

# Counterintuitive orbital mixing

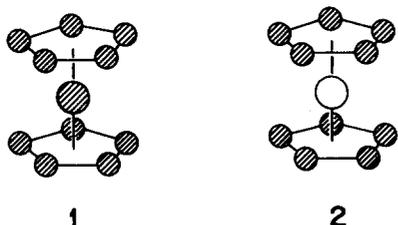
Myung-Hwan Whangbo and Roald Hoffmann

Department of Chemistry, Cornell University, Ithaca, New York 14850  
(Received 16 May 1977)

In both extended Hückel and *ab initio* SCF molecular orbital calculations instances of anomalous orbital interaction are occasionally observed. The lower energy combination of two interacting orbitals is found to be the out-of-phase, antibonding one. Such cases have been called counterintuitive orbital mixing. We present an argument based on SCF perturbation methodology demonstrating that the counterintuitive orbital mixing effect is not an artifact but a natural consequence of orbital interaction between two orbitals that differ greatly in energy but overlap significantly.

Concepts of bonding and antibonding play a central role in the molecular orbital (MO) interpretation of chemical phenomena. For a diatomic molecule bonding and antibonding MO's are formed as in-phase and out-of-phase combinations of atomic orbitals, respectively. A bonding MO leads to a buildup of electron density in the region between two nuclei, while an antibonding MO causes charge withdrawal from this region. Thus electron occupation of the former results in bond strengthening, but that of the latter leads to bond weakening. These conclusions are valid for polyatomic molecules as well. They can be given a perturbation theoretical justification and form the basis of a general set of rules governing orbital interaction.<sup>1</sup>

However, well-defined exceptions to these conclusions have been found in extended Hückel as well as *ab initio* SCF-MO calculations.<sup>2</sup> For instance one of the lower-lying occupied MO's of ferrocene, mainly 2s on the carbons, has the nodal properties shown in 2, that is it is made up of an out-of-phase combination of carbon 2s and iron 4s atomic orbitals, rather than 1, the in-phase combination intuitively anticipated:

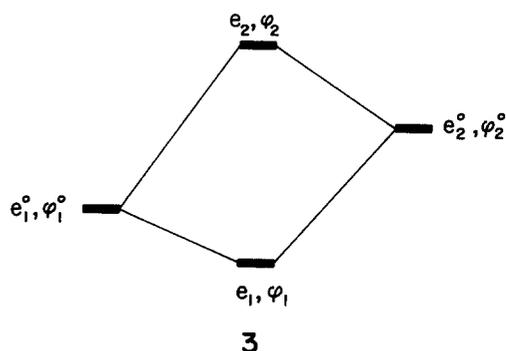


Mixing occurs in an antibonding manner. We have called this phenomenon counterintuitive orbital mixing (COM).

COM occurs in a regular manner in selected levels of limited basis set *ab initio* SCF-MO calculations on transition metal complexes. It is diminished, but does not disappear, in the extended basis calculations at hand.<sup>2</sup> The effect is also found, in a minor but noticeable way, in extended basis set *ab initio* calculations on organic molecules. It is a regular feature of semiempirical calculations of the extended Hückel type on transition metal complexes. Whenever it occurs it operates to reduce Mulliken overlap populations, sometimes even making them negative; it also may manifest itself in negative gross atomic populations. Most of the time the effects of COM are small and do not affect the valence

orbitals of the molecule. The phenomenon has often been ignored as an artifact of the population analysis or of the approximations of the particular method used. The purpose of this paper is to provide a demonstration that the effect is a natural one in the SCF scheme, and not an artifact.

Consider a typical two-level interaction diagram:



We are concerned how the interacted or composite level wavefunction  $\varphi_1$ , and its energy  $e_1$ , is related to the wavefunctions  $\varphi_1^0$  and  $\varphi_2^0$ , and their respective energies,  $e_1^0$  and  $e_2^0$ , of the interacting fragments. This is a question typically posed and easily answered within a one-electron framework. However a recent development of an SCF partitioning scheme<sup>3</sup> allows one to formulate the answer to this problem. It is easily shown that to second order<sup>4</sup>

$$e_1 = e_1^0 + \Delta_{11} + (\Delta_{12} - e_1^0 s) / (e_1^0 - e_2^0), \quad (1)$$

$$\varphi_1 = (1 - st - t^2/2) \varphi_1^0 + t \varphi_2^0, \quad (2)$$

where  $\Delta_{11}$  is the first order energy correction term, and  $\Delta_{12}$  and  $s$  are the interaction matrix element and overlap integral between  $\varphi_1^0$  and  $\varphi_2^0$ , respectively. The mixing coefficient  $t$  is expressed as

$$t = (\Delta_{12} - e_1^0 s) / (e_1^0 - e_2^0). \quad (3)$$

In Eq. (2)  $\varphi_1$  is given by a linear combination of  $\varphi_1^0$  and  $\varphi_2^0$ , where the weighting coefficient  $(1 - st - t^2/2)$  for  $\varphi_1^0$  ensures that  $\varphi_1$  to second order is normalized to unity. Equations (1)–(3) are similar in form to the expression obtained from one-electron perturbation theory.<sup>5</sup>

Since  $(e_1^0 - e_2^0) < 0$ , the second order energy correction

term  $(\Delta_{12} - e_1^0 s)^2 / (e_1^0 - e_2^0)$  of Eq. (1) is negative. It has been our common experience that  $\varphi_1^0$  and  $\varphi_2^0$  combine in phase in  $\varphi_1$ , which leads to bonding between the fragments described by  $\varphi_1^0$  and  $\varphi_2^0$ . In this case,  $t > 0$  if the overlap integral  $s > 0$ . Since the choice of the sign of  $s$  is arbitrary, it will be assumed in the following that  $s > 0$ . Equations (1) and (3) reveal that even if  $t < 0$  the second order energy correction term is still stabilizing. In such a case  $\varphi_1^0$  and  $\varphi_2^0$  combine out of phase, thereby leading to COM. Thus, from Eq. (3), the formal condition for COM can be stated as

$$\Delta_{12} - e_1^0 s > 0. \quad (4)$$

The implication of Eq. (4) may be examined by rewriting Eq. (1) as follows<sup>6</sup>

$$e_1 = \Delta_{11} + (1 - 2st - t^2)e_1^0 + 2t\Delta_{12} + t^2e_2^0 \quad (5)$$

In other words,  $e_1$  is a weighted average of  $e_1^0$ ,  $\Delta_{12}$ ,  $e_2^0$ , and  $\Delta_{11}$ . The only terms that depend on the sign of  $t$  in Eq. (5) are  $-2ste_1^0$  and  $2t\Delta_{12}$ . The former comes from the weighting of  $e_1^0$ , and the latter from that of  $\Delta_{12}$ . In most cases  $e_1^0 < 0$ , and  $\Delta_{12} < 0$ . Thus if COM occurs ( $t < 0$ ),  $-2ste_1^0 < 0$ ,  $2t\Delta_{12} > 0$ , and, from Eq. (4),  $|-2ste_1^0| > |2t\Delta_{12}|$ . Therefore the following inequality is obtained

$$-2ste_1^0 + 2t\Delta_{12} < 0. \quad (6)$$

This equation means that with the occurrence of COM the stabilization of the  $\varphi_1^0$  level resulting from the weighting of  $e_1^0$  is greater than the destabilization caused by its antibonding interaction with  $\varphi_2^0$ .

It should be noticed that Eq. (6) is also satisfied for the normal situation when  $t > 0$ . In this case,  $(\Delta_{12} - e_1^0 s) < 0$ ,  $-2ste_1^0 > 0$ , and  $2t\Delta_{12} < 0$ . Thus in the usual case, Eq. (6) indicates that the  $\varphi_1^0$  level is stabilized more by its bonding interaction with  $\varphi_2^0$  than it is destabilized by weighting  $e_1^0$  less.

Whether normal or counterintuitive mixing occurs thus depends on the sign of  $\Delta_{12} - e_1^0 s$ . There is no basic theoretical restriction on this difference, and indeed existing calculations, *ab initio* and semiempirical, show that it can be positive or negative. In the case of extended Hückel calculations it may be easily shown<sup>2</sup> that COM ( $\Delta_{12} - e_1^0 s > 0$ ) is most likely to occur when the interacting orbitals have very disparate Coulomb integrals and yet overlap significantly. The effect shows up in the lower (and higher<sup>7</sup>) molecular orbitals and not in the frontier orbitals of the molecule. A typical case is that of ferrocene, cited above, where the anomalous mixing is between Fe 4s, 4p and C 2s (very different energy, yet high overlap).

In SCF-MO *ab initio* calculations much the same ground rules for COM appear to be in force. The effect occurs primarily between a pair of orbitals where one is low energy and contracted and the other is high energy and diffuse. Again Fe 4s, 4p and C 2s are a case in point.<sup>2</sup> The in-phase combination of these orbitals causes charge buildup between the metal and ligands at the expense of charge loss in the region of the ligands, while the opposite is the case for the out-of-phase combination. Obviously the latter is more profitable in the

case of COM. This may be due to the fact that a diffuse atomic orbital leads to a preferential electron distribution in a region far removed from its center,<sup>8</sup> and thus more electron density near the attractive region of the ligand nuclei.

It may be said that COM occurs because of the inherent incompleteness of a basis set in the LCAO-MO theory. That is, a diffuse orbital is used as a polarization function for a contracted orbital, to tailor the electron density of the latter. Evidence to support this hypothesis is found from *ab initio* SCF-MO calculations on main group compounds with extended basis sets: There exist occupied MO's in which a contracted and the corresponding diffuse orbital of an atom mix in with different signs, the latter showing COM.<sup>9</sup> Within the LCAO-MO theory, completeness of a basis set is achieved by including basis set orbitals not only of various angular momenta but also of various exponents within a given angular momentum. Thus the probability of COM will persist even at the Hartree-Fock limit, in our opinion.

Are there any experimentally observable consequences of counterintuitive orbital mixing? Marsden and Bartell<sup>10</sup> have independently noticed the phenomenon and discussed it under the name of "altruistic covalent interaction." In their work an anomalous bond length relationship is correctly correlated by extended Hückel calculations, and the overlap populations that are the end product of these calculations in turn are influenced by COM. In our group the anomalous mixing, exaggerated as it is in extended Hückel calculations, was for a long time viewed as a somewhat shady character, perhaps an artifact of our deficient method, perhaps not. We no longer see it as an artifact, yet part of our earlier attitude carries over as a mild skepticism, not of the reality of the effect, but of the possibility of its experimental detection. Some further thought will have to go into the problem.

## ACKNOWLEDGMENTS

We are grateful to J. H. Ammeter, H.-B. Bürgi, and L. S. Bartell for a continuing dialogue on this problem, and to J. C. Thibeault who first analyzed the effect in our group. Our work was generously supported by the National Science Foundation.

<sup>1</sup>R. Hoffmann, *Acc. Chem. Res.* **4**, 1 (1971), and references therein.

<sup>2</sup>J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.* (in press).

<sup>3</sup>M.-H. Whangbo, H. B. Schlegel, and S. Wolfe, *J. Am. Chem. Soc.* **99**, 1296 (1977).

<sup>4</sup>Here the fragments are assumed to be closed shells in their isolated states. When they refer to functional groups, this assumption may not be valid. In such a case, fragment orbitals can be obtained by the partitioning method (Ref. 3), which does not change our discussion which follows except that  $\Delta_{11}$  vanishes.

<sup>5</sup>L. Salem, *J. Am. Chem. Soc.* **90**, 543 (1968).

<sup>6</sup>Equation (5) may be derived from the equality  $e_1 = \langle \varphi_1 | F | \varphi_1 \rangle$ ,

where  $F$  is the Fock operator, by expanding  $\varphi_1$  as in Eq. (2) and retaining the resulting terms up to second order.

<sup>7</sup>So far we have been discussing COM in the lower level. Of course an analogous effect, in the opposite sense, occurs in the higher level.

<sup>8</sup>The same point was made in the perceptive discussion of J. P. Dahl and C. J. Ballhausen, *Adv. Quantum Chem.* 4, 170

(1968), pp. 194–199.

<sup>9</sup>The effect is clearly seen in many wave functions in the compendium by L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley-Interscience, New York, 1972).

<sup>10</sup>C. J. Marsden and L. S. Bartell, *Inorg. Chem.* 15, 2713 (1976).