that the volume V be the total number of sites. The *physical size* of the unit cell is, naturally, determined by the condition that a molecule consist of l segments (unit cells).

¹⁵ The g of the auxiliary one-dimensional lattice is only an approximation to the required g, because it includes configurations in which some of the "bends" are between terminal bonds belonging to different molecules and such bends are not real in the original three-dimensional model.

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Radial Expansion of $3d$ Orbitals and the Near Degeneracy of the $^4A_{1g}$ and ^4E_g Excited States of Octahedral Mn(II) Complexes

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The relationship between the wavefunctions for mostly $3d$ molecular orbitals and the energies of the nearly degenerate $^4A_{1g}$ and ^4E_g excited states of octahedral Mn^{2+} complexes is investigated from two points of view. First, the expressions relating the energy splitting to the degree of covalency have been extended within the framework of the intermediate neglect of differential overlap (INDO) approximation to include the large but previously neglected two-center Coulomb integrals and all ligand one-center Coulomb and exchange integrals. The results resemble those previously obtained in their inability to account for the spectral assignment of the ^4E_g state below $^4A_{1g}$ for the MnF_6^{4-} complex in the salts $KMnF_3$, $RbMnF_3$, and MnF_2. Second, the assumption of identical metal-ion repulsion integrals for the e_g and t_{2g} molecular orbitals is discarded in a simple analysis of an all-electron molecular SCF calculation for the MnF_6^{4-} complex. While both the e_g and t_{2g} orbitals contain a metal-ion d orbital that is expanded relative to that for the free Mn^{2+} ion, the slightly greater radial expansion for the t_{2g} orbital is shown to qualitatively account for the observed ordering of the $^4A_{1g}$ and ^4E_g states.

INTRODUCTION

Considerable progress has been made in recent years in the interpretation of the optical absorption spectra of divalent manganese complexes. Much of this advance has resulted from studies[1-3] of antiferromagnetic salts in which the coupling of excitons and magnons produces significant changes in the intensities. One troublesome feature in the spectra is the overlapping of two electronic bands near 25 000 cm⁻¹, these being assigned as transitions from the $^6A_{1g}$ ground state of the $3d^5$ configuration to the $^4A_{1g}$ and ^4E_g excited states. The order of these states is unclear, however. These two states, which like the ground state are associated with the strong-field configuration $t_{2g}^3 e_g^2$, are degenerate in the standard cubic-field schemes. While spin–orbit coupling or low-symmetry crystalline fields produce very small ($\sim$10-cm⁻¹) second-order splittings[4] of the ^4E_g state, larger splittings have been assumed to arise from a modification of the electron repulsion integrals on which the energy of the crystal-field-independent transitions from the ground-state depends.

The introduction into the strong-field scheme of a covalency parameter for the σ-antibonding e_g electrons only was shown by Koide and Pryce[5] to result in a sizeable splitting of the two states. A similar modifica-

tion was made in the weak-field scheme by Stout,[6] while we extended[7] the strong-field description to include a covalency parameter for the π-antibonding t_{2g} electrons. The resulting expressions are also applicable to tetrahedral complexes, in which the t_2 covalency is presumably greater than that for the e orbitals. The general result obtained by considering the effects of covalency on the repulsion integrals is that the $^4A_{1g}$ state lies below ^4E_g when the degree of delocalization of the e_g electrons is slightly greater than that of the t_{2g}, but that the order reverses when the difference in degree of delocalization becomes large. For the tetrahedral case the ^4E state lies below $^4A_1$ for both small and large differences in delocalization.

Unfortunately the predictions for the octahedral case do not appear to be borne out by the careful analysis of the high-resolution spectra of several Mn(II) salts. Although Stevenson[8] did assign the $^4A_{1g}$ state to be about 100 cm⁻¹ below ^4E_g in $KMnF_3$ and $RbMnF_3$, Ferguson's inverted assignment[9] for the zero-phonon magnon sidebands appear to be the correct one for these salts. Similarly, our analysis[10] of the very weak magnetic dipole zero-phonon, zero-magnon lines associated with this same spectral region in MnF_2 demonstrated that the $^4A_{1g}$ state did not lie below both orthorhombic field components of the ^4E_g state. More specif-

ically, the lowest energy line of this group at 25 245.6 cm⁻¹ was identified by its polarization as one ortho-rhombic component of ^4E_g, while the line at 14.5-cm⁻¹ higher energy is, from its polarization, either the other component of ^4E_g or else the $^4A_{1g}$ state. The position of the third expected magnetic dipole line is unclear. One interpretation of the nature of the strong magnon sideband at 200-cm⁻¹ higher energy is as a sideband to an unobserved $^4A_{1g}$ zero-magnon origin about 150 cm⁻¹ above the ^4E_g zero-magnon origins, the latter value being based upon a 50-cm⁻¹ magnon energy.

Thus it appears to be reasonably well established that the ^4E_g state lies below $^4A_{1g}$ for Mn(II) in octa-hedral or nearly octahedral fluoride coordination. To explain this result within the usual covalency splitting requires a difference between the e_g and t_{2g} degrees of covalency that is unrealistically large for fluoride ions. For example, assuming no t_{2g} covalency at all, the fraction of d character in the e_g orbital must be less than $\frac{7}{8}$ for ^4E_g to lie below $^4A_{1g}$. Equally important, both levels will be depressed about 3500 cm⁻¹ from the free-ion value of the energy of ^4G relative to ^6S. By contrast the observed depression is only about 1550 cm⁻¹, from 26 850–25 300 cm⁻¹.

Ferguson[9] was able to account for the observed order of levels by a modification of our covalency expressions that requires the introduction of additional parameters. Specifically he uses different covalency parameters for the $^4E_g[t_{2g}{}^3(^4A_{2g})e_g{}^2(^1E_g)]$ and $^4E_g[t_{2g}{}^3(^2E_g)e_g{}^2(^3A_{2g})]$ basis states, following the idea of Craig and Magnusson[11] that the higher-energy terms should be reduced more than the lower-energy terms by a ligand field. However it seemed desirable to explore the separation of the $^4A_{1g}$ and ^4E_g states in greater detail in order to establish the relationship of the splitting to the nature of the wavefunctions for the mostly $3d$ electrons.

THE INDO APPROXIMATION TO THE REPULSION INTEGRALS

We have first re-examined the relationship between the electron repulsion integrals and the covalency parameters. Earlier we noted[7] that the formulas of Koide and Pryce,[5] as well as our own, implied a neglect of the large metal–ligand Coulomb integrals. Many other integrals are neglected as well, including ligand one-center Coulomb and exchange integrals. While these one-center types are certainly not small relative to the corresponding metal one-center integrals, their contri-bution to the repulsion integrals evaluated over molec-ular orbitals tends to be negligible because a small multiplicative factor which is the fourth power of the ligand mixing coefficient.

Consider a set of five molecular orbitals (MO's) constructed for an octahedral complex from the stand-ard real d atomic orbitals (AO's) and from ligand p AO's. Ligand s AO's are neglected. The designations of the d AO's and hence of the corresponding mostly d

MO's, are: $\xi(yz)$, $\eta(xz)$, $\zeta(xy)$, $\theta(3z^2-r^2)$, and $\epsilon(x^2-y^2)$, where the first three span the t_{2g} representation of the group O_h and are mixed with ligand p_π AO's, while the latter two e_g AO's are mixed with ligand p_σ AO's. Once a basis set of AO's is specified, each MO is characterized by the coefficient of the d AO, the ligand coefficients being determined by symmetry and the normalization condition.

In order to calculate the multiplet structure of the d^5 configuration we require electron repulsion integrals evaluated with respect to these MO's. A typical integral is denoted by the shorthand

$$[ij, kl] = \int \psi_i{}^*(1)\psi_j(1)(e^2/r_{12})\psi_k{}^*(2)\psi_l(2)d\tau_1 d\tau_2. \quad (1)$$

A useful approximation which avoids some of the short-comings of earlier treatments is based upon the neglect of differential overlap for AO's on different atoms. This is the same approximation made[12,13] in the INDO (intermediate neglect of differential overlap) semi-empirical molecular-orbital procedure. The complete neglect of differential overlap (CNDO) would result in neglect of all one-center exchange integrals, which is obviously unjustified in our case. The INDO procedure retains all one-center Coulomb and exchange integrals for both the metal and ligand atoms, and also all two-center Coulomb integrals. However, two-center ex-change integrals and all three- and four-center integrals are ignored. Two-center integrals of the type $[aa', bb']$, where a and a' are different AO's on center A, and b and b' are different AO's on center B, are also ignored. This distinguishes the approximation from that made in the related NDDO (neglect of diatomic differential overlap) procedure which retains these terms.

Using this INDO approximation the various re-pulsion integrals are given (Table I) as a sum of param-eters, each multiplied by the appropriate MO coeffi-cients. Table II expresses certain integral equivalencies, thus completing Table I. In practice we have estimated both metal–ligand and ligand–ligand two-center Cou-lomb integrals by point-charge repulsions at the ap-propriate bond distances, but this simplification is not necessary to the method. Some important features of the expressions can be noted. All Coulomb integrals with respect to MO's contain not only the large metal A parameter but also the large ligand F_0 parameter and various large two-center Coulomb integrals with respect to AO's. By contrast, most of the exchange integrals with respect to the MO's contain none of these large parameters. The exceptions are the exchange integral $[\theta\epsilon, \epsilon\theta]$ and the mixed integrals $[\xi^2, \theta\epsilon]$ and $[\eta^2, \theta\epsilon]$. These differences in the types of contributions appear to resolve the difficulty of unreasonably large matrix elements we noted earlier when covalency parameters are applied to Coulomb integrals as well as to exchange integrals. We now see that scaling the metal-ion contributions to repulsion integrals but ignor-ing any ligand contributions is more justifiable for

TABLE I. Electron-repulsion integrals.

Integral[a]	A [b]	B [b]	C [b]	F_0	F_2	V_{ML}	$V_{\text{LL}}(cis)$	$V_{\text{LL}}(trans)$
$[\xi^2, \eta^2]$	c^4 [c]	$-2c^4$	c^4	$2d^4$	$-4d^4$	$8c^2d^2$	$6(2)^{1/2}d^4$	d^4
$[\xi^2, \theta^2]$	a^2c^2	$2a^2c^2$	a^2c^2	$10b^2d^2/3$	$-20b^2d^2/3$	$4a^2d^2+4b^2c^2$	$14(2)^{1/2}b^2d^2/3$	$5b^2d^2/3$
$[\xi^2, \epsilon^2]$	a^2c^2	$-2a^2c^2$	a^2c^2	$2b^2d^2$	$-4b^2d^2$	$4a^2d^2+4b^2c^2$	$6(2)^{1/2}b^2d^2$	b^2d^2
$[\zeta^2, \theta^2]$	a^2c^2	$-4a^2c^2$	a^2c^2	$4b^2d^2/3$	$-8b^2d^2/3$	$4a^2d^2+4b^2c^2$	$20(2)^{1/2}b^2d^2/3$	$2b^2d^2/3$
$[\zeta^2, \epsilon^2]$	a^2c^2	$4a^2c^2$	a^2c^2	$4b^2d^2$	$-8b^2d^2$	$4a^2d^2+4b^2c^2$	$4(2)^{1/2}b^2d^2/3$	$2b^2d^2$
$[\theta^2, \epsilon^2]$	a^4	$-4a^4$	a^4	$4b^4/3$	$16b^4/3$	$8a^2b^2$	$20(2)^{1/2}b^4/3$	$2b^4/3$
$[\xi^2, \xi^2]$	c^4	$4c^4$	$3c^4$	$4d^4$	$16d^4$	$8c^2d^2$	$4(2)^{1/2}d^4$	$2d^4$
$[\theta^2, \theta^2]$	a^4	$4a^4$	$3a^4$	$4b^4$	$16b^4$	$8a^2b^2$	$4(2)^{1/2}b^4$	$2b^4$
$[\xi\eta, \eta\xi]$	0	$3c^4$	c^4	0	$6d^4$	0	0	0
$[\xi\theta, \theta\xi]$	0	a^2c^2	a^2c^2	0	$10b^2d^2$	0	0	0
$[\xi\epsilon, \epsilon\xi]$	0	$3a^2c^2$	a^2c^2	0	$6b^2d^2$	0	0	0
$[\zeta\theta, \theta\zeta]$	0	$4a^2c^2$	a^2c^2	0	$4b^2d^2$	0	0	0
$[\zeta\epsilon, \epsilon\zeta]$	0	0	a^2c^2	0	$12b^2d^2$	0	0	0
$[\theta\epsilon, \epsilon\theta]$	0	$4a^4$	a^4	$4b^4/3$	$16b^4/3$	0	$-4(2)^{1/2}b^4/3$	$2b^4/3$
$[\xi^2, \theta\epsilon]$	0	$2(3)^{1/2}a^2c^2$	0	$2b^2d^2/3^{1/2}$	$-4b^2d^2/3^{1/2}$	0	$-4b^2d^2/3^{1/2}$	$2b^2d^2/3^{1/2}$
$[\theta\eta, \epsilon\eta]$	0	$3^{1/2}a^2c^2$	0	0	$-2(3)^{1/2}b^2d^2$	0	0	0
$[\xi\eta, \zeta\theta]$	0	$-2(3)^{1/2}ac^3$	0	0	0	0	0	0
$[\epsilon\xi, \eta\zeta]$	0	$-3ac^3$	0	0	0	0	0	0
$[\theta\eta, \zeta\xi]$	0	$3^{1/2}ac^3$	0	0	0	0	0	0

[a] Each integral is given by the sum of the parameters at the top of the columns, with each parameter multiplied by the appropriate coefficient in the table.

[b] A, B, and C are central-ion d-electron repulsion parameters, F_0 and F_2 are ligand p-electron repulsion parameters, V_{ML} is the metal–ligand

Coulomb integral approximated as e^2/R (R is the bond length), while $V_{\text{LL}}(cis)$ and $V_{\text{LL}}(trans)$ are ligand–ligand Coulomb integrals approximated as $e^2/R(2)^{1/2}$ and $e^2/2R$, respectively.

[c] The lower case letters denote coefficients as follows: $a = C_{eM}$, $b = C_{eL}$, $c = C_{tM}$, and $d = C_{tL}$.

exchange integrals than for Coulomb integrals. Thus ignoring any change in Coulomb integrals due to covalency roughly corresponds to scaling the metal-ion contribution but also including the large ligand terms listed above.

We have used these repulsion integrals to evaluate the energies of the $^4A_{1g}$, ^4E_g(I), and ^4E_g(II) states relative to the $^6A_{1g}$ ground state from the expressions previously reported.[7] These energies do not involve the orbital splitting parameter Δ as all states are associated with the configuration $t_{2g}{}^3e_g{}^2$. The Roman numerals for the ^4E_g states indicate the association with the ^4G and ^4D free-ion terms, respectively. The ^4E_g energies are obtained by diagonalizing a 2×2 matrix of the repulsion energies evaluated with respect to the $^4E_g[t_{2g}{}^3(^2E_g)e_g{}^2(^3A_{2g})]$ and $^4E_g[t_{2g}{}^3(^4A_{2g})e_g{}^2(^1E_g)]$ basis functions. To facilitate comparison with the results obtained from an SCF wavefunction[14] for $\text{MnF}_6{}^{-4}$ by a procedure described in the next section, we chose the following parameters. For Mn^{2+}, $A = 178\ 400$ cm^{-1}, $B = 1145$ cm^{-1}, and $C = 4247$ cm^{-1}, while for F$^-$ the values are $F_0 = 169\ 584$ cm^{-1} and $F_2 = 2922$ cm^{-1}. The Mn–F distance, to which the metal–ligand Coulomb integrals are inversely proportional in a point-charge approximation, was taken as 4.006274 bohr, again to coincide with that used in the $\text{MnF}_6{}^{4-}$ SCF calculation. The remaining two parameters are the coefficients of the $3d$ AO's in the e_g and t_{2g} MO's, with the corresponding ligand AO coefficients being determined by the normalization of the MO's neglecting overlap.

Table III (upper half) gives the resulting energy difference between the $^4A_{1g}$ and ^4E_g(I) states as a function of the squares of the $3d$ coefficients. Similar results, although obtained by neglecting the ligand F_0 and F_2 parameters as well as all two-center Mn–F and F–F Coulomb integrals, are given in the bottom half of Table III. These latter results correspond, except for differences in the Mn^{2+} repulsion parameters, to the results we previously reported. Our new results, including all two-center Coulomb integrals and all ligand one-center Coulomb and exchange integrals, display several interesting features. First, except for the trivial case of pure $3d$ orbitals, the $^4A_{1g}$ and ^4E_g states are not degenerate even when the e_g and t_{2g} MO's have the same $3d$ coefficient. Second, the energy difference between the $^4A_{1g}$ state and the ^4E_g state is reduced in comparison with results based only on Mn^{2+} repulsion integrals. Thus for values of the $3d$ coefficient in the e_g MO less than that for the t_{2g} MO, as presumably holds for octahedral complexes, the prediction that $^4A_{1g}$ lies below ^4E_g is strengthened in our improved procedure for calculating the effects of covalency on the energy splitting of these states. The fact that this result appears to contradict the experimental findings strongly suggests that we must look elsewhere for an explanation of the observed ordering of the states. A key assumption in the present method is that the Mn^{2+} repulsion parameters are identical for the e_g and t_{2g} MO's, thus implying that the same $3d$ radial function is used in the construction of these MO's. The next section indicates a basis for discarding this assumption.

TABLE II. Integral equivalences.

Integral	Identical integral
$[\xi^2, \zeta^2]$	$[\xi^2, \eta^2]$
$[\eta^2, \zeta^2]$	$[\xi^2, \eta^2]$
$[\eta^2, \theta^2]$	$[\xi^2, \theta^2]$
$[\eta^2, \eta^2]$	$[\xi^2, \xi^2]$
$[\zeta^2, \zeta^2]$	$[\xi^2, \xi^2]$
$[\epsilon^2, \epsilon^2]$	$[\theta^2, \theta^2]$
$[\xi\zeta, \zeta\xi]$	$[\xi\eta, \eta\xi]$
$[\eta\zeta, \zeta\eta]$	$[\xi\eta, \eta\xi]$
$[\eta\theta, \theta\eta]$	$[\xi\theta, \theta\xi]$
$[\eta\epsilon, \epsilon\eta]$	$[\xi\epsilon, \epsilon\xi]$
$[\eta^2, \theta\epsilon]$	$-[\xi^2, \theta\epsilon]$
$[\epsilon\xi, \theta\xi]$	$-[\theta\eta, \epsilon\eta]$
$[\epsilon\eta, \zeta\xi]$	$-[\epsilon\xi, \eta\zeta]$
$[\eta\zeta, \theta\xi]$	$[\theta\eta, \zeta\xi]$
$[\eta^2, \epsilon^2]$	$[\xi^2, \epsilon^2]$

MOLECULAR-ORBITAL RESULTS FOR MnF$_6^{4-}$

We have examined in some detail a recent all-electron LCAO MO-SCF calculation[14] for the octahedral MnF$_6^{4-}$ complex. This calculation is very similar to that recently reported[15] for NiF$_6^{4-}$, in which the MO's are expanded in a large basis set of Gaussian functions. These functions have the forms (unnormalized) $\exp(-ar^2)$ for s, $x \exp(-ar^2)$ for $p(x)$, and $xy \exp(-ar^2)$ for $d(xy)$ etc. The exponential parameters are chosen by an optimization of the SCF energies of the separate Mn^{2+} and F$^-$ ions. The Mn(3d) AO in free Mn^{2+} is described by a linear combination of the five functions given in Table IV, yielding one-center repulsion integrals (in cm^{-1}) of $A = 178\,400$, $B = 1145$, and $C = 4247$. By comparison an SCF calculation[16] for Mn^{2+} using four Slater-type functions gave $A = 177\,666$, $B = 1141$, and $C = 4213$, these values being only slightly smaller than the above. The F(2p) AO used in the MnF$_6^{4-}$ calculation is also given in Table IV, this yielding one-center repulsion integrals (in cm^{-1}) of $F_0 = 169\,584$ and $F_2 = 2922$. Since this AO was chosen by an SCF procedure for the F$^-$ ion, these repulsion integrals are expectedly smaller than neutral-atom values of $F_0 = 188\,721$ and $F_2 = 3344$, these obtained[17] using seven p-type Gaussian functions.

In carrying out the molecular SCF calculation for MnF$_6^{4-}$ the various Gaussian functions were not all assumed to appear in the MO's in the same ratios as they did in the AO's. However in the interest of reducing computation time, complete linear variation was not permitted either. Instead the common compromise[18] of "contraction" was employed. Thus the first three Mn(3d) functions in Table IV were constrained to occur in any MO in the same relative proportions as given by the atomic SCF coefficients, and similarly for the two remaining functions, giving in effect two different Mn(3d) radial functions for the molecular

SCF calculation. Similar groupings were made for all other Mn and F AO's beginning with the K shell. For F(2p) two groups were chosen, these consisting of the first four Gaussians in Table IV as one function and the last Gaussian alone as the other function. The renormalized coefficients appropriate to these groupings are also given in Table IV.

The SCF calculation for the $^6A_{1g}$ ground state of MnF$_6^{4-}$ was made assuming O_h symmetry and an Mn–F bond length of 2.119924 Å = 4.006274 bohr. The calculation was of the restricted SCF variety for this open-shell complex, meaning that all MO's are doubly occupied except for the five singly occupied mostly 3d MO's. Thus the shape of the doubly occupied MO's is assumed not to depend on whether the spin of the electron is the same as, or different from, that of the unpaired electrons. The singly occupied mostly 3d t_{2g} set of MO's was characterized by coefficients of 0.5605747 and 0.6243790 for the two Mn(3d) basis functions, while the singly occupied e_g set was characterized by coefficients of 0.4980922 and 0.5425740 for the same basis functions. The coefficient of a particular Gaussian in an MO is then given by the product of one of these coefficients for a contracted grouping in an MO multiplied by the appropriate renormalized coefficient of the Gaussian in that grouping. The results are given in Table IV. The fractions of 3d character in these antibonding orbitals are given from a Mulliken population as 1.00359 and 1.02234 for the t_{2g} and e_g, respectively. The proximity of these values to unity indicates the very small extent of ligand admixture, while the fact that the fractions are greater than unity reflects the antibonding character of these MO's. The

TABLE III. INDO results for energy $^4A_{1g}$ −energy ^4E_g.[a,b]

	$C_{e_g}^2$					
$C_{t_{2g}}^2$	1.00	0.95	0.90	0.85	0.80	0.75
1.00	0	−200	−268	−272	−289	−380
0.95	361	−21	−269	−415	−520	−656
0.90	843	327	−86	−393	−629	−846
0.85	1380	789	264	−188	−567	−903
0.80	1914	1298	716	176	−318	−775
0.75	2403	1795	1204	630	77	−461

Energy difference using metal-ion repulsion integrals only

1.00	0	−169	−119	110	450	840
0.95	367	0	−155	−92	143	478
0.90	869	352	0	−141	−66	174
0.85	1443	836	338	0	−126	−40
0.80	2031	1386	803	323	0	−112
0.75	2593	1943	1328	770	309	0

[a] Energy differences in cm^{-1}.
[b] Energy parameters (in cm^{-1}) are $A = 178\,400$, $B = 1145$, $C = 4247$, $F_0 = 169\,584$, $F_2 = 2922$. Bond length is 4.006274 bohr.

TABLE IV. Gaussian basis functions and MO coefficients.

Orbital	Exponent	Coefficient in free ion	Contraction grouping and renormalized coefficients	Coefficient in t_{2g} MO	Coefficient in e_g MO	Renormalized coefficient in t_{2g} MO	Renormalized coefficient in e_g MO
Mn (3d)	27.73	0.0411132	(1) 0.0723006	0.0405299	0.0360124	0.0404407	0.0409240
	7.649	0.1946165	(1) 0.3422473	0.1918552	0.1704707	0.1914329	0.1937206
	2.558	0.4160834	(1) 0.7317130	0.4101798	0.3644605	0.4092771	0.4141680
	0.8675	0.4576896	(2) 0.7453748	0.4653964	0.4044210	0.4643721	0.4595785
	0.2942	0.2155875	(2) 0.3510971	0.2192176	0.1904962	0.2187352	0.2164772
F (2p)	44.36	0.014285	(1) 0.0200187	0.0008408	0.0014491	0	0
	10.27	0.0960340	(1) 0.1345798	0.0056523	0.0097418	0	0
	2.939	0.2766022	(1) 0.3876240	0.0162800	0.0280588	0	0
	0.9812	0.4419257	(1) 0.6193045	0.0260105	0.0448294	0	0
	0.2405	0.4559124	(2) 1.0	0.0229592	0.0602759	0	0

corresponding total ligand fractions are -0.00359 and -0.02234, respectively. These negative fractions are a consequence of the Mulliken population definitions when applied to antibonding MO's in which some coefficients are near unity with others near zero.

If we define Mn(3d) radial functions in the complex by the sets of five MO coefficients for the Mn(3d) Gaussians, we obtain, after another renormalization, a radial function for the t_{2g} electrons that differs from that for the e_g electrons. The renormalization (Table IV) involves the neglect of ligand orbitals, the most important of which are the F(2p) AO's whose coefficients are also given in Table IV. Both the t_{2g} and e_g radial functions are characterized by an expansion relative to the function for free Mn^{2+}. This expansion is indicated by the increased coefficients for the two Gaussians with smallest exponents, these functions comprising one basis function in the molecular SCF calculation and having large radial extents. Correspondingly in going from the free ion to the complex there is a reduction in the coefficients of the three Gaussians with larger exponents, these comprising the other SCF basis function and having small radial extents. However the feature relevant to our discussion of the order of the $^4A_{1g}$ and ^4E_g excited states is the difference in the radial expansion for the two types of MO's. The renormalized coefficients in Table IV show that the Mn(3d) radial function in the t_{2g} MO expands more relative to the free ion than does that for the e_g MO. Further, among all of the unrenormalized MO coefficients, those for the small exponent Gaussians in the t_{2g} MO are the only coefficients that are larger in an absolute sense than the coefficients in the free-ion AO.

We have used these renormalized radial functions to calculate the energies of the $^4A_{1g}$, $^4E_g(I)$, and $^4E_g(II)$ excited states. Numbering the $^4E_g[t_{2g}^3(^2E_g)e_g^2(^3A_{2g})]$ and $^4E_g[t_{2g}^3(^4A_{2g})e_g^2(^1E_g)]$ basis functions as 1 and 2, respectively, the expressions for the matrix elements

can, because of spherical symmetry, be written as

$$H_{11} = (9B+3C)+(4B'+2C'),$$
$$H_{22} = (6B'+3C')+(8B''+2C''),$$
$$H_{12} = 2(3)^{1/2}B'. \tag{2}$$

In the above, the parameters B and C are evaluated from the t_{2g} radial function, B' and C' from the product of the e_g and t_{2g} radial functions, and B'' and C'' from the e_g function only. The various parameters are obtained by evaluating all of the individual repulsion integrals required for the energy expressions given in Table II of Ref. 7. We obtain the combinations $3B+C = 7604$ cm^{-1}, $3B'+C' = 7632$ cm^{-1}, $4B'+C' = 8770$ cm^{-1}, and $4B''+C'' = 8803$ cm^{-1}. From the above, $B' = 1138$ cm^{-1} and $C' = 4219$ cm^{-1}, but we cannot obtain separate values for the remaining parameters.

The resulting energies are 32 471 cm^{-1} for $^4A_{1g}$, 32 451 cm^{-1} for $^4E_g(I)$, and 40 438 cm^{-1} for $^4E_g(II)$. By comparison the corresponding term energies as calculated from the free-ion SCF repulsion parameters of $B = 1145$ cm^{-1} and $C = 4247$ cm^{-1} are $10B+5C = 32\,685$ cm^{-1} for ^4G and $17B+5C = 40\,700$ cm^{-1} for ^4D. The nephelauxetic effect for these states consists of depressions of 214 and 234 cm^{-1} for $^4A_{1g}$ and $^4E_g(I)$ with respect to ^4G, and 262 cm^{-1} for $^4E_g(II)$ relative to ^4D. Thus the $^4E_g(I)$ state lies 20 cm^{-1} below $^4A_{1g}$ as a consequence of the difference in the nephelauxetic shifts.

The high computed value of the free-ion ^4G energy in comparison to the experimental value of 26 850 cm^{-1} results in part because the excited state is constructed from radial functions chosen, within the limited basis set approximation, to minimize the ^6S ground-state energy. Better than this "frozen orbital" approximation for the excited state would be a calculation of the free-ion energy difference from independent SCF calculations for the two states. The significant feature of the computed nephelauxetic effect is that the $^4E_g(I)$ state is depressed about 10% more than $^4A_{1g}$, a result

in qualitative agreement with experiment but not accounted for by the usual covalency arguments for octahedral complexes.

Another consequence of the differential radial expansion was described in a recent theoretical study[19] of the relationship between covalent binding and the neutron form factor for the Mn^{2+} ion in the MnF_6^{4-} complex. This study concluded that while the e_g MO does contain an admixture of ligand AO's, the t_{2g} MO is best described by an over-all expansion of the metal d orbital not found for the e_g MO. Consequently, the computed spherical scattering factor for the t_{2g} MO is, except at small scattering angles, less than that for the e_g MO. Over all, the scattering factor for the $^6A_{1g}$ state of MnF_6^{4-} is found to be less than that for the ^6S state of Mn^{2+}.

SUMMARY

An attempt to account for the lower energy of the ^4E_g state of the MnF_6^{4-} complex relative to the $^4A_{1g}$ state by extending the calculation of covalency effects to include, in the framework of the INDO approximation, large but previously neglected repulsion integrals is unsuccessful for reasonable choices of covalency parameters. The tabulated expressions for the integrals do, however, reveal a number of interesting relationships, particularly with regards to the distinction between those integrals containing, and those which do not contain, ligand one-center Coulomb integrals and/or two-center metal–ligand and ligand–ligand Coulomb integrals. These expressions should have a number of uses in the description of transition-metal complexes.

The application of the covalency expressions to the calculation of the $^4A_{1g}$ and ^4E_g energies assumed the identity of the radial functions for the $3d$ AO's in both the e_g and t_{2g} MO's. While this assumption can be removed in this approach, the resulting number of parameters required is unwieldy. Instead, a simple analysis of a recent all-electron LCAO MO SCF calculation for the MnF_6^{4-} complex suggests a one-center model in which the greater radial expansion of the t_{2g} orbital relative to the e_g orbital in going from the free Mn^{2+} ion to the complex qualitatively accounts for the observation of the ^4E_g state being lower in energy than the $^4A_{1g}$ state. If a covalency model were forced to account for this ordering, it is as though the t_{2g} MO displays the greater "covalency."

The "frozen orbital" approximation could be used to calculate the energies of the various crystal-field states of interest directly from repulsion integrals evaluated with respect to the MO's for the MnF_6^{4-} complex. These integrals would contain all one-, two-, three-, and four-center contributions, and thus not involve the types of approximation made here. Should these integrals become available a comparison to the results of our simpler analysis would be in order.

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