

lanthanide ions to indicate the coordination of the aqueous ion appears applicable to aqueous solutions. Although a strictly qualitative effect, there are published examples^{24,25} where the coordination of the Nd³⁺

ion can be inferred from the shape of the absorption bands. Application to other lanthanide ions, and to other systems, might permit a better understanding of lanthanide coordination behavior.

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Parameter-Free Molecular Orbital Calculations

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A method is outlined for the calculation of electronic energy levels of transition metal complexes. The procedure is completely specified for a given choice of atomic wave functions and does not involve the use of arbitrary parameters for the evaluation of the matrix elements. The method is used to calculate the energies and molecular orbitals of four octahedral and seven tetrahedral chloro complexes. The results are evaluated in terms of Δ values, nephelauxetic B and β values, bond orders, overlap populations, stretching frequencies, and chlorine nqr results. The calculations substantiate increased covalency as a function of formal oxidation state by comparison of overlap populations with stretching frequencies and the correlation between calculated and experimental nephelauxetic β values. For different transition metals in the same oxidation state, an increase in covalent character with increasing atomic number is observed.

Introduction

In our recent publications,^{2,3} we outlined a calculational procedure for estimation of the relative positions of the electronic energy levels of transition metal complexes. At that time, computational limitations necessitated the introduction of two parameters, R_σ and R_π , which were employed in the estimation of sums of two-center electrostatic interaction integrals. These two parameters were held constant for the series of fluoride complexes then under investigation. In this report, we shall indicate that not only was the assumption of constant R values a reasonable one, but also that it is possible to carry out the molecular orbital calculations without the introduction of these parameters. That is, for a proper basis set of atomic wave functions, we shall propose a calculational method which is completely specified. The procedure has been tested by application to four octahedral and seven tetrahedral chloride complexes of first-row transition metals. The accord achieved between experimental observables and the values calculated from the theoretical results are very satisfying and indicate that the calculational model holds promise for the elucidation of the electronic structures of metal complexes.

Matrix Elements of the Secular Determinant

The Diagonal Element.—As in our previous work,^{2,3} the diagonal terms involving the metal wave functions, χ_i , are given by

$$\langle \chi_i | \mathcal{H} | \chi_i \rangle = \epsilon_\chi(q_M) - \sum_{j=1}^n q_j (1/r_j | \chi_i \chi_i \rangle) \quad (1)$$

(1) Abstracted in part from the thesis submitted by D. D. Radtke in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

(2) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *Inorg. Chem.*, **5**, 951 (1966).

(3) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *ibid.*, **5**, 960 (1966).

where $\epsilon_\chi(q_M)$ is the orbital energy of the metal electron in the free ion of charge q_M , and the second term is the crystal field potential due to the ligand point charges, q_j . Both q_M and q_j are evaluated by means of the Mulliken electron population analysis⁴ and it is required that self-consistency be established between the initial choices and final calculated values of q_M and q_j .

The ligand diagonal terms, exclusive of ligand-ligand interaction, have the form

$$\langle \phi_i | \mathcal{H} | \phi_i \rangle = \epsilon_{\rho_{i1}}(q_1) - q_M (1/r_M | \rho_{i1} \rho_{i1} \rangle) + \sum_{j=2}^n (1/r_j | \rho_{i1} \rho_{i1} \rangle) \quad (2)$$

where $\epsilon_{\rho_{i1}}$ is the orbital energy of the electron in the i th orbital of ligand 1 and of charge q_1 , and the second and third terms constitute the crystal field potential due to the metal ion of charge q_M and the other ligands with charges q_j .

The concepts which led to the formulations given in eq 1 and 2 have been previously outlined.^{2,3,5} It is worthwhile to note that while eq 1 and 2 are developed from consideration of the rigorous treatment of one-electron energies of closed-shell systems, the proposed method is semiempirical and deviates from rigor for the sake of computational simplicity. Furthermore, in our previous work we employed the commonly used simplification that the orbital energies, ϵ_{χ_i} , could be obtained from the experimental values of the valence-state ionization energies (VSIE). This approximation has the undesirable feature that variations in the choice of the basis functions have no effect on the orbital

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

(5) 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., 1958.

energies, as should be the case. Since the core functions, *e.g.*, 1s through 3p inclusive on the metal, do not vary appreciably as changes occur in the outer orbitals and since the wave functions for these orbitals are reasonably well known, it was decided to determine the orbital energies, ϵ_{χ_i} , by the actual evaluation of the appropriate kinetic energy, nuclear attraction, and one-center electrostatic interaction integrals. Thus, as should be the case, when the wave function associated with an orbital is varied, not only the overlap and other multicenter integrals change, but the value of the orbital energy is also affected. Such considerations have not always been taken into account in previously reported calculational methods.⁶⁻⁸

The Off-Diagonal Elements.—The off-diagonal element involving the symmetry-adapted ligand wave function, ϕ_b , can be written in terms of the single-ligand wave functions, ρ_{il} . Thus, $(\phi_b|\mathcal{H}|\chi_i) = C(\rho_{il}|\mathcal{H}|\chi_i)$, where C is the same group factor which relates the diatomic overlap $S(\rho_{il}, \chi_i)$ to the group overlap, $G(\phi_b, \chi_i)$. In terms of the single-ligand wave function, the matrix element can be approximated by

$$(\rho_{il}|\mathcal{H}|\chi_i) = \epsilon_{\chi_i}(q_M)S(\rho_{il}, \chi_i) - \sum_{j=2} q_j(1/r_j|\rho_{il}\chi_i) + (\rho_{il}|V_1|\chi_i), \quad (3)$$

where the middle term on the right-hand side of eq 3 consists of three-center nuclear attraction integrals multiplied by the self-consistent ligand charge, q_j . The final term in eq 3 is given by

$$(\rho_{il}|V_1|\chi_i) = \sum_k \bar{b}_k \{ 2(\rho_{k1}\rho_{k1}|\rho_{il}\chi_i) - (\rho_{k1}\rho_{il}|\rho_{k1}\chi_i) \} - Z_1(1/r_1|\rho_{il}\chi_i) \quad (4)$$

In our previous work,^{2,3} it was necessary to approximate eq 4 by the relationship

$$(\rho_{il}|V_1|\chi_i) = [R_a(6 - q_1) - Z_1](1/r_1|\rho_{il}\chi_i) \quad (5)$$

where R_a was a "reduction factor" dependent upon ρ_{il} and χ_i but fixed for the complete series of fluoride complexes under study. In the present computations, we have been able to eliminate the use of arbitrary R values and thus free the calculations of all parameters. For a given choice of basis set wave functions, the computations and results are completely specified.

The elimination of the R parameters is made possible by the use of eq 4 rather than eq 5 for the evaluation of the off-diagonal elements. The former equation requires the determination of the two-center electrostatic interaction integrals.⁹ Computationally, such integrals are time consuming and expensive to obtain. Fortunately, for a series of related complexes, we have obtained evidence¹⁰ that the electrostatic interactions given in eq 4 can be quite accurately approximated by

the relationship given by eq 5. That is, once the sum of two-center electrostatic interactions given by eq 4 has been determined for one complex, say CrCl_6^{3-} , it is possible to evaluate the R values which fit the relation

$$R_a(6 - q_1)(1/r_1|\rho_{il}\chi_i) = \sum_k \bar{b}_k \{ 2(\rho_{k1}\rho_{k1}|\rho_{il}\chi_i) - (\rho_{k1}\rho_{il}|\rho_{k1}\chi_i) \} \quad (6)$$

and these R values are essentially constant when one varies the central metal, internuclear distance, and even symmetry. While this is detailed more completely elsewhere,¹⁰ it is worthwhile to reproduce some of the calculated R values to verify this important result. Table I displays the R values calculated by eq 6 for a group of chloride and fluoride complexes. Note the variations in symmetry and ligand species. The results indicate first of all that the assumption of constant R values from complex to complex which was made in our earlier calculations^{2,3} was a reasonable one. Secondly, eq 6 provides a method for the approximation of the sums of two-center electrostatic interaction integrals in terms of the corresponding nuclear attraction integrals which are easier to compute. It should be emphasized that while eq 6 again incorporates R values into the computations, these are *not* parameters to be varied but are totally determined by the exact calculation of the interaction integrals for at least one complex in a series. Because the approximations of eq 6 hold, the reintroduction of R values is for computational simplicity only and is not an inherent part of the proposed method of calculation.

It might also be noted that while the values of $R(3d\sigma, 2p\sigma)$ and $R(3d\pi, 2p\pi)$ for the fluoride complexes in Table I are close to the value of $R_\sigma = R_\pi = 0.87$ used in our previous works,^{2,3} they are not identical. Use of $R_\sigma = 0.84$ and $R_\pi = 0.89$ as suggested by Table I in a calculation identical with our previous work would yield similar wave functions but somewhat larger Δ values than previously obtained. However, the previous calculations did not involve the same size basis set as is used in the present work. This important factor is considered in detail in the next section.

TABLE I
R VALUES AS A FUNCTION OF THE COMPLEX^a

	TiCl ₄ (2.18 Å)	CrCl ₆ ³⁻ (2.34 Å)	FeCl ₆ ³⁻ (2.38 Å)	CrF ₆ ³⁻ (1.93 Å)	NiF ₆ ³⁻ (2.10 Å)
$R(3d\sigma, ns)$	0.78	0.76	0.77	0.76	0.79
$R(3d\sigma, np\sigma)$	0.84	0.83	0.84	0.83	0.86
$R(3d\pi, np\pi)$	0.88	0.88	0.90	0.88	0.90

^a All values calculated from eq 6 for the totally ionic case, *i.e.*, $q_1 = -1$ and $\bar{b}_k = 1$ for $k = ns, np$.

Calculational Considerations

As indicated by the results in Table IV of ref 2, our previous method required that the basis set used in the calculations consist of the 3d, 4s, and 4p orbitals for the first-row transition metals and the 2p fluorine ligand orbitals. At that time we showed that inclusion of the fluorine 2s orbitals increased $\Delta = 10Dq$,

(6) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).

(7) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

(8) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 369 (1967).

(9) The two-center electrostatic interaction program for the CDC 3600 computer was made available to us through the kindness of Professor F. A. Matson, Molecular Physics Group, University of Texas, Austin, Texas.

(10) D. D. Radtke and R. F. Fenske, *J. Am. Chem. Soc.*, **89**, 2292 (1967).

an effect which was not adequately corrected by inclusion of the free-ion 4d functions on the metal. We noted that the minimal reduction of Δ by the 4d orbitals was probably not because higher orbitals are ineffective but rather because of the form of the particular 4d functions obtained by minimization of the free-ion energy. That is, the *free-ion* 4d functions may not be the most appropriate functions for a *molecular* calculation.¹¹ Specifically, one notes in Table I of ref 2 that the free-ion 4d functions are so diffuse that the 4d σ -2p σ overlap is small and *negative*, while the 4d π -2p π overlap is very large.

The inability of our previous method to incorporate the ligand s orbitals imposes some limitations on its usefulness. For example, in dealing with NH₃ or CO ligands the inclusion of the σ -bonding ligand 2s orbitals is obviously desirable. Consequently, in the present work we decided not to restrict ourselves completely to the wave functions of the free ion at self-consistent charge. Of course, this raises the question as to how the wave functions should be chosen. Since this is a semiempirical calculation, there is no guarantee that the set which yields the lowest total energy, even if it could be easily calculated, is the proper choice. Thus, it was decided to formulate the wave functions in a systematic way on the basis of two considerations, both designed to maximize the contributions of a wave function to an occupied orbital.

Two factors influence the degree of participation of a metal wave function in a molecular orbital—the energy of the orbital relative to the ligand orbital energy and the overlap of the metal wave function with the ligand function. For illustrative purposes, assume an electron population analysis resulted in a metal configuration of 3d⁵4s¹4p¹. (Such a configuration might be apropos to the iron in FeCl₆³⁻ with a self-consistent charge of +1.0.) Because of the high occupancy of the 3d orbitals, alteration of the 3d radial wave functions markedly changes the 3d orbital energy. Examination of calculated orbital energies shows that the lowest orbital energy is achieved when the wave function corresponds to that of the free ion, ignoring the outer-orbital 4s and 4p contributions. Attempts to vary the wave function in order to increase overlap with ligand orbitals result in rapidly increasing orbital energies and decreasing participation of the metal orbital in the bonding orbitals of the complex. Thus, as in previous work,² the chosen 3d functions were made to correspond to the effective charge on the metal. In general, as will be shown, the effective charge for the metal 3d orbitals was approximately +2.0.

Similarly, for the chloride complexes studied in this work the effective ligand charges are reasonably close to -1.0 so that chloride functions were used. For computational convenience, minimum basis set chloride functions were constructed such that they would have maximum overlaps with the many-term functions of Clementi, *et al.*^{12,13} The final forms of these and the

metal basis functions have been filed with the American Documentation Institute.¹⁴

Because of their lower occupancy, alteration of the radial functions for the 4s and 4p metal orbitals does not result in drastic changes in the calculated orbital energies but does cause substantial changes in the overlap integrals. Consequently, it was decided that the metal 4s, 4p, and 4d wave functions would be constructed such that they would have a maximum overlap interaction with the ligand p orbitals. Since the 4p and 4d functions are capable of both σ and π bonding, a compromise between the two was effected as indicated below.

Construction of the 4s, 4p, and 4d Functions.—The form of the outer 4s and 4p metal orbitals used in this work is similar to that given by Richardson, *et al.*,^{15,16} except that Richardson's criterion was minimum free-ion energy whereas ours is maximum overlap with the ligand p functions. The metal functions are constructed from the smallest possible number of Slater-type orbitals which can be used for orthonormal functions. Thus

$$\psi(4s) = a_1\phi_{1s}(\alpha_1) + a_2\phi_{2s}(\alpha_2) + a_3\phi_{3s}(\alpha_3) + a_4\phi_{4s}(\alpha_4) \quad (7)$$

where $\phi_{ns}(\alpha_n) = N_n r^{n-1} e^{-\alpha_n r}$. The orbital exponents α_1 , α_2 , and α_3 are the same as those used for Richardson's¹⁴ $\psi(1s)$, $\psi(2s)$, and $\psi(3s)$ core functions of the metal. For a given value of α_4 , the coefficients a_1 through a_4 in $\psi(4s)$ are completely specified by the orthogonality of the function to the core functions and the normalization requirement. By variation of α_4 , that $\psi(4s)$ function can be found such that $S(\psi_M(4s), \psi_{Cl}(3p\sigma))$ is a maximum. Where known, the internuclear distances used in the overlap calculations corresponded to the experimental distances for the complexes.¹⁷ In those cases where the distances in the complexes have not been determined, the values for corresponding species were used.¹⁸

In a similar way, the 4p functions were constructed from

$$\psi(4p) = b_1\phi_{2p}(\beta_1) + b_2\phi_{3p}(\beta_2) + b_3\phi_{4p}(\beta_3) \quad (8)$$

Again, β_1 and β_2 are the same orbital exponents as the 2p and 3p core functions¹⁵ and the coefficients b_1 to b_3

(12) E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, *Phys. Rev.*, **133**, A1274 (1964).

(13) E. Clementi, IBM Research Paper, RJ-256, 1963.

(14) Material supplementary to this article has been deposited as Document No. 9839 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$2.50 for photoprints, or \$1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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

(16) J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *ibid.*, **38**, 798 (1963).

(17) (a) TiCl₄: M. Kimura, K. Kimura, M. Aoki, and S. Shibata, *Bull. Chem. Soc. Japan*, **29**, 95 (1956); (b) VCl₄: W. N. Lipscomb and A. G. Whittaker, *J. Am. Chem. Soc.*, **67**, 2019 (1945); (c) FeCl₄⁻: B. Zaslav and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957); (d) CoCl₄²⁻: B. N. Figgis, M. Gerlock, and R. Mason, *Acta Cryst.*, **17**, 506 (1964); (e) NiCl₄²⁻: P. Pauling, Ph.D. Thesis, University College, London, 1960.

(18) (a) MnCl₄²⁻ and FeCl₄²⁻: see ref 6; (b) TiCl₆³⁻ and VCl₆³⁻ from TiCl₃ and VCl₃: W. Klemm and E. Krose, *Z. Anorg. Chem.*, **253**, 218 (1947); (c) CrCl₆³⁻ from CrCl₃: B. Morosin and A. Narath, *J. Chem. Phys.*, **40**, 1958 (1964); (d) FeCl₆³⁻ from FeCl₃: N. Wooster, *Z. Krist.*, **83**, 35 (1932).

(11) See, for example, the Hartree-Fock calculations on HF by E. Clementi, *J. Chem. Phys.*, **36**, 33 (1962).

are fixed for a given value of β_3 by the orthonormality requirements. However, here β_3 will not be the same for maximum σ and π overlap. Since both of these interactions are important, it was decided to use an average β value, *i.e.*

$$\beta_3 = [\beta_3(\sigma) + \beta_3(\pi)]/2$$

where $\beta_3(\sigma)$ and $\beta_3(\pi)$ are the corresponding values for maximum σ and π overlaps.

The 4d wave functions were made orthogonal to the previously mentioned 3d functions. Since these latter functions are the sum of two Slater functions, *i.e.*

$$\psi(3d) = C_1\phi_{3d}(\gamma_1) + C_2\phi_{3d}(\gamma_2) \quad (9)$$

the 4d functions are of the form

$$\psi(4d) = C_3\psi(3d) + C_4\phi_{4d}(\gamma_3) \quad (10)$$

As in the case of the 4p functions, the value of γ_3 is the average of the ones required for maximum σ and π overlap

$$\gamma_3 = [\gamma_3(\sigma) + \gamma_3(\pi)]/2 \quad (11)$$

The general effect of using the average for β_3 and γ_3 is to contract the 4p and 4d wave functions relative to Richardson's values for the free ions. The final forms of all of the metal wave functions used for the complexes in this work have been deposited with the ADI.¹⁴

It should be noted that since the 4d wave function is orthogonal to the 3d, there is no cross-term between them in the G_{ij} matrix, *i.e.*, $S(\psi_{3d}, \psi_{4d}) = 0$. However, a term does appear in the H_{ij} matrix. Even though, in the approximations used, $(\psi(3d)| -1/2\Delta + V_M|\psi(4d)) = 0$, the interactions with the ligand centers must be evaluated. That is, $(\psi(3d)| \sum_{j=1} V_j|\psi(4d)) \neq 0$.

Effect of Basis Set Size.—Table II contains a comparison between two sets of energy levels calculated for CrCl_6^{3-} . Those in column 2 were computed using the metal 3d, 4s, and 4p and the chloride 3s and 3p orbitals. Those in column 3 were obtained using the same orbitals plus the specially constructed 4d orbital. The results are striking and their significance is apparent.

Note that the self-consistent charge and orbital coefficients in the two sets of calculations are quite similar. Indeed the only substantial differences between the two calculations occur in the relative positions of the $2t_{2g}$, $3e_g$, $3t_{2g}$, and $4e_g$ orbitals. However, the separation between the first two of these is $\Delta = 10Dq$, which is generally used as a major criterion for judging the worth of a calculational procedure! Note also the drastic alteration in the values of the $3t_{2g}$ and $4e_g$ levels. This reaffirms our earlier contention² that the value of the highest level for a given representation is subject to substantial variation. In the absence of the 4d functions, the highest levels for the t_{2g} and e_g representations are those associated with Δ . As previously mentioned, the sensitivity of these levels required that ligand s orbitals also be omitted from the calculational basis set. With the introduction of the appropriate 4d functions, such an omission is no longer necessary.

TABLE II
EFFECT OF 4d ORBITALS ON CrCl_6^{3-} ENERGY LEVELS^a

	Without 4d orbital interaction	With 4d orbital interaction
$4e_g(4d)$	22.21 ^b	91.32
$3t_{2g}(4d)$	19.48 ^b	49.58
$3e_g$	7.90	5.30
$2t_{2g}$	4.62	3.91
t_{2u}	-0.97	-1.00
t_{1g}	-0.97	-1.00
$3t_{1u}$	-1.19	-1.24
$1t_{2g}$	-1.59	-1.76
$2t_{1u}$	-2.28	-2.35
$2a_{1g}$	-3.63	-3.74
$2e_g$	-3.72	-4.20
$1e_g$	-17.45	-17.78
$1t_{1u}$	-18.06	-18.18
$1a_{1g}$	-18.46	-18.60
Charge	+1.75	+1.80
Δ^c	3.28	1.39
3d coeff $2t_{2g}$	0.96	0.93
4d coeff $2t_{2g}$	0.00	-0.09

^a All energies are in electron volts. ^b The 4d orbital energy without interaction. ^c The experimental Δ value is 1.57 eV.

This ability to include the ligand s orbitals should be substantially more important when one deals with ligand systems where the bonding to the metal might incorporate appreciable s character.

It should be emphasized that the introduction of the 4d orbitals into the calculation does not necessarily mean that there is substantial contribution by these atomic orbitals to the $2t_{2g}$ and $3e_g$ molecular orbitals. As indicated by the orbital coefficients given in Table II, the 4d contribution to either molecular orbital does not exceed 5%.

Electron Distribution.—As in our previous work, the charge on the metal ion was required to be self-consistent with that obtained *via* the Mulliken electron population analysis⁴ of the occupied molecular orbitals. Two sets of calculations were performed. In the first, method A, only the participation of the metal 3d orbitals in the molecular orbitals was used to accumulate electron density on the metal while in the second, method B, all of the orbitals in the metal basis set were included. As with our fluoride results, the calculations indicate that the two methods of electron distribution give very similar results and that for most purposes either technique can be employed as long as the same method is used for all of the complexes in a series. Some typical values are given in Table III. The results reemphasize the fact that the charge on the metal is primarily a technique to control the calculation and is not an appropriate measure of covalent character. The 3d orbital coefficients obtained by the two distributions are quite similar, despite the drastic differences in self-consistent charges. However, because the metal 3d and 4d functions belong to the same irreducible representations, it is perhaps less permissible to say that only the 3d coefficient determines the metal participation within a molecular orbital. Furthermore, when only the 3d population density is used, a dilemma arises as to the distribution of the metal charge density

TABLE III
VALUES AS A FUNCTION OF ELECTRON DISTRIBUTION:
METHOD A, 3d ORBITALS ONLY;
METHOD B, ALL METAL ORBITALS

	TiCl ₄	MnCl ₄ ²⁻	CoCl ₄ ²⁻	TiCl ₆ ³⁻	CrCl ₆ ³⁻
Metal charge					
A	1.70	1.67	1.55	1.86	1.80
B	0.33	0.20	0.09	0.60	0.44
Δ value ^a					
A	1.10	0.52	0.50	1.68	1.39
B	1.02	0.45	0.48	1.65	1.47
e coefficient ^b					
A	0.91	0.98	0.93	0.94	0.92
B	0.94	0.99	0.98	0.94	0.93
t ₂ coefficient ^b					
A	0.90	0.97	0.93	0.96	0.93
B	0.92	0.98	0.95	0.98	0.96

^a All Δ values are given in electron volts. ^b The e and t₂ coefficients refer to the coefficients of the 3d orbitals in those antibonding molecular orbitals generally associated with the metal orbitals.

associated with those higher metal orbitals not included in the population analysis. The division of this charge density between the ligand s and p orbitals is not uniquely specified and the manner in which one distributes the charge affects both the ligand electron configuration and possible charge asymmetry on the ligands. This latter consideration is important when one attempts to correlate ligand orbital charge densities with nqr data. The usual population analysis involving all orbitals avoids this problem. Consequently, it was decided to control the calculations by means of the self-consistent charge as determined by the Mulliken distribution involving all of the metal orbitals.

Ligand-Ligand Interaction.—In octahedral symmetry, the ligand π -bonding orbitals are basis functions for the irreducible representations t_{1u}, t_{2g}, t_{1g}, and t_{2u}. The latter two representations are nonbonding insofar as interactions with the metal orbitals are concerned, while the t_{1u} and t_{2g} functions can interact with the metal p and d orbitals, respectively. Under such considerations, a qualitative order of the four sets of ligand π -energy levels could be t_{1g} = t_{2u} > t_{1u} > t_{2g}. However, recent experimental results¹⁹ on the Faraday effect in IrCl₆²⁻ suggest that in that complex the order might be t_{1g} > t_{1u} > t_{2u} > t_{2g}. Such an order can most easily be explained as a consequence of the effects of ligand-ligand interactions. Hence, it would be desirable to be able to incorporate such interactions properly into the calculations.

Inclusion of ligand-ligand interactions have a two-fold effect on the matrix elements of the secular determinant. First, it removes the accidental degeneracy of certain diagonal matrix elements. For example, without ligand-ligand interaction the ligand π orbitals t_{1u}, t_{2u}, t_{1g}, and t_{2g} have the same energy levels prior to interaction with the metal orbitals. Under the influence of ligand-ligand interaction, the values of the diagonal elements are altered as indicated by the partial energy

(19) P. N. Schatz, University of Virginia, Charlottesville, Va., private communication.

level diagram for VCl₆³⁻ in Figure 1. Second, certain off-diagonal matrix elements between ligand orbitals of the same representation which were zero prior to ligand-ligand interaction can now possess nonzero values. For example, the matrix element in octahedral symmetry between the σ - and π -bonding p orbitals belonging to the t_{1u} representation becomes $\mathcal{H}(\sigma, \pi)_{t_{1u}} = \sqrt{2}[\mathcal{H}(\sigma_1, \sigma_2) - \mathcal{H}(\pi_1, \pi_2)]N_\sigma N_\pi$, where the scripts 1 and 2 refer to adjacent ligand atoms and the N's are the normalization factors for the ligand symmetry adapted wave functions.

The evaluations of the resultant terms for both the diagonal and off-diagonal elements were carried out in a manner analogous to that for metal-ligand interactions. Our early results were greeted with enthusiasm. The ordering of the calculated energy levels for VCl₆³⁻ were in accord with that suggested by the experimental results on IrCl₆²⁻. As indicated by Figure 1, the only levels appreciably altered were those associated with the occupied ligand π orbitals. Such features as the self-consistent charge and the coefficients in the molecular orbitals were substantially the same for the calculations with and without ligand-ligand interaction.

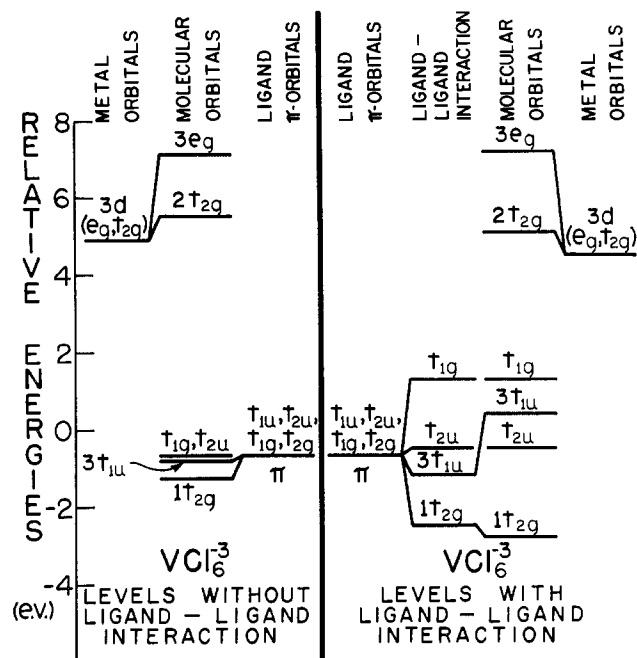


Figure 1.—Energy levels for VCl₆³⁻ with and without ligand-ligand interaction.

As additional computations were completed, our initial enthusiasm faded. One of the characteristic features of calculations carried out over a series of complexes MX₆³⁻, where M has an increasing number of d electrons, is a slowly decreasing separation between the metal d orbitals and the ligand π orbitals prior to bonding. Inclusion of ligand-ligand interaction raised the filled nonbonding t_{1g} level closer and closer to the partially occupied antibonding 2t_{2g} level until, finally, in our calculation on FeCl₆³⁻ the 2t_{2g} was below the t_{1g} level. This impossible situation has an obvious ex-

planation which becomes apparent on careful examination of the matrix elements. While the method qualitatively suggests the proper direction that the effect of ligand–ligand interaction should have, in its present technique of approximations it *overestimates* the importance of the interactions. For example, in VCl_6^{3-} the separation of the ligand diagonal terms for the t_{1g} and t_{2g} π orbitals *via* ligand–ligand interaction is calculated to be 3.78 eV, while the alteration of the metal 3d level as a result of σ -bonding interaction with the ligands is only 2.74 eV. It is extremely unlikely that ligand–ligand interactions should be more important than metal–ligand interactions in this respect.

The reason for the failure of this technique reasonably to assess ligand–ligand interaction lies in the approximations required by the computational procedure. We have already asserted in connection with metal–ligand electrostatic interactions, eq 3, that point-charge approximations for charge densities on certain centers were reasonable only if the charge density was outside the region of overlap of the two wave functions.²⁰ In the evaluation of ligand–ligand interactions, terms of the sort $(\rho_{i1}|V_M|\rho_{ij})$ arise. As illustrated crudely in Figure 2, even though M and j are not on ligand center 1 and $M \neq j$, it is still possible that the charge density V_M is in the region of overlap between ρ_{i1} and ρ_{ij} . In such cases, it is not reasonable to approximate the term by the integral $q_M(1/r_M|\rho_{i1}\rho_{ij})$ but it should be evaluated by the more complex relationship

$$(\rho_{i1}|V_M|\rho_{ij}) = \sum_k \bar{b}_k \{ 2(\chi_{kM}\chi_{kM}|\rho_{i1}\rho_{ij}) - (\chi_{kM}\rho_{i1}|\chi_{kM}\rho_{ij}) \} - Z_M(1/r_M|\rho_{i1}\rho_{ij}) \quad (12)$$

Equation 12 requires the evaluation of three-center two-electron electrostatic interaction integrals involving metal 3d and higher orbitals. At the present time, such computations are complex and time consuming. The necessity to sum such integrals over the metal orbitals of principal quantum numbers 3 and 4 makes their evaluation a prohibitive task. Consequently, we had no recourse but to eliminate the inclusion of ligand–ligand interaction from consideration in order to maintain the parameter-free character of the calculations. While this is an unfortunate limitation it does not seriously restrict the applicability of the method. As has already been mentioned, the inclusion of ligand–ligand interaction does not substantially alter the values of the orbital coefficients. The only energy levels affected by ligand–ligand interaction are those associated with the ligand π orbitals. This will affect the estimates of the energies associated with electronic transitions from these orbitals, *i.e.*, the ligand to metal charge-transfer transitions. Since such transitions involve a substantial alteration of charge distribution between the ground and excited states, it is uncertain that energy values based on one-electron separations in the ground state would achieve a high degree of correspondence

(20) For example, $(\rho_{i1}|V_j|\chi_i)$ can be approximated by $q_j(1/r_j|\rho_{i1}\chi_i)$ if $j \neq 1$ but requires the use of either eq 4 or 5 if $j = 1$.

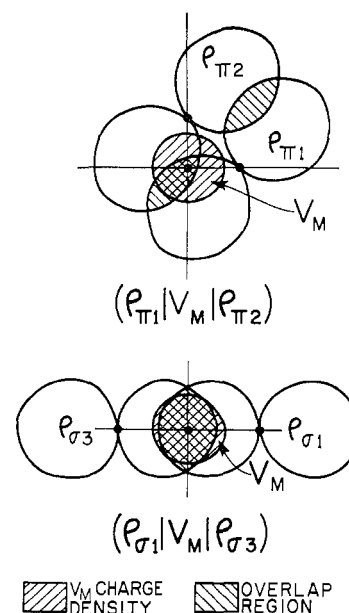


Figure 2.—Overlapping charge densities in ligand–ligand interactions.

with experimental values in any event. Even when ligand–ligand interaction is excluded, qualitative correlations between observed charge-transfer bands and the ground-state energy level separations can be made, as long as exact agreement is not expected.

Results and Discussion

Eigenvalues.—The method outlined in the previous sections was applied to four octahedral and seven tetrahedral chloride complexes of first transition row metals. The coefficients associated with the eigenfunctions have been deposited with the ADI.¹⁴ The resultant eigenvalues along with the calculated and experimental values of $10Dq$ are given in Tables IV and V. The agreement between the $10Dq$ values is extremely gratifying particularly when one recalls that the method is devoid of arbitrary parameters which can be adjusted. Since the estimates of $10Dq$ are based upon approximate calculational methods of the ground-state energies, whereas a rigorous calculation would involve the difference between ground and excited states, it would be misleading to overemphasize the significance of the correlation between the t_2 and e energy levels and the $10Dq$ values. However, it does seem that, if appropriate basis sets for the ligand and metal atoms yield a good correlation for one complex, calculations with the same size basis sets properly reflect the trends in $10Dq$ values for similar complexes even when the symmetry is altered. Furthermore, in the halide complexes studied here, the t_2 and e orbitals involved in the $10Dq$ estimate are quite similar in metal character. Hence, one would not expect a substantial change in charge distribution between the ground and excited states nor a substantial alteration of electron repulsion integrals. Thus, estimates of $10Dq$ from the ground-state energy level separations in these cases are probably more realistic than they would be in

TABLE IV
 EIGENVALUES FOR OCTAHEDRAL COMPLEXES^a

	TiCl ₆ ³⁻	VCl ₆ ³⁻	CrCl ₆ ³⁻	FeCl ₆ ³⁻
	Distance, ^b Å			
	2.47	2.45	2.34	2.38
	Charge ^c			
	0.60	0.49	0.44	0.14
1a _{1g}	-17.47	-17.40	-17.23	-17.17
1t _{1u}	-17.40	-17.18	-16.87	-16.81
1e _g	-17.16	-17.02	-16.61	-16.60
2e _g	-2.75	-2.67	-2.44	-2.38
2a _{1g}	-2.33	-2.29	-1.87	-1.92
2t _{1u}	-1.40	-1.34	-0.87	-0.82
1t _{2g}	-1.20	-1.13	-0.82	-0.90
3t _{1u}	-0.91	-0.77	-0.34	-0.31
1t _{2u}	-0.86	-0.75	-0.32	-0.34
1t _{1g}	-0.86	-0.75	-0.32	-0.34
2t _{2g}	+7.00	+5.65	+5.62	+2.69
3e _g	+8.66	+7.14	+7.09	+3.94
3t _{2g}	+34.99	+35.62	+37.64	+38.99
4t _{1u}	+60.70	+54.78	+73.46	+65.72
4e _g	+87.66	+88.62	+90.46	+93.27
3a _{1g}	+109.60	+127.16	+370.52	+248.05
10Dq(calcd)	1.66	1.49	1.47	1.25
10Dq(exptl)	1.71	1.54	1.57	1.14

^a All energies are given in electron volts. ^b Distance refers to the experimental metal-ligand distance used in the calculations. ^c Charge refers to the metal charge at self-consistency *via* the Mulliken population analysis.

Crudely, one might say that transitions from the ligand orbitals to the empty metal 3d orbitals are possible but transitions to the metal 4p orbitals are not.

The fact that in certain of the charged complexes the occupied orbitals are above zero does not mean that such complexes are unstable or the results are erroneous since it must be remembered that the basic calculation did not take into account the potential well caused by the cations. Thus, the observed correspondence between the charge on the species and the absolute values of the energy levels is to be expected. Note that if -3, -9, and -12 eV were added to the energy levels of the complexes with -1, -2, and -3 charges, respectively, not only would all occupied orbitals be below zero but the absolute values of the low-lying orbitals would be practically identical. The energies -3, -9, and -12 eV are those required to make the 1a₁ and 1t₂ energies of the -1, -2, and -3 tetrahedral species essentially equal to those of the neutral molecule.

Covalency.—In a previous paper,³ we outlined a method for the calculation of the Racah electrostatic interaction parameter, *B*(complex), and the nephelauxetic β value from the 3d orbital coefficients in the

 TABLE V
 EIGENVALUES FOR TETRAHEDRAL COMPLEXES^a

	TiCl ₄	VCl ₄	FeCl ₄ ⁻	MnCl ₄ ²⁻	FeCl ₄ ²⁻	CoCl ₄ ²⁻	NiCl ₄ ²⁻
	Distance, ^b Å						
	2.185	2.03	2.19	2.33	2.27	2.25	2.27
	Charge ^c						
	0.33	0.23	0.34	0.20	0.24	0.09	0.08
1a ₁	-30.02	-30.27	-27.32	-21.37	-21.05	-21.14	-21.18
1t ₂	-30.20	-30.35	-26.97	-21.23	-20.88	-20.89	-20.92
2a ₁	-15.90	-16.02	-12.35	-6.26	-6.05	-6.16	-6.31
2t ₂	-16.42	-16.65	-12.64	-5.88	-5.95	-5.89	-5.99
1e	-14.62	-14.96	-11.07	-4.78	-4.73	-4.69	-4.77
3t ₂	-14.34	-14.51	-10.66	-4.86	-4.76	-4.69	-4.75
1t ₁	-13.65	-13.69	-10.30	-4.67	-4.54	-4.47	-4.51
2e	-7.01	-6.85	-7.05	+3.07	+1.32	+0.21	-1.32
4t ₂	-5.99	-5.89	-6.42	+3.52	+1.84	+0.68	-0.88
5t ₂	+10.27	+13.59	+16.92	+20.40	+21.74	+21.55	+20.80
3e	+16.80	+20.57	+21.43	+25.22	+26.66	+26.98	+26.11
6t ₂	+66.39	+77.04	+66.88	+65.95	+65.64	+66.73	+65.49
3a ₁	+38.54	+64.60	+92.23	+62.03	+68.25	+76.40	+71.26
10Dq(calcd)	1.02	0.96	0.63	0.45	0.52	0.48	0.44
10Dq(exptl)	0.93	1.12	0.62	0.45	0.50	0.41	0.44

^a All energies are in electron volts. ^b Distance refers to the experimental metal-ligand distance used in the calculations. ^c Charge refers to the metal charge at self-consistency *via* the Mulliken population analysis.

systems, such as carbonyl and cyanide complexes, where one would expect substantial differences in metal character between the two orbitals.

It will be noted that the absolute values of the energy levels fall into distinct regions depending upon the charge on the complex. The neutral species TiCl₄ and VCl₄ have all their occupied orbitals below zero. Of the unoccupied orbitals in these two complexes only the 2e and 4t₂ levels are less than zero which suggests (but certainly does not prove) that transitions from filled orbitals such as 1t₁, 3t₂, etc., to these orbitals can occur but that ionization of an electron would result rather than transitions to the 5t₂ and higher orbitals.

molecular orbitals and the appropriate 3d wave functions. It might be noted here that in the estimate of *B* and β a reduction results as a consequence of both the coefficients in the molecular orbitals and the wave functions used in the *atomic* basis set. This double correction is necessary for calculational consistency. As we have previously outlined,³ the 3d wave function should reflect the effective charge seen by the 3d electron as determined by self-consistent charge calculation which is used to control the computational procedure. If a different wave function had been employed, *e.g.*, that of the formal charge on the free ion, it would affect the molecular orbital coefficients and they would not

correspond to those obtained in this self-consistent calculation. It should be kept in mind that the method outlined for estimation of the B values is only an approximate one and that in principle the full molecular orbitals should be employed. The 3d metal wave functions corresponding to lower than the formal charge were used in the estimation of the B values because they were the atomic orbitals used in the molecular orbital calculation.

Application of the method to the $2e$ and $4t_2$ orbitals in tetrahedral symmetry and the $2t_{2g}$ and $3e_g$ orbitals in octahedral symmetry yields the calculated values given in Table VI. The results are in good accord with the experimental values. Since the β values can be used as a measure of the covalency of the specified orbitals, several features are noteworthy: (1) For a given formal oxidation state of the metal there is an increasing orbital covalency as the atomic numbers of the elements increase. This is illustrated by both the tetrahedral metal(II) complexes and the octahedral metal(III) complexes. (2) As shown by the isoelectronic pair FeCl_4^- and MnCl_4^{2-} , the increased formal charge on the metal substantially increases the orbital covalency; that is, β is much smaller. (3) The calculated orbital covalencies of the two iron(III) complexes, FeCl_4^- and FeCl_6^{3-} , are essentially identical.

TABLE VI

NEPHELAUXETIC EFFECT. B AND β VALUES							
	Fe- Cl_4^-	Mn- Cl_4^{2-}	Co- Cl_4^{2-}	Ni- Cl_4^{2-}	Cr- Cl_6^{3-}	Cr- Cl_6^{3-}	Fe- Cl_6^{3-}
$B(\text{calcd})$	625 ^a	830	880	875	619	649	640
$B(\text{exptl})$	590	770	730	765	563	561	655
$\beta(\text{calcd})$	0.58	0.95	0.88	0.82	0.70	0.68	0.59
$\beta(\text{exptl})$	0.58	0.86	0.75	0.72	0.65	0.62	0.65

^a All B values are in units of cm^{-1} .

Other commonly used measures of covalent character are bond orders and overlap populations. Coulson's²¹ original definition of bond order concerned the π character between two orbitals on adjacent atoms with the simplifying assumption that the overlap integral could be neglected in computing the molecular orbital coefficients. With this assumption, two electrons in the bonding or antibonding orbital of a diatomic homopolar molecule have bond orders of +1.0 and -1.0, respectively, so the net bond order due to full occupation of both orbitals is zero. In adapting bond orders to include overlap considerations, Mulliken²² defined the bond order in such a way that the upper limit is still +1.0. However, partial or complete occupation of the antibonding orbital can result in a negative value for the bond order, the limit being $-(1+S)/(1-S)$, where S is the overlap integral.

In dealing with the symmetry-adapted functions in the present work, it is convenient to specify a given molecular orbital belonging to the irreducible representation, a , by

$$\psi_{ia} = \sum_j C_{ij} \chi_j(a) + \sum_q C_{iq} \phi_q(a) \quad (13)$$

(21) C. A. Coulson, *Proc. Roy. Soc. (London)*, **A169**, 419 (1939).

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

where C_{ij} and C_{iq} are the coefficients for the normalized symmetry-adapted wave functions on the metal, $\chi_j(a)$, and ligands, $\phi_q(a)$, respectively. Then the orbital bond order becomes

$$P_{ia}(jq) = N(ia)C_{ij}C_{iq}(1 + G_{jq}) \quad (14)$$

where $N(ia)$ is the number of the electrons in the i th orbital and $G(jq)$ is the group overlap integral of $\chi_j(a)$ with $\phi_q(a)$. The total bond order is given by

$$P_a(jq) = \sum_i P_{ia}(jq)/D_a \quad (15)$$

where D_a is the orbital degeneracy of the irreducible representation, a . Division by the orbital degeneracy is necessary to keep an upper limit of +1.0 for a fully covalent bond. Since this is an adaptation of Mulliken's definition, it is also possible that occupation of the antibonding levels can result in bond orders which are negative. A partial tabulation of the calculated bond orders for the eleven complexes is given in Table VII. The complete list of bond orders has been deposited with the ADI since the most informative trends concerning covalency can be obtained by examination of the bond orders involving the metal 3d orbitals. Several features are significant.

TABLE VII
BOND ORDERS

	3d-3s	3d σ -p σ	t_2 3d π -p π	e 3d π -p π
TiCl_3^{3-}	0.050	0.594	0.351	...
VCl_6^{3-}	0.036	0.638	0.283	...
CrCl_6^{3-}	0.046	0.664	0.230	...
FeCl_6^{3-}	-0.001	0.334	0.316	...
TiCl_4	0.052	0.544	0.434	0.716
VCl_4	0.060	0.546	0.484	0.540
FeCl_4^-	-0.018	0.268	0.181	0.346
MnCl_4^{2-}	0.006	0.130	0.034	0.062
FeCl_4^{2-}	0.012	0.167	0.069	-0.005
CoCl_4^{2-}	0.006	0.193	0.109	-0.114
NiCl_4^{2-}	0.008	0.132	0.056	-0.092

(1) The negligible values for the 3d-3s bond orders for all the complexes are indicative of the relative unimportance of the low-lying 3s chlorine orbital.

(2) A clear distinction must be made between covalency of orbitals as measured by the nephelauxetic β values and covalency of bonds as measured by the bond order. We have previously noted the increase of orbital covalency with increasing atomic number. However, whether the bond order increases or decreases depends upon the change, if any, in occupation of the antibonding orbitals in the sequence of compounds. Thus for the four octahedral chlorides, the 3d σ -3p σ bond order increases from Ti through Cr, reflecting the increasing orbital covalency, since the $3e_g$ orbital remains unoccupied. The 3d σ -3p σ bond order of FeCl_6^{3-} shows a substantial decrease because of the two electrons in the $3e_g$ orbital. Similarly the 3d π -3p π bond order decreases from Ti through Cr because of the increased occupation of the $2t_{2g}$ (antibonding) orbital. From CrCl_6^{3-} to FeCl_6^{3-} there is no change in the $2t_{2g}$

orbital occupation so the increase in bond order reflects the increased orbital covalency.

(3) For the isoelectronic pair of complexes FeCl_4^- and MnCl_4^{2-} the bond orders reflect the increased covalency as a function of increased formal oxidation state. This is analogous to the conclusion reached on the basis of the β values.

(4) The negative values for the tetrahedral e $3d\pi-3p\pi$ bond orders are indicative of the nonbonding character of these interactions because of the partial or full occupation of the antibonding $2e$ orbitals.

Rather than using bond orders, Mulliken²² expresses a strong preference for overlap populations as a measure of bond covalency. In terms of the wave function formulation given by eq 13, the overlap populations are given by

$$n(a, j, q) = 2 \sum_i N(ia) C_{ij} C_{iq} G(jq) \quad (16)$$

where $n(a, j, q)$ is the overlap population due to the interaction of $\chi_j(a)$ and $\phi_q(a)$. Once obtained, these overlap "densities" may be summed together, e.g., σ density with π density, and/or divided between the number of metal to ligand bonds in the complex. The calculated overlap populations are given in Table VIII. Only the metal $3d$ orbital interactions are listed for two reasons: it is in these populations that the greatest variations occur, and, even more important, the higher metal orbitals are so diffuse that the resultant densities are not between the metal and ligand nuclei but are actually concentrated on the ligand centers.²³ In general, the covalency characteristics suggested by the overlap populations are analogous to those obtained from the bond order results.

One thought-provoking correlation exists between the overlap populations and the infrared stretching frequencies²⁴ for the metal-chlorine bonds. The relationship is illustrated by the results in Table IX. The stretching frequencies for a particular oxidation state are fairly constant, as are the overlap populations, but between oxidation states the populations and frequencies differ substantially. While a qualitative correlation exists, there does not appear to be a quantitative relation between overlap population and the stretching frequencies. This suggests that other factors such as different charge distributions on the atoms contribute to the stretching frequencies.

Correlation with Nqr Results.—Recently Cotton and

(23) See Figure 3 of ref 2 for radial density curves of the diffuse metal orbitals.

(24) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

TABLE VIII
TOTAL OVERLAP POPULATIONS

	3d σ -	3d σ -	t ₂	e	3d σ -	3d π -	Per bond
	3s	p σ	p π	p π	lig	lig	
TiCl_5^{3-}	0.03	0.40	0.29	...	0.43	0.29	0.72
VCl_5^{3-}	0.02	0.38	0.22	...	0.40	0.22	0.62
CrCl_5^{3-}	0.03	0.38	0.16	...	0.41	0.16	0.57
FeCl_5^{3-}	0.00	0.15	0.15	...	0.15	0.15	0.30
TiCl_4	0.04	0.49	0.24	0.43	0.53	0.67	1.20
VCl_4	0.04	0.47	0.29	0.34	0.51	0.63	1.14
FeCl_4^-	-0.01	0.15	0.06	0.12	0.14	0.18	0.32
MnCl_4^{2-}	0.01	0.07	0.01	0.02	0.08	0.03	0.11
FeCl_4^{2-}	0.01	0.08	0.02	0.00	0.09	0.02	0.11
CoCl_4^{2-}	0.01	0.09	0.03	-0.03	0.10	0.00	0.10
NiCl_4^{2-}	0.01	0.06	0.01	-0.02	0.07	-0.01	0.06

TABLE IX
CORRELATION OF OVERLAP POPULATIONS
WITH METAL-CHLORINE STRETCHING FREQUENCIES

Complex	Total overlap population	Exptl str freq, cm^{-1}
TiCl_4	1.20	490
VCl_4	1.14	482
FeCl_4^-	0.32	378
MnCl_4^{2-}	0.11	285
FeCl_4^{2-}	0.11	282
CoCl_4^{2-}	0.10	310
NiCl_4^{2-}	0.06	285

Harris²⁵ proposed a method for the calculation of quadrupole coupling constants and frequencies from the LCAO-MO eigenvectors. Using their relationship we have calculated the frequencies for various complexes. The results are given in Table X. In general the agreement is quite good particularly when one considers the approximations in both calculational models. It should also be kept in mind that the nqr data for the solids were obtained on compounds in which the chlorines were bridging the metal atoms, and, since nqr results are a measure of charge asymmetry, the values for MCl_3 and MCl_3^{3-} need not be identical.

TABLE X
NQR FREQUENCIES FOR CHLORINE LIGANDS

Complex	Mc/sec		Exptl compd
	Freq, calcd	Freq, exptl	
TiCl_4	8.23	5.98	TiCl_4
TiCl_5^{3-}	7.40	7.39	$\text{TiCl}_5(\text{s})$
VCl_5^{3-}	9.05	9.40	$\text{VCl}_5(\text{s})$
CrCl_5^{3-}	9.32	12.81	$\text{CrCl}_5(\text{s})$
FeCl_5^{3-}	7.95	10.02	$\text{FeCl}_5(\text{s})$
Cl atom	...	54.8	Cl

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(25) F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S. A.*, **56**, 12 (1966).