1-difluoromethyl (1-$CHF_2$) substitution also shifts the equilibrium toward norcaradiene while 2-methyl substitution favors cycloheptatriene in analogy with oxepin.

We have looked at the kinetic stability of norcaradiene and 2-methylnorcaradiene. As reported above, both species are thermodynamically unstable with respect to conversion to cycloheptatrienes. Table IV presents the results of our studies on the energetics of these isomerizations and shows that neither norcaradiene nor its 2-methyl derivative is locked into the unstable bicyclic form. Thus, the activation enthalpy for **9** → **10** is calculated to be 10.9 kcal/mol and for 2-methylnorcaradiene → 2-methylcycloheptatriene 8.8 kcal/mol. As we found in the case of benzene oxide → oxepin, methyl substitution in the 2 position lowers the barrier to isomerization significantly. Table IV also contains the results for the benzenimine → azepin conversion and shows once again that the barrier separating **11** from **12** is low and would not be expected to prevent rapid conversion of the less stable benzenimine to azepin.

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# On MO Calculations of Dimeric Interactions and Their Applicability to Crystal Structures. $(TCNQ)_2$ and $(TTF)_2$

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**Abstract:** Ramifications of simple MO considerations on charge-transfer dimer structures are considered. The missing extended Hückel energy minimum for slipped neutral $(TTF)_2$ is found and attributed to steric repulsion between sulfurs. The dimer energy vs. slip in $(TTF)_2$ is found to be sensitive to the presence of sulfur d AOs in the basis set. Discrepancies between earlier calculations are attributed to this basis-set dependence. The relevance of dimer structure calculations to crystal structures is discussed. Symmetry restrictions in the crystal are more severe than in the dimer, so some energy-lowering effects present for the dimer are forbidden in a uniform stack in the crystal. Such effects should favor phase transitions to nonuniform stacks. It is pointed out that the four distances in TTF-TCNQ crystals (two interplanar and two slip distances) are not independent. Our data suggest that the slip value of TTF in TTF-TCNQ is a passive parameter determined by the other three (active) parameters. Our data furthermore suggest that, in pure TTF crystals, the slip value is an active parameter.

## I. Introduction

The crystalline organic charge-transfer complex tetrathiafulvene-tetracyanoquinodimethane (TTF-TCNQ) possesses an electrical conductivity (in one dimension) on the order of those of some of the less conductive metals (e.g., manganese).[1] This is many orders of magnitude more conductive than normal organic materials and has led to great interest in obtaining a detailed understanding of how the electrical properties of organic crystals are influenced by the properties of the individual molecules and also by the interactions between molecules in a crystal.[2] A facet of this problem has been to try to relate observed crystal structure to molecular structure. One approach to this restricted goal has been to perform molecular orbital (MO) calculations on "supermolecules", usually dimers, such as $(TCNQ)_2$ and $(TTF)_2$, to see whether energy minima can be found in the regions of observed stable crystal configurations. In this paper, we make some general observations concerning such calculations, and illustrate these observations by examining the results of MO calculations by us and others on the two dimer systems $(TCNQ)_2$ and $(TTF)_2$. Implications of our results for understanding TTF-TCNQ crystal structure are also discussed.

## II. Crystal Structure of TTF-TCNQ

TTF-TCNQ in the room temperature conducting phase consists of parallel stacks of like molecules, the molecules in

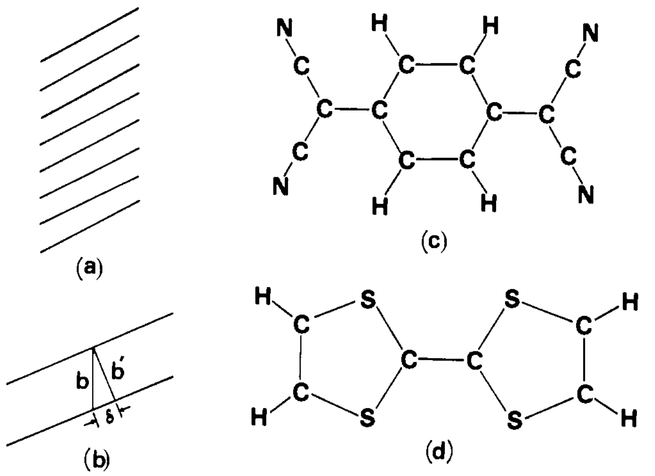

**Figure 1.** (a) Schematic diagram showing the arrangement of planar molecules in a stack. The molecules are seen edge on and the shorter in-plane molecular axis is perpendicular to the page. Each stack contains molecules of a single type in TTF-TCNQ. (b) The relation between adjacent molecules in a stack is given by the interplanar distance $b'$ and the distance of slip from the completely eclipsed arrangement, $\delta$. For TCNQ stacks, $b' = 3.17$ Å, $\delta = 2.13$ Å; for TTF stacks, $b' = 3.47$ Å, $\delta = 1.60$ Å. (c and d) The molecular structures of TCNQ and TTF.

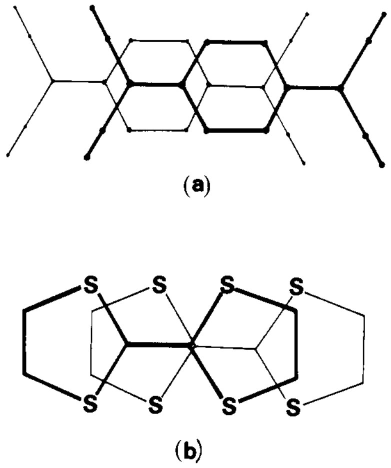

**Figure 2.** Arrangements found for neighboring molecules in stacks of (a) TCNQ, (b) TTF in TTF-TCNQ crystals.

each stack being equidistant and packed face to face, but slipped somewhat along the longer molecular axis so as not to be perfectly eclipsed[3] (see Figure 1). Electron transfer is thought to occur to the extent of about 0.6 electron being lost from each TTF molecule and gained by each TCNQ molecule.[4] Thus, the appropriate charge for a dimer which is intended to represent a segment of a crystal stack is about +1 for $(TTF)_2$ and −1 for $(TCNQ)_2$.

The degree of slip away from an eclipsed configuration corresponds, for TCNQ, to an arrangement where the six-membered ring of one molecule lies directly over a C-C double bond of each nearest neighbor, as sketched in Figure 2a. The slip in TTF is such as to allow the sulfur atoms in adjacent molecules to "nest" between each other as indicated in Figure 2b. It is these slip distances and their relationships to molecular structure and extent of charge transfer that we address here.

## III. Structural Information on Related Systems

Many charge-transfer complexes are known where TCNQ is the electron acceptor. In some of these, the TCNQ molecules do not assume the slipped structure seen in TTF-TCNQ. In general, there is a tendency for $(TCNQ)_2$ to prefer an eclipsed configuration as the degree of charge transfer approaches $(TCNQ)_2{}^{2-}$.[5,6] There is also evidence to suggest that $(TTF)_2{}^{2+}$ prefers an eclipsed configuration.[5,7] TTF molecules in the pure crystal, however, are slipped in a manner similar to that in TTF-TCNQ.[8] Thus, there is experimental evidence to support the contention[5] that the eclipsed (or nearly eclipsed) form of such dimers (or segregated stacks) is favored by a larger extent of charge transfer.

## IV. Earlier Theoretical Work on $(TCNQ)_2$

The first MO calculations on this dimer were of the $\pi$-only extended Hückel molecular orbital (EHMO) type and were reported in 1969 by Chesnut and Moseley.[9] If the interplanar distance is kept fixed at 3.17 Å and only $\delta$, the extent of slip along the long axis, is allowed to vary, those calculations show, for $(TCNQ)_2{}^0$, an energy maximum at $\delta = 0$ (i.e., eclipsed dimer) and a small minimum at $\delta \approx 2.13$ Å. For $(TCNQ)_2{}^-$, a shallow minimum appears at $\delta = 0$ and the minimum at 2.13 Å becomes deeper. For $(TCNQ)_2{}^{2-}$, even deeper minima are found at both positions. These workers investigated the potential surface in other regions as well, but for the present we are concerned only with the behavior of the energy with respect to slip along the long axis. Chesnut and Moseley pointed out that this tendency for the ionized forms of $(TCNQ)_2$ to be more strongly bound than the neutral dimer is in accord with elementary notions of MO theory: The monomer one-electron energies should be split about equally up and down by the interaction with the dimer. In the neutral dimer, all such split-pair MOs are either completely occupied or completely empty, so splitting effects on the energy largely cancel. If one of the split pair of MOs contains only two electrons (as in $(TCNQ)_2{}^{2-}$), these electrons will be in the lower energy member of the pair, stabilizing the dimer.[9]

Berlinsky et al.[10] carried out full EHMO calculations on $(TCNQ)_2$ and found energy vs. slip results in general qualitative agreement with those of Chesnut and Moseley. Most recently, Silverman[5] has repeated the investigation using instead the CNDO/2 method. His data differ from the EHMO results in some details. The CNDO/2 energy for $(TCNQ)_2{}^0$ is a maximum at $\delta = 0$, though not so pronounced as the EHMO maximum, and no minimum is found at $\delta = 2.1$ Å. $(TCNQ)_2{}^-$ and $(TCNQ)_2{}^{2-}$ are found to have energy mimima at $\delta = 0$ and 2.1 Å with the minimum at $\delta = 0$ being slightly deeper in both cases. Qualitatively, though, the CNDO/2 and EHMO results are rather similar. Other calculations[11] have been performed on $(TCNQ)_2$, but these have been concerned with calculating bandwidths rather than total energies.

## V. Earlier Theoretical Work on $(TTF)_2$

Berlinsky and co-workers[10] have reported EHMO calculations on $(TTF)_2$ (interplanar distance kept at 3.47 Å) as a function of slip distance and dimer charge (0, +1, +2). They found an energy maximum for eclipsed $(TTF)_2{}^0$ and found no minimum at the observed TTF-TCNQ crystal slip distance of 1.6 Å. For $(TTF)_2{}^+$ they found a very slight minimum at $\delta = 0$, and for $(TTF)_2{}^{2+}$ a much more pronounced minimum there, but neither of these ions was found to give minima anywhere else in the range examined ($0 < \delta < 2.0$ Å).

Silverman[5] has recently reported CNDO/2 calculations on $(TTF)_2$ as a function of charge and slip distance. Here the qualitative agreement between EHMO and CNDO/2 methods is not as good as was the case for $(TCNQ)_2$. CNDO/2 calculations show a *minimum* for eclipsed $(TTF)_2{}^0$, whereas EHMO calculations give a maximum there. Otherwise, CNDO/2 calculations agree with the EHMO results; the minimum at $\delta = 0$ gets deeper as $(TTF)_2$ becomes more positive, and no minimum is found at any slipped configuration from $\delta = 0$ out to 1.6 Å.

The failure of these calculations to predict an energy minimum around $\delta = 1.6$ Å for $(TTF)_2{}^{0,+}$ is something of a puzzle.

It has led Berlinsky[2] to speculate that "the molecules stack the way that they do because they are jammed between stacks of TCNQ molecules". However, Silverman[5] points out that TTF packs in much the same manner in pure TTF crystals, and suggests instead that the stability of slipped TTF might be understandable in terms of the simple close packing of hard atomic spheres. This implies, however, that this "steric" factor is not adequately handled by CNDO/2 or EHMO methods.

Previous theoretical work thus leads us to focus on two questions: (1) Why have neither EHMO nor CNDO/2 calculations on $(TTF)_2{}^{0,+}$ shown any energy minimum at the observed slip distance? (2) Why do these two methods disagree qualitatively on the energy at the eclipsed configuration of $(TTF)_2{}^0$, the former giving a maximum, the latter a minimum?

## VI. Some General Aspects of EHMO Calculations on Dimers

EHMO energy changes are amenable to detailed analysis in terms of Mulliken overlap population changes,[12,13] so there is nothing to prevent us from determining precisely what causes the various orbital energies to change as they do with changes in $\delta$. However, when large systems like $(TCNQ)_2$ are being treated, the complete analysis becomes unmanageably cumbersome, and a somewhat less detailed approach is more comprehensible.

Let us begin by considering the limiting case of interaction through space between two identical degenerate orbitals, $\chi_a$ and $\chi_b$ (which may be AOs or MOs), *in the absence of any other orbitals*. An MO calculation will produce two new orbitals from these. One will be "bonding", one "antibonding". We shall refer to this new pair of orbitals as an *orbital pair* (OP). In an EHMO calculation, one normally finds that the lower energy orbital is the one corresponding to phase agreement between the original orbitals, i.e.

$$\phi_{\text{lower energy}} \equiv \phi_l \equiv [2(1 + S_{ab})]^{-1/2}(\chi_a + \chi_b)$$

and

$$\phi_{\text{higher energy}} \equiv \phi_h \equiv [2(1 - S_{ab})]^{-1/2}(\chi_a - \chi_b)$$

where

$$S_{ab} \equiv \langle \chi_a | \chi_b \rangle$$

and where we are assuming that the relative orientations of $\chi_a$ and $\chi_b$ are such that their *sum* gives phase agreement in the overlap region. (There are conditions under which the case of phase agreement goes with the *higher* energy MO. This is well understood,[13] occurs only for very deep levels, and is of no practical concern here.) One further finds that the energy rise due to formation of $\phi_h$ is greater than the lowering due to $\phi_l$. This is caused by the difference in normalizing factors.[14] Therefore, a fully occupied orbital pair of this nature will contribute to a net energy rise, hence repulsion, in an EHMO calculation. Indeed, this is precisely the EHMO equivalent of what chemists refer to as repulsion between closed shells. As a rule of thumb, *the larger the overlap $S_{ab}$, the greater we expect this energy splitting, and net repulsion, to be.*[15]

By limiting ourselves to but two starting orbitals, we prevent the EHMO method from altering the above considerations in any way. Usually, however, we do have other orbitals present, and, for large "supermolecules" like $(TCNQ)_2$, these become very numerous. The variational procedure will use these, as best it can, to lower the energies of our OP further. It will do this by skewing the bonding orbital to increase the overlap in the bonding regions between the interacting systems, and by skewing the antibonding orbital in the reverse manner in order to relieve the antibonding interaction. Let us refer to this shifting of MOs into and out of the intersystem region as *overlap-induced polarization* (OIP) to distinguish it from polarization induced by an electric field (which is not present in the basic EHMO treatment).

In the language of perturbation theory, we can say that the splitting in energies associated with our original unpolarized OP is the first-order energy change. OIP results from first- (and higher) order corrections to the orbitals. Energy changes resulting from OIP represent second- (and higher) order corrections to the energy. Thus, the first-order energy change for a fully occupied OP is net positive (repulsive), and higher order energy changes may be net negative if suitable orbitals exist at higher energies.[16,17]

The approach of two ethylene $\pi$ systems end to end to form a butadiene $\pi$ system exemplifies these points. Figure 3 illustrates how the energies and orbitals appear at different stages in the two-step process just described. (We ignore the $\sigma$ systems and extra hydrogen atoms here.) The originally degenerate levels interact to first order to produce two net repulsive splittings. The MOs are shown as being unpolarized at this stage. Interaction between levels connected by arrows produces OIP and depresses the lower levels (at the expense of the upper ones, where OIP is of a nature to decrease bonding and augment antibonding). Whether this will suffice to convert the repulsive effect of the lower OP into an attractive one depends, in general, upon the availability of other OPs, not too much higher in energy, which have proper symmetry and significant overlap with the OP of interest.

A related terminology used by chemists would refer to atoms or molecules which resist OIP as "hard", and those which are highly susceptible as "soft".[18] "Repulsion between closed shells" is a phrase which tacitly assumes a hard-hard interaction. (If the two interacting species are identical, we need only refer to a "hard" interaction.)

## VII. Applications of Theory to $(TCNQ)_2$

When a pair of neutral TCNQ molecules are brought together, face to face and eclipsed (at a distance of 3.17 Å), are we dealing with a hard or a soft interaction? The fact that EHMO calculations[10] predict a repulsive interaction indicates that the interaction is hard, i.e., that the OIP is insufficient to cause a net attraction. We can understand this by examining MO energies and symmetries of TCNQ, shown in Figure 4. There are only two ways OIP can be effected. One way is by mixing together filled and empty $\pi$ MOs. This could be done so as to build up each MO at sites where it has a large bonding interaction with the other TCNQ molecule, or else to decrease it where it has a large antibonding interaction. In order to maintain proper symmetry, only $\pi$ MOs of identical symmetry can be mixed (when $\delta = 0$). Thus, the HOMO, which has $b_{1u}$ symmetry (TCNQ has $D_{2h}$ symmetry), can mix with an empty $\pi$ MO of $b_{1u}$ symmetry at $-8.3$ eV. The other mode of mixing is $\pi$-$\sigma$ mixing. This would shift an MO into or out of the region between TCNQ molecules. Again, only certain symmetry combinations are allowed, namely (in the order $\pi$-$\sigma$), $b_{2g}$-$b_{3u}$, $b_{3g}$-$b_{2u}$, $b_{1u}$-$a_g$, $a_u$-$b_{1g}$. Arrows in Figure 4 indicate some of the allowed interactions. (The same symmetry restrictions apply for charge-induced polarization.)

Neither of these mixing modes is very effective in eclipsed $(TCNQ)_2{}^0$. The $\pi$-$\pi$ mode suffers because, for a given dimer MO, every nonzero interaction between an AO on one molecule and its twin on the other must be of the same type. Hence, polarization to favor bonding between certain atoms must come at the expense of bonding between other atoms. Some advantage may be had, but it is not likely to be great. $\pi$-$\sigma$ mixing suffers because overlaps between $2p_\sigma$ AOs on one TCNQ and $2p_\pi$ AOs on the other are zero for eclipsing atoms and relatively small for more distant pairs. Overlap between the 2s AO on an atom with $2p_\pi$ AO on the eclipsing atom is more substantial, but the 2s AOs figure significantly only in MOs that are very far in energy from the frontier orbitals. (They appear in oc-

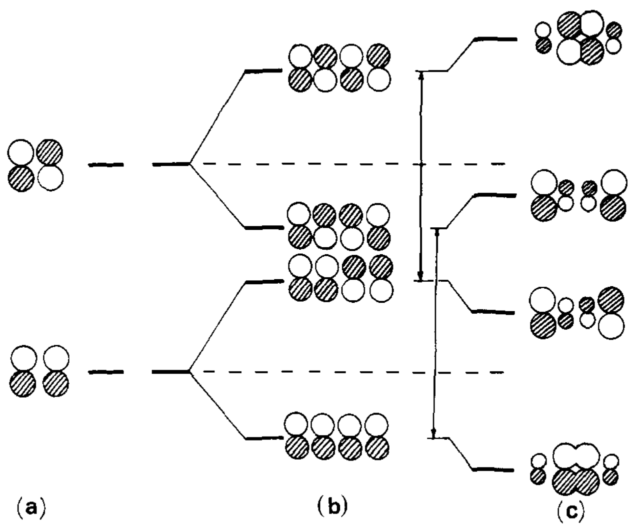

**Figure 3.** End-to-end interaction between two ethylene $\pi$ systems. (a) Before interaction. (b) Interaction to first order. (c) Interaction to all orders. The arrows in (b) indicate the levels which can interact to give the results (c).

cupied MOs at energies around −20 eV and in empty MOs at 6 eV and higher.) Thus, neither mixing mode has much opportunity to contribute, and the interaction is hard.

As the two neutral TCNQ molecules slip away from $\delta = 0$ at constant interplanar distance, two things happen to reduce the repulsion. First, the degree of overlap between each MO on one molecule with its mate on the other decreases, so the OP splittings decrease and so does the net repulsion produced by the imbalance of the splittings. Second, end-to-end polarization within each molecule becomes active as a mode of OIP. (The lower symmetry allows previously forbidden mixings to occur. Also, $\pi$-$\pi$ mixing can respond to the fact that one end of each molecule is no longer interacting strongly with the other molecule.) Hence the interaction is both reduced and softened. Because the direction of end-to-end polarization is generally opposite for the two members of an OP (into the overlapping region for the bonding member, out of this region for the antibonding member), the overall charge imbalance is quite small.[17]

If the decrease in overlap between TCNQ molecules were monotonic with increasing $\delta$, we should expect the repulsion to decrease monotonically (possibly even turning into an attraction if sufficient softening occurred). But the overlap changes in a nonuniform way. At $\delta = 0$, a total of 16 atoms (excluding hydrogens) in one TCNQ molecule eclipse those in the other. The next eclipsing comes at $\delta = 1.4$ Å, when four atoms pass over another four. At $\delta = 2.85$, 4.25, 5.65, 7.42, and 8.31 Å, there are respectively five, six, one, two, and two eclipsing pairs. We might expect some bumps in our curve of energy vs. $\delta$ as we pass through regions with large numbers of closest approaches. Such maxima resulting from hard, closed-shell interactions are simply the EHMO manifestation of "steric repulsion".

Figure 5 summarizes data from our EHMO calculations[19] on $(TCNQ)_2$ for slip values ranging from 0 to 5 Å. The upper curve corresponds to the energy of $(TCNQ)_2{}^0$ relative to the energy at infinite separation. This curve exhibits the pronounced maximum at $\delta = 0$ found by all previous workers[5,9,10] and also a ridge in the region from about 2.4 to 4.5 Å which matches the eclipsing of five or six pairs of atoms. The very shallow minimum occurring around $\delta = 2.1$ Å appears to be merely the result of slight relief from steric repulsion.

The bottom curve of Figure 5 is the energy variation of the lowest unfilled MO (LUMO) of $(TCNQ)_2{}^0$. This MO accepts electronic charge to give $(TCNQ)_2{}^-$ or $(TCNQ)_2{}^{2-}$ (or intermediate charges when we consider infinite stacks) and is sometimes called the affinity orbital. It consists mostly of a $\pi$ MO from each TCNQ molecule combined in a bonding manner. In Figure 6a is a sketch of this MO as it appears on one of the monomers. The LUMO energy local minima occurring at $\delta = 0$, 2.2, and 4.5 Å correspond to dimer configurations permitting maximum overlap between two such monomer MOs. (See Figure 6b.) (These positions are likewise those where the antibonding mate of the LUMO will have the highest energy. I.e., these are positions of maximum splitting in the OP of which the LUMO is the lower energy member. Hence, these positions correspond to local maxima in conducting bandwidth as calculated for an infinite chain.) The minimum in LUMO energy at $\delta = 0$ is the deepest because the optimum overlap between a monomer MO and its twin comes when they are eclipsed, for then the largest components of each

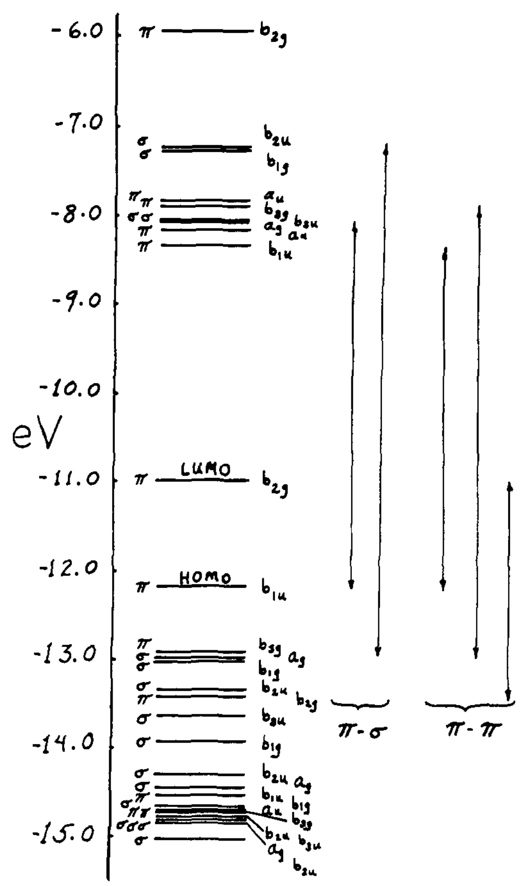

**Figure 4.** Some EHMO energy levels and MO symmetries for TCNQ. Arrows indicate mixings which are allowed for eclipsed $(TCNQ)_2$.

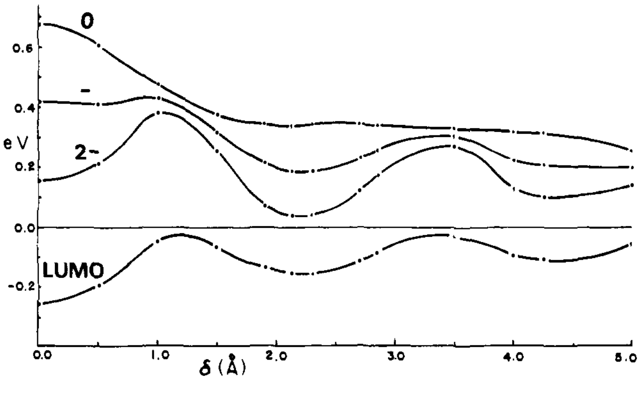

**Figure 5.** Energy vs. slip for $(TCNQ)_2{}^n$ ($n = 0$, 1−, 2−) as calculated by the EHMO method. LUMO energy is also shown. The interplanar distance is 3.17 Å, as in TTF-TCNQ.

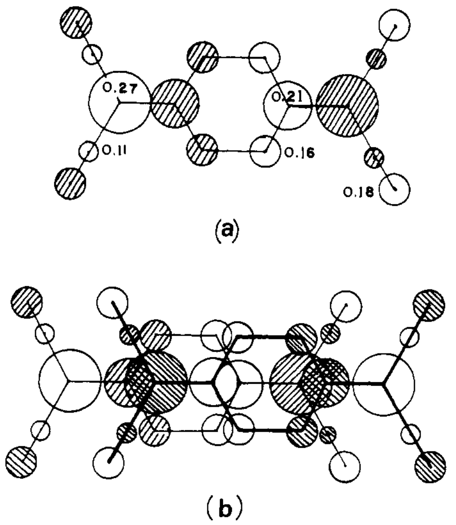

**Figure 6.** (a) The LUMO of $(TCNQ)_2{}^0$ as seen from above. Only upper lobe of each $\pi$ AO is shown. The AO lobes between TCNQ monomers are in phase agreement. (b) The LUMO of $(TCNQ)_2{}^0$ at $\delta$ = 2.13 Å. Only the AO lobes between molecular planes are shown. The LUMO energy goes through a minimum at $\delta$ = 2.13 Å because overlap between monomer orbitals is relatively large here.

MO are matched, giving the maximum overlap. The efficacy of this overlap also at $\delta$ = 2.2 Å has been noted by all earlier workers.

Since the EHMO total energy is the sum of one-electron energies, the curves of energy vs. slip for $(TCNQ)_2{}^-$ and $(TCNQ)_2{}^{2-}$ are produced by adding the lower curve once or twice to the top curve. This produces the middle two curves of Figure 5. The energy behavior at $\delta$ = 0 for these ions is clearly the result of opposite tendencies of the steric repulsive "hump" and the attractive minimum of the affinity orbital. At values of $\delta$ greater than 1.5 Å, the fluctuating affinity orbital energy dominates the contour because the "steric repulsion curve" is so featureless there.

The curve for $(TCNQ)_2{}^0$ is relatively smooth compared to that for the LUMO in Figure 5. This arises because the former curve is a sum of energies of all occupied MOs, whereas the latter gives the variation of but one MO. An individual MO will usually have much larger magnitudes on some atoms than on others, so overlap between a pair of such MOs will vary relatively greatly with slip according to whether these "favored" atoms are close together or far apart. Thus, the sensitivity of orbital energy to slip is understandable. But different orbitals will have different "favored atoms", hence different placement of maxima and minima. Also, the maxima and minima in one such curve will tend to be countered by the minima and maxima in the curve for the other member of the split orbital pair. The synthesis of many such curves produces a profile of lower contour, although the regions corresponding to *no* close approaches continue to show as minima and those of *many* close approaches as maxima. In this way a curve is generated which reflects the degree of close approach of *atoms in general*—a steric repulsion curve.

On the basis of the above, we can make the following generalizations concerning EHMO energies for face-to-face slipped dimers of planar $\pi$ systems:

(1) For closed-shell monomers comprised of atoms like C, N, and O, the interaction should be hard, or repulsive, in the neutral dimer.

(2) The repulsive curve for the neutral dimer will have a pronounced maximum at $\delta$ = 0 (eclipsed) and may reflect steric repulsion as lesser maxima at nonzero values of $\delta$.

(3) Gain or loss of up to two electrons will cause an additional attractive factor to enter. The former adds a new, bonding orbital; the latter removes some antibonding orbital character. Either way, the added attractive factor is most attractive at $\delta$ = 0, and there may be other, secondary attractive maxima at other values of $\delta$. These are qualitatively predictable from examination of the affinity or donor MO of the monomer.

(4) At low levels of electron transfer, the minima in the total energy curve will correspond to positions of *secondary* attractive maxima in the above-mentioned attractive factor. The total energy at $\delta$ = 0 will remain a maximum due to domination by underlying filled OPs. As more charge is transferred (up to two electrons per dimer) the total energy at $\delta$ = 0 will tend toward a minimum and may even become the deepest local minimum. It could even become lower in energy than the infinitely separated pair.

(5) Because the overlap between a monomer MO and its mate is a maximum at $\delta$ = 0, the following are true there: (a) Orbital pair splitting is maximized. (b) Conduction bandwidth is maximized. (c) Steric repulsion in the neutral dimer is maximized. (d) LUMO energy is minimized. (e) HOMO energy is maximized.

The suggestion[5] that increased electron transfer should favor the eclipsed dimer is consistent with the interplay among (c), (d), and (e).

We emphasize that these remarks apply to EHMO calculations, and may or may not apply to the actual physical situation. Certainly, inclusion of van der Waals interactions, electric charge repulsion, and charge-induced polarization would be desirable in a complete model.

## VIII. Application of Theory to $(TTF)_2$

$(TTF)_2$ introduces some important new features for consideration. First, sulfur atoms are much larger than carbon atoms, so we might anticipate that the intermonomer interactions will be dominated by the sulfurs. Second, we must decide whether or not to include 3d AOs on sulfur in our basis set, so it is worth considering how that decision will influence our computational results.

Berlinsky et al.[10] omitted 3d AOs on the grounds of spectroscopic considerations. Silverman[5] makes no explicit statement regarding his basis set, but the standard CNDO/2 method[20] normally does include 3d AOs on sulfur. We report below EHMO calculations on $(TTF)_2$ with and without 3d AOs on sulfur.

**A. No d Orbitals in Basis Set.** If the sulfurs dominate the steric interaction, the major interaction should come at $\delta$ = 0, when four pairs of sulfur atoms are eclipsed, and a secondary maximum interaction might be anticipated at $\delta$ = 3.2 Å, where two pairs are eclipsed. This might reasonably be expected to result in a minimum around 1.6 Å, but we have already seen that earlier calculations[5,10] failed to find such a minimum.

Figure 7 displays EHMO[19] energy vs. slip distance for a pair of TTF molecules[21] at an interplanar separation of 3.47 Å.[2] (This is the distance between TTF molecules in TTF-TCNQ and is the distance used in the earlier calculations.[5,10]) No d AOs are present in the basis set. The interaction is "hard", and we see the anticipated maxima at $\delta$ = 0 and 3.2 Å, with a significant minimum at about $\delta$ = 2.0 Å. Thus, the EHMO calculations (without d AOs) are consistent with a slipped structure for $(TFF)_2{}^0$ wherein the sulfur atoms nest between each other to reduce steric repulsion. The calculated minimum does not come exactly at the observed slip distance, and it is not clear whether this results from the operation of factors in the crystal which are not included in our treatment, or from the deficiencies of the EHMO method itself. Presumably Berlinsky et al.[10] would also have found this energy minimum if they had examined a slightly larger range of $\delta$.

Highest occupied MO (HOMO) energy vs. slip is also plotted in Figure 7. It is a positive (repulsive) energy curve (since the HOMO is the *antibonding* member of a $(TTF)_2$ OP)

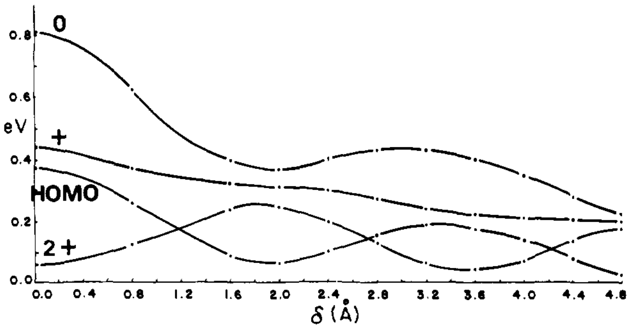

**Figure 7.** Energy vs. slip for (TTF)$_2{}^n$ ($n$ = 0, 1+, 2+) as calculated by the EHMO method without 3d AOs on sulfur. HOMO energy is also shown.

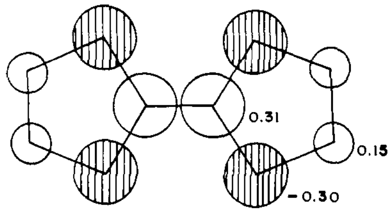

**Figure 8.** The HOMO of eclipsed (TTF)$_2{}^0$ as seen from above. The AO lobes between the TTF monomers are in phase disagreement.

and is very similar in appearance to the total energy curve for (TTF)$_2{}^0$. When we examine the HOMO (Figure 8), we see that it is concentrated heavily in the sulfur atom 3p$_\pi$ AOs, which also are the AOs which overlap most effectively between monomers. Therefore, the HOMO energy should be highest when the largest numbers of sulfur atoms are eclipsed, and it is evident that the same considerations govern both the HOMO and the total energy curves.

The HOMO of (TTF)$_2{}^0$ is the donor MO. To get the energy of (TTF)$_2{}^+$ or (TTF)$_2{}^{2+}$, we subtract the energy of the HOMO from the total energy once or twice, obtaining the other curves in Figure 7. The rather featureless curve for (TTF)$_2{}^+$ arises from subtracting curves that are so similar. (TTF)$_2{}^{2+}$ shows minima at $\delta = 0$ and 3.2 Å because these are sites of maximum sulfur–sulfur "bonding" (or greatest loss of antibonding).

Comparing these results with those for (TCNQ)$_2{}^0$, we find that the chief difference is that, for (TTF)$_2{}^0$, the steric interaction is dominated by a small subset of all the atoms, leading to a greater degree of fluctuation in steric repulsion. The HOMO interaction is dominated by AOs on the same four atoms, so it has a similar appearance to the steric repulsion curve. Otherwise, the conclusions are the same.

**B. d AOs Present in Basis Set.** Inclusion of 3d AOs on sulfur atoms[19] leads to the results graphed in Figure 9. Comparison with Figure 7 makes it clear that the 3d AOs have a dramatic effect. For (TTF)$_2{}^0$, we now find *minima* at $\delta = 0$ and 3.2 Å and a maximum at 1.6 Å. Over the range $0 \leq \delta \leq 1.6$, this resembles the results of the CNDO/2 calculation.[5] The HOMO energy behavior is qualitatively similar to what we found without d AOs (though less bumpy) and this is what we should expect, since this MO is still the antibonding member of an OP and the HOMO is still very similar to that calculated without d AOs. Because the HOMO maxima have not shifted, we again see a preferential deepening of the minimum at $\delta = 0$ as more charge is transferred out of the HOMO. The important change which has occurred upon inclusion of d AOs is that we have a much softer interaction, so that, where we had maxima for our neutral dimer, we now find minima.

It is possible to find the detailed reason for the softer interaction. In Figure 10 are plotted orbital energy levels in the frontier region for TTF. On the right are the levels computed without d AOs, and it is clear that this is consistent with a "hard" situation. (The lowest energy empty σ MO level falls off the top of the figure near 0 eV.) On the left are plotted the levels resulting when 3d AOs are present on sulfur. A large number of π–σ mixings become possible for eclipsed (TTF)$_2$. Especially noteworthy are those involving empty σ levels enclosed by the curly bracket. These MOs include large amounts of sulfur 3d$_{z^2}$ character, and the overlap between a 3d$_{z^2}$ AO on one sulfur and the 3p$_z$ AO on the eclipsing sulfur of the other monomer is (relatively) very large. Hence, these MOs mix relatively heavily with occupied π MOs. The net effect is to increase the Mulliken population of 3d$_{z^2}$ AOs in eclipsed (TTF)$_2{}^0$ by a factor of 3 over that in TTF. The effect of 3d AO inclusion is also observable in the Mulliken overlap population

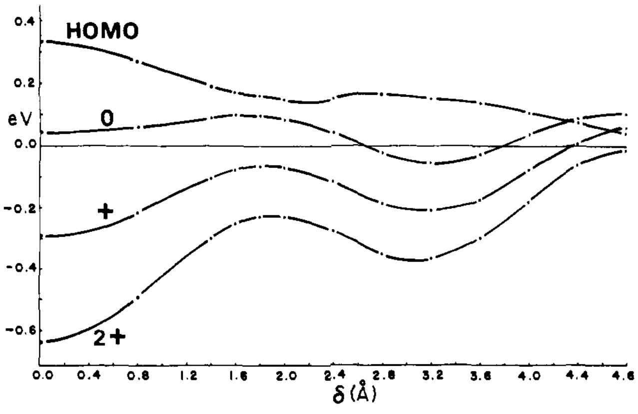

**Figure 9.** Energy vs. slip for (TTF)$_2{}^n$ ($n$ = 0, 1+, 2+) as calculated by the EHMO method with 3d AOs on sulfur. HOMO energy is also shown.

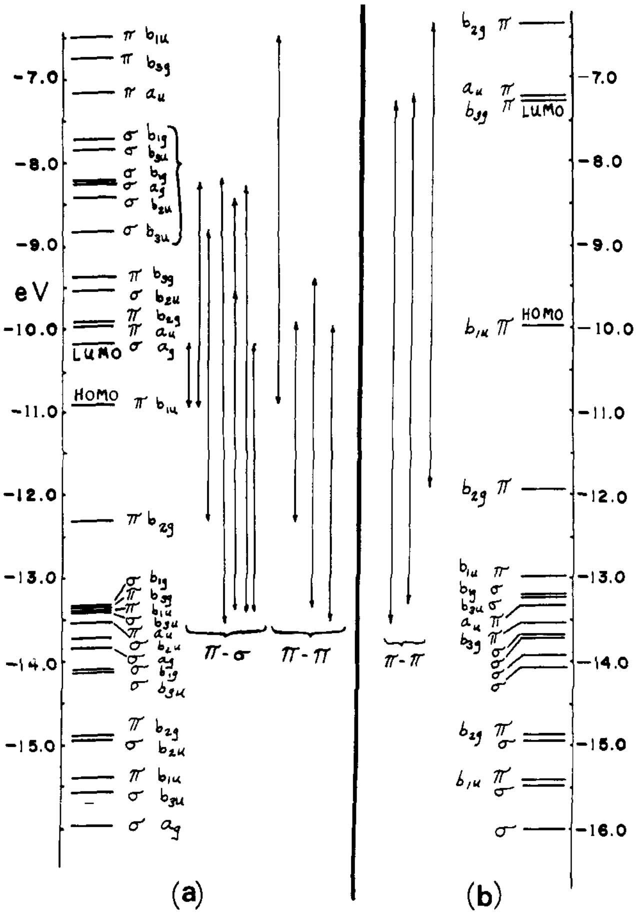

**Figure 10.** Some EHMO energy levels and MO symmetries for TTF (a) with, (b) without 3d AOs on sulfurs. Arrows indicate mixings which are allowed in eclipsed (TTF)$_2$.

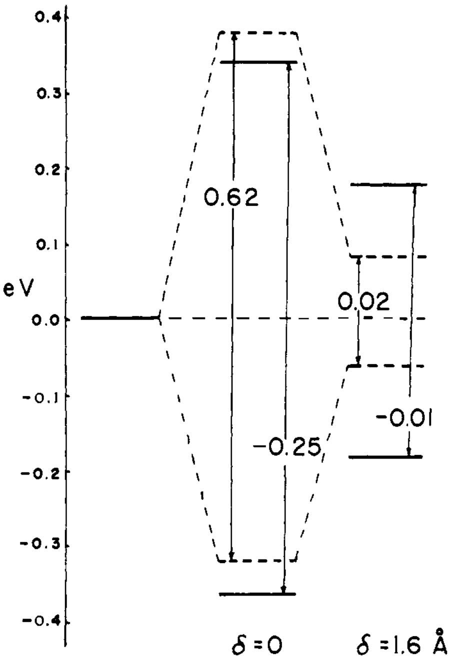

**Figure 11.** Splitting of HOMO of TTF in $(TTF)_2$ at $\delta = 0$, 1.6 Å. Dashed line is result when 3d AOs are absent. Numbers are sums of indicated orbital-pair energies in eV. A positive sum corresponds to a repulsive contribution.

between atoms in different monomers. In eclipsed $(TTF)_2{}^0$, the largest such populations by far occur for eclipsed sulfur pairs. In the absence of 3d AOs, these overlap populations are each −0.01. When 3d AOs are included, they are each +0.06. At $\delta = 3.2$ Å, these populations become −0.008 and + 0.072, respectively.

It is interesting to note that softening the interaction by including d AOs has not led to the replacement of the highest maximum by the deepest minimum for $(TTF)_2{}^0$. The energy at $\delta = 0$ is still positive, indicating that the additional OIP only partly compensates for the first-order repulsive effect.

The softening of the interaction also manifests itself as a reversal in the splitting pattern of some of the orbital pairs. Figure 11 shows how the splitting of the HOMO of TTF occurs in $(TTF)_2$. Without d AOs, the antibonding orbital rise exceeds the bonding orbital lowering—the "expected" first-order effect. With d AOs, both levels are depressed enough to reverse this and give a net attractive contribution. Note that the *size* of the splitting at $\delta = 0$ is about the same for either basis. This implies that d AOs would have little influence on the EHMO conduction bandwidth for an infinite eclipsed TTF stack.

It is awkward that 3d basis functions should have so much influence on the dimer results since it is not always clear whether (or how) to include them in a semiempirical calculation. We shall not consider this problem further here, but emphasize that basis-set choice can have profound effects on dimer configuration calculations, and that the nature of these consequences can be understood in terms of overlap-induced polarizability.

On the basis of these results, we can add to our list of conclusions about EHMO calculations on dimers.

(6) When a few large atoms are present in the monomers, their relative proximities will tend to dominate the shape of the neutral dimer energy (vs. slip) curve.

(7) The presence of d orbitals in the EHMO basis set produces important new OIP possibilities, and may cause an otherwise repulsive orientation to become attractive.

(8) The observation that d AOs in the basis have little effect on some properties does not mean they will have little effect on all properties.

## IX. Applicability of Dimer Calculations to Crystals

Dimers are important constituents of many charge-transfer complexes, and model calculations such as these are of immediate relevance in those cases. But how transferable are our results to infinite uniformly spaced stacks such as those in TTF–TCNQ? They are only *partly* transferable because *the symmetry in a uniform eclipsed stack prevents either end-to-end or $\pi$–$\sigma$ types of polarization from occurring.* Thus, except for the effects of $\pi$–$\sigma$ mixing between monomer MOs of identical symmetry (which we expect usually to be a minor effect), the one-electron MO interaction in the infinite *eclipsed* stack should produce only first-order, hence repulsive, effects.

In a *slipped* stack, symmetry considerations continue to prevent $\pi$–$\pi$ mixing but $\pi$–$\sigma$ mixing becomes allowed. Such mixing is capable of shifting charge equally to the top side of one end of a molecule and the bottom side of the other end. Thus, some ability continues to exist in the crystal for softening through OIP with slip away from a fully eclipsed arrangement. For a molecule like TCNQ, where $\sigma$ MOs are energetically far from the frontier orbitals, such $\sigma$–$\pi$ mixing is not likely to be important. Hence, for such molecules the EHMO energy vs. slip in a stack should continue to be understandable as the result of a (hard) steric interaction with a superimposed HOMO or LUMO energy effect (to the extent that charge transfer occurs). However, for a molecule like TTF, $\pi$–$\sigma$ mixing might be important in a slipped stack.

Hence, in considering TTF stacks, we are still faced with the problem of whether or not to include d AOs in a semiempirical calculation. Symmetry prevents them from playing a role at $\delta = 0$, but not at finite $\delta$, so, if they enter in an appreciable way, they could have profound effects on energy vs. slip. Ab initio calculations (which are protected by a variational lower bound) could shed light on the effects of d AOs, but are presently beyond our means. The fact that pure TTF crystals pack with a slip value of 1.6 Å suggests that our results *without* d AOs are more correct, but the point is by no means proved.

Another view of the effects of polarization argues that structural changes in the crystal which change the symmetry will be favored to the extent that this permits otherwise forbidden OIP. An example is the transition from equal spacing between monomers to a long–short–long spacing (i.e., packed dimers), which would tend to make a conducting stack become semiconducting. Thus, model calculations aimed at understanding phase transitions will require careful consideration of the role of d orbitals and the appropriate degree of softness.

## X. Determining Factors of TTF–TCNQ Structure

A motivation for these studies was the observation[5] that TTF is slipped similarly in pure TTF and in TTF–TCNQ. *If we assume that d AOs are best neglected,* then reference to Figure 7 shows that we are only part way to an understanding of these structures. $(TTF)_2{}^0$ shows a minimum in energy at about the right place, due to steric repulsion between sulfurs, so we appear to have agreement with the structure of pure TTF. But $(TTF)_2{}^+$ appears to be rather indifferent to slip value. Can it be that stacks of TTF in TTF–TCNQ are slipped in response to different factors from those in pure TTF? Investigation of this point shows that it is not only possible, it is likely! This results from the fact that, in a 1:1 crystal, specifying the distance between TCNQ molecules as well as that between TTF molecules and also the slip values in both stacks *overdetermines* the situation. Only three of these quantities are independent. This arises from the fact that the crystallographic distance $b$ (see Figure 1) must be the same in both kinds of stack. Hence, if TCNQ and TTF each have a strong preference for a certain (different) interplanar distance $b'$, and TCNQ has a strong preference for a certain slip distance $\delta$ (which Figure 5 indicates is indeed the case), and if TTF has no strong preference for a particular value of $\delta$ (as Figure 7 would suggest), then $\delta$ in TTF will be determined by the other three quantities. Indeed, if there is a strong preference for all *four* quantities, the observed values will reflect the best *compromise* among *competing* factors. It may be that the combination of three "preferred" and one "passive" dimensions results in a stability which is necessary for a segregated crystal to form in the first place. [In general, we expect the energy dependence on intermolecular distance $b'$ to be stronger than that on $\delta$ (assuming $\delta$ is varied with $b'$ fixed near the position of the van der Waals minimum). This would accord with the observation that less energy is required to cause molecules to move from their preferred relative orientation (solid-phase change or else melting) than is needed to significantly change their relative distances (vaporization, or compression).]

This analysis is reminiscent of Berlinsky's[10] suggestion, quoted earlier, that the TTF orientation results from the TCNQ orientation. Berlinsky's phraseology, however, suggests a direct interstack steric effect of some kind and does not point out the fundamental dependence among these structural parameters in 1:1 crystals in general.

## XI. Conclusions

Semiempirical calculations (EHMO, CNDO) on dimers are useful models for understanding segregated stacking in crystals. While the total energies so produced are not very meaningful (owing to lack of important physical contributions, such as van der Waals attractions, and omission of inner-shell orbital energies), the *energy changes with slip* appear to be at least qualitatively correct. The EHMO method has been shown here to be capable of displaying the effects of steric repulsion between sulfurs in $(TTF)_2^0$, a capability which previous work[5,10] had cast into doubt. [Silverman[22] has recently reexamined the steric repulsion in $(TTF)_2$ via a van der Waals radius model.] However, we have also shown that the computed effects of steric interaction between members of a $(TTF)_2$ dimer are very sensitive to one's choice as to whether to include d AOs in the basis. We suggest that the failure of CNDO calculations[5] to reveal steric repulsion in neutral $(TTF)_2$ and the qualitative differences between CNDO[5] and earlier EHMO[10] calculations on $(TTF)_2$ result from the inclusion of d AOs in the CNDO, but not the EHMO, basis set.

We have considered the ramifications of crystal symmetry on the transferability of dimer models to the crystal, and found that some polarization modes of the dimer become symmetry forbidden in the uniform stack. This suggests that interactions in uniform stacks (especially eclipsed stacks) are harder than in isolated dimers and that crystal phase changes may be at least partially controlled by OIP effects.

Finally, we have pointed out that, in a 1:1 crystal like TTF-TCNQ, only three of the four $b'$ and $\delta$ values are independent, and that the slip value for TTF is very possibly "determined" by the other three quantities.

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(14) Reference 12, p 441.
(15) The statement is rigorously correct if $\chi_a$ and $\chi_b$ are AOs. If they are MOs, the various values of valence state ionization potentials for different AOs in each MO can produce exceptions to the rule.
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(17) Our discussion of orbital energy shifts and polarizations assumes that the orbital under consideration is being perturbed by a higher energy orbital. But perturbations occur from below, too, and so MOs will be found which behave oppositely to our descriptions. However, the *net* effect on total energy depends on the perturbation of filled MOs by empty MOs. Since the empty MOs are always at higher energy (in the ground state), we can ignore the "reversed" cases.
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