The Off-Diagonal Matrix Element in Molecular Orbital Calculations for Metal Complexes

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Abstract: This work concerns an investigation of those considerations involved in the evaluation of the off-diagonal matrix elements which arise in molecular orbital calculations for metal complexes. The use of $FG_{ij}(H_{ii} + H_{jj})/2$ and related attempts to correlate H_{ij} with the group overlap integrals, G_{ij}, by a multiplicative factor, F, is examined from theoretical considerations and calculational results. It is shown that terms of considerable magnitude, which do not vary as functions of the overlap integrals, make substantial contributions to the off-diagonal elements. Hence, unpredictable fluctuations in the F factor occur, and the need for wide variations in the choices of F factors in previous calculations is understood. Evidence is also presented which indicates that sums of two-center electrostatic interaction integrals vary from complex to complex in a fashion analogous to the corresponding nuclear attraction integrals. Consequently, indications are that the former integrals may be evaluated from the latter in a systematic way.

Since the introduction of the Wolfsberg–Helmholz calculations[2] for the evaluation of the electronic energy levels in transition metal complexes, the matrix elements in the secular determinant, $|H_{ij} - EG_{ij}|$, have been approximated by a variety of techniques. In a previous paper[3], we emphasized the importance of including the two-center Coulomb and exchange integrals as well as the free-ion orbital energies for the evaluation of the metal and ligand diagonal terms. Other authors[4–6] have introduced similar adjustments to the diagonal terms using various means for approximating the integrals involved. However, most of these authors have continued to use an approximation for the off-diagonal matrix element which involves the overlap integral, S_{ij}, or the group overlap integral, G_{ij}. It is the purpose of this paper to examine the relation between the overlap integral and the off-diagonal matrix element.

It is interesting to note the various attempts to systematize the relationship between S_{ij} and the off-diagonal term. The original Wolfsberg–Helmholz calculation[2] set $H_{ij} = FG_{ij}(H_{ii} + H_{jj})/2$ with $F_\sigma = 1.67$ and $F_\pi = 2.00$. Yamatera[7] used the same expression for his calculations on $Co(NH_3)_6^{+3}$. The self-consistent charge and configuration (SCCC) method as originally applied by Ballhausen and Gray[8] to the vanadyl ion employed $H_{ij} = FG_{ij}\sqrt{H_{ii}H_{jj}}$ with $F_\sigma = F_\pi = 2.00$. Among others, this relation has been employed by Lohr and Lipscomb[9], Fischer,[10] Johansen and Ballhausen,[11] and in several applications by Gray and co-workers.[12–14] However, Cotton and Haas[15] have pointed out that in a series of ammine complexes, F_σ had to be varied from 1.82 to 2.30 in order to obtain agreement with experimental values of $\Delta = 10Dq$. Similarly, the more recent applications of the SCCC method to halide and oxide complexes[16] used $F_\pi = 2.10$ with F_σ slowly varying from 1.53 to 1.81. In all of these calcuations, the diagonal term consisted only of the free ion orbital energy and/or the ionization potential of the corresponding hydride.

Other variations for H_{ij} have been presented. Cusachs[17] suggested $H_{ij} = (2 - |S_{ij}|)(H_{ii} + H_{jj})G_{ij}/2$, while Yeranos[18] offered $H_{ij} = FG_{ij}[2(H_{ii}H_{jj})/(H_{ii} + H_{jj})]$, and Kettle[19] employed the simplest relation, $H_{ij} = KS_{ij}$ with k as a variable.

A further complication arises with the introduction of the two-center Coulomb integrals in the evaluation of H_{ii} and H_{jj}. $H_{ii} = \epsilon_{ii} +$ Coulomb repulsion terms. ϵ_{ii} is the orbital energy of the electron in the free ion which is frequently approximated by the negative of the valence-state ionization energy of the appropriate free ion. The two-center Coulomb repulsion integrals are positive. The effect of the latter terms is to raise the values of H_{ii} and H_{jj} appreciably above their original negative values, that is, to make them smaller in absolute value.

Indeed, it is possible and actually occurs[20] that in complexes of high negative charge, FeF_6^{-3} or $CrCl_6^{-3}$, for example, at self-consistent charge the Coulomb repulsion terms are larger in magnitude than the orbital energies for the metal 3d, 4s, and 4p orbitals so that H_{ii} for the metal is positive. Such a situation is possible because the calculations do not include the positive ions of the species, for example, the K^+ ions in K_3TiF_6, which are presumed to add simply a constant potential

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to the system. At the same time, the ligand diagonal term, H_{jj}, is negative so that use of the root-mean-square method results in imaginary values. To circumvent this dilemma, Ros[21] returned to the original Wolfsberg–Helmholz average. But even this method can lead to difficulty in terms of the coefficients in the molecular orbitals. Consider solving the secular equation for the eigenvalues

$$a[H(3\text{d},3\text{d}) - E] + b[H(3\text{d},3\text{p}) - EG(3\text{d},3\text{p})] = 0 \quad (1)$$

Such an expression can arise in the solution of a 2 × 2 matrix involving FeCl_6^{-3}, for example. The term a is the coefficient of the metal 3d wave function in the molecular orbital, while b is the coefficient for the symmetry adapted ligand orbitals. $H(3\text{d},3\text{d})$ is the metal diagonal matrix element, $H(3\text{d},3\text{p})$ is the off-diagonal term between the 3d and 3p orbitals, and $G(3\text{d},3\text{p})$ is the positive overlap integral. Consider the case where $H(3\text{d},3\text{d})$ is positive and $H(3\text{p},3\text{p})$ is slightly negative in value.[22] The energy of the bonding orbital, E, will be more negative than either $H(3\text{d},3\text{d})$ or $H(3\text{p},3\text{p})$ so that $[H(3\text{d},3\text{d}) - E]$ as well as $-EG(3\text{d},3\text{p})$ will be positive.

Then for a positive value of a

$$b = -\frac{a[H(3\text{d},3\text{d}) - E]}{H(3\text{d},3\text{p}) - EG(3\text{d},3\text{p})} \quad (2)$$

For b to have a positive value in keeping with the bonding character of the orbital, not only must $H(3\text{d},3\text{p})$ be negative but it must be larger in absolute value than $EG(3\text{d},3\text{p})$. But if one uses

$$H(3\text{d},3\text{p}) = FG[H(3\text{d},3\text{d}) + H(3\text{p},3\text{p})]/2$$

with the Coulomb terms included for the diagonal values, it can and does occur that $|H(3\text{d},3\text{d})| > |H(3\text{p},3\text{p})|$ so that $H(3\text{d},3\text{p})$ is positive and one is led to the erroneous conclusion that the bonding orbital is antibonding in character. In any event, the off-diagonal term is substantially decreased in magnitude if H_{ij} is evaluated from the H_{ii} terms in this way.

The situation cannot be rectified simply by the addition to the diagonal terms of some arbitrary negative potential that will allow both terms to become negative. In principle, the addition of such a term, $-Z$, to the Hamiltonian should not alter the calculated energy levels, E, relative to each other or to the starting levels, H_{ii} and H_{jj}. Without loss of generality, this can be illustrated by recourse to a simplified 2 × 2 secular determinant in which $H_{ii} = H_{jj}$. Then

$$(H_{ii} - E)^2 - (H_{ij} - EG_{ij})^2 = 0 \quad (3)$$

$$E_1 = (H_{ii} - H_{ij})/(1 - G_{ij}) \quad (4)$$

$$E_1 - H_{ii} = [(H_{ii} - H_{ij})/(1 - G_{ij})] - H_{ii} \quad (5)$$

A constant potential for the diagonal terms yields $-Z\langle\psi_i|\psi_i\rangle = -Z$ so H_{ii}' becomes

$$H_{ii}' = H_{ii} - Z \quad (6)$$

For the off-diagonal term, one obtains $-Z\langle\psi_i|\psi_j\rangle = -ZG_{ij}$ so H_{ij}' becomes

$$H_{ij}' = H_{ij} - ZG_{ij} \quad (7)$$

Substitution of these terms into

$$(H_{ii}' - E')^2 - (H_{ij}' - E'G_{ij})^2 = 0 \quad (8)$$

yields

$$E_1' = [(H_{ii} - H_{ij})/(1 - G_{ij})] - Z \quad (9)$$

Then, $E_1' - H_{ii}' = E_1 - H_{ii}$, and constancy of the levels relative to one another is maintained. But this relation holds only if $H_{ij}' = H_{ij} - ZG_{ij}$. If one applies the Wolfsberg–Helmholz approximation for the off-diagonal term, then for $H_{ii} = H_{jj}$

$$H_{ij} = FG_{ij}H_{ii}$$

However, for H_{ij}', one obtains

$$H_{ij}' = FG_{ij}(H_{ii} - Z) = H_{ij} - FG_{ij}Z \quad (10)$$

The requirement of unchanging relationships between the levels is maintained only if $F = 1.00$. Since this is never the case, introduction of a constant potential to the diagonal terms would be equivalent to the addition of another variable to the calculations, subtly altering the value of the off-diagonal term depending on the size of the chosen potential.

As an alternative to the foregoing undesirable state of affairs, Oleari, *et al.*,[4] have chosen to set $H_{ij} = FG_{ij}(\epsilon_{ii} + \epsilon_{jj})/2$ where the ϵ's are the orbital energies and $F = 1.00$ for all interactions with ligand p orbitals and $F = 0.30$ for metal–ligand interactions involving the ligand s orbitals. This removes the dilemma as to sign for the off-diagonal terms. However, as will be shown, it is our belief that the absolute magnitudes of the terms are too small.

Theoretical Considerations

Throughout the course of all the various attempts to approximate the off-diagonal terms, the considerations advanced by Richardson,[23] in an A.E.C. publication which unfortunately achieved only limited distribution, have been overlooked. Richardson shows that by application of the Mulliken[24] 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

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

where $-{}^1/_2\Delta$ is the kinetic energy operator, V_M is the potential energy due to the nucleus and electrons of the metal, and V_j corresponds to the nucleus and electrons of the jth ligand. Additional information concerning the operator forms of the potentials can be found in our recent publication.[3]

Consider the matrix element $(\phi_i|\mathcal{H}|\chi_i)$, where χ_i is a metal wave function and ϕ_i is a symmetry-adapted linear combination of ligand wave functions, ρ_{ij}, over the j ligands. Then $(\phi_i|\mathcal{H}|\chi_i) = C(\rho_{i1}|\mathcal{H}|\chi_i)$ where the constant, C, is the same coefficient which relates the diatomic overlap, $S(\rho_{i1},\chi_i)$ to the group overlap $G(\phi_i,\chi_i)$. Then the matrix element can be written as

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$$(\phi_i|\mathcal{H}|\chi_i) = C\Big\{(\rho_{i1}| -{}^1/_2\Delta + V_{\mathrm{M}}|\chi_i) + \Big(\rho_{i1}\Big|\sum_{j=2} V_j\Big|\chi_i\Big) + (\rho_{i1}|V_1|\chi_i)\Big\} \quad (11)$$

For computational reasons, the foregoing expression is a convenient form for the matrix element. However, since the Hamiltonian is Hermetian, it is also possible to write the off-diagonal term as

$$(\chi_i|\mathcal{H}|\phi_i) = C\Big\{(\chi_i| -{}^1/_2\Delta + V_1|\rho_{i1}) + \Big(\chi_i\Big|\sum_{j=2} V_j\Big|\rho_{i1}\Big) + (\chi_i|V_{\mathrm{M}}|\rho_{i1})\Big\} \quad (12)$$

If one makes the reasonable approximation that χ_i is an eigenfunction of $-{}^1/_2\Delta + V_{\mathrm{M}}$ and correspondingly ρ_{i1} is an eigenfunction of $-{}^1/_2\Delta + V_1$, then the first term in $(\phi_i|\mathcal{H}|\chi_i)$ and $(\chi_i|\mathcal{H}|\phi_i)$ becomes $\epsilon_{\chi_i}S(\rho_{i1},\chi_i)$ and $\epsilon_{\rho_{i1}}S(\rho_{i1},\chi_i)$ respectively. By considering the off-diagonal term as $H(\phi_i,\chi_i) = {}^1/_2[(\phi_i|\mathcal{H}|\chi_i) + (\chi_i|\mathcal{H}|\phi_i)]$, one can write

$$H(\phi_i,\chi_i) = C\Big\{\frac{(\epsilon_{\chi_i} + \epsilon_{\rho_{i1}})S(\rho_{i1}\chi_i)}{2} + \Big(\rho_{i1}\Big|\sum_{j=2} V_j\Big|\chi_i\Big) + {}^1/_2[(\rho_{i1}|V_{\mathrm{M}}|X_i) + (\rho_{i1}|V_1|\chi_i)] \quad (13)$$

Note that when the first term in the brackets is multiplied by C it becomes $(\epsilon_{\chi_i} + \epsilon_{\rho_{i1}})G(\phi_i,\chi_i)/2$ which is identical with the Wolfsberg–Helmholz relationship for $F = 1.00$. This latter value, it will be recalled, was employed by Oleari, *et al.*[4] Thus, their approximation assumes the additional Coulomb terms cancel one another. Correspondingly, as Richardson pointed out long ago,[23] the use of F factors larger than 1.00 in the off-diagonal term attempts to correct by *multiplicative* factors for the *added* potential terms. What Richardson was not in a position to do at the time was to explore the reasonableness of an approximation involving the overlap integral, $S(\rho_{i1},\chi_i)$, for evaluation of the two- and three-center electrostatic interactions. As a by-product of our recently completed calculations on chloride complexes in octahedral and tetrahedral symmetry,[25] we have reached the conclusion that estimations of the electrostatic interaction and nuclear attraction integrals involved in $H(\phi_i,\chi_i)$ cannot be systematically made from the corresponding overlap integral. Consequently, it is not surprising that off-diagonal terms which are estimated from a product function involving overlap integrals should require substantial adjustments, by variable F factors and the other cited methods, when going from one compound to the next. Furthermore, it does not seem likely that product functions involving the overlap integral only can be systematized to reliably reproduce the value of the off-diagonal matrix elements. Calculational evidence of these conclusions is given in the next section.

Calculations

Examination of eq 13 suggests that the Wolfsberg–Helmholz approximation for the off-diagonal matrix element would be adequate from one complex to another if one of two situations applied: (1) the additional terms, $(\rho_{i1}|\Sigma V_j|\chi_i)$, etc., nearly cancel one another so that the dominant term in the expression for $H(\phi_i,\chi_i)$ is $CS(\rho_{i1},\chi_i)(\epsilon_{\chi_i} + \epsilon_{\rho_{i1}})/2$; (2) the additional terms display the same variations from orbital to orbital and compound to compound as do the corresponding overlap integrals. Unfortunately, neither situation appears to hold.

The Magnitude of the Additional Terms. Consider the evaluation of the terms for $H(\phi_i,\chi_i)$ as given in eq 13. As we have previously indicated,[3] the values of ϵ_{χ_i}, $\epsilon_{\rho_{i1}}$, and $S(\rho_{i1},\chi_i)$ present no computational problems once appropriate consideration is given to the charges and configurations of the metal and ligand species. Furthermore, it is quite reasonable to approximate the three-center interactions by

$$\Big(\rho_{i1}\Big|\sum_{j=2} V_j\Big|\chi_i\Big) = -\sum_{j=2} q_j(1/r_j|\rho_{i1}\chi_i) \quad (14)$$

where q_j is the calculated charge on the ligand j as obtained from a Mulliken electron population analysis[26] and $(1/r_j|\rho_{i1}\chi_i)$ is a three-center nuclear attraction integral. The two remaining terms, $(\rho_{i1}|V_{\mathrm{M}}|\chi_i)$ and $(\rho_{i1}|V_1|\chi_i)$, require special consideration. In terms of our previous techniques,[3] the explicit forms of these terms are

$$(\rho_{i1}|V_1|\chi_i) = \sum_k \bar{b}_{k1}\{2(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i) - (\rho_{k1}\rho_{i1}|\rho_{k1}\chi_i)\} - Z_1(1/r_1|\rho_{i1}\chi_i) \quad (15)$$

$$(\rho_{i1}|V_{\mathrm{M}}|\chi_i) = \sum_k \bar{a}_{k\mathrm{M}}\{2(\chi_k\chi_k|\rho_{i1}\chi_i) - (\chi_k\rho_{i1}|\chi_k\chi_i)\} - Z_{\mathrm{M}}(1/r_{\mathrm{M}}|\rho_{i1}\chi_i) \quad (16)$$

where

$$(\psi_a\psi_b|\psi_c\psi_d) = \int \psi_a^*(1)\psi_b(1)1/r_{12}\psi_c^*(2)\psi_d(2)\,\mathrm{d}\tau$$

$$(1/r_{\mathrm{M}}|\psi_a\psi_b) = \int \psi_a^*(1)1/r_{\mathrm{M}}\psi_b(1)\,\mathrm{d}\tau$$

$\bar{a}_{k\mathrm{M}}$ and $\bar{b}_{k1}$ are the fractions of the electron in the kth occupied orbital on the metal and ligand 1, respectively, as determined from the electron population analysis. For simplicity it is assumed that all inner-shell electrons, for example, those below the 3d in the metal and below the 3s on a chlorine ligand, can be incorporated into Z_{M} and Z_1 which then represent the core potentials rather than the nuclear charges. Even with this simplification the number of different two-center electrostatic interaction integrals associated with eq 16 becomes quite large when χ_k includes the 3d, 4s, 4p, and 4d metal wave functions with two or more Slater functions for each of the radial terms. The routine evaluation of all these integrals is computationally time consuming and expensive, particularly when one considers the many off-diagonal terms involved in $|\rho_{i1}\chi_i)$. It is for this reason that for routine calculations we have chosen to evaluate $H(\phi_i,\chi_i)$ by eq 11, since the evaluation of $(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i)$ in $(\rho_{i1}\cdot|V_1|\chi_i)$ need be summed only over $k = n$s and np.

In the course of some recently completed computations,[25] we had an opportunity to investigate the off-diagonal term represented by eq 13 within the framework of our computational technique. If one makes the assumption[23] that the 3d orbitals are the only outer metal orbitals sufficiently contracted to result in a meaningful transfer of electron density to the metal and hence one can limit the electron population analysis to these orbitals, then $(\rho_{i1}|V_{\mathrm{M}}|\chi_i)$ becomes more computationally tractable. We have examined this and the other terms

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(26) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

of the off-diagonal element for $H(3d\sigma,3p\sigma_1)$ and $H(3d\pi,3p\pi_1)$ in $FeCl_6^{-3}$ at a self-consistent charge on the metal of +1.75. Within the framework of the Slater average of configuration approximations the calculated values for the various terms are summarized in Table I.

Table I. Terms in $(3p\sigma_1|\mathcal{H}|3d\sigma)$ and $(3p\pi_1|\mathcal{H}|3d\pi)$ of $FeCl_6^{-3}$

	$(3p\sigma_1,3d\sigma)$	$(3p\pi_1,3d\pi)$
$S(\rho_{i1},\chi_i)$	0.074	0.044
3d orbital energy, ev	−28.49	−28.49
3p orbital energy, ev	−6.86	−6.86
$(\rho_{i1}\|\sum_{j=2} V_j\|\chi_i)$, ev	+1.40	+0.89
$(\rho_{i1}\|V_M\|\chi_i)$, ev	−3.07	−1.42
$(\rho_{i1}\|V_1\|\chi_i)$, ev	−1.30	−0.42
$H(\rho_{i1}, \chi_i)$, eq 13, ev	−2.09	−0.81
$H(\rho_{i1}, \chi_i)$, eq 11, ev	−2.01	−0.77
$S(\epsilon_{3d} + \epsilon_{3p})/2$	−1.31	−0.78
F	1.60 (1.54)[a]	1.04 (0.99)[a]

[a] The F value in parentheses is that required to obtain agreement between $FS(\epsilon_{3d} + \epsilon_{3p})/2$ and $H(\rho_{i1},\chi_i)$ obtained from eq 11. The F value not in parentheses is needed to duplicate $H(\rho_{i1},\chi_i)$ by eq 13.

First of all, one notes that there is very good agreement between the values of $H(\rho_{i1},\chi_i)$ determined by eq 11 and 13. When one considers the necessary approximations in each of these computations, such agreement is very satisfying. At the very least it indicates a substantial degree of internal consistency within the model framework. It might also be noted in passing that the addition of a constant potential to the Hamiltonian operator for the diagonal terms offers no dilemma for the off-diagonal elements as given by eq 11 or 13 since they would increase by the value $-ZG(\phi_i,\chi_i)$ as required to maintain the previously mentioned constancy of separation between the eigenvalues.

It is also apparent that the formula, $FS(\rho_{i1},\chi_i)\cdot(\epsilon_{\chi_i} + \epsilon_{\rho_{i1}})/2$ with $F = 1$, does occasionally yield a value for the off-diagonal term which is approximately correct, as in the case of $(3p\pi_1|\mathcal{H}|3d\pi)$ for $FeCl_6^{-3}$. However, the relationship is not generally applicable as indicated by the values for $(3p\sigma_1|\mathcal{H}|3d\sigma)$. In general, the additional terms in eq 13 do not cancel one another, and they have an important influence on the value of the off-diagonal term.

If one assumes that the good agreement between results from eq 11 and 13 is maintained for other off-diagonal matrix elements, and that the values obtained by these equations are good estimates of the matrix elements, it is a simple task to examine the trends in F values necessary to obtain agreement between $FS\cdot(\epsilon_{\chi_i} + \epsilon_{\rho_{i1}})/2$ and the values from eq 11. The F values for the two complexes, $FeCl_6^{-3}$ and $FeCl_4^-$, are summarized in Table II. The wide variations in the values for F within and/or between the two complexes strikingly illustrates the futility of attempting to achieve identity between the sets of off-diagonal terms by means of one or two fixed values of F. It is obvious that the variations in the off-diagonal terms cannot be systematically related to the changes in overlap only.

Table II. F Values for $FS(\epsilon_{\chi_i} + \epsilon_{\rho_{i1}})/2 = (\rho_{i1}|\mathcal{H}|\chi_i)$

	$FeCl_6^{-3}$ (4.50 au)[a]	$FeCl_4^-$ (4.14 au)[a]
$(3d\sigma,3s)$	1.28	1.70
$(3d\sigma,3p\sigma)$	1.53	2.18
$(3d\pi,3p\pi)$	0.99	1.60
$(4s,3s)$	1.32	1.73
$(4s,3p\sigma)$	0.86	1.57
$(4p\sigma,3s)$	1.36	1.81
$(4p\sigma,3p\sigma)$	0.87	2.69
$(4p\pi,3p\pi)$	0.62	1.41
$(4d\sigma,3s)$	1.45	2.06
$(4d\sigma,3p\sigma)$	2.75	4.49
$(4d\pi,3p\pi)$	0.22	1.58

[a] Internuclear distance between the metal and chlorine atoms.

Variations of the Terms from Complex to Complex. There is additional evidence that one cannot expect a simple correlation of overlap with the corresponding off-diagonal element. This is exemplified by examination of the trends in the term $(\rho_{i1}|V_1|\chi_1)$, whose explicit form is given in eq 15. For simplicity of discussion, it is convenient to examine eq 15 in the ionic limit, that is, $\bar{b}_{k1} = 1$ for k = 3s and 3p. In this case, the two-center electrostatic interaction integrals then become

$$\sum_{k=3s,3p} 2(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i) - (\rho_{k1}\rho_{i1}|\rho_{k1}\chi_i)$$

In our previous paper[3] we suggested that this summation might be approximated by the relationship, $7R\cdot(1/r_1|\rho_{i1}\chi_i)$, where $(1/r_1|\rho_{i1}\chi_i)$ is the two-center nuclear attraction integral, the value of 7 accounts for the summation over the s and p orbitals, and R is a constant which depends upon ρ_{i1} and χ_i. We have now obtained some substantiation that the assumption implicit in our previous work has validity, namely, that the value of R for a given off-diagonal term is essentially invariant to changes in metal wave function, ligand wave function, and internuclear distance. To test this relationship, we carried out computations of the two-center interactions[27] for three chloride and two fluoride complexes involving octahedral and tetrahedral symmetry with internuclear distances ranging from 1.93 to 2.38 A. The values of R for the metal 3d interactions with the ligand ns and np orbitals were then computed from the equation

$$7R(1/r_1|\rho_{i1}\chi_i) = \sum_{k=3s,3p} 2(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i) - (\rho_{k1}\rho_{i1}|\rho_{k1}\chi_i) \tag{17}$$

The R values corresponding to a given ρ_{i1} and χ_i are given in the first part of Table III. Two conclusions can be drawn: (1) each set (ρ_{i1},χ_i) has its appropriate value of R; (2) the variations of R values with changing ligands, metals, symmetries, and distances are within

Table III. R and f Values as a Function of the Complex

	$TiCl_4$ (2.18 A)	$CrCl_6^{-3}$ (2.34 A)	$FeCl_6^{-3}$ (2.38 A)	CrF_6^{-3} (1.93 A)	NiF_3^- (2.01 A)
$R(3d\sigma,n s)$	0.78	0.76	0.77	0.76	0.79
$R(3d\sigma,n p\sigma)$	0.84	0.83	0.84	0.83	0.86
$R(3d\pi,n p\pi)$	0.88	0.88	0.90	0.88	0.90
$f(3d\sigma,n s)$	0.43	0.39	0.38	0.61	0.56
$f(3d\sigma,n p\sigma)$	0.46	0.44	0.42	0.60	0.55
$f(3d\pi,n p\pi)$	0.36	0.34	0.33	0.45	0.42

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(27) The two-center electrostatic interaction program adapted to the Control Data Corp. computers was kindly supplied to us by Professor F. A. Matson, Molecular Physics Group, University of Texas, Austin, Tex.

4% of one another. This latter conclusion suggests that changes in electrostatic interactions of the type given by the right-hand side of eq 17 result in a similar change in the corresponding nuclear attraction integral. Having once determined the appropriate R values by exact calculation of the electrostatic interactions for one complex, one may use the same R values for related species with reasonable confidence. That this same relation does not hold true for the overlap integrals is indicated by the values of f in Table III calculated from the relationship

$$7fS(\rho_{i1},\chi_i) = \sum_{k\,=\,3s,3p} 2(\rho_{k1}\rho_{k1}|\rho_{i1}\chi_i) - (\rho_{k1}\rho_{i1}|\rho_{k1}\chi_i)$$

As indicated by the f values, the range of values within the chlorides is of the order of 10% and changing from chloride to fluoride complexes alters the f's by about 30%. Thus, it is apparent that a single f factor times the overlap integral is incapable of properly approximating this important term in the off-diagonal matrix element.

By a similar study, it is possible to show that there is no consistent relation between the overlap integral, $S(\rho_{i1},\chi_i)$, and the three-center term, $(\rho_{i1}|\sum_{j=2} V_j|\chi_i)$, in the off-diagonal element.

Summary

It seems fairly clear that the use of F factors which multiply the overlap integrals is incapable of consistent approximation of the off-diagonal matrix elements. On the contrary, there is good indication that the additional terms given by eq 11 or 13 are related to the corresponding nuclear attraction integrals. Since it has been shown that the relative positions and separations of the final energy levels are sensitive functions of the off-diagonal terms, it is not inconceivable that energy levels in systems of low symmetry, such as tetragonal or square-planar symmetry, might be incorrectly ordered in calculations in which the off-diagonal terms have been related to overlap integrals.

On the other hand, it appears that the relation given by eq 17 offers a convenient method to circumvent the time-consuming and expensive calculation of the two-center electrostatic interaction integrals.

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