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Valence-orbital ionization potentials for third-row transition elements

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Valence-orbital ionization potentials (VOIP's) for 5*d* transition elements have been derived by performing fully relativistic self-consistent numerical local-density atomic calculations. The von Barth–Hedin–Lundqvist local exchange and correlation potential was employed. In order to evaluate the accuracy of the calculated VOIP's, theoretical ionization potentials were compared with experimental results obtained from data on the atomic spectra of neutral and of singly, doubly, and triply charged 5*d* transition elements, for the few atomic configurations for which measurements are available. Good agreement was obtained between experimentally derived and theoretical ionization potentials, the latter calculated by a "transition-state" procedure. Comparison was also made with results obtained by performing nonrelativistic local-density calculations. The use of the Kohn-Sham local exchange-only potential was also investigated, in order to assess the effect of correlation corrections included in the von Barth–Hedin–Lundqvist potential. Moment-polarized relativistic local-density calculations were also performed and compared with the available experimental results.

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I. INTRODUCTION

Semiempirical molecular-orbital (MO) calculations of the electronic structure of molecules, performed with methods derived from the zero-differential overlap (ZDO) approximation, are characterized by the use of atomic spectroscopic information in the determination of the one-center one-electron matrix elements and in the evaluation of two-electron integrals [1–6]. The one-center one-electron integrals (also called one-center "core" integrals [1]) are systematically related to valence-orbital ionization potentials (VOIP's) (or VOIP's plus electron affinities) [1], which depend on the charge and configuration of the atom. By definition, a VOIP is the energy difference between the average energy of the states pertaining to a given configuration of the ionized and neutral atom. VOIP's are also required to evaluate the one-center two-electron integrals in Pariser's approximation [7] and the two-electron two-center integrals in the empirical Weiss-Mataga-Nishimoto formula [5,8]. Electron affinities, which are often unknown for transition elements, are also estimated by an isoelectronic extrapolation using the appropriate VOIP parameters [9].

In the semiempirical extended Hückel method, the variation known as the self-consistent charge and configuration (SCCC) method for transition-metal complexes [10(b)] estimates the diagonal Hamiltonian matrix elements as linear combinations of VOIP's for several configurations, where each VOIP is assumed to have a quadratic charge dependency, in order to adequately represent the fractional populations present in the complex.

For the 3*d* and 4*d* transition elements, the dependence of the VOIP's on both charge and configuration can be obtained from the large amount of available data on atomic spectra [11], and thus complete sets of VOIP parameters have been published in the literature [12–14]. For 5*d* transition elements, however, the situation is quite different, since the experimental data are very scarce and do not allow a reliable estimate of VOIP parameters. Consequently, for third-row transition elements no complete set of VOIP's as a function of the atomic charge and configuration is available in the literature.

For these reasons, we have obtained theoretically a complete set of VOIP parameters, as a function of charge and configuration, for 5*d* transition elements by performing fully relativistic self-consistent numerical local-density (LD) atomic calculations [15]. Local-density calculations are an adequate tool to derive VOIP's, since average energies over the states of a configuration are obtained. The von Barth–Hedin–Lundqvist (VBHL) local exchange and correlation potential [16,17] was employed and the "transition-state" concept [18] was used to define ionization potentials.

In Sec. II we give a summary of some uses of VOIP's in semiempirical methods. In Sec. III we describe the theoretical method employed here. In Sec. IV we compare theoretical and experimentally derived VOIP's, when available. In Sec. V we give calculated VOIP parameters for all 5*d* elements and in Sec. VI we summarize our conclusions.

II. VOIP'S IN SEMIEMPIRICAL METHODS

Most semiempirical MO methods, derived from the ZDO approximation, estimate part or all of the diagonal matrix elements of the one-electron Hamiltonian given by (in hartrees)

$$H_{\mu\mu}^{AA}=U_{\mu\mu}^{AA}-\sum_{B\,(\neq A)} Z_B(\psi_\mu^A|R_B^{-1}|\psi_\mu^A)\ , \tag{1}$$

where

$$U_{\mu\mu}^{AA}=(\psi_\mu^A|-\nabla^2/2-Z_A R_A^{-1}|\psi_\mu^A)$$

from atomic spectroscopic data. In Eq. (1), ψ_μ^A is a valence atomic orbital (AO) centered on atom A and Z_A is the core (nucleus and inner-shell electrons) charge on atom A. The one-center term $U_{\mu\mu}^{AA}$ is essentially an atomic quantity. The remaining terms in Eq. (1) give the interaction between a valence electron in ψ_μ^A with the cores of the other atoms B.

Different semiempirical ZDO methods [complete neglect of differential overlap (CNDO), intermediate neglect of differential overlap (INDO), neglect of diatomic differential overlap (NDDO)] [1], which attempt to treat explicitly at least the most important electron repulsion integrals, differ mainly in the extent to which the ZDO approximation is invoked in these integrals. The CNDO model, for which the ZDO approximation is used for all products of different atomic orbitals $\psi_\mu\psi_\nu$, relates the one-center one-electron "core" integrals $U_{\mu\mu}^{AA}$, Eq. (1), to atomic parameters. In the conventional CNDO/1 parameterization, these integrals are obtained from atomic ionization potentials and Slater-Condon parameters [1]. In the INDO [1,4] and NDDO [1] methods, similar treatments are employed, but in these cases the one-center differential overlap integrals are no longer neglected.

An alternative procedure to evaluate the core integrals $U_{\mu\mu}$, adopted in the CNDO/2 and INDO/2 methods, is to use the average between the ionization potential and electron affinity [1]. Unfortunately, electron affinities of transition elements, even for the first-transition series, are often unknown. One procedure adopted for transition elements involves determining the electron affinities A_μ by an isoelectronic quadratic extrapolation [9] based on ionization potentials and promotion energies, for the appropriate charge and configuration, obtained from atomic spectra.

In the CNDO method, the two-center terms in Eq. (1) have to be approximated in a manner which is consistent with the way the two-electron integrals are treated in the ZDO approximation. Furthermore, the invariance conditions require these terms to be the same for all orbitals ψ_μ on atom A. Consequently, the diagonal matrix elements $H_{\mu\mu}^{AA}$ may be written as

$$H_{\mu\mu}^{AA}=U_{\mu\mu}^{AA}-\sum_{B\,(\neq A)} V_{AB}\ , \tag{2}$$

where V_{AB} represents the interaction of a valence electron in atom A with the core of atom B. In the original CNDO/1 method of Pople and co-workers [1] for an s,p basis set, V_{AB} is calculated using the atom A valence s orbital.

In the CNDO/2 [1] and INDO [1,4] methods, the electron-core potential integrals V_{AB} are not evaluated separately but are related to the electron repulsion integrals

$$\gamma_{AB}=(\psi_\mu^A\psi_\mu^A|\psi_\nu^B\psi_\nu^B)\ . \tag{3}$$

The integrals γ_{AB} are calculated replacing the basis functions ψ_μ^A and ψ_ν^B by s symmetry orbitals of the same principal quantum number.

When focusing on molecular spectroscopy, the integrals γ_{AB} are not calculated, but are determined empirically, as in the spectroscopic methods CNDO/S and INDO/S [5,7]. A procedure to determine these integrals empirically [5] is to employ the Weiss-Mataga-Nishimoto formula [8]

$$\gamma_{AB}\cong\frac{f_\gamma}{2f_\gamma/(\gamma_{AA}+\gamma_{BB})+R_{AB}}\ , \tag{4}$$

where R_{AB} is the distance between the two centers in Bohr radii and f_γ is a parameter introduced by Weiss [5]. The one-center two-electron integrals are obtained from the Pariser approximation [7]

$$\gamma_{AA}\cong I_A-A_A\ , \tag{5}$$

where I_A and A_A are the ionization potential and electron affinity, respectively, of an s, p, or d electron on atom A, for a given configuration.

The spectroscopic methods CNDO/S and INDO/S present one similarity with local-density theory. In fact, in LD theory the chemical potential, in the zero-temperature limit, is defined as the first derivative of the total electronic energy E with respect to the number of electrons N [15(a)]. The curvature of E as a function of N at 0 K, for a neutral atom or molecule, may be shown, in the finite-difference approximation, to be [15(a)]

$$\left[\frac{\partial^2 E}{\partial N^2}\right]\cong I-A\ ,$$

which is precisely the definition of the integral γ_{AA} given by Eq. (5).

The ionization potentials appearing in the semiempirical methods derived from the ZDO approximation may be related to the average of the states of a configuration (VOIP). Furthermore, the possibility of employing VOIP's pertaining to the charge and configuration of the atoms in the molecule would constitute an improvement.

In the semiempirical extended Hückel (EH) method [10(a)], the Hamiltonian of the system is not explicitly defined, as is the case in methods derived from the ZDO approximation. The diagonal matrix elements of the "effective" Hamiltonian operator are approximated as minus the VOIP of the atom for a given configuration, and the off-diagonal elements are proportional to an average of the diagonal ones weighted by the appropriate orbital overlap. Furthermore, the variation of the EH method, known as the self-consistent charge and configuration (SCCC) method for transition-metal complexes [10(b)], estimates the diagonal Hamiltonian matrix elements as linear combinations of VOIP's for several configurations, where each VOIP is assumed to have a quadratic charge dependency, in order to adequately represent the self-consistent charge and fractional populations present in the complex. This procedure requires extensive tabulations of VOIP's as a function of both charge and configuration.

III. THEORETICAL METHOD

A. Nonrelativistic

The purpose of atomic spin-polarized self-consistent local-density (LD) calculations [19] based on density-functional theory [15(a),20] is to solve the set of one-electron equations

$$(h-\varepsilon_{i\sigma})\psi_{i\sigma}(\mathbf{r})=0 \ , \tag{6}$$

where $\psi_{i\sigma}$ is an atomic spin-orbital, $\varepsilon_{i\sigma}$ the eigenvalue, and the one-electron Hamiltonian is given (in hartrees) by

$$h=-\nabla^2/2+V[\rho_\sigma(\mathbf{r})] \ . \tag{7}$$

The spin density $\rho_\sigma(\mathbf{r})$ at point $\mathbf{r}$ is defined as a sum over the spin-orbitals $\psi_{i\sigma}(\mathbf{r})$ with occupation numbers $f_{i_\uparrow}, f_{i_\downarrow}$ for either spin

$$\rho_\sigma(\mathbf{r})=\sum_i f_{i\sigma}|\psi_{i\sigma}(\mathbf{r})|^2 \ . \tag{8}$$

The potential $V[\rho_\sigma(\mathbf{r})]$ is a functional of the spin density ρ_σ and includes a Coulomb and an exchange-correlation term. The Coulomb potential V_{Coul} includes both nuclear and electronic contributions

$$V_{\text{Coul}}[\rho_\sigma(\mathbf{r})]=-\frac{z}{r}+\int\frac{\rho_\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \ . \tag{9}$$

In the exchange-only LD theory, the local exchange potential $V_x[\rho_\sigma(\mathbf{r})]$ is given by the Kohn-Sham (KS) expression [19]

$$V_x[\rho_\sigma(\mathbf{r})]=-2(3/4\pi)^{1/3}[\rho_\sigma(\mathbf{r})]^{1/3} \ . \tag{10}$$

Improvements were made in the theory, in order to include correlation effects, leading to exchange and correlation local potentials of the general form

$$V_{\text{xc}}[\rho_\sigma(\mathbf{r})]=V_x[\rho_\sigma(\mathbf{r})][1+F(\rho_\uparrow,\rho_\downarrow)] \ , \tag{11}$$

where the correction factor F is obtained by a fitting procedure to numerical calculations of the correlation energy for a uniform electron gas [16,17].

Nonrelativistic LD calculations retain the restriction of spherical symmetry for atoms. Consequently, the spin orbitals $\psi_{i\sigma}(\mathbf{r})$ which are solutions of Eq. (6) have the property of being the product of a radial function times a spherical harmonic. In spin-polarized calculations, the restriction that the radial functions $R_{nl\sigma}(r)$ have the same values for both spin-up and spin-down electrons is relaxed, leading to different radial functions and, consequently, different spin densities and self-consistent potentials for the two spin orientations.

B. Relativistic

The one-electron Dirac Hamiltonian provides the usual starting point for relativistic self-consistent LD calculations and is written (in hartrees, $c=137.037$) as [15(b)]

$$h_D=c\tilde{\alpha}\cdot[\mathbf{p}-(1/c)\mathbf{A}]+c^2(\tilde{\beta}-1)+A_0 \ , \tag{12}$$

where $\tilde{\alpha}$ and $\tilde{\beta}$ are the 4×4 Dirac matrices, $\mathbf{p}$ the momentum operator, and $(\mathbf{A}, A_0)$ a four-component vector potential describing external fields. The one-electron atomic equations are

$$(h_D-\varepsilon_{n\kappa})\psi_{n\kappa m}(\mathbf{r},s)=0 \ . \tag{13}$$

In the simplest extension of the nonrelativistic LD theory, one sets $\mathbf{A}=\mathbf{0}$ and $A_0=V[\rho_\sigma(\mathbf{r})]$, where $V[\rho_\sigma(\mathbf{r})]$ includes the Coulomb potential, Eq. (9), and the local exchange-correlation potential, Eqs. (10) and (11), as in the nonrelativistic case. The use of nonrelativistic exchange-correlation potentials in relativistic LD calculations is well justified. The effect of relativistic corrections to the nonrelativistic local potential [Eq. (10)] on the energy levels is negligible for valence shells, becoming significant only for core levels of heavy atoms [21].

The fourth-order central-field Dirac spinors are

$$\psi_{n\kappa m}(\mathbf{r},s)=\begin{bmatrix} r^{-1}P_{n\kappa}(r)\chi_{\kappa m}(\theta,\phi,s) \\ ir^{-1}Q_{n\kappa}(r)\chi_{-\kappa m}(\theta,\phi,s)\end{bmatrix} , \tag{14}$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are, respectively, the "large" and "small" components. The orbitals $\psi_{n\kappa m}(\mathbf{r},s)$ are eigenfunctions of the total angular momentum squared j^2 and of its projection j_z with eigenvalues $j(j+1)$ and m, respectively, and are of given parity. The relativistic quantum number κ is defined by

$$\kappa=\begin{cases} l & \text{if } j=l-\frac{1}{2} \\ -(l+1) & \text{if } j=l+\frac{1}{2} \ , \end{cases} \tag{15}$$

which includes both j and the parity. The two-component Pauli spinor $\chi_{\kappa m}$ is a vector-coupled function of a spherical harmonic $Y_l^m(\theta,\phi)$ and a spin function $\xi_\sigma(s)$ [15(b)].

A set of coupled radial equations is obtained, by substituting the wave function of Eq. (14) into the eigenvalue equation [Eq. (13)] [15(b)]

$$\begin{aligned} &c\frac{dQ_{n\kappa}(r)}{dr}-\frac{c\kappa}{r}Q_{n\kappa}(r)+V[\rho(r)]P_{n\kappa}(r)=\varepsilon_{n\kappa}P_{n\kappa}(r) \ , \\ &-c\frac{dP_{n\kappa}(r)}{dr}-\frac{c\kappa}{r}P_{n\kappa}(r)-2c^2Q_{n\kappa}(r)+V[\rho(r)]Q_{n\kappa}(r) \\ &\qquad\qquad\qquad\qquad\qquad=\varepsilon_{n\kappa}Q_{n\kappa}(r) \ . \end{aligned} \tag{16}$$

These equations can be solved self-consistently, in an analogous way to the nonrelativistic equations, since the potential is a functional of the electronic density

$$\rho(r)=\sum_{n,\kappa}f_{n\kappa}[P_{n\kappa}^2(r)+Q_{n\kappa}^2(r)] \ . \tag{17}$$

The moment-polarized scheme, developed by Ellis and Goodman [22], is a relativistic alternative to the spin-polarized nonrelativistic theory, since the spin component s_z is not diagonal in the four-component theory. The moment-polarized approach is based on the twofold Kramers degeneracy, which remains in the Dirac theory [23], and allows different occupancy for ↑, ↓ members of the Kramers doublets and different spatial wave functions for each component. In this case, different potentials $V[\rho_\sigma(r)]$ (one for moment up and the other for moment down) are used to determine the ↑, ↓ eigenvalues and eigenvectors, in analogy to the nonrelativistic spin-polarized case.

The radial equations, for both relativistic and nonrelativistic cases, are solved numerically by using a radial mesh of 300 points with a logarithmic distribution, which concentrates a larger number of points near the nucleus.

IV. COMPARISON BETWEEN THEORETICAL AND EXPERIMENTALLY DERIVED VOIP'S

A. Some details of the calculations

The VOIP V_{VO} for a specific electron of a specific configuration of the neutral atom is defined as [24]

$$V_{\mathrm{VO}}=V_{\mathrm{ion}}+E_I'-E_A' \ , \tag{18}$$

where V_{ion} is the first ionization potential, E_A' is the average energy of the given configuration of the neutral atom relative to its ground state, and E_I' is the average energy of the corresponding configuration of the ion relative to the ground state of the ionized atom. Similar expressions hold to derive VOIP's for singly and doubly charged atoms.

As mentioned in the Introduction, in a LD calculation the VOIP is given by

$$V_{\mathrm{VO}}=E_I-E_A \ , \tag{19}$$

where E_A and E_I are the average energies over the states of a given configuration of the neutral and ionized atom, respectively, obtained directly from the LD calculations. Both definitions [Eqs. (18) and (19)], of course, represent the same quantity.

Since the potential $V[\rho(r)]$ in the LD theory depends only on the electronic density, it is the same for all states within a configuration. Therefore, there is no need for averaging over the "*LS* configuration" (in the nonrelativistic case) or over a "*jj* configuration" (in the relativistic case), as in the Hartree-Fock-Dirac method. On the other hand, considering a single "*jj* configuration" (in the relativistic LD or Dirac-Fock methods) is meaningful only when "*jj* coupling" dominates. Furthermore, the use of pure *jj* configurations may be misleading when a comparison is made with nonrelativistic results obtained in *LS* coupling. The appropriate procedure, when dealing with open-shell systems in intermediate coupling, would therefore be to average over all the *jj* configurations associated with a single *LS* one [15(b),25]. In this case, the electronic density $\rho(r)$ [Eq. (17)] has to be replaced by the average [15(b)]

$$\langle \rho(r) \rangle = \sum_{n,\kappa} \langle f_{n\kappa} \rangle [P_{n\kappa}^2(r)+Q_{n\kappa}^2(r)] \ , \tag{20}$$

where $\langle f_{n\kappa} \rangle$ is the average occupation number

$$\langle f_{n\kappa} \rangle \equiv \langle f_{nlj} \rangle = (f_{nl}/f_{nl}^0) f_{nlj}^0 \ . \tag{21}$$

Here, f_{nl} is the occupation number of the nl main shell; f_{nl}^0 and f_{nlj}^0 are the degeneracies of the nl main shell and the nlj subshell, respectively.

The procedure described above, based on the average occupation numbers $\langle f_{n\kappa} \rangle$, was employed to derive VOIP's in the relativistic calculations reported here, since most of the available atomic experimental data have been assigned *LS* designations or are listed with miscellaneous designations owing to the departure from *LS* coupling [11]. The atomic spectra are analyzed within *jj* coupling only for elements in the vicinity of gold. Furthermore, most semiempirical MO methods are parametrized using nonrelativistic basis sets.

No account was taken of the Breit interaction term or higher-order relativistic corrections, and corrections for the finite size of the nucleus were omitted. The effect of these corrections on the VOIP's for valence shells is negligible [26].

Derivations of VOIP's would require two calculations, one to obtain the energy of the neutral atom and the other for the ionized atom. However, with the use of the "transition-state concept," only one calculation needs to be performed to obtain each VOIP. In fact, it has been demonstrated that, up to second order, the energy needed to ionize an electron from one orbital is equal to the absolute value of the orbital energy in a self-consistent calculation with $\frac{1}{2}$ an electron removed from the orbital [18]. This procedure not only reduces the computations by 50%, but also assures that in many cases better accuracy is achieved, since it avoids numerical errors due to small differences between very large numbers.

B. Comparison with experimental results

Theoretical VOIP's for several charges and configurations of 5*d* transition elements are given in Tables I–III. Nonrelativistic (NR) non-spin-polarized (NP) LD calculations employing the Kohn-Sham (KS) local exchange-only potential are designated NR-KS-NP. Fully relativistic (R) NP LD calculations were also performed employing both the KS local exchange-only potential (R-KS-NP) and the von Barth–Hedin–Lundqvist (VBHL) local exchange and correlation potential (R-VBHL-NP). The fully relativistic LD calculations, employing the von Barth–Hedin–Lundqvist local exchange and correlation potential and the moment-polarized (P) scheme developed by Ellis and Goodman [22], were designated R-VBHL-P. The experimental values presented in Tables I–III were obtained from data on the atomic spectra of neutral and of singly, doubly, and triply charged 5*d* transition elements, for the few atomic configurations for which measurements are reported [11,27–51]. Only configurations for which at least 90% of the states are known were considered, unless otherwise specified.

As is well known, the relativistic treatment gives VOIP's which are larger for the *s* and *p* electrons (the orbitals are contracted) and smaller for the *d* electrons (the

TABLE I. VOIP's for neutral $5d$ atoms in units of eV.

Configuration[a]	n	NR-KS-NP[b]	j	R-KS-NP[c]		R-VBHL-NP[d]		R-VBHL-P[e]		Expt.[f]
$5d^{n}(d)$										
Ir	9	7.7	5/2 3/2	7.0 8.1	7.4[g]	8.3 9.5	8.7[g]	7.8 9.0	8.3[g]	7.0
Pt	10	8.5	5/2 3/2	7.6 9.0	8.2	9.0 10.4	9.5	8.8 10.2	9.4	8.6
$5d^{n-1}6s(d)$										
Hf	4	5.1	5/2 3/2	4.3 4.8	4.5	5.4 5.9	5.6	6.1 6.6	6.3	5.3
Pt	10	11.2	5/2 3/2	9.5 10.9	10.1	10.9 12.3	11.5	10.2 11.7	10.8	10.8
Au	11	12.2	5/2 3/2	10.3 12.0	11.0	11.8 13.4	12.4	11.4 13.1	12.1	11.9
$5d^{n-2}6s^{2}(d)$										
Hf	4	6.7	5/2 3/2	5.3 5.8	5.5	6.5 7.1	6.7	6.9 7.4	7.1	6.5
Ta	5	8.0	5/2 3/2	6.4 7.1	6.7	7.6 8.3	7.9	8.2 8.9	8.5	7.5
Au	11	15.3	5/2 3/2	12.5 14.2	13.2	14.0 15.7	14.7	13.5 15.3	14.2	14.3
Hg	12	16.6	5/2 3/2	13.5 15.5	14.3	15.0 17.0	15.8	14.8 16.8	15.6	15.6
$5d^{n-1}6p(d)$										
Au	11	13.7	5/2 3/2	12.1 13.8	12.8	13.5 15.2	14.2	13.2 14.9	13.9	13.7
$5d^{n-1}6s(s)$										
Hf	4	5.6	1/2	6.8		7.7		8.4		7.4
Ir	9	6.4	1/2	8.2		9.4		9.8		8.4
Pt	10	6.5	1/2	8.5		9.6		9.9		8.8
Au	11	6.6	1/2	8.7		9.9		10.0		9.2
$5d^{n-2}6s^{2}(s)$										
Hf	4	6.3	1/2	7.2		8.3		7.4		7.8
Ta	5	6.7	1/2	7.7		8.8		7.7		8.5
Pt	10	7.7	1/2	9.4		10.6		10.0		9.8
Au	11	7.8	1/2	9.6		10.8		10.5		10.1
Hg	12	7.9	1/2	9.9		11.1		10.9		10.4
$5d^{n-2}6s6p(s)$										
Au	11	8.7	1/2	10.9		12.1		12.6		12.1
Hg	12	8.9	1/2	11.3		12.4		12.8		12.0
$5d^{n-1}6p(p)$										
Au	11	3.2	3/2 1/2	3.4 4.0	3.6[g]	4.3 4.9	4.5[g]	4.5 5.1	4.7[g]	4.3
$5d^{n-2}6s6p(p)$										
Au	11	3.9	3/2 1/2	3.8 4.5	4.0	4.7 5.5	5.0	5.1 6.0	5.4	5.4
Hg	12	3.9	3/2 1/2	3.8 4.6	4.0	4.7 5.6	5.0	5.1 6.0	5.4	4.9

[a] The type of electron being ionized (in parentheses) and the configuration.

[b] Nonrelativistic (NR) non-spin-polarized (NP) calculations employing the Kohn-Sham (KS) potential.

[c] Relativistic (R) non-moment-polarized (NP) calculations employing the Kohn-Sham (KS) potential.

[d] Relativistic (R) non-moment-polarized (NP) calculations employing the von Barth–Hedin–Lundqvist (VBHL) potential.

[e] Relativistic (R) moment-polarized (P) calculations employing the von Barth–Hedin–Lundqvist (VBHL) potential.

[f] Experimental values from data in Ref. [11] and [27]– [51].

[g] The j-weighted average of the $j=l\pm1/2$ VOIP's are tabulated in order to compare with those obtained nonrelativistically and with the experimental values.

TABLE II. VOIP's for singly charged $5d$ atoms in units of eV.

Configuration[a]	n	NR-KS-NP[b]	j	R-KS-NP[c]		R-VBHL-NP[d]		R-VBHL-NP[e]		Expt.[f]
$5d^n(d)$										
Hf	3	11.6	5/2	11.0	11.2[g]	12.2	12.5[g]	12.9	13.1[g]	12.2
			3/2	11.6		12.8		13.5		
Au	10	20.6	5/2	19.3	20.0	20.9	21.5	20.7	21.4	21.1
			3/2	21.0		22.6		22.4		
$5d^{n-1}6s(d)$										
Hf	3	13.7	5/2	12.5	12.7	13.8	14.0	14.4	14.7	14.3
			3/2	13.1		14.4		15.0		
Au	10	23.9	5/2	21.7	22.5	23.3	24.0	22.6	23.3	23.8
			3/2	23.5		25.1		24.4		
Hg	11	25.4	5/2	23.0	23.8	24.6	25.4	24.2	25.1	25.0
			3/2	25.0		26.6		26.3		
$5d^{n-2}6s^2(d)$										
Hf	3	15.9	5/2	14.1	14.4	15.5	15.8	15.7	15.9	16.1
			3/2	14.7		16.1		16.3		
Hg	11	29.0	5/2	25.7	26.5	27.3	28.1	26.8	27.6	28.1
			3/2	27.8		29.4		28.9		
$5d^{n-1}6p(d)$										
Hf	3	14.6	5/2	13.6	13.8	14.9	15.2	15.5	15.7	15.0
			3/2	14.2		15.6		16.1		
Au	10	25.1	5/2	23.3	24.0	24.8	25.6	24.2	24.9	25.4
			3/2	25.1		26.7		26.0		
Hg	11	26.6	5/2	24.6	25.4	26.2	27.0	25.9	26.7	26.6
			3/2	26.7		28.2		28.0		
$5d^{n-1}6s(s)$										
Hf	3	12.1	1/2	13.5		14.6		15.3		14.3
Au	10	15.0	1/2	17.7		19.0		19.3		18.5
Hg	11	15.3	1/2	18.2		19.5		19.7		18.8
$5d^{n-2}6s^2(s)$										
Hf	3	13.3	1/2	14.4		15.6		15.0		15.7
Au	10	16.4	1/2	18.9		20.2		19.6		19.6
Hg	11	16.7	1/2	19.4		20.7		20.4		19.9
$5d^{n-2}6s6p(s)$										
Hf	3	13.9	1/2	15.2		16.4		17.1		16.7
Hg	11	17.5	1/2	20.5		21.9		22.5		21.8[h]
$5d^{n-1}6p(p)$										
Hf	3	8.6	3/2	8.7	8.9[g]	9.6	9.8[g]	10.1	10.4[g]	9.5
			1/2	9.4		10.3		10.9		
Au	10	10.2	3/2	10.4	10.8	11.4	11.9	11.8	12.2	11.7
			1/2	11.6		12.7		13.0		
Hg	11	10.3	3/2	10.6	11.0	11.6	12.0	11.9	12.3	11.6
			1/2	11.8		12.9		13.2		
$5d^{n-2}6s6p(p)$										
Hf	3	9.4	3/2	9.3	9.5	10.2	10.5	10.8	11.1	11.2
			1/2	10.0		11.0		11.7		
Hg	11	11.3	3/2	11.2	11.7	12.3	12.8	12.9	13.4	13.1[h]
			1/2	12.7		13.8		14.4		

[a-g] See footnotes in Table I.

[h] 80% of states known.

orbitals are expanded), as compared to nonrelativistic calculations. These relativistic effects can be observed comparing the NR-KS-NP and the R-KS-NP results in Tables I–III. The lower energies (and the larger VOIP's) for the 6*s* and $6p_{1/2}$ orbitals, obtained in the relativistic calculations, are consistent with their penetration into the core region. The relativistic treatment allows the description of the contraction of these orbitals, which is a consequence of the proximity of the nucleus. For the orbitals that extend outside the core region, as the 5*d* orbitals, the core contraction yields a greater screening of the nucleus, and so the electrons experience a weaker potential. This indirect relativistic effect results in the higher energies, and smaller VOIP's, for the 5*d* orbitals.

In comparing the results of the NR-KS-NP and R-KS-NP calculations, as shown in Tables I–III, with the experimental values, it may be seen that the relativistic 6*s* and 6*p* calculated VOIP's are always in better agreement with the measured values, as compared to the nonrelativistic VOIP's. The same is not true for the 5*d* VOIP's, for which the nonrelativistic values compare better with experiment. This is possibly due to a compensation of errors between the use of the KS potential (no correlation) and the nonrelativistic treatment.

The von Barth–Hedin–Lundqvist exchange and correlation local potential yields VOIP's that are systematically ~1 eV higher than the values obtained using the simple exchange-only Kohn-Sham potential. The rather large effect due to correlation corrections can be observed comparing the R-KS-NP and the R-VBHL-NP results for the 5*d*, 6*s*, and 6*p* electrons in Tables I–III. Comparing with experimental values, it may be observed that consideration of correlation effects improves the VOIP's of 5*d* and 6*p* electrons in the vast majority of cases. For the 6*s* electrons no improvement may be observed on the average.

In general, a good agreement was obtained between experimentally derived and relativistic nonpolarized theoretical VOIP's, these last obtained using the von Barth–Hedin–Lundqvist exchange and correlation local potential (R-VBHL-NP), for almost all atomic configurations for which measurements are available. On

TABLE III. VOIP's for doubly charged 5*d* atoms in units of eV.

Configuration[a]	n	NR-KS-NP[b]	j	R-KS-NP[c]		R-VBHL-NP[d]		R-VBHL-P[e]		Expt.[f]
$5d^n(d)$										
Hf	2	21.4	5/2	20.4	20.7[g]	21.8	22.1[g]	22.4	22.6[g]	22.6
			3/2	21.1		22.5		23.1		
Hg	10	35.1	5/2	33.4	34.2	35.0	35.8	34.9	35.7	34.9
			3/2	35.4		37.1		36.9		
$5d^{n-1}6s(d)$										
Hf	2	23.9	5/2	22.5	22.7	23.9	24.2	24.4	24.6	24.5
			3/2	23.1		24.6		25.0		
$5d^{n-1}6p(d)$										
Hf	2	24.8	5/2	23.6	23.8	25.0	25.3	25.4	25.6	25.8
			3/2	24.2		25.7		26.0		
$5d^{n-1}6s(s)$										
Hf	2	19.9	1/2	21.5		22.7		23.2		22.5
Hg	10	25.0	1/2	28.6		29.9		30.3		28.6
$5d^{n-2}6s^2(s)$										
Hf	2	21.3	1/2	22.8		24.0		23.7		24.1
$5d^{n-2}6s6p(s)$										
Hf	2	21.9	1/2	23.5		24.8		25.3		24.7
$5d^{n-1}6p(p)$										
Hf	2	15.4	3/2	15.5	15.8	16.5	16.8	16.9	17.3	17.0
			1/2	16.4		17.5		18.0		
Hg	10	18.8	3/2	19.1	19.7	20.2	20.9	20.6	21.3	19.9
			1/2	21.0		22.2		22.6		
$5d^{n-2}6s6p(p)$										
Hf	2	16.5	3/2	16.4	16.7	17.4	17.8	18.0	18.4	17.9
			1/2	17.4		18.5		19.1		

[a–g] See footnotes in Table I.

TABLE IV. Parameters for VOIP curves as a function of the charge q ($V_{\mathrm{VO}}=C_2q^2+C_1q+C_0$) in units of eV.

	Configuration[a]	VO[b]	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
			$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=10$	$n=11$	$n=12$
C_2	d^n	$d(5/2)$	0.980	0.860	0.780	0.800	0.815	0.775	0.740		
C_2	d^n	$d(3/2)$	0.965	0.855	0.840	0.780	0.725	0.775	0.750		
C_2	d^n	d	0.925	0.830	0.825	0.770	0.770	0.815	0.715		
C_2	$d^{n-1}s$	$d(5/2)$	0.845	0.825	0.740	0.745	0.695	0.690	0.700	0.700	
C_2	$d^{n-1}s$	$d(3/2)$	0.855	0.795	0.730	0.710	0.690	0.725	0.700	0.700	
C_2	$d^{n-1}s$	d	0.900	0.855	0.695	0.780	0.665	0.650	0.750	0.700	
C_2	$d^{n-1}p$	$d(5/2)$	0.855	0.820	0.730	0.730	0.725	0.715	0.700	0.750	
C_2	$d^{n-1}p$	$d(3/2)$	0.775	0.805	0.780	0.705	0.780	0.760	0.700	0.800	
C_2	$d^{n-1}p$	d	0.815	0.855	0.690	0.770	0.750	0.650	0.750	0.700	
C_2	$d^{n-2}s^2$	$d(5/2)$		0.715	0.715	0.650	0.650	0.650	0.650	0.600	0.600
C_2	$d^{n-2}s^2$	$d(3/2)$		0.670	0.640	0.700	0.600	0.600	0.700	0.600	0.650
C_2	$d^{n-2}s^2$	d		0.705	0.685	0.700	0.650	0.600	0.650	0.550	0.650
C_1	d^n	$d(5/2)$	6.660	7.420	8.060	8.500	8.955	9.475	9.980		
C_1	d^n	$d(3/2)$	6.805	7.535	8.080	8.660	9.225	9.575	10.050		
C_1	d^n	d	6.825	7.510	8.025	8.590	9.090	9.455	10.055		
C_1	$d^{n-1}s$	$d(5/2)$	7.565	8.025	8.680	9.065	9.615	10.030	10.400	10.800	
C_1	$d^{n-1}s$	$d(3/2)$	7.635	8.215	8.810	9.270	9.730	10.125	10.600	11.000	
C_1	$d^{n-1}s$	d	7.500	8.035	8.815	9.060	9.705	10.150	10.350	10.900	
C_1	$d^{n-1}p$	$d(5/2)$	7.535	8.040	8.610	9.010	9.425	9.855	10.300	10.550	
C_1	$d^{n-1}p$	$d(3/2)$	7.775	8.185	8.660	9.185	9.460	9.920	10.400	10.600	
C_1	$d^{n-1}p$	d	7.655	8.035	8.730	8.990	9.450	10.050	10.250	10.700	
C_1	$d^{n-2}s^2$	$d(5/2)$		8.755	9.155	9.650	10.050	10.450	10.850	11.300	11.700
C_1	$d^{n-2}s^2$	$d(3/2)$		8.890	9.380	9.700	10.300	10.700	10.900	11.500	11.750
C_1	$d^{n-2}s^2$	d		8.785	9.245	9.600	10.150	10.600	10.950	11.450	11.650
C_0	d^n	$d(5/2)$	4.560	5.320	6.060	6.800	7.530	8.250	8.980		
C_0	d^n	$d(3/2)$	5.030	5.910	6.780	7.660	8.550	9.450	10.400		
C_0	d^n	d	4.750	5.560	6.350	7.140	7.940	8.730	9.530		
C_0	$d^{n-1}s$	$d(5/2)$	5.390	6.350	7.280	8.190	9.090	9.980	10.900	11.800	
C_0	$d^{n-1}s$	$d(3/2)$	5.910	6.990	8.060	9.120	10.180	11.250	12.300	13.400	
C_0	$d^{n-1}s$	d	5.600	6.610	7.590	8.560	9.530	10.500	11.500	12.400	
C_0	$d^{n-1}p$	$d(5/2)$	6.510	7.540	8.560	9.560	10.550	11.530	12.500	13.500	
C_0	$d^{n-1}p$	$d(3/2)$	7.050	8.210	9.360	10.510	11.660	12.820	14.000	15.200	
C_0	$d^{n-1}p$	d	6.730	7.810	8.880	9.940	11.000	12.000	13.100	14.200	
C_0	$d^{n-2}s^2$	$d(5/2)$		7.630	8.730	9.800	10.900	11.900	12.900	14.000	15.000
C_0	$d^{n-2}s^2$	$d(3/2)$		8.340	9.580	10.800	12.000	13.200	14.500	15.700	17.000
C_0	$d^{n-2}s^2$	d		7.910	9.070	10.200	11.300	12.400	13.500	14.700	15.800
C_2	$d^{n-1}s$	$s(1/2)$	0.600	0.570	0.550	0.510	0.505	0.535	0.460	0.475	
C_2	$d^{n-2}s^2$	$s(1/2)$	0.525	0.530	0.545	0.540	0.465	0.450	0.600	0.500	0.550
C_2	$d^{n-2}sp$	$s(1/2)$	0.560	0.585	0.550	0.550	0.550	0.500	0.500	0.550	0.500
C_2	$d^{n-1}p$	$p(3/2)$	0.615	0.585	0.615	0.590	0.655	0.570	0.575	0.680	
C_2	$d^{n-1}p$	$p(1/2)$	0.620	0.550	0.560	0.655	0.540	0.570	0.645	0.615	
C_2	$d^{n-1}p$	p	0.600	0.550	0.595	0.630	0.600	0.520	0.580	0.590	
C_2	$d^{n-2}p^2$	$p(3/2)$	0.585	0.565	0.525	0.525	0.615	0.600	0.630	0.655	0.675
C_2	$d^{n-2}p^2$	$p(1/2)$	0.580	0.605	0.560	0.605	0.585	0.560	0.630	0.595	0.605
C_2	$d^{n-2}p^2$	p	0.600	0.545	0.520	0.585	0.590	0.635	0.580	0.670	0.600
C_2	$d^{n-2}sp$	$p(3/2)$	0.610	0.580	0.530	0.520	0.600	0.620	0.535	0.650	0.660
C_2	$d^{n-2}sp$	$p(1/2)$	0.585	0.590	0.615	0.580	0.535	0.580	0.570	0.555	0.635
C_2	$d^{n-2}sp$	p	0.585	0.565	0.575	0.575	0.560	0.640	0.565	0.635	0.650
C_1	$d^{n-1}s$	$s(1/2)$	6.300	6.690	7.050	7.470	7.785	7.995	8.420	8.675	
C_1	$d^{n-2}s^2$	$s(1/2)$	6.825	7.110	7.365	7.680	8.105	8.450	8.400	8.900	9.050
C_1	$d^{n-2}sp$	$s(1/2)$	6.720	6.945	7.250	7.550	7.850	8.200	8.500	8.650	9.000
C_1	$d^{n-1}p$	$p(3/2)$	5.045	5.355	5.555	5.830	5.935	6.290	6.475	6.460	
C_1	$d^{n-1}p$	$p(1/2)$	5.340	5.750	6.020	6.135	6.580	6.790	6.865	7.155	

TABLE IV. (*Continued*).

	Configuration[a]	VO[b]	Hf $n=4$	Ta $n=5$	W $n=6$	Re $n=7$	Os $n=8$	Ir $n=9$	Pt $n=10$	Au $n=11$	Hg $n=12$
C_1	$d^{n-1}p$	p	5.160	5.550	5.715	5.910	6.200	6.540	6.660	6.830	
C_1	$d^{n-2}p^2$	$p(3/2)$	5.445	5.705	6.025	6.225	6.255	6.500	6.610	6.735	6.875
C_1	$d^{n-2}p^2$	$p(1/2)$	5.760	5.985	6.320	6.485	6.745	7.020	7.110	7.415	7.585
C_1	$d^{n-2}p^2$	p	5.500	5.865	6.140	6.245	6.430	6.595	6.860	6.890	7.200
C_1	$d^{n-2}sp$	$p(3/2)$	5.370	5.660	6.010	6.240	6.300	6.440	6.795	6.750	6.920
C_1	$d^{n-2}sp$	$p(1/2)$	5.745	6.030	6.255	6.560	6.895	7.060	7.290	7.535	7.595
C_1	$d^{n-2}sp$	p	5.545	5.805	6.075	6.275	6.520	6.580	6.905	6.995	7.150
C_0	$d^{n-1}s$	$s(1/2)$	7.700	8.140	8.500	8.820	9.110	9.370	9.620	9.850	
C_0	$d^{n-2}s^2$	$s(1/2)$	8.250	8.760	9.190	9.580	9.930	10.200	10.600	10.800	11.100
C_0	$d^{n-2}sp$	$s(1/2)$	9.120	9.670	10.200	10.600	11.000	11.400	11.700	12.100	12.400
C_0	$d^{n-1}p$	$p(3/2)$	3.950	4.050	4.130	4.180	4.210	4.240	4.250	4.260	
C_0	$d^{n-1}p$	$p(1/2)$	4.340	4.500	4.620	4.710	4.780	4.840	4.890	4.930	
C_0	$d^{n-1}p$	p	4.080	4.200	4.290	4.360	4.400	4.440	4.460	4.480	
C_0	$d^{n-2}p^2$	$p(3/2)$	4.770	4.930	5.050	5.150	5.230	5.300	5.360	5.410	5.450
C_0	$d^{n-2}p^2$	$p(1/2)$	5.460	5.710	5.920	6.110	6.270	6.420	6.560	6.690	6.810
C_0	$d^{n-2}p^2$	p	5.000	5.190	5.340	5.470	5.580	5.670	5.760	5.840	5.900
C_0	$d^{n-2}sp$	$p(3/2)$	4.220	4.360	4.460	4.540	4.600	4.640	4.670	4.700	4.720
C_0	$d^{n-2}sp$	$p(1/2)$	4.670	4.880	5.030	5.160	5.270	5.360	5.440	5.510	5.570
C_0	$d^{n-2}sp$	p	4.370	4.530	4.650	4.750	4.820	4.880	4.930	4.970	5.000

[a] n corresponds to the configuration of the neutral atom.

[b] VO stands for the valence orbital from which the electron is ionized. The fractions in parentheses are j quantum numbers. No parentheses designate the j-weighted average.

the other hand, some discrepancies should be pointed out, mainly for the $5d^n(d)$ and $5d^{n-1}6s\,(s)$ configurations of the neutral $5d$ transition elements. The discrepancies noticed are invariably an overbinding found in the calculated VOIP's, as compared to experiment. This overbinding is stronger for the $5d^n(d)$ configuration. It has been shown [52,53] for the $3d$ series that the local potential produces systematic overbinding in calculated ionization potentials. Our calculations indicate that the same is true for the $5d$ series, at least for the atoms considered here, for which experimental data was available.

Attempting to improve even further the VOIP values, we have performed relativistic moment-polarized calculations with the VBHL exchange-correlation potential (R-VBHL-P). Moment-polarized calculations usually improve the VOIP value when the ionized electron is a minority spin $5d$ electron, although the overbinding is somewhat overcorrected for some atomic configurations. The VOIP value is also improved when the ionized electron is a minority spin $6s$ electron, but only for atoms or ions that have a minority spin $5d$ electron. For atoms at the beginning of the $5d$ series, the overbinding is overcorrected. Consequently, no systematic improvement has been obtained by performing moment-polarized calculations. For this reason, we chose the moment-restricted relativistic LD method with the von Barth–Hedin–Lundqvist potential (R-VBHL-NP) to derive the complete set of VOIP's for $5d$ transition elements. The VOIP's calculated in this manner compare better with experiment on the average, for the cases in which comparison with measured data is possible. Most calculated VOIP's are within 0.5 eV of the experimental value; results are in general better for the charged atoms.

V. VOIP'S FOR 5*d* TRANSITION ELEMENTS

The calculated VOIP's were represented by a quadratic polynomial form

$$V_{\mathrm{VO}}(q)=C_2q^2+C_1q+C_0\ , \qquad (22)$$

where q is the net atomic charge. The values of the coefficients C_0, C_1, and C_2, for the VOIP's of $5d_{5/2}$, $5d_{3/2}$, $6s_{1/2}$, $6p_{3/2}$, and $6p_{1/2}$ orbitals for several configurations, are compiled in Table IV. These coefficients were obtained by fitting the calculated values for the charges $q=0$, $+1$, and $+2$. The VOIP curves coefficients for the j-weighted average of the $j=l\pm\frac{1}{2}$ VOIP's are also tabulated in Table IV.

An attempt to estimate VOIP's from experimental data for $5d$ transition elements was made by Jostes [54], for neutral atoms only. The small amount of available data on atomic spectra did not allow the determination of the charge dependence of the VOIP's. Moreover, even for neutral atoms, the experimental data were not enough to allow the calculation of the average energies of the configurations and some assumptions had to be made in order to estimate the VOIP's.

Relativistic theoretical VOIP's have been employed in semiempirical calculations of molecules containing lanthanides [55,56] and actinides [57]; however, only values for neutral atoms in the ground-state configuration were considered.

The present parameter set should prove useful for semiempirical MO calculations, since this is the only complete set of VOIP's derived for all 5*d* transition elements, as a function of both charge and configuration. Consideration of the dependence of VOIP's on charge and configuration, when parametrizing semiempirical methods, should improve the results of molecular calculations. The comparison that we have made with experimental values has proved that the present theoretical method is capable of providing accurate values. It should be observed that, in most cases, the comparisons made involve atoms at the beginning and end of the 5*d* transition series. This is due to the increased complexity (and thus difficult interpretation) of the experimental spectra of the atoms in the middle of the series. For these intermediate atoms our calculated values should prove most useful. Furthermore, the present work also provides a parameter set which can be used in "fully relativistic" semiempirical MO calculations, i.e., calculations where a *jj*-basis set is required [58].

VI. CONCLUSIONS

A complete set of VOIP's for 5*d* transition elements have been derived by performing fully relativistic self-consistent numerical local-density atomic calculations. A good agreement was obtained between theoretical and experimentally derived VOIP's, for the atomic configurations for which measurements are available. The present parameter set should prove useful in semiempirical molecular-orbital calculations for molecules containing 5*d* transition elements, in both relativistic and nonrelativistic frameworks.

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