Use of semi-empirical molecular orbital theory for study of electronic structures of transition metal complexes

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Abstract - The intention of this paper is to set forth for a potential user of approximate molecular orbital methods some of the precautions to be considered in their application and in the interpretation of the results.

INTRODUCTION

It has been interesting to observe that over the last twenty years the utilization of molecular orbital theory for the study of transition metal complexes has undergone several transformations. At the rigorous ab initio level, the advent of large scale computers has enabled theoreticians to carry out calculations within the Hartree-Fock-Roothaan (HFR) formalism (ref. 1) and even beyond to include configuration interaction (CI) (ref. 2). At what might be termed an intermediate level of rigor the advent of Xα-calculations, by either the Discrete Variational (Xα-DV) (ref. 3) or the Scattered Wave (Xα-SW) (ref. 4) Methods, have permitted studies of special properties, such as absorption spectra, that would be difficult by any other technique. However, what has been especially intriguing is that the broadened availability of mini- and micro- computers has had a substantial impact on the use of semi-empirical or approximate methods such as INDO (ref. 5), Extended Huckel Theory (EHT) (ref. 6) and the procedure developed in our laboratories known as the Fenske-Hall (FH) (ref. 7) method. I refer particularly to the use of such computational programs by research groups whose primary emphasis lies in the realm of experimental chemistry. At this point the theoretical calculations have become another tool in the hands of a synthetic chemist, or spectroscopist, or crystallographer. A tool to be used to aid in the correlation of experimental data, to assist in the rationalization of a structure or a reaction process, and to some degree, to propose additional reaction chemistry or physical properties. This closer tie between the experimentalist and the theoretician is to be applauded and encouraged. Nevertheless, it is appropriate that a few words of caution be expressed, not to discourage the use of theoretical methods, but rather that they be used with a proper understanding of both their advantages and limitations.

It is important to realize that, with the possible exception of Extended Huckel Theory, the semi-empirical methods are attempts to approximate Hartree-Fock-Roothaan calculations. Therefore, even if these approximations were extremely accurate, the results obtained would be subject to the same limitations of HFR results themselves. For example, it has been shown in several instances that the HFR method has severe shortcomings in the determination of the correct electronic structures of certain transition metal complexes unless configuration interaction is carried out as well (ref. 8,9). This adds a further level of computational sophistication to the problem.

In addition HFR with or without CI enjoys a privilege that is not extendable to approximate methods, even though many users of approximate methods invoke this privilege. I am referring to that aspect of the Variation Principle (ref. 10) which states that of two calculations (e.g. two different basis sets or two slightly different geometries) on a system, the one which yields a more negative total energy is the more accurate description of the true state of the system. It cannot be stressed strongly enough that the incorporation of approximations and parameters no longer guarantees the validity of such a conclusion. Nevertheless, the scientific literature is filled with claims of structural preferences based upon theoretical calculations which utilize approximate or semi-empirical methods to compute total energies. The conclusions may be correct but are not proven by the energy calculation. At this point I hasten to add that the employment of total energy expressions in conjunction with approximate calculations can be useful. However, such results are not definitive, per se.

It is also worthwhile to examine the complete expression for total energy. In the HFR formalism for closed shell systems it is given as

$$E = 2 \sum_{i}^{n} \varepsilon_i - \sum_{i} \sum_{j} (2J_{ij} - K_{ij}) + \sum_{A} \sum_{B} \frac{Z_A Z_B}{r_{AB}} \tag{1}$$

or alternatively

$$E = \sum_{i}^{n} \varepsilon_i + \sum_{i}^{n} h_i + \sum_{A} \sum_{B} \frac{Z_A Z_B}{r_{AB}} \tag{2}$$

In equation 1, the first term is twice the sum of the energies of the n occupied molecular orbitals. The second term subtracts the coulomb and exchange terms summed over the occupied molecular orbitals. These first two terms constitute the total <u>electronic</u> energy. The third term is the effect due to nuclear-nuclear repulsion, summed over all the nuclei with their charges, Z_A and Z_B, at their distances, r_{AB}. Frequently this last term is not stressed since for nuclei at <u>fixed</u> distances it remains a constant. Equation 2 is an alternative form for the total energy. Note that in this equation the sum of orbital energies is not multiplied by 2 and that the second expression is the sum over filled orbitals of one electron kinetic energy and nuclear attraction terms. That is,

$$h_i = \langle \phi_i | -\tfrac{1}{2} \nabla^2 - \sum_{A} \frac{Z_A}{r_{iA}} | \phi_i \rangle \tag{3}$$

The final term in equation 2 is again the nuclear-nuclear repulsion energy.

It has been somewhat surprising that in spite of the substantial magnitude of nuclear-nuclear repulsion terms several applications of semi-empirical methods have related the energetics of a system simply to the changes in orbital energies, the ε_i in equations 1 or 2. Indeed, applications of Extended Huckel Theory (ref. 11) have commonly relied upon the relationship

$$E = 2 \sum_{i} \varepsilon_i \tag{4}$$

Some justification for the simultaneous neglect of the second and third terms in equation 1 has been presented by Ruedenberg (ref. 12) based upon earlier considerations by Politser (ref. 13). These authors suggest that for molecules <u>at their equilibrium configurations</u> the sum of the second and third terms <u>approximately</u> equal one-third the total molecular energy. That is,

$$- \sum_{i} \sum_{j} (2J_{ij} - K_{ij}) + \sum_{A} \sum_{B} \frac{Z_A Z_B}{r_{AB}} \approx \frac{1}{3} E \tag{5}$$

Thus as indicated by Albright, Burdett, and Whangbo (ref. 14): "This relationship, though approximate, justifies in part the use of orbital energy changes alone in discussing molecular structure and reactivity problems."

The simplicity of dealing with sums of orbital energies is undeniable. Furthermore, the insights gained by careful examination of orbital energetics have proven themselves as illustrated by Walsh diagrams (ref. 15). What I wish to caution against is blind acceptance of the reliability of such approximations. For example, it is trivial to show that, within the framework of EHT and the simplified total energy criterion of equation 4, calculation of the bond distance in H_2 would reach a maximum when the separation of the two atoms was zero, which of course is nonsense.

FACTORS AFFECTING THE EIGENVALUES AND EIGENVECTORS

It has been my experience that in dealing with the results of molecular orbital computations it is worthwhile to first consider a simple two-atom two-wavefunction problem as follows:

Let $\psi = C_1 \phi_1 + C_2 \phi_1$ where ϕ_1 is an atomic function on center A   (6)
                                    and ϕ_2 is an atomic function on center B.

Regardless of whether one is working in the framework of EHT or an approximate HFR method the application of the variation principle to minimize the energy with respect to the coefficients leads to the relations:

$$C_1(H_{11}-E) + C_2(H_{12}-ES_{12}) = 0 \tag{7}$$

$$C_1(H_{12}-ES_{12}) + C_2(H_{22}-E) = 0 \tag{8}$$

and the secular determinant

$$\begin{vmatrix} H_{11}-E & H_{12}-ES_{12} \\ H_{21}-ES_{12} & H_{22}-E \end{vmatrix} = 0 \tag{9}$$

where $S_{12} = \int \phi_1 \phi_2 d\tau$ = overlap integral between ϕ_1 and ϕ_2. We will assume for simplicity of discussion that the coordinate systems for the atoms have been chosen so that S_{12} is positive and therefore all H_{ij} terms are negative. It will also be true that $H_{12} = H_{21}$. Furthermore we will require that ψ be normalized, that is

$$\int \psi^* \psi \, d\tau = C_1{}^2 + 2C_1C_2S_{12} + C_2{}^2 = 1 \tag{10}$$

For future reference it is useful to note here that a common approach to partition the charge of an electron in a molecular orbital between the various atoms in the molecule is the "Mulliken electron population analysis" (ref. 16). In our simple example of ϕ_1 on atom A and ϕ_2 on atom B, the distribution becomes:

$$\text{On atom A:} \quad C_1{}^2 + C_1C_2S_{12} \tag{11a}$$

$$\text{On atom B:} \quad C_2{}^2 + C_1C_2S_{12} \tag{11b}$$

Since the wavefunctions are normalized to unity the values in equations 11a and 11b when multiplied by 100 are frequently designated as the "percent character" of an atomic orbital in the molecular orbital. I shall discuss some problems associated with the Mulliken analysis later in this paper. However, let us first return to the secular determinant and examine the situation in which $H_{11} = H_{22}$, that is, the energies of ϕ_1 and ϕ_2 are equal. (See Figure 1a) Insertion of this into the secular determinant yields

$$(H_{11}-E)^2 - (H_{12}-ES_{12})^2 = 0 \tag{12}$$

and the two solutions for the energies are:

$$E_b = \frac{H_{11}+H_{12}}{1+S_{12}} \quad \text{and} \quad E_a = \frac{H_{11}-H_{12}}{1-S_{12}} \tag{13}$$

where E_b equals the energy of the bonding orbital and E_a is the energy of the antibonding orbital.

Upon insertion of the value of E_b into equation 7, one obtains the intuitively obvious relationship for the coefficients of the bonding orbital:

$$C_1 = C_2 = 1/[2(1+S_{12})]^{1/2} \tag{14}$$

An analogous relation is obtained for the coefficients of the antibonding wavefunction, except for sign reversals:
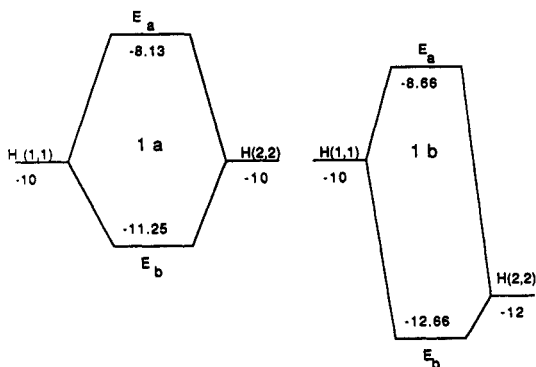
$$C_1 = -C_2 = 1/[2(1-S_{12})]^{1/2} \tag{15}$$
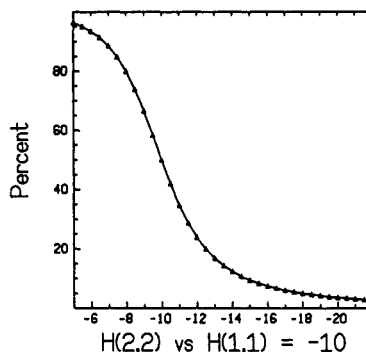

Fig. 1. Energy levels from a 2x2 secular determinant.

Fig. 2. Percent character of ϕ_a in bonding orbital.

The important points to note are that in this situation the energies of the bonding and anti-bonding orbitals relative to H_{11} are directly dependent on H_{12} while the coefficients of the wavefunctions are completely independent of the H_{12} values. While these relationships are not exact when the two diagonal terms differ from one another it is true, nevertheless, that to a first approximation the _eigenvectors_ are primarily dependent upon the values of the diagonal terms relative to one another while the _eigenvalues_ are sensitive to the magnitudes of the off-diagonal terms.

Figure 2 demonstrates the sensitivity of the eigenvectors to the relative values of the diagonal terms. With one of the diagonal terms fixed at -10 eV a change of the other from -8 eV to -12 eV alters the character of the lower molecular orbital from 80% on atom A to 76% on atom B. In addition to illustrating the sensitivity of the eigenvectors to small changes in the diagonal terms when they are nearly degenerate, the diagram also illustrates that the closer the value of a diagonal term is to a final eigenvalue the greater will be the participation of the atomic orbital in the molecular orbital. Thus, as diagrammed in Figure 1b, when ϕ_2 has an energy of -12 eV and ϕ_1 an energy of -10 eV, then by EHT methods the bonding eigenvalue at -12.66 eV has 76% ϕ_2 character. Naturally the antibonding molecular orbital at an energy of -8.66 eV is primarily ϕ_1 in character (again 76% in this simple example).

The high sensitivity of the eigenvectors to the relative positions of the diagonal terms should be a consideration in the evaluation of a theoretical method. It is very important to determine exactly how the procedure calculates or fixes the positions of these terms. A bond between two atoms can be easily altered from ionic to covalent or vice-versa by what might appear to be only small adjustments in the input values of the method. One can either consciously or unintentionally bias the output to favor ones preconceptions of what the correct answers should be. In such instances the results can be simply a facade and not an independent reinforcement of a concept.

Table 1 illustrates the effects associated with alteration of the value of the off-diagonal term, H_{12}. To simplify our considerations we have employed the EHT formalism to evaluate this term although the conclusions we shall reach are equally applicable to other approximate methods. In EHT

$$H_{12} = F \cdot \frac{(H_{11}+H_{22})}{2} \cdot S_{12} \tag{16}$$

In most recent applications $F = 1.75$ although historically other values, expecially $F = 2.00$ have been used. In Table 1 the values of H_{11} and H_{22} have been kept constant at -10 and -12 eV respectively. As indicated by the table, if one alters F from 1.75 to 2.00 the eigenvalue of the bonding orbital is stabilized by almost 0.4 eV with only a minor change (from 24% to 29%) in the character of the eigenvector. Similarly, if one chooses a different set of wavefunctions to substantially alter the overlap integral from 0.2 to 0.4 there is a stabilization of almost 1 eV in the eigenvalue with only a small percentage change in the character of the eigenvector.

Therefore, whether one is evaluating the validity of a literature article or choosing an approximate calculational method for one's own use, it is imperative that one understands how the diagonal terms (which affect the eigenvectors) and the off-diagonal terms (which affect the eigenvalues) are determined.

COUNTER INTUITIVE ORBITAL MIXING

If the coordinate systems of two atoms in a molecule are chosen such that the overlap integral, S_{12}, between an atomic orbital on each atom is positive (See Figure 3), then the wavefunction of the bonding molecular orbital:

$$\psi_b = C_1\phi_1 + C_2\phi_2 \tag{6}$$

should have positive coefficients for both C_1 and C_2. One can rearrange equation 7 for the coefficients to yield:

$$C_1 = -C_2 \frac{(H_{12}-ES_{12})}{(H_{11}-E)} \tag{17}$$

Recall that H_{11}, H_{12} and E are all negative and since the bonding orbital is more stable than H_{11} then the absolute magnitude of E is greater than the absolute magnitude of H_{11}. Therefore the denominator of equation 17, i.e. $(H_{11}-E)$, will be positive. Then in order for C_1 and C_2 to both be positive it is necessary that $(H_{12}-ES_{12})$ be negative. Since E is negative and S_{12} is positive it is clear that not only must H_{12} be negative but it must be larger in absolute value than ES_{12}, that is.

$$|H_{12}| > |ES_{12}| \tag{18}$$

TABLE 1. Effects of changes in H_{ij}

H_{11} = -10 eV		H_{22} = -12 eV		H_{12} = $F \cdot (H_{11}+H_{22}) \cdot S_{12}/2$		
F	S_{12}	H_{12}	E_b	E_a	$\%\phi_1$
1.75	0.20	-3.85	-12.66	-8.66	24
2.00	0.20	-4.40	-13.05	-8.03	29
1.75	0.40	-7.70	-13.51	-5.35	35

TABLE 2. Counter intuitive orbital mixing

H_{11} = -43.00	H_{22} = -3.00	H_{12} = -16.00	S_{12} = 0.400
E_b = -43.031	E_a = 3.602	$E_b \cdot S_{12}$ = -17.21	H_{12}-ES_{12} = +1.21

ψ_b = 1.011 ϕ_a - 0.028 ϕ_b

% Character of ϕ_a = 101.06%   % Character of ϕ_b = -1.06%

In particular circumstances that are frequently encountered in dealing with organometallic systems, both Extended Huckel Theory and the Fenske-Hall method (and very probably other approximate methods as well) fail to satisfy equaiton 18. The consequence is that in the bonding orbital, ψ_b, C_1 and C_2 will have opposite signs and therefore the wavefunction appears to be anti-bonding instead of bonding. Hoffmann and co-workers (ref. 17) called this anomalous behavior "counter-intuitive orbital mixing" and in their original discussion imply that in certain circumstances it may be valid. I maintain that it is wrong and is simply a consequence of the failure of approximate methods to properly evaluate H_{ij}.

Let us examine the conditions under which it can arise. Again, for simplicity of calculation we shall employ EHT. Table 2 illustrates the circumstances within the framework of our 2x2 determinant. Note that one of the two diagonal terms is much larger in magnitude than the other. Naturally for the bonding orbital the value of E is larger still. What is clear is that H_{12} is smaller in magnitude than ES_{12}. The conclusions in Table 2 can be generalized. With F = 1.75, the usual EHT value, equation 16 yields

$$H_{12} = 0.875 (H_{11}+H_{22}) \cdot S_{12} \tag{19}$$

When H_{11} is much larger than H_{22}, then to a good approximation

$$(H_{11}+H_{22}) \simeq H_{11} \tag{20}$$

and
$$E \simeq H_{11} \tag{21}$$

Both equation 20 and 21 are demonstrated by the results in Table 2. Substitution of these relations into $(H_{12}-ES_{12})$ yields

$$(H_{12}-ES_{12}) \simeq 0.875 H_{11}S_{12} - H_{11} \cdot S_{12} = H_{11} \cdot S_{12}(0.875-1)$$

$$(H_{12}-ES_{12}) \simeq -0.125 \, H_{11} \cdot S_{12} \tag{22}$$

Since H_{11} is negative and S_{12} is positive, equation 22 shows that $(H_{12}-ES_{12})$ will be positive instead of negative as required.

A characteristic indication that the counter-intuitive breakdown has occurred appears in the Percent Characters of the orbital participations in the molecular orbital. As demonstrated in Table 2, one of the percent characters of greater than 100% while the other is negative. The consequence of this effect is that when the Mulliken Population Analysis is used to calculate the electron distributions to the various atoms more than two electrons per orbital can be assigned to one center at the expense of positive charge being assigned to the other. In those approximate methods, such as the Fenske-Hall approach, in which the computations are cycled to self-consistent charge distributions, these errors have some effect on the eigenvalues as well.

As Table 2 illustrates, the differences between H_{11} and H_{22} must be substantial in order that the approximation in equation 20 is valid. Nevertheless, as mentioned earlier, the counter-

intuitive breakdown is quite common in certain organometallic systems. One such class of compounds are those which contain cyclopentadienyl rings (η^5-$C_5H_5^-$). Why this occurs can be illustrated thusly:

While the diagonal terms of individual carbon atoms in the Cp ring have values of -15 eV and -25 eV for the carbon -2p and carbon -2s orbitals respectively, their bonding interaction with each other to form the sigma framework of the Cp ring stabilizes these sigma levels to values such as -37, -33, and -28 eV. These low lying sigma framework levels can interact with the very diffuse virtual s- and p-orbitals of the transition metal whose diagonal term energies can be at -9 to -5 eV. The diffuse character of these metal orbitals results in substantial overlap integrals with the sigma framework, creating precisely the conditions required for equations 20-22 to apply.

To avoid the problems associated with the counter-intuitive mixing, Hoffmann and co-workers (ref. 17) include an algorithm which essentially increases the value of F in equation 16 to increase H_{ij} so that the requirement of equation 18 is satisfied. Since the Fenske-Hall method does not employ parameters such as the F-value of equation 18 an alternative method had to be found. We call it the frozen ligand core orbital approximation. To illustrate this, let us return to the example of the Cp ring. The ten most stable orbitals in the Cp fragment are associated with the sigma bonds between carbon-carbon and carbon-hydrogen atoms. Since they are so low in energy (large negative values) and the metal s- an p-orbitals are so very high in energy, the considerations of the earlier section of this paper (Figures 1b and 2) require that the resultant final molecular orbitals should be esentially 100% ligand orbitals (for those levels, E_b, that are stabilized) or 100% metal orbitals (the antibonding counterparts to the interaction). Our approach is to require these orbitals to be 100% ligand or metal. That is, we transform our diagonal and off diagonal terms from an atomic basis to a "ligand" basis composed of fragments of the molecule. Such a similarity trans- formation does not alter any of the values. However, once transformed, we treat the low lying ligand orbitals as "frozen", that is, non-interacting with the metal, by setting the new off-diagonal term between the metal and these transformed orbitals to zero. This is completely equivalent to "freezing" the atomic cores such as the 1s orbitals on carbon or the 1s through 3p orbitals on a chromium atom and interacting only the "valence" orbitals of the atoms in a molecule. During each iterative cycle in the FH procedure, the ligand orbitals interact to form the core sigma framework which are then frozen from further interaction while the pi orbitals of the Cp ring do interact with the metal system.

The effects associated with the frozen core approximation in the Fenske-Hall method are demonstrated in Table 3 which compares results on the CpRe (CO)(NO)(PH$_3$)$^+$ ion with and without freezing the ligand core orbitals. Substantial differences in the charges on the atoms are especially apparent. Note also that when the ligand core orbitals are not frozen the rhenium 6p orbitals have negative electron populations and the lowest lying sigma frame- work orbital appears to be occupied with 2.385 electrons. Such extremes as to result in the unrealistic negative population are not common but this does represent a dramatic illustration of the errors that can result. With the exception of the negative electron population in the rhenium orbital these erroneous occupations are not obvious if the electrons are examined only in an atomic basis rather than transformed to the ligand orbital basis. This emphasizes the usefulness of the transformation of the atomic results to ligand fragments for purposes of data analysis.

Finally, the counter-intuitive breakdown is most readily detected in negative percent characters of atomic orbitals in particular molecular orbitals or in occupations of greater than two electrons in ligand fragment orbitals when basis transformations have been carried out. The computer print out of the very low lying orbitals should be carefully inspected for signs of this effect.

SOME CONSEQUENCES OF THE CHOICES OF ATOMIC BASIS FUNCTIONS

A discussion of the effects of atomic wavefunctions on the results obtained by approximate molecular orbital methods is complicated somewhat by the varying degrees in which the methods actually utilize the basis functions. This is particularly true in regard to the determination of the diagonal terms of the secular equation. For example, in EHT the diagonal terms for the valence orbitals are completely independent of the choice of basis functions. They are determined from experimental ionization energies of the neutral atoms and remain unchanged throughout the calculations. (In earlier versions, still occasionally used, the metal diagonal terms were dependent on the charge on the metal but were still independent of the atomic wavefunctions.) At the other extreme, the Fenske-Hall method calculates the one center coulomb and exchange integrals so that the diagonal terms can be quite sensitive to the choice of atomic functions used in the basis set. In INDO, the diagonal terms are generated from a combination of experimental ionization energies, electron affinities, and computed one-center coulomb intergrals. Hence, the effect of altering the basis sets on the diagonal terms is even more difficult to generalize. However, all three methods utilize wavefunctions to evaluate the off-diagonal term.

TABLE 3. Frozen and unfrozen ligand core
calculations on $CpRe(CO)(NO)(PH_3)^+$

Orbital	Mulliken Electron Population	
	Frozen	Unfrozen
Re 6s	.420	.176
Re 6px	.298	-.095
Re 6py	.262	-.104
Re 6pz	.054	-.392
Cp σ-1	2.000	2.385
Re charge	-.045	+1.717
Cp charge	+.073	-0.751
S (6pz,σ-1)	0.640	0.640[a]
H (6p,6p)	-10.18 eV	-6.13 eV
H (σ-1,σ-1)	-38.54 eV	-36.75 eV
H (6pz,σ-1)	0	-18.46 eV
E (bonding)	-38.54 eV	-38.38 eV
$(H_{ij} - ES_{ij})$	*	+6.10 eV

[a]This is the "group overlap" with the linear
combination of atomic orbitals for the
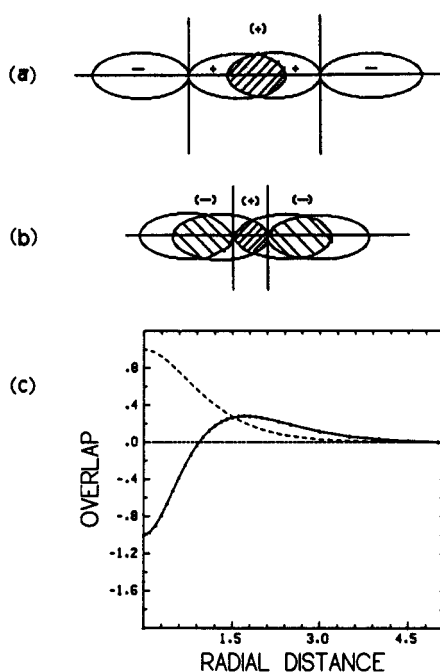sigma framework of the Cp ring.

Fig. 3. Qualitative and quantitative
orbital overlaps.

Equation 16 has already presented the evaluation of H_{ij} for EHT and from it we see that H_{ij}
is proportional to S_{ij}, the overlap integral. Equations 23 and 24 present the expressions
for the Fenske-Hall (ref. 7) and INDO (ref.5) methods respectively:

$$H_{ij} = (\epsilon_{iu} + \epsilon_{jv}) \cdot S_{ij} + \sum_{w \neq u,v} \langle \chi_{iu}|Q_w|\chi_{jv}\rangle - \langle \chi_{iu}|-\tfrac{1}{2}\nabla^2|\chi_{jv}\rangle \qquad (23)$$

$$H_{ij} = \tfrac{1}{2}(\beta_A^\circ + \beta_B^\circ) S_{ij} - P_{ij}\gamma_{AB} \qquad (24)$$

Thus it is clear that all three methods involve the use of the overlap integral, S_{ij}, in
the estimation of H_{ij}.

Consider two identical sigma bonding p-orbitals on adjacent atoms in which the coordinate
systems are such that the positive lobes face one another as in Figure 3a. The overlap
integral is positive. Now envision the two atomic centers slowly approaching one another.
Initially the overlap integral may increase as the positive lobes overlap more and more.
Eventually, however, the situation depicted in Figure 3b must ultimately occur. Note that
part of the positive lobe of one atom overlaps with the negative lobe of the other. In fact
as the two centers merge the final overlap integral would equal minus 1 as can be imagined
by the exact overlay of the positive lobe of one orbital with the negative lobe of the other.
Thus, a plot of overlap as a function of distance for sigma p-orbitals yields the curve
presented in Figure 3c. Several factors are noteworthy. First of all, there is a point at
which the overlap integral equals zero and then becomes negative. This distance can be
quite removed from merging the two centers. It is very doubtful that H_{ij} follows the same
behavior. Similarly whether H_{ij} reaches a maximum when S_{ij} does is also highly questionable.
Such inappropriate behavior by H_{ij} as a function of distance is undoubtedly why approximate
methods are generally inadequate for total energy calculations for bond length estimations.

All of this becomes quite obscure in dealing with real systems. For example, two identical
p-pi orbitals increase their overlap to a maximum of 1 as the internuclear distances goes
to zero, (Figure 3c), while an s-orbital on one center and a p-orbital on the other reach
some maximum value and then decrease to zero as the bond distance goes to zero. Consequently
the overall trends in the energies of a complete set of occupied molecular orbitals can be
quite complex. Whether a maximum total energy is obtained and at what internuclear distance
depends upon the system under study and which equation is used to evaluate the total energy.
For example, since two adjacent 1s orbitals approach a maximum of plus 1 as the bond
distance goes to zero then, as previously indicated, the theoretical maximum energy for H_2
would also be at R = 0 if equations 4 and 16 were universally good approximations.

It is important to realize that near zero values of S_{ij} (and therefore of H_{ij}) are not restricted to changes in bond length. It can be observed at normal bond distances between a diffuse orbital on one center and a tight orbital on the second center. In fact this is a common occurrence when one uses orbitals for transition metals that are generated from a single atom, i.e. atomic, calculation regardless of how rigorous that atomic calculation was performed. This is demonstrated in Figure 4a and 4b. These figures plot the value of $\psi^2 r^2$ (the electron density of the atomic wavefunction ψ) as a function of the radial distance, r, from the atomic nuclei. The manganese atom is centered at r = 0 and the carbon atom at 3.555 atomic units (1.886 Angstroms) from the manganese. The radial distribution of the carbon atom both toward and away from the manganese is plotted. Because of the sign of the angular portion of the carbon p-z orbital, the overall function will be positive on one side and negative on the other. Thus the value of the integrand in an overlap calculation on one side of the carbon will tend to be cancelled by the integrand of opposite sign on the other side of the carbon. Notice that the diffuse orbital obtained from an SCF calculation on an isolated manganese atom spreads to both sides of the carbon function. The tighter manganese function employed in Figure 4b will obviously have a larger sigma overlap. The actual overlap integral values for the two manganese functions are given in Table 4. It is clear from these results that the valence 4s and 4p orbitals for the first transition row elements (or the 5s, 5p and 6s, 6p orbitals for the second and third row elements) that are available from literature sources or computer programs should <u>not</u> be used in molecular calculations. This warning is not limited to approximate methods but has been shown to be equally important in rigorous calculations as well.
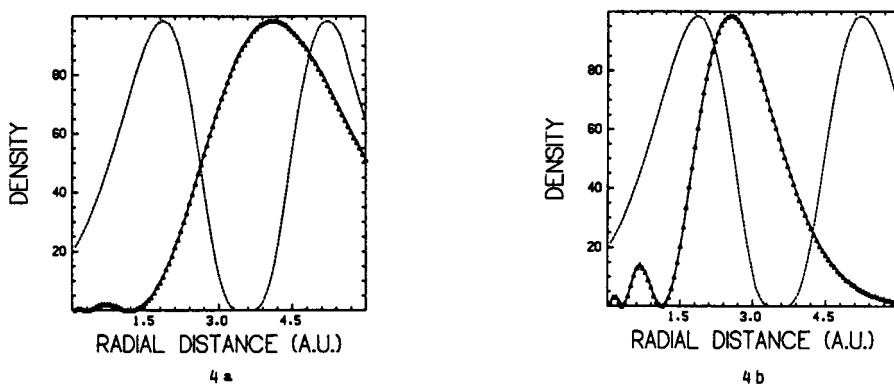

Fig. 4. a. Mn (atomic) and C (atomic) p-orbital radial densities.
         b. Mn (maximum overlap) and C (atomic) p-orbital radial densities.

TABLE 4.   Overlap integrals between manganese and carbon functions

ψ_{4p} (atomic) = 0.02365ϕ (2,10.085) − 0.08169ϕ (3,3.975) + 1.0030ϕ (4,0.975)

ψ_{4p} (max overlap) = 0.08585ϕ (2,10.086) − 0.31057ϕ (3,3.975) + 1.0428ϕ (4,1.617)

ψ_{2p} (atomic carbon) = 0.80168ϕ (2,1.25572) + 0.26048ϕ (2,2.72625)

where $\phi(n,\alpha) = N \, r^{n-1} \, e^{-r\alpha}$

	Mn(atomic)	Mn(max overlap)
S (4pσ,2pσ)	0.009	0.286
S (4pπ,2pπ)	0.285	0.264

The foregoing discussion naturally raises the question as to how the proper atomic wave-functions should be chosen. The traditional approach in our laboratories has been to use neutral atom functions for the ligands, for example, the carbon, nitrogen, and oxygen 1s, 2s, and 2p functions of Clementi (ref. 18) are curve fit to single zeta exponents. The Slater functions for the transition metals are then generated by curve fitting to Herman-Skillman atomic Xα calculations by the method we have already presented in the literature (ref. 19). This latter approach yields very good core functions, 1s through 3p on a first transition row element for example, as well as the metal d-orbitals. A series of calculations are then performed with varying zeta values for the 4p functions with the further requirement that the 4p orbital be orthogonal to the 2p and 3p core functions. At the bond distance available from crystallographic data the sigma and pi overlap integrals between the 4p functions and the neighboring ligand atom are computed. The quantity S is calculated from

$$S = S(4p\sigma, \text{ligand } p\sigma) + 2S(4p\pi, \text{ligand } \pi). \tag{25}$$

Equation 25 yields a weighted maximum sigma and pi overlap between the 4p and the ligand atom as a function of the 4p orbital exponent, zeta. This zeta value is then assigned as the exponent for both the 4s and 4p functions appropriately orthogonalized to their core orbitals.
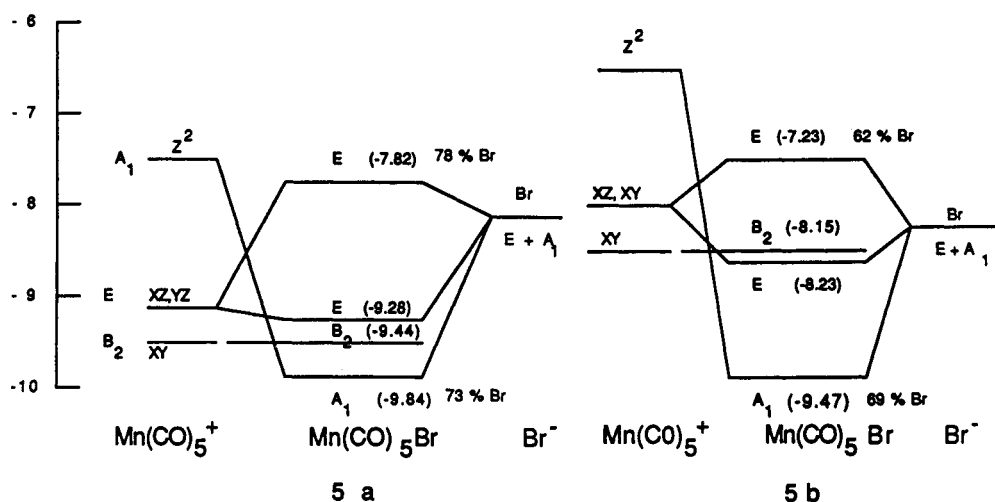
Fig. 5. Mn(CO)₅Br highest filled orbitals. a. Atomic 4s and 4p Mn
    functions. b. Maximum overlap 4s and 4p Mn functions.

Figure 5 demonstrates that the choice of virtual s- and p-functions can have a dramatic
effect on both the sequence of eigenvalues of occupied orbitals and the character of the
eigenvectors associated with the energy levels. When the diffuse atomic 4s and 4p functions
on the manganese are chosen as part of the basis set the HOMO (highest occupied molecular
orbital) consists of a pair of orbitals highly localized on the bromine atom. When more
contracted 4s and 4p orbitals are used, the bonds between the manganese and bromine are
quite covalent, in accord with experimental evidence. In passing, one should note the
effectiveness of utilizing ligand fragments in the analysis of the results. In both 5a and
5b the diagonal terms are those of the fragment Mn(CO)₅⁺ which splits the d-orbitals by the
stabilizing effect of the carbonyl ligand interactions.   This fragment approach
clarifies the covalent character of the pi interactions by the proximity in energy of the
"metal" and bromine e-orbitals.

CHARGES ON ATOMS IN MOLECULES

In spite of our acceptance of the concept within molecular orbital theory that an occupied
orbital spans the entire molecule, there is a strong tendency to wish to divide the charge
density and assign it to the individual atoms. This has been mitigated somewhat by the
ability of present day computers to efficiently compute density maps associated with an
individual orbital or a sum of the occupied orbitals. Nevertheless a variety of techniques
have been proposed to calculate the charges on the atoms with the most commonly employed
method being the Mulliken electron population analysis refrred to earlier in this paper.

One of the uses to which charges on atoms have been put is to rationalize or predict the site
of electrophilic attack in the reaction chemistry of organometallic complexes (ref. 20). In
my view this is a reasonable course of action as long as certain limitations are recognized
and appropriate precautions are taken. To illustrate this let us return again to the inter-
action of the valence s- and p-orbitals of a transition metal and their interaction with the
nearest neighbor atoms.

TABLE 5. Mulliken populations in Mn(CO)₅Br

A: From a single orbital:
 $\psi = .3655\ d_{z^2} + .2357\ p_z + .381\ C_s + .444\ C_z$ + other terms
Population in d_{z^2} = $(.3655)^2 + (.3655)(.381)(.130) + (.3655)(.444)(.119)$ = .1706
    Ratio = .1336/.1706 = 78%
Population in p_z = $(.2357)^2 + (.2357)(.381)(.495) + (.2357)(.444)(.285)$ = .1299
    Ratio = .0556/.1299 = 42%

B: Total Orbital Populations (Manganese 4s and 4p)   4s = .388 $4p_x$ = .435 $4p_y$ = .435 $4p_z$ = .400

C: Mulliken Charges
    Mn = -0.305 (+1.353)
    C = +0.193 (-0.083)
    Br = -0.331 (- .414)

It will be recalled for equation 11 that in the Mulliken Population Analysis the two contributions to the assignment of electron density to an atom are the square of the coefficient of that atomic orbital in the molecular orbital and the sum of all the cross terms times their respective overlap integrals. A typical example of such contributions are illustrated in Table 5 for a single orbital in $Mn(CO)_5Br$ for the bond between the manganese and the carbon trans to the bromine atom. In the case of the d-electron population, 78% of the contribution comes from the square of the coefficient of the d_{z^2} orbital in the molecular orbital. However, for the $4p_z$ orbital, 58% of the "occupation" comes from the cross terms with the carbon orbitals, $C_iC_jS_{ij}$. From Figure 4, it is clear that most of this cross term is in closer proximity to the carbon nucleus than it is to the manganese nucleus. Furthermore, Figure 4 reminds us that even for the "tighter" manganese 4p function much of its density maximizes in the vicinity of the carbon atom. Thus in the case of these diffuse valence orbitals of the transition metal assignment of their density to the metal rather than to their nearest neighbors will tend to place too much negative charge on the metal atom. Table 5, part B, lists the total occupations of the 4s and 4p orbitals on the manganese. Part C lists the final atomic charges via the Mulliken analysis. The values in parentheses list the charges when the 4s and 4p populations are re-distributed to the six nearest neighbors to the manganese. The latter values are probably a much more reliable indication of the charge density distribution in the molecule. In any event it should be apparent that atomic charges, especially those on the central transition element and its nearest neighbors, should be treated very cautiously.

FINAL COMMENTS

While this paper has focusssed on possible pitfalls in the utilization of approximate molecular orbital methods I have done so with the hope and expectation that these approaches will continue to be used in the years ahead. They have provided insight into the electronic structures of systems too large to be treated by rigorous methods and by so doing have advanced our understanding of coordination chemistry.

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