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A Method for Molecular Orbital Calculations for Metal Complexes

By RICHARD F. FENSKE, KENNETH G. CAULTON, DOUGLAS D. RADTKE, and CAROL C. SWEENEY

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A method is proposed for the calculation of the relative values of one-electron energy levels in transition metal complexes. Approximations to more rigorous considerations are made in terms of free-ion orbital energies and point-charge interactions. The effects of ligand–ligand interaction, size of basis sets, methods for electron population analysis, and parameter variations are evaluated.

MO Theory for Metal Complexes

The goal of any theoretical calculation involving many-atom inorganic systems is to achieve reasonable correlation with the experimental observables coupled with an improved insight into the nature of the chemical bonding in such systems. From a practical standpoint, since completely exact calculations are impossible at the present time, one turns to semiempirical methods for the actual computations. Ideally, such methods should not only predict reasonable values of the observables but should entail approximations which are in accord with more rigorous approaches.

In the past few years, the modified Wolfsberg and Helmholz method[1-4] has been used for the calculation of the electronic energy levels in transition metal complexes. As a result of previous work in this laboratory,[5,6] we became convinced that this method entailed certain assumptions concerning the estimation of the values of the diagonal and off-diagonal matrix elements which were not in accord with more rigorous considerations. We further felt that, as an automatic consequence of these assumptions, the approach resulted in molecular orbitals which were frequently too covalent in character.[6] Consequently, one would expect poor correlation with those experimental observables whose interpretation involved the nature of the molecular orbitals. For example, the modified Wolfsberg–Helmholz calculation on permanganate[4] indicates the e-antibonding orbital to be approximately 60% ligand in character, yet $t_1 \rightarrow e^*$ transition intensity[5] in MnO_4^- and the esr results[7] in MnO_4^{2-} indicate that this orbital should involve no more than 10% ligand participation.

It is the purpose of this report to outline a semiempirical approach for the transition metal complex systems which we believe is in better accord with theoretical considerations and which shows some promise of leading to results in better agreement with experimental information. Application of the method to the relatively simple fluoride systems is carried out in order to define the ground rules under which the approach may be extended to complexes containing ligands of greater complexity.

Initial Considerations

Accepting the fact that a rigorous, complete, one-electron calculation for systems of transition metal complexes is not feasible at the present time, the choice of the approach to be used depends upon the degree of compromise between rigor and simplicity of calculation. In this context it is worthwhile to consider the one-electron energies of a closed-shell system in terms of an LCAO–SCF calculation.

The one-electron molecular orbitals, Ψ_i, are approximated by a linear combination of symmetry-adapted atomic orbitals, for example[8]

$$\Psi_i = a_i\chi_i + b_i\phi_i$$

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(1) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

(2) H. D. Bedon, S. M. Horner, and S. Y. Tyree, Jr., *Inorg. Chem.*, **3**, 647 (1964).

(3) H. D. Bedon, W. E. Hatfield, S. M. Horner, and S. Y. Tyree, Jr., *ibid.*, **5**, 743 (1965).

(4) A. Viste and H. B. Gray, *ibid.*, **3**, 1113 (1964).

(5) R. F. Fenske and C. C. Sweeney, *ibid.*, **3**, 1105 (1964).

(6) R. F. Fenske, *ibid.*, **4**, 33 (1965).

(7) D. S. Schonland, *Proc. Roy. Soc.* (London), **A254**, 111 (1959).

(8) J. W. Richardson and R. E. Rundle, "A Theoretical Study of the Electronic Structure of Transition Metal Complexes," Ames Laboratory, Iowa State College, ISC-830, U. S. Atomic Energy Commission, Technical Information Service Extension, Oak Ridge, Tenn., 1956. In actual practice the Ψ_i frequently contain more than two terms. Since the treatment of the additional coefficients and functions follows the same pattern outlined here, this simpler case was chosen for brevity and clarity. The reader is referred to the foregoing reference for a more complete discussion.

Here a and b are coefficients, χ_i is a normalized metal function, and ϕ_i is the normalized symmetry-adapted combination of ligand wave functions associated with the n ligands

$$\phi_i = \sum_{j=1}^{n} C_{ij}\rho_{ij}$$

where ρ_{ij} is an atomic orbital on the jth ligand. Without loss of generality, we can simplify this discussion by assuming that all ρ_{ij} are orthonormal; *i.e.*, $\int \rho_{ij}\rho_{ik}\mathrm{d}\tau = \delta_{jk}$. Then $\sum_j C_{ij}^2 = 1$.

Since the metal wave function, χ_i, is not orthogonal to ϕ_i, one defines the group overlap integral

$$G(\chi_i, \phi_i) = \int \chi_i\phi_i\mathrm{d}\tau = \sum_j C_{ij}S(\chi_i, \rho_{ij})$$

where $S(\chi_i, \rho_{ij})$ is the diatomic overlap integral.

The charge distribution Ψ_i^2 is given by

$$\Psi_i^2 = a_i^2\chi_i^2 + 2a_ib_i\sum_j C_{ij}\chi_i\rho_{ij} + b_i^2\sum_j\sum_k C_{ij}C_{ij}\rho_{ij}\rho_{ik}$$

where the coefficients are such that integration of Ψ_i^2 over all space is unity. Hence

$$a_i^2 + 2a_ib_i\sum_j C_{ij}S(\chi_i, \rho_{ij}) + b_i^2\sum_j C_{ij}^2 = 1$$

It is convenient to divide this latter quantity, the charge density, between the metal and ligand centers. For this purpose, use can be made of the Mulliken method[9]

$$\bar{a}_i = a_i^2 + a_ib_i\sum_j C_{ij}S(\chi_i, \rho_{ij}) = \text{fraction on the metal}$$

$$\bar{b}_i = \sum_j\{b_i^2C_{ij}^2 + a_ib_iC_{ij}S(\chi_i, \rho_{ij})\} = \sum_j \bar{b}_{ij}$$

$$\bar{b}_{ij} = b_i^2C_{ij}^2 + a_ib_iC_{ij}S(\chi_1, \rho_{ij}) = \text{fraction on ligand } j$$

If one considers a rigorous SCF calculation, multicenter electrostatic integrals arise which are extremely difficulty to evaluate exactly. Consequently, use is made of another Mulliken[10] approximation, namely, that for the estimation of two-electron electrostatic interaction integrals. By this approximation

$$(\rho_A\rho_B|\rho_C\rho_C) \approx [(\rho_A\rho_A|\rho_C\rho_C) + (\rho_B\rho_B|\rho_C\rho_C)]S(\rho_A, \rho_B)/2$$

where $(\rho_A\rho_B|\rho_C\rho_C) = \int \rho_A{}^*(1)\rho_B(1)1/r_{12}\rho_C{}^*(2)\rho_C(2)\mathrm{d}\tau$, and the ρ's are one-electron wave functions on atoms A, B, and C, and $S(\rho_A, \rho_B)$ is the overlap integral between ρ_A and ρ_B. Consider an integral of the type

$$(\Psi_i\Psi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) = a_i^2(\chi_i\chi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) + 2a_ib_i\sum_j C_{ij}(\chi_i\rho_{ij}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) + b_i^2\sum_j\sum_k C_{ij}C_{ik}(\rho_{ij}\rho_{ik}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}})$$

Since we have assumed that $S(\rho_{ij}, \rho_{ik})$ equals δ_{ik}, by the Mulliken approximation the last term in the equation above simplifies to $b_i^2\sum_j C_{ij}^2(\rho_{ij}\rho_{ij}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}})$. Similarly

$$2a_ib_i\sum_j C_{ij}(\chi_i\rho_{ij}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) = a_ib_i\sum_j C_{ij}S(\chi_i, \rho_{ij})[(\chi_i\chi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) + (\rho_{ij}\rho_{ij}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}})]$$

Therefore

$$(\Psi_i\Psi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) = [a_i^2 + a_ib_i\sum_j C_{ij}S(\chi_i, \rho_{ij})](\chi_i\chi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) + \sum_j[b_i^2C_{ij}^2 + a_ib_iC_{ij}S(\chi_i, \rho_{ij})](\rho_{ij}\rho_{ij}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}})$$

which can be written as

$$(\Psi_i\Psi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) = \bar{a}_i(\chi_i\chi_i|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}}) + \sum_j \bar{b}_{ij}(\rho_{ij}\rho_{ij}|\rho_{\mathrm{ml}}\rho_{\mathrm{ml}})$$

Thus, by the Mulliken approximations, coulomb integrals involving the molecular charge distribution, Ψ_i^2, can be greatly simplified.

In a long overlooked report on MO theory for transition metal complexes, Richardson[8] shows that by application of the Mulliken multicenter integral approximation to both coulomb and exchange parts of the Fock operator in Roothaan's method for closed shells, the one-electron operator becomes

$$\mathcal{H} = -{}^1/_2\Delta + V_{\mathrm{M}} + \sum_j^n V_j$$

where $-{}^1/_2\Delta$ is the kinetic energy operator. V_{M} is given by

$$V_{\mathrm{M}} = \sum_i \bar{a}_i\{2(\chi_i\chi_i| - (\chi_i\,|\chi_i\,\} - Z_{\mathrm{M}}(1/r_{\mathrm{M}}|$$

in which $(\chi_i\chi_i|$, $(\chi_i\,|\chi_i$, and $Z_{\mathrm{M}}(1/r_{\mathrm{M}}|$, indicate the coulomb, exchange, and nuclear attraction operators, respectively. V_j is the corresponding operator for the electrons and nucleus of the jth ligand

$$V_j = \sum_i \bar{b}_{ij}\{2(\rho_{ij}\rho_{ij}| - (\rho_{ij}\,|\rho_{ij}\} - Z_j(1/r_j|$$

It is pertinent to note the relationship between Richardson's formulation and that given by Shulman and Sugano[11] for their ionic model calculation on $KNiF_3$. In the extreme of a completely ionic species in which overlaps between metal and ligand wave functions are neglected, the $\bar{a}_i$ and $\bar{b}_{ij}$ in V_{M} and V_j are either 1 or 0, and Richardson's operator becomes identical with that of Shulman and Sugano.

Matrix Elements of the Secular Determinant

The Metal Diagonal Elements.—Application of the variation principle and the methods of group theory lead to the factored secular determinant: $|H_{ij} - EG_{ij}| = 0$. The diagonal terms involving the metal wave functions, χ_i, are given by

$$H_{ii} = (\chi_i|\mathcal{H}|\chi_i) = (\chi_i|-{}^1/_2\Delta + V_{\mathrm{M}}|\chi_i) + (\chi_i|\sum_j V_j|\chi_i)$$

If one considers the Shulman and Sugano ionic model, the first term is simply the orbital energy of the electron whose wave function is χ_i in the free gaseous ion, and the second term is the electrostatic interaction of the electron with all of the ligand electrons and nuclei. Insofar as the species is not ionic, that is, as far as there is participation of the metal orbitals in the bonding MO's, there is a transfer of charge from the ligands to the central metal. This transfer of charge is reflected

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(9) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955).

(10) R. S. Mulliken, *J. Chim. Phys.*, **46**, 497, 675 (1949).

(11) R. G. Shulman and S. Sugano, *Phys. Rev.*, **130**, 517 (1963).

in the values of the $\bar{a}_i$ in the V_{M} operators summed over all of the occupied molecular orbitals. Therefore, in terms of the Mulliken population analysis, the first term in the diagonal element can be approximated as the orbital energy associated with the ion of that charge indicated by the population analysis of the calculated MO's. Our calculational procedure then requires that the assumed starting charge on the metal be the same as that calculated from the Mulliken population analysis of the final molecular orbitals. In this respect the calculations are analogous to the modified Wolfsberg and Helmholz calculations.

Again, if one considers the purely ionic model, V_j is the nuclear attraction and electronic repulsion of the anionic ligand, for example, F^- in $TiF_6{}^{3-}$. However, insofar as charge is transferred to the metal *via* covalent bonding, the ligand electron population on the *j*th ligand is decreased and consists of $\sum\limits_{i=1}\bar{b}_{ij}$, where the summation is over all occupied MO's.

Examination of the exact calculations of the electrostatic interaction integrals by Shulman and Sugano indicates that to a fair degree of approximation

$$\sum_i\{2(\rho_{ij}\rho_{ij}|3\mathrm{d}3\mathrm{d}) - (\rho_{ij}3\mathrm{d}|\rho_{ij}3\mathrm{d})\} \approx Q(1/r_j|3\mathrm{d}3\mathrm{d})$$

where *i* is summed over the 2s and 2p fluoride electrons and *Q* is 8, *i.e.*, the two 2s electrons and the six 2p electrons. This implies that a point-charge approximation for the ligand electrons is fairly reasonable,[8] and hence, since the $\bar{b}_{ij}$ are not unity, the term for the metal diagonal element becomes

$$(\chi_i|V_j|\chi_i) \approx \sum_i\bar{b}_{ij}(1/r_j|\chi_i\chi_i) - Z_j(1/r_j|\chi_i\chi_i)$$

where Z_j is the nuclear charge minus the two electrons in the 1s orbital. However $\sum\limits_i\bar{b}_{ij} - Z_j$ is simply minus the charge on the *j*th ligand as calculated by the Mulliken population analysis. Hence, $(\chi_i|V_j|\chi_i) \approx -q_j(1/r_j|\chi_i\chi_i)$, where q_j is the algebraic charge on ligand *j*. When summed over all *n* ligands, this term is seen to be completely analogous to a "crystal field" potential where the point charge on each ligand, q_j, is that in accord with the electron population analysis.[12] Thus, the metal diagonal term is approximated by

$$(\chi_i|\mathcal{H}|\chi_i) = \epsilon_\chi(q_{\mathrm{M}}) + \mathrm{CF}(q_j)$$

where $\epsilon_\chi(q_{\mathrm{M}})$ is the orbital energy of the metal electron in the free ion of charge q_{M}, and $\mathrm{CF}(q_j)$ is the crystal field potential[13] due to the ligand point charges, q_j.

Ligand Diagonal Elements.—The ligand diagonal matrix elements are readily obtained by rearrangement of the terms in the one-electron operator. This is most easily done by consideration of the interactions of an electron in one ligand atom and then relating this matrix element to the matrix element for the entire symmetry-adapted ligand function. Thus, for the electron in the *i*th orbital on ligand atom 1, ρ_{i1}

$$(\rho_{i1}|\mathcal{H}|\rho_{i1}) = (\rho_{i1}| -{}^1/_2\Delta + V_1|\rho_{i1}) + (\rho_{i1}|V_{\mathrm{M}} + \sum_{j=2}V_j|\rho_{i1})$$

If ligand–ligand overlap is neglected, this matrix element equals the desired matrix element $(\phi_i|\mathcal{H}|\phi_i)$. If it is not neglected, suitable adjustments can be made by addition of terms such as $(\rho_{i1}|\mathcal{H}|\rho_{i2})$ and renormalization as outlined by Viste and Gray.[4] For simplicity of discussion of the method, we will consider only the situation where ligand–ligand overlap is neglected.

By the same considerations as those given for the metal diagonal term, the ligand term becomes

$$(\phi_i|\mathcal{H}|\phi_i) = \epsilon_\phi(q_j) - q_{\mathrm{M}}(1/r_{\mathrm{M}}|\phi_i\phi_i) - \sum_{j=2}q_j(1/r_j|\phi_i\phi_i)$$

That is, it is equal to the orbital energy of the ligand ion of charge q_j plus the crystal field potential due to the central metal ion of charge q_{M} and the remaining ligands of charge q_j.

The Off-Diagonal Elements, $(\phi_i|\mathcal{H}|\chi_i)$.—It will be convenient to consider the matrix element $(\rho_{i1}|\mathcal{H}|\chi_i)$ which involves the wave function of an electron on only one ligand atom, ρ_{i1}, and then relate this to the desired matrix element $(\phi_i|\mathcal{H}|\chi_i)$. Thus, $(\phi_i|\mathcal{H}|\chi_i) = C(\rho_{i1}|\mathcal{H}|\chi_i)$, where the constant, *C*, is the same coefficient which relates the diatomic overlap, $S(\rho_{i1}, \chi_i)$, to the group overlap, $G(\phi_i, \chi_i)$.

The matrix element can be written as

$$(\rho_{i1}|\mathcal{H}|\chi_i) = (\rho_{i1}| -{}^1/_2\Delta + V_{\mathrm{M}}|\chi_i) + (\rho_{i1}|V_i|\chi_i) + \sum_{j=2}(\rho_{i1}|V_j|\chi_i)$$

Since χ_i is assumed to be an eigenfunction of the operator, $-{}^1/_2\Delta + V_{\mathrm{M}}$, the first term becomes: $(\rho_{i1}| -{}^1/_2\Delta + V_{\mathrm{M}}|\chi_i) = \epsilon_{\chi i}(q_{\mathrm{M}})S(\rho_{i1}, \chi_i)$. The last term in the expression for the matrix element involves the wave functions of ligand atom 1 and the central metal with the charge distributions on all of the other ligand atoms. Here we employ an approximation analogous to that used by Shulman and Sugano, namely, that the sum of the nuclear and electron charge densities on these centers is considered to be a point charge equal to the charge on each ligand. Thus, the term becomes a sum of three center integrals

$$\sum_{j=2}(\rho_{i1}|V_j|\chi_i) = -\sum_{j=2}q_j(1/r_j|\rho_{i1}\chi_i)$$

Computation of the resultant three-center nuclear attraction integrals, $(1/r_j|\rho_{i1}\chi_i)$, is discussed in the Appendix.

The middle term, $(\rho_{i1}|V_1|\chi_i)$, in the equation for the matrix element requires special consideration. Because ρ_{i1} and V_1 are on the same center, a point-

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(12) It should be noted that for anionic ligands this crystal field term splits the 3d orbitals in the usual crystal field order, e_g above t_{2g} for octahedral symmetry, while Shulman and Sugano's calculations[11] show the reverse order because of the exchange integrals arising from the V_j operator. However, this difference is small compared to the over-all effect of the crystal field term on the position of metal diagonal elements relative to those of the ligands.

(13) It should be remembered that this latter potential must include the term $Y_{00}(1/r_>)$ in the expansion of the crystal field potential. This term, which can be ignored in a crystal field calculation involving only the 3d metal orbitals, is of primary importance in the placement of the metal energy levels relative to those of the ligands.

charge approximation for V_1 similar to that used for the three-center integrals is not only unreasonable in principle but also gave unacceptable results in trial calculations. If we consider the explicit form of the term, we obtain

$$(\rho_{i1}|V_1|\chi_i) = \sum_k \bar{b}_{k1}\{2(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i) - (\rho_{k1}\rho_{i1}|\rho_{k1}\chi_i)\} - Z_1(1/r_1|\rho_{i1}\chi_i)$$

where the sum of *k* is over all occupied orbitals on atom 1. Only the last term in the above expression, which involves the nuclear attraction, is a point-charge interaction; the coulomb and exchange interactions involve spread-charge distributions. At best, only those integrals in which ρ_{k1} is the fluoride 1s orbital might be reasonably approximated by $(1/r_1|\rho_{i1}\chi_i)$. This approximation, first utilized by Shulman and Sugano, can be expressed by the same formula given above but with Z now equal to the nuclear charge minus two and the summation of $\bar{b}_{k1}$ only over the orbitals considered in the bonding. However, the problem involving the evaluation of the outer orbitals on the ligand remains.

Two approaches can be considered: (1) the actual evaluation of the two-center electrostatic interaction integrals and (2) the approximation of the sum of these interactions by a point-charge integral multiplied by a correction factor to adjust for the diffuse character of the charge distribution, $\rho_{k1}\rho_{k1}$. Calculations in which the integrals are evaluated exactly, method 1, are presently being studied in our laboratory. Method 2, which has the advantage of an appreciable reduction in the number of integrals which must be calculated, has been used to obtain the results presented in this report. It involves the approximation

$$\sum_k \bar{b}_{k1}\{2(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i) - (\rho_{k1}\rho_{i1}|\rho_{k1}\chi_i)\} \approx (6 - q_1)R_{\mathrm{a}}(1/r_1|\rho_{i1}\chi_i)$$

In the above expression $R_{\mathrm{a}}(1/r_1|\rho_{i1}\chi_i)$ approximates the coulomb and exchange integrals. The term $(+6 - q_1)$ accounts for the electron distribution[14] on ligand atom 1 as given by its starting charge, q_1.

Substitution of the above relationship into the expression for $(\rho_{i1}|V_1|\chi_i)$ yields

$$(\rho_{i1}|V_1|\chi_i) \approx [R_{\mathrm{a}}(6 - q_1) - Z_1](1/r_1|\rho_{i1}\chi_i)$$

The subscript, a, on R allows for a choice in reduction factors depending on whether ρ_{i1} and χ_i are σ- or π-bonding orbitals.

Some feeling for the order of magnitude of the R values can be obtained from the calculations by Shulman and Sugano[11] on $KNiF_3$. Their integrals show that $R_\sigma = 0.86$ and $R_\pi = 0.90$ for the terms in $(2p\sigma_1|V_1|3d\sigma)$ and $(2\rho\pi_1|V_1|3d\pi)$, respectively. In our calculations, we determine which values of R_σ and R_π would yield the correct Dq value for one complex, TiF_6^{3-}, and then require that these same values remain fixed for all calculations involving the same ligand, fluoride.

Evaluation of the Matrix Elements

Basis Sets, Wave Functions, and Integrals.—Because of obvious extensions to other systems, we shall limit our discussion to the TiF_6^{3-} species. During the course of our investigations, basis sets of various sizes have been considered. The largest involves the 2s and 2p orbitals on fluoride and the 3d, 4s, 4p, and 4d orbitals on titanium. As will be seen, our final calculations suggest the use of Ti^{2+} wave functions. Hence, in the reported calculation, overlap integrals, two- and three-center nuclear attraction integrals, and the "crystal field" integrals for the diagonal elements are computed using those atomic orbitals of Ti^{2+} developed by Richardson.[15,16] The fluoride functions are the same as those employed by Shulman and Sugano.[11] A metal–fluorine distance 1.97 A and appropriate ligand–ligand distances from octahedral geometry were used in the calculation of all desired integrals. 1.97 A corresponds to that for Ti and F in TiF_3 which has been shown to have six fluorines octahedrally oriented about the titanium atom.[17] The wave functions and group overlaps are given in Table I. It should be noted that, because of the method for obtaining the 4d wave function, it is not orthogonal to the 3d. Hence, an off-diagonal term connecting the 3d and 4d wave functions appears in both the G and H matrices. Even if the 4d wave function were orthogonal to the 3d, a term connecting the two would still appear in the H matrix because the potential energy term, $(3d|\sum_i V_i|4d)$, would not be zero.

TABLE I

WAVE FUNCTIONS AND OVERLAP INTEGRALS FOR TiF_6^{3-}

Wave Functions[a]

$$\Psi(3d) = 0.4623\phi_3(4.55) + 0.6910\phi_3(1.80)$$

$$\Psi(4s) = -0.02231\phi_1(21.40) + 0.07751\phi_2(8.05) - 0.1985 \times \phi_3(3.64) + 1.0164\phi_4(1.20)$$

$$\Psi(4p) = +0.07355\phi_2(8.80) - 0.28678\phi_3(3.31) + 1.03721 \times \phi_4(1.31)$$

$$\Psi(4d) = -0.18794\phi_3(2.82) + 1.0175\phi_4(0.97)$$

$$\Psi(2s) = 1.02182\phi_2(2.425) - 0.21736\phi_2(8.700)$$

$$\Psi(2p) = 0.50258\phi_2(3.7374) + 0.63388\phi_2(1.3584)$$

Group Overlap Integrals, R = 1.97 A

$G(3d\sigma, 2s)$	= 0.2506	$G(4d\sigma, 2s)$	= 0.6574
$G(3d\sigma, 2p\sigma)$	= 0.2231	$G(4d\sigma, 2p\sigma)$	= −0.0968
$G(3d\pi, 2p\pi)$	= 0.2158	$G(4d\pi, 2p\pi)$	= 0.6084
$G(4s, 2s)$	= 0.5891	$S(3d, 4d)$	= 0.1740
$G(4s, 2p\sigma)$	= 0.3276		
$G(4p\sigma, 2s)$	= 0.5380		
$G(4p\sigma, 2p\sigma)$	= 0.2255		
$G(4p\pi, 2p\pi)$	= 0.3956		

[a] $\phi_{\mathrm{a}}(\alpha)$ is a normalized Slater-type orbital as defined in ref 15 and 16.

Orbital Energies, ϵ_χ and ϵ_ϕ.—In a crystal field calculation, the titanium would, of course, be Ti^{3+}

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(14) Six is used rather than seven because ρ_{i1} is also on atom 1, and an electron cannot interact with itself, a fact which is automatically adjusted for on the left-hand side of the equation by the equivalence of the coulomb and exchange integrals when $\rho_{k1} = \rho_{i1}$.

(15) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(16) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 796 (1963).

(17) S. Siegel, *Acta Cryst.*, **9**, 684 (1956).

with a single d electron in the t_{2g} orbital. However, in the present MO approach, transfer of charge from the fluorides *via* the bonding orbitals will result in a decrease of charge from +3. Calculations of orbital energies are consequently dependent upon both the charge on the ion and the orbital configuration. The calculations for a given charge were interpolated linearly from values obtained for integral charges. Values for different configurations were weighted and averaged to achieve the energy of the appropriate configuration by the same methods employed in the modified Wolfsberg and Helmholz technique.[3,4] However, it should be stressed that calculated orbital energies, and not experimental valence state ionization energies, were used for the values of ϵ_χ and ϵ_ϕ. The orbital energies were calculated from the usual one-center kinetic energy, coulomb, and exchange integrals in which the core electrons, 1s to 3p on the metal and 1s on the fluoride, as well as the outer orbitals, 3d, 4s, etc., were those appropriate to the charge on the titanium[15,16] and the fluoride.[11] The orbital energies, for the configurations finally used, are given in Table II.

TABLE II

ORBITAL ENERGIES AS A FUNCTION OF CHARGE[a]

	Ti^0	Ti^+	Ti^{2+}	Ti^{3+}	F^0	F^-
3d	0.127[b]	11.534	26.272	44.272	...	...
4s	4.668	12.117	19.865	27.793	...	...
4p	3.021	9.154	16.147	25.711	...	...
4d	0.918	5.016	10.078	14.819	...	...
2s	...	...	...	...	42.633	28.526
2p	...	...	...	...	19.707	4.908

[a] The configurations are $3d^n$, $3d^{n-1}4s^1$, $3d^{n-1}4p^1$, $3d^{n-1}4d^1$ for the 3d, 4s, 4p, and 4d orbitals, respectively. [b] All values are in electron volts. The orbital energies are the negative of the values given in the table.

In principle, the preceding discussion is valid only for closed-shell configurations while in application we must frequently deal with subshells which are only partially occupied. To stay within the framework of the closed-shell system the orbital energies are calculated by the use of Slater's average of configuration method.[18] Furthermore, this is in keeping with our inability to assign the spins of the electrons donated to the metal *via* the bonding orbitals.

Two- and Three-Center Integrals.—The two- and three-center nuclear attraction integrals, $(1/r_1|\rho_{i1}\chi_i)$ and $(1/r_j|\rho_{i1}\chi_i)_{j\neq 1}$, were calculated by the method of Shavitt[19] with modifications as indicated in the Appendix. The values of these integrals for $\rho_{i1} = 2p_1$, $\chi_i =$ 3d, 4s, 4p are given in Table III.

The two-center integrals, $(1/r_j|\chi_i\chi_i)$ and $(1/r_M|\rho_{i1}\rho_{i1})$, for the "crystal field" interactions are also a type of nuclear attraction integral but are a great deal easier to calculate. See, for example, Ballhausen,[20] keeping in mind that one must include the $Y_{00}(1/r_>)$ term in the expansion of the potential. (Values of these integrals are also given in Table III.)

TABLE III

TWO- AND THREE-CENTER NUCLEAR ATTRACTION INTEGRALS, $(1/r_i|\rho_{i1}\chi_i)$

$\|\rho_{i1}, \chi_i)$	r_1[a]	r_4	r_2	r_3
$\|2s, 4s)$	5.074[b]	0.911	1.293	1.293
$\|2s, 4p\sigma)$	8.383	1.444	2.047	2.047
$\|2s, 3d\sigma)$	3.511	0.605	0.846	3.846
$\|2s, 4d\sigma)$	8.736	1.377	1.948	1.948
$\|2p\sigma, 4s)$	1.762	0.721	1.312	1.012
$\|2p\sigma, 4p\sigma)$	2.819	3.767	1.157	1.157
$\|2p\sigma, 3d\sigma)$	2.565	0.583	0.780	0.780
$\|2p\sigma, 4d\sigma)$	−0.139	−0.037	−0.082	−0.082
$\|2p_x, 4p_x)$	2.533	0.803	1.256	1.075
$\|2p_x, 3d_{xz})$	1.525	0.462	0.694	0.635
$\|2p_x, 4d_{xz})$	4.276	1.108	1.678	1.536

[a] The subscripts on the r designate the ligand location of the point charge. The ligand locations are numbered identically with those used by ref 20, p 154. [b] The values of the integrals are given in units of electron volts.

Computational Methods

Once the values of the integrals tabulated in Tables I–III are obtained, the matrix elements of the secular determinant become functions of q_M, R_σ, and R_π since q_j is fixed by the relations among the charge on the metal, q_M, the number of ligands, n, and the over-all charge on the complex, q; that is, $q_j = (q - q_M)/n$. For chosen values of R_σ and R_π, the computations are completely determined by the requirement of self-consistency between the starting value of q_M and that determined by the electron population analysis.

In the method for the determination of that charge which will be self-consistent, one cannot arbitrarily choose a starting charge, carry out a computation, and use the new charge calculated from the population analysis for a second calculation. A simple example will illustrate why this is so. If one chooses $q_M = +2.97$ for the TiF_6^{3-} complex, the calculated charge q_M is −2.12. If it were possible to evaluate orbital energies for such a titanium species, the next iteration would put the calculated q_M at approximately +3. Thus, the computations would oscillate between extremes, and self-consistency would not be achieved. Rather, one starts at some low q_M, say zero, and slowly increments this value until the calculated value first falls below the starting value. The self-consistent charge must then be a value between the last starting charge and the one preceding it. Comparison of these two charges with their corresponding calculated charge distributions allows a self-consistent value to be chosen by interpolation.

Results and Discussion

This report is concerned with an examination of conditions under which the approach will yield answers in best agreement with experiment, the sensitivity of the results to changes in these conditions, etc. For this reason, all discussions will be limited to TiF_6^{3-}.

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(18) J. C. Slater, "Quantum Theory of Atomic Structure," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 322.

(19) I. Shavitt, "Methods in Computational Physics," Vol. 2, Academic Press Inc., New York, N. Y., 1963, p 1.

(20) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., N_w York, N. Y., 1962, p 57.

Results for a series of octahedrally coordinated fluorides appear in the following paper.

Pertinent to the method of calculation are such considerations as the size of the basis sets, the values of the R_σ and R_π parameters, the method and scope of the electron population analysis, and the inclusion of ligand–ligand overlap. Table IV summarizes some of the results obtained.

Table IV

Metal Charges and Δ Values ($R_\sigma = R_\pi = 0.80$)

Computation	Basis set[a]	Lig–lig overlap[b]	Population analysis[c]	Charge on metal ion	Δ value,[d] ev
1	A	Yes	M	1.02	4.63
2	A	Yes	a_i^2	1.72	4.80
3	A	No	M	1.01	2.73
4	A	No	a_i^2	1.52	2.88
5	A	No	d^n	1.75	2.73
6	B	Yes	M	1.30	9.75
7	B	Yes	a_i^2	2.04	9.49
8	B	No	M	1.08	7.46
9	B	No	a_i^2	1.79	7.74
10	B	No	d^n	1.77	7.48
11	C	Yes	M	0.38	7.67
12	C	Yes	a_i^2	1.79	8.84

[a] Basis sets: A = 2p ligand; 3d, 4s, 4p metal. B = 2s, 2p ligand; 3d, 4s, 4p metal. C = 2s, 2p ligand; 3d, 4s, 4p, 4d metal. [b] Lig–lig refers to whether or not ligand–ligand overlaps and H matrix elements were included. [c] Population analysis: M refers to regular Mulliken method; d^n refers to Mulliken method only for the 3d interactions; for details and explanation of a_i^2 method, see text. [d] Experimental Δ value = 1.98 ev.

Ligand–Ligand Matrix Elements.—Despite the fact that the overlaps of 2s and 2p orbitals on adjacent fluorides are very small, one sees what is apparently a large influence on the calculated values of Δ when this interaction is included. For example, computations 1 and 3 differ in approach only by this consideration, yet the Δ value changes by approximately 2 ev. It is believed that such results are entirely spurious, caused by the approximations of the method. The off-diagonal interaction term between central metal and ligand involves the two-center interaction, $(\rho_{i1}|V_1|\chi_i)$, which is approximated by $[-R_a(-6 + q_j) - Z](1/r_1|\rho_{i1}\chi_i)$, where R_a is chosen to yield a correspondence between the point-charge approximation and the spread-charge electrostatic interaction. An analogous term is involved in the ligand–ligand interaction, $(\rho_{i1}|V_1|\rho_{i2})$, and by the computational method the same factor, R_a, is used. However, a correction factor between metal and ligand interactions at a distance r should not necessarily apply to ligand–ligand interactions involving more contracted functions at a distance $\sqrt{2}r$. Indeed, the point-charge approximation should be more correct in this latter case; that is, R_a should be larger. However, a larger R_a would decrease the size of the off-diagonal interaction, decreasing its effect on Δ. Consequently, the use of the same R_a for metal–ligand and ligand–ligand interactions is probably incorrect.[21] Therefore, it appears preferable to ignore ligand–ligand interaction entirely unless one evaluates the two-center electrostatic interactions exactly.

Size of Basis Set.—Comparisons of any three sets of data in Table IV in which only the sizes of the basis sets are changed all show the same distinct trend: the basis set A results in the smallest, set B in the largest, and set C in the intermediate values. Comparable conditions between sets A and B result in approximately a 5-ev increase in the calculated value of Δ. This effect is analogous to that which occurs in the modified Wolfsberg and Helmholz method.[6] In both calculations, inclusion of the 2s basis functions causes little change in the metal or ligand character of the molecular orbitals or in the values of any of the energy levels except the *highest* energy levels of those in which the 2s participates. However, in the basis sets A and B, the e_g level which determines Δ is the orbital of highest energy, and consequently inclusion of the 2s results in an incorrect result for the calculated value of Δ.

Calculations with set C basis show what happens when an attempt is made to use an expanded basis set in order to reduce the value of Δ. Specifically set C includes the 4d atomic orbital on the metal. A slight reduction is Δ is achieved but not enough to compensate for the presence of the 2s. There is good reason to conclude that the minimal reduction was caused not because higher orbitals are ineffective but rather because the form of the particular 4d orbitals one obtains by minimization of free-ion energies may not be adequate. That is, higher atomic orbitals obtained for the free ion may not necessarily be the most desirable for the molecular orbital calculations.[22,23] Specifically, one notes that the σ-bonding overlap of the 4d with the 2p is negative and quite small, while the π overlap is very large, because the 4d orbitals from the free-ion calculations are very diffuse. Preliminary calculations have shown that contraction of the orbital by increase of the orbital exponent causes a decrease in π overlap, together with a change in sign and increase in σ overlap, without substantial alteration in orbital energy. Because of the location of the 4d level, such changes should have the effect of decreasing the calculated Δ value. In any event, it is clear that, if one uses free-ion atomic orbitals with this method, the best approximations to the molecular energy levels are obtained by use of the minimal set A. It should be stressed that, while the calculations reveal little change in molecular orbital character on exclusion of the 2s orbitals, use of set A is not meant to imply that they do not participate in the bonding. Rather, it would appear that a single reduction factor for both types of σ interactions tends to overestimate the role of the 2s. We are presently investigating the entire problem of wave function forms and basis sets in a more rigorous framework in order to clarify this situation.

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[21] A similar conclusion was reached by us in regard to the modified Wolfsberg and Helmholz approach.[6]

[22] While there is a convenience in the use of free-ion AO's as basis functions, there is no theoretical requirement that they be used, particularly for the higher energy orbitals. Indeed, as illustrated by Hartree–Fock calculations on hydrogen fluoride,[23] there is evidence that such AO's are frequently not the best functions with which to construct the LCAO–MO's.

[23] E. Clementi, *J. Chem. Phys.*, **36**, 33 (1962).

Electron Population Analysis.—The values in Table IV also allow comparison of three methods for electron population analysis. Those labeled M refer to the previously described Mulliken method in which the analysis includes all of the orbitals in the basis set. Those symbolized by d^n indicate that the Mulliken method was applied to the 3d orbitals only. That is, the a_i of the 3d orbitals only were used to calculate the charge on the central metal with all remaining charge presumed to be on the ligands. In the method labeled a_i^2 for a calculated MO of the form $\Psi_i = a_i\chi_i + b_i\phi_i$, the coefficents a_i and b_i were renormalized such that $a_i^2 + b_i^2 = 1$ prior to the summation of the a_i^2 of the occupied molecular orbitals.

One need only examine curves of the radial functions of the AO's used in the basis sets to see why such a study was made. Figures 1 and 2 show that, while the region of overlap between the 3d metal and 2p ligand orbitals is between the two atoms, the overlaps of the 2p with the other more diffuse metal orbitals are essentially on the ligand. Furthermore, Figure 3 indicates that the charge densities of the 4s and 4p wave functions are also primarily on the ligands. Consequently, if we consider coulomb interaction of the type $\bar{a}_{4p}(4p4p|3d3d)$, it is not unreasonable to approximate this by $\bar{a}_{4p}(1/r_j|3d3d)$, that is, the interaction of the 3d charge density with the $\bar{a}_{4p}$ charge density acting as a point charge *on the ligand.*

From this point of view, the self-consistent charge takes on a clearer meaning which should be emphasized. It is primarily a means of control for estimation of self-consistency between the final coefficients, a_i and b_i, and those implied in the choice of starting charge. To interpret the self-consistent charge as the "true" ionic charge of the metal in the complex is misleading. Furthermore, Mulliken[24] has pointed out that the charge distribution by his method is dependent upon the size of the basis set and that unbalanced sets on two atoms would automatically favor an *apparent* transfer of charge to the atom with the larger basis set.

These considerations more than justify the use of only the 3d–2p interactions to distribute the charge. It is further affirmed by the a_i^2 method of analysis. This approach tends to assign the cross term in the charge density, $2a_ib_iG$, to the ligands. One notes from Table IV the general similarity between the charge *via* the d^n and a_i^2 methods. This emphasizes that the transfer of charge to the metal in the 4s, 4p, and 4d MO's in the Mulliken method comes from the a_ib_iG contribution. However, as Figure 1 indicates, for these diffuse metal orbitals this distribution should really be associated with the ligand and not the metal.

It is interesting to note that, all other considerations being equal, all three methods give approximately the same Δ value. However, the foregoing considerations suggest that the Mulliken method involving only the 3d orbitals is the most reasonable approach to use. Since this method presumes all metal electrons above the filled 3p shell to be in the 3d orbitals in the ground state, a simplification occurs in the evaluation of the orbital energies. One need no longer consider the contributions of such configurations as $3d^{n-1}s$, $3d^{n-2}sp$, etc., to the 3d orbital energies, but only those arising from the $3d^n$ configuration. Similarly the 4s, 4p, and 4d energies come from the $3d^{n-1}4s$, $3d^{n-1}4p$, $3d^{n-1}4d$ configurations, respectively. This appreciably simplifies their calculation.

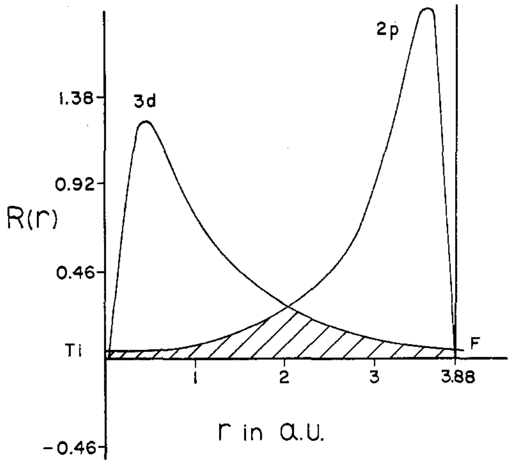

Figure 1.—Radial functions of TiF_6^{3-}, 3d metal–2p ligand.

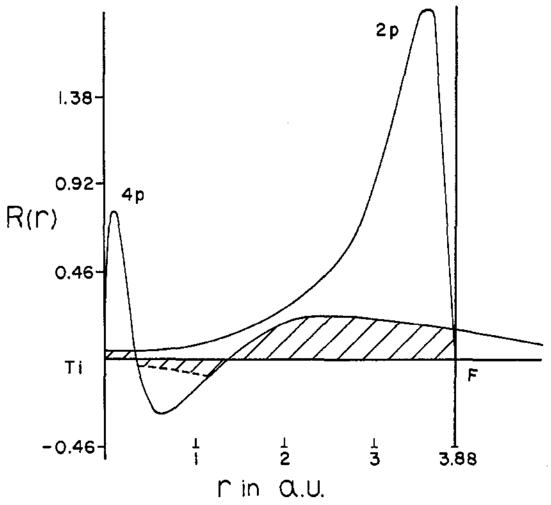

Figure 2.—Radial functions of TiF_6^{3-}, 4p metal–2p ligand.

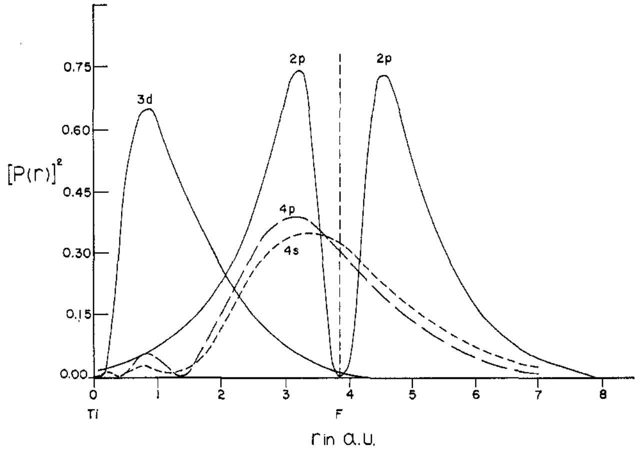

Figure 3.—Charge densities of radial functions of TiF_6^{3-}. $P(r) = R(r)r$.

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(24) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).

The Choice of R Parameters.—Under the assumption that the difference in the t_{2g}^* and e_g^* levels reflects the Δ value for TiF_6^{3-}, none of the results given in Table IV agree well with the experimental value[25] of 1.98 ev. Table V summarizes the results of interest for the calculations as a function of R_σ and R_π.

TABLE V

RESULTS AS A FUNCTION OF REDUCTION PARAMETERS

R_σ	R_π	Charge	Δ	Electron populations[a] $2t_{2g}^*$	$2e_g$	$1t_{2g}$	$1e_g$
0.90	0.90	2.07	1.68[b]	0.904	0.887	0.096	0.113
0.85	0.85	1.90	2.19	0.891	0.862	0.109	0.138
0.85	0.80	1.82	1.23	0.868	0.870	0.132	0.130
0.85	0.75	1.75	0.24	0.848	0.877	0.152	0.123
0.80	0.80	1.77	2.73	0.878	0.840	0.122	0.160
0.87	0.87	1.98	1.98	0.897	0.873	0.103	0.127

[a] Electron population values given for that fraction of one electron on the metal atom. [b] Values of Δ given in electron volts.

Disregarding for the moment that set of values which yield the best estimate of Δ, one notes the sensitivity of Δ and the relative insensitivity of the orbital coefficients and self-consistent charge to the choice of reduction parameters. For example, computations 3 and 4 in Table V show a change in Δ of 0.20 ev for 0.01 change in the R_π value. This kind of result affirms that not only are the values of the off-diagonal term very sensitive to the value of the integral $(\rho_{i1}|V_1|\chi_i)$, but also the antibonding energy levels are extremely sensitive to the value of the off-diagonal matrix element. This is further illustrated by comparison of the t_{2g} secular determinants for computations 3 and 4 of Table V. The determinants, their eigenvalues, and the differences between the H(3d, 3d) elements and their respective antibonding levels are given in Table VI. It is seen that a change of the R_π scaling factor from 0.80 to 0.75 results in an increase of 0.87 ev in $t_{2g}^* - H(3d, 3d)$. This sensitivity of the antibonding levels, and consequently of the estimates of Δ, to small variations in the off-diagonal term was first noted by us[2] in connection with the modified Wolfsberg and Helmholz method. It raises serious questions as to the ability of any semiempirical method to reproduce *exact* Δ values.

TABLE VI

t_{2g} SECULAR DETERMINANTS AND EIGENVALUES

$R_\sigma = 0.85 \quad R_\pi = 0.80$

$$\begin{vmatrix} 11.26 - E & -4.84 - GE \\ -4.84 - GE & -1.24 - E \end{vmatrix} \qquad \begin{array}{l} E_1 = -2.60 \text{ ev} \quad E_2 = 15.26 \text{ ev} \\ E_2 - H(3d, 3d) = 4.00 \text{ ev} \end{array}$$

$R_\sigma = 0.85 \quad R_\pi = 0.75$

$$\begin{vmatrix} 11.82 - E & -5.74 - GE \\ -5.74 - GE & -1.28 - E \end{vmatrix} \qquad \begin{array}{l} E_1 = -2.30 \text{ ev} \quad E_2 = 16.69 \text{ ev} \\ E_2 - H(3d, 3d) = 4.87 \text{ ev} \end{array}$$

On the other hand, one is seldom interested in Δ for its own sake. Certainly in the case of simple complexes such as hexahalides, hexaammines, etc., it is well known from crystal field considerations. What is of interest is the nature of the bonding. If calculations of a theoretical nature are to have significance, it will be because of the insight they give us into covalency, the importance of π bonding, etc. This is precisely the information one can obtain by consideration of the coefficients of the atomic orbitals in the molecular orbitals, and these have been shown to be relatively insensitive to changes in the scaling parameters. It is suggested, therefore, that instead of concentrating one's effort on the exact reproduction of Δ, one may use the experimental value as a means of fixing parameters such as R_σ and R_π and thereby correlate the results of the calculations with other experimental data. This approach will be examined more fully in the following article.

The foregoing discussion does not mean to imply that one should be free to choose R_σ and R_π in an entirely arbitrary fashion. For example, for computation 1 of Table V, the reduction factors of $R_\sigma = R_\pi = 0.90$ resulted in an off-diagonal term for the A_{1g} secular determinant of insufficient magnitude so that the coefficient of the 4s orbital in the bonding wave function was negative and a negative population on the metal was calculated by the population analysis. The latter is physically meaningless. Furthermore, the negative coefficient would imply that a decrease in charge density between the atoms occurs on bond formation; *i.e.*, the molecular orbital has the form of an antibonding orbital. In terms of the limited basis set employed, it is much more likely that the reduction factor does not adequately reflect the proper degree of electrostatic repulsion, and such choices should be discarded.

Similarly, it would seem that since the correction involves the ligand charge distribution, $\sum_i \bar{b}_{ij}\rho_{ij}\rho_{ij}$, one could expect that reduction factors for a given ligand should be fairly independent of the metal ion or its oxidation state. That this seems to hold is shown in the following paper which covers a series of hexafluoride complexes.

From Table V, it is seen that, when reduction factors of $R_\sigma = R_\pi = 0.87$ are employed, the calculated value equals the experimental Δ. More complete details of this calculation are given in Table VII. From the tabulated coefficients and the $\bar{a}_i$ values, one notes the moderate degree of π bonding in the fluoride complex, a result in accord with that obtained by Shulman and Sugano on $KNiF_3$. Likewise, it is seen that, although some covalency exists, the complex is essentially ionic as indicated by the high degree of metal character in the t_{2g}^* and e_g^* orbitals. Participation in the bonding of the 4s and 4p orbitals does not appear to be substantial.

In accord with experimental observations, the wide separation of the t_{2g}^* and e_g^* orbitals from the nearest filled pure ligand orbital, t_{1u}, eliminates the possibility of observing charge-transfer transitions in the visible or ultraviolet region. On the other hand, transitions from t_{2g}^* to a_{1g}^* would appear to be energetically observable in TiF_6^{3-}. In fact, the same vibrations,

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[25] Previous considerations of TiF_6^{3-} suggested a Δ value of 2.15 ev. However, as will be shown in the following paper, our results suggest the lower value might be more apropos. In any event, the values of Δ in Table IV are all too high.

TABLE VII

ENERGY LEVELS AND EIGENVECTORS OF TiF_6^{3-}

Level	Energy, ev	Eigenvector coefficients					$\bar{a}_i$
		3d	4s	4p	2pσ	2pπ	
$3t_{1u}$	24.92	...	...	1.113	−0.303	−0.533	0.932
$2a_{1g}$	15.44	...	1.058	...	−0.379	...	0.988
$2e_g$	15.01	0.990	...	...	−0.484	...	0.873
$2t_{2g}$	13.03	0.996	...	...	...	−0.446	0.897
t_{1g}	−1.37	...	...	...	...	1.000	0.000
t_{2u}	−1.37	...	...	...	...	1.000	0.000
$2t_{1u}$	−1.62	...	...	0.102	−0.182	0.944	0.043
$1t_{2g}$	−2.19	0.237	...	...	...	0.922	0.103
$1a_{1g}$	−2.41	...	0.034	...	0.988	...	0.012
$1t_{1u}$	−2.48	...	...	0.072	0.970	0.125	0.025
$1e_g$	−3.69	0.27	...	...	0.905	...	0.127

t_{1u} and t_{2u}, make both the $t_{2g} \rightarrow e_g$ and $t_{2g} \rightarrow a_{1g}$ transitions vibronically allowed. It is interesting to note that there are two absorption maxima in TiF_6^{3-}. While the existence of two peaks has been previously rationalized[2] as due to Jahn–Teller distortion in the excited state, it is tempting to speculate that the second maximum might be due, at least in part, to the $t_{2g} \rightarrow a_{1g}$ transition. Additional consideration of this and other results are given in the following paper on the hexafluorides.

Summary

The proposed method for the calculation of electronic energy levels in transition metal complexes attempts to simplify a more rigorous SCF calculation by means of reasonable approximations. The use of limited free-ion basis sets and point-charge approximations yields results which are in accord with present chemical concepts concerning the bonding in such complexes. The results appear to be sufficiently encouraging to warrant further investigation of the method.

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Appendix

Computation of Three-Center Nuclear Attraction Integrals

Shavitt[18] has indicated the usefulness of the Laplace transform in the evaluation of multicenter integrals involving Slater orbitals

$$R_n(r) = [(2\alpha)^{2n+1}/(2n)!]^{1/2}r^{n-1}e^{-\alpha r}$$

Application of this method to the computation of three-center nuclear attraction integrals,[26] $(\phi_A|r_C^{-1}|\chi_B)$, can be facilitated by the following considerations.

Both nuclear attraction and hybrid integrals require modified Bessel functions of the second kind of integral order, while eq 119–135 of ref 19 presume half-integral order. By rearranging terms in the series for J_{nm} (eq 115) one can show, in the notation of Shavitt[19]

$$T_{lm} = \sum_{i=1}^{l-n-1/2} S_{li}(\sigma, \tau) + \sum_{i=0}^{\infty} R_{li}(\sigma, \tau)$$

TABLE VIII

SUBDIVISION OF THE INTERVAL OF INTEGRATION

Ratio of orbital exponents	L_1	L_2
≥18	0.95	0.99
14–18	0.95	0.98
10–14	0.90	0.95
8–10	0.82	0.91
6–8	0.78	0.88

where l is half an odd integer, with

$$S_{li} = \frac{k_i(\varkappa)}{\Gamma(l+1-i)(2\tau)^i}$$

and

$$R_{li} = \frac{k_i(\varkappa)}{(l+1+i)(2\rho)^i}$$

With these definitions of R and S the recursion relations follow readily; in particular, eq 131 of ref 19 becomes

$$T_{l+1,m} = (lT_{lm} + \sigma T_{l-1,m} - S_{l-1,\,l-m-1/2})/\tau$$

To avoid the time-consuming generation[27] of the Bessel functions K_i, when i is integral, use can be made of a very accurate analytic approximation[28] to K_0 and K_1. The maximum error in this approximation is about 1 part in 10^7, much less than the error introduced by the numerical quadrature.

Accurate evaluation of the integrals is strongly dependent upon the location of the one-dimensional numerical integration points in the interval (0, 1). For certain integrals the integrand behaves erratically near the limits, and subdivision of the interval is necessary. Since it is desirable that the quadrature be automatic, a study has been made to determine a suitable criterion and method for the subdivision. While it is true that for large x the Bessel functions $K_i(x)$ in the series go as $e^{-x}(\pi/2x)^{1/2}$ for all i, it is not possible to use x alone as an indication of the size of the integrand since the series is infinite. However, it has been determined that, when the ratio α_A/α_B is large, the only significant contribution to the integrand comes from a very narrow maximum located near the limit 1. When this ratio is very small, similar behavior is exhibited near zero. When $1/6 \leqslant \alpha_A/\alpha_B \leqslant 6$, the integrand is reasonably uniform over the entire interval. Consequently, the ratio of the α values is indicative of the behavior of the integrand and is a useful criterion for placing more points in the interval where the integrand is largest and most erratic.

When use is made of the best available atomic functions,[15,16] one deals with ratios of orbital exponents of 20:1 or less. Our calculations indicate that, for such functions, use of 16 Gauss–Legendre points, with the interval properly subdivided,[29] yields values accurate to 1 part in 10^5 or 10^{-5} au, whichever is the less stringent.

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[26] Note that it is the implicit assumption of Shavitt that the $+Z$ axis at center A points away from center B; this is opposite to the convention in the overlap formulas of R. Mulliken, C. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[27] I. Stegun and M. Abramowitz, "Mathematical Tables and Other Aids to Computation," Vol. XI, 1957, p 255.

[28] E. Allen, ref 27, Vol. X, 1956, p 162.

[29] Without subdivision, errors for a given pair of Slater functions can be as great as 50%.

When $20 \geqslant \alpha_A/\alpha_B \geqslant 6$, the points are allocated in groups of 3, 5, and 8 in the intervals $(0, L_1)$, (L_1, L_2), $(L_2, 1)$, respectively, where the L values for the appropriate ratio are given in Table VIII. For $6 \geqslant \alpha_A/\alpha_B \geqslant {}^1/_6$, no subdivision is necessary. For $20 \geqslant \alpha_B/\alpha_A \geqslant 6$, the 3, 5, and 8 points are placed in the intervals $(1 - L_2, 1)$, $(1 - L_2, 1 - L_1)$, and $(0, 1 - L_2)$, respectively.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

Energy Levels, Spin Densities, and the Nephelauxetic Effect in Metal Hexafluorides

BY RICHARD F. FENSKE, KENNETH G. CAULTON, DOUGLAS D. RADTKE, AND CAROL C. SWEENEY

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The relative electronic energy levels of MF_6^{3-}, where M = Ti, V, Cr, Fe, and Co, are calculated from semiempirical molecular orbital theory. The calculated $\Delta = 10Dq$ values compare well with experimental results. The molecular orbitals indicate less covalent character than previous calculations. Spin density estimates from the 2p orbitals are in good accord with results from nmr and epr measurements. Comparison of calculated and experimental B and β values shows excellent agreement and allows an interpretation of the nephelauxetic effect to be made.

Introduction

In the preceding paper,[1] a method was outlined for the calculation of the relative energy levels of transition metal complexes. This report concerns the application of the procedure to the series MF_6^{3-}, where M = Ti, V, Cr, Fe, and Co. Since full details have already been given, we shall simply summarize the pertinent restrictions.

The calculations are fully specified by the wave functions, internuclear distances, and choice of reduction parameters, R_σ and R_π. The basis set for the metal consisted of the +2 wave functions for the 3d, 4s, and 4p orbitals as tabulated by Richardson and coworkers.[2,3] The fluoride 2p radial function is the same as that used by Shulman and Sugano[4] in their work on $KNiF_3$. With the exception of CrF_6^{3-} where the internuclear distance is known[5] the internuclear distances between the metals and the fluorines were obtained from the tabulation given by Peacock[6] for the neutral compounds MF_3. In each case, octahedral symmetry of fluorines about the metal is evident. In accord with the calculations[1] on TiF_6^{3-}, reduction parameters of $R_\sigma = R_\pi = 0.87$ were employed in the approximation of the two-center interactions for the off-diagonal terms of the secular determinant.

Calculated Energy Levels

The relative values of the energy levels, the self-consistent charges, and the calculated and experimental $\Delta = 10Dq$ values for the five complexes are summarized in Table I. For each system, the levels through t_{1g} are completely filled. The occupation of the $2t_{2g}$ and $2e_g$ levels is then specified by the number of d electrons on the metal distributed in accord with the "weak field" nature of the complexes. It should be noted that the level values are *relative* positions and that the positive values of the $2t_{2g}$ and higher levels result because the potential of the cations was not included in the calculations.

In view of the sensitivity of calculated Δ values to small variations in reduction parameters, the degree of agreement between calculated and experimental results is quite gratifying. As has been shown,[1] minor adjustment of the reduction parameters would have resulted in exact agreement of Δ values with little change in the eigenvector coefficients; these results show that approximate Δ values can be obtained without such adjustment.

The values of the energy levels suggest that charge-transfer transitions from the nonbonding t_{2u} state should not be observable in the visible or ultraviolet regions except in the case of CoF_6^{3-} where the one-electron energy difference $2t_{2g} - t_{2u}$ is 5.20 ev. Of course, this latter quantity does not account for possible electrostatic interaction changes as a result of the charge transfer. Unfortunately, the experimental absorption spectrum for this species[7] is not reported above 20,000 wavenumbers (2.48 ev) so a comparison is not presently possible.

It is also noteworthy that for the titanium complex the transition $2t_{2g} \rightarrow 2a_{1g}$ is expected to appear at 2.41 ev. Since the same vibrations, t_{1u} and t_{2u}, which make the $2t_{2g} \rightarrow 2e_g$ transitions vibronically allowed also make $2t_{2g} \rightarrow 2a_{1g}$ possible, one is tempted to speculate that the higher energy absorption maximum in TiF_6^{3-}

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