

# MOLECULAR ORBITAL THEORY FOR $\pi$ -DONOR AND $\pi$ -ACCEPTOR COMPLEXES

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## ABSTRACT

The capabilities and limitations of approximate methods for molecular orbital (MO) calculations are discussed. In particular, the apparent ability of approximate methods to obtain agreement with experimental absorption spectra is critically examined both from the point of view of theoretical considerations and comparison of eigenvectors obtained by different investigators on the same complexes.

Applications of an approximate MO method to the interpretation of photoelectron spectra and carbonyl force constants are illustrated. These latter calculations suggest that changes in both the sigma and pi antibonding orbitals of the carbonyls are necessary for interpreting the trends in force constants.

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While the first attempt to apply molecular orbital theory to transition metal complexes was reported by Wolfsberg and Helmholz<sup>1</sup> in 1952, intensive study of the method did not occur until the 1960s. The eight year delay is quite understandable when one recalls that it was in this period that 'crystal field theory' and its modification 'ligand field theory' were at the peak of their popularity. The initial success of the latter theories in the interpretation of the weak absorption bands in the visible and ultra-violet regions resulted in a flurry of activity by both the theorists and the experimentalists. The pioneering work of Orgel, McClure, Jørgensen, Liehr, Tanabe, Sugano and Ballhausen comes quickly to mind<sup>2</sup>. While their studies gave the basic understanding of such spectra, at the same time they showed the fundamental limitations of the models. The reduction of the electron repulsion integrals ( $F_2$  and  $F_4$  in Slater-Condon notation, or  $B$  and  $C$  in Racah's terminology) from free ion to complex not only led to a thorough study of what Jørgensen<sup>2b</sup> termed the 'nephelauxetic effect', but it also required that these quantities be treated as variables to be estimated with the cubic field parameter,  $\Delta$  or  $10Dq$ , and the spin-orbit coupling term,  $T$ . In order to treat systems whose symmetry was lower than cubic, additional parameters,  $D_s$  and  $D_t$ , had to be included. This proliferation of variables made band assignment less unambiguous. Another shortcoming of the model was its inability to treat the intense charge transfer bands which have their origins in electronic transitions either from the ligands to the metal or vice versa. Thus, while ligand field theory was and is an excellent starting point for many considerations involving absorption spectra and is still used, its utility is more restricted. An alternative approach was sought within the framework of molecular orbital theory.

The preoccupation of theoretical inorganic chemists with interpretation of absorption spectra has had a significant influence in the emphasis given to molecular orbital calculations for transition metal complexes. It was no accident that two very influential papers on the subject were presented at the same Symposium on Ligand Field Theory at the Chicago meeting of the American Chemical Society in 1961: the paper by Ballhausen and Gray<sup>3</sup> on 'The electronic structure of the vanadyl ion' and the one on 'Covalency effects in  $\text{KNiF}_3$ ' by Sugano and Shulman<sup>4</sup>. While both works dealt with molecular orbital considerations, the differences between the two are most striking. Despite the term 'covalency' in the title, the calculations of Sugano and Shulman were based upon an ionic model, viz.  $\text{Ni}^{2+}$  surrounded by six  $\text{F}^-$  ions and suggested that the covalent character was quite small. The method included the exact evaluation of kinetic energy, overlap, one and two centre nuclear attraction integrals, and one and two centre coulomb and exchange integrals. By contrast, Ballhausen and Gray (B and G) employed wavefunctions for the evaluation of overlap integrals only. Like its precursor, the Wolfsberg-Helmholz technique, it evaluated the diagonal terms in the secular determinant,  $H_{ii}$  and  $H_{jj}$ , from experimental valence state ionization energies. For the off-diagonal terms, B and G used a modification of the original Wolfsberg-Helmholz formula. The latter used  $H_{ij} = F \times S_{ij}(H_{ii} + H_{jj})/2$  with  $F$  as a variable depending on whether sigma or pi interactions were involved. In the vanadyl calculation, B and G employed  $H_{ij} = -2S_{ij}(H_{ii}H_{jj})^{1/2}$ . Over the years, this general procedure has been used in a variety of applications, particularly by Gray and co-workers<sup>5</sup> under the title 'SCCC method'. Certain modifications were introduced, such as varying only the  $H_{ii}$  terms associated with the metal atom while keeping those of the ligands fixed. In the evaluation of the off-diagonal term, a return was made to the original Wolfsberg-Helmholz form. In the SCCC applications,  $F_\sigma$  has been varied from 1.32 to 1.96 and  $F_\pi$  from 2.00 to 2.45 depending upon the system under investigation. It can be shown that such alterations have substantial effects upon the resultant eigenvalues but they were necessary in order to achieve accord between the experimental absorption energy and the orbital energy separation of the two molecular orbitals presumed to be involved in the electronic transition, viz.

$$\Delta E(i \rightarrow a)_{\text{exptl}} = \varepsilon_a - \varepsilon_i$$

In the past, no one has been a more severe critic of the SCCC method than I have and I am still convinced that the basic procedure is inadequate for general application to transition metal complexes<sup>6</sup>. Rather than review what I believe are shortcomings of the procedure, particularly since they are already in the literature, I would prefer to emphasize the important role that these calculations have played, namely that molecular orbital considerations can lead to an understanding of absorption spectra, at least in a qualitative if not always quantitative sense. Furthermore, the work of Gray and co-workers played a key part in directing the attention of coordination chemists to the utility and importance of molecular orbital theory for the understanding of bonding in metal complexes.

It is one of those intriguing paradoxes of scientific research that while interest in MO theory arose from a desire to interpret absorption spectra,

quantitative determination of transition energies is among the most difficult to achieve via rigorous considerations. If one applies Hartree-Fock LCAO-MO theory to a closed shell system in its ground state, Roothaan<sup>7</sup> has shown that the transition energy associated with the spin allowed excitation of an electron from an occupied molecular orbital,  $\phi_i$ , to an unoccupied orbital,  $\phi_a$ , is *not* the difference between the two orbital energies,  $\varepsilon_a$  and  $\varepsilon_i$ , but rather

$$\Delta E(i \rightarrow a) = \varepsilon_a - \varepsilon_i - J_{ia} + 2K_{ia}$$

where  $J_{ia}$  and  $K_{ia}$  are coulomb and exchange integrals between the two molecular orbitals involved. While the  $K_{ia}$  integrals are of the order of 1 eV, the coulomb integrals,  $J_{ia}$ , range between 5 and 10 eV, i.e. between 40000 and 80000 wavenumbers. Particularly when one recalls that even the above expression depends upon the rather uncertain assumption that all the other occupied MOs remain unchanged as a result of the electronic transition, the hope that molecular orbital calculations will be able to unambiguously assign different transitions with energy separations of the order of 2000 to 3000 wavenumbers is slim indeed. As Dahl and Ballhausen<sup>8</sup> have stated, '... extremely extensive calculations are required to place states of different symmetry in the correct order, and also to evaluate energy differences between states of the same symmetry correctly'. Recently I received a preprint from Richardson<sup>9</sup> of an article dealing with his excellent calculations on  $\text{NiF}_6^{4-}$ . These very rigorous computations are capable of making the appropriate transition assignments. Even if one did not know that a substantial portion of Richardson's research over the last ten years has been devoted to developing this computational ability, a cursory reading of the article will convince the reader of the complexities involved.

It is my contention that for some time to come the assignments of absorption maxima to various electronic transitions will be primarily the domain of the experimental chemist using such techniques as single crystal polarized light, low temperature studies, MCD and MORD, and related methods. This is not to imply that they cannot be aided by qualitative and quantitative molecular orbital considerations. Rather, I mean that unambiguous transition assignments for metal complexes, except on the basis of selection rules imposed by symmetry or similar restrictions, are not possible using MO computations which involve approximate calculational methods. There is a necessary corollary to such an ascertainment: the ability to obtain apparent agreement between observed and calculated transition energies does not, *per se*, guarantee the reasonableness, much less the accuracy, of the eigenvectors. There are several examples in the literature where the same compounds were calculated by various methods, all achieving 'agreement' with observed transition energies, but yielding substantially different eigenvectors and hence different interpretations of the nature of the bonding in the species. Some of these are compared in *Table 1*.

Theoretical chemistry has three goals: to develop models for the correlation of known experimental information; through the models, to gain insight into the nature of chemical bonding; and ultimately to have predictive value which will suggest additional experiments. For the theoretical inorganic chemist, the second and third goals impose special challenges because they mean that he must deal with systems of relevance to the modern experi-

Table 1. Composition of pi-bonding molecular orbitals by various approximate methods

Complex	MO	% Metal	% Ligand	Ref.
TiCl <sub>4</sub>	2e	69	31	5a
		90	10	10
		88	12	6c
CrO <sub>4</sub> <sup>2-</sup>	2e	49	51	5a
		72	28	6c
		80	20	11
MnO <sub>4</sub> <sup>1-</sup>	2e	40	60	5a
		48	52	8
		78	22	11

mentalist. The ability of a quantum chemist to calculate accurately the dipole moment of gaseous HF may be of significance to other quantum mechanicians but it will be of little interest to those experimentalists attempting to evaluate the relative importance of sigma and pi bonding in transition metal carbonyl complexes or the significance of  $d\pi-d\pi$  bonding in complexes containing phosphine and phosphite ligands.

Within the last few years, the advent of larger computers and the introduction of Gaussian basis sets have permitted exact or nearly exact SCF-LCAO-MO calculations to be carried out on molecules of greater complexity, including some on transition metal complexes. I have already mentioned Richardson's work of NiF<sub>6</sub><sup>4-</sup>. Such calculations serve an extremely important purpose. Nevertheless, not only from the standpoint of computer time and expense but also from the computational limits still present, there is and will be a continuing need for approximate methods. Indeed, there appears to be a growing interest on the part of researchers who have been traditionally associated with rigorous and exact treatment of small molecules to search for approximations which will permit the treatment of larger systems.

Various approximate methods for molecular orbital calculations are available in the literature. We have already discussed the SCC modification of the Wolfsberg-Helmholz technique. Cotton and Harris<sup>12</sup> proposed another modification which is similar to the 'Omega variation of Hückel theory' familiar to organic chemists. Ballhausen, Dahl and co-workers<sup>8, 10</sup> have investigated a modified CNDO approach which incorporates aspects of both Löwdin and Schmidt orbital orthogonalization. Our method had its origins in the considerations presented by Sugano and Shulman together with unpublished work by Richardson. Other investigators<sup>13</sup> examined further modifications, such as employing the Cusachs<sup>14</sup> approximation for the off-diagonal term  $H_{ij} = (2 - |S_{ij}|)S_{ij}(H_{ii} + H_{jj})/2$ . This list is by no means an exhaustive compilation of the many important studies being carried out throughout the scientific community.

Invariably, there exists little similarity between the systems examined by the procedures, so it is difficult to make comparisons between them. I have evolved a personal set of questions I pose when judging the potential merits of an approximate method. They are :

1. Are the calculations used to study a single compound or a series of compounds.
2. Are parameters used in the evaluation of the elements in the secular determinant? If the answer is yes, then
  - (a) how many are employed?
  - (b) are they held constant throughout the series of compounds? If not, what criteria are used to vary them?
  - (c) if they are varied, is there any statement made as to the sensitivity of the eigenvalues and eigenvectors to the variations in the parameters?
3. If a modification of a previously employed procedure is incorporated, what reasons are given for the change and what alterations, if any, occur in the results?
4. Does the method remain internally consistent throughout its applications to different systems?
5. How closely does the approximate calculation adhere to the considerations and/or conclusions of more rigorous theory?
6. What experimental results are correlated by the calculations? How independent are these correlations of possible parameter variations?

These questions reflect a rather critical attitude which I believe is very desirable. A calculation involving extensive approximations if applied to a single molecule or complex is of uncertain value. If substantial alterations of parameters are required and there is no *a priori* method for their selection, the extension of the approach to new or different systems causes substantial uncertainties. A method must be internally consistent in the guidelines it lays down for itself.

Ultimately, it is the last two questions which are the most significant. Insofar as accord with rigorous calculations is concerned, it is my contention that *no* approximate method presently in the literature can be completely justified. In particular, an adequate treatment of two centre exchange and hybrid integrals, such as  $\langle \phi_a(1)\phi_b(2) | 1/r_{12} | \phi_b(1)\phi_a(2) \rangle$  and  $\langle \phi_a(1)\phi_a(2) \times | 1/r_{12} | \phi_a(1)\phi_b(2) \rangle$ , is invariably lacking. Thus, 'exact' agreement between rigorous and approximate methods is not presently possible. Nevertheless, it is possible that approximate calculations are capable of reasonable accord with more precise treatments and, more important, are able to yield trends within a series of related species which are analogous to those obtained via rigorous methods. Furthermore, approximate methods of molecular orbital calculations do yield values which can be correlated with experimental results and consequently not only possess predictive capabilities for related systems for which the experimental results are unknown but also lead to an understanding of the nature of the electronic structure and chemical bonding in the systems studied.

To illustrate the kinds of information that can be obtained from approximate molecular orbital calculations I would like to report on the results of studies carried out in our laboratories. I will briefly describe the method which attempts to approximate the Hartree-Fock LCAO-MO technique. For the diagonal terms in the Fock matrix, we use:

$$F_{ii} = \langle \chi_{iu} | F | \chi_{iu} \rangle = \epsilon_{iu} + \sum_{v \neq u} \langle \chi_{iu} | Q_v | \chi_{iu} \rangle$$

where  $\chi_{iu}$  is the  $i$ th atomic orbital on atom  $u$ , and

$$\varepsilon_{iu} = \langle \chi_{iu} | -\frac{1}{2}\nabla^2 - Z_u/r_u | \chi_{iu} \rangle + \sum_{k \neq i} m_k^u \times g(i,k)^u + (m_i^u - 1) g(i,i)^u$$

in which  $-\frac{1}{2}\nabla^2$  is the kinetic energy operator,  $Z_u$  is the nuclear charge on atom  $u$ ,  $m_k^u$  is the Mulliken population<sup>15</sup> of all the electron orbitals on atom  $u$  with the same  $n$  and  $l$  values (for example  $m_{2p}^u$  represents the total population of the  $2p$  orbitals on atom  $u$ ),  $g(i,k)^u$  is Slater's average energy of configuration<sup>16</sup> for the interactions of the set of  $i$  functions with quantum numbers  $n_i$  and  $l_i$  with the set of  $k$  functions, with quantum numbers  $n_k$  and  $l_k$ , both sets of functions,  $i$  and  $k$ , are AOs on atom  $u$ .

$$Q_v = q_v (-Z_v + \sum_s m_s^v)/r_v$$

in which (analogous to the expressions involved in  $\varepsilon_{iu}$ )  $Z_v$  is the nuclear charge on atom  $v$ ;  $r_v$  is the distance from the nucleus  $v$  to the electron; and  $m_s^v$  is the Mulliken population of the electron orbitals on atom  $v$  with the same  $n$  and  $l$  quantum numbers. In very recent work, we have found that the entire expression for  $\langle \chi_{iu} | Q_v | \chi_{iu} \rangle$  can be approximated by  $q_v/R_{vu}$ , where  $R_{vu}$  is the internuclear distance between centres  $u$  and  $v$ .

The off-diagonal elements of our approximate Fock matrix are obtained using the formula:

$$F_{ij} = \langle \chi_{iu} | F | \chi_{jv} \rangle = S_{ij}(\varepsilon_{iu} + \varepsilon_{jv}) + \sum_{w \neq u, v} \langle \chi_{iu} | Q_w | \chi_{jv} \rangle - \langle \chi_{iu} | -\frac{1}{2}\nabla^2 | \chi_{jv} \rangle$$

where  $S_{ij}$  is the overlap integral of  $\chi_{iu}$  and  $\chi_{jv}$ ,  $\langle \chi_{iu} | Q_w | \chi_{jv} \rangle$  is estimated via the Mulliken approximation<sup>17</sup> and a point charge simplification, namely

$$\langle \chi_{iu} | Q_w | \chi_{jv} \rangle = (-Z_w + \sum_t m_t^w) \times \frac{1}{2} S_{ij} (1/R_{uw} + 1/R_{vw})$$

The third term in the expression for  $F_{ij}$  consists of a two centre kinetic energy integral which is evaluated by standard methods.

The rationalization of the forms of the expressions for  $F_{ii}$  and  $F_{ij}$  will not be discussed here. However, it should be pointed out that the calculations are completely specified by the choices for the internuclear distances, the size of the atomic basis set, and the wavefunctions of the basis set. When the structures are known, the internuclear distances are obtained from the crystallographic data. If such data for the particular species are unavailable, information from known compounds of related structures or covalent radii, or both, are employed. The size of the basis set for the AOs of the first transition metal series include all orbitals up to the  $4d$  with the  $3d$ ,  $4s$ ,  $4p$  and  $4d$  acting as valence orbitals and the others as 'inner' or 'core' electrons. For the ligands, C, O, N, halogen etc., the AOs involve those normally employed, with the outermost  $s$  and  $p$  orbitals as the valence orbitals. The forms of the wavefunctions for the atomic orbitals are those which are available for the free atoms or ions of the same charge as determined from the Mulliken electron distribution. The exceptions to this are the outer 'virtual' orbitals of the metal, the  $4s$ ,  $4p$  and  $4d$ , the construction of which is described elsewhere<sup>6c</sup>. Thus the calculations are devoid of parameters, do not rely upon

experimental information except for internuclear distances, and involve a systematic method for choice of wavefunctions.

## APPLICATIONS

### Photoelectron spectroscopy

In his paper on Hartree-Fock LCAO-MO theory, Roothaan<sup>7</sup> indicated that within the limits of Koopmans' theorem<sup>18</sup> the orbital energy,  $\epsilon_i$ , of a molecular orbital,  $\phi_i$ , should be equal to the ionization energy of an electron in the molecular orbital. With the development of photoelectron spectroscopy<sup>19</sup> by Vilesov, Kurbatov and Terenin in Russia, Turner in England, and Siegbahn in Sweden, the theoretical chemist was given experimental data with which to compare the values of his molecular orbital calculations. Continued study in this field has indicated that correlation between orbital energies and the observed ionizations may not be as direct as one might originally have hoped. Nevertheless, valuable information is obtainable from a combination of these experiments with theory. For example, a molecular orbital calculation by Nieuwpoort<sup>20</sup> on  $\text{Ni}(\text{CO})_4$  indicated that the upper filled levels were in the sequence  $e < t_2$ , that is, rather than having the  $t_2$  orbitals above the  $e$  as one would expect from crystal field consideration for tetrahedral symmetry, the reverse sequence was obtained. However, Price applied photoelectron spectroscopy to gaseous  $\text{Ni}(\text{CO})_4$  and obtained two bands at 8.8 and 9.8 electron volts with an intensity ratio of three to two, clearly indicating that the tetrahedral ordering was correct and Nieuwpoort's calculations were inadequate.

We undertook a calculation on  $\text{Cr}(\text{CO})_6$  and obtained<sup>21</sup> a clear separation of the six 'metal  $3d$ ' electrons of  $t_{2g}$  representation from the lower lying carbonyl electrons. Our calculations indicated that the  $3d$   $t_{2g}$  orbitals were stabilized, in accord with the long-held view of pi-acceptor ability of the carbonyl groups by virtue of their vacant antibonding ( $2\pi$ ) orbitals. We then initiated studies<sup>22</sup> on the series of compounds,  $\text{Mn}(\text{CO})_5\text{L}$ , where  $\text{L} = \text{H}$ ,  $\text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ . Our purpose was to examine the influence of a group which had no pi-acceptor ability (the  $\text{H}^-$  ion), or was a traditional pi donor such as the halides. Before our computations were completed, the photoelectron spectra of these systems became available<sup>23</sup> and the agreement with our calculations was very gratifying. Removal of one carbonyl group and replacement by the hydride ion led to the expected splitting of the  $t_{2g}$  degeneracy which was present in octahedral symmetry. The loss of some pi stabilization for the  $d_{xz}$  and  $d_{yz}$  orbitals (assuming the hydrogen to be located along the  $z$  axis), places the resultant  $e$  level above the  $b_2$ . This is exactly what is observed in the spectrum of the complex. But the major surprise and the most satisfying agreement came upon examination of the halide complexes. Evans and co-workers' photoelectron spectra definitely indicated that the sequence of upper orbitals was  $e < e < b_2$  with the highest of these being primarily halogen rather than metal in character. Our calculations are in agreement with this conclusion. Prior to this work, the placement of the halogen at such a high position was so contrary to what one might expect from 'chemical intuition', not to mention a completely opposite assignment on the basis of an SCCC calculation previously in the literature, that I frankly admit that I

would have been very hesitant about publishing the results were it not for their substantiation from the photoelectron data.

In their examination of various  $\text{Mn}(\text{CO})_5\text{L}$  species, Evans and co-workers<sup>23</sup> encountered an apparent anomaly in the spectrum of  $\text{Mn}(\text{CO})_5\text{CH}_3$ . If one were to consider the bonding characteristics of the  $\text{CH}_3^-$  group as similar to that of  $\text{H}^-$ , i.e. that it is not a pi-acceptor, then one would expect the order of the two highest occupied levels to be  $e < b_2$ , as in  $\text{Mn}(\text{CO})_5\text{H}$ . Contrary to this expectation, the first two bands in  $\text{Mn}(\text{CO})_5\text{CH}_3$ , at 8.46 and 9.10 eV, had an intensity ratio of approximately one to two which led the investigators to postulate an inversion of the two levels. We have recently completed some preliminary calculations on this compound and are able to offer an alternative explanation. The sequence of the upper two levels is the same as in the hydride, that is,  $e < b_2$ . However, there is an occupied orbital of  $a_1$  symmetry in close proximity to the  $b_2$  level. The eigenvector of this orbital indicates that it is the sigma bonding orbital between the metal atom and the group. While the eigenvalue of this orbital is not identical with that of the  $b_2$  orbital, they differ by about 2 eV, differences in orbital rescaling and correlation effects upon ionization could make their ionization energies essentially identical. Such rescaling would reduce the observed energy from the value of the orbital energy and would be different for sigma orbitals compared to pi orbitals. Since the character of this bonding orbital is so substantially different from that of the  $b_2$  and  $e$  orbitals, the simple intensity relations need no longer apply. The interaction cross section could be such that its intensity combined with the  $b_2$  band could appear to be twice that of the first observed band.

The above discussion is a plausible interpretation. Approximate molecular orbital calculations are not in a position to prove an hypothesis but can give it a degree of credibility. It is certain that they will continue to play an important role with respect to interpretation of photoelectron spectra.

### Infra-red frequencies and force constants

It has long been held that when such ligands as carbon monoxide bond to a transition metal a primary contribution to the reduction in the force constant, and hence the related stretching frequencies, has been the pi-acceptor ability of these ligands by virtue of their energetically available anti-bonding pi-orbitals. Furthermore, Cotton<sup>24</sup> postulated that in  $\text{M}(\text{CO})_5\text{L}$  systems, alterations in the CO force constants could be ascribed to changes in pi bonding within the CO group. This latter concept has been challenged by Darensbourg and Brown<sup>25</sup> who contend that both sigma and pi changes are required to account fully for the observed variations in the stretching frequencies.

During our studies of the  $\text{Mn}(\text{CO})_5\text{L}$  systems<sup>22</sup>, we noted two particular phenomena. First, application of the Mulliken population analysis to evaluate electron distribution indicated that the only orbitals that differed in their occupancies from those of free CO were the  $5\sigma$  and the  $2\pi$ , that is, in every complex the electronic distribution of the carbonyl group could be described by  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi_x)^2(1\pi_y)^2(5\sigma)^a(2\pi_x)^b(2\pi_y)^c$ . While the  $5\sigma$  is primarily located on the carbon atom and roughly corresponds to the carbon lone pair in valence bond terms, it is actually an antibonding orbital with respect to the carbonyl group. The  $2\pi$  orbitals are the familiar pi-acceptor

orbitals which are vacant in free carbon monoxide. Secondly, we noted that there were variations in both the  $5\sigma$  and  $2\pi$  occupancies. Because all the complexes involved the same central metal these variations were relatively small although they clearly displayed the *trans*-influence, i.e. the orbital occupancies of the carbonyl groups *trans* differed from those which were *cis* to the L group. Consequently we decided to investigate these observations by studying a wider range of complexes.

Fortunately, there exist a substantial number of complexes of the forms  $M(\text{CO})_5\text{L}$ ,  $M(\text{CO})_4\text{L}_2$ , and several dimeric species  $[M(\text{CO})_5\text{L}]_2$ , where  $M = \text{Cr}$ ,  $\text{Mn}$  and  $\text{Fe}$ , and  $\text{L} = \text{H}$ ,  $\text{CH}_3$  and the halides. Furthermore, the relative force constants<sup>26</sup> for the *cis* and *trans* carbonyl groups have been estimated via the Cotton-Kraihanzel<sup>27</sup> model. Although the absolute values of such force constants may be open to question, their relative values are meaningful. While the study is incomplete, particularly with respect to the dimeric systems, we have accumulated sufficient data to indicate that correlations do exist which give insight and have predictive value.

Table 2. Correlation of force constants with antibonding orbital occupancies

Compound	CO group	$k_{(\text{obs.})}$	$k_{(\text{calc.})}$	( $5\sigma$ )	( $2\pi_x$ )	( $2\pi_y$ )
$\text{Fe}(\text{CO})_5\text{Br}^+$	<i>cis</i>	19.00	18.98	1.325	0.171	0.193
$\text{Fe}(\text{CO})_4\text{Br}_2$	<i>cis</i>	18.26	18.32	1.338	0.205	0.205
$\text{Fe}(\text{CO})_4\text{I}_2$	<i>cis</i>	17.95	17.95	1.337	0.221	0.221
$\text{Fe}(\text{CO})_5\text{Br}^+$	<i>trans</i>	17.93	18.16	1.287	0.233	0.233
$\text{Fe}(\text{CO})_5\text{Br}_2$	<i>trans</i>	17.53	17.43	1.295	0.250	0.272
$\text{Mn}(\text{CO})_5\text{Cl}$	<i>cis</i>	17.46	17.52	1.393	0.212	0.219
$\text{Fe}(\text{CO})_4\text{I}_2$	<i>trans</i>	17.43	17.26	1.293	0.252	0.285
$\text{Mn}(\text{CO})_5\text{Br}$	<i>cis</i>	17.39	17.40	1.392	0.213	0.229
$\text{Mn}(\text{CO})_5\text{I}$	<i>cis</i>	17.29	17.25	1.392	0.213	0.242
$\text{Mn}(\text{CO})_4\text{Br}_2^-$	<i>cis</i>	16.91	16.78	1.406	0.242	0.242
$\text{Mn}(\text{CO})_5\text{I}$	<i>trans</i>	16.37	16.32	1.349	0.286	0.286
$\text{Mn}(\text{CO})_5\text{Br}$	<i>trans</i>	16.32	16.31	1.350	0.286	0.286
$\text{Mn}(\text{CO})_5\text{Cl}$	<i>trans</i>	16.28	16.28	1.352	0.286	0.286
$\text{Cr}(\text{CO})_5\text{Br}^-$	<i>cis</i>	15.56	15.57	1.456	0.261	0.282
$\text{Mn}(\text{CO})_4\text{Br}_2^-$	<i>trans</i>	15.50	15.58	1.357	0.302	0.325
$\text{Cr}(\text{CO})_5\text{Br}^-$	<i>trans</i>	14.10	14.17	1.405	0.353	0.353

At the time of writing we have completed calculations on the eight complexes listed in Table 2. It will be noted that the force constants span a range from 14.1 to 19.0 md/Å and involve both the *cis* and the *trans* carbonyl groups so that the eight complexes provide sixteen observables. Table 2 also displays the calculated occupancies of the corresponding  $5\sigma$  and  $2\pi$  carbonyl orbitals. A computer programme was designed to obtain a statistical analysis of the data in accord with the general equation

$$k = a + b(2\pi) + c(5\sigma)$$

where  $k$  is the force constant,  $(2\pi)$  and  $(5\sigma)$  are the occupancies of these orbitals as determined from a Mulliken population analysis and  $a$ ,  $b$  and  $c$  are the coefficients to be obtained. The results were extremely satisfying. The equation is of the form:

$$k(\text{md}/\text{\AA}) = 36.42 - 11.76(2\pi) - 9.93(5\sigma)$$

The standard error in the estimate of a particular  $k$  value from this equation is  $0.10 \text{ md}/\text{\AA}$ . All the usual tests of statistical significance are above the 99 per cent confidence level. When one considers that the Cotton-Kraihanzel model is quite approximate, the degree of agreement is particularly pleasing. The calculated force constants are given in *Table 2*.

With the limited amount of data, it is not possible to ascertain whether the coefficients for the sigma and pi contributions are significantly different from one another. It is obvious, of course, that both effects do contribute to the observed force constant which is in accord with the conclusion of Professor T. L. Brown. Notice that both coefficients are negative, as would be expected from the antibonding character of the  $2\pi$  and  $5\sigma$  orbitals.

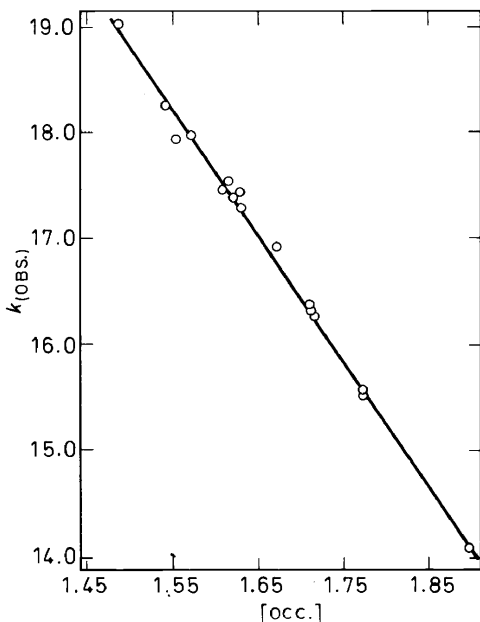


Figure 1. Force constants versus antibonding orbital occupancy.

It is possible to rewrite the equation in a form which will permit a two-dimensional relationship to be plotted. Thus:

$$k(\text{md}/\text{\AA}) = 36.42 - 11.76[\text{occ}]$$

where

$$[\text{occ}] = [(2\pi_x) + (2\pi_y) + 0.845(5\sigma)]$$

that is, the term  $[\text{occ}]$  represents the total occupancy of the  $2\pi$  and  $5\sigma$  orbitals, weighted in accord with the calculated equation. The resultant linear relationship is plotted in *Figure 1* and displays the excellent agreement obtained.

## SUMMARY

What I have tried to do in this paper is to illustrate some of the present assets and liabilities in approximate molecular orbital calculations applied

to coordination complexes. They should never be considered as a substitute for definitive experimentation. Rather, when properly carried out in combination with experiments they are capable of correlating results, giving additional insight into chemical bonding, and stimulating the imagination for additional experimentation.

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