Inorganica Chimica Acta, 9 (1974) 245–250

Investigations in Semi-empirical Molecular Orbital Methods. IV. A Modified Wolfsberg–Helmholz Method for Inorganic Systems

L. E. HARRIS
Pitman–Dunn Laboratory Frankford Arsenal Philadelphia, Pa. 19137, U.S.A.
and
E. A. BOUDREAUX*
Department of Chemistry Louisiana State University in New Orleans New Orleans, La. 70122, U.S.A.
Received November 12, 1973

Semiempirical molecular orbital calculations were performed for MF_6^{3-} where $M = Ti^{3+}$, V^{3+}, Cr^{3+}, Fe^{3+} and Co^{3+}, MnF_6^{4-}, MnF_6^{2-}, $MnCl_6^{4-}$, $MnCl_4^{2-}$, $MnCl_2$, VCl_6^{2-} and VCl_4, using a modified semi-empirical MWH method. The method of calculation is derived from the HF–SCF equations using approximations appropriate to the highly polar bonds in transition metal halides. The final equations used also take account of the site potential present for the charged molecular ion. This method is compared to other recent semi-empirical computational methods including the conventional MWH method. The computed atom charges are in better agreement with experimentally estimated atom charges than those of previous semi-empirical calculations. The ligand field molecular orbital coefficients are also in good agreement with coefficients estimated from NMR and EPR spectroscopy. This method of calculations also gives results that agree with the trends shown by experimentally determined 10 Dq values and charge transfer transition energies and are in good numerical agreement with the experimental 10 Dq values.

Introduction

The Mulliken–Wolfsberg–Helmholz (MWH) method[1–3] has been used extensively in recent years to rationalize the electronic properties of transition metal complexes. The theoretical foundations of these calculations, however, have been poorly understood. Additionally, recent estimates of the charges on the atoms from x-ray emission spectral data[4] and ligand field orbital coefficients from EPR and NMR spin densities[5] indicate that the conventional MWH approach underestimates the ionicity of transition metal halides. To correct these deficiencies, a modified method of calculation was derived from Richerdson's simplified SCF hamiltonian for transition metal complexes.[6a,b] Prior to the work of Boudreaux and Dutta–Ahmed[6a,b] a more simplified MWH approach was developed by Harris and Boudreaux,[7] which differs in several respects from the case reported here. A similar method has been proposed and used by Hillier[8] for calculations on transition metal carbonyl complexes. The m-MWH method is applied here to transition metal fluorides and chlorides. The results obtained are in better agreement than previous semi-empirical calculations[5,9] not only in regard to experimental estimates of the ground state charge distribution but also with the experimentally determined values of 10 Dq and the first charge transfer transition energies of transition metal halides. This improvement in the reliability of the m-MWH method should be most useful in those cases where, at present, reasonably accurate descriptions of the electronic structures of transition metal complexes are necessary to interpret experimental results but are difficult, if not impossible, to obtain from the more rigorous methods of molecular orbital calculation.

Method of Calculation

A molecular orbital, Ψ_i, for a transition metal halide complex, MX_n^{-Q}, can be written as

$$\Psi_i = m_i u_i + l_i \Phi_i$$

$$\Phi_i = \sum_j^N c_{ij} v_{ij}$$

where u_i is a metal atomic orbital and the coefficients, c_{ij}, symmetry adapt the atomic orbitals, v_{ij}, localized on the j^th^ ligand to give the symmetry orbital, Φ_i. Richardson[10] has shown that Roothaan's formulation of the HF equations for transition metal complexes can be greatly simplified using Mulliken's multicenter integral approximation. Following Fenske's[5] further approximation to Richardson's hamiltonian for the highly polar transition metal fluorides, the diagonal

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* To whom correspondence should be addressed.

element of the metal, HM, and the diagonal of the ligand, H_X, with respect to Φ_i can be written as

$$H_M = \xi_{u_i}\ (q_M) - Nq_X <1/r_j|u_iu_i> \qquad (1)$$

$$H_X = [\xi_{v_{il}}\ (q_X) - q_X <1/r_M|v_{il}v_{il}> - \sum_{j=2} q_X <1/r_j|v_{il}v_{il}>]X_i \qquad (2)$$

where ξ_k is the orbital energy of the kth atomic orbital, q_M and q_X are the charges on the metal and ligand and X_i is a correction factor for ligand–ligand overlap.[11] If a point charge electrostatic approximation in used for the nuclear attraction integrals, these equations reduce to[6a]

$$H_M = \xi_{u_i}\ (q_M) - Nq_X/R \qquad (3)$$

$$H_X = [\xi_{v_{il}}\ (q_X) - q_M/R_X - (N-1)q_X/R_{XX}]X_i \qquad (4)$$

Where R_{MX} and R_{XX} are the metal–ligand and ligand–ligand internuclear distances, respectively.

The effect of the potential of the site that the complex occupies should be incorporated into the computations. The effect can be approximated in a manner consistent with the level of the other approximations, by assuming that the stabilizing potential at the site of the complex, MX_N^{-Q}, is uniformly distributed within a sphere of radius R, upon whose surface resides a quantity of positive charge, Q. Thus this model is even a simpler one than that proposed previously.[6a] Since the complex is in a potential well of depth, –Q/R, equations (3) and (4) become

$$H_M = \xi_{u_i}\ (q_M) - Nq_X/R_{MX} - (N-1)q_X/R_{MX} \qquad (5)$$

$$H_X = \{\xi_{v_{il}}\ (q_X) + [N/R_{MX} - (N-1)/R_{XX}]q_X\}X_i \qquad (6)$$

Application of the same approximations used for the diagonal element leads to the following expression for the off-diagonal elements[7]

$$H_{MX} = G\frac{(u_i,\Phi_i)}{2}\{H_M + H_X/X_i - \frac{q_X}{2}[<1/r>_X - 1/R_{MX} - \frac{q_M}{2}[<1/r>_M - 1/R_{MX}]\} \qquad (7)$$

where $<1/r>_X$ and $<1/r>_M$ are the expections values of the ligand and metal functions.

Alternatively, if the Rudenberg approximation[12]

$$T(u_i,v_{il}) = kS(u_i,v_{il})|S(u_i,v_{il})|\{T(u_i,u_i) + T(v_{il},v_{il})\}$$

for two center kinetic energy integrals such as, $T(u_i,v_{il})$, is used, we obtain the expression

$$H_{MX} = (2-k|S(u_i,v_{il})|)G(u_i,\Phi_i)(H_M + H_X)/2 \qquad (8)$$

where $G(u_i,\Phi_i)$ is the group overlap integral between the metal and ligand symmetry adapted orbital and k is a correction factor for the kinetic energy terms. analogous expressions may be developed for the ligand–ligand off-diagonal elements.

Equations (5), (6) and (8) were used in these calculations. It can easily be shown that these equations hold for basis sets having more than one atomic orbital basis set chosen included the 4s, 4p and 3d metal orbitals and the 2s and 2p ligand orbitals. The orbital energies, $\xi(q)$'s, were evaluated from the VOIE's of Basch *et al.* The orbital populations and atom charges were obtained from a population analysis of the Lowdin orbitals.[6a,14] This method of population analysis as opposed to the conventional Mulliken population analysis[15] avoids the occurrence of negative populations and is in better accord with experiment in the calculation of atomic charges and dipole moments.[6b,7,16,17] The overlap integrals were calculated by numerical (16 point Gaussian) integration using the metal, +1, functions of Richardson *et al.*[18] and the fluoride and chloride functions of Clementi.[19] The calculations were iterated using a damping scheme[20] until both charges and populations were self-consistent to within ± 0.01.

Thus the equations used in the limit of zero charge separation are the same as the conventional MWH equations using the Wolfsberg–Helmholz approximation

$$H_{ij} = F(H_{ii} + H_{jj})/2 \qquad (9)$$

for the off diagonal elements with F given by the Cusachs approximation[21]

$$F = 2-/S_{ij}/$$

However, the derivation of these equations from the HF–SCF hamiltonian leads to additional charge dependent terms (excluding the site potential).[6a] The necessity of these terms had previously been only intuitively justified.[22] These additional charge dependent terms are important since their magnitude can be larger than the orbital energies in the metal atom diagonal elements of highly ionic species such as TiF_6^{3-}. In the case of highly covalent molecules, the neglect of these terms may not be important since the charges on the atoms are usually much smaller. These terms take into account the interatomic coulombic energy, that is the energy due to the effect that the charge on one atom has on another.

The site potential, although crudely approximated here, is a physically real effect. Its inclusion was found to be necessary to obtain results in accord with experiment.[6b,7] In the absence of this term, the metal diagonal elements become very positive while the ligand diagonal elements remain negative. Consequently this large numerical discrepancy between the diagonal elements may cause the vital Mulliken multicenter integral approximation to fail. Thus, an important function of the site potential, over and above its representation of the influence of the environment on the complex, may be to allow the numerical values of the diagonal element to fall within a range where the Mulliken approximation is valid.

TABLE I. Self-consistent Atom Charges and Orbital Populations of Transition Metal Halides.[a]

Complex	q_M	M(4s)	M(4p)	M(3d)	q_v	X(2s)	R(‹)
$TiF_6^{3-}(d^1)$	1.65	0.20	0.35	1.90	–0.77	1.93	1.97[b]
$VF_6^{3-}(d^2)$	1.51	0.22	0.38	2.91	–0.75	1.91	1.94[b]
$CrF_6^{3-}(d^3)$	1.47	0.24	0.48	3.91	–0.75	1.91	1.93[b]
$FeF_6^{3-}(d^5)$	1.24	0.29	0.46	6.03	–0.70	1.90	1.92[b]
$CoF_6^{3-}(d^6)$	1.17	0.30	0.46	7.06	–0.70	1.90	1.89[b]
$MnF_6^{4-}(d^5)$	0.82	0.25	0.41	5.50	–0.80	1.92	2.12[b]
$MnF_6^{2-}(d^3)$	1.81	0.24	0.35	4.60	–0.63	1.90	1.74[b]
$MnCl_6^{4-}(d^5)$	0.20	0.43	0.77	5.61	–0.70	1.89	2.51[c]
$MnCl_4^{2-}(d^5)$	0.46	0.42	0.44	5.69	–0.62	1.89	2.33[b]
$MnCl_2(d^5)$	0.83	0.72	0.52	8.93	–0.41	1.75	2.09[d]
$VCl_6^{2-}(d^1)$	0.81	0.40	0.72	3.07	–0.46	1.85	2.30[d]
$VCl_4(d^1)$	0.67	0.33	0.75	3.25	–0.17	1.79	2.03[b]

[a] A complete listing of the eigenvalues and eigenvectors is available from the authors upon request. [b] Taken from ref. 8. [c] Taken from «Tables of Interatomic Distances and Configurations in Molecules and Ions», Special Publications, No. 11, Chemical Society, London, 1958. [d] Estimated.

Some justification for the use of an electrostatic approximation for the nuclear attraction integrals has already been given elsewhere.[6a]

Results and Discussion

The atom charges and orbital populations calculated by this method are given in Table I. The charge on the ligand, q_X, can be used as a measure of the ionicity of the complex, which shows an apparent decrease both with atomic number across the transition metal series and with the oxidation number of the metal ion, but increases with the number of ligands attached to the metal ion and with the electronegativity of the ligand expected. These trends are all chemically reasonable. The magnitude of the computed charges and orbital populations are compared to values estimated from x-ray emission spectroscopy[4] in Table II. Both in CrF_6^{3-} and FeF_6^{3-} the charges computed by the method are in better agreement with experiment than those obtained from either the SCCC calculations of Basch *et al.*[9] or the calculations of Fenske *et al.*[5] The SCCC calculations of Basch *et al.* are of the conventional MWH variety using equation 9 for the off-diagonal elements and with the ligand diagonal elements held fixed. The method of Fenske *et al.*[5] utilizes equations (1) and (2) with Xi (set to one) and a comparable equation for the off-diagonal elements. In their method the nuclear attraction integrals (even the three centered nuclear attraction integrals) are evaluated by numeric integration. The m-MWH method of calculation gives metal atom charges intermediate between those of Basch *et al.* and Fenske *et al.* and in agreement with the metal atom charges estimated from x-ray emission data.[4]

Besides the estimation of charge distribution given by the x-ray emision data, the unpaired spin density in the ligand orbitals can be obtained from NMR and EPR spectra. The actual coefficients in the pertinent molecular orbitals, for a half-filled shell in octahedral symmetry, are related to the experimentally determined spin density, f_i, in the i^th^ atomic orbital by the equations[6b]

$$f_s = l_s^2/_3$$

$$f_\sigma - f_\pi = l_\sigma^2/_3 - l_\pi^2/_4$$

where l_s and l_σ are the coefficients of the ligand 2s and 2pσ symmetry adapted orbitals in the 3eg molecular orbital, and l_π is the coefficient of the ligand 2pπ symmetry adapted orbital in the $2t_{2g}$ molecular orbital.

TABLE II. Comparison of Experimental and Theoretical Atomic Charges and Orbital Populations of Transition Metal Halides.

CrF_6^{3-}	M(3d)	M(4s)	q_M
Obs.[a]	4.40[d]	0.07	1.53
This Work	4.39	0.24	1.47
SCCC[b]	4.76	0.52	0.97
Fenske *et al.*[c]	4.09	–	1.92

FeF_6^{3-}	M(3d)	M(4s)	q_M
Obs.[a]	6.30[d]	0.37	1.33
This Work	6.49	0.29	1.24
SCCC[b]	6.76	0.48	0.86
Fenske *et al.*[c]	6.01	–	1.96

[a] Taken from ref. 4. [b] Taken from ref. 8. [c] Taken from ref. 5. [d] The observed 3d population is really a combination of the 3d and 4p populations.

Thus, the extent of agreement between the calculated and measured spin density is a sensitive test of the correctness of the calculated coefficients in the ground state molecular orbitals. As is shown in Table III, the calculated and measured spin densities are indeed in good agreement.

Thus, our method gives reasonable results for the ground state charge distribution of these complexes. Although the primary objective was to obtain good ground state properties, correlations were also made to properties involving excited electronic states. In conventional MWH calculations such as those of Basch *et al.*,[9] the F factor in the off-diagonal element expression given by equation 9 must be adjusted for each complex to obtain a good match between the orbital energy difference of the $2t_{2g}$ and $3e_g$ molecular orbitals a and experimentally determined value of 10 Dq. Basch *et al.* found that with F_π set at 2.10, the 10 Dq values of many octahedral and tetrahedral halide complexes of transition metals were exactly matched by varying $F\sigma$ according to the equation

$$F\sigma = 0.027\eta + 1.546 \pm 0.02$$

where for Ti, $\eta = 0$, for V, $\eta = 1$, ...*etc.* In the calculations of Fenske *et al.*[5] a factor, R, in the off-diagonal element approximation was adjusted such that the difference of the $2t_{2g}$ and $3e_g$ orbital energy agreed with the experimental value of 10 Dq in Ti F_6^{3-}. Calculations on the other halide complexes are then performed without further adjustment. In the m-MWH calculations, the 10 Dq values obtained as orbital energy differences from calculations with k set to one in equation 8 are listed under Calculation I in Table IV. As is shown in Table IV, these computed 10 Dq values, while they are larger than the experimental values, in all cases exhibit the same trend as experimental values.

In the m-MWH calculations, as in those of Fenske *et al.*, which are based on derivations from the HF–SCF hamiltonian, the difference between the $2t_{2g}$ and $3e_g$ orbital energy would be expected to be larger than the experimental values of 10 Dq since the appropriate electron repulsion integrals should be subtracted from

TABLE III. Comparison of Experimental and Theoretical Spin Densities in Transition Metal Halides.

Complex	f_s(%)		$f_\sigma - f_\pi$(%)	
	Obs.	Calc.	Obs.	Calc.
$CrF_6^{3-}(d^3)$	–0.02 ± 0.01[a,b]	0.00	–4.9 ± 0.8[a] –6.0 ± 1.0[b]	–3.07
$FeF_6^{3-}(d^5)$	0.8 ± 0.1[c]	0.77	3.4 ± 1.0[c]	2.80
$MnF_6^{4-}(d^5)$	0.4 ± 0.04[c]	0.41	1.6 ± 0.8[c]	1.82
$MnCl_6^{4-}(d^5)$	0.4 ± 0.04[d]	0.56	3.9 ± 0.4[d]	3.42

[a] R. G. Shulman and K. Knox, *Phys. Rev. Letters, 4,* 603 (1960). [b] L. Helmholz, A. V. Guzzo, and R. N. Sanders, *J. Chem. Phys., 35,* 1349 (1961). [c] L. Helmholz, *J. Chem. Phys., 31,* 172 (1959). [d] F. Tsay and L. Helmholz, *J. Chem. Phys., 50,* 2642 (1969).

TABLE IV. Comparison of Experimental and Theoretical 10 Dq Values and Charge Transfer Transition Energies (eV).

Complex	10Dq				First Allowed L → M Charge Transfer: $3t_{1u} \rightarrow 2t_{2g}$	
	Obs	Calc				
		Calc I	Calc II	Other Work[f]	Obs[g]	Calc II
$Tif_6^{3-}(d^1)$	2.2[a]	4.3	2.0	2.0	>6.2[a]	8.9
$VF_6^{3-}(d^2)$	2.0[b]	3.8	2.1	2.0	>5.0[g]	7.8
$CrF_6^{3-}(d^3)$	1.9[c]	3.6	2.1	2.1	>4.6[g]	6.8
$FeF_6^{3-}(d^5)$	1.7[d]	2.7	2.0	2.0	>3.7[e]	4.1
$CoF_6^{3-}(d^6)$	1.6[d,e]	2.6	2.1	2.0	–	3.3
$MnF_6^{2-}(d^5)$	2.7[d]	7.2	2.7	–	>3.5	5.5
$MnF_6^{3-}(d^3)$	1.0[d]	2.2	1.8	–	>5.3[g]	6.7

[a] H. Bedon, S. M. Horner, and S. Y. Typree, Jr., *Inorg. Chem., 3,* 647 (1964). [b] C. J. Ballhausen and F. Winter, *Acta Chem. Scand., 13,* 1729 (1959). [c] W. Low, *Phys. Rev. 109,* 247, 256 (1959). [d] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison-Wesley, Reading, Massachusetts, 1962, pp. 110–111 and pp. 284–289. [e] C. K. Jørgensen, *Advan. Chem. Phys. 5,* 62, 85 (1962). [f] Taken from Ref. 5. [g] Taken from Ref. 8.

the orbital energy difference to correctly compute the value of 10 Dq.[23] Calculations are underway to correct the 10 Dq values given by Calculation I with the appropriate electron repulsion integrals.[16] However, to directly compare these calculations to both those of Fenske *et al.* and those performed in the conventional MWH manner, further calculations were performed in which the off-diagonal elements were adjusted to obtain an orbital energy of the ligand field orbital that matched the experimental value of 10 Dq. Blyholder and Coulson[24] have found that the necessity of an F factor in conventional MWH formulations of the off-diagonal elements arises from the kinetic energy of the hamiltonian. Equation 8 was derived such that the kinetic energy is separated from the potential energy. Therefore, only the kinetic energy terms that depend on the overlap squared are adjusted by making use of the parameter, k, in equation 8. Additionally, Carroll and McGlynn[25] have shown that the value of k necessary to match SCF off-diagonal elements in a series of test calculation is, on the average equal to one; however, any individual k factor may be very different from one. Consequently, k was set equal to one except in the e_g matrix, where it was determined through a series of test calculations on TiF_6^{3-} by allowing it to vary until the orbital energy difference of the ligand field orbitals equaled the experimental value of 10 Dq in TiF_6^{3-}. The value of $k = 3.5$ in the e_g matrix, determined in the test calculations on TiF_6^{3-} was used in subsequent calculations for the transition metal fluorides, which are listed under Calculation II in Table IV, and chlorides, which are listed in Table V. It is emphasized that the difference between the calculations performed with $k = 1$ and $k = 3.5$ are not consequential except for the calculation of 10 Dq. Thus, the atom charges are not significantly different and the spin densities are in agreement with experiment in the calculations performed both with k–1 and 3.5. The computed quantities listed in Tables I–IV are for $k = 3.5$, in Table IV and V the values listed under calculation II are for $k = 3.5$.

TABLE V. Comparison of Experimental and Theoretical Value of 10 Dq and Charge Transfer Transitions (eV).

Complex	10 Dq			First Allowed L→M Charge Transfer	
	Obs.	Calc			
		This Work	Other Work	Obs.	Calc.
$MnCl_6^{4-}$	1.0[a]	1.3	–	–	4.2
$MnCl_4^{2-}$	0.5[b]	0.5	0.5	3.8[b]	4.0
VCl_6^{2-}	~2	2.7	–	–	3.1
VCl_4	1.1[c]	0.4	1.0	3.0[d]	4.5

[a] J. W. Stout, *J. Chem. Phys., 33,* 303 (1960). [b] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Am. Chem. Soc., 84,* 167 (1962). [c] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw–Hill, New York, N.Y., 1962, p. 228. [d] C. Dyikgnaaf, *Spectrochim. Acta, 21,* 769 (1965).

The computed values of 10 Dq for the transition metal fluorides listed under Calculation II in Table IV are in the correct order and in most cases the agreement with experiment is quite food. The 10 Dq values calculated by Fenske *et al.* are also given in Table IV. In all cases, the 10 Dq values given by our method are very close to and in as good agreement with experiment as those of Fenske *et al.* The computed values of 10 Dq for the transition metal chlorides are given in Table V. These results were obtained using the same parameters that were used for the transition metal fluorides. The results, except for those obtained for VCl_4, are in good agreement with experiment and for $MnCl_4^{2-}$ in good agreement with the results of Fenske and Radtke.[26] Since VCl_4 and $MnCl_6^{4-}$ are according to the results the most covalent of the complexes, it is not surprising that the largest discrepancy with experiment occurs in these complexes since many of the point charge approximations made are in the Zeroth-order approximation and are probably least valid for these complexes. Furthermore, in these two cases, it should be expected that another value of k would be necessary to successfully calculate 10 Dq by scaling the off-diagonal elements. The calculated spin densities and 10 Dq for both of these complexes are so close to those obtained by Fenske *et al.*[5] that they argue against the contention[5] that reasonable results cannot be obtained for transition metal complexes using the Wolfsberg–Helmholz off-diagonal element approximation.

Moreover, the m-MWH calculations performed here allow interpretation of charge transfer spectra whereas those of Fenske *et al.* do not. The calculated energies for the first X→M charge transfer transitions are compared to experiment in Table IV for the fluorides, and in Table V for the chlorides. The experimental data for the first charge transfer transitions are based on results obtained from the band onset of the maxima and are not very precise. The first two allowed ligand to metal charge transfers transitions in the octahedral complexes, $2t_{2g} \leftarrow 3t_{1u}$ and $2t_{2g} \leftarrow t_{2u}$, are computed to have nearly the same energy but the $2t_{2g} \leftarrow 3t_{1u}$ always is at slightly lower energy. Consequently, the experimental band onsets are assigned to the $2t_{2g} \leftarrow 3t_{1u}$ transition. However, the intensity of the charge transfer transition is probably derived from the $2t_{2g} \leftarrow t_{2u}$ transition. The charge transfer transitions occurring in the two tetrahedral complexes are assigned to the $2e \leftarrow t_1$ transition. The computed transitions energies are in all cases, correctly larger than the observed band onsets, and also are consistent with the trends in the experimental data. These transitions energies could, presumably, be brought into closer numerical agreement with experiment by the inclusion of configuration interaction.

A recent application of the m-NWH method has been made in comparing the calculated effective atomic charges and population in FeF_6^{3-} and CrF_6^{3-} with those obtained by x-ray emission data.[27] The agreement between the calculated and observed data was found to be very good indeed.

The m-MWH method of calculation provides some insight into previous MWH calculations. The form of what would correspond to an F factor in the off-diagonal elements that we have used is very similar to that used for the F_σ factor in the calculations of Basch *et al.*[9] Moreover, the value of the parameter k in the e_g matrix brings the values calculated by the expression corresponding to the F factor in our calculation very close to the value given by the empirical expression of Basch *et al.* for F_σ. In many previous MWH calculations[9] on transition metal complexes, reasonable results were obtainable only if the ligand diagonal elements were arbitrarily set to a value close to the VOIP of the neutral atoms. The effect of the terms added to the orbital energy in equation 6 is largely to cancel out the charge dependence of the ligand VOIP. Thus, the additional terms in equation 6 obtained from a systematic derivation justify the previous practice of arbitrarily setting the ligands at their neutral atom value.

References

1 M. Wolfsberg and L.J. Helmholz, *J. Chem. Phys., 20,* 837 (1952).
2 D.R. Davies and G.A. Webb, *Coord. Chem. Rev., 6,* 95 (1971).
3 D.G. Carroll, A.T. Armstrong and S.P. McGlynn, *J. Chem. Phys., 41,* 1865 (1966).
4 G. Leonhardt and A. Meisel, *J. Chem. Phys., 52,* 6189 (1970).
5 R.F. Fenske, K.G. Caulton, D.D. Radtke and C.C. Sweeney, *Inorg. Chem., 5,* 951 (1966); *5,* 960 (1966).
6 (a) A. Dutta–Ahmed and E.A. Boudreaux, *Inorg. Chem., 12,* 1590 (1973); (b) *ibid,* pg. 1597.
7 L.E. Harris, Doctoral Dissertation, Louisiana State University in New Orleans (1969).
8 I.H. Hillier, *J. Chem. Soc., A,* 878 (1969).
9 H. Basch, A. Viste and H.B. Gray, *J. Chem. Phys., 44,* 10 (1966).
10 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.
11 C.J. Ballhausen and H.B. Gray, "Molecular Orbital Theory", Benjamin, New York, N.Y., 1965.
12 K. Rudenberg, *J. Chem. Phys., 34,* 905 (1961).
13 H. Basch, A. Viste and H.B. Gray, *Theoret. Chim. Acta, 3,* 458 (1965).
14 P.O. Lowdin, *Phys. Rev., 97,* 1474 (1955).
15 R.S. Mulliken, *J. Chem. Phys., 23,* 1841 (1955).
16 L.E. Harris and E.A. Boudreaux, to be published.
17 E.W. Stout, Jr. and P. Politzer, *Theoret. Chim. Acta, 13,* 379 (1968).
18 J.W. Richardson, W.C. Nieuwport, R.R. Powell and W.F. Edgell, *J. Chem. Phys., 36,* 1057 (1962); J.W. Richardson, R.R. Powell and W.C. Nieuwport, *J. Chem. Phys., 38,* 796 (1963).
19 E. Clementi, *J. Chem. Phys., 40,* 1944 (1964); IBM Report RJ–256.
20 D.G. Carroll, A.T. Armstrong and S.P. McGlynn, *J. Chem. Phys., 44,* 1865 (1966).
21 L.C. Cusachs, *J. Chem. Phys., 42,* 1575 (1965).
22 C.K. Jørgensen, *Int. J. Quantum Chem., 1,* 191 (1967).
23 J.P. Dahl and C.J. Ballhausen, "Molecular Orbital Theories of Inorganic Complexes" in "Advences in Quantum Chemistry", Vol. 4, Per-Olov Lowdin Ed., Acedemic Press, New York, N.Y., 1968.
24 G. Blyholder and C.A. Coulson, *Theoret. Chim. Acta, 10,* 316 (1968).
25 D.G. Carroll and S.P. McGlynn, *J. Chem. Phys., 45,* 3827 (1966).
26 R.F. Fenske and D.D. Radtke, *Inorg. Chem., 7,* 479 (1968).
27 L.E. Harris and E.A. Boudreaux, *Chem. Phys. Letters, 20,* 434 (1973).