

## Relativistic density-functional calculations of interconfigurational energies in transition-metal atoms

Hornng-Tay Jeng and Chen-Shiung Hsue

*Institute of Physics, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China*

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The relativistic local-spin-density approximation and the relativistic generalized gradient approximation (RGGA) are employed to calculate interconfiguration energies including  $4s$ - $3d$  transition energies,  $4s$  ionization energies, and  $3d$  ionization energies for the first transition-metal atoms. For  $3d$  ionizations, the RGGA, which includes relativistic corrections as well as gradient effects, yields the best results. For  $4s$ - $3d$  transitions, the relativistic effects also systematically improve the accuracies of the results. However the  $4s$  removal energies from the relativistic schemes are slightly too large, whereas the self-interaction-correction local-spin-density approximation, which provides correct long-range effective potentials, gives accurate results.

The Hohenberg-Kohn-Sham density-functional theory (DFT)<sup>1,2</sup> has been extensively used to study ground-state electronic structures of many-body systems such as atoms, molecules, and solids.<sup>3</sup> Following Kohn and Sham's<sup>2</sup> local-density approximation, various extensions such as the local-spin-density (LSD) approximation,<sup>4</sup> the self-interaction-correction local-spin-density (SIC-LSD) approximation,<sup>5</sup> and the generalized gradient approximation (GGA)<sup>6</sup> were proposed. In the relativistic density-functional theory (RDFT),<sup>7,8</sup> the Schrödinger-like Kohn-Sham equations of the DFT are replaced by Dirac-like equations. The relativistic corrections to the exchange-correlation potential-energy functional were also obtained based on quantum electrodynamics arguments<sup>7,8</sup>.

Recently Kotochigova *et al.*<sup>9</sup> presented atomic structure calculations across the Periodic Table using the relativistic local-density approximation. Tong and Chu<sup>10</sup> performed RDFT calculations using the optimized effective potential<sup>11</sup> with self-interaction correction for various atoms in the Periodic Table. In a previous work,<sup>12</sup> we calculated the ground-state total energies for a series of atoms using the  $B$ -spline basis<sup>13</sup> for the RDFT. Researches on relativistic effects have become more active recently for various systems.<sup>14-16</sup>

Interconfiguration energies (ICE's) are often taken as tests for various theoretical approaches. Gunnarsson and Jones<sup>17</sup> tested the performances of the SIC-LSD (Ref. 5) functional, and concluded that the SIC-LSD approximation does not yield systematic improvement over the LSD results for the iron series. Martin and Hay<sup>18</sup> calculated ICE's of the three transition series in the Hartree-Fock (HF) approximation using the Cowan and Griffin<sup>19</sup> scheme for relativistic corrections. They found that relativistic corrections are large even for the first transition series. Lagowski and Vosko<sup>20</sup> investigated the  $J$ -independent relativistic contributions on  $s$ - $d$  ICE's, and confirmed that even in the first transition series the perturbatively calculated relativistic effects are non-negligible. Kutzler and Painter<sup>21</sup> presented ICE's of the  $3d$  atoms obtained from both the LSD approximation and the GGA.<sup>6</sup> They concluded that gradient functionals provide some improvement over the LSD approximation, but the remaining errors are still large.

ICE's involve mainly valence-shell electrons moving in

the outermost atomic regions where the relativistic effects are expected to be rather small. However, relativistic effects cause the electron orbitals in the inner shell to shrink, and result in a better screening of the nuclear charges for the outer electrons.<sup>12</sup> The importance of relativistic effects on ICE's of the iron series were demonstrated perturbatively in Refs. 18, 20, and 21. In this work, we calculate ICE's within the fully relativistic LSD (RLSD) and GGA (RGGA) schemes. Results from the SIC-LSD approach are also included for comparisons.<sup>22</sup>

In RDFT, we self-consistently solve the Dirac equations

$$\frac{dF_{\sigma i}(r)}{dr} - \frac{\kappa}{r} F_{\sigma i}(r) = \alpha [V_{\text{eff}}^{\sigma}(r) - \epsilon_{\sigma i}] G_{\sigma i}(r), \quad (1)$$

$$\frac{dG_{\sigma i}(r)}{dr} + \frac{\kappa}{r} G_{\sigma i}(r) = \alpha \left[ \frac{2}{\alpha^2} + \epsilon_{\sigma i} - V_{\text{eff}}^{\sigma}(r) \right] F_{\sigma i}(r),$$

where  $G_{\sigma i}(r)$  and  $F_{\sigma i}(r)$  are the major and minor components of the radial Dirac wave functions with spin  $\sigma$ .<sup>12</sup> The effective potential  $V_{\text{eff}}^{\sigma}(r)$  is given by

$$V_{\text{eff}}^{\sigma}(r) = -\frac{z}{r} + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}^{\sigma}[\rho_+, \rho_-]. \quad (2)$$

The total electron density can be expressed as

$$\rho(r) = \rho_+(r) + \rho_-(r) = \sum_{\sigma i} [ |G_{\sigma i}(r)|^2 + |F_{\sigma i}(r)|^2 ], \quad (3)$$

where  $\rho_+$  and  $\rho_-$  denote the spin-up and -down densities. Strictly speaking, the spin-density concept in the relativistic treatment is a good approximation for the valence orbitals only. But in our case, the spin-density concept can be used, since all the electrons for the inner-shell orbitals are spin paired. The exchange-correlation potential is obtained by

$$v_{xc}^{\sigma}[\rho_+, \rho_-] = \frac{\delta E_{xc}[\rho_+, \rho_-]}{\delta \rho_{\sigma}}, \quad (4)$$

TABLE I.  $4s$ - $3d$  transition energies (eV) ( $4s^23d^{n-2} \rightarrow 4s^13d^{n-1}$ ).

	Expt. <sup>a</sup>	(rel) <sup>b</sup>	GGA <sup>c</sup>	GGA(rel) <sup>c</sup>	LSD <sup>c</sup>	LSD(rel) <sup>c</sup>	SIC <sup>d</sup>	SIC(rel) <sup>d</sup>	RLSD <sup>e</sup>	RGGA <sup>e</sup>
Sc	1.43	0.12	0.91	1.03	0.69	0.81	0.50	0.64	0.81	1.02
Ti	0.81	0.14	-0.03	0.11	-0.27	-0.13	-0.42	-0.26	-0.11	0.13
V	0.25	0.17	-0.91	-0.74	-1.17	-1.00	-1.27	-1.09	-0.99	-0.72
Cr	-1.00	0.21	-1.74	-1.53	-2.03	-1.82	-2.08	-1.86	-1.82	-1.53
Mn	2.15	0.20	1.25	1.45	1.05	1.25	1.07	1.30	1.17	1.38
Fe	0.87	0.26	0.39	0.65	0.16	0.42	0.23	0.51	0.34	0.60
Co	0.42	0.30	-0.46	-0.16	-0.71	-0.41	-0.59	-0.26	-0.46	-0.17
Ni	-0.03	0.36	-1.30	-0.94	-1.57	-1.21	-1.39	-1.00	-1.24	-0.95
Cu	-1.49	0.43	-2.16	-1.73	-2.44	-2.01	-2.16	-1.72	-1.98	-1.72
$\overline{\Delta E}$			-0.83	-0.59	-1.08	-0.83	-1.06	-0.79	-0.85	-0.60

<sup>a</sup>Reference 24.<sup>b</sup>Reference 18.<sup>c</sup>Reference 21.<sup>d</sup>Reference 22.<sup>e</sup>This work.

with the energy functional  $E_{xc}[\rho_+, \rho_-]$ . The energy functional used here for both RLSD and RGGA calculations are deduced from the Monte Carlo results of Ceperley and Alder,<sup>23</sup> as fitted by Perdew and Zunger<sup>5</sup> with relativistic corrections given by MacDonald and Vosko.<sup>8</sup> The gradient functionals from Perdew and Wang<sup>6</sup> are used for the RGGA. The total energy of the ground state is given by a minimization of the energy functional

$$E_G[\rho_+, \rho_-] = T[\rho] + \frac{1}{2} \int d^3r d^3r' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + \int d^3r \rho(\vec{r}) V_{\text{ext}}(\vec{r}) + E_{xc}[\rho_+, \rho_-], \quad (5)$$

where  $T[\rho]$  is the noninteracting kinetic energy functional and  $V_{\text{ext}}(\vec{r})$  is the external potential.

The lowest experimental terms,<sup>24</sup> which concern the valence electrons moving mainly in the nonrelativistic regions, are designated by the nonrelativistic configurations. Since for each nonrelativistic configuration there exist, in general, several relativistic configurations, the calculated total energies are averaged over all the relevant relativistic configurations in the uncoupled scheme for simplicity, as discussed in Ref. 25.

The  $4s$ - $3d$  transition energy is defined by

$$\Delta_{sd} = E(\text{core}, 4s^1 3d^{n-1}) - E(\text{core}, 4s^2 3d^{n-2}), \quad (6)$$

where  $n$  is the number of valence electrons. It is well known that the local-density approximation tends to overstabilize

TABLE II.  $4s$  ionization energies (eV) from the  $s$ -rich configuration ( $4s^23d^{n-2} \rightarrow 4s^13d^{n-2}$ ) for all elements, and from the  $d$ -rich configuration ( $4s^13d^{n-1} \rightarrow 4s^03d^{n-1}$ ) for Cr, Ni, and Cu.

	Expt. <sup>a</sup>	(rel) <sup>b</sup>	GGA <sup>c</sup>	GGA(rel) <sup>c</sup>	LSD <sup>c</sup>	LSD(rel) <sup>c</sup>	SIC <sup>d</sup>	SIC(rel) <sup>d</sup>	RLSD <sup>e</sup>	RGGA <sup>e</sup>
Sc	6.56	0.02	6.77	6.79	6.60	6.62	6.57	6.62	6.67	6.84
Ti	6.83	0.04	7.05	7.09	6.89	6.93	6.85	6.89	6.95	7.13
V	7.06	0.03	7.29	7.32	7.12	7.15	7.07	7.13	7.18	7.36
Cr	7.28	0.04	7.49	7.53	7.33	7.37	7.27	7.34	7.37	7.56
Mn	7.43	0.05	7.67	7.72	7.52	7.57	7.45	7.53	7.55	7.75
Fe	7.90	0.06	8.21	8.27	8.07	8.13	7.99	8.10	8.14	8.33
Co	8.28	0.08	8.68	8.76	8.54	8.62	8.45	8.57	8.65	8.82
Ni	8.67	0.11	9.10	9.21	8.97	9.08	8.85	9.00	9.11	9.26
Cu	9.04	0.13	9.52	9.65	9.40	9.53	9.22	9.40	9.53	9.67
Zn	9.39	0.16	9.84	10.00	9.71	9.87	9.57	9.78	9.93	10.06
$\overline{\Delta E}$			0.32	0.39	0.17	0.24	0.08	0.19	0.26	0.43
Cr*	6.76	0.09	7.55	7.64	7.48	7.57	7.16	7.28	7.59	7.65
Ni*	7.62	0.15	8.44	8.59	8.26	8.41	7.87	8.07	8.43	8.59
Cu*	7.72	0.15	8.50	8.65	8.35	8.50	8.02	8.24	8.59	8.75
$\overline{\Delta e}$			0.80	0.93	0.66	0.79	0.32	0.50	0.84	0.96

<sup>a</sup>Reference 24.<sup>b</sup>Reference 18.<sup>c</sup>Reference 21.<sup>d</sup>Reference 22.<sup>e</sup>This work.

TABLE III.  $3d$  ionization energies (eV) from the  $s$ -rich configuration ( $4s^23d^{n-2} \rightarrow 4s^23d^{n-3}$ ) for all elements, and from the  $d$ -rich configuration ( $4s^13d^{n-1} \rightarrow 4s^13d^{n-2}$ ) for Cr, Ni, and Cu.

	Expt. <sup>a</sup>	(rel) <sup>b</sup>	GGA <sup>c</sup>	GGA(rel) <sup>c</sup>	LSD <sup>c</sup>	LSD(rel) <sup>c</sup>	SIC <sup>d</sup>	SIC(rel) <sup>d</sup>	RLSD <sup>e</sup>	RGGA <sup>e</sup>
Sc	8.00	-0.10	8.89	8.79	9.01	8.91	9.49	9.30	8.78	8.67
Ti	9.92	-0.10	10.61	10.51	10.75	10.65	11.16	10.94	10.45	10.33
V		-0.14	12.18	12.04	12.35	12.21	12.70	12.45	11.98	11.84
Cr	12.40	-0.17	13.65	13.48	13.84	13.67	14.14	13.86	13.41	13.25
Mn	14.30	-0.15	15.05	14.90	15.26	15.11	15.51	15.18	14.76	14.60
Fe	10.71	-0.20	12.03	11.83	12.22	12.02	12.45	12.12	11.88	11.72
Co	12.88	-0.22	13.71	13.49	13.94	13.72	14.10	13.73	13.53	13.32
Ni			15.32		15.57		15.65	15.24	15.07	14.83
Cu	15.04	-0.30	17.20	16.90	17.48	17.18	17.14	16.67	16.57	16.32
Zn	17.30	-0.55	18.35	17.80	18.62	18.07	18.56	18.04	17.98	17.73
$\overline{\Delta E}$			1.12	0.89	1.32	1.10	1.50	1.16	0.85	0.67
Cr*	8.29	-0.17	9.23	9.15	9.36	9.19	9.35	9.20	9.20	9.09
Ni*	8.70	-0.25	10.40	10.15	10.54	10.29	10.23	10.00	10.35	10.22
Cu*	10.53	-0.30	11.68	11.38	11.84	11.54	11.38	11.12	11.52	11.39
$\overline{\Delta e}$			1.26	1.05	1.41	1.17	1.15	0.93	1.18	1.06

<sup>a</sup>Reference 24.

<sup>b</sup>References 18 and 21.

<sup>c</sup>Reference 21.

<sup>d</sup>Reference 22.

<sup>e</sup>This work.

$3d$  orbitals relative to  $4s$  orbitals. As shown in Table I,  $4s$ - $3d$  transition energies from both the LSD (column 6)<sup>21</sup> and SIC-LSD (column 8)<sup>22</sup> approximations are on average 1 eV lower than experimental values (column 2).<sup>24</sup> The GGA (column 4),<sup>21</sup> which takes into account the gradient effects, gives smaller mean errors ( $\overline{\Delta E}$ ).

By including relativistic contributions,<sup>18,22</sup> results are systematically improved within the GGA(rel) (column 5),<sup>21</sup> the LSD(rel) (column 7),<sup>21</sup> and the SIC(rel) (column 9).<sup>22</sup> Note that the relativistic corrections of both the GGA(rel) and LSD(rel) used in Ref. 21 are the HF relativistic contributions (column 3) taken from Ref. 18. On the other hand, the relativistic corrections in the SIC(rel) are calculated perturbatively with SIC-LSD wave functions.<sup>22</sup> The RLSD (column 10) and the RGGA (column 11) give results quite close to the values from the LSD(rel) and the GGA(rel) respectively. The average relativistic corrections from the RLSD and the RGGA amount to 0.23 eV which is in agreement with the average HF relativistic contributions of 0.24 eV.

The  $4s$  ionization energy is given explicitly by

$$\Delta_{s-ion} = E(\text{core}, 4s^1 3d^{n-2}) - E(\text{core}, 4s^2 3d^{n-2}). \quad (7)$$

In Table II, the initial configurations  $4s^2 3d^{n-2}$  are the experimental ground-state configurations for most of the iron series atoms. The  $4s$  removal energies from the ground-state configurations  $4s^1 3d^{n-1}$  for Cr, Ni, and Cu are also included in the lower half of the table.

The GGA approach gives worse results than the simpler LSD scheme. The relativistic corrections systematically promote the nonrelativistic  $4s$  binding energies with growing errors across the iron series. The most involved RGGA scheme yields the worst results. This is due to the fact that for  $4s$  ionization energies, the major contributions come

from the energy differences of the outermost  $4s$  orbital electrons. The gradient effects and the relativistic corrections to the inner-shell electrons cancel each other out. In fact, the  $4s$  binding energies<sup>22</sup> from the SIC-LSD scheme,<sup>5</sup> which includes electron-electron self-interaction corrections, are in much better agreement with the experimental results. This is in line with the results in Ref. 22, where the SIC-LSD scheme is very successful in yielding accurate oscillator strengths for the valence  $s$  electrons of the alkali isoelectron atoms, which depend very sensitively on the wave functions involved.

For Cr, Ni, and Cu from  $4s^1 3d^{n-1}$  configurations, the mean errors ( $\overline{\Delta e}$ ) are much larger as compared with  $4s$  ionization energies from  $4s^2 3d^{n-2}$  configurations. Kutzler and Painter<sup>21</sup> calculated the  $4s$  ionization energy for potassium, and obtained much smaller errors, which indicates that the local-density functionals are subject to considerable errors in calculating the interaction energy between the  $4s$  electron with the  $3d$  subshell.

The  $3d$  ionization energy is defined as

$$\Delta_{d-ion} = E(\text{core}, 4s^2 3d^{n-3}) - E(\text{core}, 4s^2 3d^{n-2}). \quad (8)$$

Since the experimental energies of the relevant  $s$ -rich configurations for  $3d^2 4s^2$  of V and  $3d^7 4s^2$  of Ni were not tabulated in Ref. 24, the experimental ionization energies of V and Ni are not presented in Table III. We also calculate the  $3d$  removal energies in the transition  $4s^1 3d^{n-1} \rightarrow 4s^1 3d^{n-2}$  for Cr, Ni, and Cu. The calculated errors are larger than the corresponding errors for both  $4s$ - $3d$  transitions and  $4s$  ionizations. This results from the difficulties of describing the  $3d$  electrons accurately. The GGA results are

better than both the LSD and SIC-LSD results, which indicates that the gradient effects are quite important in the  $3d$  orbitals.

For  $3d$  ionizations from  $4s^2 3d^{n-2}$  configurations, Martin and Hay<sup>18</sup> reported HF relativistic corrections for Zn only. Kutzler and Painter<sup>21</sup> instead used HF relativistic contributions from  $4s^1 3d^{n-1}$  states<sup>18</sup> for the other atoms. Both perturbative and fully relativistic approaches systematically improve the nonrelativistic results. The RLSD approximation and RGGA give average relativistic effects of  $-0.47$  and  $-0.45$  eV, respectively, which is much larger than  $-0.34$  eV of the SIC-LSD approximation and  $-0.22$  eV of the HF approximation. It was discussed in Ref. 12 that for  $3d$  atoms, the differences in total energies between the perturbative and RDFT schemes are of the order of 0.01%. Nevertheless, for  $3d$  removal energies, differences between the HF relativistic corrected values and the RDFT results increase to about 2%.

For Cr, Ni, and Cu, both the fully relativistic and the perturbative approaches yield similar  $3d$  binding energies from the  $4s^1 3d^{n-1}$  state. The best results are given from the SIC-LSD scheme. Since for both  $4s$  ionization and  $4s$ - $3d$  transition energies, results from RDFT are roughly equal to the HF relativistic corrected results, this is also the case in  $3d$  ionization from the  $4s^1 3d^{n-1}$  state, which is equivalent

to the difference between  $4s$  ionization and  $4s$ - $3d$  transition energies. The SIC-LSD scheme yields the best  $4s$  ionization energies; hence it gives smaller errors here.

To conclude, for  $3d$  ionizations, both gradient effects and relativistic corrections play important roles. There is a significant improvement of the results obtained from the RGGA scheme. As a  $3d$  electron is ionized, the  $3d$  orbitals shrink further, and the relativistic effects are stronger than for the neutral atoms. This may explain why perturbative treatments are not adequate for  $3d$  ionization energies as compared with the RDFT results. On the other hand, the total numbers of electrons are not changed in  $4s$ - $3d$  transitions, so that the shrinkage is not as dramatic as that in ionized atoms. Perturbative relativistic approaches give similar results as given from RDFT. As for  $4s$  ionizations, the SIC-LSD scheme, which provides correct long-range effective potentials for the outermost  $4s$  electrons, yields the most accurate results. Since the relativistic effects on the outermost  $4s$  electrons are relatively small, the differences between RDFT and the perturbatively corrected results are not as large as that in  $3d$  transitions.

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