}ns\ ^{1,3}P$ ($n=4\sim 8$) of Mg. The ground-state energy -200.0744 (a.u.).

	$-E$ (a.u.)	ΔE (eV)			
States	Present work[a]	Present work[a]	Other theory[b]	Expt. MZ[c]	NE[d]
$2p^{-1}4s\ ^3P$	198.0557	54.9323	53.72	54.801	54.801
^1P	198.0538	54.9849		55.065	55.065
$2p^{-1}5s\ ^3P$	198.0044	56.3272	55.99	56.278	56.280
^1P	198.0038	56.3457		56.544	56.545
$2p^{-1}6s\ ^3P$	197.9852	56.8499	56.56	56.777	56.785
^1P	197.9849	56.8586		57.039	
$2p^{-1}7s\ ^3P$	197.9759	57.1038			
^1P	197.9757	57.1087		57.302	57.305
$2p^{-1}8s\ ^3P$	197.9707	57.2464			
^1P	197.9706	57.2478			57.456

[a] From LYP potential.
[b] CIIOO [26].
[c] Reference [27].
[d] Reference [28].

$\rho_\sigma(r)=(1/4\pi)\Sigma_{nl}^{v_\sigma} w_{nl\sigma}(R_{nl\sigma}/r)^2$. The potential in Eq. (2) qualifies for excited-state calculation because it is self-interaction free, has correct long-range behavior, and depends on symmetry of atomic state [3,4]. The exchange potential in Krieger, Li, and Iafrate (KLI) procedure [5], an approximation of the exact exchange optimized effective potential (OEP) [6], is an approximation of the SLHF exchange potential [3,4]. For atoms with nuclear charge $Z \geqslant 8$, the GGA correlation potential $v_{c\sigma}(r)$ is taken to be that proposed by Lee, Yang, and Parr (LYP) [7]. For atoms with $Z < 8$, due to the overestimation of the LYP potential [3,7], the GGA correlation potential will be taken to be that proposed by Perdew and Wang (PW) [8].

The spin-orbitals are obtained by solving the radial KS equation (1) using the generalized pseudospectral (GPS) method [9]. The GPS 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. Furthermore, the GPS method allows for nonuniform and optimal spatial discretization with the use of only a modest number of grid points. It has been shown to be a very effective and efficient numerical algorithm for high-precision solution of KS equation [10–12]. From the spin-orbitals of an electronic configuration, a single Slater determinant for a multiplet state is constructed and its total energy calculated. For a multiplet state that cannot be determined by a single determinant, Slater's diagonal sum rule [13] is used to calculate the multiplet energy [3].

TABLE V. Total energies (E) and excitation energies (ΔE) of inner-shell excited states $2s^{-1}np\ ^{1,3}P$ ($n=3\sim8$) and $2s^{-1}ns\ ^{1,3}S$ ($n=4\sim8$) of Mg.

States	$-E$ (a.u.) Present work[a]	ΔE (eV) Present work[a]	Other theory[b]
$2s^{-1}3p\ ^3P$	196.6721	92.5820	91.72
^1P	196.6630	92.8288	
$2s^{-1}4p\ ^3P$	196.5181	96.7718	96.18
^1P	196.5170	96.8026	
$2s^{-1}5p\ ^3P$	196.4871	97.6164	97.11
^1P	196.4865	97.6317	
$2s^{-1}6p\ ^3P$	196.4738	97.9775	
^1P	196.4735	97.9863	
$2s^{-1}7p\ ^3P$	196.4669	98.1667	
^1P	196.4667	98.1721	
$2s^{-1}8p\ ^3P$	196.4628	98.2782	
^1P	196.4626	98.2820	
$2s^{-1}4s\ ^3S$	196.5499	95.9065	94.65
^1S	196.5447	96.0502	
$2s^{-1}5s\ ^3S$	196.4984	97.3079	97.07
^1S	196.4966	97.3585	
$2s^{-1}6s\ ^3S$	196.4792	97.8325	97.64
^1S	196.4783	97.8565	
$2s^{-1}7s\ ^3S$	196.4698	98.0872	
^1S	196.4693	98.1003	
$2s^{-1}8s\ ^3S$	196.4645	98.2301	
^1S	196.4642	98.2382	

[a]From LYP potential.
[b]CIIOO [26].

TABLE VI. Total energies (E) and excitation energies (ΔE) of inner-shell excited states $1s^{-1}np\ ^{1,3}P$ ($n=3\sim8$) and $1s^{-1}ns\ ^{1,3}S$ ($n=4\sim8$) of Mg.

States	$-E$ (a.u.) Present work[a]	ΔE (eV) Present work[a]	Other theory[b]
$1s^{-1}3p\ ^3P$	152.1433	1304.2822	1303.25
^1P	152.1353	1304.5002	
$1s^{-1}4p\ ^3P$	151.9851	1308.5868	1307.86
^1P	151.9839	1308.6192	
$1s^{-1}5p\ ^3P$	151.9536	1309.4453	1308.80
^1P	151.9533	1309.4521	
$1s^{-1}6p\ ^3P$	151.9401	1309.8108	
^1P	151.9399	1309.8179	
$1s^{-1}7p\ ^3P$	151.9331	1310.0018	
^1P	151.9329	1310.0062	
$1s^{-1}8p\ ^3P$	151.9290	1310.1145	
^1P	151.9289	1310.1172	
$1s^{-1}4s\ ^3S$	152.0171	1307.7160	1306.29
^1S	152.0144	1307.7895	
$1s^{-1}5s\ ^3S$	151.9649	1309.1362	1308.77
^1S	151.9640	1309.1618	
$1s^{-1}6s\ ^3S$	151.9454	1309.6660	1309.35
^1S	151.9450	1309.6780	
$1s^{-1}7s\ ^3S$	151.9360	1309.9226	
^1S	151.9358	1309.9297	
$1s^{-1}8s\ ^3S$	151.9307	1310.0663	
^1S	151.9306	1310.0706	

[a]From LYP potential.
[b]CIIOO [26].

The above procedure is now used to calculate the total and excitation energies of inner-shell excited states of closed-shell atomic systems: Be, B^+, Ne, and Mg. For simplicity, an abbreviation $(nl)^{-1}(n'l')$ is used to represent an electronic configuration of an electron in an inner subshell (nl) being excited to a subshell $(n'l')$. For instance, $1s^{-1}\ 2p$ of Be represents $1s2s^2 2p$. Throughout the paper, 1 a.u. $=27.2116$ eV is used.

In Table I we present the total and excitation energies of inner-shell excited states $1s^{-1}np\ ^{1,3}P$ ($n=2\sim8$) of Be. For comparison, we also list the theoretical results of density work functional approach (WF) [14] and saddle-point complex-rotation method (SPCR) [15,16], and available experimental results (Expt.) [17–19]. The maximum relative discrepancies of our total energies to the WF and SPCR results are 0.10% and 0.27%, respectively. The maximum relative deviations of our excitation energies to the WF, SPCR, and experimental results are 0.18%, 0.35%, and 0.37%, respectively. Hence our results agree very well with the experimental and other theoretical results.

To explore the feasibility of the approach to inner-shell excitation of atomic ions, we also apply the procedure to the calculation of inner-shell excitation of B^+. The results for the excited states $1s^{-1}np\ ^{1,3}P$ ($n=2\sim8$) are given in Table II along with the theoretical results of Dirac-Fock method (DF) [20] and experimental results [20]. The relative deviations of our excitation energies to the DF and experimental results are less than 0.32% and 0.29%, respectively. Thus our results are in very good agreement with the experimental and other theoretical results.

In Table III we present the total and excitation energies of inner-shell excited states $1s^{-1}ns\ ^{1,3}S$ and $1s^{-1}np\ ^{1,3}P$ ($n=3\sim8$) of Ne. For comparison we also list the theoretical results of density work functional approach (WF) [14] and configuration-interaction model (CI) [21], and experimental results (Expt.) [22–25]. For the excited states $1s^{-1}ns\ ^{1,3}S$, the relative deviations of our total energies to the WF results are not more than 0.02%. The relative discrepancies of our excitation energies to the experimental results are less than 0.02%, while the maximum relative discrepancies of the WF and CI results to the experimental results are 0.08% and 0.03%, respectively. For the excited states $1s^{-1}np\ ^{1,3}P$, the relative deviations of our total energies to the WF results are not more than 0.02%. The maximum relative discrepancy of our excitation energies to the experimental results is 0.02% while the maximum relative deviations of the WF and CI results to the experimental results are 0.07% and 0.02%, respectively. Thus our excitation energies are very close to the CI results and better than the WF data.

The total and excitation energies of inner-shell excited states $2p^{-1}ns\ ^{1,3}P$, $2s^{-1}np\ ^{1,3}P$ and $2s^{-1}ns\ ^{1,3}S$, as well as $1s^{-1}np\ ^{1,3}P$ and $1s^{-1}ns\ ^{1,3}S$ for $n\leqslant8$ of Mg are shown in Tables IV–VI, respectively. For comparison, the theoretical results of configuration-interaction calculation with improved and optimized orbitals (CIIOO) [26] and experimental results (Expt.) [27,28] are also shown in these tables. For the excited states $2p^{-1}ns\ ^{1,3}P$ in Table IV, the only ones for which experimental excitation energies are available, the CIIOO excitation energies are smaller than both the experimental results and our results. The maximum relative deviations of our excitation energies and the CIIOO results to the experimental results are 0.36% and 1.97%, respectively. Thus our results are more accurate than the CIIOO results. For the excited states in Tables V and VI, the CIIOO excitation energies are again smaller than ours. The maximum relative deviations of our results to the CIIOO results are 0.94%, 1.33%, 0.08%, and 0.11% for the excited states $2s^{-1}np\ ^{1,3}P$, $2s^{-1}ns\ ^{1,3}S$, $1s^{-1}np\ ^{1,3}P$, and $1s^{-1}ns\ ^{1,3}S$, respectively.

In summary, a SLHF density-functional approach is presented and applied to calculate the total energies and excitation energies of inner-shell excited states of closed-shell atomic systems: Be, B^+, Ne, and Mg. The results are in overall good agreement with the available, more sophisticated *ab initio* theoretical results and experimental data. The relative discrepancies of our calculated excitation energies to the available experimental results are not more than 0.40%, demonstrating that the SLHF density-functional approach provides a powerful and computationally efficient scheme for the accurate calculation of inner-shell excited states of closed-shell atomic systems within DFT. Finally, we present also a number of new results for highly excited inner-shell states.

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