Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam - Printed in The Netherlands

MOLECULAR ORBITAL CALCULATIONS ON TRANSITION METAL COMPOUNDS

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(Received February 26th, 1970)

CONTENTS

A. INTRODUCTION

By means of symmetry arguments Bethe[1] first demonstrated qualitatively the nature of the splitting patterns for atomic orbitals in various chemically important geometries. Bethe regarded the ligands as point negative charges. Since these qualitative results could arise either by an electrostatic or a covalent mechanism, this model has proved useful in discussions of those physical properties of transition metal complexes which are largely dependent upon the splitting of the d orbitals, such as the $d \rightarrow d$ transitions and magnetic moments.

In spite of some early success the electrostatic model is rather unrealistic; for example, it is unable to account for the ordering of the ligands in the spectrochemical series. In 1935 Van Vleck[2] showed that $Fe(CN)_6^{3-}$ has a low-spin configuration and FeF_6^{3-}

a high-spin one but did not indicate why CN^- produces a much larger orbital splitting than F^-. Since then the results of many experiments have been reported which are best interpreted by assuming that some covalent bonding exists between the metal and ligands[3]. On this basis the spectrochemical series reflects the ability of a ligand to be a π donor or acceptor. A ligand–metal π-bond formed by ligand π orbitals which are lower in energy than the metal t_{2g} orbitals destabilises the t_{2g} orbitals and gives a smaller value for the orbital separation, $10Dq$, in an octahedral complex. Conversely, if the ligand π orbitals are higher in energy than the metal t_{2g} orbitals, upon overlap the latter are stabilised and the value of $10Dq$ increases. Between these two extremes are the non-π-bonding ligands which are arranged approximately in the order of their dipole moments. The theoretical model which is most frequently used to account for the covalent bonding in transition metal complexes is based on molecular orbital (MO) theory. This has the advantage of retaining the most important feature of the earlier crystal field theory namely the symmetry arguments.

It will be assumed that the reader is conversant with the basic ideas of group theory and MO theory as discussed in the books of Cotton[4] and of Ballhausen and Gray[5]. This review is not intended to be fully rigorous, however it should enable the reader to approach the original literature on this subject with a fair degree of confidence.

B. CALCULATIONS EMPLOYING THE CRYSTAL FIELD MODEL

The majority of the more demanding calculations that have been reported for transition metal complexes have been concerned with the estimation of the crystal field parameter $10Dq$ [6]. Since the basic concepts of crystal field theory are incorporated in the MO approach, we propose to deal briefly with the crystal field model.

It is generally assumed that in a molecule the atomic orbitals may be divided into two categories. Those which are not considered to be involved in bonding are assumed to be the same as in a free atom and are designated "core orbitals"; whereas those concerned with the bonding in the molecule are referred to as the "valence orbitals". The valence orbitals are $3d$, $4s$ and $4p$, for a first row transition metal, and usually $2s$ and $2p$ for a ligand.

In a crystal field calculation with an octahedral transition metal complex the one-electron core Hamiltonian operator is defined by

$$\hat{H}^{\text{core}}(1) = \hat{T}(1) + \sum_x \hat{V}_x(1) \tag{1}$$

where $\hat{T}(1)$ represents the kinetic energy of the valence electron, (1), and $\hat{V}_x(1)$ the potential felt by electron (1) due to the nucleus x and its core electrons. The sum over x includes the metal and ligand nuclei. The form of $\hat{V}_x(1)$ is given more explicitly as

$$\hat{V}_x(1) = -\frac{Z_x e^2}{r_{1x}} + \sum_{j \text{ on } x} (2\hat{J}_j^{\text{core}} - \hat{K}_j^{\text{core}}) \tag{2}$$

The first term in Eqn. (2) describes the energy of attraction felt by electron (1) due to nucleus x with charge Z_x; the second term describes the repulsive potential that electron (1) feels from all the core electrons on nucleus x. $\hat{J}_j^{\text{core}}$ expresses the coulomb repulsive potential experienced by like charges; $\hat{K}_j^{\text{core}}$ accounts for the exchange potential and expresses the fact that the total electronic energy of a system is lower if it has electrons with parallel spins rather than with anti-parallel spins, (Hund's Rule). Since the only variables in Eqn. (1) are the space coordinates of electron (1), the Hamiltonian, $\hat{H}^{\text{core}}$, is known as a one-electron operator.

For an octahedral metal complex $10Dq$ may be defined[7] in the absence of any inter-electronic repulsions among the d orbitals as

$$10Dq = \langle e_g | H^{\text{core}} | e_g \rangle - \langle t_{2g} | H^{\text{core}} | t_{2g} \rangle \qquad (3)$$

where the $3d$ orbitals are denoted by the symmetry labels e_g and t_{2g} appropriate to octahedral symmetry. In crystal field calculations with first row transition metal ions the $3d$ orbitals are usually the only metal valence orbitals considered. All the occupied ligand orbitals are included in the core.

In early calculations on this model the core potentials V_x were taken to be due to point dipoles or point charges centered on the ligands and the exchange potentials were neglected. By taking hydrogen-like functions for the metal d orbitals Van Vleck[8] obtained a satisfactory estimate for $10Dq$ which he thought was probably accidental due to the approximations involved.

Kleiner[9] has used Slater type functions[10] for the d orbitals in his calculation on chrome alum. He calculated the integrals arising from $\hat{J}_j^{\text{core}}$ in Eqn. (2) but ignored those associated with $\hat{K}_j^{\text{core}}$. By this means he obtained a value of $-5500\ \text{cm}^{-1}$ for $10Dq$ compared with the experimental value of $17500\ \text{cm}^{-1}$. This lack of agreement gave rise to the first serious doubts of the crystal field model and showed the necessiry of using more contracted orbital functions. The conditions which cause the contraction and expansion of atomic orbitals by ligands have been discussed by Craig and Magnusson[11].

By using non-contracted d wave functions Kleiner obtained the wrong sign for $10Dq$ which may be seen from Fig.1.

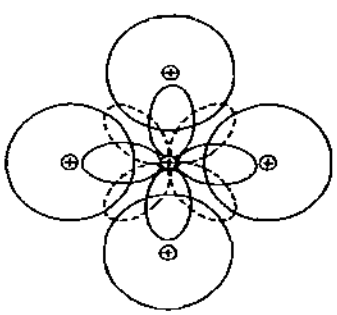

Fig.1. A representation of part of an octahedral metal complex. The electron clouds on the four ligands are shown by sections through spheres. The lobes of an e_g type of metal orbital are drawn with full lines and those of a t_{2g} type of metal orbital with dashed lines. The positive charges on the metal and ligand nuclei are also shown.

If an electron occupies an e_g orbital, which has lobes directed at the ligand atoms, it will be strongly attracted by the net positive charge of the core which tends to compensate for the repulsion experienced from the ligand electron cloud. For an electron in a t_{2g} orbital the repulsive effect of the electron cloud is almost as great as it is for the e_g electron but the attraction of the core is much smaller. Consequently an electron in an e_g orbital is of lower energy than one in a t_{2g} orbital which is contrary to the normal point charge arguments for an octahedral complex. When contracted d wavefunctions are used the orbital splitting is reversed[12]. Freeman and Watson[12] used self consistent field (SCF) d wavefunctions, in a calculation on chrome alum, which are more contracted than the functions Van Vleck used. They obtained a value of 500 cm^{-1} for $10Dq$, supporting the doubts expressed by Van Vleck about the wavefunctions that he had used.

Tanabe and Sugano[13] obtained a value of $10Dq = 47500$ cm^{-1} for chrome alum. In their calculation they included the contributions from the operators $\hat{K}_j^{core}$ in Eqn. (2) and orthogonalised the metal d and core orbitals to each other to account for the deformation of the Cr d orbitals upon complex formation.

The necessity for considering mixing between metal and ligand orbitals has been demonstrated by Offenhartz[7]. He has reported an open-shell calculation of $10Dq$ for NiF_6^{4-}. The important stages in the calculation are summarised in Fig.2.

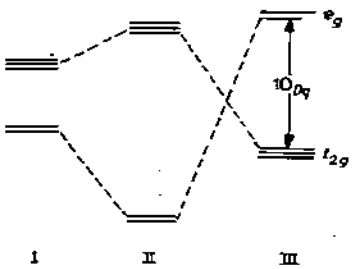

Fig.2. Three stages in the open-shell calculation of $10Dq$ for NiF_6^{4-} (after Offenhartz[7])*.

At stage I $10Dq$ is considered as the energy difference between the metal t_{2g} and e_g orbitals under a potential due only to the ligands. This corresponds to the crystal field value of $10Dq$ and it is seen to have the wrong sign. Stage II considers again only pure metal orbitals and an operator which describes the kinetic energy of the electrons and the potential energy due to the metal and the ligands. This leads to a larger value of $10Dq$ with the incorrect sign. The third stage, III, includes the effect of mixing metal and ligand orbitals, which gives the correct sign to $10Dq$.

The mixing of metal and ligand orbitals of the appropriate symmetry types is implicit in molecular orbital (MO) theory. The disappointing results of $10Dq$ from the crystal field model has led to an increase in interest in semi-empirical MO procedures. Although these calculations are less rigorous, the MO model appears to be more satisfactory.

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C. MOLECULAR ORBITAL (MO) CALCULATIONS

In MO calculations not only the orbital energies are evaluated but the values of the coefficients of the atomic orbitals comprising the MO's are also found. The calculated energies may be compared with experimental estimations of $10Dq$ including data derived from photoelectron spectroscopy[14], (Section D). The calculation of the atomic orbital coefficients provides an estimate of covalent bonding which may be compared with experimental data arising from NMR, ESR, NQR, Mössbauer, vibrational and electronic spectra and in some cases magnetic susceptibilities, (Section E).

It is usual to represent the MO's, ϕ_i, as linear combinations of the valence atomic orbitals (LCAO's), χ_p, extending over all atoms in the molecule. Hence

$$\phi_i = \sum_p C_{ip}\chi_p \tag{4}$$

where the subscripts $i, j, k, \ldots$ refer to MO's and $p, q, r, s, t, \ldots$ to atomic orbitals. The coefficients C_{ip}, which give the relative amounts of the various atomic orbitals in each LCAO set, are to be determined. To be satisfactory wavefunctions the MO's must be normalised eigenfunctions of a Hamiltonian operator $\hat{H}$ such that

$$\hat{H}\phi_i = \epsilon_i\phi_i \tag{5}$$

Physical meaning is given to the orbital energies, ϵ_i, of the occupied MO's by Koopman's theorem[68]. It states that for closed shells the energy required to ionize an electron from the i^{th} MO, with the geometry fixed at that of the neutral molecule (vertical ionization potential), is $-\epsilon_i$, provided that the other MO's are not appreciably affected by the ionization process.

The electronic Hamiltonian operator $\hat{H}$ is approximated as a sum of one-electron operators by

$$\hat{H} = \sum_i \hat{H}^{\text{core}}(1) + \sum_{i<j} \frac{e^2}{r_{ij}} + V_{xx} \tag{6}$$

where the summation is taken over all of the valence electrons. $\hat{H}^{\text{core}}$ is defined by Eq. (1) for each of the valence electrons. The second term in Eq. (6) accounts for the electrostatic interaction between the valence electrons, and the last term represents the internuclear repulsion. For a fixed nuclear configuration V_{xx} affects the electronic energy levels by a uniform amount. Since it is usual in calculations on transition metal compounds to consider only a single nuclear configuration, V_{xx} becomes a constant and will not be considered further.

To satisfy the antisymmetry requirement in the general case, the electronic wavefunction for a particular state of the system is represented as a linear combination of Slater determinants[5]. Each determinant Ψ being of the form given by Eq. (7).

$$\Psi = |\psi_a\psi_b \ldots \ldots \psi_k| \tag{7}$$

where $\psi_a, \psi_b, \ldots \psi_k$ are spin-orbitals which are simple products of the space MO's, $\phi_i, \phi_j, \ldots$ and the spin functions α and β.

The expectation value of the energy E, of a system is found by means of the Hamiltonian operator described by Eqn. (6) operating upon a linear combination of determinantal functions as,

$$E = 2\sum_k H^c_{kk} + \sum_{k,l}(2J_{kl} - K_{kl}) + f[2\sum_m H^c_{mm} + f\sum_{m,n}(2aJ_{mn} - bK_{mn}) + 2\sum_{k,m}(2J_{km} - K_{km})] \quad (8)$$

where k,l refer to closed-shell orbitals and m,n to open-shell orbitals; a, b and f are numerical constants depending upon the particular case considered. Using i,j to denote either open- or closed-shell orbitals, then in Eqn. (8)

$$H^c_{ii} = \int \phi_i^*(1)\, \hat{H}^{\text{core}}(1)\, \phi_i(1)\, d\tau_1 \quad (9)$$

$$J_{ij} = \int\int \phi_i^*(1)\, \phi_j^*(2) \frac{e^2}{r_{12}} \phi_i(1)\, \phi_j(2)\, d\tau_1\, d\tau_2 \quad (10)$$

$$K_{ij} = \int\int \phi_i^*(1)\, \phi_j^*(2) \frac{e^2}{r_{12}} \phi_j(1)\, \phi_i(2)\, d\tau_1\, d\tau_2 \quad (11)$$

The Coulomb integral, J_{ij}, is analogous to the classical electrostatic interaction between the charge distributions of electrons (1) and (2). K_{ij} has no classical analogue and is known as the exchange interaction between the charge distributions $\phi_i^*(1)\, \phi_j(1)$ and $\phi_j^*(2)\, \phi_i(2)$.

For the closed-shell case the electronic energy is given by the first two summations presented in Eqn. (8). The third and fourth summations represent the open-shell energy, the final term in Eqn. (8) accounts for the interaction between the open- and closed-shell orbitals. The fractional occupation of the open-shell orbitals is given by f, for a single electron in a set of d orbitals $f = 0.1$.

The Hartree–Fock or SCF MO's, $\phi_1, \phi_2, \ldots \phi_i$ are obtained from the application of the variation principle to Eqn. (8) such that the energy E is minimised. This leads to the Hartree–Fock equations for the orbitals ϕ_i

$$\hat{F}\phi_i(1) = \epsilon_i \phi_i(1) \quad (12)$$

The SCF operator, $\hat{F}$, is defined in terms of the orbital ϕ which is a solution of Eqn. (12), hence an iterative technique is adopted in solving equations of this type. Formally Eqn. (12) describes both open- and closed-shell configurations, the major difference between these two cases being in the form of the SCF operator. For the closed-shell case in which there are $2n$ valence electrons in n MO's, $\hat{F}$ is defined by

$$\hat{F} = \hat{H}^{\text{core}}(1) + \sum_{i=1}^{n}(2\hat{J}_i - \hat{K}_i) \quad (13)$$

The coulomb and exchange operators $\hat{J}_i$ and $\hat{K}_i$ are defined as

$$\hat{J}_i\phi_j(1) = \int \phi_i^*(2)\, \phi_i(2) \frac{e^2}{r_{12}}\, d\tau_2\, \phi_j(1) \quad (14)$$

and $$\hat{K}_i\phi_j(1) = \int \phi_i^*(2)\, \phi_j(2) \frac{e^2}{r_{12}}\, d\tau_2\, \phi_i(1) \quad (15)$$

If the SCF orbitals are represented by the LCAO approximation then Eqn. (4) is substituted into Eqn. (12). This generates a set of linearbomogeneous equations which are called the secular equations. These may be written as

$$\sum_q C_{iq}(F_{pq} - \epsilon_i S_{pq}) = 0 \tag{16}$$

where the atomic overlap integrals, S_{pq}, are defined by

$$S_{pq} = \int \chi_p^* \chi_q \, d\tau \tag{17}$$

and $$F_{pq} = \int \chi_p^* \hat{F} \chi_q \, d\tau \equiv \langle \chi_p \mid F \mid \chi_q \rangle \tag{18}$$

The secular equations are also known as Roothaan's SCF-MO equations[66]. Roothaan[67] has produced a set of secular equations analogous to those given by Eq. (16) for the open-shell case where $\hat{F}$ is now the open-shell SCF operator. At present, calculations on transition metal compounds using Roothaan's open-shell formalism are not common, instead further approximations are usually introduced so that open-shell calculations may be treated by closed-shell techniques which are simpler[6,7]. It is usually assumed that a single Slater determinant adequately represents the open-shell wavefunction. Often the secular equations appropriate to the closed-shell case are solved for α and β spins separately[261]. It has been argued that the approximations involved in this method are unimportant since the SCF MO's are insensitive to them. However cases do exist where they are important[51,52,262]. Consequently there appears to be little point in persuing approximate methods further when accurate solutions to the SCF open-shell problem are available[263]. Perhaps the advent of larger and faster computers will provide the impetus for a series of open-shell SCF calculations on some transition metal compounds soon.

In MO calculations the main mathematical problem rests in the evaluation of the integrals of the SCF operator, $\hat{F}$, (Sections C, iv and C, v). Owing to the difficulties experienced in exact calculations computational simplifications are often introduced. If these simplifications are introduced in a systematic manner using well defined approximations a semi-quantitative approach is evolved (Section C, iv). Alternatively if the approximations are not explicitly listed and some of the terms in the SCF operator are directly related to experimentally determined quantities then a semi-empirical approach to the problem is obtained similar to that formulated by Wolfsberg and Helmholz (WH)[15] (Section C, ii).

(i) General comments on semi-empirical MO calculations

In the Hückel formalism $\hat{H}$ of Eqn. (5) is an undefined one-electron operator; however, the repulsion terms in Eqn. (6) are ignored. Upon application of the variation procedure the secular Eqn. (19) are obtained

$$\sum_q C_{iq}(H_{pq} - \epsilon_i S_{pq}) = 0 \tag{19}$$

In the Hückel approximation, $S_{pq} = 1$ if $p = q$ and $S_{pq} = 0$ if $p \neq q$; the H_{pq} represent

the Coulomb ($p = q$) and resonance ($p \neq q$) integrals defined as

$$H_{pq} = \int \chi_p^* \hat{H} \chi_q \, d\tau \tag{20}$$

The set of secular Eqn. (19) lead to the formulation of the secular determinant (21)

$$| H_{pq} - \epsilon_i S_{pq} | = 0 \tag{21}$$

from which the energies ϵ_i of the MO's can be evaluated. These solutions may then be used to determine the coefficients, C_{iq}, in Eqn. (19)[16].

By considering the matrix corresponding to the determinant in Eq. (21), it is apparent that the diagonal elements are $H_{pp} - \epsilon_i$ and the off-diagonal elements are H_{pq}. Consequently the terminology of matrix elements is often used when referring to the integrals defined by Eqn. (20).

By using wavefunctions which are adapted to the symmetry of the molecule a considerable simplification of the secular determinant is obtained[5]. For each irreducible representation of the point group to which the molecule belongs there is at most one simplified determinant.

In calculations on transition metal complexes the two-centre overlap integrals S_{pq} are replaced in Eqns. (19) and (21) by group overlap integrals G, which are defined by

$$G = \int \chi_q^* (\sum_r C_{rr} \chi_r) \, d\tau \tag{22}$$

where χ_q is a normalised metal valence orbital and $\sum_r C_{rr} \chi_r$ represents a normalised ligand LCAO set. The integrals G should include the effects of ligand–ligand overlap[5]. The group overlap integrals may then be expressed in terms of two-atom overlap integrals appropriate to the symmetry implied by various molecular geometries[5,6].

The simple Hückel theory was developed to deal only with π electrons but has been extended to include σ electrons[17]. Additionally, the extended Hückel molecular orbital (EHMO) formalism does not neglect S_{pq} when $p \neq q$ and H_{pq} is taken to be proportional to S_{pq}. Since H_{pq} describes the energy of interaction between the orbitals on atoms p and q it is intuitively appropriate that a relationship between H_{pq} and S_{pq} should exist. However, as discussed in section C, v, this relationship is not necessarily a simple one.

(ii) The Wolfsberg–Helmholz (WH) procedure

Wolfsberg and Helmholz first applied the principles of the EHMO model to transition metal complexes[15]. They approximated the resonance integrals H_{pq} by

$$H_{pq} = \frac{K}{2} G(H_{pp} + H_{qq}) \tag{23}$$

where K is a constant chosen to be 1.67 for σ overlaps and 2.00 for π overlaps. The Coulomb integrals H_{pp} and H_{qq}, give an estimate of the energy of an electron in the p^{th} or

q^{th} orbital in the field of the core and the remaining valence electrons. These are assumed to be approximately the same as the valence state ionization energies (VSIE). The 'valence state' is not a well defined concept. It assumes a meaning when the molecular wavefunction is written in terms of detailed atomic wavefunctions assigned to definite centers[18,19]. This allows the separation of the integrals, involving the functions assigned to a particular atom from a molecular wavefunction. Consequently the 'valence state' may be considered to be a statistical average[20] of stationary states of an atom chosen so as to have, as closely as possible, the same interactions between the atomic electrons as they have when the atom is part of a molecule. This may be visualised, for a given atom in a molecule, as arising from the removal of all the other atoms from the molecule without allowing any electronic rearrangement[18,21].

Consequently the atomic 'valence state' is composed of electrons occupying particular hybridised orbitals with averaged spin orientations. The VSIE is the energy required to remove an electron from the valence state of an atom, and values of it have been tabulated by Hinze and Jaffé[22,23].

By using these approximations, Eqns. (21) and (19) are solved and the coefficients C_{iq} evaluated, from which the charge distribution in the molecule is obtained. In the original WH calculation the values chosen for H_{pp} were varied until the calculated first and second electronic excitation energies were in qualitative agreement with the experimental values[15].

A further requirement is that the resulting charge distribution be approximately the same as that assumed in setting up the atomic orbital wavefunctions whose VSIE's are chosen for the integrals H_{pp}.

Since the original WH calculation on permanganate and some related tetrahedral anions the procedure has been widely used for transition metal complexes, largely in an amended form. Criticism has been raised over the use of atomic VSIE values in the estimation of H_{pp}[24,25]. Mulliken's definition of VSIE assumes that the electrons are in orbitals with definite spatial parameters. In MO calculations it is unnecessary to use hybridized orbitals, the atomic orbitals used should be as independent as possible of the arrangement of electrons occupying other orbitals of the same atom. Thus, since the electrons are assumed to be separated into valence and core sets, the ionization potential of a valence electron is expected to be a function of the orbital from which the ionization occurs, the occupancy of that orbital and the total number of valence electrons of the atom. Additionally, a molecular orbital wavefunction is frequently analysed in terms of non-integral occupation numbers of the atomic orbitals from which it is constructed. Consequently it has been proposed[26] that valence orbital ionization potentials (VOIP's) be used, since they refer to an electron with random spin and space orientations within a given configuration. Unfortunately many authors whilst using the definition of VOIP, suggested by Basch, Viste and Gray[26], retain the older abbreviation VSIE or VSIP (valence state ionisation potential).

The available atomic spectral data[5,26] show that the values taken for the VOIP's are highly dependent upon the charge and orbital configuration of the metal atom. It is therefore assumed that for a charge q on the metal ion the value of the VOIP is given by the quadratic relationship

$$\text{VOIP}(q) = Aq^2 + Bq + C \qquad (24)$$

where A, B and C are tabulated parameters[26,27]. This relationship is found to be satisfactory in many cases[28].

Average energy of configuration VOIP's have been obtained for the elements between H and Kr in various configurations and states of ionization.

By means of Eqn. 24 the VOIP can be evaluated as a continuous function of charge on the metal ion. This, in collaboration with a Mulliken population analysis[29] in which the overlap population between two atoms is equally divided, enables the values of H_{pp} to be adjusted to accommodate variation in the charge on the metal ion. This has been used in self-consistent charge and configuration (SCCC) MO calculations. In a SCCC-MO calculation[27,30,31] the ligands are usually assigned a constant VOIP value; the metal VOIP value is calculated from an assumed input charge distribution and configuration; and the secular Eqns. (19) are solved for the MO eigenvalues and eigenvectors. A Mulliken population analysis is performed on each of the MO's producing a new charge and configuration for the metal. A new VOIP, corresponding to the new metal charge, is then assigned to the matrix elements involving metal orbitals. The procedure is repeated until self-consistency of charge and configuration is obtained to within defined limits.

As the difference in the Coulomb energies H_{pp} and H_{qq} becomes larger it is not unreasonable to expect the resonance energy H_{pq} to decrease more rapidly than the arithmetic mean indicated by Eqn. (23). It has been suggested that for transition metal complexes H_{pq} may be more suitably approximated by the geometrical mean[30,32].

$$H_{pq} = -KG\sqrt{H_{pp}H_{qq}} \tag{25}$$

A disadvantage of Eqn. (25) is that it makes the positions of the antibonding orbitals unusually sensitive to the values chosen for H_{pp} and H_{qq}.

The use of a single value of K in Eqn. (23), for the same type of overlap in a series of related molecules has been challenged by Cotton and Haas[33]. They have shown that in order to account for the experimental values of $10Dq$ in a series of transition metal hexammines it is necessary to take values of K_σ ranging from 1.82 for $[Cr(NH_3)_6]^{3+}$ to 2.30 for $[Co(NH_3)_6]^{3+}$. Additionally a single value of K_σ is not necessarily satisfactory for a given metal in different oxidation states; a value of 2.00 is required for Co^{II} and 2.30 for Co^{III}. Since the overlap integrals between the metal $3d$ and ligand orbitals tend to decrease along the first transition series, it appears very probable that the values of H_{pq} remain fairly constant for hexammine complexes throughout. However these results are not in agreement with those obtained from a SCCC type of WH calculation on some first row octahedral and tetrahedral metal complexes with simple halide and chalcogenide ligands[27]. In calculating values of $10Dq$ it was found that reasonable agreement with experiment was obtained by assuming K_π to be constant and allowing K_σ to change only very slowly in passing along the first transition series metals. It was also reported that a single value of K_σ was found to be sufficient to account for both octahedral and tetrahedral complexes of a given metal when the same set of atomic orbitals were used. Although the results of Cotton and Haas[33] and those of Basch, Viste and Gray[27] appear to be in disagreement, it is necessary to remember that neither the details of the calculations nor the complexes considered are identical.

In constructing ligand combinations of σ orbitals many authors have considered that the $2s_\sigma$ and $2p_\sigma$ orbitals are hybridized and use only one basis set to describe them in the

LCAO[30,34-36]. This has been criticised by Fenske[37] who suggests that it is preferable to use different basis sets for the $2s_\sigma$ and $2p_\sigma$ orbitals.

The effects of the fields of neighbouring atoms on the energy of an electron have been largely neglected in many WH calculations[38]. In the case of some transition metal oxides and halides this has led to the prediction of unusually high covalencies[39-41]. To account for this Cusachs[42] has suggested approximating H_{pq} as

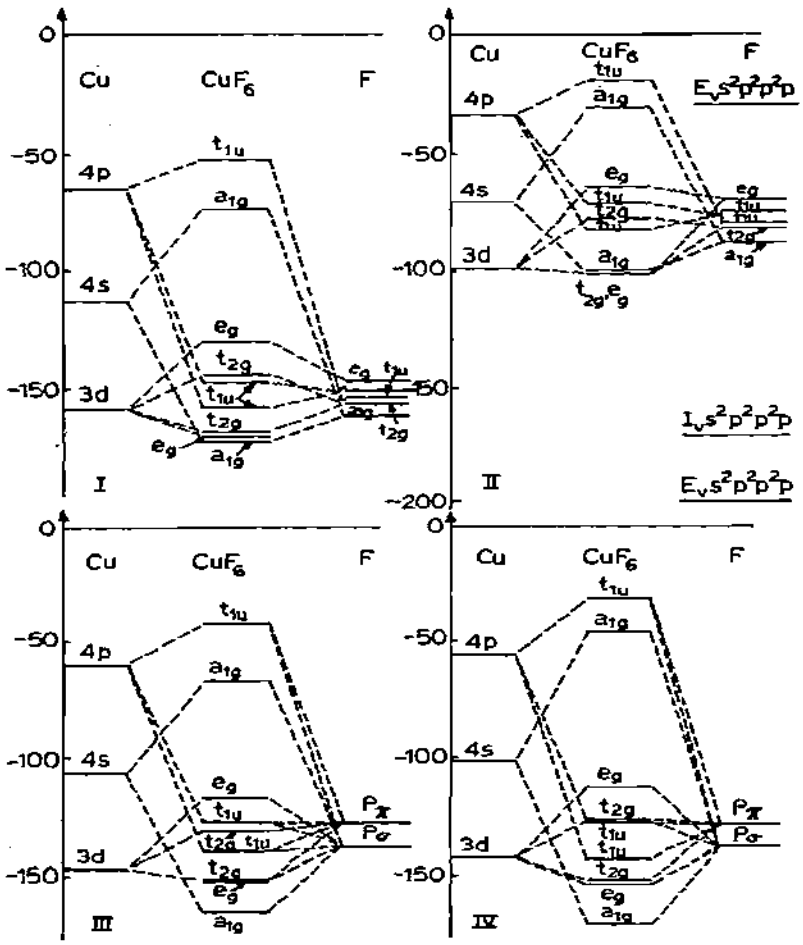
$$H_{pq} = \tfrac{1}{2}(H_{pp} + H_{qq})S_{pq}(2 - |S_{pq}|) \tag{26}$$

which has been employed satisfactorily in some calculations on porphyrins[43-45]. Additionally the neighbouring fields may be described by a constant potential, $-Z$, which is added to H_{pp}. It appears in the expression for H_{pq} as an additional term $-ZS_{pq}$ [46]. However it has been reported that the effects of neglecting these corrections for H_{pp} and H_{pq} largely cancel[24,25].

Johansen and Ballhausen[47] have reported four WH calculations on CuF_6^{4-} in which the fluoride VSIE and WH factor K were varied. The fluoride 2*s* orbitals were ignored and only the $2p_\sigma$ functions considered. The VOIP for copper was estimated from Eqn. (24) and the H_{pq} values derived from Eqn. (25). The results of these calculations are given in Fig.3. The first calculation shows the anticipated large negative charge on fluoride indicating that the use of a neutral atom VSIE is unrealistic. In the other calculations the charge on fluoride is made self-consistent and is either derived from the hydride ionisation potentials or by interpolation between the neutral atom VSIE and electron affinity. The first calculation also shows that the chosen configuration for copper provides a reasonable approximation to the final charge distribution and forms the basis of the ones used in the other three calculations. Taking $10Dq$ to be the energy difference between the e_g and t_{2g} orbitals the values obtained are all about 14000 cm^{-1}, which appears to be reasonable. A small variation in K does not appear to have an important effect on the calculated value of $10Dq$ although the overall energy level pattern tends to spread out as K increases. Consequently the interpretation of charge transfer spectra is likely to be very dependent upon the value of K chosen.

(iii) Choice of atomic orbitals

The results of MO calculations depend very critically not only upon the choice of approximations involved in the calculation but also on the choice of radial functions used in the constituent atomic orbitals. From a population analysis it is found that fractional charges are assigned to atoms, consequently it becomes necessary to choose radial functions for the atomic orbitals which most closely reflect the calculated electronic configuration. So far there appears to be no simple way to estimate the best radial functions. In order to satisfy the orthogonality requirement, free atom orbitals are often chosen[6]. Where necessary the valence orbitals may be orthogonalised to the core orbitals by means of the Schmidt procedure[6].



(I) Self-consistent calculation using the valence-state ionization-energy for neutral fluorine. Cu: input $q^{0\cdot6689}d^{9\cdot6466}s^{0\cdot4487}p^{0\cdot2358}$; output $q^{0\cdot6688}d^{9\cdot6466}s^{0\cdot4487}p^{0\cdot2358}$. F: output charge $-0\cdot7781$, '$10Dq$' = $14\cdot66 \times 10^3$ cm^{-1}. Wolfsberg–Helmholz factor 2·00. (II) Self-consistent calculation, also with respect to F using valence-state ionization-energies (interpolation between E_v and $I_v s^2p^2p^2p$). Cu: input $q^{0\cdot00845}d^{9\cdot89563}s^{0\cdot69377}p^{0\cdot40215}$; output $q^{0\cdot00844}d^{9\cdot89563}s^{0\cdot69378}p^{0\cdot40215}$. F: input $q = -0\cdot6681$; output $q = -0\cdot6681$; '$10Dq$' = 13·137 cm^{-1}. Wolfsberg–Helmholz factor 2·00. (III) Self-consistent calculation using hydride ionization potentials for fluorine. Cu: input $q^{0\cdot6180}d^{9\cdot7968}s^{0\cdot3454}p^{0\cdot2397}$; output $q^{0\cdot6180}d^{9\cdot7968}s^{0\cdot3454}p^{0\cdot2397}$. F: output charge $-0\cdot7697$; '$10Dq$' = $13\cdot48 \times 10^3$ cm^{-1}. Wolfsberg–Helmholz factor 1·75. (IV) Self-consistent calculation using hydride ionization potentials for fluorine. Cu: input $q^{0\cdot4643}d^{9\cdot6954}s^{0\cdot42725}p^{0\cdot41305}$; output $q^{0\cdot4643}d^{9\cdot6954}s^{0\cdot42725}p^{0\cdot41305}$. F: output charge $-0\cdot7440$; '$10Dq$' = $14\cdot01 \times 10^3$ cm^{-1}. Wolfsberg–Helmholz factor 2·00. Units on figure: 10^3 cm^{-1}.

Fig.3. The energy levels derived from four different WH type of MO calculations on CuF_6^{4-} (reproduced from Johansen and Ballhausen[47]).

Accurate analytical functions for elements from the first period are available[48] and satisfactory functions for elements of the second and third periods have been reported[49–53]. Frequently the radial functions have been approximated as single exponential Slater[10] analytical functions, given by Eqn. (27).

$$\chi_{(n,l,m)} = Nr^{(n-l)}\exp(-\zeta r)Y_l^m(\theta,\phi) \tag{27}$$

where N is a normalising constant, n, l and m are quantum numbers, $Y_l^m(\theta,\phi)$ are Tesseral harmonics, r relates to the nucleus–electron separation and ζ is a variable depending upon the effective nuclear charge.

However, radial functions in which the exponential term has been optimized for SCF wavefunctions have been reported by Clementi and Raimondi[54,55]. They are often more appropriate than Slater functions particularly for ligand atoms. Clementi[56] has shown that a linear combination of exponential functions gives energies much closer to the Hartree–Fock SCF energies than does a single exponential function. However use of these more complicated functions tends unfortunately to increase the length of the calculation.

To minimise the difficulties of evaluating the electron repulsion integrals obtained from Slater functions, Gaussian functions of the form given by Eqn. (28) have been employed[57].

$$\chi_{(n,l,m)} = Nr^{n-l}\exp(-\zeta r^2)Y_l^m(\theta,\phi) \tag{28}$$

The evaluation of the repulsion integrals is now simplified since the product of two Gaussian functions on two centers may be expressed as a single Gaussian function on a third center situated on a line joining the other two centers. This leads to simpler integrals but increases the number that is required to obtain a wavefunction whose energy is comparable to that obtained with a given number of Slater functions[58–60]. A further disadvantage of Gaussian functions is their behaviour both close to, and at a large distance from, the nucleus[57]. To date Gaussian functions have not been widely used in calculations on transition metal complexes.

In some WH type of calculations on porphyrins Watson's[53,61] contracted $3d$ functions have been used to estimate the overlap integrals between the metal $3d$ and nitrogen orbitals[44,45]. It is found that the overlap integrals estimated in this manner can be reproduced by a single exponential function with a value of ζ lying between the Slater and Clementi values.

Richardson, Powell and Nieuwpoort[62,63] have reported $3d$, $4s$ and $4p$ metal functions which have been widely used in calculating metal ligand overlap integrals although their $4p$ functions may be too diffuse[43].

The accuracy with which analytical functions fit experimental data is often found to improve when the orthogonality requirement for orbitals with the same value of l but different values of n is relaxed.

So far the majority of MO calculations on transition metal complexes that have been reported have been concerned with first row metals. Herman and Skillman[64] have computed numerical functions for second and third row metals from which approximate analytical s,p,d and f orbitals have been constructed[65].

(iv) Semi-quantitative MO calculations

In semi-empirical MO calculations the Hamiltonian operator $\hat{H}$, given by Eqn. (5), is not specifically defined. Quantitative MO theory is concerned with calculating the matrix elements H_{pp} and H_{pq} in which due consideration is given to all of the interactions between the electrons and the nuclei, however a quantitative calculation on a transition metal complex has not yet been reported. In order to make the problem tractable approximations are introduced in a systematic manner such that semi-quantitative MO calculations become possible. For a closed-shell system described by Eqn. (28) the values of ϵ_i may be found by equating the associated secular determinant to zero, as shown in Eqn. (29).

$$|F_{pq} - \epsilon_i S_{pq}| = 0 \tag{29}$$

To determine the eigenvalues ϵ_i of the matrix corresponding to this determinant, the values of the matrix elements F_{pq} of the SCF operator have to be found. To achieve this the F_{pq} are usually considered to consist of two parts[69].

$$F_{pq} = H_{pq}^{\text{core}} + G_{pq} \tag{30}$$

Where H_{pq}^{core} is derived from the one-electron part of the total electronic Hamiltonian operator, and G_{pq} from the two-electron part. These integrals have the forms shown in Eqns. (31) and (32).

$$H_{pq}^{\text{core}} = \int \chi_p (\hat{T} + \sum_x \hat{V}_x) \chi_q \, d\tau \tag{31}$$

where $\hat{T}$ is the one-electron kinetic energy term, and $\hat{V}_x$ is the potential due to nucleus x and its core electrons

$$G_{pq} = \sum_{s,t} p_{st} [<pq|st> - \tfrac{1}{2} <pt|qs>] \tag{32}$$

where

$$<pq|st> = \int\int \chi_p^*(1) \chi_s^*(2) \frac{e^2}{r_{12}} \chi_q(1) \chi_t(2) \, d\tau_1 \, d\tau_2 \tag{33}$$

and $$p_{st} = 2 \sum_i^{\text{occ}} C_{is} C_{it} \tag{34}$$

Eqn. (33) describes the interaction between two electrons, (1) and (2), distributed amongst the atomic orbitals χ_p, χ_q, χ_s and χ_t. The elements of the charge and bond order matrix p_{st} are described by Eqn. (34) where the summation extends over all of the doubly occupied MO's ϕ_i.

It is important to realise that the one-electron operator matrix elements H_{pq} given by Eqn. (19) are significantly different in form from the F_{pq} of Eqn. (16). Eqns. (32) to (34) show that in the latter case the matrix elements are a function of the coefficients which are required, whereas this is not the case with the matrix elements of Eqn. (19). Hence to obtain solutions of Eqn. (16) it is necessary to adopt an iterative procedure.

The large number of multicenter two-electron integrals which have to be evaluated leads to computational difficulties[57,70–72]. Computer programs for such calculations are available. However, they require a lot of computer time and so far few 'ab initio' calculations have been reported for transition metal complexes. Usually approximations for the multicenter integrals are introduced which reduce the computational effort without too severely affecting the estimated electron distribution in the molecule[73].

Sugano and Shulman[77] have reported a semi-quantitative MO calculation on the ion NiF_6^{4-}; they obtained a value of 6350 cm^{-1} for $10Dq$ compared to the experimental value[78] of 7250 cm^{-1}. In their model they assumed that the ion NiF_6^{4-} could be considered as a separate entity in the crystal and that it had a negligible amount of covalency in the Ni–F bonds. Consequently, they neglected overlap and used orbitals more appropriate to a crystal field than to a MO model. Nevertheless, when solving for the MO's they evaluated the two- and three-center integrals, and demonstrated that the only contributions to $10Dq$ with the correct sign came from the off-diagonal matrix elements which are the elements associated with covalency. They also demonstrated that the effects of π bonding between Ni and F are not negligible. When evaluating $10Dq$ they assumed that only the energies of the antibonding orbitals are affected by an electronic transition. However, if the energies of both the bonding and the antibonding orbitals are allowed to change the calculated value of $10Dq$ is reduced to[79] 2800 cm^{-1}. It has been pointed out that the effects of electron correlation have been omitted from the Sugano and Shulman calculation[80]. This omission has been corrected by a configuration interaction approach resulting in a value of 5400 cm^{-1} for $10Dq$ [81]. It has also been demonstrated that by the use of a large basis set, MO calculations excluding configuration interaction can account for the correlation effects in transition metal fluorides[82]. Some of the apparent discrepancies that exist in different authors calculated values of $10Dq$ for NiF_6^{4-} and other similar fluorides could lie with their definitions of this parameter[7].

A SCF-MO calculation on NiF_6^{4-} in which 74 contracted Gaussian functions are used as basis orbitals has been reported[83]. In this calculation all the poly-center molecular integrals were accurately calculated[83], with a resulting value of 17933 cm^{-1} for $10Dq$ when the Ni 4*s* and 4*p* functions are excluded, and 29194 cm^{-1} when they are included. These results are in qualitative agreement with those obtained when a basis of Slater orbitals is used[84]. Even so, the poor agreement of these results with the experimental value of $10Dq$ indicates that the validity of the cluster model for a solid with a Perovskite structure is open to criticism.

However, SCF-MO calculations have been recently reported on the clusters TiF_6^{3-}, CrF_6^{3-}, FeF_6^{4-} and NiF_6^{4-} which have restored some confidence in 'ab initio' calculations on these systems[85]. The MO's were constructed from linear combinations of free-ion atomic orbitals which are orthogonal at each center. Slater atomic orbitals which approximate the Hartree–Fock orbitals were employed for the fluoride ions and the metal orbitals. All the one-

and two-center integrals were obtained exactly whereas the three-center integrals were obtained using Mulliken's approximation[86,87] (Section C, iii). Integrals containing products of two atomic orbitals on different fluoride ions were found to be negligible. For NiF_6^{4-} the calculated value of the lowest electronic $d \rightarrow d$ transition usually taken as the $10Dq$ value, is 7922 cm^{-1} when the Ni 4*s* and 4*p* basis functions are excluded and 7126 cm^{-1} when they are included. The agreement with the experimental value of 7250 cm^{-1} is obviously good and gives encouragement for further semi-quantitative MO calculations on transition metal complexes.

A number of MO calculations have also been reported on complexes which are usually considered to be more covalent than metal fluorides. In many cases the overlap integrals are much larger than those encountered in calculations on the metal fluorides, and, often rather drastic approximations are applied in the evaluation of the necessary matrix elements, as discussed in sections C, v and C, vi.

Semi-quantitative MO calculations on transition metal complexes involve more effort than semi-empirical ones both in understanding the problems involved, and in performing the actual calculation. Until a more comprehensive range of complexes has been treated by semi-quantitative MO methods it seems likely that the semi-empirical calculations, which give meaningful results for series of related molecules, will be preferred by chemists.

(v) Relationships between semi-quantitative and semi-empirical MO formulations

One of the most common approximations that have been made in attempts to solve Roothaan's equations (Eqn. (16)) is the zero differential overlap (ZDO) approximation. It was originally introduced into the Pople–Pariser–Parr (PPP) theory of conjugated hydrocarbons[74] and involves the following approximations

(a) all overlap integrals are neglected;
(b) in the evaluation of two electron integrals the charge distribution $\chi_p\chi_q$ is neglected if χ_p and χ_q belong to different centers;
(c) the matrix elements H_{pq}^{core} are equated to zero unless χ_p and χ_q either belong to the same center or are nearest neighbours.

An extension of this scheme involving the complete neglect of differential overlap (CNDO) has been introduced by Pople, Santry and Segal[75,76]. In the CNDO model the charge distribution $\chi_p\chi_q$ is neglected even if the two orbitals belong to the same atomic center.

These approximations simplify Roothaan's equations by avoiding the evaluation of polycenter integrals. Recently some justification for using them in calculations on transition metal complexes has been presented[6]. CNDO type of calculations have been reported for the permanganate ion[6,88,89] and titanium tetrachloride[90,91]. Reasonable agreement has been reported between the results of the CNDO calculations on the permanganate ion and those from a SCCC model using matrix elements corrected by the inclusion of ligand field terms[92], and those from an 'ab initio' SCF-MO calculation[93]. However, the assignment of the electronic spectrum of the permanganate ion has been the subject of much experiment, discussion and controversy[15,27,31,89,94–98]. Consequently it is not reasonable to claim a general success for a particular MO description on the basis of a prediction of the electronic

spectrum of this ion. The small energy separations derived from the CNDO and 'ab initio' SCF-MO calculations indicate that any estimation of transition energies should include the effects of configuration interaction. From the results obtained it does seem that the CNDO approach, when consistently formulated, is able to supply a reasonably accurate and detailed description of the electronic structures of the permanganate ion and titanium tetrachloride.

The ZDO approximation of the SCF-LCAO-MO formulation can be interpreted in two ways[99–101]. One consists of a regrouping of terms followed by a consistent use of the Mulliken approximation[85,86] for multicenter electron interaction integrals in Eqn. (33). The second interpretation involves the use of an orthogonalised atomic orbital (OAO) basis set as suggested by Löwdin[102,103].

Löwdin has chosen to define the OAO's by

$$\lambda = \chi S^{-\frac{1}{2}} \tag{35}$$

where λ is a row matrix describing the OAO set, χ is a row matrix of the starting atomic orbital set and S is a square matrix defined in terms of the overlap integrals S_{pq} given by Eqn. (17). The OAO set is chosen such that S^{λ}_{pq} is zero if $p \neq q$. They also approximately satisfy the ZDO requirement which may be expressed as

$$<pq\,|\,st>^{\lambda} = <pp\,|\,ss>^{\lambda} \delta_{pq} \cdot \delta_{st} \tag{36}$$

where the λ superscript denotes that OAO's are being used, the δ's are Kronecker delta functions. The equivalence of the use of the ZDO approximations and of OAO basis sets has been demonstrated by the numerical evaluation of some two-center repulsion integrals[104–106]. However, OAO's do not appear to have been widely employed yet in calculations on transition metal complexes. Instead Mulliken's approximation[85,86] for multicenter integrals is often adopted. Whilst Mulliken was concerned with integrals, the approximation is usually written as[107]

$$\chi_p(1)\,\chi_q(1) = \tfrac{1}{2} S_{pq} [\chi_p(1)\,\chi_p(1) + \chi_q(1)\,\chi_q(1)] \tag{37}$$

For this approximation to be valid, the centers to which the atomic orbitals χ_p and χ_q belong should be close neighbours, different atomic orbitals on the same center should be orthogonal and the atomic orbitals concerned should be of the same type.

By means of Eqn. (37), the multicenter electron interaction integrals of Eqn. (32) may be approximated in terms of products of two-center repulsion integrals and atomic overlap integrals, such that

$$<pq\,|\,st> \simeq \tfrac{1}{4} S_{pq} S_{st} [<pp\,|\,ss> + <pp\,|\,tt> + <qq\,|\,ss> + <qq\,|\,tt>] \tag{38}$$

and $$<pt\,|\,qs> \simeq \tfrac{1}{4} S_{pt} S_{qs} [<pp\,|\,qq> + <pp\,|\,ss> + <tt\,|\,qq> + <tt\,|\,ss>] \tag{39}$$

However the approximation given by Eqn. (39) is not a very accurate one[88,89].

The evaluation and tabulation of one- and two-center integrals has been discussed by numerous authors[57,108–116]. In some cases these integrals have been calculated exactly using the DIATOM programs of Corbato and Switendick[117].

From Eq. (31) H_{pq}^{core} is the sum of kinetic energy and core attraction terms; treatment of the latter by the Mulliken approximation, shows that it is proportional to the overlap integral S_{pq} as indicated in Eq. (40).

$$\int \chi_p^* \sum_x \frac{Q_x}{r_x} \chi_q \, d\tau \simeq \frac{S_{pq}}{2} \left[\int \chi_p^* \sum_x \frac{Q_x}{r_x} \chi_p \, d\tau + \int \chi_q^* \sum_x \frac{Q_x}{r_x} \chi_q \, d\tau \right] \tag{40}$$

where a point charge approximation is used for V_x. Mulliken's approximation cannot be used on the kinetic energy term which is expected to be large if $p \equiv q$. If p and q are adjacent atoms it should be small, and negligible otherwise. Hence if p and q are immediately neighbouring atoms H_{pq} and S_{pq} should not be directly proportional due to the presence of the kinetic energy term. Proportionality is only to be expected if p and q are second neighbours or further apart. If χ_p and χ_q belong to the same atom the kinetic energy part of H_{pq} will be sufficiently large to give the matrix element a value very different from those of the other H_{pq} elements[118]. Hence, it is apparent from Eq. (23) that it is necessary to have $K \neq 1$ if the kinetic energy part of the Hamiltonian is to be taken into account.

In discussing the role of electronic kinetic energy in molecules, Ruedenberg has considered the changes which occur in the atomic electronic distribution as atoms move from infinite separation to the positions that they eventually occupy in a molecule[265,266]. At infinite separation a rearrangement of the electrons in each atom takes place such that the atom is promoted to its valence state. The electronic rearrangement is considered to produce two effects, hybridization and contraction of the atomic orbitals. Hybridization results in an increase in the electronic potential energy and corresponds in semi-empirical MO calculations on first row transition metal compounds to the use of the $4s$ and $4p$ valence orbitals. Although particular orbitals may expand there is always an over-all contraction of atomic orbitals when an atom is promoted to its valence state. This results in a considerable decrease in the potential energy and a slightly larger increase in the kinetic energy of the electrons. Consequently the net effect, on the electronic energy, of valence state promotion is a large increase in kinetic energy.

Before bond formation occurs the interelectronic interaction between two atoms is a repulsive one. Upon bond formation some electrons become common to both atoms such that the interatomic electronic repulsive energy is decreased. However, since the electronic charge cloud of each atom has effectively increased there is an increase in the intra-atomic electronic repulsion energy. Ruedenberg concludes that it is the over-all decrease in electronic kinetic energy which is the major factor contributing to the stabilization of covalent bonds. Since this decrease is derived from both intra- and inter-atomic electronic sources it is to be expected that the kinetic energy term should affect the diagonal and off-diagonal matrix elements differently. However the off-diagonal contribution is often as important as the diagonal one[38,123]. In semi-empirical MO calculations on transition metal compounds the kinetic energy is normally assigned to $\hat{H}^{\text{core}}$ and is thus estimated from the

VOIP's for the separated atoms. Consequently changes in the electronic kinetic energy upon bond formation are ignored in all but the most complete calculations because approximate forms of the Hamiltonian operator (section C, i) do not explicitly allow for them*. The importance of the kinetic energy contribution to the off-diagonal elements has been recognised by some authors[38,45,119,123]. Consequently it is not surprising that a different value of K has been required for each type of bond in order to account for experimental values of $10Dq$, and that K_σ should depend upon the metal and its oxidation state[33].

It has been claimed that the approximated integrals obtained from the Mulliken procedure should be treated as theoretical quantities to be calculated rather than to be assigned empirical values[120]. This requirement has been overlooked in many calculations on transition metal complexes. Richardson and Rundle[121] have applied Mulliken's approximation to the Coulomb and exchange parts of Roothaan's closed-shell form of the SCF operator. This results in a one-electron operator of the form given by Eqn. (41)

$$F = T - \sum_x \frac{Q_x}{r_x} + \sum_i \sum_p \sum_q C_{ip}\, C_{iq}\, S_{pq} [2 < |pp> - <p|p>] \tag{41}$$

This operator has been the basis of several series of semi-empirical MO calculations on transition metal complexes[38,40,92,122-124]. Eqn. (41) is an exact equivalent of the ZDO approximation to the SCF operator when OAO's are used. However, as mentioned previously OAO's do not appear to have been used in many calculations on transition metal complexes. The operator of Eqn. (41) may be written as[40,122]

$$F = T + V_w + \sum_x V_x \tag{42}$$

where V_w describes the potential due to atom w,

$$V_w = \sum_p a_p \{2 < |pp> - <p|p>\} - \frac{Q_w}{r_w} \tag{43}$$

where a_p is the gross orbital population in the atomic orbital χ_p on atom w, the terms inside the brackets $\{\ \}$ describe the contribution of the valence electrons of w to the effective field acting upon a given valence electron and $\frac{Q_w}{r_w}$ describes the effective field at the valence electron due to the core of atom w. The term V_x in Eqn. (42) is the operator for atom x, of the same form as Eqn. (43); the summation is taken over all of the atoms in the molecule.

The secular determinant corresponding to Eqn. (29) now becomes

$$|F_{pw,qx} - \epsilon_i S_{pw,qx}| = 0 \tag{44}$$

*We are very grateful to a referee for bringing this point to our attention.

where the atomic orbital χ_{qx} is associated with atom x and the operator F takes the form given by Eqn. (42). The diagonal matrix elements of this operator become

$$F_{pw,pw} = <\chi_{pw} \mid T + V_w \mid \chi_{pw}> + <\chi_{pw} \mid \sum_{x \neq w} V_x \mid \chi_{pw}> \tag{45}$$

The first term in Eqn. (45) may be evaluated by taking the basis orbitals χ_{pw} to be eigenfunctions of the operator $T + V_w$ with eigenvalues $\epsilon_{pw}(Q_w)$, where Q_w is the charge on atom w corresponding to the configuration obtained from a Mulliken population analysis[29]. Hence,

$$F_{pw,pw} = \epsilon_{pw}(Q_w) + <\chi_{pw} \mid \sum_{x \neq w} V_x \mid \chi_{pw}> \tag{46}$$

Using a point-charge approximation for V_x allows Eqn. (46) to be written as

$$F_{pw,pw} = \epsilon_{pw}(Q_w) + \sum_{x \neq w} Q_x <\chi_{pw} \mid \frac{1}{r_x} \mid \chi_{pw}> \tag{47}$$

In the WH procedure the first term of Eqn. (47) is identified with the negative of the VOIP and the second term is neglected. The second term accounts for the effect of separated charges within a molecule upon the electronic energy levels[40]. It has been described as a Madelung term[39] or ligand field correction term which may be evaluated exactly[40,92,122].

The off-diagonal matrix elements of the type $F_{pw,qx}$ are considered in different ways by various authors. The Goeppart–Mayer–Sklar approximation[125] is often used in this context[40,92,122–124]. This approximation assumes that the atomic function χ_{qx} is an eigenfunction of the operator $T + V_w$. Hence

$$<\chi_{pw} \mid T + V_w \mid \chi_{qx}> = S_{pw,qx} \cdot \epsilon_{qx}(Q_x) \tag{48}$$

so that the off-diagonal matrix elements may be written as,

$$F_{pw,qx} = S_{pw,qx}(\epsilon_{pw}(Q_w) + \epsilon_{qx}(Q_x)) - \tfrac{1}{2} S_{pw,qx} \left[\sum_{y \neq w,x} \left\{ <\chi_{pw} \mid V_y \mid \chi_{pw}> + <\chi_{qx} \mid V_y \mid \chi_{qx}> \right\} \right] - T_{pw,qx} \tag{49}$$

Fenske et al. have considered that the matrix elements inside the brackets [ ] in Eqn. (49), which contain the ligand field corrections in the diagonal elements of the atomic orbitals χ_{pw} and χ_{qx}, may be either evaluated[122], or approximated as a modified point charge integral[40]. Additionally Hillier et al.[92,123,124] have assumed a point charge approximation, using the atomic charge obtained from a Mulliken population analysis. The two-center kinetic energy integrals $T_{pw,qx}$ may be numerically evaluated.

Neglect of the last two terms in Eqn. (49) results in an expression similar to the WH approximation of the off-diagonal matrix elements, Eqn. (23). For molecules with small

charge separations the major deviation from the WH formalism can be seen from Eqn. (49) to occur through the two-center kinetic energy integrals $T_{pw,qx}$.

For more ionic molecules the ligand field corrections to the off-diagonal elements predominate.

Calculations based upon the approximations given in Eqns. (47) and (49) have been reported for the permanganate ion[122] and some organometallic molecules[92]. The results obtained appear to be in reasonable agreement with those of other approximate calculations and experimental data.

Harris[126] has recently criticised the use of iterative techniques in semi-empirical calculations such as the SCCC method. In these calculations the Hamiltonian matrix elements are assumed to be dependent upon the MO coefficients through the charge and bond order matrix, Eqn. (34). Consequently this dependence should be considered when the Variation Principle is applied to the expression for the total energy; this leads to the secular equations

$$(F_{pq} - \epsilon_i S_{pq})C_i = 0 \tag{50}$$

where ϵ_i are orbital energies in the SCF sense and F_{pq} are the matrix elements of an SCF type of Hamiltonian operator. In the SCCC calculations the secular equations that are solved are

$$(H_{pq} - \epsilon_i S_{pq})C_i = 0 \tag{51}$$

where H is the total energy Hamiltonian whose matrix elements are chosen by the usual WH procedures. It has been reported[127] that the use of Eqn. (51) rather than Eqn. (50) will not lead to a proper minimum of the total energy; this point should be considered when interpreting the results of iterative WH calculations.

Criticism of calculations using the operator defined by Eqn. (41) is based upon the inconsistent use of Mulliken's multicenter integral approximations[6]. One result of this inconsistency is that an electron is allowed to interact with itself[6,128,129].

Although any semi-empirical theory may be readily criticised for the approximations that it employs, it is not unreasonable to expect the approximations to be used consistently. Otherwise, the significance to be attached to the results obtained is not at all clear.

(vi) Electron population analyses

The Mulliken population analysis[29], consists of equally dividing the electronic overlap population between the metal and ligands and has been used extensively[6,40,89,91]. A more refined version of the Mulliken approximation due to Löwdin[130], takes account of the fact that the overlap population need not be distributed symmetrically between two atoms. Löwdin distributes the charges in a manner which preserves the dipole moment.

The Mulliken approximation may be written for two centres v and w as,

$$\chi_v\chi_w = a_v\chi_v^2 + b_w\chi_w^2 \tag{52}$$

where

$$a_v + b_w = S_{vw} \tag{53}$$

by comparison the Löwdin approximation is

$$a_v = S_{vw}(\tfrac{1}{2} - \langle x \rangle / R) \tag{54}$$

where S_{vw} is defined by Eqn. (53) and

$$\langle x \rangle = \frac{\int \chi_v \chi_w \, d\tau}{S_{vw}} \tag{55}$$

and R is the distance between the two atoms. The Löwdin approximation reduces to the Mulliken formulation when χ_v and χ_w differ only in the centres with which they are associated.

An alternative method of distributing the overlap charge considers the electronic charge Q_v on an atom v defined as[25,40,131]

$$Q_v = \frac{\sum_i N_i \left[\sum_p C_{ip}^2\right]}{\left[\sum_p C_{ip}^2 + \sum_q C_{iq}^2\right]} \tag{56}$$

where N_i is the number of electrons in the i^{th} MO, p refers to the atomic orbitals on atom v, and q to those on a neighbouring atom. This has been referred to as the modified Mulliken (MM) method[132]. Calculations on transition metal complexes, comparing the Mulliken and MM methods, have shown that the resulting electron population is similar for both approximations[40,41].

A further method of population analysis called the mid-plane method is similar to Löwdin's[133]. In this approximation a plane midway between atoms v and w, and perpendicular to the line joining them, divides the overlap charge between them such that

$$a_v = \int_{-\infty}^{0} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \, \chi_v \chi_w \tag{57}$$

where the coordinate x is measured from the midpoint between the atoms.

The mid-plane and Löwdin approximations have been compared with the Mulliken and MM methods[132,134,135]. With SCCC type calculations the Löwdin and mid-plane partitions produce charge distributions which show the same trend for the permanganate ion and the sulphate ion[135]. However, when compared to the results of a Mulliken population analysis, both of these methods show a significant movement of electron density away from the central atom onto the oxygen atoms. These results provide

confirmation of Mulliken's remark[136] that his method of population analysis would automatically favour the atom with the larger basis set if unbalanced sets on two atoms were used.

Stout and Politzer[132] have reported SCCC calculations using Cusachs[42] off-diagonal matrix element approximation, for some simple heteronuclear diatomic molecules. They have demonstrated that the Löwdin, Mulliken and MM methods of population analysis produce three significantly different charge distributions and the wavefunctions obtained by these methods have different energies and predict different dipole moments.

The wavefunction giving the most satisfactory agreement with experimental data was that obtained using the Löwdin method for the population analysis.

Doggett has used Mulliken's and Löwdin's methods in calculations on a series of hydrides[134]. He found that in the majority of cases the dipole moments obtained from Mulliken's method were seriously in error.

SCCC calculations that have been reported for transition metal complexes invariably incorporate Mulliken's method of population analysis. Since this leads to a transfer of charge to the metal, due to its relatively large basis set, an apparently high degree of covalency results.

Although Löwdin's approximation appears in many ways to be the best choice it has not been widely used in calculations on transition metal complexes. The use of a single type of population analysis in calculations on a series of related molecules can show valuable trends in electron density distributions. The qualitative nature of such results need not detract from their overall significance.

(vii) The angular overlap model

It is appropriate in a review article dealing with MO calculations on transition metal complexes to mention the angular overlap model, although it appears to be of limited application and seems not to be widely adopted. The model recognises the importance of the group overlap integral in the WH procedure, Eqn. (11), and considers its behaviour for each electronic energy level. The other terms in Eqn. (11) remain unchanged during this process. In this way the electronic structures of a number of related molecules can be rationalised by using very few assumptions other than the relative magnitudes of group overlap integrals[137,138].

The ligand symmetry functions are approximated by Kronecker δ functions, such that a linear combination of ligand σ orbitals may be written as

$$\psi_L = \sum_{i=1}^{N} N_i \, \delta(x - x_i)\delta(y - y_i)\delta(z - z_i) \tag{58}$$

where the coefficients N_i are normalised in the usual way.

The metal orbitals, ψ_M are considered as a product of angular and radial components, A_l and R_{nl} respectively, so that

$$\psi_M = A_l(x,y,z) \cdot R_{nl}(r) \tag{59}$$

which can form MO's with a combination of ligand σ orbitals having the same symmetry. The group overlap integrals are expressed in terms of two-center overlap integrals, S_{MX}, between the metal M and one of the ligand set X. The S_{MX} are then written as the product of two functions, an angular function Ξ, and a radial one S^*_{MX}.

$$S_{MX} = \Xi S^*_{MX} \tag{60}$$

where the angular function depends only upon the coordinates of the ligands, (x_i,y_i,z_i), and the atomic angular function, A_l, of the metal orbital, so that,

$$\Xi = \sum_{i=1}^{N} N_i A_l(x_i,y_i,z_i) \tag{61}$$

By means of second order perturbation theory the relative σ antibonding effects on the various orbitals of a given metal valence shell, denoted by the quantum number l, are found to be approximately proportional to Ξ^2. The introduction of a radial parameter σ^*, allows the relative energy of the antibonding orbitals formed by the l shell to be written as $\Xi^2 \overset{*}{\delta}$. If the WH parameter $K = 2$ in Eqn. (23) and the ligands in the complex are identical and at equal distance from the metal ion, then

$$\overset{*}{\delta} \simeq \frac{(S^*_{MX})^2 H_X{}^2}{H_M - H_X} \tag{62}$$

where $\overset{*}{\delta}$ has the same value for metal orbitals of the same valence shell but with different symmetry properties in the molecule.

The energies of the MO's derived mainly from the metal valence shell with quantum number l become dependent upon the symmetry of the molecule through the angular overlap function Ξ which is related to the molecular geometry by Eqn. (61).

Interest in the angular overlap model rests largely in low symmetry complexes of the lanthanides and transthorium elements[139–142], although it has recently been applied to the assignment of geometrical isomers of a Co^{III} complex[143]. The model appears to be most useful in qualitative discussions on metal complexes containing metal–ligand bonds with a small degree of covalency and in which the symmetry is sufficiently low to permit the metal valence shell orbitals to transform as different irreducible representations in the σ antibonding set.

As originally proposed the angular overlap model takes account of σ, π and δ antibonding as well as bonding orbitals[138]. However, this more general model does not yet appear to have found any practical application in transition metal chemistry.

D. MO CALCULATIONS OF SOME ELECTRONIC ENERGY LEVELS IN TRANSITION METAL COMPOUNDS

The purpose of many MO calculations on transition metal compounds has been the estimation of $10Dq$. Reasonable agreement with experiment has been obtained in many cases by the introduction of scale factors in semi-empirical calculations. It is often assumed that these scale factors compensate for the approximations employed in the calculation, unfortunately this is not always the case. In order to extensively test a theoretical calculation it is necessary to compare its predictions with more than one experimental parameter.

The significance that can be attached to the energies and wavefunctions derived from semi-empirical MO calculations has been the subject of considerable discussion[6,37,98]. In general the results obtained from semi-empirical MO calculations depend very closely upon the initial assumptions made in the calculation.

(i) General comments on the ordering of electronic energy levels

Most reported MO calculations have not dealt explicitly with the intensities of the electronic bonds. The order of energy levels obtained by calculation is usually compared with the electronic spectrum of the metal complex. In the case of any ambiguity arising from comparison with experimental data, it is usually assumed that the parity forbidden $d \rightarrow d$ bonds have the lowest intensities, the molar extinction coefficient ϵ ranging from 1 to 500 (litre · mole^{-1} · cm^{-1}). Charge transfer bands usually have ϵ values between 1000 and 10,000 and any ligand→ligand bands can be even more intense[144]. The latter can usually be recognised by comparison with the spectrum of the free ligand. However, some workers have estimated oscillator strengths from wavefunctions computed for the molecular ground state[15,30].

TABLE 1 [a]

ANALYSIS OF THE ELECTRONIC SPECTRUM OF $VOSO_4 \cdot 5\,H_2O$

Transition	*Energy (cm^{-1})*		*Oscillator strength* $\times 10^4$	
	Predicted (polarisation)	*Observed (polarisation)*	*Predicted*	*Observed*
$^2B_2 \rightarrow {}^2E^{I}$	12,502 (⊥)	13,060 (⊥)	3.9	1.1
$^2B_2 \rightarrow {}^2B_1$	18,794	16,000	vibronic	0.45
$^2B_2 \rightarrow {}^2A_1$	44,766	covered	vibronic	
$^2B_2 \rightarrow {}^2E^{II}$	38,800	41,700 (⊥)	26.4	50.3
$^2B_2 \rightarrow {}^2B_2$	44,000 (∥)	~50,000	44.7	150

[a] Taken from Ballhausen and Gray[30]. The experimentally observed energies and oscillator strengths refer to aqueous solution, 0.01–0.10 *M* in H_2SO_4. In the $VOSO_4 \cdot 5H_2O$ crystal the $^2B_2 \rightarrow {}^2E^{I}$ and the $^2B_2 \rightarrow {}^2E^{II}$ bands are observed at the same energies in ⊥ polarization only.

(ii) Octahedral compounds

The energies and intensities of the electronic transitions derived from a WH calculation[30] on the vanadyl ion are compared with experimental values in Table 1. The first three transitions in Table 1 are essentially $d \rightarrow d$ in character, whilst the $^2B_2 \rightarrow {}^2E^{II}$ and $^2B_2 \rightarrow {}^2B_2$ are charge transfer bands. It is noteworthy that in agreement with experiment the calculated oscillator strengths for these latter bands are greater than for the vibronically allowed $d \rightarrow d$ bands.

In the spectra of octahedral complexes exhibiting ligand to metal charge transfer bands mixing may occur between the $d \rightarrow d$ and charge transfer transitions. Fenske[145] has shown from theoretical arguments that the mixing involves those ligand to metal charge transfer transitions in which the final states involve the e_g but not the t_{2g} orbital of the metal. By taking this mixing into account reasonable agreement has been found between the calculated and experimental relative intensities for octahedral transition metal complexes.

Numerous MO calculations of various types have been reported for the hexahalide complexes of the first row transition metal ions. The estimated values of $10Dq$ and of the energy of the first L→M charge transfer band, taken to be $t_{2u} \rightarrow 2t_{2g}$ for the configurations d^0 to d^7, are recorded in Table 2.

Although in some cases, not all authors agree on the experimental value of $10Dq$ it can be seen from Table 2 that reasonable agreement between the calculated and experimental parameters can be obtained by both semi-empirical and semi-quantitative MO calculations. However it should be remembered that agreement between the calculated and experimental results does not necessarily substantiate the validity of the theoretical method used[37]. It is necessary in all cases of discussion of calculated molecular parameters to consider the approximations involved. Ballhausen and Johansen[146], have estimated the static Jahn–Teller effect in CuF_6^{4-} by means of WH type calculations. They calculate that the difference in bond lengths due to the Jahn–Teller distortion will be 0.16 Å if the WH factor $K = 2.0$ and 0.20 Å if $K = 1.75$. This results in reasonable agreement with the experimental difference of 0.13 Å [147]. However they are not able to predict whether the stable conformation should be an elongated or a compressed octahedron. Barnum[148,149] has reported some semi-empirical MO calculations on trivalent metal acetylacetonates, $M(acac)_3$, where M = Ti, V, Cr, Mn, Fe, Co in which only the metal t_{2g} set and the ligand π electrons were considered. He estimated the integrals H_{pp} from atomic electronegativities and H_{pq} for the ligand system from bond energies. The metal–oxygen exchange integral was left as a variable that is determined by fitting the calculated energy levels to the observed electronic spectrum. The effect of varying the metal–oxygen exchange integral on the energy levels of $Co(acac)_3$ is shown in Fig.4. Reasonable agreement is found between the electronic spectrum and the energy levels given in Fig.4 when the metal–oxygen exchange integral is given a value of 14,000 cm^{-1}. Due to the drastic approximations made in the model used for the calculation this agreement is probably largely fortuitous; however the model does provide a description of the three $\pi \rightarrow \pi^*$ and the two charge transfer $d \rightarrow \pi^*$ transitions observed in the electronic spectrum of $Co(acac)_3$.

Recently Barnum's calculations have been shown to be in error in that an orthogonalization of symmetry orbitals has been assumed which is invalid[150]. The

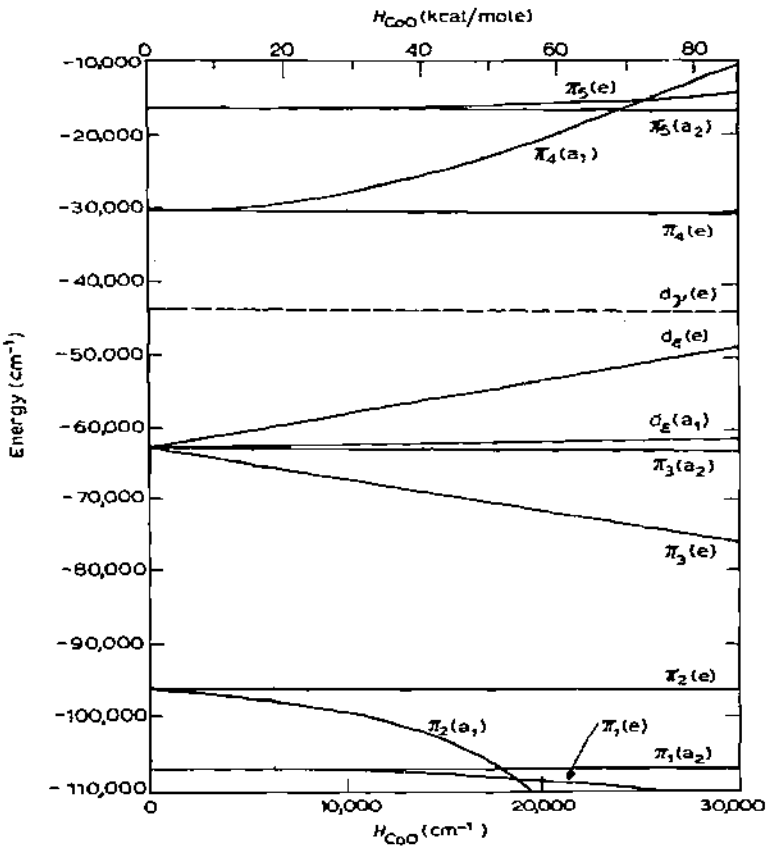


Fig.4. The effect of metal–oxygen π bonding on the energy levels of $Co(acac)_3$ (reproduced from Barnum[149]).

correction of this error permits a qualitative discussion of the electronic spectra of metal tris-acetylacetonates similar to that given by Barnum. However neither of these calculations is able to account for the first appearance potentials of the ions $M(acac)_3^+$ which are identified with the ionization potentials of $M(acac)_3$, and it has been suggested[151] that Koopmans' theorem may not apply to this system. Apart from the gross approximations involved in these calculations it seems likely that the inclusion of some σ orbitals in the calculation would provide a more satisfactory description of the $M(acac)_3$ complexes, as has been demonstrated[152] in the case of $Co(acac)_3$.

Semi-empirical MO calculations relating to the electronic structure and bonding in some transition metal carbonyls has been reported[153–158]. Satisfactory agreement has been found between the calculated energies and oscillator strengths and the observed transitions and their intensities in the spectrum of chromium hexacarbonyl and some of its arene derivatives[154].

Koopman's theorem allows the calculation of ionisation potentials to within 10% of

TABLE 2

COMPARISON OF CALCULATED AND OBSERVED VALUES OF $10Dq$ AND THE FIRST ALLOWED L → M CHARGE-TRANSFER BAND FOR SOME OCTAHEDRAL HALIDE COMPOUNDS OF FIRST ROW TRANSITION METAL IONS (all energies are given in 10^3 cm^{-1})

Compound	*10Dq*		*Type of calculation*	*First L → M charge-transfer band*		*Ref.*
	Calculated	*Observed*		*Calculated*	*Observed*	
TiF_6^{3-}	15.97		WH	54.18		34
	17.3	17.5	SCCC	59.0	>50	27
	17.5		Semi-empirical	116.2		41
	17.18		SCF without Ti 4*s* and 4*p* orbitals			85
	17.15		SCF with Ti 4*s* and 4*p* orbitals			85
	25.7		WH with L–L overlap and free ion approx.			37
	27.5		WH without L–L overlap			37
	30.6		WH with L–L overlap and hydride approx.			37
$TiCl_6^{3-}$	13.4	13.8	SCCC	37.0	≳38	27
	13.4		Semi-empirical	63.4		122
$TiBr_6^{3-}$	13.1	13.0	SCCC	25.8	<38	27
VF_6^{2-}	20.75	20.1	WH	42.7	–	35
VF_6^{3-}	16.0	15.9	SCCC	48.4	>40	27
	16.22		Semi-empirical	100.1		41
	17.2		WH	43.2		35
VF_6^{4-}	12.1	12.0	SCCC	45.0	⩾40	27
VCl_6^{3-}	12.02		Semi-empirical	51.7		122
	13.7	13.9	SCCC	27.7	≳40	27
CrF_6^{3-}	15.6	15.2	SCCC	38.9	>37	27
	12.7		SCF closed shell			7
	18.45		SCF open shell			7
	16.54		Semi-empirical	83.8		41
	6.88		SCF with ionic Hamiltonian			81
	16.864		SCF without Cr 4*s* and 4*p* orbitals			85
	15.879		SCF with Cr 4*s* and 4*p* orbitals			85
$CrCl_6^{3-}$	13.6	13.8	SCCC	21.8	>37	27
	11.86		Semi-empirical	48.0		122
$CrBr_6^{3-}$	13.3	13.2	SCCC	12.8	<37	27
MnF_6^{2-}	21.9	21.8	SCCC	36.9	>28	27
MnF_6^{4-}	8.4	8.4	SCCC	29.6	>43	27

Compound	*10Dq*		*Type of calculation*	*First L → M charge-transfer band*		*Ref.*
	Calculated	*Observed*		*Calculated*	*Observed*	
FeF_6^{3-}	13.7	14.0	SCCC	23.5	>30	27
	15.97		Semi-empirical	53.5		41
	10.95		SCF Closed Shell			7
	13.9		SCF Open Shell			7
	7.5		Semi-quantitative			264
	7.3		SCF with ionic Hamiltonian			81
FeF_6^{4-}	8.496	7.660	SCF without Fe, 4*s* and 4*p* orbitals			85
	8.090		SCF with Fe, 4*s* and 4*p* orbitals			85
$FeCl_6^{3-}$	10.08	9.2	Semi-empirical	24.5		122
CoF_6^{3-}	13.1	13.1	SCCC	16.9		27
	15.5		Semi-empirical	42.0		41
NiF_6^{4-}	7.3	7.25	SCCC	17.6	>60	27
	18.3		SCF closed shell			7
	7.25		SCF open shell			7
	17.93		Unrestricted SCF without Ni, 4*s* and 4*p* orbitals			83
	29.19		Unrestricted SCF with Ni, 4*s* and 4*p* orbitals			83
	10.8		Unrestricted Hartree–Fock SCF			84
	4.67		SCF with a contracted Gaussian basis set			267
	4.04		SCF with ionic Hamiltonian			82
	7.922		SCF without Ni, 4*s* and 4*p* orbitals			85
	7.126		SCF with Ni, 4*s* and 4*p* orbitals			85
	6.35		SCF			77
	2.8		SCF			79
	5.4		Semi-quantitative			81
CuF_6^{4-}	13.137		WH			47
	13.48		WH			47
	14.01		WH			47
	14.66		WH			47

the observed vertical ionization potential; this is demonstrated in Table 3 for some orbitals of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ derived from semi-empirical MO calculations[153,156].

Evaluation of the overlap populations derived from the same calculation shows that the σ bond between carbon and oxygen is apparently unchanged upon bonding to a transition metal[153]. This suggests that π-back-bonding is responsible for the reduction in the carbon–oxygen force constant when compared with the carbon monoxide molecule. In the case of $V(CO)_6^-$, Beach and Gray[156] have shown that π-back-donation accounts for the largest redistribution of electron density when the complex is formed. They have also demonstrated that as the positive charge on the metal increases in an isoelectronic series the

TABLE 3

COMPARISON OF CALCULATED AND OBSERVED IONIZATION POTENTIALS FOR $Cr(CO)_6$, $Mo(CO)_6$ AND $W(CO)_6$

Molecule	*Orbital symmetry*	*Vertical ionization potential (eV)*		*Ref.*
		Calculated	*Observed*	
$Cr(CO)_6$	$2t_{2g}$	8.19	8.40	153
	$4t_{1u}$	14.02	13.32	153
	$1t_{1u}$, $1t_{2u}$, $3t_{1u}$	14.90, 14.95, 14.97	14.12	153
	$3a_{1g}$	15.23	14.49	153
	$3e_g$	16.14	15.2	153
	$1t_{2g}$	16.24	15.6	153
	$2t_{1u}$	17.69	17.48	153
	$2a_{1g}$	18.51	18.7	153
	$2e_g$	19.01	19.3	153
$Cr(CO)_6$	$2t_{2g}$	8.38	8.41	156
	$2e_g$	13.14	13.32	156
	$3t_{1u}$	13.28	14.12	156
	$2a_{1g}$	14.98	14.49	156
	$1t_{1g}$	15.64		156
	$1t_{2u}$	16.46		156
	$2t_{1u}$	17.02	17.48	156
	$1t_{2g}$	18.52	~18.5	156
$Mo(CO)_6$	$2t_{2g}$	8.45	8.41	156
	$2e_g$	13.34	13.10	156
	$3t_{1u}$	13.41	14.05	156
	$2a_{1g}$	15.03	14.60	156
	$1t_{1g}$	15.76	15.12	156
	$1t_{2u}$	16.52		156
	$2t_{1u}$	17.04	17.63	156
	$1t_{2g}$	18.47		156
$W(CO)_6$	$2t_{2g}$	8.54	8.34	156
	$2e_g$	13.41	13.22	156
	$3t_{1u}$	13.44	14.12	156
	$2a_{1g}$	14.95	14.54	156
	$1t_{1g}$	15.88	15.11	156
	$1t_{2u}$	16.56		156
	$2t_{1u}$	16.97	17.6	156
	$1t_{2g}$	18.33		156

degree of back-donation falls off sharply. Additionally Caulton and Fenske have demonstrated that there is no bonding between the metal and oxygen atoms and that the metal–carbon overlap populations decrease as the metal oxidation state increases[153]. The observed metal–carbon stretching frequencies for a series of hexacarbonyls supports this suggestion; similar agreement has been reported for some hexacyanides of transition metals with the d^6 configuration[159]. It has also been demonstrated that charge density calculations on octahedral hexacarbonyl complexes provide an explanation of the reactivity of the hexacarbonyls towards nucleophiles[153].

The relative π acceptor abilities of NO^+, CN^- and CO have been deduced from calculations on metal complexes containing these species as ligands[156,159–161]. By comparing the calculated π populations on these ligands the order of π acceptor ability is $NO^+ \gg CO >$ CN. This agrees with the domination of the electronic structure of the nitroprusside ion by a very strong Fe–NO bond which has been demonstrated by a SCCC–MO calculation and a polarized electronic spectrum from a single crystal sample[160].

Recently Fenske and DeKock[157] have reported non-parameterized calculations on $Mn(CO)_5L$ where L = H, Cl, Br, I. They obtain energies for the highest filled orbitals in very good agreement with data from photoelectron spectroscopic studies[162] as shown in Table 4.

Other calculations on octahedral metal complexes include some WH type calculations on some hexammines[33,163] and ZDO calculations[164] on $Cu(H_2O)_6^{2+}$ and $Cu(NH_3)_6^{2+}$. In the latter the electronic structures are discussed and the tetragonal distortion due to the Jahn–Teller effect is accounted for by the calculations.

Cotton and Haas[33] have shown the need to vary the WH parameter K as a function of metal and of oxidation state in a series of hexammine complexes to account for experimental values of $10Dq$. However by using better radial functions, including ligand–ligand overlap

TABLE 4[a]

COMPARISON OF CALCULATED AND OBSERVED ORBITAL ENERGIES IN eV FOR MEMBERS OF THE SERIES $Mn(CO)_5L$

Molecule	*Orbital symmetry*	*Orbital energy (eV)*	
		Calculated	*Observed*
$Mn(CO)_5H$	$8e$		
	$7e$	9.80	9.00
	$2b_2$	10.36	10.60
$Mn(CO)_5Cl$	$8e$	8.61	8.80
	$7e$	10.40	10.43
	$2b_2$	10.65	11.00
$Mn(CO)_5Br$	$8e$	7.92	8.76
	$7e$	10.15	10.04
	$2b_2$	10.47	10.80
$Mn(CO)_5I$	$8e$	7.46	8.35–8.65
	$7e$	9.95	9.57
	$2b_2$	10.29	10.32

[a] Taken from Fenske and De Kock[157].

TABLE 5

COMPARISON OF CALCULATED AND OBSERVED VALUES OF $10Dq$ AND THE FIRST ALLOWED L → M CHARGE-TRANSFER BAND FOR SOME TETRAHEDRAL COMPOUNDS OF FIRST ROW TRANSITION METAL IONS (all energies are given in 10^3 cm^{-1})

Compound	*10Dq*		*Type of calculation*	*First L → M charge-transfer band*		*Ref.*
	Calculated	*Observed*		*Calculated*	*Observed*	
$TiCl_4$	8.23		Semi-empirical	53.6		122
	8.7	8.7	SCCC	40.2	34.8	27
	53.4		CNDO	88.8		91
$TiBr_4$	7.5	7.6	SCCC	32.0	29.0	27
VCl_4	7.74		Semi-empirical	55.2		122
	9.0	9.0	SCCC	37.7	24.2	27
VCl_4^-	5.6	5.6	SCCC	37.0		27
CrO_4^{2-}	26.0	26.0	SCCC	48.2	26.8	27
	18.2		Semi-quantitative	37.4		167
	26.6		Semi-empirical	80.5		95
MnO_4^{2-}	19.2	19.0	SCCC	34.6	22.9	27
MnO_4^{3-}	14.8	14.8	SCCC	33.7	30.8	27
$MnCl_4^{2-}$	3.6	3.6	SCCC	21.5	30.0	27
	3.63		Semi-empirical	62.5		122
$FeCl_4^-$	5.0	5.0	SCCC	13.7	27.2	27
	5.08		Semi-empirical	25.2		122
$FeCl_4^{2-}$	4.1	4.0	SCCC	17.2		27
	4.2		Semi-empirical	47.3		122
$CoCl_4^{2-}$	3.7	3.7	SCCC	14.9	42.5	27
	3.87		Semi-empirical	41.5		122
$CoBr_4^{2-}$	3.1	3.1	SCCC	9.4	23.4	27
$NiCl_4^{2-}$	3.6	3.54	SCCC	8.4	35.8	27
	3.55		Semi-empirical	43.4		122
	3.9		SCCC	31.6		166

and using a value for the ionization potential of ammonia derived from photoionization data Wirth[163] has shown that the WH model is suitable for discussing the electronic structure of $Co(NH_3)_6^{3+}$, and by implication other metal hexammines. Cotton and Harris[165] have reported WH type of calculations on the series MCl_6^{2-} where M = Re^{IV}, Os^{IV}, Ir^{IV} and Pt^{IV}. They have used atomic orbital energies for the metal ions very close to those of the uncharged atoms and obtained satisfactory agreement with the experimental *d* orbital splittings and charge-transfer spectra.

(iii) Tetrahedral compounds

Some results taken from MO calculations of electronic energy levels of tetrahedral metal complexes are presented in Table 5. The first allowed L→M charge transfer band is considered to occur between MO's corresponding to the irreducible representations $t_1 \rightarrow 2e$ for metals with the configurations $d^0 \rightarrow d^5$ and from $t_1 \rightarrow 4t_2$ for the configurations d^7 and d^8.

The much debated permanganate ion (see section C, v) is purposely omitted from this tabulation since it has been discussed in detail in a recent review article[6], where the superiority of CNDO calculations[89] over the WH approach has been demonstrated. Since then a series of SCCC calculations[123] and an 'ab initio' calculation[93] have been reported for this ion, there appears to be reasonable agreement between these results and those from CNDO calculations.

The value of $10Dq$ is taken to correspond to the energy difference of the $2e$ and $4t_2$ MO's. Since a number of the complexes listed in Table 5 have metals with d^0 configurations a $d \rightarrow d$ transition corresponding to $10Dq$ is often obtained experimentally as the energy difference between two L → M charge transfer bands. During a charge-transfer excitation the ligand field, and consequently the anti-bonding MO energy separation, changes[95] such that experimental values of $10Dq$ for these complexes may not be reliable.

In addition to the permanganate ion, CNDO type calculations have also been reported by Dahl et al.[91,167] for the isoelectronic series CrO_4^{2-}, VO_4^{3-} and $TiCl_4$. These calculations show that the order and nature of the excited states vary from one of these tetrahedral systems to the next. This is in contrast to the findings obtained from semi-empirical MO calculations[27] which predict the same MO energy level diagram for all the tetrahedral molecules of first-row transition metals. Agreement with the results of the ordering of the excited states of MnO_4^- and CrO_4^{2-} from the CNDO calculations is reported from a calculation employing the ZDO approximation and empirically evaluated integrals[95].

However it is surprising that with the exception of MnO_4^- the order of the energy levels shown for the species in Fig.5 is inverted when compared to that expected from crystal field arguments. The $4t_2$ and $2e$ orbitals are those which correspond to the metal *d* orbitals in the crystal field case, hence $2e$ is expected to be lower in energy than $4t_2$ in a tetrahedral environment. A tentative assignment of electronic transitions has been proposed based on the electronic energy levels given in Fig.5. However this must be considered with great caution[167].

The position of the $2e$ orbital is very dependent upon the form of the radial functions used. However in order to significantly change the energy level scheme given in Fig.5, for

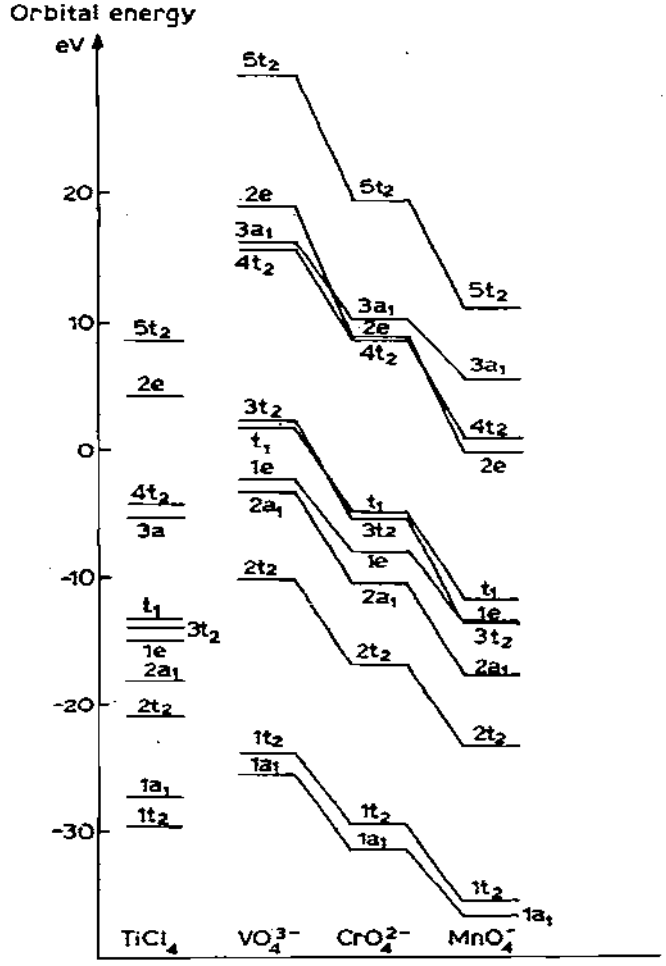


Fig.5. MO energy level diagram for some tetrahedral species. The filled orbitals are $1a_1$, $2a_1$, $1t_2$, $2t_2$, $3t_2$, $1e$ and t_1 in all cases (reproduced from Dahl and Johansen[167]).

$TiCl_4$, drastic changes in the radial functions would be necessary[167]. In a CNDO calculation on $TiCl_4$ the metal and ligand valence orbitals have been extensively varied.

Slater-type radial functions have been chosen which have been Schmidt orthogonalised to the core orbitals[91].

The effect of varying the $3d$ orbitals corresponding to the configurations $3d^1$ to $3d^8$ whilst the metal $4s$ and $4p$, and the ligand orbitals remain unchanged is shown in Fig.6. It is surprising that there is very little variation of the MO energy levels with respect to each other with change in the $3d$ orbital function. In each case the empty orbitals remain in the order $5t_2 > 2e > 4t_2 > 3a_1$. This ordering appears not to be any more sensitive to changes in the Ti, $4p$ and $4s$ orbitals.

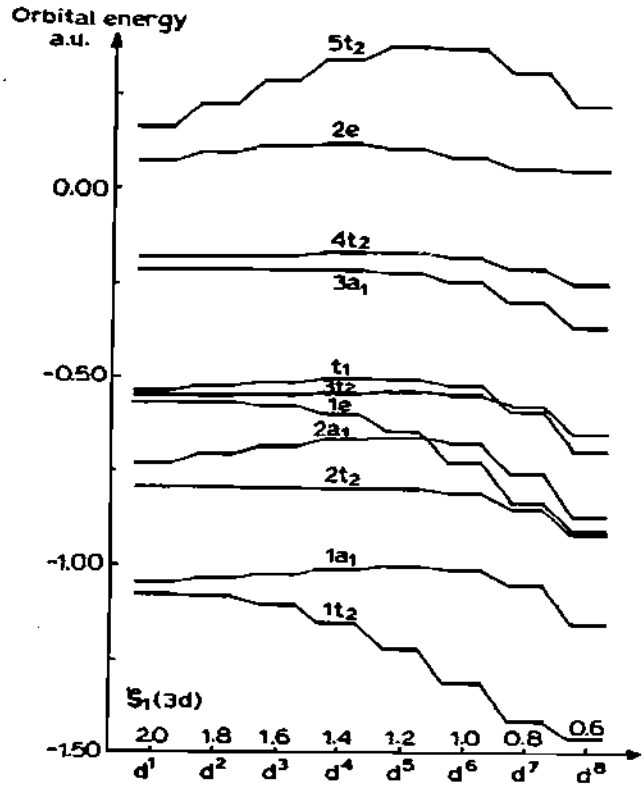


Fig.6. Variation of the one-electron MO levels, in $TiCl_4$, with changes in the Ti 3*d* orbitals. The metal 4*s* and 4*p* and the chlorine valence orbitals are unchanged (reproduced from Becker and Dahl[91]).

The six band spectrum of gaseous $TiCl_4$ over the range 4000–1100 Å has been tentatively assigned on the basis of these CNDO calculations[90]. This assignment is not in agreement with others on $TiCl_4$. It seems likely that any future assignment of the electronic spectrum of $TiCl_4$ will have to be considered together with MO calculations.

Valenti and Dahl[166] have reported a WH type of calculation on $NiCl_4^{2-}$. In discussing electronic transition energies they have considered electron–electron repulsion; consequently, their energy levels allow a more satisfactory estimate of the position of the first L → M charge-transfer band than that derived from SCCC data in which the electron repulsion effects were not considered[27]. The estimated value of $10Dq$ does not seem to be seriously effected by this omission (see Table 5).

Semi-empirical MO data relating to the static Jahn–Teller effect in VCl_4, $NiCl_4^{2-}$, $CuCl_4^{2-}$ and CuF_6^{4-} have been reported[168,169]. The energy level splittings derived from these calculations appear to be in reasonable agreement with those obtained from experimental data[170].

Recently SCF calculations including all electrons have been reported for the non-existent molecules ScH_3NH_3 and TiH_3F[171]. In addition to describing the electronic

structures these calculations have provided parameters which may be transferred to more complicated molecules containing Sc and Ti. The hope is that SCF data may be obtained for more complicated molecules without performing the full SCF calculation.

(iv) Square planar compounds

The ordering of the metal *d* orbitals in the d^8 square planar tetrahalide complexes of Pd^{II}, Pt^{II} and Au^{III} has been the subject of many reports. Crystal field[172] and simple MO [173] arguments have been produced in favour of the orbital sequence $d_{xz}, d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$. The electronic spectrum of K_2PtCl_4 both in the solid state and in various solvents can be interpreted using this sequence and $d_{z^2} < d_{xz}, d_{yz} < d_{xy} < d_{x^2-y^2}$, which has been supported by SCCC and WH type of MO calculations[174–176]. The WH calculations have used a wide range of values for the Pt, VOIP's and wavefunctions and the WH factor *K*. More sophisticated spectroscopic measurements lend support to this latter orbital sequence[177–179].

The relatively low energy accorded to the $5d_{z^2}$ orbital in $PtCl_4^{2-}$ probably arises from the large participation of the Pt 6*s* orbital in the σ bonding[174]. Since both the $5d_{z^2}$ and 6*s* orbitals bond with the same ligand combination the large participation of the 6*s* orbital leaves the $5d_{z^2}$ in a relatively stable position. However the d_{z^2} need not be the lowest energy *d* orbital in all square planar complexes. It has been suggested that it is the lowest in the tetrahalides because of the low spectrochemical position of the halide ligands, indicating good π donor and poor $\sigma \rightarrow d$ donor properties[174]. Ligands with better π acceptor or $\sigma \rightarrow d$ donor potential, or both, can cause the d_{z^2} orbital to be above the d_{xz}, d_{yz} pair. This is in agreement with predictions for $Ni(CN)_4^{2-}$ for which a substantial ring current has been claimed due to electron delocalization through the cyanide system[173]. Support for this proposal is also given from the detailed assignments of the electronic spectra of complexes of the type $[MX_4]^{z}$ where $M = Pd^{II}, Pt^{II}, Au^{III}$ and $X = Cl^-, Br^-, CN^-, NH_3$ [172]. The halide complexes show strong ligand → metal charge-transfer bands, the cyanides show metal → ligand bands and the ammine complexes exhibit allowed $d \rightarrow p$ transitions[176]. A semi-empirical MO calculation[204] has been reported for $PdCl_4^{2-}$ in which the electronic spectrum is discussed in terms of the level ordering $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$.

WH type of calculations have been reported for square planar Ni^{II} complexes of maleonitriledithiolate[180] and dithioglycerol[181]. The results of these calculations have been used to satisfactorily assign the electronic spectra of complexes of Ni^{II}, Pd^{II}, Pt^{II} and Au^{III} with some sulphur ligands[180,182].

The results of an SCCC-MO calculation on Zeise's salt have been shown to be qualitatively in agreement with the $d \rightarrow d$ transitions assigned from polarized crystal spectra[183]. However in order to account for the charge-transfer bands a correction of approximately 15,000 cm^{-1} is required.

WH calculations including both σ and π orbitals have been reported for some square planar bis(β-ketoenolate) Cu^{II} and Ni^{II} complexes in which the Coulomb integrals of the oxygen atoms are used as variables. The calculations have given rise to reasonable assignments for most of the observed bands in the electronic spectra of these complexes

including agreement with some band polarization measurements[184-187]. This tends to support the approximations made in the calculations and the bonding scheme signified by them.

Other MO calculations reported on square planar complexes include a semi-empirical ZDO calculation on copper bis(dimethylglyoxime)[188] and a WH type of calculation on nickel bis-(dimethylglyoxime)[189]. An explanation of the dimerization of the copper complex in the crystalline state has been offered as a result of these calculations. Whereas in the nickel complex no evidence was found for bonding between adjacent metal atoms in the ground state. In both cases a satisfactory explanation of the electronic spectra was afforded by the calculations.

Gouterman et al. have reported a series of calculations on porphyrins[190-192] and metalloporphyrins with a view to understanding their electronic structure[43-45,193-197]. The biologically interesting porphyrins have metals present such as Mg, Fe and sometimes Cu. Some authors have performed WH type calculations on Fe porphyrin using only π electron orbitals, sp^2 hybrids on the central N atoms and $3d$, $4s$ and $4p$ orbitals of iron[198-201]. However in the calculations reported by Gouterman et al. all the valence orbitals of the H, C and N atoms as well as the metal $3d$, $4s$ and $4p$ orbitals are included.

The electronic spectra of the various metal porphyrins are reasonably similar indicating that the interaction between the metal orbitals and the porphyrin π system is rather weak. The energy level scheme, as obtained from a WH type of calculation, for the top filled and lowest empty orbitals of some metal porphyrins is given in Fig.7. In order to obtain agreement with the transition energies of the two lowest $\pi \rightarrow \pi^*$ transitions, $a_{2u} \rightarrow e_g$ and $a_{1u} \rightarrow e_g$, an interaction parameter in the H_{pq} matrix elements was adjusted[43-45].

In the Cu and Zn complexes the d orbitals are mainly of low energy and are thoroughly mixed with the ligand orbitals. The relatively high energy b_{1g} orbital has more metal $d_{x^2-y^2}$ character in the Cu complex than in the Zn complex and contains the

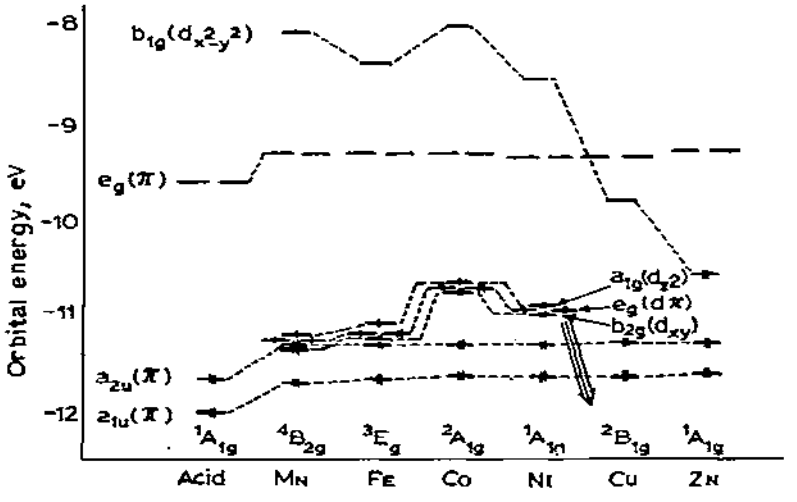


Fig.7. The calculated energies and symmetries of the top filled and lowest empty orbitals of some porphyrins (reproduced from Zerner and Gouterman[43]).

unpaired electron. In the other metal complexes the metal orbitals are largely unmixed and lie closely together between the highest filled porphyrin $a_{2u}(\pi)$ and the lowest empty porphyrin $e_g(\pi^*)$ orbitals. With the assistance of Fig.7 it is possible to make predictions of the energies of some electronic transitions, of magnetic properties and of the ease of reduction of the metal porphyrins. Some of these predictions are born out by experiment, others have yet to be verified. It is predicted that Ni^{II} porphyrin has a diamagnetic $^1A_{1g}$ ground term and that it can become paramagnetic if a pyridine molecule coorinates with the Ni atom at a distance of approximately 2 Å. The calculation predicts that the paramagnetism arises from the raising of the $3d_{z^2}$ orbital and the lowering of the $3d_{x^2-y^2}$ orbital to give a $^3B_{1g}$ ground term. This agrees with the experimental evidence for paramagnetism when Ni porphyrins are dissolved in pyridine.

Recently Ake and Gouterman[197] have reported WH type calculations on the luminescence energy levels in VO, Co and Cu porphyrins. The effect of an unpaired d electron on the triplet state of porphyrin is to give a tripdoublet and a quartet. From the calculations the intensity of the luminescence transitions can be reproduced. Predictions have been made that the tripdoublet-quartet energy gap will be dependent upon the substituents of the porphyrin ring and that the radiative lifetime of the quartet will depend upon the metal. Some of these predictions have yet to be verified experimentally.

Day[202] has reported some PPP calculations on vitamin B_{12} whose structure is similar to that of the cobalamin given in Fig.8. The π electron conjugation of the corrin ligand extends over a bent chain of thirteen atoms. Since vitamin B_{12} is diamagnetic it is assumed

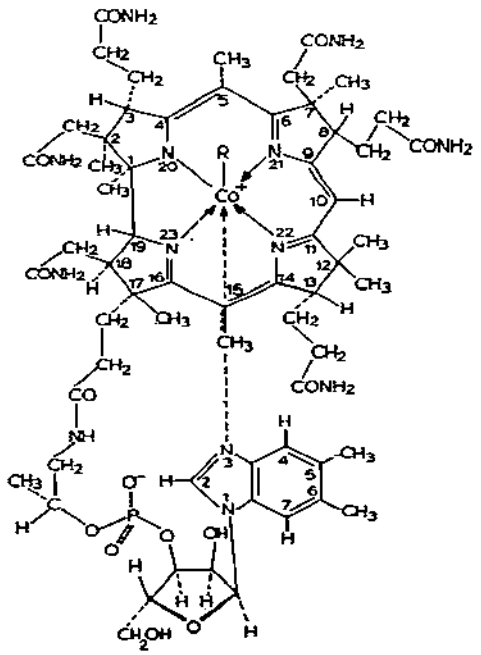


Fig.8. The structural formula of a cobalamin, related to vitamin B_{12} showing the bent chain of the partially conjugated corrin ligand from atom N_{20} to N_{23} (reproduced from Day[202]).

that the Co atom is trivalent and that the ligand has a formal charge of minus one enabling it to be treated as a fourteen π electron system.

The visible and near UV spectrum of vitamin B_{12} consists entirely of ligand transitions, hence the PPP calculation is expected to provide a reasonable account of this part of its electronic spectrum. As the axial ligand R in Fig.8 becomes a progressively better σ donor the amount of charge on the four N atoms of the corrin ligand (atoms N_{20} to N_{23}) is expected to increase. This has been allowed for in the calculation by using a range of values for the VSIP's of the four N atoms. It is found from the calculation that some of the one-electron promotion energies are very strongly dependent upon the values chosen for the N atom VSIP's whereas others are not. This leads to the possibility of mixing occurring between excited states for some of the values of the VSIP's. Consequently, it is to be expected that the intensities of some of the $\pi \rightarrow \pi^*$ transitions will vary as the σ donor strength of the group R changes; this is in agreement with the experimental observations. This effect is not predicted by the simple Hückel theory. The PPP calculation also gives a reasonable account of the effect of substituents within the conjugated chain on the $\pi \rightarrow \pi^*$ transitions and their polarizations.

PPP type calculations have recently been reported for the fully conjugated 26 π electron corrole system which is assumed to be planar[203]. Although no experimental geometry is available for the corrole system, it is anticipated to be planar in the Co^{III}, Ni^{II} and Cu^{II} derivatives. Consequently these calculations should be of interest in problems relating to the electronic structures of these and similar metal derivatives.

(v) Some metal compounds with other structures

A simple WH type of calculation[36] has been used to describe the electronic spectrum of $CuCl_5^-$, and a SCCC approach appears to be a suitable basis for discussing the electronic structures of some trigonal bipyramidal Ni^{II} complexes[205]. In the latter case proposals are made concerning the relative importance of various electronic factors in determining whether a low-spin d^6 system will favour a square planar or a trigonal bipyramidal structure.

Metal to metal bonding has been the subject of semi-empirical MO calculations. In the case of binuclear complexes of Cu^{II} different energy level schemes have been reported which may be interpreted in favour of σ or δ bonding between the copper atoms[206,207]. Cotton and Harris[208] have performed a WH type of calculation on $Re_2Cl_8^{2-}$. By evaluating the bond order of the Re to Re bond from the MO coefficients they have reported that the major components of the bond have π symmetry. The total π bonding is estimated to be five times as strong as the δ bonding and three times as strong as the σ bonding. They have also indicated that the potential well provided by the δ bond is sufficient to stabilise the molecule in the eclipsed (D_{4h}) rather than the staggered (D_{4d}) configuration.

Several semi-empirical theoretical investigations have been carried out for ferrocene in order to obtain an understanding of its electronic structure. Usually the MO description has considered the π electrons of the cyclopentadienyl rings and the metal $3d$ electrons[92,209–218]. Various approximations have been employed for the matrix elements used in the calculations, in general terms the results obtained are not in very good agreement with each other. An

SCCC type of calculation on ferrocene, vanadocene and nickelocene has resulted in a common ordering of the highest filled and lowest empty orbitals in these three molecules, namely $e_{2g} < a_{1g} < e_{1g}$ which are predominantly metal $3d$ in character[218]. This ordering provides reasonable agreement with reported optical and magnetic measurements on these complexes[219] and the photoelectron spectrum of ferrocene[14]. The calculations also indicate that the charge on the vanadium nucleus in vanadocene is higher than that on the iron and nickel nuclei in their sandwich complexes; this is in agreement with measurements of conductivities and dipole moments[218].

Semi-quantitative MO calculations including electron interaction and all valence electrons have been reported for palladium bis π-allyl and dibenzene chromium[92,220]. The results for the former indicate that of the two possible isomers, C_{2v} and C_{2h} symmetry, the C_{2v} type is likely to be more stable.

Small linear transition metal molecules have been treated by SCCC and limited basis set 'ab initio' SCF-MO calculations. The simple SCCC method predicts the order $\delta < \sigma < \pi$ for the MO's derived from the free ion d orbitals in TiO and CuO which is fairly satisfactory since the diatomic metal oxides are a difficult case[38]. 'Ab initio' calculations have been reported for TiO[221,222], ScO[223], TiN[224], VO[225], ScF[212,226] and CuF_2 [227].

Basch et al.[227] have used contracted Gaussian basis sets in their SCF-MO calculations on CuF_2 in an attempt to resolve questions about its geometry and electronic states. In the $^2\Sigma_g$ ground term they have calculated harmonic force constants and vibrational frequencies in very good agreement with the limited experimental data. Comparison of their predictions for the excited $^2\Delta_g$ and $^2\Pi_g$ terms with experimental data must await the results of further experiments.

In general, good agreement is found between the calculated energy levels and the electronic spectra of these simple molecules.

The WH method has been applied to europium tetraacetylacetonate with reasonable success[228]. The angular overlap model is able to predict the orbital energies of lanthanide elements in good agreement with experimental results in many cases. The results obtained for some enneaaquo ethylsulphates of various lanthanides (Fig.9) show good agreement with experiment, especially for the complexes with configurations f^1 and f^2.

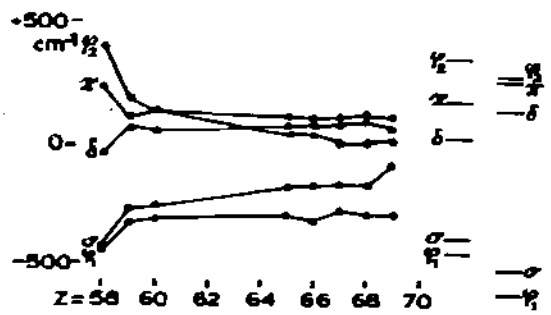


Fig.9. Comparison of predicted orbital energies for some lanthanide enneaaquo ethylsulphates and experimental values (reproduced from Jørgensen, Pappalardo and Schmidtke[137]).

E. MO RESULTS RELATING TO COVALENCY IN METAL–LIGAND BONDS

The amount of covalency or bond order of a metal–ligand bond, as defined by Mulliken[29,229] can be calculated from the overlap integrals and the coefficients of the atomic orbitals in the MO's.

Experimentally there are a number of techniques which provide some evidence for covalent character in metal–ligand bonds. However, in order to reduce the experimental data to a set of molecular orbital coefficients severe approximations are introduced such that a reliable quantitative estimate of the covalent bonding is usually not available. Consequently in this section we provide only a superficial account of the covalency data available.

(i) The orbital reduction factor K

The reduction in the orbital component of the g tensor, and in some cases of the magnetic moment, has been described by a factor K the various facets of which have recently been reviewed[3,233,234].

Formally K is defined

$$K_{rq} = \frac{\int \phi_r \hat{L}_z \phi_q \, \delta\tau}{\int \chi_r \hat{L}_z \chi_q \, \delta\tau} \tag{63}$$

where $\hat{L}_z$ is the z component of the orbital angular momentum operator, ϕ_r and ϕ_q are MO wave functions and χ_r and χ_q are atomic d wavefunctions. In an octahedral complex

$$K = 1 - \frac{\left(\frac{C^2}{2}\right)(1 - S_{trans} + 6S_{cis})}{1 + C(4S_{m,p}) + \left(\frac{C^2}{2}\right)(2 - 2S_{trans} + 4S_{cis})} \tag{64}$$

where $C/2$ is the mixing coefficient between the metal atomic d functions and the appropriate ligand LCAO sets, $S_{m,p}$ represents the overlap integral between a metal d orbital and a single ligand p_π orbital, S_{trans} and S_{cis} involve ligand orbitals only, they represent the overlap integrals between p orbitals on the ligands in *trans* and *cis* positions of the octahedron respectively.

S_{cis} may be resolved into both $p_\sigma - p_\sigma$ and $p_\pi - p_\pi$ components whereas S_{trans} consists of a $p_\pi - p_\pi$ type overlap only. These integrals may be evaluated by using general expressions[233].

The relationship between experiment and theory is Eqn. (64) since C and $S_{m,p}$ may be theoretically estimated and K obtained from magnetic susceptibility[233,235–238] or ESR data[30,183,184,161,230–232,239–243,214]. The rather complicated form of Eqn. (64) shows why simple correlations between π acceptor properties of the ligands and K are often not

available. In general the ESR data are fairly satisfactorily accounted for by semi-empirical MO calculations of the WH type.

A semi-empirical MO calculation of the zero-field splitting of Cr^{3+} ions in non-cubic sites has demonstrated the possibility of calculating g tensor anisotropy on a MO basis[246].

It has been demonstrated that for octahedral complexes the spin density f_π, which is considered to be the fraction of unpaired metal t_{2g} electron that is transferred to the ligands[244,245] is related to K by[3]

$$K = 1 - 2f_\pi \tag{65}$$

In the case of $IrCl_6^{2-}$ the value of the g tensor gives $f_\pi = 8\%$ which agrees with the estimate made from the observed superhyperfine structure of the chlorine ligands[3]. Reasonable agreement between calculated and experimental values of f_π have also been obtained[41] for CrF_6^{3-} and FeF_6^{3-}. Ligand hyperfine structure may also be determined by NMR measurements[244]. The NMR spectrum of a ligand nucleus in a paramagnetic complex may be interpreted in terms of a contact shift which is dependent upon the amount of unpaired spin residing on the ligand[165,244,247–253]. For simple ligands such as F^-, the spin density on the ligand can be obtained from a MO calculation including all of the atoms in the molecule. In the case of molecules with large ligands it is usual to perform a MO calculation on the ligand, treating it as a free radical formed by electron transfer between metal and ligand. By evaluating the amount of electron transfer that occurs a qualitative estimate of the metal–ligand bond order and bond type may be obtained from the measured contact shifts[244].

Eqns. (64) and (65) relate only to electron delocalisation by π bonding between metal t_{2g} and ligand orbitals, when σ bonding with the metal e_g orbitals becomes important the form of K is altered[3]. Under these circumstances it is possible to estimate the relative amounts of σ and π electron delocalisation in a complex. ESR and ^{19}F NMR data have been reported for a number of transition metal fluorides with the perovskite structure such as $KNiF_3$. Semi-quantitative MO calculations, which assume discrete octahedral species, have been performed to obtain values of f_s and f_σ which denote the fractions of unpaired electron in the fluorine $2s$ and $2p_\sigma$ orbitals respectively[254]. The poor agreement between the calculated and experimental spin densities, as shown by Table 6, could arise from the assumption of discrete octahedral species in $KNiF_3$ since in the perovskite structure the transition metal ions share ligands between them. Poor agreement was also noted between the experimental and many of the calculated values of $10Dq$ for $KNiF_3$ (Table 2).

(ii) The nephelauxetic series

Upon complex formation the Racah parameter B, representing interelectronic repulsion, is often reduced from its free ion value. The extent to which the value of B in the complex is reduced, for a given metal ion with different ligands, decides the position of the ligands in the nephelauxetic series proposed by Jørgensen[255]. For some common ligands the order in terms of values of B is given by

No ligands $> F^- > H_2O > NH_3 > NCS^- > Cl^- \simeq CN^- > Br^- > S^{2-} > I^-$

TABLE 6
SPIN DENSITIES IN THE FLUORINE 2s AND $2p_\sigma$ ORBITALS OF $KNiF_3$

f_s (%)	f_σ (%)	*Source*	*Ref.*
0.54	3.8	Experiment	77
0.4	5.2	SCF–MO calculation	77
0.3	0.96	SCF–MO calculation	79
0.37	1.63	SCF–MO calculation	82
0.5	3.3	MO calculation plus configuration interaction	81
0.173	31.7	SCF–MO calculation excluding Ni 4s and 4p	83
7.2	19.3	SCF–MO calculation including Ni 4s and 4p	83
0.18	1.26	SCF–MO calculation using a contracted Gaussian basis set	267

which roughly corresponds to the order of the electronegativities of the donor atoms. The nephelauxetic effect is thought to arise from two sources, (a) central field covalency, this describes the expansion of the radial part of the metal *d* wavefunctions as a result of the reduction of the metal ion's effective charge due to covalent bonding, and (b) symmetry restricted covalency, this results from the delocalization of metal electrons largely arising from the π overlap between the metal t_{2g} and ligand π orbitals.

Both of these effects tend to reduce the interelectronic repulsion between metal electrons and have been taken into account in MO calculations of *B* for some transition metal complexes[41,77,122]. The calculated values of *B* are compared with some experimental results in Table 7.

TABLE 7 [a]
COMPARISON BETWEEN SOME EXPERIMENTAL AND CALCULATED VALUES OF THE RACAH PARAMETER *B*

Complex ion	*B* (cm^{-1})	
	Calculated	*Experimental*
$(FeCl_4)^-$	625	590
$(MnCl_4)^{2-}$	830	770
$(CoCl_4)^{2-}$	880	730
$(NiCl_4)^{2-}$	875	765
$(VCl_6)^{2-}$	619	593
$(CrCl_6)^{3-}$	649	561
$(FeCl_6)^{3-}$	640	655

[a] Taken from Fenske and Radtke[122].

(iii) Spin–orbit coupling

In a complex ion the value of the spin–orbit coupling constant, λ, is usually smaller than the free-ion value for reasons similar to those producing the nephelauxetic effect. The reduction in λ is related to the coefficients of the metal *d* orbitals in the MO wavefunctions.

In many cases the expressions for the major components of the *g* tensor contain λ [170]. Experimental measurement of these components of *g* provide an experimental estimate of the *d* orbital coefficients that can be compared with the calculated values. Reasonable agreement has been obtained between the calculated and experimental coefficients for some metal porphyrins[44], copperbis(dimethyl glyoxime)[188], the vanadyl ion[30], and other metal complexes. Magnetic susceptibility measurements can also provide an estimate of the value of λ in a metal complex[235–238].

From Mössbauer spectra it is often possible to obtain isomer shifts and quadrupole splitting parameters. The latter may be related to λ so that covalency can be estimated from quadrupole splitting data[170,256,257]. However, it has recently been reported that a simple relationship between the quadrupole splitting measured at the iron nucleus in a series of compounds and the degree of covalency cannot be demonstrated from experimental data[258]. Since the isomer shift of a nucleus provides a measure of the electron density of its surroundings, it can provide an estimate of covalency in metal–ligand bonds[258].

(iv) Electric field gradients at the nucleus

The electric field gradient at the nucleus plays a part in producing the quadrupole splitting observed in Mössbauer spectra and in nuclear quadrupole resonance (NQR) spectra. From ^{35}Cl NQR measurements it is possible to obtain an estimate of the covalent character of a metal–chlorine bond, this may also be obtained from MO data[259,260]. The comparison between experimental and calculated NQR frequencies, from semi-empirical MO calculations on a series of transition metal chlorides, is given by Table 8.

TABLE 8

COMPARISON BETWEEN SOME EXPERIMENTAL AND CALCULATED ^{35}Cl NQR FREQUENCIES

Complex	*Frequency (MHz)*		*Ref.*
	Calculated	*Experimental*	
$TiCl_4$	8.23	5.98	122
$(TiCl_6)^{3-}$	7.40	7.39	122
$(VCl_6)^{3-}$	9.05	9.40	122
$(CrCl_6)^{3-}$	9.32	12.81	122
$(FeCl_6)^{3-}$	7.95	10.02	122
$(ReCl_6)^{2-}$	16	13.9	259
$(OsCl_6)^{2-}$	19	16.9	259
$(IrCl_6)^{2-}$	22	20.8	259
$(PtCl_6)^{2-}$	25.5	26.0	259
$(PtCl_4)^{2-}$	17	18.05	259

In general very good agreement is found between the experimental and theoretical frequencies. The lower frequencies of the first row metal complexes indicate a higher ionic character in the metal–chlorine bond than found for the metals of the later transition series.

A comparison of covalency determined by ESR and NQR data has been presented for some transition metal halides[260]. Unfortunately the amount of data available for comparison is rather meagre. However, it does seem that both of these experimental techniques are able to provide estimates of covalent bonding in reasonable agreement with values obtained from MO calculations.

(v) Metal–ligand stretching frequencies

Often the metal–ligand stretching frequency can be taken as an indication of the degree of covalency of the metal–ligand bond. Hence it is not unreasonable to expect a correlation between metal–ligand overlap populations and stretching frequencies. This appears to be the case with the series of metal halogen complexes given[122] in Table 9. The stretching frequencies for a given oxidation state and the overlap populations are fairly constant. However, between oxidation states the populations and frequencies differ

TABLE 9[a]

COMPARISON OF OVERLAP POPULATIONS AND METAL–CHLORINE STRETCHING FREQUENCIES

Complex	*Total overlap population*	*Experimental stretching frequency* (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

[a] Taken from Fenske and Radtke[122].

considerably. Hence a quantitative relationship between overlap population and stretching frequency does not appear to exist for these molecules. In the case of $V(CO)_5^-$, $Cr(CO)_6$ and $Mn(CO)_6^+$, the decrease in metal–carbon stretching frequency as the metal oxidation state increases has been explained on the basis of decreased interaction between the metal $3d\pi$ and ligand antibonding 2π orbitals as a result of MO calculations[153]. For a series of manganese pentacarbonyl halides the force constants, k, and orbital occupancies of the CO groups are given[157] in Table 10.

The differences in force constant values for carbonyl groups *cis* and *trans* to the halide are attributed to differences in total 2π occupation.

TABLE 10[a]

COMPARISON OF FORCE CONSTANTS AND ORBITAL OCCUPANCIES OF THE CO GROUPS IN THE SERIES $Mn(CO)_5X$

	5σ	$2\pi_y$	$2\pi_x$	2π total	K_{cis} (m dynes/Å)
For cis CO groups					
X = Cl	1.382	0.203	0.194	0.397	17.50
X = Br	1.381	0.212	0.194	0.406	17.41
X = I	1.381	0.224	0.195	0.419	17.28
					K_{trans} (m dynes/Å)
For trans CO groups					
X = Cl	1.352	0.263	0.263	0.526	16.22
X = Br	1.349	0.263	0.263	0.526	16.26
X = I	1.345	0.264	0.264	0.528	16.30

[a] Taken from Fenske and De Kock[157].

In the series of *cis* complexes changes in the occupation of the $2\pi_y$ orbital correlates with changes in the force constant. In the *cis* carbonyl groups the $2\pi_y$ orbital can interact directly with the π bonding orbital of the halogen ligand as shown in Fig.10.

The degree of interaction should increase as the halogen π orbital becomes more diffuse, and more of the halogen charge can be transferred directly to the $2\pi_y$ orbitals. The corresponding increase in the antibonding $2\pi_y$ population then results in a decrease in the carbonyl force constant.

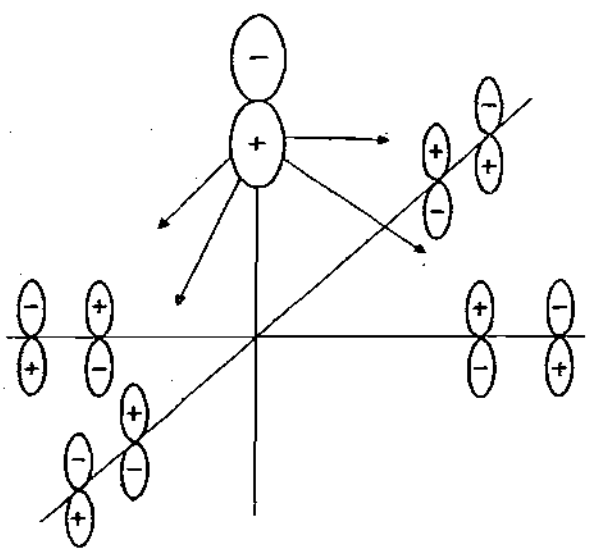


Fig.10. Direct interaction between an orbital on the halide atom and the $2\pi_y$ antibonding orbital of the four CO groups which are *cis* to the halide in the series $Mn(CO)_5X$ (reproduced from Fenske and De Kock[157]).

A further example of a correlation between overlap population and stretching frequency has been reported for several of the bonds in europium tetraacetylacetonate[228]. No doubt more will appear in the future.

In conclusion it may be noted that the results obtained from many semi-empirical MO calculations on transition metal compounds are reasonably compatible with a variety of experimental data. Although there are a number of arguments that may be raised, from the theoretical viewpoint, against this type of calculation it appears that the results are widely applicable as a guide for the experimentalist. The success of any MO calculation should be measured not only by the accuracy with which it can predict experimental parameters but also by the number of them correctly predicted. The recent successful application of the CNDO method to tetrahedral metal compounds raises hopes that, in the absence of more widespread 'ab initio' calculations, this type of calculation will soon find further application to transition metal complexes.

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