An Intermediate Neglect of Differential Overlap Model for Second-Row Transition Metal Species

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Abstract

An intermediate neglect of differential overlap (INDO) model for elements of the second transition series is described. Values of exponents for the radial portion of the Slater basis atomic orbitals, the orbital ionization energies, and the beta (or bonding) parameters for these elements are reported. Use of the model to investigate equilibrium geometries, relative energy ordering of geometric isomers, spectroscopic transition energies, energy ordering of state wave functions of different symmetry, trends in dipole moments, and equilibrium stretching frequencies is reported. The results indicate that the INDO method is capable of yielding quality results for species containing atoms of the second transition series.

Introduction

In recent years, interest in the second-row transition metals has been increasing steadily. The study of catalysts and advanced materials has spurred this interest. A short list of examples include Y in superconductors [1], Mo [2]- and Ru [3]-based oxidation catalysts, Tc radiopharmaceuticals [4], Zr organometallics[1] [5], Rh hydroformylation catalysts [6], adsorption of molecular hydrogen by Pd [7], and silver oxide catalysts for the epoxidation of olefins [8]. As with any area of chemistry, it is of interest to carry out theoretical investigations to elucidate the pertinent electronic structural factors. The application of ab initio methods to these second-row species has been hampered by the large size of many of the systems of interest, the presence of many low-energy excited states in the transition metals, and the increasing importance of relativistic effects with increased atomic number[2] [9,10]. Semiempirical intermediate neglect of differential overlap (INDO) models have been used extensively to investigate systems containing first-row transition metals [11]. In contrast, the application of the NDO methods to second-row species has been limited [12]. The aims of the current paper are

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[1] Marks and Toney discuss the hydrolysis of $ZrCp_2Cl_2$ and its implications for anti-tumor agents in Ref. 5.

[2] Some of these problems are discussed in Ref. 9.

twofold: first, to describe a set of parameters for second-row transition metals that extends the INDO model proposed previously by Bacon and Zerner [13] for first-row transition metals; and second, to study a wide variety of molecular properties to test the strengths and weaknesses of this INDO model.

Theoretical Model

The model is an extension of intermediate neglect of differential overlap models described in some detail previously [13,14]. Briefly, solutions of the secular equations are sought:

$$FC = \Delta C\varepsilon, \tag{1a}$$

with F the Fock or energy matrix, Δ the overlap matrix,

$$\Delta_{\mu\nu} = \langle\mu|\nu\rangle = \langle X_u|X_v\rangle = \delta_{\mu\nu}, \tag{1b}$$

for the INDO model; ε, the diagonal matrix of molecular orbital "energies"; and C, a square matrix the columns of which are the MO coefficients,

$$(\phi_1, \phi_2, \ldots \phi_n) = \Phi = XC. \tag{1c}$$

In the above, Φ is a row matrix of molecular orbitals and X is a row matrix of atomic orbitals. Equation (1a), one equation with one Fock matrix, refers to the closed-shell case. Open-shell cases can be treated by the unrestricted Hartree–Fock (UHF) [15] or by restricted open-shell Hartree–Fock (ROHF) theory [16]. The basic parameters for the model, however, are expressed with a single Fock operator with no loss in generality:

$$F_{u\nu} = h_{\mu\nu} + \sum_{\sigma, \lambda} P_{\sigma\lambda}\left[(\mu\nu\,|\,\sigma\lambda) - \frac{1}{2}(\mu\sigma\,|\,\nu\lambda)\right]. \tag{2a}$$

In the above, P is the first-order density matrix with the elements given by

$$P_{\sigma\lambda} = \sum_a c^*_{\lambda a} n_a c_{\sigma a}, \tag{2b}$$

with n_a being the occupation of MO Φ_a, $n_a = 0$ or 2 for the closed-shell cases being discussed here. The INDO model as employed herein includes all one-center, two-electron integrals. Of the many multicentered two-electron integrals of the form $(\mu\sigma\,|\,\nu\lambda)$, only the two-center integrals $(\mu\mu/\nu\nu)$ are maintained. Furthermore, in order to keep rotational invariance, the orbitals X_μ and X_ν must be considered to be "s" types, $\mu \rightarrow \bar{\mu}$:

$$(\mu\mu\,|\,\nu\nu) = (\bar{\mu}\bar{\mu}\,|\,\bar{\nu}\bar{\nu}) = \gamma_{\mu\nu}. \tag{3}$$

The orbital $X_{\bar{\mu}}$ has the same radial extent as X_μ. In the nonspectroscopic version of INDO considered here, these integrals are calculated ab initio, as are the one-center Slater–Condon F° integrals. The higher Slater–Condon factors needed to build the one-center two-electron integrals are calculated and scaled by 0.6. This scaling is recommended by examining Slater–Condon factors obtained empirically from spectroscopy for both the first- and second-row transition series, in

those cases when the spectroscopy is complete enough for such a study. This scaling has very little effect in the prediction of molecular geometry, but does improve spectroscopic predictions. This leads to

$$F_{\mu\mu}^{AA} = U_{\mu\mu}^{A} + \sum_{\sigma,\lambda}^{A} P_{\sigma\lambda}\left[(\sigma\lambda\,|\,\mu\mu) - \frac{(\sigma\mu\,|\,\lambda\mu)}{2}\right] + \sum_{B\neq A}^{B}\sum_{\sigma} P_{\sigma\sigma}\gamma_{u\sigma} - \sum_{B\neq A} Z_B\left(\mu\left|\frac{1}{R_B}\right|\mu\right)$$

(4a)

$$F_{\mu\nu}^{AA} = H_{\mu\nu}^{AA} + \sum_{\sigma,\lambda}^{A} P_{\sigma\lambda}\left[(\sigma\lambda\,|\,\mu\nu) - \frac{(\mu\sigma\,|\,\nu\lambda)}{2}\right]$$

(4b)

$$F_{\mu\nu}^{AB} = H_{\mu\nu}^{AB} - \frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}.$$

(4c)

$U_{\mu\mu}$ is the one-center core integral, essentially an integral dependent on atom A and orbital X_{μ}:

$$U_{\mu\mu} = \left\langle\mu\left|-\frac{1}{2}\nabla^2 - \frac{Z_A}{R_A} + V\right|\mu\right\rangle,$$

(5a)

and this integral will be obtained from ionization potentials [13]:

$$U_{ss} = -I_s - (\ell - 1)F^{\circ}(ss) - m\left[F^{\circ}(sp) - \frac{G^1(sp)}{6}\right] - n\left[F^{\circ}(sd) - \frac{G^2(sd)}{10}\right]$$

(5b)

$$U_{pp} = -I_p - (m - 1)\left[F^{\circ}(pp) - \frac{2F^2(pp)}{25}\right]$$

$$- \ell\left[F^{\circ}(sp) - \frac{G^1(sp)}{6}\right] - n\left[F^{\circ}(pd) - \frac{G^1(pd)}{15} - \frac{3G^3(pd)}{70}\right]$$

(5c)

$$U_{dd} = -I_d - (n - 1)\left[F^{\circ}(dd) - \frac{2\{F^2(dd) + F^4(dd)\}}{63}\right]$$

$$- \ell\left[F^{\circ}(sd) - \frac{G^2(sd)}{10}\right] - m\left[F^{\circ}(pd) - \frac{G^1(pd)}{10} - \frac{3G^3(pd)}{70}\right]$$

(5d)

for a transition element with electronic configuration $s^1p^md^n$. The ionization potentials used in Eqs. (5b)–(5d) are averaged and smoothed throughout each series, s^1d^{n-2}, sd^{n-1}, spd^{n-2}, and d^n, and the appropriate U averaged as described in Section B. For balance between U and the two-electron part of the Fock matrix, all G^1, G^2, G^3, F^2, and F^4 are scaled as previously described.

The nuclear attraction integral is taken equal to the appropriate two-electron integral to maintain balance between one-electron attraction terms and two-electron repulsions,

$$\left(\bar{\mu}\left|\frac{1}{R_B}\right|\bar{\mu}\right) = (\bar{\mu}\bar{\mu}\,|\,BB).$$

(6)

$H_{\mu\nu}^{AA}$ is traditionally set to zero, and

$$H_{\mu\nu}^{AB} = \frac{(\beta_\mu^A + \beta_\nu^B)}{2} * S_{\mu\nu},\tag{7}$$

introducing pure parameters β_μ^A and β_ν^B that are characteristic of an atom and an orbital. In general, $\beta_s = \beta_p \neq \beta_d$. The use of Eq. (7) is perhaps the poorest approximation of this model; its justification is a posteriori.

The INDO equations of this work then become

$$F_{\mu\mu}^{AA} = U_{\mu\mu}^A + \sum_{\sigma,\lambda}^{A} P_{\sigma\lambda}\left[(\sigma\lambda\,|\,\mu\mu) - \frac{(\sigma\mu\,|\,\mu\lambda)}{2}\right]$$

$$+ \sum_{B\neq A}^{B}\sum_{\sigma} P_{\sigma\sigma}\gamma_{\mu\sigma} - \sum_{B\neq A}^{B}\sum_{\sigma} n_\sigma\gamma_{\sigma\mu}\tag{8a}$$

$$F_{\mu\nu}^{AA} = \sum_{\sigma,\lambda}^{A} P_{\sigma\lambda}\left[(\sigma\lambda\,|\,\mu\nu) - \frac{(\sigma\mu\,|\,\mu\nu)}{2}\right]\tag{8b}$$

$$F_{\mu\nu}^{AB} = \frac{(\beta_\mu^A + \beta_\nu^A)S_{\mu\nu}}{2} - \frac{P_{\mu\nu}\gamma_{\mu\nu}}{2}.\tag{8c}$$

In Eq. (8c), $S_{\mu\nu}$ is a "weighted" overlap given by

$$S_{ss'}^{AB} = \langle s\,|\,s'\rangle\tag{9a}$$

$$S_{sp'}^{AB} = \langle s\,|\,p\sigma'\rangle g(s\sigma')\tag{9b}$$

$$S_{pp'}^{AB} = \langle p\sigma\,|\,p\sigma'\rangle g(p\sigma p\sigma')f_{\sigma\sigma'} + f_{\pi\pi'}[g(\pi_x\pi_x') + g(\pi_y\pi_y')]\langle p\pi\,|\,p\pi'\rangle\tag{9c}$$

$$S_{sd'}^{AB} = \langle s\,|\,d'\rangle g(sd)\tag{9d}$$

$$S_{pd'}^{AB} = \langle p\sigma\,|\,d\sigma'\rangle g(p\sigma d\sigma) + f_{p\pi d\pi'}[g(p\pi_x d\pi_x') + g(p\pi_y d\pi_y')]\langle p\pi\,|\,d\pi'\rangle\tag{9e}$$

$$S_{dd'}^{AB} = \langle d\sigma\,|\,d\sigma'\rangle g(d\sigma d\sigma') + f_{d\sigma d\sigma'} + f_{d\pi d\pi'}[g(d\pi_x d\pi_x') + g(p\pi_y d\pi_y')]$$

$$* \langle d\pi\,|\,d\pi'\rangle + f_{d\delta d\delta}[g(d\delta_{xy}d\delta_{xy}') + g(d\delta_{x2-y2}d\delta_{x2-y2}')]\langle d\delta\,|\,d\delta'\rangle,\tag{9f}$$

with $g(\sigma\lambda)$ the rotational factors required to transform the local coordinate system in which the integrals are evaluated to the molecular fixed axes and $f_{\sigma\lambda}$ empirical factors required to position the molecular orbital eigenvalue in proper order:

$$f_{\sigma\sigma'} = 1.267\tag{10a}$$

$$f_{\pi\pi'} = 0.640\tag{10b}$$

$$f_{d\sigma d\sigma} = f_{d\pi d\pi} = f_{d\delta d\delta} = 1.\tag{10c}$$

For this work, (A) orbital basis sets to calculate integrals, (B) ionization energies to evaluate core integrals $U_{\mu\mu}$, and (C) values of β_μ^A successful in reproducing the structure of model systems are needed. These are discussed, in order, below.

Determination of Parameters for Second-Transition Series Elements

A. Orbital Exponents

A basis set of Slater-type orbitals was used to calculate overlap integrals and values of the Slater–Condon $F°$ integral. Values of single Slater orbital exponents, ζ_0, were chosen that gave good agreement with $F°$ values obtained from the multiple-zeta near-Hartree–Fock wave functions of Clementi–Roetti [17]. The exponents necessary to give the correct theoretical $F°$ values are given in Table I, and they are obtained from

$$F°(\text{multiple } \zeta, 4d) = \zeta°(4d) \times 0.200905 \tag{11a}$$

$$F°(\text{multiple } \zeta, 5s) = \zeta°(5s) \times 0.164761. \tag{11b}$$

The $5s$ orbital exponents determined above for Y (^2D), Mo (^7S), and Ag (^2S) were used to calculate overlap integrals with sulfur $3s$ and oxygen $2s$ orbitals. These integrals were compared with similar values obtained using Clementi–Roetti functions [17] for the metal and oxygen atoms and the Watson function [18] for the sulfur. At typical bond distances, the difference between the two sets of overlap integrals is 12% or less. Therefore, the single-ζ exponents derived for $F°$ from Eq. (11b) will be used for the $5s$ and $5p$ orbitals.

TABLE I.   Values of Slater exponents ($\zeta°$) the second transition series.[a]

Element	Configuration	F (4d)	$\zeta°$ (4d)	$F°$ (5s)	$\zeta°$ (5s)
Y	s^2d^1	0.377407	1.879	0.21008	1.275
Zr	s^2d^2	0.434097	2.161	0.22086	1.340
	s^1d^3	0.395993	1.971	0.21620	1.312
Nb	s^2d^3	0.479881	2.389	0.23013	1.397
	s^1d^4	0.413974	2.060	0.22685	1.377
Mo	s^2d^4	0.521410	2.594	0.23840	1.447
	s^1d^5	0.488614	2.432	0.23547	1.429
Tc	s^2d^5	0.561502	2.795	0.24550	1.490
	s^1d^6	—	—	0.23929	1.452
Ru	s^2d^6	0.594174	2.957	0.25351	1.539
	s^1d^7	0.561853	2.797	0.24218	1.470
	s^0d^8	0.529716	2.637	—	—
Rh	s^2d^7	—	—	0.26106	1.584
	s^1d^8	0.598266	2.978	0.24418	1.482
	s^0d^9	0.567051	2.822	—	—
Pd	s^2d^8	—	—	0.26781	1.625
	s^1d^9	—	—	0.24670	1.497
	s^0d^{10}	0.602215	2.998	—	—
Ag	s^2d^9	—	—	0.27399	1.663
	s^1d^{10}	0.667273	3.321	0.24822	1.507
Cd	s^2d^{10}	0.726671	3.617	0.27999	1.699

[a]$F°$ values were calculated using Clementi–Roetti multiterm functions [17].

The accuracy of the $4d$ exponents determined through $F°$ ($4d4d$) for the calculation of two-electron integrals was tested by calculating the values of $(ns, ns \mid 4s, 4s)$ at different r values, assuming $4s$ exponents in the range of 1.5–3.5. The limiting value of this integral should be $1/r$ in each case. An analysis of the data indicated that this integral is insensitive to the value of the exponent on the metal (within 1%) for all exponents ≥ 2.0 at distances ≥ 2.5 Å. The variation is less than 5% for exponents ≥ 2.0 at distances ≥ 2.0 Å. The ($4s, 4s \mid 4s, 4s$) integral is the most sensitive to the exponent, as expected. These results indicate that the exponents in Table I obtained from fitting one-center $F°$ ($4d4d$) are satisfactory for calculating the required two-electron integrals at all distances.

Based on the procedure used to parameterize the first transition series elements [13, 14b], an attempt was made to use a function of the type $\zeta(R) = A + B/R$ to obtain the correct overlap between metal $4d$ orbitals and sulfur $3s$ and $3p$ orbitals at typical Mo—S bond distances. Unlike the first transition series, however, no single values of A and B could be obtained for each element that gave good agreement for both sigma and pi overlaps. Therefore, two-term functions were used at the expense of increased computational time. The double-zeta functions of Clementi and Roetti [17] were reduced to two-term functions by dropping the coefficients that were mostly $3d$ in nature and renormalizing. The overlap-weighted average error between the calculated overlaps using the renormalized two-term functions and those obtained with the five-coefficient Clementi–Roetti functions in the range 1.40–3.00 Å was 7%, 5%, and 13% for σ, π, and δ overlaps, respectively. Values of the coefficients, C_1 and C_2, and orbital exponents, ζ_1 and ζ_2, for these two-term functions are given in Table II.

In summary, a single value of $\zeta(d)$ is used for calculating two-electron integrals, and a double-zeta function is used to calculate all other properties, based on the observations given above.

TABLE II.   Renormalized two-term Clementi–Roetti double-zeta $4d$ functions.

Metal	C_1	C_2	ζ_1	ζ_2
Y	0.28655	0.82468	3.83698	1.73900
Zr	0.39924	0.71381	3.63923	1.80383
Nb	0.47775	0.65432	3.59080	1.71750
Nb	0.44775	0.66301	3.77410	1.92510
Mo	0.50051	0.62684	3.81446	1.86369
Mo	0.48013	0.62892	3.95409	2.04659
Tc	0.51241	0.59542	4.12429	2.15492
Ru	0.53423	0.59271	4.25911	2.09384
Ru	0.52248	0.58711	4.35709	2.26533
Rh	0.54409	0.58137	4.48485	2.21685
Rh	0.53881	0.57193	4.56078	2.36478
Pd	0.54902	0.57561	4.72335	2.34159
Pd	0.55017	0.56104	4.77173	2.47121
Ag	0.55763	0.55359	4.98896	2.58374
Cd	0.56165	0.54887	5.21258	2.70557

B. Effective Ionization Energies

Average valence state energies for the elements of the second transition series were calculated from data in Moore's tables [19]. These energies were used to calculate the VSIE's for the $5s$, $5p$, and $4d$ orbitals. Since many of the required microstate energies have not been reported, the raw VSIE's were fit to a function of the type IP $= a + bZ + cZ^2$, where $Z = 3$ for Y, 4 for Zr, etc. When performing the fit, the percentage of known states was taken into account by using weighting factors of 5 (100% of states known), 4 (80% of states known), ... 2 (40% of states known). The resulting fitting equations are shown in Table III.

To calculate the most appropriate value of the core integral for the $5s$, $5p$, and $4d$ orbitals of the second transition series, it was necessary to determine a weighting factor for the various electronic configurations. First, state promotion energies, Eq. (12), were calculated for each element and the promotion energies fit quadratically to Z:

$$E(d^{n-2}s^2) \longrightarrow E(d^{n-1}s^1) \longrightarrow E(d^n). \qquad (12)$$

To determine the mixing coefficients between electronic states, a procedure similar to the one employed previously for the first transition series elements [14c] was used. The following matrix equation was solved for two different values of the mixing parameter, δ:

$$\begin{vmatrix} E(d^{n-2}s^2) & \delta & \delta \\ \delta & E(d^{n-1}s^1) & \delta \\ \delta & \delta & E(d^n) \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix} = \varepsilon \begin{vmatrix} C_1 \\ C_2 \\ C_3 \end{vmatrix}. \qquad (13)$$

Although there is no good criterion for choosing the value of the mixing parameter, a value of $\delta = 5000$ cm^{-1} causes the states to merge into one another gradually. Therefore, this value was used to obtain the coefficients. The squares of the resulting coefficients obtained from the lowest-energy solution of Eq. (13) are listed in Table IV. Interestingly, enough, such a procedure is necessary for the model to reproduce accurately geometries throughout the second transition series.

To determine whether the same set of weighting factors can be used to obtain $5p$ ionization energies, a set of mixing coefficients was derived from the $d^{n-2}sp$

TABLE III.   Equations determined in least squares quadratic fit of experimental valence state ionization energies versus group number.[a]

s^2d^{n-2}:	VSIE($4d$) $= 15.17 + 13.47Z - 0.2375Z^2$	($\sigma = 3.1, N = 4$)	
s^1d^{n-1}:	VSIE($4d$) $= 11.77 + 9.170Z - 0.09719Z^2$	($\sigma = 2.9, N = 9$)	
s^0d^n:	VSIE($4d$) $= 8.536 + 5.726Z + 0.03017Z^2$	($\sigma = 0.6, N = 4$)	
s^2d^{n-2}:	VSIE($5s$) $= 33.78 + 7.385Z - 0.3489Z^2$	($\sigma = 1.7, N = 10$)	
s^1d^{n-1}:	VSIE($5s$) $= 28.64 + 7.487Z - 0.4302Z^2$	($\sigma = 2.1, N = 10$)	
p^1d^{n-1}:	VSIE($5p$) $= 16.33 + 5.368Z - 0.3821Z^2$	($\alpha = 1.4, N = 10$)	
$s^1p^1d^{n-2}$:	VSIE($5p$) $= 22.23 + 4.509Z - 0.2670Z^2$	($\sigma = 1.0, N = 6$)	

[a]σ is the average error in units of 1000 cm^{-1}, and N is the number of points used to obtain the least-squares fit.

TABLE IV. Valence bond mixing of $d^x s^y$ states ($\delta = 500$ cm^{-1}).

	$C_1^2(d^{n-2}s^2)$	$C_2^2(d^{n-1}s^1)$	$C_3^2(d^n)$
Sr	0.9411	0.0522	0.0066
Y	0.9193	0.0732	0.0074
Zr	0.8774	0.1145	0.0080
Nb	0.7846	0.2087	0.0067
Mo	0.5567	0.4429	0.0005
Tc	0.1869	0.7781	0.0350
Ru	0.0117	0.7044	0.2839
Rh	0.0031	0.3170	0.6800
Pd	0.0068	0.1224	0.8709
Ag	0.0000	1.0000	0.0000
Cd	1.0000	0.0000	0.0000

and $d^{n-1}p$ states from $E(d^{n-2}sp)$ and $E(d^{n-1}p)$ and a δ value of 5000 cm^{-1}. The effective $5p$ ionization energies calculated using squares of these coefficients as weighting factors for the two states were compared with ionization energies obtained using modified (renormalized) coefficients $(C_1')^2$ and $(C_2')^2$ obtained from the coefficients in Table III by employing equations 14a and 14b:

$$(C_1')^2 = C_1^2 \div \{C_1^2 + C_2^2\} \tag{14a}$$

$$(C_2')^2 = C_2^2 \div \{C_1^2 + C_2^2\}. \tag{14b}$$

The resulting I_p values were similar using the $d^{n-2}sp/d^{n-1}p$ and modified $d^{n-2}s^2/d^{n-1}s$ coefficients because the weighting factors were similar in the cases in which the ionization energies were different, and the ionization energies were similar at places where the weighting factors were different. Therefore, the coefficients in Table IV are used to evaluate the core energies. These values can also be used to produce effective ionization energies for those atoms in molecular environments. A summary of the effective $5s$, $5p$, and $4d$ ionization energies for elements 37–48 is given in Table V.

C. Calculation of the Beta or Bonding Parameter

The bonding parameter, β_μ^A, is used in the calculation of the off-diagonal Fock-matrix elements. These atomic quantities can be estimated from the known β values of those atoms that immediately precede it in the same group of the periodic table [14a]:

$$\beta_\mu^A = \beta_\mu^C * [U_A(s) + U_A(p)]/[U_C(s) + U_C(p)], \tag{15a}$$

an expression that can be generalized to spd-basis transition metals:

$$\beta_\mu^A = \beta_\mu^C * [U_A(s) + U_A(p) + U_A(d)] \div [U_C(s) + U_C(p) + U_C(d)]. \tag{15b}$$

These initial β values can then be refined in model molecular calculations. For this purpose, $U_{\mu\mu}$, the local core integral, is estimated under the CNDO approximation [14a] from Eqs. (5b)–(5d), settling all higher Slater–Condon factors ($F^k, G^k, k \geq 1$) to zero.

TABLE V. Effective ionization energies (eV).[a]

Element	I_s	I_p	I_d
Rb	4.43	2.64	1.77[b]
Sr	5.81	3.71	3.68
Y	6.49	4.10	6.46
Zr	7.07	4.40	7.80
Nb	7.51	4.61	8.91
Mo	7.71	4.65	9.51
Tc	7.64	4.49	9.35
Ru	7.58	4.33	9.03
Rh	7.60	4.19	8.71
Pd	7.58	4.00	8.96
Ag	7.31	3.61	12.51
Cd	8.95	4.70	17.68

[a]Based on the weighting factors in Table IV and the VSIES obtained using the fitting equations in Table III.
[b]Based on the d^n configuration only.

The β parameters for the second-row transition metals obtained in this fashion are given in Table VI. These bonding parameters, β, have been used for all the INDO/1 calculations performed herein. No refinements were made, although choosing these parameters specifically to yield more accurate results might be desirable.

D. Description of the Calculations

The molecular orbital calculations carried out in the present work were run using the program ZINDO [13, 14b]. Geometry optimizations were of the gradient-driven type [20]. Convergence to a stationary point on the potential energy surface was assumed when the maximum component of the gradient was less than 5×10^{-4} Hartrees/bohr. Calculations on open-shell species were performed using the restricted open-shell Hartree–Fock formalism [16]. Values of the orbital exponents used are summarized in Tables I and II.

TABLE VI. Beta values for second transition series elements (eV).

Element	$\beta(5s) = \beta(5p)$	$\beta(4d)$
Y	−1.0	−14.14
Zr	−1.0	−17.03
Nb	−1.0	−19.81
Mo	−1.0	−21.83
Tc	−1.0	−23.55
Ru	−1.0	−26.29
Rh	−1.0	−27.17
Pd	−1.0	−27.59
Ag	−1.0	−27.94

E. Calculation of Molecular Properties Using the Parameters Derived

1. Geometry Optimization of Second-Row Transition Metal Secies: The results of geometry optimizations on second-row transition metal species are, in general, quite good. The average percent error for all species is 4.4% (or 10 pm; $N = 48$). The average errors are measured using $\{\Sigma(R_{INDO} - R_e)^2/N\}^{1/2}$. N is the number of distinct M—X bonds, e.g., in a trigonal bipyramidal structure $N = 2$ (M—X_{axial} and M—$X_{equatorial}$). The average error for each individual transition metal ranges from 2.6% (3 pm; $N = 4$) for Ru and Nb (5 pm; $N = 7$) to 9.7% (22 pm; $N = 4$) for Ag. Several other points that deserve mentioning are an average error of 3.3% for charged species ($N = 15$), 3.7% for diatomic metal-oxo species, and a 3.3% average error for those molecules with coordination number greater than or equal to 4 about the central metal atom. This average error corresponds to 10 pm. A somewhat detailed analysis of these predicted geometries appears in a preliminary report on this work [21]; it was noted that four- to seven-coordinate species were well handled by this theory. Also, the INDO theory described here could be used to compare the total energies of different geometric isomers at their respective optimized structures with success.

2. Properties Other Than Geometry: Compared to the abundance of MO calculations on main-group species and the steadily increasing number of MO calculations on first-row transition metal molecules, the number of ab initio calculations on second-row transition metal species is small. Many of the calculations are of diatomics (MH [22] MO [23], etc.) and polyatomics of limited chemical interest (MoH$_6$ [24], RhH$_2$ [25], etc.). The further development of pseudopotential methods [26] should increase the size of the molecules that will be investigated by ab initio methods. To our knowledge, the only set of ab initio calculations for an entire class of second-row transition metal compounds are those of Bauschlicher and co-workers on the hydrides, MH [22]. INDO/1 geometry optimizations were performed for each of these species and compared to the results of Bauschlicher et al. and experimental data (where available). These molecules, with very "soft" potential energy curves, probably represent the most difficult test for the INDO method (or any method). In these calculations, the hydrogen is negatively charged, in agreement with the ab initio results. As a result, a more diffuse hydrogen (smaller orbital exponent) $1s$ AO was examined. The H $1s$ exponent value used in the previous calculations was the standard value of 1.2. Using $\zeta_H = 1.0$ gave hydrides that were too "hydridic," as evidences by dipole moments much larger than calculated by the ab initio methods and a significant decrease in the $4d$ population of the metal. $\zeta_H = 1.2$ led to poor predictions for equilibrium bond lengths. $\zeta_H = 1.1$ was found to provide the best compromise. The results are listed in Table VII.

Dipole Moments: The dipole moment is very sensitive to the level of theory employed. For example, in YH ($^1\Sigma^+$), a dipole moment of approximately 1.55 D is calculated using relativistic effective core potentials (RECPS) [22]. Going to an all-electron calculation, and correlating only the four valence orbitals of Y and H, results in a calculated dipole moment of 1.51 D using the coupled pair func-

TABLE VII.   INDO/1 geometry optimization results for diatomic metal hydrides[a]

Species	State (INDO)	State (ab initio)	r_e (Å) (INDO)	r_e (Å) (ab initio)
YH	$^1\Sigma^+$	$^1\Sigma^+$	1.772	1.915–1.982
YH	$^3\Delta$	$^3\Delta$	1.816	1.999–2.035
ZrH	$^2\Delta$	$^2\Delta$	1.727	1.845–1.857
ZrH	$^4\Phi$	$^4\Phi$	1.765	1.901–1.902
NbH	$^3\Phi$	$^3\Phi$	1.695	1.788–1.792
NbH	$^5\Delta$	$^5\Delta$	1.724	1.749–1.760
MoH	$^6\Sigma^+$	$^6\Sigma^+$	1.698	1.743–1.747
TcH	$^5\pi$	$^5\Sigma^+$	1.705	1.667–1.674
TcH	$^7\Sigma^+$	$^7\Sigma^+$	1.763	1.830–1.832
RuH	$^4\Phi$	$^4\Phi$	1.694	1.641–1.650
RuH	$^6\Delta$	$^6\Delta$	1.747	1.770–1.781
PdH	$^2\Sigma^+$	$^2\Sigma^+$	1.764	1.523–1.548
AgH	$^1\Sigma^+$	$^1\Sigma^+$	1.809	1.627–1.721

[a]Ab initio results come from Ref. 22 and the equilibrium bond length varies with basis set, level of correlation, and correlation formalism.

tional (CPF) approach [22]. Inclusion of the subvalent Y 4s and 4p electrons raises the value to 1.81 D, quite close to the 1.85 D calculated from the INDO wave function of the $^1\Sigma^+$ state. For AgH ($^1\Sigma^+$), using RECPS and correlating 12 electrons, yields dipole moments of 2.90 D (CPF) and 3.38 (SDCI) [22]. Switching to an all-electron calculation, 20 electrons correlated, yields 4.37 D (SDCI) and 3.18 D (CPF) at $r_e = 1.70$ Å. The INDO result is 4.47 D at $r_e = 1.66$ Å. These results are summarized in Table VIII. The relative orderings and trends in the dipoles are fairly well represented.

State Energies: The INDO calculations reproduce the correct ground states for all the systems examined except for YF$^+$ ($^2\Sigma^+$-calcd.; $^2\pi$-expt.), RuO$^+$ ($^4\Phi$-calcd.; $^4\Delta$-calcd.) (GVB-CI)), PdO (triplet), and AgO. In the case of RuO$^+$, the $^4\Delta$ (Ru$-\delta^3\pi_-^1\pi_+^1$) state is very close in energy to the $^4\Phi$ (Ru$-\delta^3\pi_-^1\sigma_n^1$) state, and, in fact, becomes the ground state on a slight stretching of the Ru$-$O bond [27]. This is not surprising since the transition from the $^4\Phi$ to the $^4\Delta$ involves the excitation from the nonbonding σ_n (5s and $4d_{z^2}$ mixing to polarize the orbital away from oxygen) to the antibonding RuO π^*. In the case of AgO and PdO (triplet), there is uncertainty in the correct symmetry of the ground state [23]. There is theoretical and experimental evidence in support of the state found by the INDO calculations, PdO($^3\pi$) and AgO($^2\Sigma^+$).

The relative ordering of the lowest-energy states of a given multiplicity are described quite well by the INDO wave function for the diatomic hydrides listed in Table IX. Of the five compounds in Table IX, the same ordering as the ab initio calculations of Bauschlicher et al. [22] is predicted in at least four cases. In the fifth case, ZrH, the predicted ground state depends on the level of theory. Using RECPS and the SDCI formalism, the $^4\Phi$ state is lower than the $^2\Delta$ state by 0.04 eV and higher by 0.06 eV employing the CPF formalism.

TABLE VIII.   Calculated dipole moments.[a]

Species	State (INDO)	μ_e (D) (INDO)	μ_e (D) (ab initio)
YH	$^1\Sigma^+$	1.85	1.48–1.81
YH	$^3\Delta$	2.04	2.78–3.30
ZrH	$^2\Delta$	2.26	1.28–1.54
ZrH	$^4\Phi$	1.75	2.22–2.44
NbH	$^3\Phi$	2.72	1.89–2.08
NbH	$^5\Delta$	1.81	2.28–2.48
MoH	$^6\Sigma^+$	2.46	3.00–3.18
TcH	$^5\pi$	2.99	2.57–3.08
TcH	$^7\Sigma^+$	0.02	0.73–0.81
RuH	$^4\Phi$	2.98	2.63–3.37
RuH	$^6\Delta$	0.66	0.13–0.31
RhH	$^3\Delta$	3.21	2.17–2.99
PdH	$^2\Sigma^+$	3.69	1.96–2.79
AgH	$^1\Sigma^+$	4.47	2.90–4.37

[a]INDO/1 values were calculated at what was determined by Bauschlicher and co-workers [22] to be the equilibrium bond length (using the coupled pair formalism [CPF] for electron correlation and including the valence orbitals in the active correlation space).

Stretching Frequencies: The stretching frequencies are expected to be too high. Indeed, this is the case (Table X). A remedy similar to that taken for ab initio calculations [28], i.e., scaling, could be employed. The scaling factor obtained is 1.41.

Spectroscopy: For the second-row transition metal hydrides, the ground and low-energy excited states for YH [29] and AgH [30] are relatively well explored.

TABLE IX.   State energies.[a]

Species	Ab initio	INDO/1
YH($^1\Sigma^+$)	−0−[b]	−0−
YH($^3\Delta$)	0.34 to 0.96	0.54
ZrH($^2\Delta$)	−0−	−0.31
ZrH($^4\Phi$)	−0.04 to 0.06	−0−
NbH($^5\Delta$)	−0−	−0−
NbH($^3\Phi$)	0.80 to 1.01	0.97
TcH($^5\pi$)	0.20 to 0.27	0.27
TcH($^7\Sigma^+$)	−0.11 to 0.14	−0−
RuH($^4\Phi$)	−0−	−0−
RuH($^6\Delta$)	0.82 to 1.06	0.14

[a]Relative energies in eV. The INDO/1 energy differences were calculated by subtracting the SCF energy of the excited state from the SCF energy of the ground state at the r_e determined by the INDO/1 method for the ground state. The ab initio results are from Ref. 23.
[b]−0− denotes the calculated ground state.

TABLE X.   Calculated equilibrium stretching frequencies.

Species	w_e (INDO/1) cm^{-1} [a]	w_e (INDO/1)$_{corr}$ [b]	w_e (cm^{-1}) [c]
$AgH(^1\Sigma^+)$	2182	1553	1760
$MoO(^7\pi)$	726	517	455–470[d, e]
$PdO(^1\Sigma^+)$	787	560	630–670[d]
$NbO(^3\Sigma^+)$	1322	941	989
$PdO(^3\pi)$	679	483	480–570[d]
$RhC(^2\Sigma^+)$	1666	1186	1050
$YCl(^1\Sigma^+)$	421	300	381
$YO(^2\Sigma^+)$	1143	814	861
$ZrO(^2\Sigma^+)$	1283	913	970
$RuO(^5\Delta)$	881	627	801[f], 855[g]
$YH(^1\Sigma^+)$	2364	1683	1513–1559
$YH(^3\Delta)$	2676	1905	1384–1412
$ZrH(^4\Phi)$	2967	2112	1525–1535
$MoH(^6\Sigma^+)$	2042	1453	1639–1662
$TcH(^7\Sigma^+)$	2479	1764	1742–1902
$PdH(^2\Sigma^+)$	2327	1656	1505–1755

[a]W_e was calculated from a quadratic fit of E vs. $(1/r)$ at four points ($r_e - 5\%r_e$, $r_e, r_e + 5\%r_e$, $r_e + 10\%r_e$).

[b]W_e(INDO/1) $\div$ 1.405.

[c]The "best" available value, i.e., experiment (if available); otherwise, a high-level ab initio calculation. Reported values are from Ref. 22 for the metal-hydrides; others are from Ref. 30 unless otherwise noted.

[d]Ref. 26

[e]If a range of values or more than one value is given, then w_e(INDO)/w_e is calculated with respect to the average.

[f]From an analysis of the data in Ref. 27.

[g]From a Ru—oxo porphyrin complex, Ref. 28

The theoretically determined transition energies (calculated using single excitation CI) are shown in Table XI.

The results show quite good agreement with the experimental values, in spite of the fact that no new parameters were introduced to obtain these results. In general, the very successful INDO/S (spectroscopic) model requires the use of empirical two-electron integrals set to match atomic spectroscopy [13, 14b].

Summary

It has been the aim of the present research to show that the INDO/1 method, although not specifically parameterized to favor any experimental quantity, does a reasonable job in describing the electronic structure of second-row transition metal species. Equilibrium bond lengths are predicted in good agreement with experimental data and higher level ab initio calculations. For properties other than bond lengths, there is a paucity of information available. Most of the available experimental data (e.g., stretching frequencies, transition energies, etc.) are for diatomic species. These species are in most cases of limited chemical interest. Also, the small size of these systems lends itself to the use of high-level ab initio

TABLE XI.   Spectroscopy for AgH and YH.[a]

Species	State	T_e(exp)	T_e(INDO/1)	r_e(exp) (Å)
AgH	$X - {}^1\Sigma^+$	$-0-$	$-0-$	1.62
	${}^1\Sigma^+$	3.27	3.71	1.67
	${}^1\pi$	4.98	5.12	1.61
	${}^3\pi$	5.17	5.18	1.64
	${}^3\Delta$	5.52–5.79[b]	5.14	1.87
	${}^1\pi$	5.79	5.31	1.80
YH	$X - {}^1\Sigma^+$	$-0-$	$-0-$	
	${}^3\Delta$	0.33–0.96	0.64	
	${}^3\pi$	0.94–1.01	0.77	
	${}^1\pi$	1.35	1.37	
	${}^1\Sigma^+$	1.77	1.89	
	${}^1\pi$	2.43	3.16	

[a]Experimental and calculated T_e's are in eV. Data are from Refs. 22 and 29 for AgH and YH, respectively.
[b]There is uncertainty as to the exact placement of this band [30].

calculations (with relativistic and electron correlation corrections) to accurately map the ground and low-energy excited states. The metal-hydrid systems probably represent the worse possible case for the INDO/1 calculations. Nevertheless, a comparison of INDO/1 calculations with the ab initio results of Bauschlicher and co-workers [22] for the diatomic hydrides showed good agreement. For polyatomic systems such as transition-metal complexes, organometallic systems, etc., the INDO/1 method was shown to yield results that were quite good in comparison to lower level ab initio calculations. In many of these cases, the size of the system studied with the INDO/1 method would make an ab initio calculation difficult.

There are many refinements to the model that can be made. Foremost among these is a careful parameter search. In particular, no specific fitting to experimental results have been made. The parameters used are atomic in nature, except for β, which has been extrapolated from the first transition series. Of interest is that such a crude parameterization works so well.

Acknowledgments

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