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Application of density-functional theory to atomic resonances

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Density-functional theory in the local-spin-density approximation has been applied to calculate the energy positions of low-lying resonance (autoionization) states of neutral atoms and positive ions. This method is very convenient for a quick, approximate prediction of excitation energies in collision experiments.
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Density-functional theory (DFT) was originally designed for many-electron systems in their ground state [1]. Various modifications of the original method have been applied to atomic, molecular, and solid state systems [2], usually in their ground states. There are also applications of DFT for excited states [3]; a time-dependent formalism has been applied to photoabsorption cross-section [4] and photoionization cross-section [5] calculations for rare gas atoms. To the knowledge of the authors there is no systematic application of the time-independent form of DFT to atomic autoionization (AI) states.

Autoionization is a time-dependent process. There are several methods presented in the literature using either a time-dependent or a time-independent formalism for AI states [6]. These methods, however, usually require more computational effort compared to conventional bound-state calculations.

In this paper we report results of relativistic calculations based on the single-particle Dirac equation in which we have applied an approximate time-independent DFT to the low-lying AI states of neutral atoms and positive ions. The calculations require a computational effort similar to ground-state DFT calculations.

The method of calculation is based on the self-consistent solution of N one-particle Dirac equations (Kohn-Sham orbital equations) of the form (in Rydberg atomic units)

$$[-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla}+(\beta-1)\tfrac{1}{2}c^2+v_{\mathrm{eff}}^{\sigma}]\psi_{\sigma,i}=\varepsilon_{\sigma,i}\psi_{\sigma,i}, \tag{1}$$

where

$$v_{\mathrm{eff}}^{\sigma}(\mathbf{r})=v(\mathbf{r})+2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{\mathrm{xc}}^{\sigma}(\mathbf{r}). \tag{2}$$

In these equations σ is a quantum number that labels the solutions according to their spin state. The wave functions ψ are four-vectors, but can be described by two radial functions only. The spin-dependent charge density $\rho_\sigma(\mathbf{r})$ is obtained self-consistently, and defined as

$$\rho_\sigma(\mathbf{r})=\sum_i^{N_\sigma}|\psi_{i,\sigma}(\mathbf{r})|^2 \tag{3}$$

and

$$\rho=\sum_\sigma \rho_\sigma. \tag{4}$$

$v(\mathbf{r})$ is the Coulomb potential between electron and nucleus, and $v_{\mathrm{xc}}^{\sigma}(\mathbf{r})$ is the exchange-correlation potential. The total energy of the atom consists of the kinetic energy of the electrons, the electron-nucleus Coulomb potential energy, and

TABLE I. Comparison of calculated AI energies with experimental values and other calculations for some neutral atoms with $Z\leqslant 10$. Energies are in eV and with respect to the ground state of the corresponding system.

Atom (state)	Present calc.	Expt. value [Ref.]	Ratio $E_{\mathrm{calc}}/E_{\mathrm{expt}}$	Difference $E_{\mathrm{cal}}-E_{\mathrm{expt}}$	Other calc. [Ref.]
He($2s^2$)	56.54	57.64 [9]	0.981	-1.10	57.85 [26]
He($2p^2$)	58.15	58.30 [9]	0.997	-0.15	58.32 [27]
Li($1s2s^2$)	55.69	56.35 [10]	0.988	-0.66	56.32 [28]
F($1s^22s2p^6$)	18.34	20.99 [12]	0.874	-2.65	20.68 [30]
Ne($2p^43p4s$)	52.66	53.68 [13]	0.981	-1.02	
Ne($2p^43p5s$)	54.02	54.73 [13]	0.987	-0.71	
Ne($2s2p^63p$)	41.75	45.55 [14]	0.917	-3.80	46.25 [5]
Ne($2s2p^64p$)	43.38	47.12 [14]	0.921	-3.74	47.40 [5]
Ne($2s2p^65p$)	44.05	47.69 [14]	0.924	-3.64	47.81 [5]

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TABLE II. Same as Table I for some neutral atoms with $Z \geqslant 12$.

Atom (state)	Present calc.	Expt. value [Ref.]	Ratio $E_{\text{calc}}/E_{\text{expt}}$	Difference $E_{\text{calc}}-E_{\text{expt}}$	Other calc. [Ref.]
$\mathrm{Mg}(2p^5 3s^2 4s)$	54.83	54.81 [15]	1.000	+0.02	
$\mathrm{Mg}(2p^5 3s^2 3d)$	55.78	55.49 [15]	1.005	+0.29	
$\mathrm{Mg}(2p^5 3s 3p^2)$	56.27	54.96 [15]	1.024	+1.31	
$\mathrm{Al}(3s 3p 3d)$	8.22	8.43 [16]	0.975	−0.21	8.03 [31]
$\mathrm{Cl}(3s 3p^5 4p)$	22.82	22.20 [17]	1.028	+0.62	
$\mathrm{Cl}(3s 3p^5 5p)$	24.21	23.35 [17]	1.037	+0.86	
$\mathrm{Cl}(3s^2 3p^3 4s^2)$	23.37	22.12 [18]	1.057	+1.25	
$\mathrm{Cl}(3s^2 3p^3 3d 4s)$	23.99	23.03 [18]	1.042	+0.96	
$\mathrm{Ar}(3s 3p^6 4p)$	27.38	26.61 [19]	1.029	+0.77	26.85 [5]
$\mathrm{Ar}(3s 3p^6 5p)$	28.81	27.99 [19]	1.029	+0.82	28.12 [5]
$\mathrm{Ar}(3s 3p^6 6p)$	29.43	28.51 [19]	1.032	+0.92	28.53 [5]
$\mathrm{Cu}(3d^9 4s 5s)$	8.67	7.80 [20]	1.112	+0.87	
$\mathrm{Kr}(4s 4p^6 5p)$	25.91	24.99 [22]	1.037	+0.92	25.20 [5]
$\mathrm{Kr}(4s 4p^6 6p)$	27.26	26.31 [22]	1.036	+0.95	26.45 [5]
$\mathrm{Sr}(4d 5d)$	6.14	6.37 [23]	0.964	−0.23	
$\mathrm{Ag}(4d^9 5s^2)$	4.35	3.75 [24]	1.160	+0.60	
$\mathrm{Xe}(4d^9 5s^2 5p^6 6p)$	66.02	65.11 [25]	1.014	+0.91	

the exchange-correlation energy of the electrons. The total energy can be determined from the self-consistent resultant charge density as

$$E[\rho]=\sum_{\sigma,i} \varepsilon_{\sigma,i}-\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d(\mathbf{r})d(\mathbf{r}')+E_{\text{xc}}[\rho_\sigma] -\sum_{\sigma} \int v_{xc}^{\sigma}(\mathbf{r})\rho_\sigma(\mathbf{r})d(\mathbf{r}). \tag{5}$$

The local-spin-density approximation has been used for the exchange-correlation energy in the form due to Von Barth and Hedin, and parametrized by Janak [7]:

$$v_{\text{xc}}^{\sigma}(\mathbf{r})=\frac{\delta E_{\text{xc}}}{\delta\rho_\sigma(\mathbf{r})}, \tag{6}$$

where the functional $E_{\text{xc}}[\rho]$ is defined as

$$E_{\text{xc}}[\rho]=\sum_{\sigma} \int \rho_\sigma(\mathbf{r})\varepsilon_{\text{xc}}^{\sigma}(\rho(\mathbf{r}))d\mathbf{r}. \tag{7}$$

As is normally done in this approach, the spin states are defined by the large components only. We have divided the electrons in two groups, labeled by σ. If we use the potential for $\sigma=+1$ we solve the Dirac equations and choose the large component to be spin up. Similarly, for $\sigma=-1$ we choose spin down. The small components will have a mixture of both spins, but the effects of this spin mixing are small compared with the energy differences we are trying to obtain. In the calculations each occupied orbital is defined by an occupation number; in this work we only consider integral occupation of states.

Since Hund's second rule is not obeyed in the local-spin-density approximation, it is not possible to determine the term values of the electron configuration exactly. Calculated energies correspond to a spherical average of the low-lying terms of each configuration. This is the main source of error

TABLE III. Same as Table I for some positive ions.

Atom (state)	Present calc.	Expt. value [Ref.]	Ratio $E_{\text{calc}}/E_{\text{expt}}$	Difference $E_{\text{calc}}-E_{\text{expt}}$	Other calc. [Ref.]
$\mathrm{Li}^{+}(2s^2)$	71.70	70.62 [10]	1.015	+1.08	70.58 [29]
$\mathrm{B}^{2+}(1s 2s^2)$	191.05	193 ±0.5 [11]	0.990	−1.95	192.70 [11]
$\mathrm{B}^{2+}(1s 2s 2p)$	191.70	195 ±1 [11]	0.983	−3.30	194.75 [11]
$\mathrm{O}^{5+}(1s 2s^2)$	547.49	551 ±1.5 [11]	0.994	−3.51	551.45 [11]
$\mathrm{O}^{5+}(1s 2s 2p)$	548.55	556 ±3 [11]	0.987	−7.45	555.23 [11]
$\mathrm{N}^{4+}(1s 2s^2)$	408.21	411 ±1 [11]	0.993	−2.79	410.68 [11]
$\mathrm{N}^{4+}(1s 2s 2p)$	409.13	415 ±2 [11]	0.986	−5.87	413.59 [11]
$\mathrm{F}^{6+}(1s 2s^2)$	707.27	711 ±1 [11]	0.995	−3.73	710.31 [11]
$\mathrm{F}^{6+}(1s 2s 2p)$	708.48	716 ±2 [11]	0.989	−7.52	714.07 [11]
$\mathrm{Cu}^{18+}(2p^5 3p 4p)$	1350.44	1337.59 [21]	1.010	+12.85	

TABLE IV. Comparison of energy differences between the AI states $(1s2l3l')$ and $(1s2s2p)$ in three-electron ions. Energies are in eV. (a) represents the difference between the states $(1s2s3d)$ and $(1s2s2p)$, (b) represents the difference between the states $(1s2p3p)$ and $(1s2s2p)$.

Ion	Present calc.	Expt. value [32]	Ratio $E_{\mathrm{calc}}/E_{\mathrm{expt}}$	Difference $E_{\mathrm{calc}}-E_{\mathrm{exp}}$	Other calc. [33]
C^{3+}(a)	42.85	43.73	0.980	-0.88	43.71
C^{3+}(b)	46.43	47.65	0.974	-1.22	47.63
N^{4+}(a)	62.95	64.12	0.982	-1.17	64.12
N^{4+}(b)	67.23	68.74	0.978	-1.51	68.72
O^{5+}(a)	86.83	88.32	0.983	-1.49	88.33
O^{5+}(b)	91.83	93.61	0.981	-1.78	93.60
F^{6+}(a)	114.49	116.95	0.979	-2.46	116.33
F^{6+}(b)	120.24	122.34	0.983	-2.10	122.29

in our calculations. The aim of this study is to investigate how large these errors are.

Comparisons of the present calculations with the available experimental values and some other available calculations for the same configurations for the AI states of some neutral atoms are given in Table I for the elements with $Z \leqslant 10$, and in Table II for the elements with $Z \geqslant 12$. A similar comparison for some positive ions is given in Table III. Only one example is chosen both from experimental values and other calculations. The energy differences of the states $(1s2l3l')$ and $(1s2s2p)$ in three-electron ions are compared with experimental values and perturbation theory calculations in Table IV. A comparison of the present calculations with that of the complex-rotation method [8] for $(1s2s2p)$ states in lithiumlike ions is given in Table V.

From the data given in Table I one can see that the time-independent DFT calculations predict the energy positions of the AI states reasonably well for low-lying states, which are located just above the first ionization threshold. For the neutral atoms with nuclear charge less than 11 the relative error (as compared to the experimental values) is within 2% for valence electron excitations. For core electron excitations, however, the error increases up to 8%. The largest relative error (13%) is in the F$(1s^2 2s2p^6)$ system, which has a hole in the inner subshell of the outhermost shell. For these atoms all calculated values are smaller than the corresponding experimental values.

From the data for the neutral atoms with nuclear charge larger than 11, given in Table II, one can see that the present calculations predict the energy positions of the AI states reasonably well again for low-lying states. The relative error (again compared to the corresponding experimental values) for this group of elements is within 4%, except for Cu and Ag. Almost all calculated values are larger than the corresponding experimental values for this group of atoms, except for Al and Sr.

From the data given in Table III for the positive ions, one can see that the agreement of the present results and the experimental values is even better. The relative error is within 1%. Almost all calculated values are smaller than the corresponding experimental values, except for Li^{+} and Cu^{18+} ions.

TABLE V. Comparison of the present calculations with that of the complex-rotation method [8] for $(1s2s2p)$ states in lithiumlike ions. Values are absolute energies in hartree units.

Z	Present calc. (E_{PC})	Other calc. (E_{OC})	Ratio $E_{\mathrm{PC}}/E_{\mathrm{OC}}$	Difference $E_{\mathrm{PC}}-E_{\mathrm{OC}}$
3	-5.29832	-5.36848	0.98693	0.07016
4	-9.95118	-10.06848	0.98835	0.11730
5	-16.10515	-16.27246	0.98972	0.16731
6	-23.76099	-23.98006	0.99086	0.21907
7	-32.91994	-33.19201	0.99180	0.27207
8	-43.58348	-43.90953	0.99257	0.32605
9	-55.75332	-56.13421	0.99321	0.38089
10	-69.43134	-69.86794	0.99375	0.43660
11	-84.61967	-85.11274	0.99421	0.49307
12	-101.32063	-101.87104	0.99460	0.55041
13	-119.53679	-120.14537	0.99493	0.60858
14	-139.27090	-139.93863	0.99523	0.66772
15	-160.52599	-161.25386	0.99549	0.72787
16	-183.30528	-184.09438	0.99571	0.78909
17	-207.61227	-208.46370	0.99592	0.85143
18	-233.45065	-234.36559	0.99610	0.91493

The agreement in the results of the present calculation and that of the complex-rotation method for the AI state $(1s2s2p)$ in lithiumlike ions given in Table IV is good. Differences of the two calculations increase as the nuclear charge increases. The present results are slightly higher than that of the complex-rotation calculation results. The differences are within the 1% range.

The energy differences between the resonance states $(1s2l3l')$ and $(1s2s2p)$ in three-electron ions given in Table V are calculated within 2% error with the corresponding experimental values. The present results are smaller than the experimental values.

From the results presented in this work one concludes that the energy positions of the AI states and energy differences between resonance states for neutral atoms and positive ions can easily be predicted with an error of a few percent by a simple and quick calculation. The present method takes at most 1 minute CPU time on an IBM-RISC/6000 workstation. Other methods require a much larger computational effort in comparison to the present method. Of course, the quality of the results calculated by these other methods is much better. They describe the physics of the many-body effects in much greater detail, which is essential for our basic understanding of the electronic structure of atoms. In the local-density approximation these many-body effects are included only in an approximate way. In this paper we have investigated the resultant errors in the energy of AI states. Whether the errors reported in this paper are large or small depends on the context in which they are needed. Our only conclusion is that if for a given application the errors reported in this paper are considered to be small DFT is useful. In such cases the time-independent form of DFT can easily be applied to atomic systems for predicting the approximate excitation energies needed in, e.g., experiments studying collisions of atoms.

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