

# Relativistic density-functional calculations of interconfigurational energies for second and third transition-metal rows

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The fully relativistic density-functional theory (RDFT) is employed to calculate interconfigurational energies (ICE's), including  $s$ - $d$  transition energies,  $s$ - and  $d$ -ionization energies for the second and the third transition-metal atoms. Relativistic results from local-spin-density approximation (RLSD), the generalized gradient approximation (RGGA), and the approximation within the framework of the Krieger-Li-Iafrate treatment of the optimized effective potential (ROEP) incorporated by an explicit self-interaction correction term are reported. In addition, results from the simple perturbation procedure are also calculated for comparisons. Among these three exchange-correlation functionals, it is found that the RGGA yields the most accurate ICE's for both the  $5s$ - $4d$  and  $6s$ - $5d$  transition and  $4d$  ionization. For the  $5s$  and the  $6s$  ionization, the ROEP, which is expected to give a good description of the ICE's due to its correct long-range behavior, does not surpass the RLSD and RGGA. It is surprising to find that the simple perturbation method yields the same ICE's with those of the fully RDFT for the second transition-metal atoms. The validity of the perturbative procedure still persists for the lanthanum atom ( $Z=57$ ) and then fails dramatically for the rest of the third transition metals, with the  $f$  electrons being fully filled. From the similarity of calculations by means of the fully RDFT and the standard perturbation method, we are optimistic that the simple perturbation method not only greatly speeds up the computations in practice, but yields the reliable ICE's, up to La.

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## I. INTRODUCTION

The Hohenberg-Kohn-Sham density-functional theory (DFT) (Refs. 1 and 2) has become a powerful tool in the study of electronic structures and has been applied to a wide variety of systems such as atoms, molecules, and solid. The simplest form of DFT for practical applications is the local-density approximation (LDA), which is based on the properties of uniform electron gas. Various refinements of the LDA have been proposed by the introduction of improved versions of the exchange-correlation (xc) potential. For example, the local-spin-density (LSD) approximation,<sup>3</sup> in which the xc potential is formulated with a separate accumulation of the charges with up and down spins, gives a more accurate description for the studied systems than the LDA. Another important refinement of the LDA is the so-called generalized gradient approximation (GGA).<sup>5</sup> In general, this semilocal extension, based on the gradient expansion, significantly improves results over the standard LDA. Furthermore, the self-interaction-correction (SIC) concept,<sup>4</sup> which removes the spurious self-interaction by the electron, provides the proper asymptotic behavior and yields rather accurate ionization potential. For high- $Z$  systems relativistic effects should be included for the kinetic energy as well as the xc energy. In fact, even for systems with moderate  $Z$  the importance of the relativistic contributions have been addressed in the literature. For example, Kotochigova *et al.*<sup>6</sup> presented benchmark atomic calculations across the Periodic Table using the relativistic local-density (RLSD) approximation. Tong and Chu,<sup>7</sup> employing the optimized effective potential (OEP) with self-interaction correction, performed the relativistic density-functional (RDFT) calculations for atoms with  $Z$

$=2-106$ . Varga and co-workers<sup>8</sup> demonstrated the four-component RDFT results for diatomic molecules with Cu, Ag, and Au constituents, for a consistent examination of the importance of the relativistic effects. Researches on the relativistic effects for various systems have become more active recently.

Since the energy differences between the  $s$  and the  $d$  orbitals of transition metals are fairly small, interconfiguration energies (ICE's) provide a severe test for various DFT calculations. Martin and Hay<sup>9</sup> calculated ICE's of the three transition series within the Hartree-Fock (HF) framework with use of the Cowan and Griffin<sup>10</sup> scheme for relativistic corrections and found that the relativistic contributions for the ICE's are appreciable even for the first transition metals. Kutzler and Painter<sup>11</sup> presented ICE's of the  $3d$  atoms with the LSD and the GGA, respectively, and concluded that the gradient functionals provide some improvements over the LSD approximation, but the remaining errors are still large. Gritsenko *et al.*<sup>12</sup> reported calculations of the  $s$ - $d$  promotion for the first and the second transition-metal rows by using the weighted spin-density approximation. The scalar-relativistic<sup>13</sup> variant of their method nicely approximates the experiment for the first transition row but worsens the values of the corresponding nonrelativistic scheme for the  $4d$  atoms. Recently, Jeng and Hsue<sup>14</sup> investigated systematically the ICE's of the  $3d$  atoms within the RLSD and the fully relativistic generalized gradient approaches (RGGA) and concluded that the fully relativistic scheme seems to surpass the performance of the traditional perturbative treatment.

ICE's involve mainly valence electrons moving in the outermost atomic regimes where the relativistic effect is ex-

pected to be small. However, such effect causes the electron orbitals in the inner shells to shrink and results in a better screening of the nuclear charge for the outer electrons. Consequently, the relativistic effect indirectly influences the ICE's of the transition-metal atoms.

Relativistic effects can be investigated by utilizing the standard perturbation method, scalar relativistic scheme, or the fully relativistic approach. Among these frameworks the first is the simplest and is the least time-demanding. In the scalar relativistic approximation both the mass velocity and the Darwin corrections, instead of being treated as perturbative terms in the traditional perturbation method, are included in the Hamiltonian, and therefore the shrinkage of the wave functions for the inner orbitals are taken into account automatically. The ground electronic energies via this moderate scheme are supposed to be more accurate than those from the perturbation procedure. In the fully relativistic approach the spin-orbital splitting are inherently taken into account by replacing the Schrödinger-like Kohn-Sham equation with the Dirac-like one and therefore the calculated results should be the most reliable. It is the aim of the present work to create highly precise benchmark ICE's for the second and the third transition metals via the fully relativistic approach. The differences of results from the standard perturbation will also be examined. Here the LSD,<sup>3</sup> the GGA,<sup>5</sup> and the OEP (Ref. 7) schemes are employed to evaluate systematically the ICE's, including the *s-d* promotion energies, the *s*-ionization energies and the *d*-ionization energies. In addition, the calculated results presented in this paper are compared with those for the first transition-metal row.<sup>14</sup>

## II. FORMALISM

All the calculations carried out here are in the central-field approximation. Atomic units, i.e.,  $e = m = \hbar = 1$ , are adopted throughout and the energy is in the Hartree.

In the nonrelativistic limit, one solves self-consistently the classical Kohn-Sham (KS) equation

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\text{eff}}^\sigma(\vec{r}) \right\} \psi_{i\sigma}(\vec{r}) = \epsilon_{i\sigma} \psi_{i\sigma}(\vec{r}), \quad (1)$$

with the effective potential

$$v_{\text{eff}}^\sigma(\vec{r}) = -\frac{z}{r} + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}^\sigma(\vec{r}). \quad (2)$$

The total electron density is constructed from the wave function  $\psi_{i\sigma}(\vec{r})$  by

$$n(\vec{r}) = \sum_{i\sigma} |\psi_{i\sigma}(\vec{r})|^2, \quad (3)$$

where the sum is over all the occupied orbitals indexed by *i* with spin  $\sigma$ . The xc potential is obtained by

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

The xc energy functionals  $E_{xc}[n_+, n_-]$  used in this work are deduced from the Monte Carlo results of Ceperley and Alder,<sup>15</sup> as fitted by Perdew and Zunger.<sup>4</sup> The gradient functionals from Perdew and Wang<sup>5</sup> are employed for the GGA. The total energy of the ground state is given by a minimization of the energy functional

$$E_G = T_0[n] + \int d\vec{r} \left( -\frac{z}{r} \right) n(\vec{r}) + \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_{xc}[n_+, n_-]. \quad (5)$$

$T_0[n]$  is denoted as the noninteracting kinetic energy functional.

The implementation of the Krieger-Li-Iafate (KLI) approach of the optimized effective potential (OEP) by the incorporation of an explicit self-interaction correction (SIC) term<sup>7</sup> slightly modifies the KS equation. Following the KLI-OEP procedure,<sup>7</sup> we add the right-hand side of Eqs. (2) with an additional term, i.e.,

$$v_{\text{eff}}^\sigma(\vec{r}) = -\frac{z}{r} + \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + v_{xc}^\sigma(\vec{r}) + V_{SIC,\sigma}(\vec{r}), \quad (6)$$

where

$$V_{SIC,\sigma}(\vec{r}) = \frac{\sum_i n_{i\sigma}(\vec{r}) \{v_{i\sigma}(\vec{r}) + [\bar{V}_{SIC,i\sigma} - \bar{v}_{i\sigma}]\}}{\sum_i n_{i\sigma}(\vec{r})}, \quad (7)$$

$$v_{i\sigma}(\vec{r}) = - \int d\vec{r}' \frac{n_{i\sigma}(\vec{r}')}{|\vec{r}-\vec{r}'|} - \frac{\delta E_{xc}[n_{i\sigma}, 0]}{\delta n_{i\sigma}(\vec{r})}, \quad (8)$$

and

$$\bar{V}_{SIC,i\sigma} = \langle \psi_{i\sigma} | V_{SIC,\sigma}(\vec{r}) | \psi_{i\sigma} \rangle, \quad (9)$$

$$\bar{v}_{i\sigma} = \langle \psi_{i\sigma} | v_{i\sigma}(\vec{r}) | \psi_{i\sigma} \rangle. \quad (10)$$

The total energy functional is now given by

$$E_G^{SIC}[\{\psi_{i\sigma}\}] = E_G - \{J[n_{i\sigma}] + E_{xc}[n_{i\sigma}, 0]\}. \quad (11)$$

Here

$$J[n_{i\sigma}] = \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n_{i\sigma}(\vec{r})n_{i\sigma}(\vec{r}')}{|\vec{r}-\vec{r}'|}, \quad (12)$$

and  $E_G$  is given in Eqs. (5).

The complete RDFT,<sup>16</sup> based on the underlying quantum field theory, has been addressing inherently the formidable question of renormalization. Thus, while RDFT provides a rather general and extremely powerful approach to relativistic problems in principle, some physically motivated approximations are unavoidable in order to make RDFT a workable scheme in practice. Since the purpose of this work only aims at electronic structure calculations, the omission of

TABLE I.  $5s$ - $4d$  transition energies (eV).

Atom	Expt. <sup>a</sup>	NHF <sup>b</sup>	HFR <sup>b</sup>	LSD	RLSD	LSD (rel)	GGA	RGGA	GGA (rel)	OEP	ROEP	OEP (rel)
Y	1.36	0.42	0.75	0.71	1.05	1.06	0.88	1.22	1.23	0.53	0.89	0.88
Zr	0.59	-0.40	-0.01	-0.32	0.09	0.10	-0.15	0.27	0.27	-0.51	-0.09	-0.09
Nb	-0.18	-1.24	-0.80	-1.38	-0.92	-0.90	-1.21	-0.74	-0.73	-1.59	-1.11	-1.11
Mo	-1.47	-2.89	-2.37	-2.46	-1.95	-1.92	-2.30	-1.79	-1.76	-2.69	-2.17	-2.15
Tc	0.41	0.20	0.75	-0.66	-0.08	-0.05	-0.40	0.17	0.20	-0.89	-0.28	-0.27
Ru	-0.87	-1.42	-0.74	-1.70	-1.00	-1.00	-1.46	-0.77	-0.77	-1.95	-1.22	-1.23
Rh	-1.63	-2.19	-1.40	-2.77	-1.95	-1.97	-2.56	-1.77	-1.78	-3.04	-2.20	-2.22
Pd	-2.43	-3.01	-2.09	-3.87	-2.98	-2.98	-3.69	-2.83	-2.82	-4.16	-3.24	-3.24
Ag	-3.97	-4.91	-3.86	-4.99	-4.00	-4.00	-4.84	-3.89	-3.88	-5.29	-4.31	-4.28
$ \Delta E $		0.81	0.43	1.03	0.40	0.39	0.84	0.26	0.25	1.27	0.62	0.62

<sup>a</sup>Reference 18.<sup>b</sup>Reference 9.

the radiative corrections (often called no-sea approximation) should be appropriate. Under such a situation, the fully RDFT can be obtained from the nonrelativistic DFT by substituting the relativistic kinetic energy operator  $-i\hbar c\vec{\alpha}\cdot\vec{\nabla}$  for its nonrelativistic counterpart  $-\frac{1}{2}\vec{\nabla}^2$  and using the relativistic version of the xc energy functionals. The relativistic wave functions, in spherically symmetric approximations, satisfy the following coupled-differential equations:

$$\begin{aligned} \frac{dF_{i\sigma}(r)}{dr} - \frac{\kappa}{r}F_{i\sigma}(r) &= \frac{1}{c}[v_{\text{eff}}^{\sigma}(r) - \epsilon_{i\sigma}]G_{i\sigma}(r), \\ \frac{dG_{i\sigma}(r)}{dr} + \frac{\kappa}{r}G_{i\sigma}(r) &= \frac{1}{c}[2c^2 + \epsilon_{i\sigma} - v_{\text{eff}}^{\sigma}(r)]F_{i\sigma}(r), \end{aligned} \quad (13)$$

where  $F_{i\sigma}(r)$  and  $G_{i\sigma}(r)$  are the major and minor components of the radial Dirac wave functions with spin  $\sigma$ . The index  $\kappa$  is the usual Dirac's quantum number and  $c$  is the speed of light, which is set as 137.035 989 5 throughout this work. The total electron density then reads

$$n(r) = \sum_{i\sigma} [ |G_{i\sigma}(r)|^2 + |F_{i\sigma}(r)|^2 ]. \quad (14)$$

It is well known that the electron spin is not a good quantum number in the relativistic theory due to the spin-orbital interaction and therefore the spin-density concept in the RDFT is only an approximation. But in our case, such an approximation is quite good since the electron spin-spin interaction can still compete with the spin-orbit interaction for the valence orbitals, while for the inner-shell orbitals, all the electrons are spin paired. The xc energy functional is corrected relativistically due to MacDonald and Vosko.<sup>17</sup> The experimental data from Ref. 18 are presented in terms of the nonrelativistic notations. However, for each notation there involves, in general, several relativistic configurations. Therefore the surveys from the fully RDFT are averaged over all the relevant relativistic configurations in the uncoupled scheme for simplicity, as discussed in Ref. 19.

Relativistic contributions may also be studied in a simpler fashion, on the basis of the perturbation theory. Under the condition that the effective potential  $v_{\text{eff}}^{\sigma} \ll c^2$ , the four-component Dirac equations can be approximated, to order of  $1/c^2$ , by

$$\left[ -\frac{1}{2}\nabla^2 + v_{\text{eff}}^{\sigma}(\vec{r}) - \frac{\mathbf{p}^4}{8c^2} + \frac{\nabla\cdot\mathbf{E}}{8c^2} \right] \Psi_{i\sigma} = \epsilon_{i\sigma} \Psi_{i\sigma}, \quad (15)$$

where  $\Psi_{i\sigma}$  is the nonrelativistic limit of the major part  $G_{i\sigma}$ . The third and last terms in the bracket in Eqs. (15) are the mass-velocity term and the Darwin shift, respectively. The spin-orbital coupling effect is not considered throughout this work. With the unperturbed wave functions in hand, which will be achieved self-consistently from Eqs. (1) to (3), it is legitimate in most situations to treat both corrections as perturbative terms. Thus the relativistic many-electron properties can be demonstrated by the perturbative manipulation of the nonrelativistic wave functions.

### III. RESULTS AND DISCUSSION

#### A. Second transition row

##### 1. $5s$ - $4d$ transition energies

The  $5s$ - $4d$  transition energy is the energy difference between the  $s$ -rich and the  $d$ -rich configurations, viz., the energy needed for one of the valence electrons to transit from  $5s$  to  $4d$  orbitals. It is defined by

$$\Delta_{sd} = E(\text{core}, 5s^1 4d^{n-1}) - E(\text{core}, 5s^2 4d^{n-2}), \quad (16)$$

where  $n$  is the number of valence electrons in the atom. In Table I, we list the calculations of the LSD, the GGA, and the OEP. Relativistic results with the fully RDFT, labeled as RLSD, RGGA, and ROEP, and with the perturbation procedure (labeled "rel") are also shown in this table. The nonrelativistic (NHF) and relativistic (HFR) Hartree-Fock calculations by Martin and Hay<sup>9</sup> are included for comparisons. The results clearly show that the LSD understates the  $5s$ - $4d$  transfer energy, followed by a mean error  $\Delta E$  1.03 eV. This

TABLE II. Total energies of various configurations of Ag from both the fully RGGGA and the standard perturbation method, with the unit in hartree. Here  $P4$  and  $Dw$  stand for the mass-velocity correction and the Darwin shift, respectively.

Configuration	GGA	P4	Dw	GGA (rel)	RGGA
$5s^24d^9$	-5200.1257	-396.4851	285.3651	-5311.2457	-5310.5490
$5s^14d^{10}$	-5200.3036	-396.4056	285.3208	-5311.3884	-5310.6917
$5s^14d^9$	-5199.8070	-396.4452	285.3408	-5310.9114	-5310.2137
$5s^24d^8$	-5199.4971	-396.5527	285.4011	-5310.6487	-5309.9511

is similar to what occurs in the  $4s$ - $3d$  transfer energy of the first transition metals.<sup>11,14</sup> The OEP, which warrants a more correct description of the asymptotic behavior, actually yield an even worse result than the LSD with an error  $\overline{\Delta E}$  of 1.27 eV. On the other hand, the GGA, which accounts for the gradient effects, provides improved results with a smaller mean deviation of 0.84 eV.

By including the relativistic contributions, significantly improved results are obtained from RGGGA with the  $\overline{\Delta E}$  being 0.26 eV. This is about half the mean error of 0.43 eV from the HFR scheme by Martin and Hay,<sup>9</sup> where the non-spherical effects are taken into account. The improvement by the relativistic effect is also seen in the results from the RLSD and the ROEP, of which the mean errors are considerably reduced to 0.40 and 0.62 eV, respectively. Actually, the subtle competitions of the  $s$ - and the  $d$ -orbital energies make it difficult to achieve accurate theoretical results for  $s$ - $d$  transitions. For some atoms such as Zr and Tc, even the signs of the results are not correct in most situations. Yet, as shown in Table I, the RGGGA reproduces the correct signs of the  $5s$ - $4d$  ICE's throughout the whole row. Therefore both the relativistic and gradient effects play a very important role in dealing with the  $s$ - $d$  promotion of the second transition-metal series.

Note that the relativistic DFT calculations by the perturbation approach yield almost the same results with those obtained by solving the Dirac equations directly. This is evident by comparing columns 6 and 7 in Table I for the local-spin density approximation, columns 9 and 10 for the gradient functional, and columns 12 and 13 for the refined optimized effective potential, respectively. This conclusion is slightly surprising considering that the magnitude of the perturbation contributions for the atoms concerned here with atomic numbers range  $Z=40$ -48. In this respect, we display in Table II the calculated total energies of various configurations for the silver atom, obtained from both the GGA and RGGGA approaches. The mass velocity ( $P4$ ) and the Darwin ( $Dw$ ) corrections for the nonrelativistic calculations are also shown in the table. As expected, the total energies from the GGA and the RGGGA differ by a substantial amount. With the perturbation correction for the relativistic effects, the total energies differ from the RGGGA by about 20 eV. However, when calculating the difference between the corrected total energies according to Eqs. (16), we obtain the same ICE's from both approaches. This means that the relativistic modifications of the wave functions in the inner orbitals have the same effect on the energies of the valence  $5s$  and  $4d$  orbit-

als. To probe the range for this cancellation, we also investigate the third transition metal and will discuss later. In short, for the ICE's, which deal with the energy differences between different configurations, the perturbative correction to the relativistic effects seems to be a good approximation, at least up to Cd ( $Z=48$ ).

## 2. $5s$ Ionization energies

In contrast to the case for the first transition-metal row, the valence electrons in the second row tend to favor the  $d$  orbitals rather than the  $s$  orbital. The configurations of the experimental ground states for the  $4d$  atoms are summarized into three categories:  $5s^24d^{n-2}$  for Y, Zr, Tc, and Cd;  $5s^14d^{n-1}$  for Nb, Mo, Ru, Rh, and Ag; and  $5s^0d^{10}$  for Pd. For convenience we will select the  $5s^24d^{n-2}$  configurations as the initial state, and define the  $5s$  ionization energy as

$$\Delta_{\text{ion}} = E(\text{core}, 5s^14d^{n-2}) - E(\text{core}, 5s^24d^{n-2}). \quad (17)$$

The calculated results are listed in Table III, in which the labels are the same as those in Table I.

The calculated  $5s$  removal energies agree quite well with the experiment. Table III displays that the results from the GGA approach, which includes the gradient corrections to take care of the nonuniformity of the charge densities, yields the smallest deviations among all the approaches. The  $\overline{\Delta E}$  of the nonrelativistic GGA (column 8) is 0.10 eV, and the corresponding mean errors from the LSD and OEP are 0.15 eV (column 5) and 0.17 eV (column 11), respectively. This situation differs from the case for the first transition-metal atoms,<sup>14</sup> where the SIC-LSD rather than the GGA yielded the smallest mean error for the  $4s$  ionization energy. Similar to the SIC-LSD, the OEP approach provides a proper description for the long-range potential of the outer electron and is expected to give the best  $5s$  binding. Our results seem to imply that the gradient correction plays a more important role in the  $5s$  orbitals. It is clear from Table III that all the nonrelativistic DFT results underestimate the  $s$ -ionization energies for the first half of the series but are in good agreement with the experiment for the second half, especially those from the LSD and the OEP approaches.

The fully RDFT results systematically predict stronger binding of the  $5s$  electrons across the  $4d$  series. Table III shows that the inclusion of relativistic corrections causes a positive shift from the nonrelativistic calculations. Therefore the RDFT improves the  $5s$ -ionization energies for the first half of the second transition-metal series, but overestimate

TABLE III.  $5s$  ionization energies (eV).

Atom	Expt. <sup>a</sup>	NHF <sup>b</sup>	HFR <sup>b</sup>	LSD	RLSD	LSD (rel)	GGA	RGGA	GGA (rel)	OEP	ROEP	OEP (rel)
Y	6.61	4.72	4.81	6.28	6.42	6.42	6.43	6.57	6.57	6.23	6.38	6.38
Zr	6.95	5.05	5.18	6.57	6.74	6.75	6.71	6.89	6.89	6.53	6.71	6.70
Nb	6.93	5.15	5.29	6.77	6.98	6.97	6.91	7.12	7.11	6.74	6.95	6.96
Mo	7.22	5.23	5.37	6.93	7.16	7.15	7.06	7.29	7.28	6.91	7.14	7.14
Tc	7.28	5.29	5.43	7.06	7.31	7.30	7.18	7.43	7.42	7.05	7.30	7.30
Ru	7.59	5.68	5.87	7.58	7.90	7.88	7.67	7.97	7.96	7.56	7.88	7.88
Rh	7.98	6.03	6.28	7.98	8.36	8.34	8.05	8.41	8.39	7.97	8.34	8.33
Pd	8.32	6.36	6.66	8.32	8.75	8.73	8.38	8.78	8.76	8.31	8.74	8.72
Ag	8.64	6.66	7.02	8.62	9.10	9.07	8.67	9.12	9.10	8.60	9.09	9.07
Cd	8.99	6.93	7.34	8.89	9.42	9.39	8.94	9.43	9.41	8.87	9.41	9.39
$ \overline{\Delta E} $		1.94	1.73	0.15	0.26	0.24	0.10	0.27	0.26	0.17	0.24	0.25

<sup>a</sup>Reference 18.<sup>b</sup>Reference 9.

the ionization energies with growing errors in the second half. The mean errors of the RDFT are 0.26, 0.27, and 0.24 eV for the RLSD, RGGA, and ROEP, respectively. By comparison of columns 6 and 7 for the LSD (rel), columns 9 and 10 for the GGA (rel), and columns 12 and 13 for the OEP (rel), it indicates that both the perturbation method and the fully relativistic approach yield the similar ICE's of the  $5s$  ionization. The maximum difference between these two approaches is 0.03 eV.

The Hartree-Fock results by Martin and Hay<sup>9</sup> are also included in Table III for comparisons. These mean errors, with 1.94 and 1.73 eV for NHF and HFR, respectively, are much larger than all the results obtained from the DFT, with or without the relativistic corrections. The Hartree-Fock scheme consistently underestimates the  $5s$  binding energy by a significant amount.

### 3. $4d$ ionization

The  $d$  ionization energy is usually defined as the energy needed to ionize a  $d$ -shell electron in  $s$ -rich configurations. In this work we define the  $d$  ionization as

$$\Delta_{dion} = E(\text{core}, 5s^2 4d^{n-3}) - E(\text{core}, 5s^2 4d^{n-2}). \quad (18)$$

Our calculations are shown in Table IV. Due to the lack of the relevant values from Ref. 18, the experiment for Nb, Mo, Tc, Rh, and Pd is not presented in this table. Martin and Hay<sup>9</sup> reported the calculation for  $d$  ionization from the  $5s^2 4d^{10}$  state of the Cd atom but no data are available for the ionization from the  $5s^2 4d^{n-2}$  states of the other  $4d$  transition metals.

Since the energies needed to ionize the  $d$  electron is larger due to the stronger binding and localization, the calculated ICE's have a wider variation as the number of  $d$  electrons changes. As shown in this table, all the nonrelativistic DFT results overestimate the  $4d$  ionization energies. The mean errors for the  $4d$  ionization are much larger than those of the  $5s$  ionization, reflecting the difficulties for a successful description of the  $4d$  binding. The GGA yields a mean error of 0.79 eV (column 6) which is slightly smaller than 0.89 eV (column 3) of the LSD. The OEP, which essentially aimed at a better description for the asymptotic behavior of the outermost  $5s$  electrons, actually yields the worst  $\overline{\Delta E}$  of 1.21 eV

TABLE IV.  $4d$  ionization energies (eV).

Atom	Expt. <sup>a</sup>	LSD	RLSD	LSD (rel)	GGA	RGGA	GGA (rel)	OEP	ROEP	OEP (rel)
Y	6.54	6.89	6.51	6.49	6.85	6.47	6.45	7.12	6.72	6.72
Zr	8.67	8.61	8.18	8.16	8.56	8.13	8.11	8.86	8.41	8.41
Nb		10.25	9.76	9.75	10.21	9.72	9.71	10.52	10.01	10.02
Mo		11.85	11.31	11.29	11.82	11.28	11.26	12.15	11.58	11.59
Tc		13.42	12.85	12.80	13.40	12.83	12.78	13.75	13.16	13.13
Ru	10.77	12.05	11.44	11.39	11.80	11.20	11.14	12.39	11.76	11.73
Rh		13.82	13.12	13.10	13.60	12.90	12.88	14.18	13.46	13.47
Pd		15.55	14.75	14.76	15.37	14.57	14.58	15.93	15.10	15.14
Ag	15.58	17.25	16.41	16.38	17.11	16.27	16.25	17.65	16.78	16.79
Cd	17.86	18.93	18.01	17.98	18.83	17.91	17.89	19.36	18.46	18.42
$ \overline{\Delta E} $		0.89	0.43	0.42	0.79	0.36	0.34	1.21	0.65	0.65

<sup>a</sup>Reference 18.

TABLE V.  $6s$ - $5d$  transition energies (eV).

Atom	Expt. <sup>a</sup>	NHF <sup>b</sup>	HFR <sup>b</sup>	LSD	RLSD	LSD (rel)	GGA	RGGA	GGA (rel)	OEP	ROEP	OEP (rel)
La	0.36	-0.98	-0.30	-0.54	0.14	0.13	-0.41	0.28	0.27	-0.71	0.00	-0.03
Hf	1.69	-0.38	0.95	-0.10	1.35	1.20	0.14	1.60	1.46	-0.26	1.23	1.05
Ta	1.04	-1.28	0.21	-1.15	0.45	0.30	-0.90	0.72	0.57	-1.33	0.32	0.12
W	-0.18	-2.95	-1.29	-2.22	-0.50	-0.64	-1.98	-0.24	-0.38	-2.42	-0.66	-0.83
Re	1.76	-0.04	1.76	-0.59	1.35	1.19	-0.32	1.55	1.38	-0.81	1.18	0.97
Os	0.75	-1.63	0.55	-1.60	0.83	0.41	-1.31	0.90	0.63	-1.84	0.51	0.19
Ir	0.40	-2.43	0.09	-2.63	-0.09	-0.42	-2.37	0.17	-0.22	-2.90	-0.22	-0.65
Pt	-0.64	-3.28	-0.40	-3.70	-0.88	-1.28	-3.47	-0.74	-1.12	-4.00	-1.11	-1.52
Au	-1.74	-5.13	-1.86	-4.78	-1.71	-2.17	-4.61	-1.62	-2.06	-5.08	-1.95	-2.42
$\overline{\Delta E}$		2.39	0.47	2.31	0.30	0.52	2.07	0.15	0.32	2.53	0.46	0.73

<sup>a</sup>Reference 18.<sup>b</sup>Reference 9.

(column 9). A similar trend was found in the  $3d$  row.<sup>14</sup> Hence the gradient effect is dominant in the  $4d$ -electron removal due to the rapid variation of the electron density in these inner regimes.

With the relativistic corrections, all the fully RDFT approaches lead to lower results for the  $4d$  ionization energies. The RGGA, the RLSD, and the ROEP create better binding energies with mean errors of 0.36, 0.43, and 0.65 eV, respectively. Inclusion of relativistic effects reduces the deviations from the nonrelativistic results by half.

Looking at columns 5, 8, and 11 in Table IV, we again come to the conclusion that perturbation corrections for the relativistic effects agree very well with those obtained from the fully RDFT approaches. To sum up, the similarity of the three kinds of ICE's concerned in the present work by the perturbation and the fully RDFT demonstrates the usefulness and accuracy of the perturbative procedure. Thus the perturbation approach is not only computationally more efficient but maintains good precision.

### B. Third transition row:

#### 1. $6s$ - $5d$ transition energies

The  $6s$ - $5d$  transition energy is the energy needed for one of the valence electrons to transit from  $6s$  to  $5d$  orbitals, which is defined as

$$\Delta_{sd} = E(\text{core}, 6s^1 5d^{n-1}) - E(\text{core}, 6s^2 5d^{n-2}), \quad (19)$$

with  $n$  valence electrons in the atom. The corresponding results are listed in Table V. Similar trends with the  $4d$  row are concluded in this table. That is, the LSD (column 5) understates the  $6s$ - $5d$  transfer energy with a mean error  $\overline{\Delta E}$  2.31 eV; the OEP (column 11) results in the worse values than the simple LSD with an error  $\overline{\Delta E}$  of 2.53 eV; and the GGA (column 8) provides improved results with a smaller mean deviation of 2.07 eV.

Solving the Dirac equation directly leads to significantly better results. The  $\overline{\Delta E}$  are reduced markedly to 0.30, 0.15, and 0.46 eV for RLSD (column 6), RGGA (column 9), and

ROEP (column 12), respectively. The RGGA, just like the treatment for the second transition metal, not only obtains the best values among these three exchange-correlation functionals but gives the correct signs throughout the whole row. The HFR (column 4), in which the nonspherical effect is involved, is accompanied with the  $\overline{\Delta E}$  of 0.47 eV, three times larger than that of the RGGA. Therefore, combined with the preceding conclusion of the  $4d$  row and that of Ref. 14, it is certainly confirmed that both the relativistic and gradient effects are indeed two important factors in dealing with the  $s$ - $d$  promotion for all the transition-metal atoms.

It is interesting to note that the similarity of the calculations by the perturbation approach and the fully RDFT is valid only for the lanthanum ( $Z=57$ ), the first atom of the  $5d$  row, and fails dramatically for the rest. This conclusion should not be surprising since there are 14 lanthanide elements between the lanthanum and the hafnium atom ( $Z=72$ ), with the  $4f$  orbital being fully filled. This abrupt increase of the atomic number so large that the extension of the simple perturbative procedure is damaged. By numerical comparisons in Table V it is also observed that the calculations from the perturbative approaches (columns 7, 10, and 13) are always between those of the nonrelativistic treatments and of the fully RDFT schemes. This is no doubt a consequence of the incomplete treatment of relativistic corrections for atoms with heavier atomic number.

#### 2. $6s$ ionization energies

The  $6s$  ionization energy is the energy needed to remove one of the outermost  $6s$  electrons from the  $6s^2 5d^{n-2}$  configuration and defined as

$$\Delta_{s\text{ion}} = E(\text{core}, 6s^1 5d^{n-2}) - E(\text{core}, 6s^2 5d^{n-2}). \quad (20)$$

The final results are summarized in Table VI. The experimental data of the hafnium and iridium ( $Z=77$ ) from Ref. 18 are indeterminate and hence not listed in this table. Several aspects of these calculations is noteworthy to be pointed out here.

TABLE VI.  $6s$  ionization energies (eV).

Atom	Expt. <sup>a</sup>	NHF <sup>b</sup>	HFR <sup>b</sup>	LSD	RLSD	LSD (rel)	GGA	RGGA	GGA (rel)	OEP	ROEP	OEP (rel)
La	5.87	4.13	4.29	5.57	5.82	5.81	6.70	5.96	5.93	5.53	5.79	5.77
Hf		5.07	5.61	6.68	7.49	7.31	6.85	7.66	7.49	6.64	7.44	7.28
Ta	7.90	5.13	5.71	6.86	7.75	7.55	7.01	7.92	7.71	6.83	7.73	7.53
W	7.94	5.17	5.77	6.99	7.96	7.73	7.13	8.11	7.88	6.98	7.95	7.74
Re	7.88	5.19	5.79	7.10	8.14	7.88	7.22	8.27	8.00	7.09	8.14	7.90
Os	8.77	5.58	6.40	7.61	8.88	8.57	7.69	8.92	8.62	7.61	8.88	8.60
Ir		5.94	6.97	8.00	9.47	9.10	8.06	9.46	9.11	8.00	9.48	9.13
Pt	9.22	6.26	7.51	8.33	9.97	9.54	8.37	9.93	9.53	8.32	9.99	9.58
Au	9.76	6.56	8.03	8.60	10.43	9.93	8.64	10.36	9.89	8.61	10.45	9.98
Hg	10.43	6.83	8.51	8.85	10.84	10.28	8.87	10.75	10.22	8.87	10.87	10.35
$ \overline{\Delta E} $		2.87	1.97	0.98	0.30	0.18	0.98	0.31	0.15	0.99	0.32	0.19

<sup>a</sup>Reference 18.<sup>b</sup>Reference 9.

First, in contrast to those in Table III in the present work and Table II in Ref. 14, which both show that the calculated  $s$  ionizations from the fully RDFT is even worse than those from the nonrelativistic DFT for the first two transition-metal rows, Table VI displays the usually intuitive conclusion, i.e., the values from the RDFT are much improved than those without relativistic effects. This means that the fully RDFT, which becomes increasingly more important with increasing atomic number, could alter the trends exhibited. The reductions are 0.98–0.30 eV for the LSD (columns 5 and 6), 0.98–0.31 eV for the GGA (columns 8 and 9), and 0.99–0.32 eV for the OEP (columns 11 and 12), respectively.

Second, the mean errors of (R)LSD, (R)GGA, and (R)OEP are qualitatively the same. With more detailed analyses about the data in this table, it is found that the (R)LSD are very close to the (R)OEP and slightly different from the (R)GGA. Actually, the complete fullness of the  $4f$  orbital will enhance the shielding effect and result in more diffusion of the outermost  $6s$  electrons. And quite likely it is seems to indicate that the charge density of the outermost regime is adequately dilute so that both (R)LSD and (R)OEP give the same description for the  $6s$  ionization yet with the gradient expansion of charge densities in such regimes some minor contributions still arise.

Third, the perturbative results accurately reproduce the fully RDFT ones for the La atom whereas such similarity is destroyed for the rest of the  $5d$  row, in line with the conclusion of the  $6s$ - $5d$  promotion. However, it is very surprising that the mean deviations yielded from the perturbation, which are 0.18, 0.15, and 0.19 eV for the LSD (rel) (column 7), the GGA (rel) (column 10), and the OEP (rel) (column 13), respectively, are much smaller than those with the RDFT. This seems somewhat contradictory to the expectation that the fully RDFT should describe more reliably such a situation. No definitive explanation is offered for this observation because the standard perturbation is insufficient to give a precise description for heavy atoms. Maybe this reflects indirectly that the application of the fully RDFT in this situation should be reexamined since the fully RDFT is

based on the single-particle approximation and drops some delicate effects mentioned in Sec. II.

Finally, the HFR (column 4) yields the  $\overline{\Delta E}$  of 1.97 eV, almost six times larger than the present calculations. Hence our computations of the  $6s$  ionization based on the density-functional theory surpass those with the Hartree-Fock approach, which accounts for the nonspherical effect.

### 3. $5d$ ionization

Analogous to the  $4d$  ionization, the  $5d$  ionization is defined as

$$\Delta_{d-ion} = E(\text{core}, 6s^2 5d^{n-3}) - E(\text{core}, 6s^2 5d^{n-2}). \quad (21)$$

The present computations are shown in Table VII along with the available experiment from Ref. 18, no theoretical calculations in the work by Martin and Hay<sup>9</sup> were reported and the relevant HF values are missing in this table.

Again, for the lanthanum atom both the perturbation approach and the fully RDFT yield similar ionization energies. Moreover, it is found that this coincidence also holds for other atoms, especially for the first half of the  $5d$  series. This opposite behavior exhibited in the  $5d$  ionization as compared to the previous conclusion of the  $6s$ - $5d$  promotion and  $6s$  removal is at first sight puzzling. One possible explanation for this phenomenon is that the  $5d$  electrons are influenced by a relatively smaller effective atomic number  $Z^*$ , primarily due to the shielding from the  $4f$  shell, and so the perturbation procedure is once again valid in this situation. One may throw doubt upon this argument since the  $6s$  electron is shielded, too, yet the perturbation is broken down in the treatment of the  $6s$  ionization. However, one should keep in mind that only could the orbital with the quantum number  $l$  being zero, i.e., the  $s$  orbital, have opportunities of being near the nucleus. Numerical analyses show that in the region  $r \leq 0.1a_H$  there are several percentages of the  $6s$  electron for the  $5d$  row. This portion plays an important role in considering the relativistic effect since it is not screened by the outer shells. Furthermore, the relativistic effect of this part is

TABLE VII.  $5d$  ionization energies (eV).

Atom	Expt. <sup>a</sup>	LSD	RLSD	LSD (rel)	GGA	RGGA	GGA (rel)	OEP	ROEP	OEP (rel)
La	5.76	7.38	6.64	6.64	7.34	6.62	6.61	7.53	6.79	6.82
Hf	7.23	8.29	7.07	7.05	8.17	6.97	6.95	8.47	7.19	7.25
Ta	8.77	9.80	8.41	8.45	9.67	8.29	8.32	10.02	8.58	8.68
W		11.27	9.80	9.80	11.15	9.67	9.67	11.51	10.00	10.06
Re	9.70	12.73	11.19	11.13	12.63	11.07	11.02	13.01	11.43	11.43
Os		11.55	9.93	9.88	11.26	9.69	9.63	11.85	10.19	10.22
Ir		13.19	11.35	11.40	12.89	11.07	11.12	13.51	11.64	11.76
Pt	12.97	14.78	12.74	12.87	14.51	12.47	12.60	15.13	13.03	13.25
Au	14.24	16.35	14.26	14.31	16.13	14.03	14.09	16.72	14.58	14.71
Hg		17.91	15.66	15.73	17.75	15.49	15.56	18.30	16.01	16.15
$ \Delta E $		1.78	0.52	0.50	1.63	0.61	0.57	2.04	0.56	0.61

<sup>a</sup>Reference 18.

significantly large due to being very close to the nuclear charge. As a result, the penetration into the proximity of the nucleus, which does not occur in the  $d$  electron, will enhance the relativistic contributions of the  $s$  ionization considerably. Maybe this assertion could offer guidance to investigate the puzzling conclusions shown in Table III in the present work and Table II in Ref. 14 that the calculated  $s$  ionizations for the atoms of the first two transition-metal rows ( $3d$  and  $4d$  atoms) with the RDFT are even worse than those with non-relativistic DFT treatments.

All the RDFT approaches improve the  $5d$  binding energy. The lowerings of the deviations are from 1.78 to 0.52 eV for the LSD (columns 3 and 4), 1.63 to 0.61 eV for the GGA (columns 6 and 7), and 2.04 to 0.56 eV for the OEP (columns 9 and 10), respectively. Consequently, this means, with the previous conclusions, that the solving of the Dirac equation directly serves as a more suitable tool to study the ICE's of the transition-metal rows.

#### IV. CONCLUSIONS

In this work, the fully RDFT, including the RLSD, the RGGA, and the ROEP, as well as the perturbative procedures are employed to investigate the relativistic contributions to the ICE's of the  $s$ - $d$  transition, the  $s$  ionization, and the  $d$  ionization for the second and the third transition-metal rows. Among these the RGGA obtains the best values for the  $5s$ - $4d$ , the  $6s$ - $5d$  transition, and the  $4d$  ionization. This seemingly indicates that both the gradient corrections and

relativistic effects are dominant in dealing with such ICE's, especially for the cases involving the  $d$  electron with the rapid variation of the electronic density.

For the  $5s$  and the  $6s$  ionizations, no improvement over the results from the RLSD and the RGGA was furnished from the ROEP approach, in spite of the fact that the ROEP gives a correct description for the long-range potential of the outermost electrons. Nevertheless, this scheme yields results in excellent agreements with the experiment for the first half of both the  $4d$  and  $5d$  rows. Consideration of relativistic corrections for the  $5s$  binding energies leads to the worse values than those with the nonrelativistic approach. Thus further work will be expected to appear.

The ICE's achieved by the simple perturbation procedure are essentially identical to those from the fully RDFT throughout the second transition-metal row. This identity is also true for the first atom of the third row and then fails for the rest, with the  $4f$  orbital being fully filled. Moreover, the perturbation provides a successful description of the  $5d$  ionization due to the nice shielding by the closed  $f$  shell. The similarity of ICE's by means of the fully RDFT and the standard perturbation method suggests that the latter is not only computationally much less expensive but create precisely reliable ICE's, up to La ( $Z=57$ ).

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