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Investigations in Semiempirical Molecular Orbital Methods.
I. Theoretical Considerations of a Parameter-Free Method for Inorganic Systems

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A semiempirical MO method for coordination complexes has been derived from basic Hartree–Fock considerations which also incorporates the electrostatic effects of the environment. The model is virtually free of any arbitrary scaling parameters so long as the point-charge and Mulliken multicenter integral approximations are applied systematically to the molecular integrals involved, and a correct choice of VOIE's is incorporated into the diagonal elements of the Hamiltonian. Calculated one-electron energy levels are amenable to a "spin-pairing energy" correction, which compensates essentially for the initial neglect of multicenter exchange integrals in the Hamiltonian. The concept of an average, effective spin for each MO is introduced and shown to be an adequate representation in the LCAO-MO approximation. Finally, the importance of employing Lowdin orthogonalization in an iterative procedure to arrive at orbital populations and net atomic charges and the external electrostatic effects of the environment are shown to be an essential feature of the method.

Introduction

The formalism of semiempirical molecular orbital methods has embodied such gross oversimplifications that such methods have been branded highly unreliable and of limited practical value. However the more exacting methods, in particular the *ab initio* approaches using gaussian orbitals and the UHF-SCF (unrestricted Hartree–Fock self-consistent field) procedure, require large computer facilities and virtually unlimited computational time for all but the simplest molecules of primary inorganic interest. Thus the need for a simple but reliable MO method still exists.

Since its original formulation the semiempirical MO scheme has been subjected to various modifications. However, the major objections to the basic format have remained essentially unaltered. This point has been well taken by Dahl and Ballhausen.[1] The major objections may be itemized as follows: (a) procedure for calculating off-diagonal matrix elements and arbitrary scaling factors; (b) choice and/or dependence of VOIE (valence orbital ionization energy) on both metal and ligand orbitals; (c) arbitrary scaling or no scaling of ligand σ and π orbitals; (d) the neglect of splitting factors which differentiate the energies of metal basis orbitals which are similar but belong to different irreducible representations of the molecular point group; (e) the absence of explicit consideration for the stabilizing effects of the environment on the complex ion. Additional objections not related to these include the choice of basis functions (with or without hybridization) and the disregard of electron repulsion in the calculated MO's. All of these factors have been considered in the more sophisticated methods in one instance or another, but for the sake of simplicity and computational expedience semiempirical procedures have not been subjected to similar treatment.

The present investigation was undertaken with the aim to remove the major objections while still retaining the simplicity of a semiempirical model with minimal computational requirements. In this vein, the present paper takes a closer look into the formalism of the one-electron model and off-diagonal elements based on quantities having a sound physical basis. The work of Harris contains most of the features of the present method but in a more approximate form.[2] In this respect, the only other related published work is that of Hillier,[3] which lacks many of the features given explicit consideration here. Other related methods have either been basically computational in nature and are therefore not strictly semiempirical or have employed the simple Wolfsberg-Helmholz approximation for the off-diagonal elements.[4] In part I of this series the basic format of the model is developed, while part II is devoted to the computational results vindicating the method.

In the present paper, it will be shown how the one-electron operator approximation to the exact Hartree–Fock operator can lead to a semiempirical model which is virtually free of the major objections cited above.

For the case in point we shall consider an isolated cluster of the general formula $[\mathrm{ML}_N]^Q$, where Q is the net electronic charge on the complex, M is the central metal atom, and the L's are nonmetal ligands which in principle may be the same or different. Initially we shall not be concerned with the very important stabilizing effects of the environment but will give this explicit consideration later on.

Fundamental Hartree–Fock SCF Considerations

To arrive at an accurate solution to the molecular problem we must consider the effective molecular Hamiltonian, $\mathbf{H}_{\mathrm{eff}}{}^{\mathrm{mol}}$, associated with the solutions to the HF-SCF equations. A general expression for either open- or closed-shell systems is[5,6]

$$\mathbf{H}_{\mathrm{eff}}^{\mathrm{mol}} = \mathbf{H}^{\mathrm{core}} + {}^1/_2 \sum_j N_j \mathbf{J}_j - {}^1/_2 \mathbf{K}_j \left[\sum_j N_j(\alpha) + \sum_j N_j(\beta) \right] \quad (1)$$

where N_j is the occupation number of the jth molecular orbital, Ψ_j ($N_j = 2$ or 1 for doubly or singly occupied MO's, respectively, and 0 otherwise), α and β are the spin labels of the electrons, $\mathbf{J}_j$ and $\mathbf{K}_j$ are the respective two-electron Coulomb and exchange operators, and $\mathbf{H}^{\mathrm{core}}$ includes the kinetic energy operator (${}^1/_2 \nabla_i{}^2$) and all interactions of the valence electrons with the atomic cores.

Ideally the molecular orbitals should satisfy the Hartree–Fock equations

$$\mathbf{H}_{\mathrm{eff}}^{\mathrm{mol}} \Psi_j = \mathbf{E}_j \Psi_j \quad (2)$$

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(1) J. P. Dahl and C. J. Ballhausen, *Advan. Quantum Chem.*, 4, 170 (1968).

(2) L. E. Harris, Doctoral Dissertation, Louisiana State University in New Orleans, New Orleans, La., 1969.

(3) I. H. Hillier, *J. Chem. Soc. A*, 878 (1969).

(4) N. J. Trappeniers, G. DeBrouckere, and C. A. Ten Seldam, *Chem. Phys. Lett.*, 8, 327 (1971).

(5) P. O'D. Offenhartz, "Atomic and Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(6) F. L. M. A. H. De Laat, Doctoral Thesis, Eindhoven, The Netherlands, 1968.

In the LCAO approximation, the Ψ_j have the form

$$\Psi_j = \sum_N C_{Nj} \chi_N \tag{3}$$

where χ_N are the basis atomic orbitals for the valence electrons of the N atoms in the complex, and C_{Nj} are the orbital coefficients.

If we divide the N atoms of the complex ion into metal, M, and ligand, L, atoms respectively, where the index m is over the orbitals χ_N itself, and the indices l run through the orbitals centered on any ligand atom, then the variational principle provides the eigenvalues of (2) through the secular determinant

$$|\mathbf{H}_{mN,lN'} - \mathbf{S}_{mN,lN'}\mathbf{E}| = 0 \tag{4}$$

where $\mathbf{S}_{mN,lN'}$ forms the overlap matrix and $\mathbf{H}_{mN,lN'}$ the energy matrix with respect to all orbitals m and l centered on atoms N and N', including all cases for which $N = N'$ and $N \neq N'$. Systematic application of well-grounded approximations[7] reduces all integrals to one- and two-center types for the matrix elements which have the form

$$\mathbf{H}_{mN,lN'} = \langle \chi_{mN} | -{}^1\!/_2 \mathbf{T}_{N_i}{}^2 + \mathbf{V}_N | \chi_{lN'} \rangle + \\ \langle \chi_{mN} | -{}^1\!/_2 \mathbf{T}_{N'_i}{}^2 + \mathbf{V}_N | \chi_{lN'} \rangle + \langle \chi_{mN} | \sum_{k \neq N,N'} \mathbf{V}_k | \chi_{lN'} \rangle \tag{5}$$

where

$$\mathbf{V}_N = \sum_m P_m{}^N [\mathbf{J}_{Nm} - {}^1\!/_2 \mathbf{K}_{Nm}] - Z_{N/r}$$

$$\mathbf{V}_{N'} = \sum_l P_l{}^{N'} [\mathbf{J}_{N'l} - {}^1\!/_2 \mathbf{K}_{N'l}] - Z_{N'/r}$$

with the P factors equal to the net effective populations in each MO, $\mathbf{T}_N$ and $\mathbf{T}_{N'}$ are kinetic energy operators, and $\mathbf{V}_k = -q_{k/r_k}$, where $-q_k$ is the net charge on atom k obtained from a population analysis. Thus the last term in (5) provides for the ligand field splitting of degenerate orbitals relative to the point group symmetry at the kth atom.

Modified Method of Calculation

On invoking the following approximations to the terms in eq 5 simplification results through systematic application of the following formalism: (a) The one-electron operator approximation to the exact Hartree–Fock operator is employed. (b) Only one-electron integrals are considered. Two-electron integrals between valence electrons in the molecular framework are not treated explicitly. These, however, are compensated for in a "spin pairing energy" correction to the calculated one-electron MO's, which is described in detail in section 5. (c) All parts of the Hamiltonian which are identifiable with the atomic cores are set equal to the orbital ionization energy with restricted charge dependence. (See Appendix II.) (d) All multicenter integrals are simplified using the Mulliken approximation.[8] (e) Only overlap integrals are calculated exactly; all other integrals which are not accounted for in (c) are evaluated on the basis of the point-charge approximation. (See Appendix I.) (f) Lowdin orthogonalization is employed in the final analysis to arrive at populations.[9] (g) Explicit consideration is given to an external potential for stabilizing the complex ion.

1. **The Hamiltonian.** The complete, effective Hamiltonian operator for the $[\mathrm{ML}_n]^Q$ complex ion, $\mathbf{H}_{\mathrm{eff}}{}^{\mathrm{com}}$, may be broken up into components

$$\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}} = \mathbf{H}_{\mathrm{T}} + \mathbf{H}_{\mathrm{V_M}} + \mathbf{H}_{\mathrm{V_L}} + \mathbf{H}_{\mathrm{G}} + \mathbf{H}_{\mathrm{ex}} \tag{6}$$

$\mathbf{H}_{\mathrm{T}}$ is the kinetic energy operator, $-{}^1\!/_2 \nabla_i{}^2$. $\mathbf{H}_{\mathrm{V_M}}$ is the potential energy operator due to the metal charge center; as a crude approximation, $\mathbf{V}_{\mathrm{M}} = -q_{\mathrm{M}}/r_k$, where r_k refers to an electron having its origin of coordinates at any center, k, including the case $k = \mathrm{M}$. $\mathbf{H}_{\mathrm{V_L}}$ is the potential energy operator due to ligand charge centers. There are as many such charge centers as there are ligands.

$$\sum_{j=1}^{n} \mathbf{V}_j = \sum_{j=1}^{n} \frac{(-q_{\mathrm{L}})_j}{r_k}$$

$\mathbf{H}_{\mathrm{G}}$ is the geometric potential energy operator. This results because of the approximations to $\mathbf{H}_{\mathrm{V_M}}$ and $\mathbf{H}_{\mathrm{V_L}}$ and is identifiable with "ligand field splitting" which differentiates the energies of similar AO's in different MO irreducible representations. Thus it also compensates for the difference in energies of σ and π orbitals on the ligands.

$$\mathbf{V}_{\mathrm{G}} = \sum_k (q_{\mathrm{L}}/r)_k + \sum_k (q_{\mathrm{M}}/r)_k$$

where $(1/r)_k$ are expanded in terms of associated Legendre polynomials using the spherical harmonics. The $\mathbf{Y}_0{}^0$ harmonics are excluded since these have already been considered in the $\mathbf{H}_{\mathrm{V_M}}$ and $\mathbf{H}_{\mathrm{V_L}}$ operators. Matrix elements derived from this operator are hereafter referred to as "splitting parameters" (SP). $\mathbf{H}_{\mathrm{ex}}$ is the potential energy operator due to the external environment. This accounts for stabilizing the entire complex ion by neutralizing the net charge Q. Thus it vanishes when $Q = 0$. In order that this be independent of the unique geometric positions of counteracting ions in the crystalline or solution lattice, the charge centers are symmetrically and equally distributed at each ligand site.

$$\sum_{j=1}^{n} (\mathbf{V}_{\mathrm{ex}})_j = \frac{-(-Q/n)}{R_{\mathrm{ML}}}$$

where R_{ML} is the internuclear metal–ligand bond distance, and $-Q$ is the total external charge. (See Discussion.)

2. **The Diagonal Element Approximation.** In the LCAO approximation, the molecular orbitals of a complex ion having the general formula $[\mathrm{ML}_N]^Q$ may be written as

$$\Psi_i = a_i \chi_i + b_i \phi_i \tag{7}$$

where χ_i is a metal orbital and ϕ_i is a set of symmetry-adapted orbitals having the general form $\phi_i = \Sigma_j C_{ij} v_j$, where v_j are ligand AO functions.

The diagonal matrix elements of the Hamiltonian consist of both metal ($\mathbf{H}^{\mathrm{M}}{}_{ii}$) and ligand ($\mathbf{H}^{\mathrm{L}}{}_{jj}$) components respectively.

A. **Metal Diagonal Elements.** If we consider the one-electron operator approximation in the form of eq 6, the diagonal elements of the metal are

$$\mathbf{H}^{\mathrm{M}}{}_{ii} = \langle \chi_i | \mathbf{H}_{\mathrm{eff}}^{\mathrm{com}} | \chi_i \rangle = \langle \chi_i | -{}^1\!/_2 \nabla_i{}^2 + \mathbf{V}_{\mathrm{M}} | \chi_i \rangle + \\ \langle \chi_i | \sum_{j=i}^{n} \mathbf{V}_j | \chi_i \rangle + \langle \chi_i | \mathbf{V}_{\mathrm{G}} | \chi_i \rangle + \langle \chi_i | \mathbf{V}_{\mathrm{ex}} | \chi_i \rangle \tag{8}$$

Since χ_i is assumed to be an approximate eigenfunction of $|-{}^1\!/_2 \nabla_i{}^2 + \mathbf{V}_{\mathrm{M}}|$, we may set the first term in (8) equal to ϵ_i, the orbital ionization energy of the electron in χ_i. However, in an iterative procedure to achieve self-consistent charge and orbital configuration (SCCC) the values of ϵ_i will vary as a function of the metal charges, q_{M}. Thus, some procedure must be adopted to arrive at this charge dependence. (See Appendix II.)

The second term in (8) represents integrals of electrostatic charge potential between an electron in a metal orbital and

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[7] (a) K. Ruedenberg, *J. Chem. Phys.*, 19, 1433 (1951); (b) M. Geoppert-Moyer and A. L. Sklar, *ibid.*, 6, 645 (1938).

[8] R. S. Mulliken, *J. Chim. Phys. Physicochim. Biol.*, 46, 675 (1949).

[9] P. O. Lowdin, *J. Chem. Phys.*, 18, 365 (1950).

the j ligands. These neighbor atom potential terms are called Madelung terms by Jorgensen, *et al.*,[10] since they reflect Madelung type electrostatic interactions as encountered in the ionic crystal model.

To a good degree of accuracy[11,12] it is possible to write $\mathbf{V}_j \simeq -(q_\mathrm{L})_j/r_j$, where q_L is the effective charge on the jth ligand and r is its radius vector to the metal orbital charge distribution, $\chi_i{}^*\chi_i$. Substituting this expression into the second term in (8) and using a point-charge approximation for the integrals $\langle 1/r|\chi_i\chi_i\rangle$ yield the result

$$\langle\chi_i|\sum_{j=1}^{n}\mathbf{V}_j|\chi_i\rangle \simeq -nq_\mathrm{L}/R_\mathrm{ML} \tag{9}$$

where R_ML is the metal–ligand bond distance. We shall return to the consequences of this point-charge approximation later.

The third term in (8) has the form

$$\langle\chi_i|\sum_{j=1}^{n}(q_\mathrm{L})_j\sum_{n'=0}^{\infty}\sum_{m=m'}^{n'}\left(\frac{4\pi}{2n'+1}\right)\left(\frac{r^{n'}}{R^{n'+1}}\right)\times$$
$$\mathbf{Y}_{n'j}{}^{m}\mathbf{Y}_{n'i}{}^{m*}|\chi_i\rangle \tag{10}$$

For d orbitals in regular octahedral and tetrahedral complexes, only the $\mathbf{Y}_4{}^0$, $\mathbf{Y}_4{}^4$, and $\mathbf{Y}_4{}^{-4}$ harmonics need be considered. Thus for octahedral complexes, for example, (10) has the explicit form

$$\sum_{j=1}^{n}(q_\mathrm{L})_j\left(\frac{4\pi}{9}\right)\frac{\langle r_\mathrm{d}{}^4\rangle}{R_\mathrm{ML}{}^5}\langle\chi_i|[\mathbf{Y}_4{}^0 + (5/14)^{1/2}(\mathbf{Y}_4{}^4 +$$
$$\mathbf{Y}_4{}^{-4})][\mathbf{Y}_4{}^{0*} + (5/14)^{1/2}(\mathbf{Y}_4{}^{4*} + \mathbf{Y}_4{}^{-4*})]|\chi_i\rangle =$$
$$(q_\mathrm{L})_j\frac{\langle r_\mathrm{d}{}^4\rangle}{6R_\mathrm{ML}{}^5}F_\mathrm{M} \tag{11}$$

where F_M are the integration factors pertinent to the symmetry of the ligand field.

The last term in (8) has the general form, $nq_\mathrm{ex}/R_\mathrm{ML}$ where the net external potential, $-Q$, for convenience, is distributed equally to give a net charge of q_ex at each of the n ligands. Thus $q_\mathrm{ex} = -Q/n$.

Finally the metal diagonal elements become

$$\mathbf{H^M}_{ii} = \epsilon_i(q_\mathrm{M})_i - n(q_\mathrm{L} +$$
$$q_\mathrm{ex})\left(\frac{1}{R_\mathrm{ML}}\right) + q'_\mathrm{L}\frac{\langle r_\mathrm{d}{}^4\rangle}{6R_\mathrm{ML}{}^5}F_\mathrm{M} \tag{12}$$

As stated above, the external potential is equally distributed over each of the n ligands; thus in the last term $q'_\mathrm{L} = q_\mathrm{L} + q_\mathrm{ex}$. In cases of dissimilar L ligands the adequacy of this procedure would have to be reconsidered.

B. Ligand Diagonal Elements. From eq 7 the ligand diagonal elements may be expressed as

$$\mathbf{H^L}_{jj} = \langle\phi_j|\mathbf{H}_\mathrm{eff}^\mathrm{com}|\phi_j\rangle = \sum_j C_{ij}{}^2\langle v_j|\mathbf{H}_\mathrm{eff}^\mathrm{com}|v_j\rangle +$$
$$\sum_{j\neq k}\sum C_{ij}C_{ik}\langle v_j|\mathbf{H}_\mathrm{eff}^\mathrm{com}|v_k\rangle \tag{13}$$

The normalizing condition requires that

$$\mathbf{H^L}_{jj} = N_i{}^2\langle\phi_j|\mathbf{H}_\mathrm{eff}^\mathrm{com}|\phi_j\rangle$$

whence from eq 13 it follows that

$$N_i{}^2 = \frac{1}{1 + (\mathrm{IF})_\mathrm{C} + (\mathrm{IF})_\mathrm{T}} \tag{14}$$

where N_i is the normalizing constant, and $(\mathrm{IF})_\mathrm{C}$ and $(\mathrm{IF})_\mathrm{T}$ are integration factors for cis and trans ligands, respectively, dependent upon the particular molecular geometry and irreducible representation.

Proceeding as before from eq 6, we may expand the first term of (13) as

$$\langle v_j|\mathbf{H}_\mathrm{eff}^\mathrm{com}|v_j\rangle = \langle v_j| -{}^1\!/_2\nabla_i{}^2 + \mathbf{V}_j|v_j\rangle + \langle v_j|\mathbf{V}_\mathrm{M}|v_j\rangle +$$
$$\langle v_j|\sum_{j'=2}^{n}\mathbf{V}_{j'}|v_j\rangle + \langle v_j|\mathbf{V}_\mathrm{G}|v_j\rangle + \langle v_j|\mathbf{V}_\mathrm{ex}|v_j\rangle \tag{15}$$

where the numerical coefficients, $C_{ij}{}^2$, have been omitted for clarity. The first term in eq 15 may be set equal to $\epsilon_j(q_\mathrm{L})_j$, the orbital ionization energy of the electron in v_j with restricted charge dependence, as was done previously. The second and third terms have the respective forms

$$-q_\mathrm{M}/R_\mathrm{ML}$$
$$-q_\mathrm{L}(n-2)/(R_\mathrm{LL})_\mathrm{C} - q_\mathrm{L}/(R_\mathrm{LL})_\mathrm{T} \tag{16}$$

where $(R_\mathrm{LL})_\mathrm{C}$ and $(R_\mathrm{LL})_\mathrm{T}$ are the ligand–ligand internuclear distances of cis and trans ligands, respectively.

The fourth term is handled in the manner analogous to what has already been done in section 2A, except the spherical harmonics are all referred to a single coordination site of linear geometry ($C_{\infty v}$).

The last term has the form

$$-(q_\mathrm{ex})\left[\frac{n-2}{(R_\mathrm{LL})_\mathrm{C}} + \frac{1}{(R_\mathrm{LL})_\mathrm{T}}\right] \tag{17}$$

Returning to eq 13 and again omitting the $C_{ij}C_{ik}$ coefficients, the matrix elements of the second term are

$$\langle v_j|\mathbf{H}_\mathrm{eff}^\mathrm{com}|v_k\rangle = \langle v_j| -{}^1\!/_2\nabla_i{}^2 + \mathbf{V}_j|v_k\rangle + \langle v_j|\sum_{k'\neq j}\mathbf{V}_{k'}|v_k\rangle +$$
$$\langle v_j|\mathbf{V}_\mathrm{M}|v_k\rangle + \langle v_j|\mathbf{V}_\mathrm{G}|v_k\rangle + \langle v_j|\mathbf{V}_\mathrm{ex}|v_k\rangle \tag{18}$$

The first term of (18) may be set equal to $\epsilon_{v1}(q_\mathrm{L})_1\langle v_j|v_k\rangle$, where $\langle v_j|v_k\rangle$ is the ligand–ligand overlap. The last three terms are the same as the analogous ones of eq 15 and have the forms given in (16) and (17). However, the second term of (18) is dependent on the coordinates of each ligand and has the form

$$\langle v_j|\sum_{k'\neq j}\mathbf{V}_{k'}|v_k\rangle = -q_\mathrm{L}\left\{(\mathrm{IF})_\mathrm{C}\left[\frac{n-2}{(R_\mathrm{LL})_\mathrm{C}} + 1/(R_\mathrm{LL})_\mathrm{T} +\right.\right.$$
$$\left.{}^1\!/_2\langle 1/r_\mathrm{p}\rangle(-{}^1\!/_2(R_\mathrm{LL})_\mathrm{C})\right] - (\mathrm{IF})_\mathrm{T}\left[\frac{n-2}{(R_\mathrm{LL})_\mathrm{C}} +\right.$$
$$\left.\left.1/(R_\mathrm{LL})_\mathrm{T} + {}^1\!/_2\langle 1/r_\mathrm{p}\rangle(-{}^1\!/_2(R_\mathrm{LL})_\mathrm{T})\right]\right\} =$$
$$-q_\mathrm{L}\left\{\frac{n-2}{(R_\mathrm{LL})_\mathrm{C}} + 1/(R_\mathrm{LL})_\mathrm{T} + {}^1\!/_2\langle 1/r_\mathrm{p}\rangle -\right.$$
$$\left.(\mathrm{IF})_\mathrm{C}/2(R_\mathrm{LL})_\mathrm{C} - (\mathrm{IF})_\mathrm{T}/2(R_\mathrm{LL})_\mathrm{T}\right\} \tag{19}$$

where $\langle 1/r_\mathrm{p}\rangle$ is the expectation value for the ligand p orbital, and the values of $(\mathrm{IF})_\mathrm{C}$ and $(\mathrm{IF})_\mathrm{T}$ are different for different irreducible representations. In tetrahedral cases, for example, $(R_\mathrm{LL})_\mathrm{C} = (R_\mathrm{LL})_\mathrm{T}$ and $(\mathrm{IF})_\mathrm{C} = (\mathrm{IF})_\mathrm{T} = 1$.

Since

$$N_i{}^2[\sum_j C_{ij}{}^2 + (\mathrm{IF})_\mathrm{C} + (\mathrm{IF})_\mathrm{T}] = 1$$

the final form of (19) is

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[10] C. K. Jorgensen, S. M. Horner, W. E. Hatfield, and S. Y. Tyree, *Int. J. Quantum Chem.*, 1, 191 (1967).

[11] D. D. Radtke and R. F. Fenske, *J. Amer. Chem. Soc.*, **89**, 2292 (1967).

[12] R. F. Fenske, K. G. Coulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, 5, 951, 960 (1966).

$$\mathbf{H}^{\mathrm{L}}{}_{jj} = \epsilon_j(q_{\mathrm{L}})_j - q_{\mathrm{M}}/R_{\mathrm{ML}} - [q_{\mathrm{L}} + q_{\mathrm{ex}}]\left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right] - \frac{q_{\mathrm{M}}\langle r_{\mathrm{p}}{}^2\rangle}{5(R_{\mathrm{ML}})^3} - (q'_{\mathrm{L}})(F_{\mathrm{L}})\langle r_{\mathrm{p}}{}^2\rangle/5 \times \left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right] + \frac{(q'_{\mathrm{L}})(N_i^2)}{2}\left\{(\mathrm{IF})_{\mathrm{C}} \times \left[1/(R_{\mathrm{LL}})_{\mathrm{C}} - \langle\frac{1}{r_{\mathrm{p}}}\rangle\right]\right\} + (\mathrm{IF})_{\mathrm{T}}\left[1/(R_{\mathrm{LL}})_{\mathrm{T}} - \langle\frac{1}{r_{\mathrm{p}}}\rangle\right] \quad (20)$$

where q'_{L} is a consequence of the external potential, as stated earlier.

3. The Off-Diagonal Element Approximation. It follows from the form of the molecular Hamiltonian that the off-diagonal elements are of two types, namely, metal–ligand, $\mathbf{H}^{\mathrm{ML}}{}_{ij}$, and ligand–ligand, $\mathbf{H}^{\mathrm{LL}}{}_{ij}$.

A. Metal–Ligand Off-Diagonal Elements.

$$\mathbf{H}^{\mathrm{ML}}{}_{ij} = \mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}(\phi_i, \chi_i) = {}^1/_2[\langle\phi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\chi_i\rangle + \langle\chi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_i\rangle] \quad (21)$$

where $\langle\phi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\chi_i\rangle = \langle v_{ii}|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\chi_1\rangle$ and $X_{ij} = G(\phi_i, \chi_i)/S(v_{i1}, \chi_i)$ is the geometric factor which relates the group overlap, G, for the LCAO symmetry-adapted orbitals to the two-center overlap, S, between the AO's. Expanding further

$$\langle\phi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\chi_i\rangle = \mathbf{X}_{ij}\langle v_{i1}|-{}^1/_2\nabla_i^2 + \mathbf{V}|\chi_i\rangle + \langle v_{i1}|\sum_{j=2}^{n}\mathbf{V}_j|\chi_i\rangle + \langle v_{i1}|\mathbf{V}_1|\chi_i\rangle + \langle v_{i1}|\mathbf{V}_{\mathrm{G}}|\chi_i\rangle + \langle v_{i1}|\mathbf{V}_{\mathrm{ex}}|\chi_i\rangle \quad (22a)$$

$$\langle\chi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_i\rangle = \mathbf{X}_{ij}[\langle\chi_i|-{}^1/_2\nabla_i^2 + \mathbf{V}_1|v_{i1}\rangle + \langle\chi_i|\sum_{j=2}^{n}\mathbf{V}_j|v_{i1}\rangle + \langle\chi_i|\mathbf{V}_{\mathrm{M}}|v_{i1}\rangle + \langle\chi_i|\mathbf{V}_{\mathrm{G}}|v_{i1}\rangle + \langle\chi_i|\mathbf{V}_{\mathrm{ex}}|v_{i1}\rangle] \quad (22b)$$

On recognizing that in the first term in (22a) and (22b) χ_i and v_{i1} are assumed to be eigenfunctions of $|-{}^1/_2\nabla_1{}^2 + \mathbf{V}_{\mathrm{M}}|$ and $|-{}^1/_2\nabla_1{}^2 + \mathbf{V}_1|$, respectively, we may invoke the orbital ionization energy approximation for these terms. Subsequently the expression for the off-diagonal elements according to (21) becomes

$$\mathbf{H}^{\mathrm{ML}}{}_{ij} = \mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}(\phi_i, \chi_i) = {}^1/_2\mathbf{G}^{\mathrm{ML}}{}_{ij}[\epsilon_i(q_{\mathrm{M}})_i + \epsilon_j(q_{\mathrm{L}})_j + 2\langle v_{i1}|\sum_{j=2}^{n}V_j|\chi_i\rangle + \langle v_{i1}|\mathbf{V}_1|\chi_1\rangle + \langle\chi_i|\mathbf{V}_{\mathrm{M}}|v_{i1}\rangle + 2\langle v_{i1}|\mathbf{V}_{\mathrm{G}}|\chi_i\rangle + 2\langle v_{i1}|\mathbf{V}_{\mathrm{ex}}|\chi_i\rangle] \quad (23)$$

where $G^{\mathrm{ML}}{}_{ij}$ is the group overlap between metal and ligands. The third and fourth terms in (23) are two-center terms while the remaining terms are three center. Applying the point-charge and Mulliken multicenter integral approximations to these terms reduces them as

$$\langle v_{i1}|\sum_{j=2}^{n}\mathbf{V}_j|\chi_i\rangle = -\frac{q_{\mathrm{L}}}{2}S(v_{i1}, \chi_i)\left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + \frac{1}{(R_{\mathrm{LL}})_{\mathrm{T}}} + \frac{n-1}{(R_{\mathrm{ML}})}\right] \quad (24a)$$

$$\langle v_{i1}|\mathbf{V}_1|\chi_i\rangle = -\frac{q_{\mathrm{L}}}{2}S(v_{i1}, \chi_i)\left[\langle\frac{1}{r_{i1}}\rangle_{\mathrm{L}} + 1/R_{\mathrm{ML}}\right] \quad (24b)$$

$$\langle\chi_i|\mathbf{V}_{\mathrm{M}}|v_{i1}\rangle = -\frac{q_{\mathrm{M}}}{2}S(\chi_i, v_{i1})\left[\langle\frac{1}{r_i}\rangle_{\mathrm{M}} + 1/R_{\mathrm{ML}}\right] \quad (24c)$$

$$\langle v_{i1}|\mathbf{V}_{\mathrm{G}}|\chi_i\rangle = {}^1/_2[\langle v_{i1}|\mathbf{V}_{\mathrm{G}}|v_{i1}\rangle + \langle\chi_i|\mathbf{V}_{\mathrm{G}}|\chi_i\rangle] \quad (24d)$$

$$\langle v_{i1}|\mathbf{V}_{\mathrm{ex}}|\chi_i\rangle = {}^1/_2[\langle v_{i1}|\mathbf{V}_{\mathrm{ex}}|v_{i1}\rangle + \langle\chi_i|\mathbf{V}_{\mathrm{ex}}|\chi_i\rangle] \quad (24e)$$

where the $\langle 1/r_{i1}\rangle_{\mathrm{L}}$ and $\langle 1/r_i\rangle_{\mathrm{M}}$ are expectation values of the appropriate orbitals at the L and M atoms, respectively, and the forms of the matrix elements in (24d) and (24e) have already been written out explicitly in eq 11, 12, 16, and 17. Substitution of these equations into (23) and recognizing the form of the diagonal elements (12) and (20) lead to the final result

$$\mathbf{H}^{\mathrm{ML}}{}_{ij} = {}^1/_2G^{\mathrm{ML}}{}_{ij}\left[\mathbf{H}^{\mathrm{M}}{}_{ii} + \mathbf{H}^{\mathrm{L}}{}_{jj} - \frac{q_{\mathrm{M}}}{2}\langle\frac{1}{r_i}\rangle_{\mathrm{M}} + q'_{\mathrm{L}}\langle\frac{1}{r_{i1}}\rangle_{\mathrm{L}} + (q_{\mathrm{M}} + q'_{\mathrm{L}})/2R_{\mathrm{ML}}\right] \quad (25)$$

where the appearance of q'_{L} is a consequence of the effect of the external potential as given previously.

B. Ligand–Ligand Off-Diagonal Elements. The ligand–ligand off-diagonal elements may be treated in the manner of eq 19 after the formalism of 21 is adopted

$$\mathbf{H}^{\mathrm{LL}}{}_{ij} = \mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}(\phi_i, \phi_j) = {}^1/_2[\langle\phi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_j\rangle + \langle\phi_j|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_i\rangle] \quad (26)$$

$$\langle\phi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_j\rangle = N_iN_j[\sum_{s}C_{is}C_{js}\langle\phi_{is}|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_{js}\rangle + \sum_{t\neq u}\sum C_{it}C_{ju}\langle\phi_{it}|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_{ju}\rangle] \quad (27)$$

The first term in (27) is zero, and hence the evaluation of the integrals for the second term follows along the same lines as that given for the second term in eq 13.

$$\langle\phi_i|\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}|\phi_j\rangle = N_iN_j\{[\sum_{t\neq u}\sum C_{it}C_{ju}S'_{\mathrm{C}} + \sum_{t'\neq u'}\sum C_{it'}C_{ju'}S'_{\mathrm{T}}] \times [\epsilon_i(q_{\mathrm{L}})_i - q_{\mathrm{M}}/R_{\mathrm{ML}} - q_{\mathrm{L}}\left(\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right) - (U_{\mathrm{L}})_i - (U^{\mathrm{L}}{}_{\mathrm{ex}})_i - {}^1/_2\langle\frac{1}{r_{\mathrm{L}}}\rangle_i]\} + q'_{\mathrm{L}}\frac{N_iN_j}{2} \times [\sum_{t\neq u}\sum C_{it}C_{ju}S'_{\mathrm{C}}/(R_{\mathrm{LL}})_{\mathrm{C}} + \sum_{t'\neq u'}\sum C_{it'}C_{ju'}S'_{\mathrm{T}}/(R_{\mathrm{LL}})_{\mathrm{T}}] \quad (28)$$

where U_{L} and $U^{\mathrm{L}}{}_{\mathrm{ex}}$ are splitting and external potential terms, respectively, and

$$N_iN_j = \frac{G_{ij}}{\sum_{t\neq u}\sum C_{it}C_{ju}S'_{\mathrm{C}} + \sum_{t'\neq u'}\sum C_{it'}C_{ju'}S'_{\mathrm{T}}}$$

Simplifying (28) by writing the whole term within the braces as $(\mathbf{H}'_{\mathrm{L}})_i$ reduces (26) to the form

$$\mathbf{H}_{\mathrm{eff}}^{\mathrm{com}}(\phi_i, \phi_i) = (G_{ij}/2)[(\mathbf{H}'_{\mathrm{L}})_i + (\mathbf{H}'_{\mathrm{L}})_j + q'_{\mathrm{L}}N_iN_j \times [\sum_{t\neq u}\sum C_{it}C_{ju}S'_{\mathrm{C}}/(R_{\mathrm{LL}})_{\mathrm{C}} + \sum_{t'\neq u'}\sum C_{it'}C_{ju'}S'_{\mathrm{T}}/(R_{\mathrm{LL}})_{\mathrm{T}}]] \quad (29)$$

4. Orbital Ionization Energies. A modified approach to evaluating orbital ionization energies as an approximation to the one-center terms in the molecular integrals is presented in detail in Appendix II.

5. "Effective Spin" Interaction in One-Electron MO's. The calculated results provide one-electron MO's in principle. However, because of the semiempiricism of the method, multielectron interactions have been accounted for at least in the one-center terms. Also the greater portion of the multicenter interactions have been reduced to weighted averages of one center terms, which are further treated in the point-charge approximation. Yet there is still some residue owing to the multicenter, two-electron interactions, which have been totally neglected so far as the exchange interactions are concerned. Thus a relatively small but important "spin-pairing" energy correction to the calculated one-electron MO's should be accounted for. It is proposed that the following "effective spin" recipe can be applied for these purposes.

Jorgensen[13] has discussed interelectronic repulsion and spin-pairing energy corrections in some detail. The mathematical basis for Jorgensen's approach has been verified independently by Slater.[14] If we wish to apply these same concepts to a molecular orbital, it must be recognized that the MO is a linear combination of atomic functions, and the eigenvectors multiply both spin and spatial parts of the AO's. Thus the spin-interaction corrections derived by Jorgensen and Slater for atomic configurations can be incorporated as follows.

We will assume a nondegenerate, one-electron LCAO-MO function composed of the atomic bases χ_1 and ϕ_2 with orbital coefficients C_1 and C_2, respectively. The effective distribution of the electron spin is $S_{\mathrm{eff}}^{(1)} = C_1^2\,|^1/_2|$ and $S_{\mathrm{eff}}^{(2)} = C_2^2\,|^1/_2|$, so that fractional components are assigned to χ_1 and ϕ_2. It is assumed that C_1 and C_2 are close to being the correct coefficients for the MO even though it is not an accurate spin orbital. The interaction between these components may be expressed according to the Hamiltonian

$$\mathbf{H}_{\mathrm{s}}{}^{\mathrm{eff}} = K_{\mathrm{s}} S_{\mathrm{eff}}^{(1)} \cdot S_{\mathrm{eff}}^{(2)} \tag{30}$$

where K_{s} is a constant of energy. The total effective spin, $\bar{S}$, may be taken as $\bar{S} = S_{\mathrm{eff}}^{(1)} + S_{\mathrm{eff}}^{(2)}$, whence

$$S_{\mathrm{eff}}^{(1)} S_{\mathrm{eff}}^{(2)} = {}^1/_2[\bar{S}^2 - (S_{\mathrm{eff}}^{(1)})^2 - S_{\mathrm{eff}}^{(2)}]$$

and the Hamiltonian becomes

$$\mathbf{H}_{\mathrm{s}}{}^{\mathrm{eff}} = \frac{K_{\mathrm{s}}}{2}[\bar{S}^2 - (S_{\mathrm{eff}}^{(1)})^2 - (S_{\mathrm{eff}}^{(2)})^2]$$

Thus the energy for this interaction is

$$E_{\mathrm{s}}{}^{\mathrm{eff}} = \frac{K_{\mathrm{s}}}{2}[\bar{S}(\bar{S}+1) - S_{\mathrm{eff}}^{(1)}(S_{\mathrm{eff}}^{(1)}+1) - S_{\mathrm{eff}}^{(2)}(S_{\mathrm{eff}}^{(2)}+1)] \tag{31}$$

The second and third terms within the brackets of eq 31 have fixed values, depending on the spins of the two electrons, while the first term may assume different values. This will give rise to different eigenvalues for any fixed set of spin-spin interactions. The average of the energies associated with all the different possible values of $\bar{S}$ should represent that amount of energy by which the calculated one-electron MO deviates from its correct eigenvalue.

In order to evaluate (31) it must be recognized that the constant term K_{s} includes both the electron repulsion parameter and the spin-pairing energy parameter as defined by Jorgensen.[15] This is in addition to the bulk of the repulsion already accounted for on the basis of selecting the various diagonal matrix elements for the calculation of the MO's. In fact, it is reasonable to write the parameter as $D^{\mathrm{eff}} = \Sigma_i C_i^2 D_i$, where D^{eff} is the effective parameter for the MO's and D_i is the analogous quantity for the ith AO in the MO. The latter parameters have been given by Jorgensen for various atomic configurations.[15] Also if an average value of $\bar{S}$ is found by calculating $\langle\bar{S}(\bar{S}+1)\rangle$ then eq 31 becomes

$$E_{\mathrm{s}}{}^{\mathrm{av}} = {}^1/_2\sum_i C_i D_i[\langle\bar{S}(\bar{S}+1)\rangle - S_{\mathrm{eff}}^{(1)}(S_{\mathrm{eff}}^{(1)}+1) - S_{\mathrm{eff}}^{(2)}(S_{\mathrm{eff}}^{(2)}+1)]$$

For any MO described as a linear combination of atomic orbitals having the electron occupation number n, the total distribution is $n\Sigma_i C_i^2$. Now in determining $S_{\mathrm{eff}}^{(j)}$, each electron or fraction is considered as a separate entity so that the individual entities interact with each other, but no one entity interacts with itself. Thus there may be a maximum of $(n + 2)$ and a minimum of n entities in any given MO. Hence the general expression for the average energy of the spin interaction is

$$E_{\mathrm{s}}{}^{\mathrm{av}} = \sum_i C_i D_i[\langle\bar{S}(\bar{S}+1)\rangle - \sum_j S_{\mathrm{eff}}^{(j)}(S_{\mathrm{eff}}^{(j)}+1)] \tag{32}$$

Any attempt to evaluate $\langle\bar{S}(\bar{S}+1)\rangle$ should consider that in a given LCAO-MO the n electrons have a distribution over the component AO's proportional to C_i^2; thus the average spin is found by weighting every possible spin combination (within the limits of n), or fraction thereof, by the total spin multiplicity. Jorgensen has derived the relation[15]

$$\langle\bar{S}(\bar{S}+1)\rangle = \frac{n(n+2)}{4} - \left(\frac{2l+1}{4l+1}\right)\frac{n(n-1)}{2}$$

for pure atomic configurations, l^n. The term $n(n+2)/4$ is actually S_{max} whereas the second term is a correction according to n and the "l" degeneracy. The analogy between this relation and eq 32 is that the average spin is an "effective average" dependent on the composition of the MO, and the spin interactions have been introduced directly rather than as a correction to S_{max}.

6. Evaluation of Integrals and Method of Computation. Diatomic Integrals. The computerized program is based on integration by numerical quadrature. There are no restrictions on the number of Slater type terms occurring in the atomic wave functions.

Group Overlap Integrals. The computerized program takes the diatomic overlap integrals and computes group overlap integrals as a function of symmetry. The proper transformation of coordinates from diatomic to group overlap integrals is incorporated. The integrals include the normalization factor due to ligand–ligand overlap. In the latter evaluation, transformation of coordinates is also considered in the evaluation of the normalization factor, so that rotational invariance is preserved throughout.

H Matrices. All H matrices are constructed according to the procedures proposed here, and the usual diagonalization routine is carried out.

Orbital Energies. The entire computation is iterated to self-consistent charge and configuration (SCCC) within an interval of ±0.01 unit of atomic charge and orbital population.

Orbital Population Analysis. Lowdin orthogonalization[9] is employed in the final stages of calculation to arrive at a population analysis, since a recent investigation has shown that only the Lowdin procedure is capable of reproducing the correct magnitude and sign of electric dipole moments for small molecules.[16] Furthermore, calculations on first-row transition metal–hexafluoro complexes show that reliable nuclear hyperfine parameters associated with electron spin density at fluorine are attained only with Lowdin population.[2]

Discussion

Of course the success of this method of calculation depends upon the accuracy of the Mulliken multicenter integral and point-charge approximations. The first of these has been used with considerable success in calculations on transition metal complexes wherein the integrals were calculated in

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(13) C. K. Jorgensen, "Modern Aspects of Ligand Field Theory," American Elsevier, New York, N. Y., 1972, and references therein.

(14) J. C. Slater, *Phys. Rev.*, 165, 655 (1968).

(15) (a) C. K. Jorgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1969, Chapter 2; (b) *Solid State Phys.*, 13, 375 (1962).

(16) E. W. Stout, Jr., and P. Politzer, *Theor. Chim. Acta*, 13, 379 (1968).

closed form rather than approximated.[12] Furthermore a numerical comparison to exact SCF-LCAO-MO computations show that this approximation is quite satisfactory for most purposes.[17] The only instance where the approximation is not valid is in the computation of multicenter exchange integrals,[1] which, fortunately, are not directly involved in the present computational model.

We turn our attention now to the point-charge approximation. In order to assess the accuracy of this approximation, the values of $1/R_{ML}$ and $1/R_{LL}$ for $CuCl_4^{2-}$ are compared with the nuclear attraction integrals calculated exactly for copper 3d, 4s, and 4p and chlorine 3s and 3p orbitals.[2,18] These results as presented in Appendix I show that the approximation is quite satisfactory at the specified internuclear distances. The largest errors occur when p orbitals are involved, particularly if these are diffuse 4p orbitals. However even in these cases the consequences are not drastic since such terms wherein the point-charge approximation is employed make only a very minor contribution to the energy. Of course, it is not anticipated that the results will be equally good at small internuclear distances, although similar comparisons of such integrals in CH_4 ($R_{CH} = 1.09$ Å; $R_{HH} = 1.26$ Å) and CF_4 ($R_{CF} = 1.32$ Å; R_{FF} 2.16 Å) do not exceed the errors given in Appendix I.[19] Fortunately in most molecules of inorganic interest the bond distances are in a range of $\geqslant 2$ Å.

One last point of consideration is the potential due to the external charge. The important consequences of this have been clearly demonstrated in the recent work of Brown, *et al.*,[20] and in the results presented in part II.

This is not regarded merely as a spherical potential as has been the case hitherto.[2] The logical assumption, which is supported by crystal structures of specific examples, is that the external potential (of the lattice) exerts a greater effect on the ligands than on the metal since the lattice charges are situated much closer to the ligands than to the metal. Hence, the off-diagonal element due to the external potential is nonvanishing. The radial variation of a spherical potential transfers metal and ligand electrons to the center of the molecule, and thus the effect on both metal and ligand electrons is the same. Also, because of its spherical distribution, such a potential has no off-diagonal elements. For the sake of convenience of treating complex ions both in the solid and in solution, where in the latter instance the exact positions of the external lattice charges are not known, the external potential is superimposed on each of the ligands.

All of the features of this computational model are considered in detail in part II of this series, where specific calculations are presented and the results are compared both with experiment and with other more sophisticated computational methods.

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Appendix I. Approximation to Nuclear Attraction Integrals

Table I. Values of Nuclear Attraction Integrals for $CuCl_4^{2-}$ [a]

Exact value[b]	Dev from $|1/R)$[c] %
$R = 2.21$ Å; $|1/R) = 0.23843$[c]	
$(\chi_{4s}|1/r_{Cl}|\chi_{4s}) = 0.23741$	−0.43
$(\chi_{4p\sigma}|1/r_{Cl}|\chi_{4p\sigma}) = 0.28316$	+18.70
$(\chi_{4p\pi}|1/r_{Cl}|\chi_{4p\pi}) = 0.20662$	−13.30
$(\chi_{3d\delta}|1/r_{Cl}|\chi_{3d\delta}) = 0.24185$	+1.43
$(\chi_{3d\pi}|1/r_{Cl}|\chi_{3d\pi}) = 0.24084$	+1.01
$(\chi_{3d\delta}|1/r_{Cl}|\chi_{3d\delta}) = 0.23387$	−1.91
$(\upsilon_{3s}|1/r_{Cu}|\upsilon_{3s}) = 0.23832$	−0.05
$(\upsilon_{3p\sigma}|1/r_{Cu}|\upsilon_{3p\sigma}) = 0.25910$	+8.67
$(\upsilon_{3p\pi}|1/r_{Cu}|\upsilon_{3p\pi}) = 0.22741$	−4.61
$R = 3.62$ Å; $|1/R) = 0.14599$	
$(\upsilon_{3s}|1/r_{Cl}|\upsilon_{3s}) = 0.14611$	+0.08
$(\upsilon_{3p\sigma}|1/r_{Cl}|\upsilon_{3p\sigma}) = 0.15067$	+3.20
$(\upsilon_{3p\pi}|1/r_{Cl}|\upsilon_{3p\pi}) = 0.14344$	−1.75

[a] All values in atomic units. [b] From ref 18. [c] From ref 2.

The one-electron, two-center nuclear attraction integrals are of the general form $\langle\chi_N|1/r_{N'}|\chi_{N'}\rangle$, where χ is an orbital centered on atom N and the point of integration over $1/r_{N'}$ is at any other atom N'.

If Slater orbitals are employed, exact integration results in an exponential power series in terms of the orbital parameters n and ζ and the internuclear separation $R_{NN'}$. In the point-charge approximation $\rho = (\zeta r) \rightarrow \infty$, and the integral reduces to $1/R_{NN'}$. Although in actual situations this approximation is far from exact, other compensating factors seem to ensure that the point-charge approximation appears to be an adequate representation for such purposes. The data presented in Table I for $CuCl_4^{2-}$ compare the relative merits of the point-charge approximation and an exact calculation.

Appendix II. Bonding Orbital Ionization Energies

The integrals involving that part of the operator which refers to the atomic cores $(-{}^1/_2\nabla_i^2 + \mathrm{V}_i)$ are taken to be equal to the ionization energy of the particular orbital involved on the atom, as a function of its atomic charge within the molecule. Of the various methods of calculation suggested, those made by Basch, *et al.*,[21,22] are widely used. Other workers[23-26] have also suggested some nominal modifications.

Basch, *et al.*,[21,22] emphasized the role of all spectral terms within a specified valence configuration, and the weighting of the VOIE's as a function of the atomic charge. The latter is allowed to vary quadratically for a fixed computed orbital configuration of the atom in the molecule. Cusachs, *et al.*,[23,24] averaged the energies of the various configurations and then related these averages to both the atomic populations and charges. The derived relation may be either linear or quadratic.

In any event the objective is to relate the matrix elements of $\mathbf{H}^{\text{core}}$ with some experimentally determined quantity. The crux of the problem is to determine suitable values from atomic spectral data to approximate the integral. It is common practice to write the average energy as a single determinant representation of a given atomic configuration with minimum M_L and M_S values, which can be written as a linear combination of all the spectral terms belonging to that configuration. For the purposes of MO calculations,

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(23) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, 43, 3160 (1965).

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(26) T. Anno, *Theor. Chim. Acta*, 18, 223 (1970).

these configurations have been limited to bonding orbital configurations only.

However, it is a well-known fact that configuration interaction involving other orbitals plays a major role in determining the average energy of ionization. Hence the only plausible way of accounting for this is to limit the spectroscopic terms energetically according to the electron density of the atom in the molecule, irrespective of the bonding orbital configuration. In order to accomplish this the following procedure is proposed.

(1) No *a priori* limitation should be imposed on the atomic orbital configurations, and certainly not on the AO basis considered for bonding only.

(2) Since the ionization energies are functions of the net charge in the atom (not the orbital alone) which may even be fractional, then the term energies contributing to the ionization should be restricted accordingly. It is proposed that if the net atomic charge on the bonded atom is $q + x$ $(x > 1)$, then the highest spectral terms that should be considered in the average are those limited to x times the ionization potential of the atom bearing the charge q. To avoid confusion, we shall call these orbital energies BOIE (bonding orbital ionization energies) rather than VOIE.

The BOIE for an atom in the interval of the integral ionization stages n to $n + 1$ is represented as

$$(\mathrm{BOIE})_{n\rightarrow n+1} = (\mathrm{IP})_{n+1} + \bar{E}_{n+1} - \bar{E}_{n'} \qquad (1\text{-AII})$$

$$n' = n + x \quad (x > 1)$$

where IP is the ionization potential and $\bar{E}$ is the weighted average of the acceptable term energies. As a typical example, the possible atomic terms contributing to the BOIE of the 3d electron in the Ni atom within the interval 1 < atomic charge < 2 are given in Table II.

As assumed above, the values for $\bar{E}_1$ for each of the configurations depend upon the charge on the atom. The values are zero when the electron does not "attain" the configuration. For example, for a charge less than $(1 + 51.558/146.408)$, $\bar{E}_1(\mathrm{s})$ values for $3d^8 4p$ and $3d^8 5s$ are zero, and for a charge higher than this but less than $(1 + 91.799/146.408)$, $\bar{E}_1$ for $3d^8 5s$ only is zero. The orbitals considered for bonding are 3d, 4s, and 4p only, but configurations $3d^8 4s5s$, $3d^9 4d$, and $3d^9 6s$ are not considered, as there are no corresponding configurations in Ni(II). However, for $(\mathrm{BOIE})^{4s}{}_{0\rightarrow 1}$ $3d^8 4s5s \rightarrow 3d^8 5s$ should be considered along with $3d^8 4s^2 \rightarrow 3d^8 4s$, $3d^9 4s \rightarrow 3d^9$, and $3d^8 4s4p \rightarrow 3d^8 4p$.

In any case, the overall configuration weighted or simple arithmatic averages $(\mathrm{BOIE})_{0\rightarrow 1}$ for $q = 0$, $(\mathrm{BOIE})_{1\rightarrow 2}$ for $q = 1$, and $(\mathrm{BOIE})_{2\rightarrow 3}$ for $q = 2$ are taken, and the BOIE(q) curve is constructed. The shape the curve will assume depends on both the number of electrons of interest $(\ldots l^x \ldots)$ in the configurations as well as on the charge. A summary is given in Table III.

The parameters of the resulting equations are "derived" parameters for the charge but not fitted parameters of a quadratic equation, or any equation for that matter.

Method of Cumputation. 1. Cationic Species. The ionization potentials, the atomic configurations, and the energies above the ground level, as well as their corresponding J values, are the inputs for a computerized program. The program calculates the weighted averages of energies for each configuration at an interval of $0.05(\mathrm{IP})_{n+1}$ and finally the total average. From the IP's and the averages, the BOIE's are calculated utilizing equation 1-AII for different ionized stages. The charge dependence parameters are then calculated regarding $(\mathrm{BOIE})_{0\rightarrow +1}$ for $q = 0$ and $(\mathrm{BOIE})_{+1\rightarrow +2}$ for $q = 1$. The parameters vary for different ranges of respective atomic charges. These parameters, in turn, are the inputs for final MO calculations (see part II) and the appropriate parameters are picked according to respective atomic charges.

2. Anionic Species. In MO calculations the BOIE's of anionic species are also needed. The present method requires a fairly detailed knowledge of the pertinent spectroscopic terms and their energies. Unfortunately, such data for anionic states are not readily available. However, the procedure suggested below for such cases is again better than the extrapolation method.

Table II. Condensed Spectroscopic Energy Levels of Ni (First IP = 61.579 kK; Second IP = 146.408 kK; Third IP = 283.700 kK)

Ni(I)		Ni(II)		Ni(III)	
Confign[a]	Energy[b]	Confign[a]	Energy[b]	Confign[a]	Energy[b]
$3d^8 4s$	0.000	$3d^9$	0.000	$\underline{3d^8}$	0.000
		$\underline{3d^9}$	1.507		
$\underline{3d^9 4s}$	0.205	$\underline{3d^8 4s}$	8.394		17.231
	3.410		32.523	$\underline{3d^7 4s}$	53.704
$\underline{3d^{10}}$	14.729	$\underline{3d^8 4p}$	51.558		79.143
$3d^8 4s$	22.102		79.924	$\underline{3d^7 4p}$	110.212
$3d^8 4s4p$	25.753	$\underline{3d^8 5s}$	91.799		133.691
$\underline{3d^9 4p}$	28.569		94.727	$\underline{3d^7 5s}$	181.019
	32.982				183.053
$\underline{3d^9 5s}$	42.621				
	44.262				
$3d^8 4s4p$	47.030				
$3d^8 4s5s$	48.467				
$3d^9 5p$	48.715				
$3d^9 4d$	48.953				
$3d^8 4s5s$	50.466				
$3d^9 5p$	50.689				
$3d^9 4d$	50.754				
$3d^9 6s$	52.197				

[a] Those configurations which are underlined are the ones to be employed for $\bar{E}_0$, $\bar{E}_1$, and $\bar{E}_2$ in calculating the BOIE's. [b] All values given in kK (kilokaisers).

Table III. Shape of BOIE(q) Curves

	Charge interval		
$\ldots l^x \ldots$	0–1	1–2	2–3
$\ldots l^1 \ldots$	Linear	Linear[a]	Linear[b]
$\ldots l^2 \ldots$	(Parallel to q axis)		
$\ldots l^2 \ldots$	(Parallel to q axis)	Linear	Linear[b]
$\ldots l^3 \ldots$	(Parallel to q axis)	Linear	Quadratic[c]

[a] If there is only one set of configurations, the linear curve will be parallel to the q axis. If there are two different sets such as $3d^9 4s \rightarrow 3d^9$ for $(\mathrm{BOIE})_{0\rightarrow 1}$ and $3d^8 4s \rightarrow 3d^8$ for $(\mathrm{BOIE})_{1\rightarrow 2}$, the slope may not be zero. The BOIE's then, must be arithmetic averages. [b] In some cases quadratic for consideration stated in *a* above. [c] For $l^x > {}^3$ and charge >3, the polynomial of degree greater than 2 can be used.

Table IV. A Representative Comparison of VOIE's Calculated by Basch, *et al.*,[21,22] with BOIE's of the Present Work[a]

	3d of Ni		4s of Ni		4p of Ni	
Charge	VOIE	BOIE	VOIE	BOIE	VOIE	BOIE
1.1	205.7	185.2	163.2	148.8	113.7	41.9
1.2	220.7	191.5	172.3	146.8	121.6	45.7
1.4	249.3	227.6	190.9	152.8	137.7	120.7
1.5	264.0	235.7	200.4	157.9	146.0	118.5
1.6	278.8	243.7	210.1	163.0	154.5	118.8
1.8	309.4	286.9	229.9	173.3	171.9	128.9
1.9	325.1	298.2	240.0	178.4	180.8	133.9

[a] In both calculations arithmetic averages rather than configuration weighted averages have been considered for simplicity. All values in kilokaisers.

Electron affinities can be taken as approximate IP's. As the ionization energies of anionic species are fairly low, the higher excited states are easily attained. A reasonable guess can be made about these excited states and their energies by comparing them to those of other isoelectronic cases for which the required information is known. As shown in part II, values calculated on this basis are well suited to the MO calculations, as the results are excellent. A more detailed treatment of anionic species will appear in a subsequent publication.

Results and Discussion. To exemplify the proposed method, the evaluation of BOIE's of 3d, 4s, and 4p orbitals of Ni are documented elsewhere.[27] A comparison of the overall VOIE's of Ni and their respective charge dependence calculated by the present method and those by Basch, *et al.* is shown in Table IV.

$(\mathrm{BOIE})_{n\rightarrow n+1}$ attains a limiting value when the highest term of the configurations considered is reached. Thus, when the electron attains the highest term of the configurations, the $(\mathrm{BOIE})_{n\rightarrow n+1}$ would be independent of charge. One implication is that if the charge on the atom gives a limiting energy which exceeds that corresponding to the highest term of the configurations considered, the bonding may "involve" orbitals other than those already considered. In other words, the charge on the atom would depend, among other things, on the orbitals involved in bonding.

By the present method of evaluation of orbital ionization energies, it will be possible to attain more accurate information regarding the participation of virtual orbitals in bonding. To support this contention, a comparison between observed and calculated molecular properties which show a critical dependence on atomic charge distribution is presented and discussed in detail in part II. Also discussed in part II are the implications and consequences of the very significant difference in the numerical values of calculated properties using the proposed BOIE's and those using the usual VOIE's.

It is obvious that the proposed method relies heavily on a knowledge of spectroscopic states. In cases where such data are incomplete, or lacking, it is possible to arrive at suitable information by acceptable extrapolation techniques. Although the latter procedure will of necessity lack the accuracy of experimental data, this in no way will impair the basic approach to the calculation of VOIE proposed here.

(27) A listing of BOIE's as a function of charge for the 3d, 4s, and 4p orbitals of Ni will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1590.

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Investigations in Semiempirical Molecular Orbital Methods. II. Computational Results for Octahedral Fluorides TiF_6^{3-}, CrF_6^{3-}, FeF_6^{3-}, and NiF_6^{4-}

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A new parameter-free method for doing semiempirical molecular orbital calculations has been applied to octahedral fluoro complexes MF_6^{n-} ($M = Ti^{3+}, Cr^{3+}, Fe^{3+}, Ni^{2+}$). Calculations of ligand field splittings, superhyperfine coupling constants, and spin densities are found to be in excellent agreement with experiment. In all cases the results obtained are at least as good as the best SCF calculations done on these complexes thus far.

Introduction

A new approach to performing semiempirical molecular orbital calculations on inorganic coordination complexes and molecules has been developed in part I of this series.[1] In this part of the series we present computational results on the model systems TiF_6^{3-}, CrF_6^{3-}, FeF_6^{3-}, and NiF_6^{4-} (in the salt $KNiF_3$). This selection is based on the fact that in these particular species it is possible to compare the results of this study with those of other theoretical studies having varying degrees of sophistication. Also these complexes allow a comparison to be made between the experimental and calculated data regarding ligand field splitting ($10Dq$), charge-transfer spectra, superhyperfine coupling constants and spin densities (derived from epr and nmr), and net atomic charges (derived from X-ray absorption). Consequently a very crucial test of the accuracy and applicability of the method is thus provided.

Method of Calculation

Details of the computational approach have already been given previously.[1] Thus only the basic features of the method will be reiterated here.

The diagonal elements of the Hamiltonian are

$$\mathbf{H}^{\mathrm{M}}{}_{ii} = \epsilon_i(q_{\mathrm{M}})_i - n(q_{\mathrm{L}} + q_{\mathrm{ex}})(1/R_{\mathrm{ML}}) + q'_{\mathrm{L}} \frac{\langle r_{\mathrm{d}}{}^4\rangle}{6R_{\mathrm{ML}}{}^5} F_{\mathrm{M}} \quad (1)$$

$$\begin{aligned}\mathbf{H}^{\mathrm{L}}{}_{jj} = {} & \epsilon_j(q_{\mathrm{L}})_j - q_{\mathrm{M}}/R_{\mathrm{ML}} - [q_{\mathrm{L}} + q_{\mathrm{ex}}]\left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + \right. \\ & \left. 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right] - \frac{q_{\mathrm{M}}\langle r_{\mathrm{p}}{}^2\rangle}{5R_{\mathrm{ML}}{}^3} - q'_{\mathrm{L}}(\langle r_{\mathrm{p}}{}^2\rangle/5)\left[\frac{n-2}{(R_{\mathrm{LL}})_{\mathrm{C}}} + \right. \\ & \left. 1/(R_{\mathrm{LL}})_{\mathrm{T}}\right] + \frac{q'_{\mathrm{L}}N_i{}^2}{2}\left\{(\mathrm{IF})_{\mathrm{C}}\left[1/(R_{\mathrm{LL}})_{\mathrm{C}} - \langle\frac{1}{r_{\mathrm{p}}}\rangle\right] + \right. \\ & \left. (\mathrm{IF})_{\mathrm{T}}\left[1/(R_{\mathrm{LL}})_{\mathrm{T}} - \langle\frac{1}{r_{\mathrm{p}}}\rangle\right]\right\} \quad (2)\end{aligned}$$

where $\mathbf{H}^{\mathrm{M}}{}_{ii}$ and $\mathbf{H}^{\mathrm{L}}{}_{jj}$ refer to the metal and ligands, respec-

(1) Part I: A. Dutta-Ahmed and E. A. Boudreaux, *Inorg. Chem.*, 12, 1590 (1973).