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An intermediate neglect of differential overlap (INDO) technique for lanthanide complexes: studies on lanthanide halides

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An intermediate neglect of differential overlap method of use for examining the electronic structure of lanthanide complexes is developed. It is characterized by a basis set obtained from relativistic Dirac–Fock atomic calculations, the inclusion of all one-center two-electron integrals, and a parameter set based on molecular geometry.

Lanthanide halides MX_2, MX_3 and MX_4 are studied here, as well as initial results for the twelve coordinate $Ce(NO_3)_6^{-2}$ ion. Geometries obtained are in excellent agreement with experimental values when available. Many MX_3 complexes are found to be pyramidal, and $EuCl_2$ and $YbCl_2$ are calculated to be bent even at the SCF level. Models invoking London type forces are therefore *not* required. Ionization potentials are calculated for the trihalides (ΔSCF) and are in reasonable agreement with experiment.

Contrary to conclusion of others, *f*-orbital participation, although small, is required - at least in this model - to obtain the spread of metal to halide bond distance observed in these complexes. However *f*-orbital participation does not seem to be significant even in the twelve coordinate $Ce(NO_3)_6^{-2}$ complex: rather the large coordination number seems to be a consequence of the relatively large size of the lanthanide ion.

Key words: INDO method for lanthanides — Lanthanide halides — $Ce(NO_3)_6^{2-}$

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1. Introduction

The past decade has seen a dramatic increase in interest and activity in lanthanide and actinide chemistry. Not only has considerable knowledge been gained in the traditional area of inorganic *f*-element chemistry, but much modern work is concerned with organo-*f*-element reactions [1], and the use of lanthanides and actinides as very specific catalysts [2, 3]. Unlike the corresponding chemistry involving the *d* metals, very little explanation is offered for much of this chemistry.

The electronic structure of these systems is difficult to calculate from quantum chemical means for several reasons. Most of the complexes of real experimental interest are large. In addition, very little about *f*-orbitals as valence orbitals is known, although experience is now being gained on the use of *f*-orbitals as polarization orbitals. Finally, the *f*-orbital elements are sufficiently heavy that relativistic effects become important. Very few *ab initio* molecular orbital studies have been reported on *f*-orbital systems [4]. Extended Hückel calculation, however, have been successful in explaining some of this chemistry [5]. Scattered wave and DVM Xα studies of *f*-orbital systems have also proven effective, especially in examining the photoelectron spectroscopy of reasonably complex systems [6–8].

In this paper, we examine an Intermediate Neglect of Differential Overlaps (INDO) technique for use in examining *f*-orbital complexes. At the Self-Consistent Field (SCF) level this technique executes as rapidly on a computer as does the Extended Hückel method, and considerably more rapid than the scattered wave Xα method. Since the electrostatics of the INDO method are realistically represented, molecular geometries can be obtained using gradient methods [9] as we shall demonstrate below. Since the INDO method we examine contains all one-center two-electron terms it is also capable of yielding the energies of various spin states in these systems. With configuration interaction (CI) this model should also be useful in examining the UV-visible spectra of *f*-orbital complexes. Preliminary studies of *f*-orbital chemistry using an INDO model have been disclosed by Clack and Warren [10] and, more recently, by Li Le-Min et al. [11]. The method we examine will differ from their methodology in several areas, as discussed below.

Several problems unique to a INDO tratment of these systems must be considered, and we have very little *ab initio* work to guide us. As mentioned, what role do relativistic effects play? Although we might hope to parameterize scalar contributions through the choice of orbitals and pseudo-potential parameters, spin orbit coupling, often larger than crystal field effects, will need to be considered at some later stage. Since *f*-orbitals are generally tight, and ligand field splittings thus small, a great many states differing only in their *f*-orbital populations lie very close in energy. These near degeneracies often prevent "automatic" SCF convergence, a problem with which we must deal for an effective model. The nature of the valence basis set itself is in question. Are the filled 5p and the vacant 6p of the lanthanides both required for a proper description of their compounds?

2. The model

The INDO model Hamiltonian that we use was first disclosed by Pople and collaborators [12], and then adjusted for the spectroscopy [13] and extended to the transition metal series [14–16]. The details of this model are published elsewhere [14–16]. To extend this model Hamiltonian to the *f*-orbital systems we need first a basis set that characterizes the valence atomic orbitals, and that is subsequently used for calculating the overlap and the one- and two-center two-electron integrals.

Subsequent atomic parameters that enter the model are the valence state ionization potentials used for calculating one-center one-electron "core" integrals and the Slater–Condon F^k and G^k integrals that are used for the formation of one-center two-electron integrals. The evaluation of these integrals using experimental information has traditionally made this model highly successful in predicting optical properties [17, 18].

We employ in this model one set of pure parameters, the resonance or $B(k)$ parameters; for each lanthanide atom we decided to use $B(s)=B(p)$, $B(d)$ and $B(f)$. These parameters will be chosen to give satisfactory geometries of model systems. Another choice is one that gives good predictions of UV-visible spectroscopy [13, 15]. These values seldom differ much from those chosen to reproduce molecular geometry.

In this initial work all two-center two-electron integrals required for the INDO model Hamiltonian are calculated over the chosen basis set, as are the one-center two-electron F^0 integrals. An alternate choice would be one that focuses on molecular spectroscopy. In such a case, and one that we have to investigate subsequently, the one-center two-electron F^0 could be chosen from the Pariser approximation [19] $F^0(n)=\mathrm{IP}(n)-\mathrm{EA}(n)$, (IP = Ionization Potential, EA = Electron Affinity) and the two-electron two-center integral from one of the more successful functions established for this purpose [20–22].

At the SCF level, we seek solutions to the pseudo-eigenvalue problem

$$\boldsymbol{F}\boldsymbol{C}=\boldsymbol{C}\boldsymbol{\varepsilon} \tag{1}$$

with $\boldsymbol{F}$, the Fock or energy matrix, $\boldsymbol{C}$, the matrix compound of Molecular Orbital (MO) coefficients, and $\boldsymbol{\varepsilon}$, a diagonal matrix of MO eigenvalues. The above equation is for the closed shell case (all electrons paired). The unrestricted Hartree Fock case is discussed in detail elsewhere [14], as is the open shell restricted case [23–25]. Although nearly all *f*-orbital systems are open shell, consideration of the closed shell case demonstrates the required theory and is considerably simpler.

Within the INDO model, elements of $\boldsymbol{F}$ are given by:

$$\begin{aligned} F_{\mu\mu}^{\mathrm{AA}} &= U_{\mu\mu}^{\mathrm{AA}} + \sum_{\substack{[\sigma,\lambda] \\ \subset \mathrm{A}}} P_{\sigma\lambda}[(\mu\mu|\sigma\lambda)-\tfrac{1}{2}(\mu\sigma|\mu\lambda)] \\ &\quad + \sum_{\substack{\sigma\subset \mathrm{B} \\ \neq \mathrm{A}}} P_{\sigma\sigma}(\bar{\mu}\bar{\mu}|\bar{\sigma}\bar{\sigma}) - \sum_{\mathrm{B}\neq \mathrm{A}} Z_{\mathrm{B}}(\bar{\mu}\bar{\mu}|s^{\mathrm{B}}s^{\mathrm{B}}) \end{aligned} \tag{2a}$$

$$F_{\mu\nu}^{\mathrm{AA}}=\sum_{\sigma,\lambda}^{\mathrm{A}} P_{\sigma\lambda}[(\mu\nu|\sigma\lambda)-\tfrac{1}{2}(\mu\sigma|\nu\lambda)] \qquad \mu\neq\nu \tag{2b}$$

$$F_{\mu\nu}^{\mathrm{AB}}=\tfrac{1}{2}(B_{\mathrm{A}}(\mu)+B_{\mathrm{B}}(\nu))S_{\mu\nu}-\tfrac{1}{2}P_{\mu\nu}(\bar{\mu}\bar{\mu}|\bar{\nu}\bar{\nu}) \qquad \mathrm{A}\neq\mathrm{B} \tag{2c}$$

where

$$(\mu\nu|\sigma\lambda)=\int \mathrm{d}\tau(1)\,\mathrm{d}\tau(2)\chi_{\mu}^{*}(1)\chi_{\nu}(1)r_{12}^{-1}\chi_{\sigma}^{*}(2)\chi_{\lambda}(2). \tag{3}$$

P is the first order density matrix, and since one assumes that the Atomic Orbital (AO) basis $\{\chi_\mu\}$ is orthonormal it is identical to the charge and bond order matrix, given by

$$P_{\mu\nu}=\sum_{a}^{\mathrm{MO}} C_{\mu a}C_{\nu a}n_a, \tag{4}$$

with n_a the occupation of MO Φ_a, $n_a=0,1,2$. In Eqs. (2), $F_{\mu\nu}^{\mathrm{AB}}$ refers to a matrix element $\langle\chi_\mu^{\mathrm{A}}|F|\chi_\nu^{\mathrm{B}}\rangle$ with AO χ_μ^{A} centered on atom "A". The core integral

$$U_{\mu\mu}^{\mathrm{AA}}=\left(\chi_\mu^{\mathrm{A}}\left|-\frac{1}{2}\nabla^2-\frac{Z_{\mathrm{A}}}{R}+\hat{V}^{\mathrm{A}}\right|\chi_\mu^{\mathrm{A}}\right) \tag{5}$$

is essentially an atomic term and will be estimated from spectroscopic data as described below. $\hat{V}^{\mathrm{A}}$ is an effective potential that keeps the valence orbital χ_μ^{A} orthogonal and non-interacting from the neglected inner-shell orbitals. The choice of an empirical procedure of $U_{\mu\mu}^{\mathrm{AA}}$ will remove the necessity for explicit consideration of this term. The bar over an orbital in an integral, such as $(\bar{\mu}^{\mathrm{A}}\bar{\mu}^{\mathrm{A}}|$ indicates that the orbital χ_μ is to be replaced with an s symmetry orbital of the same quantum number and exponent. The appearance of such orbitals in the theory is required for rotational symmetry and compensates for not including other two center integrals of the NDDO type [26], i.e. $(\mu^{\mathrm{A}}\nu^{\mathrm{A}}|$, $\chi_\mu\neq\chi_\nu$. The last term in Eq. (2a) represents the attraction between an electron in distribution $\chi_\mu^{\mathrm{A}*}\chi_\mu^{\mathrm{A}}$ and all nuclei but A. The rationale for replacing integral

$$(\mu^{\mathrm{A}}|R_{\mathrm{B}}^{-1}|\mu^{\mathrm{A}})\leftarrow(\bar{\mu}^{\mathrm{A}}\bar{\mu}^{\mathrm{A}}|s^{\mathrm{B}}s^{\mathrm{B}}) \tag{6}$$

is given elsewhere, and compensates for neglected two center inner shell-valence shell repulsion [27, 28] and neglected valence orbital (symmetrical) orthogonalization [28, 29]. Z_{B} is the core charge of atom B and is equal to the number of electrons of neutral atom B that are explicitly considered; i.e. 4 for carbon, 8 for iron, 4 for cerium, etc.

S of Eq. (2c) is related to the overlap matrix **Δ**, [13–15] and is given by

$$S_{\mu\nu}=\sum_{l=0} f_{\mu(1)\nu(1)}g_{\mu(1)\nu(1)}(\mu(1)|\nu(1)), \tag{7}$$

where $g_{\mu(1)\nu(1)}$ is the Eulerian transformation factor required to rotate from the local diatomic system to the molecular system, $(\mu(1)|\nu(1))$ are the sigma ($l=0$), pi ($l=1$), delta ($l=2$) or phi ($l=3$) components to the overlap in the local system, and $f_{\mu(1)\nu(1)}$ are empirical weighting factors chosen to best reproduce the molecular orbital energy spread for model *ab initio* calculations. We have made little use of this f factor, and set all $f=1$ except between p symmetry orbitals *viz* [13-15, 20].

$$S_{pp} = 1.267 g_{p\sigma p\sigma}(p\sigma|p\sigma) + 0.585 g_{p\pi p\pi}(p\pi|p\pi) \tag{8}$$

A. *The basis set*

In general ZDO methods choose a basis set of Slater Type Orbitals (STO)

$$R_{nlm} = \left[\frac{(2\zeta)^{2n+1}}{2n!}\right]^{1/2} r^{n-1}\, e^{-\zeta r} Y_1^m(\theta, \phi), \tag{9a}$$

where $Y_1^m(\theta, \phi)$ are the real, normalized spherical harmonics. Atomic orbitals χ_μ are expressed as fixed contractions of these $\{R_{nlm}\}$

$$\chi_\mu = \sum a_{nlm} R_{nlm}. \tag{9b}$$

In general a single R_{nlm} function describes the s and p orbitals for most atoms. The d orbitals of the transition metals, however, require at least a double-ζ type function (two terms in 9b) for an accurate description of both their inner and outer regions. For the lanthanides we have examined basis sets suggested by Li Le-Min et al. [10, 11], by Bender and Davidson [30], and by McLean and McLean [31]. In the latter case, the two major contributors of Eq. (9b) in the valence orbitals of the double-ζ atomic calculations were selected, and these functions were renormalized with fixed ratio to yield the required nodeless double-ζ functions for INDO. We were unable with any of these choices to develop a systematic model useful for predicting molecular geometries (see later discussion of resonance integrals).

We have adapted the following procedure on selecting an effective basis set [32]. The lanthanides and their mono-positive ions were calculated using the numerical Dirac–Fock relativistic atomic program of Desclaux [33]. From these wavefunctions radial expectation values $\langle r\rangle$, $\langle r^2\rangle$ and $\langle r^3\rangle$ are calculated for $6s$, $6p$, $5d$ and $4f$ functions. The $6s$, $5d$ and $4f$ wavefunctions were obtained by Dirac–Fock calculations on the promoted, $4f^{m-3}5d^1 6s^2$ configuration; the $6p$ from calculations in which a $5d$ electron was promoted, $4f^{m-3}6s^2 6p^1$. Wavefunctions for the mono-positive ions are obtained from $4f^{m-3}5d^1 6s^1$ and $4f^{m-3}6s^1 6p^1$ respectively. A generalized Newton procedure was then used to determine exponents (ζ) and coefficients α_{nlm} for a given set of $\langle r\rangle$, $\langle r^2\rangle$ and $\langle r^3\rangle$ with functions of the form of Eq. (9b). Again, as in the transition metal atoms, we found that a single ζ function fits the ns and np atomic functions well in the regions where bonding is important, but the $(n-1)d$, and now the $(n-2)f$ require at least two terms in the expansion of Eq. (9b). This is demonstrated for the Ce^+ ion in Fig. 1, where it is shown that a single-ζ expansion is poor for the outer region of the $4f$ function..

In Fig. 2 the value of $\langle r\rangle$ is plotted versus atomic number. the contraction of the $6s$ and $6p$ orbitals due to relativistic effects (DF vs. HF) is quite apparent here,

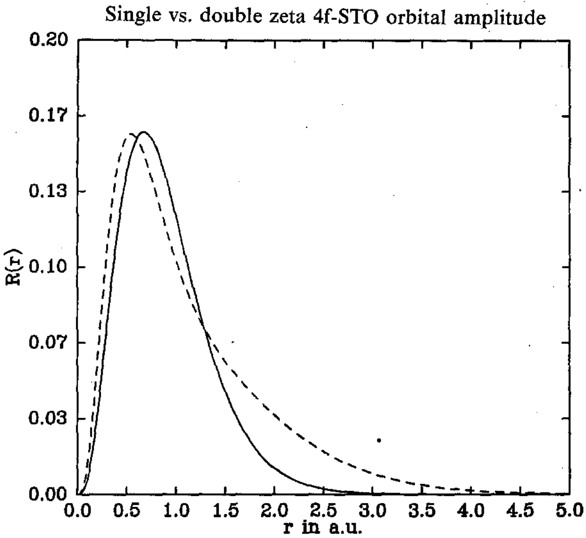

Fig. 1. Radial wavefunction for the 4*f* orbital of Ce^+ with single-ζ and double-ζ Slater type orbitals (STOs). ---, double zeta; ——, single zeta

and is a consequence of the greater core penetration of these orbitals. Subsequent expansion of the 4*f* and 5*d*, now with increased shielding, results. After some experimentation we use the Dirac-Fock values obtained from the mono-positive ions. The basis set adopted is given in Table 1.

The 4*f* and 5*d* functions are quite compact. At typical bonding distance $(4f4f|\mu\mu)$ and $(5d5d|\mu\mu)$ are essentially R_{AB}^{-1}. Because of this we calculate all two-center

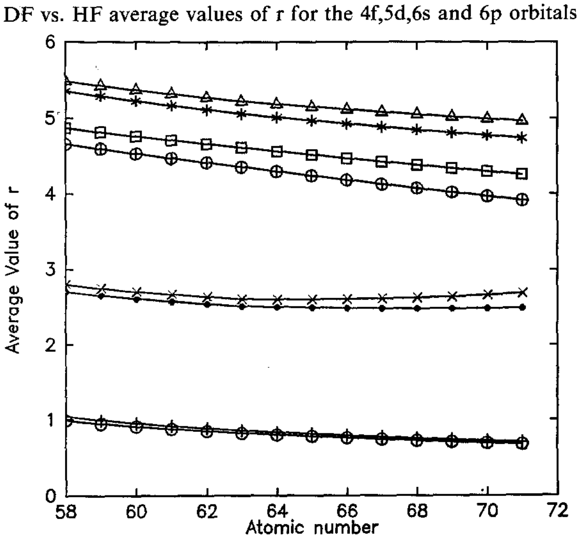

Fig. 2. Average value of *r* for the valence orbitals of the lanthanides from a relativistic calculation (DF) and a non-relativistic calculation (HF). *: DF−6*p*; △: HF−6*p*; ⊕: DF−6*s*; □: HF−6*s*; ×: DF−5*d*; ●: HF−5*d*; +: DF−4*f*; O: HF−4*f*

Table 1. Slater type orbital (STO) basis functions for the lanthanide atoms. The single ζ functions are listed for the $4f$, $5d$, $6s$ and $6p$ orbitals along with the double ζ functions for the $4f$ and $5d$ orbitals

	Single ζ exponents				Double ζ							
					Exponents				Coefficients			
Atom	$4f$	$5d$	$6s$	$6p$	$4f$		$5d$		$4f$		$5d$	
Ce	4.439	2.061	1.548	1.361	6.118	2.522	3.077	1.581	0.7159	0.4575	0.5003	0.6334
Pr	4.657	2.102	1.571	1.380	6.393	2.646	3.126	1.598	0.7175	0.4542	0.5104	0.6257
Nd	4.681	2.138	1.593	1.398	6.648	2.757	3.169	1.612	0.7196	0.4510	0.5202	0.6182
Pm	5.053	2.171	1.614	1.415	6.889	2.858	3.208	1.623	0.7220	0.4479	0.5295	0.6112
Sm	5.236	2.201	1.635	1.432	7.120	2.951	3.244	1.633	0.7247	0.4450	0.5238	0.6046
Eu	5.414	2.229	1.656	1.448	7.342	3.038	3.278	1.640	0.7275	0.4421	0.5466	0.5986
Gd	5.565	2.243	1.678	1.463	7.523	3.091	3.288	1.634	0.7332	0.4375	0.5562	0.5916
Tb	5.717	2.254	1.700	1.478	7.707	3.148	3.298	1.628	0.7379	0.4337	0.5648	0.5857
Dy	5.869	2.262	1.723	1.492	7.892	3.206	3.307	1.621	0.7421	0.4304	0.5724	0.5808
Ho	6.019	2.269	1.745	1.507	8.076	3.264	3.316	1.613	0.7461	0.4273	0.5791	0.5768
Er	6.168	2.274	1.767	1.521	8.258	3.320	3.324	1.605	0.7498	0.4243	0.5852	0.5735
Tm	6.316	2.277	1.789	1.535	8.438	3.375	3.332	1.596	0.7534	0.4214	0.5905	0.5709
Yb	6.462	2.279	1.812	1.549	8.616	3.428	3.338	1.587	0.7570	0.4186	0.5952	0.5690
Lu	6.607	2.278	1.834	1.562	8.791	3.480	3.343	1.577	0.7605	0.4159	0.5994	0.5676

two-electron integrals with ζ_1 values in Table 1. This value is chosen to match the accurate F^0 Slater-Condon Factors obtained from the numerical atomic calculations by a single exponent, via

$$F^0(4f4f) = 0.200905\ \zeta\ (4f) \tag{10a}$$

$$F^0(5d5d) = 0.164761\ \zeta\ (5d) \tag{10b}$$

$$F^0(6s6s) = 0.139803\ \zeta\ (6s) \tag{10c}$$

$$F^0(6p6p) = 0.139803\ \zeta\ (6p). \tag{10d}$$

The error in calculating two-centered two-electron integrals at typical bonding distances with this single-ζ approximation is well under 1%, and this procedure is much simpler.

B. Core integrals

The average energy of a configuration of an atom or ion is given by [34, 35]

$$\begin{aligned} E(s^k p^m d^n f^q) = {} & kU_{ss} + mU_{pp} + nU_{dd} + qU_{ff} + \frac{k(k-1)}{2} W_{ss} \\ & + \frac{m(m-1)}{2} W_{pp} + \frac{n(n-1)}{2} W_{dd} + \frac{q(q-1)}{2} W_{ff} + kmW_{sp} \\ & + knW_{sd} + kqW_{sf} + mnW_{pd} + mqW_{pf} + nqW_{df}, \end{aligned} \tag{11}$$

with W_{ij}, the average two electron energy of a pair of electrons in orbitals χ_i and χ_j given by

$$\begin{aligned} W_{ss} &= F^0(ss) \\ W_{pp} &= F^0(pp) - 2/25F^2(pp) \\ W_{dd} &= F^0(dd) - 2/63F^2(dd) - 2/63F^4(dd) \\ W_{ff} &= F^0(ff) - 4/195F^2(ff) - 2/143F^4(ff) - 100/5577F^6(ff) \\ W_{sp} &= F^0(sp) - 1/6G^1(sp) \\ W_{sd} &= F^0(sd) - 1/10G^2(sd) \\ W_{sf} &= F^0(sf) - 1/14G^3(sf) \\ W_{pd} &= F^0(pd) - 1/15G^1(pd) - 3/70G^3(pd) \\ W_{pf} &= F^0(pf) - 3/70G^2(pf) - 2/63G^4(pf) \\ W_{df} &= F^0(df) - 3/70G^1(df) - 2/105G^3(df) - 5/231G^5(df). \end{aligned} \tag{12}$$

The core integrals U_{ii}, Eq. 5, are then evaluated by removing an electron from orbital χ_i, and equating the difference in configuration energy between cation and neutral to the appropriate observed IP(n). We prefer this procedure rather than that suggested by others that average the value obtained from IP(n) and EA(n) [29, 34, 36].

There are a great many low lying configurations of the lanthanide atoms and their ions. The lowest terms of Ce, Gd and Lu come from $f^{n-3}ds^2$, while the remaining lanthanide atoms have the structure $f^{n-2}s^2$. Two processes are then possible for $6s$ electron ionization:

I $f^{n-3}d^1s^2 \to f^{n-3}d^1s^1 + (s)$

II $f^{n-2}s^2 \to f^{n-2}s^1 + (s)$.

The ionization energy of a $6s$ electron from I is systematically 0.4–0.5 eV larger than that obtained from II. When combined with Eq. (11), the estimate for U_{ss} differ by less than 0.1 eV. That is, choosing the values of process I, the use of Eq. (11) predicts the values of process II within 0.1 eV. We thus choose the values of process I shown in Table 2. These values are obtained from the promotion energies of Brewer [37, 38] and then smoothed by a quadratic fit throughout the series. For completeness, we also give the values of process II.

The lowest configuration containing a $5d$ electron is $f^{n-3}d^1s^2$ throughout the series, and $5d$ ionizations are obtained from

III $f^{n-3}d^1s^2 \to f^{n-3}s^2 + (d)$.

The ionization potentials for the $6p$ can be obtained from two processes:

IV $f^{n-2}s^1p^1 \to F^{n-2}s^1 + (p)$

V $f^{n-3}s^2p \to f^{n-3}s^2 + (p)$.

Ionization from process IV is nearly constant at 3.9 eV, from V at 4.6 eV. The $f^{n-2}s^2$ configuration is lower for all the lanthanides except Ce($fdsp$), and Gd

Table 2. Smoothed ionization potentials for processes I–VII and configuration mixing coefficients derived from Brewer's tables. The entries in the column labeled 1 are the mixing coefficients for the configuration $f^{n-3}ds^2$, in column 2 the $f^{n-2}s^2$ configuration mixing coefficients are listed

	Smoothed ionization potentials								
					process			Mixing coefficients	
	s		p		d	f			
Atom	I	II	IV	V	III	VI	VII	1	2
Ce	5.93	5.36	3.69	4.60	6.74	12.17	7.24	0.7558	0.2442
Pr	5.89	5.42	3.76	4.62	6.77	12.79	7.27	0.2764	0.7236
Nd	5.93	5.48	3.82	4.67	6.77	13.35	7.29	0.1772	0.8228
Pm	5.98	5.55	3.87	4.65	6.74	13.85	7.31	0.1465	0.8535
Sm	6.04	5.63	3.91	4.70	6.73	14.27	7.35	0.0557	0.9423
Eu	6.10	5.69	3.95	4.74	6.68	14.62	7.39	0.0236	0.9764
Gd	6.17	5.77	3.99	4.76	6.61	14.90	7.44	0.9037	0.0936
Tb	6.25	5.85	4.03	4.80	6.54	15.13	7.49	0.4821	0.5179
Dy	6.34	5.93	4.05	4.84	6.42	15.27	7.55	0.1564	0.8436
Ho	6.42	6.01	4.08	4.89	6.30	15.35	7.61	0.1533	0.8467
Er	6.52	6.09	4.10	4.92	6.16	15.36	7.69	0.1661	0.8339
Tm	6.62	6.17	4.12	4.97	6.10	15.30	7.76	0.0731	0.9269
Yb	6.73	6.26	4.13	5.02	5.96	15.18	7.84	0.0273	0.9727
Lu	6.77	—	—	—	5.31	16.11	—	1.000	—

and Tb($f^{n-3}s^2p$). Using the ionization potentials of process IV, and Eq. (11), we predict the values of process V to within 0.2 eV. We do not consider this error significant, and thus use the smoothed values from IV given in Table 2. The values from process V are also given in the table for comparison.

For a f orbital ionization, we consider the two processes

VI $f^{n-3}ds^2 \rightarrow f^{n-4}ds^2 + (f)$

VII $f^{n-2}s^2 \rightarrow f^{n-3}s^2 + (f)$

(compare with I and II). As seen in Table 2 the values from the two processes are very different. From Eq. (11)

$$U_{ff}(\mathrm{VI}) = \mathrm{IP(VI)} - (m-4)\,W_{ff} - 2\,W_{ff} - W_{df} \tag{13a}$$

$$U_{ff}(\mathrm{VII}) = \mathrm{IP(VII)} - (m-3)\,W_{ff} - 2\,W_{sf}. \tag{13b}$$

Unlike the analogous situation for the $6s$ and $6p$ orbitals, use of Eq. (13a) to find U_{ff}, and use of this value in Eq. (13b) to predict IP(VII) is not successful, and would require the scaling of the large $F^0(ff)$ integral often performed in methods parameterized on molecular spectroscopy [13, 15, 19].

As with the transition metal nd orbitals we might envision the following procedure. We assume that the lanthanide atom in a molecule is a weakly perturbed atom. The lowest energy configuration of the atom should then be most important in determining U_{ff}. We create a two-by-two interaction matrix

$$\begin{pmatrix} E(f^{n-3}ds^2) - \lambda & V \\ V & E(f^{n-2}s^2) - \lambda \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0, \tag{14a}$$

where V is an empirical mixing parameter, and C_1^2 and C_2^2 determines the relative amounts of each of the two configurations that are important. The exact value of V would depend on a given molecular situation. C_1^2 is then given by

$$C_1^2 = \frac{\chi^2}{1+\chi^2} \tag{14b}$$

$$\chi = C_1/C_2 = \frac{E(f^{n-3}ds^2) - E(f^{n-2}s^2)}{2V} + \sqrt{\left(\frac{E(f^{n-3}ds^2) - E(f^{n-2}s^2)}{2V}\right)^2 + 1}. \tag{14c}$$

The values of C_1^2 appear in Table 2, where we have used the values of $E(f^{m-3}ds^2)$ and $E(f^{m-2}s^2)$ obtained for the promotion energies of Brewer [37, 38], and a fixed value of $V = 0.02$ au. Then U_{ff} could be obtained from

$$U_{ff} = C_1^2 U_{ff}(\mathrm{VI}) + C_2^2 U_{ff}(\mathrm{VII}). \tag{15}$$

In the case of the $3d$ orbitals this valence bond mixing between $3d^{n-2}s^2$ and $3d^{n-1}s$ was important in obtaining reasonable geometric predictions [15], an observation now confirmed in careful *ab initio* studies [39]. For the lanthanide integrals and their labels in the MOLECULE [43] format only the additional integrals need be included. These integrals are generated in explicit form via a computer program that we have used in the past [15] and they have also been recently published by Jug [41]. To our knowledge all these integrals do not appear in the literature for s, p, d and f basis, although we have checked those of $(\mu\mu|\nu\nu)$ and $(\mu\nu|\nu\mu)$ against the formulas of Fanning and Fitzpatrick [35].

Integrals of the form $(\mu\mu|\nu\nu)$ and $(\mu\nu|\nu\mu)$ can be obtained through atomic spectroscopy, and their components, F^k and G^k, evaluated via least square fits

$$(\mu\mu|\nu\nu)=\sum_k a_kF^k$$

$$(\mu\nu|\nu\mu)=\sum_k b_kG^k.$$

These F^k and G^k can then be used to evaluate all integrals of the "F" or "G" type, even those that do not appear in atomic spectra because of high symmetry (i.e. $(d_{x^2-y^2}d_{yz}|d_{xz}d_{xy})$). Integrals of the "$R$" type, however, cannot be evaluated in this manner; viz. $(sd|dd)$, $(sp|pd)$, $(sd|pp)$, $(sd|ff)$, $(sf|df)$, $(pp|pf)$, $(dd|pf)$, $(pd|df)$, $(sd|pf)$, $(pd|sf)$, $(sp|df)$, and $(pf|ff)$. For this reason we evaluate all one-center two-electron integrals of the lanthanides using the basis set of Table 1, which yields the exact F^0 value obtained from the Fock-Dirac numerical calculations. All F^k, G^k and R^k integral for $k>0$ are then scaled by 2/3. This value of the scaling is obtained from a comparison of the calculated and empirically obtained [10, 44-46] $F^2(ff)$, $F^4(ff)$ and $F^6(ff)$ values that implies 0.66 ± 0.04. Empirically obtained values of $G^k(fd)$ and $F^k(fd)$ are far more uncertain and are much smaller, and are thus not used to obtain this scaling value between calculated and experimental values. At this point is seems appropriate to point out the differences of the present INDO model to that suggested by Li Le-Min *et al* [11]. In the latter formalism only the conventional one-center two-electron integrals are included leading to rotational variance. In addition, the Wolfsberg-Helmholz approach is used for the resonance integral B, $B_{ij}=(\mathrm{IP}(i)+\mathrm{IP}(j))S_{ij}/2$. No geometry optimization has been reported within their model [11]. Further differences are the restriction to single-ζ STOs and the smoothing of the valence orbital ionization potentials for the lanthanides via Anno-type expressions [11].

3. Procedures

The input to the INDO program consists of molecular coordinates and atomic numbers. Molecular geometries are obtained automatically via a gradient driven quasi-Newton update procedure [9], using either the restricted or unrestricted Hartree-Fock formalism. All UHF calculations are followed by simple annihilation [14].

Self-consistent field convergence is a problem with many of these systems. For this reason electrons are assigned to molecular orbitals that are principally f in nature according to the number of f-electrons in the system, and the symmetry of the system. Orbitals with large lanthanide $5d$ character are sought and assigned no electrons. A procedure is then adopted that extrapolates a new density for a given Fock matrix based on a Mulliken population analysis of each SCF cycle [47].

Often this procedure is not successful. In such cases all *f* orbitals are considered degenerate, and they are equally occupied in the highest spin configuration using the RHF open shell method [23]. These vectors (orbitals) are then stored, and the SCF repeated with the specific *f* orbital assignments as described above.

In cases of slow convergence, a singles or small singles and doubles, CI is performed to check the stability of the SCF, and the appropriateness of the forced electron assignment to obtian the desired state [48].

4. Results

The geometries of $CeCl_3$ and $LuCl_3$ were used to determine an optimal set of resonance integrals and configurational mixing coefficients. No further fitting was performed, and thus the structures of all other compounds are "predictions". The resonance parameters for the other lanthanides were determined by interpolation from the values for Ce and Lu (see Table 4). The INDO optimized geometries as well as the remaining cerium and lutetium trihalides are listed in Table V. In addition to the trihalides reported, the geometry of CeF_4 is also listed in Table 5. One can see the agreement with experiment is good in all cases.

The potential energy of the trihalides as a function of the out of plane angle is very flat. Although we have optimized all structures until the gradients are below 10^{-4} au/bohr, the angles are converged only to $\pm 3^0$. We note, however, that all are predicted non-planar, in agreement with experiments [6b, 49, 50].

The experimental range of the bond lengths from LnF_3 to LnI_3 is greater than we calculate. Our predicted values for the trifluorides and trichlorides are in good agreement, while bond lengths for the tribromides and triiodides are too short. Since these are the more polarizable atoms it is possible that configuration

Table 5. Geometry and ionization potentials for Cerium and Lutetium trihalides. Cerium tetrafluoride is also included in this table. The bond distances are given in angstroms, angles in degrees and IPs and eV. Experimental[a] results are also shown where available

	Bond distance		Bond angle		Ionization potential	
Molecule	INDO	Exp.	INDO	Exp.	INDO	Exp.
CeF_3	2.204	2.180	106.8	—	8.4	8.0
$CeCl_3$	2.570	2.569	115.6	111.6	10.0	9.8
$CeBr_3$	2.668	2.722	115.8	115.0	9.6	9.5
CeI_3	2.844	2.927	119.8	—	9.9	—
CeF_4	2.099	2.040	109.5	109.5	—	—
LuF_3	2.045	2.020	107.4	—	[b]	19.0
$LuCl_3$	2.415	2.417	108.2	111.5	18.6	(17.4 – 18.7)
$LuBr_3$	2.528	2.561	108.6	114.0	17.8	(16.8 – 18.4)
LuI_3	2.726	2.771	115.6	114.5	17.7	(16.2 – 18.1)

[a] [6b, 49] and [50]. Estimated values for CeF_3, CeI_3, and LuF_3 from [55]

[b] The SCF calculation on the ion of LuF_3 would not converge therefore no IP is reported

complexes of this study the $4f$ orbitals are quite compact, and this valence bond mixing does not greatly affect geometries. However, the calculation of ionization potentials that result in states with reduced f-orbitals occupation is influenced.

There are many refinements one can make in the formation of a "mixing" matrix such as Eq. (14a). One might be to make V dependent on the calculated population of the $4f$ and $5d$ atomic orbitals. However, the values of the promotion energies we obtain from Brewer are so different than those that we obtain from our own numerical calculations on the average energy of a configuration, Table 3, that for the moment we choose a 76% : 24% mix of $E(f^{m-3}ds^2):E(f^{m-2}s^2)$ for all the atoms of the series. This mix gives reasonable geometries and ionization potentials for all molecules of this study. Further refinements will require more accurate atomic promotion energies and numerical experience with the model.

C. The resonance parameters, $B(k)$

Each lanthanide atom has three $B_\mu(k)$ values, $B(s)=B(p)$, $B(d)$ and $B(f)$, and those we choose are summarized in Table 4. They are obtained by fitting the geometries of the trihalides, and the more covalent valent bis-cyclopentadienyls to be reported elsewhere.

Bond lengths are most sensitive to $B(d)$ and bond angles to $B(p)$. These angles can be reproduced solely on a basis set including $6p$ orbitals, and we have been able to obtain satisfactory comparisons with experiment without the necessity of including the $5p$ orbitals. On the other hand, orbitals of p symmetry do seem to be required for accurate predictions of geometry [10, 11].

Table 3. Average configuration energy from Dirac-Fock, calculations[a] on the $f^{n-3}ds^2$ and the $f^{n-2}s^2$ configurations for all the lanthanide atoms

	Average configuration energy	
Atom	$f^{n-3}d^1s^2$	$f^{n-2}s^2$
Ce	−8853.71494569	−8853.64980000
Pr	−9230.41690970	−9230.37981848
Nd	−9616.94751056	−9616.93446923
Pm	−10013.4526061	−10013.4606378
Sm	−10420.0710475	−10420.0976615
Eu	−10836.9533112	−10836.8834715
Gd	−11264.0945266	−11264.0439334
Tb	−11701.7877496	−11701.7482691
Dy	−12150.1565528	−12150.1286785
Ho	−12609.3663468	−12609.3484161
Er	−13079.5686394	−13079.5585245
Tm	−13560.9236801	−13560.9201649
Yb	−14053.5770354	−14053.5786047
Lu	−14557.7153258	—

[a] [33]

Table 4. Resonance integrals (beta values) for the Lanthanide atoms in eV. The beta for the *s*-orbital is set equal to the beta for the *p*-orbital

Atom	$B(s)$	$B(p)$	$B(d)$	$B(f)$
Ce	−8.00	−8.00	−17.50	−80.00
Pr	−7.61	−7.61	−17.58	−80.00
Nd	−7.23	−7.23	−17.65	−80.00
Pm	−6.85	−6.58	−17.73	−80.00
Sm	−6.46	−6.46	−17.81	−80.00
Eu	−6.08	−6.08	−17.88	−80.00
Gd	−5.69	−5.69	−17.96	−80.00
Tb	−5.31	−5.31	−18.04	−80.00
Dy	−4.92	−4.92	−18.11	−80.00
Ho	−4.54	−4.54	−18.19	−80.00
Er	−4.15	−4.15	−18.27	−80.00
Tm	−3.77	−3.77	−18.35	−80.00
Yb	−3.38	−3.38	−18.42	−80.00
Lu	−3.00	−3.00	−18.50	−80.00

It has been argued that the $4f$ orbitals are not used in the chemical bonding of those complexes except in the more covalent cases [7, 8]. From the present study we are lead to the conclusion that some, albeit small, contribution is required of these obitals to obtain the excellent agreement between experimental and calculated bond lengths for the series MF_3, MCl_3, MBr_3 and MI_3 and for the comparative values obtained for CeF_3 and CeF_4. This is indicated in Table 4 by the large values of $|B(f)|$. The latter values are a consequence of the fact that the f-orbitals are more compact than one usually expects for orbitals important in chemical bonding. Use of $5d$ orbitals alone will predict the trends in these two series, but underestimates the range of values experimentally observed.

D. Two electron integrals

Several different interpretations have been given to the INDO scheme. The simplest of those schemes is to include only one-centered integrals of the coulomb or exchange type

$$(\mu\mu\,|\,\nu\nu) \text{ or } (\mu\nu\,|\,\nu\mu).$$

For an *s*, *p* basis these are complete. For an *s*, *p*, *d* or *s*, *p*, *d*, *f* basis they are not, and the omission of the remaining integrals will lead to rotational variance. To restore rotational invariance, integrals of this type might be rotationally averaged [40], but from a study of spectra it appears that all one-center integrals should be evaluated [15]. For example, in the metallocenes the integral $(d_{x^2-y^2}d_{xy}\,|\,d_{xy}d_{yz})$ is required to separate the two transitions that arise from the $e_{1g}(d) \rightarrow e_{2g}(d)$ transitions that lead to the ${}^1E_{1g}$ and ${}^1E_{2g}$ excited states. In addition, it appears that the inclusion of all one-center integrals improves the predictions of angles about atoms with *s*, *p*, *d* basis sets [41, 42] and considerably improves the predictions of angles about the lanthanides. For these reasons we include all the one-center two-electron integrals. Since the INDO programs we use process interaction will have its largest affect on these systems. The calculated change in bond length of 0.11 Å in going from CeF_3 to CeF_4 is also smaller than the 0.14 Å observed.

Ionization potentials (IPs) are also reported in Table 5. In all cases the INDO values fall within the experimental ranges. These values are calculated using the ΔSCF method, and only the first IP is calculated. Experimentally [6b, 51] these valued are somewhat uncertain, but they are split by both crystal field effects, and by the large spin-orbit coupling not yet included in our calculations. However, the latter interaction is treated implicitly in the DVM Xα calculations [6b] based on the Dirac equation. Therefore, the Xα result for the ionization potentials show better agreement with the experiment in this aspect, but it is quite remarkable that the present INDO approach is able to reproduce the experimental trend in the first IP of the series, CeX_3, $X = F$, Cl, Br with a maximum value for the chloride, a feature noticeably missing in the DVM Xα results [6b].

The initial success of the INDO model as implemented here lead us to calculate both geometries and IPs for the remaining lanthanide trichlorides. These results are shown in Table 6. The experimental geometries [6b, 49, 50] are very well reproduced by the INDO calculations. The INDO IPs reproduce the characteristic "W" pattern of the lanthanide atoms, and fall within the experimental ranges.

To test the applicability of our model to lanthanide atoms not formally charged +3, we calculated the geometries and IPs for $SmCl_2$, $EuCl_2$ and $YbCl_2$ molecules. The results are given in Table 7. The INDO model gives optimized geometries that are bent and in good agreement with experimental results [52]. We note that this bending is a result of a small amount of p-orbital hybridization. It is not necessary to invoke London type forces, and thus correlation, to explain this effect.

Table 6. Geometries and Ionization Potentials (IPs) for the lanthanide trichlorides. Bond distances are reported in angstroms, bond angles in degrees and IPs in eV. Experimental[a] results are also given where available

	Bond distance		Bond angle		Ionization potential	
Atom	INDO	Exp.	INDO	Exp.	INDO	Exp.
Ce	2.570	2.569	115.6	111.6	10.0	9.8
Pr	2.566	2.553	108.5	110.8	11.8	(10.9 – 11.2)
Nd	2.563	2.545	112.7	—	13.3	12.0
Pm	2.556	—	112.7	—	14.4	—
Sm	2.544	—	113.0	—	15.3	(13.7 – 17.0)
Eu	2.532	—	113.2	—	16.4	—
Gd	2.514	2.489	110.0	113.0	17.7	(15.5 – 16.5)
Tb	2.496	2.478	109.8	109.9	13.0	(13.0 – 20.5)
Dy	2.479	—	110.1	—	14.3	(14.0 – 20.0)
Ho	2.464	2.459	112.0	111.2	15.0	(15.5 – 20.0)
Er	2.448	—	110.9	—	15.6	(11.5 – 16.0)
Tm	2.430	—	108.5	—	15.9	(15.3 – 21.0)
Yb	2.421	—	109.6	—	15.9	(15.5 – 21.0)
Lu	2.415	2.417	108.2	111.5	18.6	(17.4 – 18.7)

[a] [6b, 49] and [51]

Table 7. Geometry and ionization potential for $SmCl_2$, $EuCl_2$, and $YbCl_2$. Bond distances are given in angstroms, bond angles in degrees, and ionization potentials in eV. Experimental results[a] are listed where available

	Bond distance		Bond angle		Ionization potential	
Molecule	INDO	Exp.	INDO	Exp.	INDO	Exp.
$SmCl_2$	2.584	—	143.3	130±15	5.3	—
$EuCl_2$	2.576	—	143.2	135±15	6.6	—
$YbCl_2$	2.400	—	120.2	126±5	3.2	—

[a] Ref. 52

We chose $Ce(NO_3)_6^{-2}$ as our last example because it is one of the few known examples of a twelve coordinate metal. The optimized geometry is summarized in Table 8 and a plot of the optimized geometry is shown as Fig. 3. As one can see from Table 8 INDO predicts a geometry that is in excellent agreement with the experimental crystal structure [53]. Table 9 shows a population study of this complex. Although there is some *f*-orbital participation, it appears that this unusual twelve coordinate T_h structure results from electrostatic forces between the ligands and the relatively large size of the Ce(IV) ion.

5. Conclusions

We develop an Intermediate Neglect of Differential Overlap (INDO) method that includes the lanthanide elements. This method uses a basis set scaled to reproduce Dirac-Fock numerical functions on the lanthanide mono-cations, and is characterized by the use of atomic ionization information for obtaining the one-center one-electron terms, and including all of the two-electron integrals. This latter refinement is required for accurate geometric predictions, some of which are represented here, and for accuracte spectroscopic predictions, to be reported latter.

We have applied this method to complexes of the lanthanide elements with the halogens. The geometries calculated for these complexes are in good agreement

Table 8. Average bond distances and bond angles for $Ce(NO_3)_6^{-2}$ ion INDO optimized geometry and the X-ray crystal structure[a]. Distances are in angstroms and angles in degrees. The *c* subscript on the oxygen atoms denotes that the oxygen is bonded to the cerium and the *n* subscript signifies a non-bonded oxygen

Geometric parameter	INDO	Exp.
$r(Ce—O_c)$	2.52	2.508
$r(N—O_c)$	1.27	1.282
$r(N—O_n)$	1.22	1.235
$\theta(O_c—N—O_c)$	121.5	114.5
$\theta(O_c—Ce—O_c)$	50.9	50.9

[a] [53]

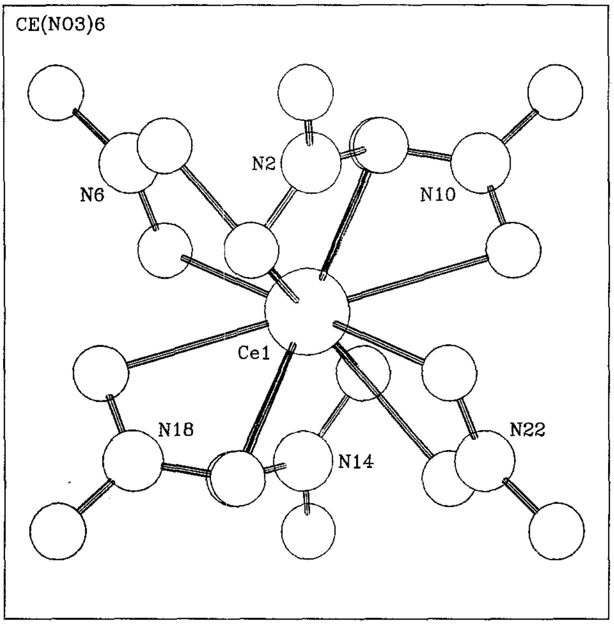

Fig. 3. Plot of the twelve coordinate $Ce(NO_3)_6^{-2}$ ion. Nitrogens 2, 18 and 22 are above the plane of the paper, while nitrogens 6, 10 and 14 lie below the plane of the paper

Table 9. Population analysis of $Ce(NO_3)_6^{-2}$. The oxygen atoms that are coordinated to the cerium are indicated by O_c. The Wyberg bond index is also given. A Wyberg index of 1.00 is characteristic of a single bond

Atom	Orbital	Atomic population	Total valency
Ce	*s*	0.23	—
	p	0.33	—
	d	1.67	—
	f	0.46	—
	Net	1.31	6.37
N	Net	0.59	3.82
O_c	Net	−0.38	1.85
O_n	Net	−0.39	1.68

Bond	Wyberg bond index
Ce—O_c	0.50
N—O_c	1.18
N—O_n	1.46

with experiment, when experimental values are available. The trihalides are calculated to be pyramidal in agreement with observation. The potential for the umbrella mode, however, is very flat. The dichlorides of Sm, Eu and Yb are all predicted to be bent even at the SCF level, again in agreement with experiment. This bending is caused by a small covalent mixing of ungerade 6*p* and 4*f* orbitals, and one need not invoke London forces to explain this observation. Again the potential for bending is very flat.

Within this model, *f*-orbitals participation in the bonding of these ionic compound through covalent effects is small. Nevertheless *f*-orbitals participation does contribute to the pyramidal geometry of the trihalides and the bent structure of the dihalides. In addition, although the trend of bond lengths within the series LnF_3, $LnCl_3$, $LnBr_3$, and LuI_3, and CeF_3 and CeF_4 are reproduced without *f*-orbital participation, the range of values calculated is considerably improved when *f*-orbitals are allowed to participate. For the twelve coordinate $Ce(NO_3)_6^{-2}$ complex reported here, *f*-orbital participation appears minor. A stable complex of near T_h symmetry is obtained regardless of the *f*-orbital interaction [54].

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