Counterintuitive Orbital Mixing in Semiempirical and ab Initio Molecular Orbital Calculations

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Abstract: In both extended Hückel and limited basis set ab initio SCF molecular orbital calculations an intriguing phenomenon occurs, especially in calculations on transition metal complexes. Some of the lower orbitals, which are made up primarily of ligand 2s combinations, mix into themselves the metal virtual orbitals, 4s and 4p, in an out-of-phase manner, opposite to what one would have predicted from a simple perturbation analysis. We call this counterintuitive orbital mixing (COM). The consequences of COM are lowered metal to ligand overlap populations and negative Mulliken gross atomic populations of the virtual orbitals. We analyze the prerequisites for occurrence of COM in both semiempirical and SCF methods and propose a modified Wolfsberg-Helmholz formula for reducing the magnitude of the effect in EH calculations.

I. Introduction. Extended Hückel Molecular Orbital (EHMO) Models

After the pioneering work of Wolfsberg and Helmholz in 1952,[2a] semiempirical LCAO-MO calculations of the "extended Hückel" (EH) type have been performed with varying degrees of success for numerous organic and inorganic molecules. In spite of the well-known shortcomings of all simple one-electron models the EHMO scheme often gives a reasonable qualitative picture of the electronic structure of molecules, as can be seen from comparisons with accurate ab initio calculations. The main reasons for this partial success are likely to be:

1. The Hartree-Fock ground state determinant of most molecules remains by far the most important term in a more accurate configuration interaction (CI) wave function, i.e., the concept of a preponderant electron configuration is valid.

2. The LCAO expansion of a molecular Hartree-Fock ground state determinant converges rapidly, if a suitable AO basis is chosen.

3. The use of empirical valence state ionization energies as diagonal elements H_{ii} and the use of expressions like $H_{ij} = kS_{ij}(H_{ii} + H_{jj})/2$ (original Wolfsberg-Helmholz expression[2a]) or $H_{ij} = (2 - |S_{ij}|)S_{ij}(H_{ii} + H_{jj})/2$ (Cusachs expression[2b]) or $H_{ij} = kS_{ij}(H_{ii}H_{jj})^{1/2}$ (Ballhausen-Gray expression[3]) as off-diagonal elements of the EH secular determinant $|H_{ij} - \epsilon S_{ij}|$ lead—in most cases—to eigenvalues and eigenvectors that are qualitatively similar to those obtained from ab initio theories.

The qualitative behavior of the molecular one-electron energy levels relative to the atomic energy levels and the buildup of MOs from AOs may be described in terms of three AO-interference rules that are obtained from perturbation arguments and from experience:

1. Constructive interference of AOs leads to bonding MOs exhibiting one-electron energies lowered relative to the weighted average of the diagonal elements H_{ii} of the contributing AOs, while destructive interference leads to antibonding MOs exhibiting one-electron energies raised relative to the corresponding weighted average of H_{ii}'s.

2. The energetic interference effect decreases with increasing difference of H_{ii}'s (principle of energy resonance).

3. In bonding LCAO eigenvectors the contribution of low-lying AOs predominates, while in antibonding MOs the contribution of high-lying AOs predominates.[4]

Nevertheless, in some cases results have been obtained in the course of EH calculations on metal complexes which contradict these rules and are, therefore, hard to rationalize; these findings will be discussed in the following section.

II. Negative Mulliken AO Charges and Overlap Populations in Extended Hückel Calculations

On several occasions we and other authors[5-9] have noted that EH calculations have led to unexpectedly large negative gross atomic populations for 4s and 4p metal AOs of various first-row transition metal complexes and also to negative metal-ligand overlap populations. We would hazard the opinion that since the effect appears undesirable it does not enter the literature as often as it is observed. Perhaps the time has come to make it explicit. This we do here by discussing a specific case, that of a metallocene.

The results of an SCCC Wolfsberg-Helmholz (WH) EH calculation on ferrocene are presented in Tables I and II, with computational details given in the Appendix. Table I shows the total electronic populations (column 1, WH) and compares them to those obtained from two recent ab initio SCF calculations[10,11] on the same system (columns 3 and 4) to be discussed in section III and also to those of a modified EH calculation (column 2) to be discussed in section V. Similar to earlier EH calculations on ferrocene[5,6] our WH calculation gives substantial negative metal 4s and 4p populations as well as a strongly negative total metal to ligand overlap population. An analysis of the various MOs (Table II) revealed the surprising result that the dominant contributions to the negative metal-ligand overlap population and to the negative 4s and $4p_z$ Mulliken charges originated from the lowest MOs (no. 1 and 2 in Table II, of a_2'' and a_1' symmetry), being mainly carbon 2s in character! For ferrocene the weakly negative 4s population of -0.072 and the strongly negative $4p_z$ population of -0.557 as well as the negative metal-carbon overlap population of -0.177 (per C atom) are mainly caused by the large *antibonding* admixtures of 4s and $4p_z$ to the orbitals of a_1' and a_2'' symmetry, respectively. To make the anomalous nature of this mixing explicit we sketch the resultant orbitals in **1** and **2**, with some exaggeration of the 4s and 4p admixture. In order

1 (a_1') 2 (a_2'')
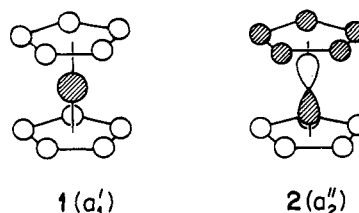
to find out whether the lowest ligand MOs were stabilized or destabilized by these destructively interfering 4s and $4p_z$ admixtures we performed additional calculations for the ligand $(C_5H_5^-)_2$ without the metal atom. The result shows that the

Table I. Comparison of Gross Orbital Populations and Overlap Populations for Various SCF and EH Calculations on Ferrocene

			Extended Hückel (this work)		Ab initio SCF	
			WH[a]	Modified[b]	I, ref 10	II, ref 11
Fe	3d	z^2	1.977	1.978	1.93	1.95
		xz, yz	0.976	0.847	0.43	0.395
		$x^2 - y^2, xy$	1.912	1.901	1.86	1.83
		Total	7.752	7.474	6.51	6.40
	4s		−0.072	0.013	0.00	0.23
	4p	x, y	0.057	0.140	0.12	
		z	−0.557	−0.232	0.01	
		Total	−0.444	0.049	0.25	
C	2s		1.254	1.195	1.12	
	2p	x, y	0.914	0.918	1.065	
		z	0.994	1.021	1.06	
		Total	2.823	2.856	3.19	
H	1s		0.999	0.995	0.81	0.933
Atomic charge		Fe	+0.763	+0.464	+1.228	+1.388
		C	−0.077	−0.052	−0.311	−0.206
		H	+0.000	+0.005	+0.188	+0.067
Overlap populations		M–C	−0.117	+0.049	−0.067	+0.072
		M–H	−0.022	−0.013	−0.009	−0.008
		M–Lig	−1.393	+0.360	−0.760	+0.633
		C_1–C_2	+1.134	+1.081	+1.090	
		C_1–H_1	+0.844	+0.837	+0.853	

[a] Wolfsberg–Helmholz expression used for H_{ij}. [b] Modified H_{ij} formula used; see section V.

lowest a_1' and a_2'' carbon 2s MOs of $(C_5H_5^-)_2$ are stabilized by −0.137 and −1.565 eV in ferrocene by the antibonding 4s and $4p_z$ admixtures of Fe, in clear violation of all three AO-interference rules mentioned in the Introduction.

Is this anomalous effect a consequence of the failure of the Mulliken population analysis scheme? In principle there is nothing mysterious about negative Mulliken AO populations; it is well known that in antibonding MOs of the form

$$\phi = c_1\chi_1 - c_2\chi_2 \qquad (c_1 > c_2 > 0)$$

obeying the normalization condition

$$c_1^2 + c_2^2 - 2c_1c_2S_{12} = 1$$

negative Mulliken population contribution are obtained for AO χ_2 whenever half the (negative) overlap population $c_1c_2S_{12}$ dominates the one-center term c_2^2, i.e.

$$\rho(\chi_2) = c_2^2 - c_1c_2S_{12} < 0$$

The effect discussed here does *not* represent a failure of the Mulliken population analysis scheme. Both the negative orbital populations and negative overlap populations are a direct consequence of a deeper lying effect, an anomalous orbital mixing, an apparent violation of the AO interference rules outlined above.[12] Since we will need to refer to this phenomenon several times, we would like to call it counterintuitive orbital mixing (abbreviated COM).

Before the reader jumps to the extrapolation that COM is an artifact of the extended Hückel method, let us see what ab initio calculations give for the same molecules in which COM is observed by semiempirical procedures.

III. Counterintuitive Orbital Mixing in ab Initio SCF Calculations

There are numerous literature examples of COM occurring in ab initio SCF calculations with basis sets of relatively low quality.

For instance, a calculation on cyclobutadieneiron tricarbonyl[13] shows substantial negative populations of the Fe 4s and 4p (a') orbitals. There are negative overlap populations between Fe 4s and 4p and some carbon orbitals as well as negative

4s and 4p atomic populations in some of the individual orbitals (see Table 1 of ref 13), among the most prominent being those levels which are mainly C 2s, exactly the same ones that would show COM in EH. An extended Hückel calculation on the same molecule gives for the population of the $4p_z$ orbital −0.32 whereas the ab initio result is −0.12. The EH 4s population is positive (the SCF calculation gave −0.17), but if we examine the MOs individually there is evidence for COM in the EH calculations as well, with negative populations in lower MOs outweighed by positive populations in higher ones.

An SCF calculation on butadieneiron tricarbonyl[14] shows prominent negative atomic populations for 4s and all 4p orbitals. Discrete variational $X\alpha$ calculations on $Cr(CO)_6$ and $Ni(CO)_4$ show negative atomic populations,[15] as do ab initio SCF calculations on the latter molecule.[16] The effect appears to be present in a calculation of $B_3C_2H_7Fe(CO)_3$.[17]

Perhaps the most striking instance of COM in ab initio calculations is for dibenzenechromium.[18] The population of 4s and 4p Cr orbitals adds up to −1.128. It is once again concentrated in orbitals that are mainly 2s on carbon.

Given the common occurrence of COM in ab initio calculations, one is led to inquire whether improvement of the basis set will make the effect disappear. We do not have a clearcut answer to this question, but report what we have observed.

For ferrocene there are two SCF calculations using Gaussian basis sets in the literature, the first by Coutière, Demuynck, and Veillard,[10] the second by Bagus, Walgren, and Almlöf.[11] Total electronic populations are given in the third and in the fourth column of Table I; information on the basis sets used and on the salient features of the Mulliken population analysis is reported in Tables III and IV.

The calculation by Bagus et al. uses a significantly more flexible basis than the calculation by Coutière et al.; this is clearly reflected by the numbers for the total energies (Table III). On the other hand, the calculation by Bagus et al. does not include suitable basis functions for a proper description of the 4p shell of Fe.

Inspection of Table I shows that neither of the two SCF calculations produces negative total orbital populations. However, the two calculations differ in the sign of the total metal to ligand overlap population! Tables III and IV show that

Table II. Wolfsberg–Helmholz EH Calculation for $Fe(cp)_2$; $k = 1.75$; Eigenvalues, Eigenvectors, and Mulliken Population Analysis

No.	Γi	Metal coefficient[a]	Coefficients on C_1 and H_1[b]		ϵ_i, eV	n_i	Metal AO gross populations	C_1 and H_1 AO gross populations		OP(M-L)[c]
1	a_2''	$+0.3710\,z$	-0.2659 s	$+0.0308\,\pi$	-30.713	2	$-0.5621\,z$	$+0.2295$ s	$-0.0019\,\pi$	-0.8374
			$+0.0388\,\sigma$	-0.0377 H				$+0.0157\,\sigma$	$+0.0129$ H	
2	a_1'	$-0.0060\,z^2$	$+0.2349$ s	$-0.0088\,\pi$	-29.537	2	$-0.0011\,z^2$	$+0.2081$ s	$+0.0004\,\pi$	-0.0012
		-0.1183 s	$-0.0029\,\sigma$	$+0.0213$ H			-0.1718 s	$+0.0012\,\sigma$	$+0.0076$ H	-0.1998
3	e_1'	$-0.1168\,x$	$+0.3244$ s	$-0.0228\,\pi$	-24.597	4	$-0.1214\,x$	$+0.2941$ s	$+0.0008\,\pi$	-0.1487
			$+0.0052\,\sigma$	$+0.1001$ H				$+0.0011\,\sigma$	$+0.0609$ H	
4	e_1''	$-0.0321\,xz$	-0.3159 s	$-0.0039\,\pi$	-24.177	4	$+0.0111\,xz$	$+0.2843$ s	$+0.0002\,\pi$	$+0.0090$
			$-0.0049\,\sigma$	-0.0952 H				$+0.0009\,\sigma$	$+0.0559$ H	
5	e_2'	$-0.0431\,x^2-y^2$	-0.2144 s	$+0.0043\,\pi$	-19.042	4	$+0.0097\,x^2-y^2$	$+0.1084$ s	$+0.0001\,\pi$	$+0.0060$
			$-0.1305\,\sigma$	-0.2040 H				$+0.0762\,\sigma$	$+0.1497$ H	
6	e_2''		-0.2153 s	$-0.0044\,\pi$	-18.825	4		$+0.1076$ s	$+0.0001\,\pi$	
			$-0.1343\,\sigma$	-0.2092 H				$+0.0766\,\sigma$	$+0.1519$ H	
7	a_1'	$+0.0697\,z^2$	-0.0002 s	$+0.0219\,\pi$	-16.698	2	$+0.0258\,z^2$	-0.0000 s	$+0.0026\,\pi$	$+0.0161$
		-0.0682 s	$-0.1590\,\sigma$	-0.1519 H			$+0.0118$ s	$+0.1210\,\sigma$	$+0.0726$ H	$+0.0025$
8	a_2''	$-0.0771\,z$	-0.0036 s	$-0.0098\,\pi$	-16.517	2	$-0.0301\,z$	-0.0000 s	$+0.0001\,\pi$	-0.0420
			$-0.1707\,\sigma$	-0.1568 H				$+0.1272\,\sigma$	$+0.0757$ H	
9	a_1'	$-0.0020\,z^2$	-0.0142 s	$-0.2103\,\pi$	-15.861	2	$-0.0000\,z^2$	-0.0002 s	$+0.1894\,\pi$	-0.0000
		$+0.0798$ s	$-0.0121\,\sigma$	-0.0363 H			$+0.0732$ s	$+0.0012\,\sigma$	$+0.0022$ H	$+0.0605$
10	a_2''	$-0.0481\,z$	-0.0082 s	$+0.2458\,\pi$	-14.597	2	$+0.0353\,z$	$+0.0001$ s	$+0.1963\,\pi$	$+0.0307$
			$-0.0026\,\sigma$	-0.0054 H				$+0.0000\,\sigma$	$+0.0000$ H	
11	e_1''	$+0.3477\,xz$	-0.0764 s	$-0.0618\,\pi$	-13.842	4	$+0.3164\,xz$	$+0.0076$ s	$+0.0110\,\pi$	$+0.0746$
			$-0.2515\,\sigma$	-0.2247 H				$+0.1646\,\sigma$	$+0.1237$ H	
12	e_1'	$-0.0986\,x$	-0.0906 s	$+0.0222\,\pi$	-13.748	4	$+0.03318\,x$	$+0.01186$ s	$+0.0021\,\pi$	$+0.0137$
			$+0.2751\,\sigma$	$+0.2480$ H				$+0.1924\,\sigma$	$+0.1464$ H	
13	e_2'	$+0.2043\,x^2-y^2$	$+0.0092$ s	$-0.0125\,\pi$	-13.182	4	$+0.1064\,x^2-y^2$	$+0.0002$ s	$+0.0004\,\pi$	$+0.0229$
			$-0.1303\,\sigma$	-0.1735 H				$+0.0364\,\sigma$	$+0.0592$ H	
14	e_2''		-0.0106 s	$-0.0006\,\pi$	-12.940	4		$+0.0003$ s	$+0.0000\,\pi$	
			$+0.1312\,\sigma$	$+0.1729$ H				$+0.0362\,\sigma$	$+0.0576$ H	
15	e_1'	$-0.1288\,x$	$+0.0236$ s	$+0.3895\,\pi$	-12.510	4	$+0.1448\,x$	$+0.0000$ s	$+0.3665\,\pi$	$+0.1116$
			$-0.0318\,\sigma$	-0.0126 H				$+0.0027\,\sigma$	$+0.0008$ H	
16	e_1''	$-0.5356\,xz$	$+0.0424$ s	$+0.3096\,\pi$	-12.154	4	$+0.6479\,xz$	$+0.0020$ s	$+0.2096\,\pi$	$+0.0742$
			$-0.1117\,\sigma$	-0.0980 H				$+0.0257\,\sigma$	$+0.0203$ H	
17	e_2'	$+0.9483\,x^2-y^2$	-0.0015 s	$-0.0906\,\pi$	-11.355	4	$+1.7956\,x^2-y^2$	$+0.0000$ s	$+0.0163\,\pi$	-0.0029
			$+0.0140\,\sigma$	$+0.0136$ H				$+0.0004\,\sigma$	$+0.0003$ H	
18	a_1'	$+0.9997\,z^2$	-0.00872 s	$-0.0127\,\pi$	-11.136	2	$+1.9529\,z^2$	$+0.0001$ s	$+0.0002\,\pi$	-0.0459
		-0.0888 s	$+0.0271\,\sigma$	$+0.0338$ H			$+0.0148$ s	$+0.0009\,\sigma$	$+0.0020$ H	-0.00097

[a] 4p orbitals: $x(y)$, z; 4s orbital, s; 3d orbitals, z^2, xz (yz), $x^2 - y^2$ (xy). [b] 2s orbital: s; $2p_z$ orbital, π; $2p_x$ orbital, σ; 1s orbital, H. [c] Metal to ligand overlap population (normalized for an occupation number of unity).

Table III. Comparison of Mulliken Overlap Populations in SCF Wave Functions on Ferrocene with Different Basis Sets

		Calculation I, Coutière et al., ref 10		Calculation II, Bagus et al., ref 11	
Basis sets		Fe 12s/7p/5d	$\rightarrow$ 4s/3p/2d	Fe 12s/6p/4d	$\rightarrow$ 8s/4p/3d
		C 8s/4p	$\rightarrow$ 2s/1p	C 7s/3p	$\rightarrow$ 4s/2p
		H 3s	$\rightarrow$ 1s	H 4s/1p	$\rightarrow$ 2s/1p
Total energy		-1634.125 au		-1645.766 au	
Overlap populations[a]	Fe-C	$(a_1')^{16}$	-0.0734	$(a_1')^{16}$	$+0.0029$
		$(a_2'')^{12}$	-0.0210	$(a_2'')^{12}$	-0.0074
		$(e_1')^{24}$		$(e_1')^{24}$	-0.0105
		$(e_2')^{16}$	$+0.0274$	$(e_2')^{16}$	$+0.0296$
		$(e_1'')^{16}$		$(e_1'')^{16}$	$+0.0571$
		$(e_2'')^{12}$	0	$(e_2'')^{12}$	0
		total	-0.0669	total	$+0.0717$
	Fe-H		-0.0091		-0.0084
	Fe-Lig		-0.7604		$+0.6327$

[a] Sums over all MOs of a given irreducible representation.

there is substantial COM in the lower quality wave function, even in some valence orbitals. In the higher quality wave function the COM effect is significantly diminished, but still persists, most noticeably in the 2s a_1' combination.

From the ferrocene discussion one is led to the conclusion that COM is diminished as the wave function is improved. This is not always so. For compounds composed of main group elements the change from a single ζ to a double ζ basis (without adding higher l functions) sometimes leads to COM for the second, more diffuse function. This may be seen in various diatomic calculations[19] but perhaps most clearly in the compendium of polyatomic double ζ functions by Snyder and

Table IV. Contributions to the Fe-C Overlap Populations from the Individual MOs of a_1' and a_2'' Symmetry in SCF Calculations I and II (in Units of 10^{-3}e)

MO type	Calcd I[a]	Calcd II[b]	MO type	Calcd I[a]	Calcd II[b]
1s Fe	−0.02	−0.00	$2p_z$ Fe	−0.23	+0.02
2s Fe	−0.11	−0.11	1s C	−0.31	+0.00
1s C	−0.19	−0.69	$3p_z$ Fe	+2.02	+4.64
3s Fe	−5.93	+0.52	2s C	−27.40	−4.21
2s C	−23.76	−22.36	2σ C	−5.70	−1.29
2σ C	+6.79	+14.33	2π C	+10.65	−6.60
2π C	−28.26	+7.40			
$3d_{z^2}$ Fe	−21.93	+2.41			
$(a_1')^{16}$	−73.40	+2.88[c]	$(a_2'')^{12}$	−20.97	−7.44[c]

[a] Reference 10. [b] Reference 11. [c] See footnote a, of Table III.

Basch.[20] Occasionally the gross populations are negative (e.g., allene on p 117, diazomethane on p 133, methyl isocyanide on p 171 of ref 20). More often one has to dig into the molecular orbitals in detail to see it. The general effect is that, if a contracted orbital mixes in with one sign (intuitive, or in accord with perturbation theory), then the diffuse orbital mixes in with the other (counterintuitive, opposite to simplistic perturbation theory).

Our working hypothesis on COM in ab initio calculations is that it is in some part a real effect, in some part a consequence of unavoidable imbalances in the basis set. The metal virtual orbitals are "used" by the molecule as polarization functions for the C 2s orbitals, to tailor the electron density of these deeper lying orbitals. Consider the electron density along a line passing through the metal atom and the centers of the cyclopentadienyl rings, in an orbital of a_1' symmetry. Suppose the electron density from a calculation omitting metal 4s functions is given by the solid line in **3**, but the true electron

3
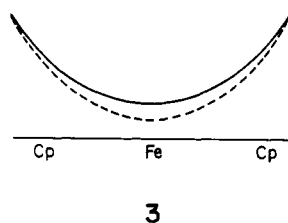
density is given by the dashed line. Addition of the 4s function on the metal will result in its mixing in a counterintuitive way, for only in that way does the electron density approach the true value.

Whether or not COM will decrease as one approaches the Hartree-Fock limit by enlarging the basis set is not clear from the computational evidence at hand. Further calculations are needed. Arguments by one of us for the case that COM will persist at the Hartree-Fock level are presented elsewhere.[21] We should also note that the effect, under the more positive name of "altruistic covalent interaction", has been independently discovered, analyzed, and given a physical interpretation by Marsden and Bartell.[22] This effect may also be responsible for a fraction of the absorption energy of small hydrocarbons on iron clusters and surfaces.[23a] Similar interactions and shifts of the lowest lying σ framework orbitals have also been discussed for acetylene and ethylene on the Ni(111) surface.[23b] Indeed such shifts counteract the effects of CC bond stretching and CH bond bending away from the surface so that, even when distorted to the extent seen in x-ray structures of transition metal coordination compounds, chemisorbed acetylene has σ framework energy levels close to those in free acetylene.[23c] Actual photoemission spectra for acetylene on Ni(111) do indeed show minor σ framework shifts, and so it has been
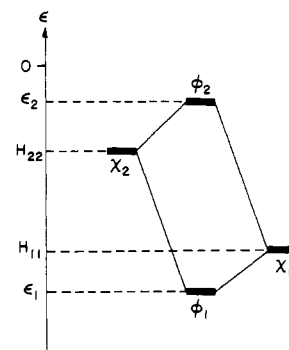
suggested by Anderson[23] that a physical manifestation of the COM effect may be at hand.

Whatever the final resolution of the question of the persistence of COM at the Hartree-Fock level, its occurrence in ab initio calculations makes one feel less compelled to brand this phenomenon an artifact of the extended Hückel procedure. Nevertheless, it is clear that in comparison with better ab initio calculations EH gives too much COM. Because the method is so transparent, let us see if we can analyze the origin of COM in the extended Hückel method, with a twofold purpose: to learn what we can do about the effect, so that perhaps we can gain some insight into its occurrence in the SCF procedures, and also to design a strategy for diminishing its excessive nature in EH.

IV. Simple Model Cases. Two or Three Interacting AOs

For two interacting orbitals (e.g., He-H or He-H$^+$, Figure 1) the Wolfsberg-Helmholz secular determinant takes the simple form

$$\begin{vmatrix} H_{11} - \epsilon & \left[\dfrac{k}{2}(H_{11} + H_{22}) - \epsilon\right]S_{12} \\ \left[\dfrac{k}{2}(H_{11} + H_{22}) - \epsilon\right]S_{12} & H_{22} - \epsilon \end{vmatrix} = 0$$

involving four independent parameters: H_{11}, H_{22}, k, and S_{12}. Since the eigenvectors depend only on the relative values of H_{11} and H_{22}, we can rewrite the secular equations in units of H_{11} by introducing the ratio $Q = H_{22}/H_{11}$:

$$\begin{vmatrix} 1 - E & \left[\dfrac{k}{2}(1 + Q) - E\right]S_{12} \\ \left[\dfrac{k}{2}(1 + Q) - E\right]S_{12} & Q - E \end{vmatrix} = 0$$

where $E = \epsilon/H_{11}$ is now the orbital energy in units of H_{11}.

Instead of looking for the two solutions of this secular determinant we merely ask for the conditions within the three-dimensional (k, Q, S_{12}) parameter space, under which the AO-interference rule (1) (section I) holds, i.e., under which the coefficients of the eigenvector

$$\phi_i = c_{11}\chi_1 + c_{12}\chi_2$$

associated with the lower eigenvalue ϵ_1 have the same sign. Since H_{11}, H_{22}, $\epsilon_1 < 0$; k, $S_{12} > 0$, $E_1 \geq 1$, and $0 < Q < 1$, inspection of the off-diagonal element shows that ϕ_i will be bonding if

$$(k/2)(1 + Q) > E_1$$

and antibonding if

$$(k/2)(1 + Q) < E_1$$

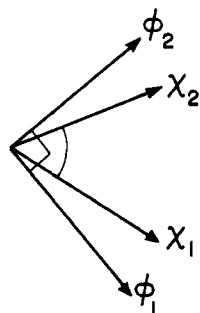independent of the value of the overlap integral S_{12}. Since for

Figure 1. Energy diagram for two interacting orbitals, χ_1 and χ_2.

Figure 2. Eigenvectors ϕ_1 and ϕ_2 both of which represent out-of-phase combinations of the basis vectors χ_1 and χ_2.

the special case of the crossing point

$$(k/2)(1 + Q) = E_1$$

the off-diagonal element vanishes, the lower eigenvector is just χ_1, and $\epsilon_1 = H_{11}$ (or $E_1 \equiv 1$). Therefore, the analytical condition for "normal" behavior can be formulated as

$$k > \frac{2}{1 + Q}$$

In other words, for the case $H_{11} = H_{22}$ ($Q = 1$) k must be greater than 1, while for the extreme case $|H_{11}| \gg |H_{22}|$ ($Q \rightarrow 0$) k has to be chosen greater than 2.

$$\begin{vmatrix} (H_{11} + H_{12})(1 + S_{12})^{-1} - \epsilon & 0 & 2(H_{13} - S_{13}\epsilon)(2 + 2S_{12})^{-1/2} \\ 0 & (H_{11} - H_{12})(1 - S_{12})^{-1} - \epsilon & 0 \\ 2(H_{13} - S_{13}\epsilon)(2 + 2S_{12})^{-1/2} & 0 & H_{33} - \epsilon \end{vmatrix} = 0 \qquad (I)$$

If k is chosen too small, i.e., if

$$k < \frac{2}{1 + Q}$$

the lower eigenvector will show the anomalous behavior we have termed COM, exhibiting a negative overlap population and a stabilization energy $|\epsilon_1 - H_{11}|$ increasing with decreasing value of k. Please note that the crossing point between "normal" and COM behavior is independent of S_{12}; but of course the negative orbital charges and overlap populations can only grow large if S_{12} is large.

A graphical interpretation of the above discussion rests on the fact that secular determinants in the EH theory exhibit the form of an eigenvalue problem in a nonorthogonal coordinate system. The basis vectors are $\chi_1, \chi_2 \ldots$ and χ_i; the angles α_{ij} between these are related to the respective overlap integrals by

$$\cos \alpha_{ij} = S_{ij}$$

It is at once obvious from Figure 2 that, for certain choices of H_{ii}'s, H_{ij}'s, and S_{ij}'s, none of the two eigenvectors ϕ_1 and ϕ_2 will lie in the positive "quadrant", i.e., both contain a positive *and* a negative contribution, corresponding to antibonding admixtures in both the upper and lower orbitals of the two-center two-orbital system.

The simple two-AO two-center model thus reveals the conditions which lead to COM within the extended Hückel framework: *there must be AOs centered on different nuclei which happen to exhibit large differences in ionization potentials and at the same time overlap substantially.* These conditions are not all that different from what we have learned about COM in ab initio SCF calculations. There the phenomenon occurs for diffuse, not occupied orbitals or for the second more diffuse component of a double ζ function. In either case such orbitals would differ substantially from other orbitals in their diagonal value of the Fock operator (of which the EH

H_{ii} is an analogue), and yet would have significant overlaps with other basis functions. The analogy of COM in the SCF case and in the EH case is not complete, however. In SCF calculations the mixing between AOs on different atoms is governed not only by two-center H_{ij} integrals (as in EH calculations) but also by one-center H_{ij} integrals arising, in general, from the use of atomic basis orbitals with different radial but equal angular parts.

Returning to the extended Hückel model, let us consider an example with more than two orbitals on two centers. For the special case of three orbitals χ_1, χ_2, χ_3 on three centers with $H_{11} = H_{22} \neq H_{33}, H_{12} \neq H_{13} = H_{23}$ and $S_{12} \neq S_{13} = S_{23}$ the secular determinant takes the form

$$\begin{vmatrix} H_{11} - \epsilon & H_{12} - S_{12}\epsilon & H_{13} - S_{13}\epsilon \\ H_{12} - S_{12}\epsilon & H_{11} - \epsilon & H_{13} - S_{13}\epsilon \\ H_{13} - S_{13}\epsilon & H_{13} - S_{13}\epsilon & H_{33} - \epsilon \end{vmatrix} = 0$$

This type of determinant arises when χ_1 and χ_2 are related by symmetry. We therefore introduce symmetry-adapted linear combinations

$$\chi_1' = (\chi_1 + \chi_2)/(2 + 2S_{12})^{1/2}$$
$$\chi_2' = (\chi_1 - \chi_2)/(2 - 2S_{12})^{1/2}$$

After transformation to the new basis we obtain the factorized

determinant I. We have thus reduced the three-dimensional problem to a two-dimensional one. We now assume, as before, no mixing between χ_1' and χ_3 in the energetically low linear combination; i.e., we assume $\epsilon_1 = (H_{11} + H_{12})(1 + S_{12})^{-1}$ and cancellation of the terms in the off-diagonal element of the above determinant. With symbols that are analogous to those in the two-AO two-center case, we obtain for "normal" behavior

$$k > \frac{2}{(1 + Q)(1 + aS_{12}) - 2aS_{12}} \qquad (a = 1)$$

This condition is seen to depend not only on Q but also on S_{12} and on a numerical constant a whose value depends on the number of symmetry equivalent orbitals included in the analysis. The inequality also shows that, for this particular example, we cannot specify a value of k that assures "normal" behavior.

In a general, polyatomic case the conditions for COM are more difficult to formulate. Nevertheless, the argument illustrated in Figure 2 may be generalized to any number of dimensions: for certain choices of H_{ii}'s, H_{ij}'s, and S_{ij}'s all eigenvectors ϕ_i will show at least one negative contribution. This implies antibonding admixtures in all MOs, even in the most stable one, i.e., it implies COM. We were unable to determine a value of k which will guarantee the absence of COM and indeed we and others[5] have observed the phenomenon for $k = 2.0$ and larger.

V. A Simple Modification of the Wolfsberg–Helmholz Formula

While our previous discussion left open the question of whether all of COM is an artifact of semiempirical calculations or poor basis sets in SCF computations, there is no doubt that in some cases the extended Hückel method produces a surfeit of the effect. We have examined a number of modifications to

Table V. "Weighted H_{ii}" EH Calculation for Fe(cp)$_2$; K = 1.75; Eigenvalues, Gegenvectors, and Mulliken Population Analysis. Abbreviations as in Table II

No.	Γ_i	Metal coefficient	Coefficients on C_1 and H_1		ϵ_i, eV	n_i	Metal AO gross populations	C_1 and H_1 AO gross populations		OP(M–L)
1	a_2''	+0.1577 z	−0.2315 s	+0.0116 π	−29.514	2	−0.2516 z	+0.2013 s	−0.0007 π	−0.3013
		+0.0289 σ	−0.0362 H					+0.0121 σ	+0.0125 H	
2	a_1'	−0.0022 z^2	+0.2180 s	−0.0040 π	−29.432	2	−0.0004 z^2	+0.1933 s	+0.0002 π	−0.0004
		−0.0460 s	−0.0103 σ	+0.0252 H			−0.0689 s	+0.0044 σ	+0.0090 H	−0.0731
3	e_1'	+0.0394 x	−0.0309 s	+0.0094 π	−24.861	4	−0.0439 x	+0.2809 s	+0.0004 π	−0.0470
			−0.0059 σ	−0.0928 H				+0.0012 σ	+0.0557 H	
4	e_1''	−0.0321 xz	−0.3076 s	−0.0043 π	−24.610	4	+0.0111 xz	+0.2765 s	+0.0002 π	+0.0090
			−0.0063 σ	−0.0926 H				+0.0012 σ	+0.0540 H	
5	e_2'	+0.0384 $x^2 - y^2$	+0.2214 s	−0.0041 π	−19.443	4	+0.0083 $x^2 - y^2$	+0.1126 s	+0.0001 π	+0.0054
			+0.1318 σ	+0.1972 H				+0.0768 σ	+0.1435 H	
6	e_2''		+0.2223 s	+0.0044 π	−19.225	4		+0.1118 s	+0.0001 π	
			+0.1354 σ	+0.2023 H				+0.0771 σ	+0.1457 H	
7	a_1'	−0.0546 z^2	+0.0003 s	−0.0221 π	−16.714	2	+0.0185 z^2	−0.0000 s	+0.0027 π	+0.0125
		+0.0753 s	+0.1580 σ	+0.1543 H			+0.0150 s	+0.1191 σ	+0.0748 H	+0.0037
8	a_2''	−0.0707 z	−0.0035 s	−0.0089 π	−16.522	2	−0.0271 z	−0.0000 s	+0.0001 π	−0.0371
			−0.1682 σ	−0.1601 H				+0.1247 σ	+0.0779 H	
9	a_1'	−0.0027 z^2	−0.0125 s	−0.2123 π	−15.824	2	−0.0001 z^2	−0.0001 s	+0.1911 π	−0.0001
		+0.0579 s	−0.0117 σ	−0.0382 H			+0.0514 s	+0.0012 σ	+0.0026 H	+0.0447
10	a_2''	−0.0633 z	−0.0066 s	+0.2444 π	−14.616	2	+0.0468 z	+0.0001 s	+0.1952 π	+0.0388
			−0.0039 σ	−0.0039 H				+0.0000 σ	+0.0000 H	
11	e_1'	+0.1055 x	+0.0828 s	−0.0303 π	−13.809	4	+0.0365 x	+0.0096 s	+0.0035 π	+0.0142
			−0.2737 σ	−0.2494 H				+0.1916 σ	+0.1494 H	
12	e_1''	+0.2889 xz	+0.0758 s	−0.0477 π	−13.807	4	+0.2277 xz	+0.0074 s	+0.0068 π	+0.0608
			−0.2596 σ	−0.2326 H				+0.1744 σ	+0.1323 H	
13	e_2'	−0.1537 $x^2 - y^2$	−0.0115 s	+0.0089 π	−13.165	4	+0.0645 $x^2 - y^2$	+0.0003 s	+0.0002 π	+0.0173
			+0.1331 σ	+0.1764 H				+0.0380 σ	+0.0614 H	
14	e_2''		−0.0123 s	−0.0004 π	−12.948	4		+0.0003 s	+0.0000 π	
			+0.1335 σ	+0.1756 H				+0.0376 σ	+0.0598 H	
15	e_1'	−0.1333 x	+0.0249 s	+0.3872 π	−12.550	4	+0.1479 x	+0.0003 s	+0.3629 π	+0.1124
			−0.0375 σ	−0.0165 H				+0.0037 σ	+0.0012 H	
16	e_1''	−0.5090 xz	+0.0307 s	+0.3332 π	−11.987	4	+0.6079 xz	+0.0010 s	+0.2392 π	+0.0897
			−0.0896 σ	−0.0796 H				+0.0160 σ	+0.0131 H	
17	e_2'	−0.9546 $x^2 - y^2$	−0.0006 s	+0.0979 π	−10.914	4	+1.8286 $x^2 - y^2$	+0.0000 s	+0.0185 π	+0.0061
			−0.0079 σ	−0.0053 H				+0.0001 σ	+0.0000 H	
18	a_1'	−1.0005 z^2	+0.0077 s	+0.0124 π	−10.665	2	+1.9600 z^2	+0.0001 s	+0.0002 π	−0.0420
		+0.0918 s	−0.0250 σ	−0.0313 H			+0.0155 s	+0.0006 σ	+0.0016 H	−0.0014

the EH procedure designed to reduce COM to a level commensurate to that found in SCF calculations.

As was deduced earlier in the specific case of the two-orbital problem, the condition for normal behavior is

$$(k/2)(1 + Q) > 1$$

For a typical k of 1.75 this condition is not satisfied for small Q, i.e., $H_{11} \gg H_{22}$. For $Q \to 0$ the problem as we saw it was that H_{12} was too small, or that the usual Wolfsberg–Helmholz formula

$$H_{12} = (kS/2)(H_{11} + H_{22})$$

was giving too much emphasis to H_{22}, and thus decreasing H_{12}. We wanted a formula that in the limit of $Q \to 0$ would make H_{12} proportional to H_{11} alone, i.e., one which would "weight" the lower orbital more.

To be more precise we introduce an orbital asymmetry parameter Δ defined as follows:

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}} = \frac{1 - Q}{1 + Q}$$

We then construct a formula for H_{ij} which has the following limiting forms:

$$\Delta = 0 \qquad H_{ij} = (k/2)S_{ij}(H_{ii} + H_{jj})$$
$$\Delta = 1 \qquad H_{ij} = S_{ij}H_{ii}$$
$$\Delta = -1 \qquad H_{ij} = S_{ij}H_{jj}$$

This formula, which is in no way unique, has the form

$$H_{ij} = C(S_{ij}/2)[(1 + \Delta)H_{ii} + (1 - \Delta)H_{jj}] \qquad (1)$$

with C a function of Δ, specifically

$$C = k - (k - 1)\Delta^2$$

Equation 1 may be rewritten alternatively as

$$H_{ij} = k'(S_{ij}/2)(H_{ii} + H_{jj}) \qquad (2)$$

with $k' = k + \Delta^2 + \Delta^4(1 - k)$, which illustrates that in a sense this modification operates by increasing k for those interactions where Δ is different from zero. The above formulas assume that all H_{ii} are negative. We note here that a similar weighted H_{ij} scheme has been suggested by Ballhausen and Gray.[24]

The "weighted H_{ij} formula" (eq 1 or 2) operates in an interesting way. It produces virtually no change in the composition and energy of the valence orbitals, but reduces COM in the lowest orbitals, the ones most prone to the effect. This may be seen in Table V, which shows the details of weighted H_{ij} results for ferrocene, and in the second column of Table I, showing now a positive total metal to ligand overlap population in spite of a still negative 4p$_z$ population.

Appendix

The Wolfsberg–Helmholz EH calculations with self-consistent charge and configuration (SCCC) were performed on $Fe(C_5H_5)_2$ using a model with D_{5h} symmetry and the following bond distances: $d(C-C) = 1.42$ Å, $d(C-H) = 1.1$ Å, d(Fe-center of C_5H_5) = 1.65 Å.

The multiexponential radial functions of Richardson[25] were used for 3d, 4s, and 4p orbitals of Fe. Double ζ orbitals of Sakai and Anno[26] were used for 2s(C) and 2p(C) with $H_{2s2s}(C) = -21.4$ eV and $H_{2p2p}(C) = -11.4$ eV. For hydrogen $\zeta = 1.2$ and $H_{1s1s} = -13.6$ eV were chosen. The SCCC iterations for the Fe H_{ii}'s were performed with the parameter set of Basch et al.[27]

In Tables II and V only one representative of degenerate MOs is listed. Also, only coefficients for one selected carbon (C_1) and hydrogen (H_1) are given. Coefficients for the remaining representatives of degenerate MOs and for the remaining carbon and hydrogen atoms are then determined by the D_{5h} symmetry of the ferrocene molecule. The notation π for $2p_z(C)$ and σ for $2p_x$ and $2p_y(C)$ refers to the planar ligand C_5H_5.

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Interaction between Matrix Isolated Nickel Difluoride and Carbon Monoxide. An ab Initio Molecular Orbital Study

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Abstract: The interaction between Ar matrix isolated NiF_2 with CO is studied by an ab initio molecular orbital method. First the electronic structures of NiF_2, CO, and CO^+ are investigated using a Gaussian lobe basis set. The NiF_2 bond angle is found to be 162° in good agreement with the experimental determination; also the NiF bond has a slightly covalent character. The electronic structure of NiF_2CO is then determined and the emphasis is put on the modification of the CO bond from free CO to NiF_2CO. It is shown that the presence of the dipositive nickel atom induces a polarization of the charges leading to a strengthening of the bond. This is consistent with the experimental observation of a 70-cm^{-1} shift of the CO frequency toward higher wavenumbers. Comparison of the dipole moment of the "complex" with the component dipoles shows equally a polarization effect on the CO bond.

I. Introduction

Coordinately unsaturated metal dihalides and diatomic molecules isolated in rare gas matrices can interact as has been

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shown by infrared spectroscopy.[12] If the effect of the matrix on each member of the associated species is known from a separate experiment,[2,4] it is then possible to determine what modifications of the spectra are due to the intermolecular forces.

The goal of the present work is to study the interaction of