# A Cautionary Comment on the Use of Orthogonal Localized Molecular Orbitals for the Quantitative Analysis of Through-space and Through-bond Orbital Interactions

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The quantitative dissection of orbital interactions into through–space (TS) and through–bond (TB) contributions using orthogonal localized MOs (LMOs), as originally proposed by Heilbronner and Schmelzer, is critically discussed, using as a test case, cyclohexa-1,4-diene. It was found that the (HF/STO-3G) TS interaction energies for this molecule, obtained using three different orbital localization procedures (Foster–Boys, the Weinhold natural bond orbitals and the Weinhold natural localized orbitals) are unsatisfactory in the sense that the calculations give a relatively small splitting between the $\pi_+$ and $\pi_-$ orbitals and an inverted sequence of $\pi^*$ orbitals resulting from supposedly pure TS interactions. This result contradicts the Hoffmann conceptual model of orbital interactions. The source of the problem is traced to the presence of the 'orthogonalization' tails associated with the LMOs. An alternative strategy for dissecting orbital interactions, termed the 'cluster' approach is discussed using an ethene dimer model as an example.

The conceptual dissection of orbital interactions into through-space (TS) and through-bond (TB) types by Hoffmann *et al.*[1,2] has been extremely fruitful and has led to refreshing insights into many chemical processes,[3] including recently, the most fundamental of all chemical processes, electron transfer.[4]

It is desirable to have a method for quantitatively dissecting the splitting between canonical Hartree–Fock (HF) molecular orbitals (CMOs) into TB and TS components. In our opinion, such a method should preserve the essential features of the original conceptual framework of TS and TB interactions as laid down by Hoffmann.[1,2] This framework has been described more formally by Heilbronner and Schmelzer,[5] and we shall adopt this description in this paper. Central to the Hoffmann model is the stepwise construction of the fully delocalized CMOs from 'pure' localized basis (molecular) orbitals. Taking the π orbital interactions in planar ($D_{2h}$) cyclohexa-1,4-diene as an example (Figure 1), one begins the analysis with the degenerate pure localized π orbitals, $\pi_1$ and $\pi_2$. These orbitals are 'pure' in the sense that they are strictly two-centre orbitals having no contributions from atomic orbitals other than those centred on the carbon atoms that formally comprise the double bonds. It is important to note that these π orbitals are not orthogonal.

Through–space interactions between $\pi_1$ and $\pi_2$ are then said to result if the Hamiltonian matrix element of the interaction, $H_{12} = \langle\pi_1|H|\pi_2\rangle$, has a significant non-zero value.[5] In this paper we adopt the usually accepted sign convention that in-phase overlap of the basis orbitals, as measured by the overlap integral $S_{12} = <\pi_1|\pi_2\rangle$, is a positive quantity. In this case $H_{12}$ is negative. Within the HF SCF formalism, the magnitude of the TS interaction is obtained by solving the (2 × 2) matrix equation (1), in which $F^\pi$ and $S^\pi$ are the Fock and overlap

$$F^\pi C = S^\pi CE \qquad (1)$$

matrices, respectively, in the basis of $\pi_1$ and $\pi_2$. Solution of equation (1) results in the formation of two symmetry-adapted semi-localized π MOs (SLMOs), $^{SL}\pi_+$ ($b_{1u}$) and $^{SL}\pi_-$ ($b_{3g}$) [equations (2) and (3)] having corresponding energies $E(^{SL}\pi_+)$ and $E(^{SL}\pi_-)$ where $F_{ij} = \langle\pi_i|F|\pi_j\rangle$. For purposes of brevity, we shall henceforth omit the normalization constants from the expressions for $^{SL}\pi_+$ and $^{SL}\pi_-$ and simply describe them as ($\pi_1 + \pi_2$) and ($\pi_1 - \pi_2$), respectively.

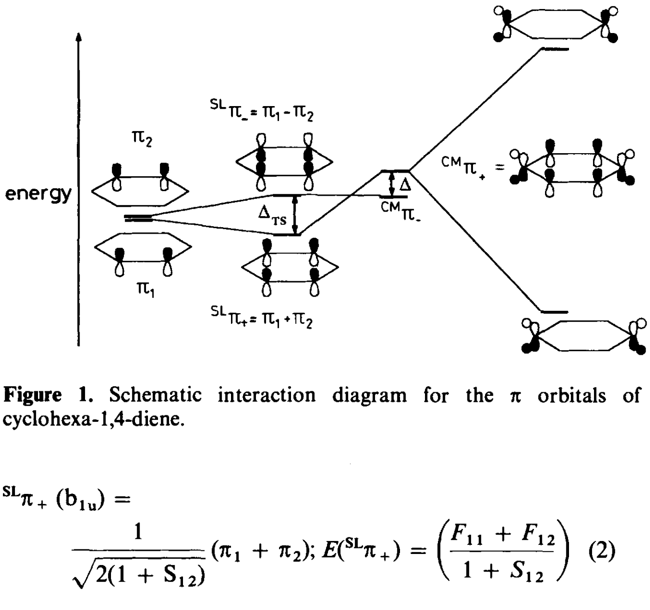


**Figure 1.** Schematic interaction diagram for the π orbitals of cyclohexa-1,4-diene.

$$^{SL}\pi_+\ (b_{1u}) = \frac{1}{\sqrt{2(1 + S_{12})}}(\pi_1 + \pi_2);\ E(^{SL}\pi_+) = \left(\frac{F_{11} + F_{12}}{1 + S_{12}}\right) \qquad (2)$$

$$^{SL}\pi_-\ (b_{3g}) = \frac{1}{\sqrt{2(1 - S_{12})}}(\pi_1 - \pi_2);\ E(^{SL}\pi_-) = \left(\frac{F_{11} - F_{12}}{1 - S_{12}}\right) \qquad (3)$$

From the sign convention used in this paper (*vide supra*), the $^{SL}\pi_+$ level lies energetically below the $^{SL}\pi_-$ level. This sequence of levels, that is, $E(^{SL}\pi_+) < E(^{SL}\pi_-)$, has been termed the natural sequence of orbitals,[5] and always obtains for pure TS interactions.[1,2,5] The magnitude of the TS interaction energy is given by the quantity, $\Delta_{TS} = E(^{SL}\pi_-) - E(^{SL}\pi_+)$, and this is always a positive quantity.[1,2,5]

Through-bond interactions are now admitted into the scheme through mixing of ${}^{SL}\pi_+$ and ${}^{SL}\pi_-$ with other SLMOs of the appropriate symmetry.[1,2,5] For cyclohexa-1,4-diene, there are no SLMOs with the correct symmetry to mix with ${}^{SL}\pi_-$ (providing the basis set contains only s and p functions on C atom, and s functions on H atoms). Consequently, ${}^{SL}\pi_-$ is identical in energy and shape with the final $\pi_-$ CMO, hereafter denoted by ${}^{CM}\pi_-$. In contrast, ${}^{SL}\pi_+$ can mix with the $b_{1u}$ SLMO comprised of the CH $\sigma$ and $\sigma^*$ localized orbitals of the $CH_2$ groups (Figure 1). The overall effect of these mixings is to elevate the ${}^{SL}\pi_+$, so that the final $\pi$ CMO of $b_{1u}$ symmetry (${}^{CM}\pi_+$) lies *above* ${}^{CM}\pi_-$; this gives rise to an inverted sequence of CMO levels,[5] where $E({}^{CM}\pi_-) < E({}^{CM}\pi_+)$.

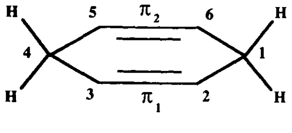
Placing the Hoffmann TS/TB model on a quantitative footing was first carried out by Heilbronner and Schmelzer, using the HF SCF theoretical model.[5,6] The essence of the Heilbronner–Schmelzer (H–S) method is to transform the set of occupied CMOs of the system in question to a set of localized molecular orbitals (LMOs). The latter may be obtained using any one of a variety of localization procedures, such as that of Foster and Boys,[7] Edmiston and Ruedenberg[8] and, the Weinhold group.[9,10] There are two principal advantages in using LMOs $\{\varphi_i\}$ as basis orbitals: Firstly, they are transferable in the sense that their self-energies, $\langle\varphi_i|F|\varphi_i\rangle$, and the matrix elements of their interaction, $\langle\varphi_i|F|\varphi_j\rangle$, are approximately independent of the surrounding molecular environment.[11,12] Secondly, the LMOs generated from any of the above procedures are orthogonal. Not only is the use of orthogonal orbitals free of any technical criticisms that can be justifiably levelled against the use of non-orthogonal LMOs,[13] but orthogonal LMOs naturally lead to a simple Hückel type treatment. A possible objection to the use of LMOs is that their shapes and self-energies are somewhat dependent on the localization criterion used to generate them. Notwithstanding this non-uniqueness problem, LMOs are particularly well-suited to the analysis of orbital interactions.

In the H–S scheme then, the magnitude of TS interactions between two orthogonal LMOs, $\varphi_1$ and $\varphi_2$, is given by $\Delta_{TS} = -2\langle\varphi_1|F|\varphi_2\rangle$ [*cf.* equations (2) and (3) with $S_{12} = 0$]. The differences between the resulting SLMO levels and the final CMO levels give the TB interaction energies. Decomposition of the TB interaction energies into contributions from various SLMOs, comprising the sigma ($\sigma$) bond relays, can be carried out,[5] although this aspect does not concern us here. Subsequent to the pioneering H–S paper on the quantitative assessment of TS and TB interactions,[5] Imamura *et al.* published a similar strategy,[14] which is identical to the H–S scheme for estimating the TS interaction energy, but differs in the way in which the TB interactions are decomposed into individual contributions.

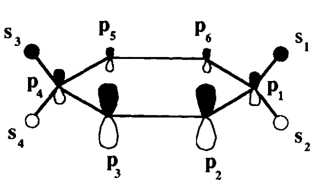
The H–S and Imamura schemes have been applied to a variety of molecules,[5,6,14] and have provided the chemist with some fascinating insights into the interplay between TS and TB effects. The object of this paper is to draw attention to the possible problems that may arise in analysing TS interactions using these schemes, based on the use of orthogonal localized MOs, as they can, and do, give results that contradict the Hoffmann model.

## Results and Discussion

We illustrate our point with the case of $\pi$ and $\pi^*$ orbital interactions in cyclohexa-1,4-diene, (**1**). The geometry of this molecule† was optimized at the HF/3-21G level, within $D_{2h}$ symmetry constraint, using the GAUSSIAN 82 suite of programs.[15] The H–S analysis was carried out on this geometry using the STO-3G[16a] and 3-21G[16b] basis sets. However, because both basis sets gave similar results, only the STO-3G data will be reported here. Three different orbital localization schemes were used, namely the Foster–Boys,[7] the Weinhold natural bond orbital,[9] and the Weinhold natural localized MO schemes.[10] The Foster–Boys LMOs (FBLMOs) were obtained using the GAUSSIAN 86 program,[17] and the Weinhold LMOs (WNBOs and WNLMOs) were obtained using the program of Reed and Weinhold as implemented for GAUSSIAN 82.[18] All three localization methods were used to generate both occupied, $\{\sigma,\pi\}$, and virtual, $\{\sigma^*,\pi^*\}$, sets of LMOs. Such procedures therefore have the potential for analysing interactions between $\pi^*$ orbitals, and thus could be of use for interpreting experimental data obtained from electron transmission spectroscopic studies.[19,]‡



(**1a**)



(**1b**)

The Fock matrix elements between the various LMOs are given in Table 1. For brevity, the matrix elements involving the $\pi$ and $\pi^*$ and LMOs are defined by:

$$F_{ij} = \langle\pi_i|F|\pi_j\rangle$$

$$F_{ij}^* = \langle\pi_i^*|F|\pi_j^*\rangle$$

Through-space interaction energies between the $\pi$ LMOs ($\Delta_{TS}$), and between the $\pi^*$ LMOs ($\Delta_{TS}^*$) are given in Table 1. These are calculated from the expressions $\Delta_{TS} = -2F_{12}$ and $\Delta_{TS}^* = -2F_{12}^*$. The energies of the $\pi$ and $\pi^*$ CMOs of cyclohexa-1,4-diene are also given in Table 1. We note that the FBLMO and WNLMO analysis of the $\pi$ manifold give practically identical results. This is in keeping with Reed and Weinhold's conclusions that their occupied NLMOs are very similar to the occupied LMOs determined by the Foster–Boys and Edmiston–Ruedenberg methods.[10] We also find that with the STO-3G basis set, the virtual WNLMOs and FBLMOs are nearly identical. This fact has apparently not been previously noted. The TS and TB interaction energies between the $\pi$

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† HF/3-21G optimized geometrical parameters [see structure (**1a**) for atom labelling]: $r_{C=C}$ 1.316 Å; $r_{C-C}$ 1.511 Å; $r_{C(1)-H}$ 1.088 Å; $r_{C(2)-H}$ 1.075 Å; C(1)–C(2)–C(3) 123.8°; C(2)–C(1)–C(6) 112.4°; H–C(1)–C(2) 109.5°; H–C(1)–H 106.4°; H–C(2)–C(3) 119.9; H–C(2)–C(1) 116.3°.

‡ We point out that the calculation of $\pi^*$ levels (and all positive energy virtual orbital levels for that matter) is not as straightforward as calculating $\pi$ (filled) levels. This is because the $\pi^*$ levels are in the continuum and hence do not converge to unique values as the basis set is enlarged. Nevertheless, there is a wide body of data showing that small basis sets, such as STO-3G, are useful for studying intramolecular interactions involving unfilled orbitals and for studying trends in unfilled orbitals along a series of related compounds.

**Table 1.** HF/STO-3G Fock matrix elements ($F_{ij}$, $F^*_{ij}$) for various LMOs of (**1**), $\Delta_{TS}$ and $\Delta^*_{TS}$ values for (**1**), π and π* CMO energies for (**1**), and $\Delta_{TS}$ and $\Delta^*_{TS}$ values for (**2**), (energies in eV).

| | FBLMO[a] | WNLMO[b] | WNBO[c] | CMO[d] |
|---|---|---|---|---|
| $F_{11}$ | −8.98 | −8.94 | −8.68 | |
| $F_{12}$ | −0.31 | −0.27 | −0.01 | |
| $F^*_{11}$ | 9.69 | 9.63 | 9.20 | |
| $F^*_{12}$ | 0.68 | 0.64 | 0.19 | |
| $\Delta_{TS}(1)$[e] | 0.62 | 0.54 | 0.02 | |
| $\Delta^*_{TS}(1)$[e] | −1.36 | −1.24 | −0.38 | |
| $E(^{CM}\pi_-)$[e] | | | | −8.67 |
| $E(^{CM}\pi_+)$[e] | | | | −7.65 |
| $E(^{CM}\pi^*_+)$[e] | | | | 8.93 |
| $E(^{CM}\pi^*_-)$[e] | | | | 9.01 |
| $\Delta_{TS}(2)$[f] | | | | 0.93 |
| $\Delta^*_{TS}(2)$[f] | | | | 0.76 |

[a] Using Foster–Boys LMOs. [b] Using Weinhold NLMOs. [c] Using Weinhold NBOs. [d] Canonical molecular orbital energies. [e] Values for (**1**). [f] Values for (**2**).

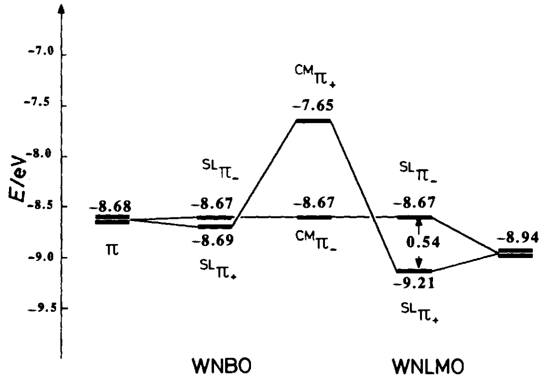


**Figure 2.** HF/STO-3G interaction diagram for the π orbitals in cyclohexa-1,4-diene based on orthogonal LMOs: (*a*) WNLMOs; (*b*) WNBOs.

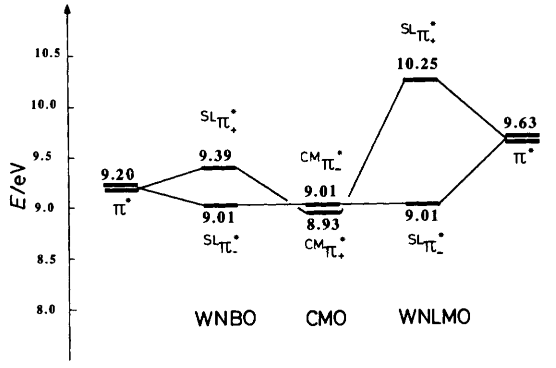
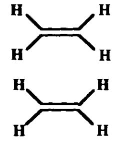
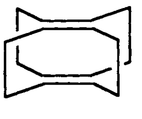


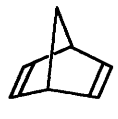
**Figure 3.** HF/STO-3G interaction diagram for the π* orbitals in cyclohexa-1,4-diene based on orthogonal LMOs: (*a*) WNLMOs; (*b*) WNBOs.



(**2**)



(**3**)



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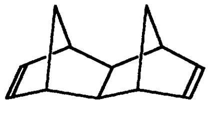

(**5**)

orbitals and between the π* orbitals are illustrated in Figures 2 and 3, respectively. Because of the similarity between the FBLMO and the WNLMO results, only the latter have been included in these figures.

$\Delta_{TS}$ is positive for both the WNBOs (0.02 eV) and WNLMOs (0.54 eV) in accordance with the Hoffmann model, indicating that the natural sequence of orbitals obtains. Also, the $^{SL}\pi_-$ orbital in all three localization schemes is identical to the final $^{CM}\pi_-$ CMO (in both energy and shape), as expected in the absence of any σ and σ* SLMOs having $b_{3g}$ symmetry. However, the small magnitude of $\Delta_{TS}$, particularly the near zero value obtained using WNBOs, is unexpected, since calculations using the ethene dimer (**2**) ('cluster' approach, *vide infra*) give a much larger $\Delta_{TS}$ value of 0.93 eV, almost twice that calculated for cyclohexa-1,4-diene, using WNLMOs.

The results of the LMO analysis of TS interactions for the π* space of cyclohexa-1,4-diene are even more surprising than those for the π manifold in that all three localization procedures lead to an inverted sequence of π* SLMOs ($^{SL}\pi^*$) *i.e.* they result in the $^{SL}\pi^*_-(a_u)$ level lying below the $^{SL}\pi^*_+(b_{2g})$ level. This result runs counter to the Hoffmann conceptual model.

The small TS splittings predicted between the π levels and the inverted order of the π* SLMOs are due to the use of orthogonal LMOs. Such LMOs are not purely localized two-centre orbitals, but have orthogonalization 'tails'. In other words, the LMOs, in order to maintain orthogonality, are 'delocalized' onto neighbouring atoms. This is clearly revealed in Figure 4 where the $\pi_1$ and $\pi^*_1$ LMOs of cyclohexa-1,4-diene are expressed in terms of the basis atomic orbitals. As can be seen from the coefficients, both $\pi_1$ and $\pi^*_1$ have sizeable tails on C1 and C4 as well as on the H atoms attached to these atoms. The π and π* LMOs may be expressed by the general forms given in equations (4)–(7) where p and s refer,

$$\begin{aligned}\pi_1 &= a_1[p_2 + p_3] + a_2[p_5 + p_6] + a_3[p_1 + p_4] + \\ &\quad a_4[s_1 - s_2 + s_3 - s_4] \\ &= a_1A_1 + a_2A_2 + a_3A_3 + a_4A_4 \qquad (4)\end{aligned}$$

$$\begin{aligned}\pi_2 &= a_1[p_5 + p_6] + a_2[p_2 + p_3] + a_3[p_1 + p_4] + \\ &\quad a_4[s_1 - s_2 + s_3 - s_4] \\ &= a_1A_2 + a_2A_1 + a_3A_3 + a_4A_4 \qquad (5)\end{aligned}$$

$$\begin{aligned}\pi^*_1 &= a^*_1[p_2 - p_3] + a^*_2[p_6 - p_5] + a^*_3[p_1 - p_4] + \\ &\quad a^*_4[s_1 - s_2 - s_3 + s_4] \\ &= a^*_1A^*_1 + a^*_2A^*_2 + a^*_3A^*_3 + a^*_4A^*_4 \qquad (6)\end{aligned}$$

$$\begin{aligned}\pi^*_2 &= a^*_1[p_6 - p_5] + a^*_2[p_2 - p_3] + a^*_3[p_1 - p_4] + \\ &\quad a^*_4[s_1 - s_2 - s_3 + s_4] \\ &= a^*_1A^*_2 + a^*_2A^*_1 + a^*_3A^*_3 + a^*_4A^*_4 \qquad (7)\end{aligned}$$

respectively, to the carbon 2p and hydrogen 1s basis atomic orbitals, and the numbering scheme and phase relationships between the basis orbitals are shown by (**1b**). The coefficients, for $\pi_1(a_i)$ and $\pi^*_1(a^*_i)$ are displayed in Figures 4(*a*) and 4(*b*), respectively; those for $\pi_2$ and $\pi^*_2$ are related to $\pi_1$ and

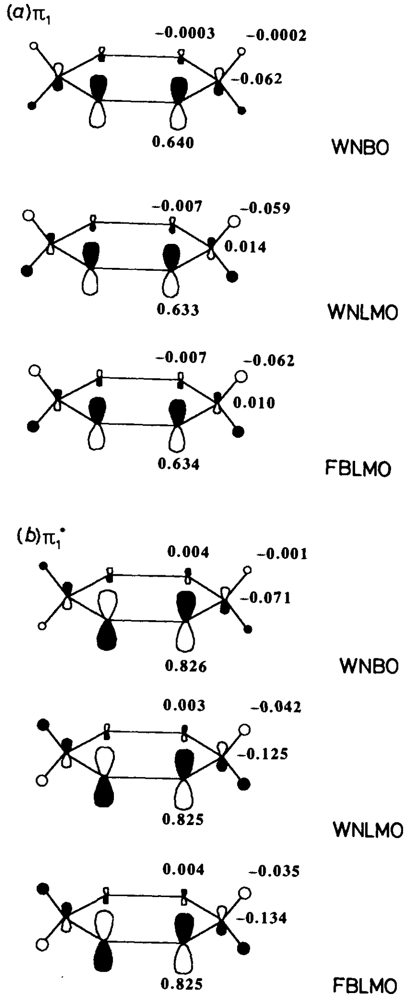

**Figure 4.** Representation of the (*a*) $\pi_1$ and (*b*) $\pi_1^*$ LMOs in terms of the valence-shell AO basis orbitals. Top: using WNBOs; middle: using WNBOs; bottom: using FBLMOs.

$\pi_1^*$ by symmetry. The TS interaction energies, $\Delta_{TS}$ and $\Delta_{TS}^*$, can then be expressed in terms of the coefficients $a_i$ and $a_i^*$, and the Fock matrix elements by $F_{ij}^A = \langle A_i | F | A_j \rangle$ and $F_{ij}^{*A} = \langle A_i^* | F | A_j^* \rangle$. By making use of molecular symmetry, the number of terms are reduced, and $\Delta_{TS}$ and $\Delta_{TS}^*$ may then be expressed as:

$$\begin{aligned} -\Delta_{TS} &= 2F_{12} = 2\langle \pi_1 | F | \pi_2 \rangle \\ &= 2F_{12}^A[a_1{}^2 + a_2{}^2] + 4F_{11}^A a_1 a_2 + 4F_{13}^A[a_1 a_3 + a_2 a_3] \\ &+ 4F_{14}^A[a_1 a_4 + a_2 a_4] + 4F_{34}^A a_3 a_4 + 2F_{33}^A a_3{}^2 + 2F_{44}^A a_4{}^2 \end{aligned} \tag{8}$$

$$\begin{aligned} -\Delta_{TS}^* &= 2F_{12}^{*A}[a_1^{*2} + a_2^{*2}] + 4F_{11}^{*A} a_1^* a_2^* + 4F_{13}^{*A}[a_1^* a_3^* + a_2^* a_3^*] \\ &+ 4F_{14}^{*A}[a_1^* a_4^* + a_2^* a_4^*] + 4F_{34}^{*A} a_3^* a_4^* + 2F_{33}^{*A} a_3^{*2} + 2F_{44}^{*A} a_4^{*2} \end{aligned} \tag{9}$$

For brevity we denote the various terms of expressions (8) and (9) by $T_{ij}$ and $T_{ij}^*$ where, for example, $T_{34} = 4F_{34}^A a_3 a_4$. Thus:

$$-\Delta_{TS} = T_{12} + T_{11} + T_{13} + T_{14} + T_{34} + T_{33} + T_{44} \tag{8a}$$

$$-\Delta_{TS}^* = T_{12}^* + T_{11}^* + T_{13}^* + T_{14}^* + T_{34}^* + T_{33}^* + T_{44}^* \tag{9a}$$

The negative of the first term on the right-hand side of each of equations (8) and (9) corresponds to the contribution one would conceptually associate with 'pure' TS interactions since both $A_1(A_2)$ and $A_1^*(A_2^*)$ are, respectively, pure localized 'tail-less' (but non-orthogonal) $\pi$ and $\pi^*$ orbitals. The estimates of the TS splittings (1.3–1.6 eV) thus obtained are significantly larger than those obtained from the dimer model discussed below. Additional studies are required in order to establish the general utility of associating $T_{12}$ and $T_{12}^*$ with the TS splittings. The remaining terms of equations (8) and (9) represent contributions from the orthogonalization tails. Values for the various terms using WNBOs and WNLMOs are given in Table 2. Because WNLMOs and FBLMOs gave nearly identical results, only those obtained using WNLMOs have been tabulated. Clearly, the orthoganolization tails make significant contributions to both $\Delta_{TS}$ and $\Delta_{TS}^*$ and in the case of the latter, the combined contribution of the orthogonalization tails is even larger than the 'pure' TS ($T_{12}^*$) contribution.

The almost zero value for $\Delta_{TS}$ using WNBOs is due to the near cancellation of the TS term $T_{12}$ by the 'tail' term $T_{13}$, the former tending to generate the natural sequence of ${}^{SL}\pi$ orbitals and the latter tending to generate an inverted sequence. The $T_{13}$ term represents an *antibonding* interaction between $[p_1 + p_4]$ and $[p_2 + p_3]$, and between $[p_1 + p_4]$ and $[p_5 + p_6]$, and this is clearly shown in the resulting ${}^{SL}\pi_+$ SLMO [Figure 5(*a*)]. Note that the ${}^{SL}\pi_-$ SLMO is unaffected by the $CH_2$ groups (because of symmetry). The presence of (antibonding) contributions from the $CH_2$ groups in the ${}^{SL}\pi_+$ SLMO may be interpreted as a TB effect, the full measure of which leads to the (final) CMO, ${}^{CM}\pi_+$.

Although a sizeable (0.54 eV) $\Delta_{TS}$ interaction energy is calculated using WNLMOs (and FBLMOs), the 'tail' terms are far from insignificant. Interestingly, $T_{13}$ becomes negative for these LMOs because the C1 and C4 p orbitals of the $\pi_1(\pi_2)$ WNLMO and FBLMO have the same phase as the C2 and C3 (C5 and C6) p orbitals [Figure 4(*a*)]. Countering this is a strong out-of-phase (antibonding) relationship between the orbitals of the H atoms of the $CH_2$ groups and the double bond p orbitals [Figure 4(*a*)] which leads to a large positive value for $T_{14}$. The $\pi_1$ and $\pi_2$ WNLMOs and FBLMOs, unlike the WNBOs, have sizeable tails at the other double bond carbon atoms, leading to a significant positive value for $T_{11}$.

The inverted sequences of the $\pi^*$ SLMOs are due primarily to the very large positive 'tail' term, $T_{13}^*$, (see Table 2) caused by the large coefficients of $p_1$ and $p_4$ in the $\pi_1^*$ and $\pi_2^*$ LMOs [Figure 4(*b*)]. Consequently, the ${}^{SL}\pi_+^*$ SLMO contains quite large antibonding contributions from the $CH_2$ orbitals as shown, for example, in Figure 5(*b*) where WNLMOs were used in constructing the SLMO. Thus, our results indicate that the so-called TS interaction energy $\Delta_{TS}^*$, determined from the LMOs, is actually dominated by TB effects and leads to an inverted sequence of $\pi^*$ SLMOs.

In summary, the orthogonalization tails in the LMOs automatically introduces orbitals, other than those associated with the double bonds, into the TS analysis. As a direct consequence, a certain amount of TB interaction is introduced at the 'TS' stage, and in the case of cyclohexa-1,4-diene, this leads to unsatisfactory values for $\Delta_{TS}$ and $\Delta_{TS}^*$, particularly with respect to the latter where even the sign of the interaction is opposite to that demanded by the Hoffmann conceptual model for TS interactions. This problem cannot be completely avoided if one adheres to using orthogonal LMOs.

An alternative method for estimating TS interaction energies that largely overcomes the orthogonalization tail problem is to use what can be termed the 'cluster' approach. This method has been used to investigate $\pi$ and $\pi^*$ interactions in the diene (3) and related polyenes.[20] In applying this approach to cyclohexa-1,4-diene, the LMOs are represented by the pure localized $\pi(\pi^*)$ CMOs of ethene. An ethene dimer (2) is then constructed in which the geometrical relationship between the double bonds is identical with that obtained in cyclohexa-1,4-diene. The $\pi(\pi^*)$

**Table 2.** Breakdown of the $\Delta_{TS}$ and $\Delta^*_{TS}$ interaction energies for cyclohexa-1,4-diene ($10^{-3}$ eV) according to equations (8*a*) and (9*a*).

| | WNBO | WNLMO | | WNBO | WNLMO |
|---|---|---|---|---|---|
| $T_{12}$ | −1 566.1 | −1 532.7 | $T^*_{12}$ | −1 284.4 | −1 282.1 |
| $T_{11}$ | 18.2 | 420.9 | $T^*_{11}$ | 172.6 | 141.5 |
| $T_{13}$ | 1 648.0 | −362.5 | $T^*_{13}$ | 1 646.6 | 2 903.1 |
| $T_{14}$ | 2.5 | 968.8 | $T^*_{14}$ | 22.6 | 863.6 |
| $T_{34}$ | −1.5 | 127.5 | $T^*_{34}$ | −11.5 | −807.0 |
| $T_{33}$ | −127.4 | −6.5 | $T^*_{33}$ | −159.9 | −497.1 |
| $T_{44}$ | 0.0 | −158.4 | $T^*_{44}$ | 0.0 | −78.7 |
| $\Delta_{TS} = -\Sigma T$ | 26.3 | 542.9 | $\Delta^*_{TS} = -\Sigma T^*$ | −386.0 | −1 243.3 |

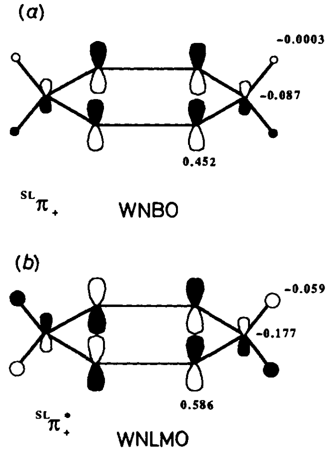

**Figure 5.** Representation of various π MOs in terms of the AO basis orbitals: (*a*) $^{SL}\pi_+$ SLMO using WNBOs; (*b*) $^{SL}\pi^*_+$ SLMO using WNLMOs.

splitting energies in this dimeric ethene 'complex' are then taken to be the $\Delta_{TS}(\Delta^*_{TS})$ interaction energies in the actual molecule and these are given in Table 1. Thus $\Delta_{TS}$ and $\Delta^*_{TS}$ for cyclohexa-1,4-diene are calculated by this method to be 0.93 and 0.76 eV, respectively (Table 1). Net TB splitting energies are then calculated as the difference between $\Delta_{TS}(\Delta^*_{TS})$ and the overall split between the $\pi(\pi^*)$ CMOs. These are 1.95 and 0.68 eV for the π and π* manifolds, respectively. However, the 'cluster' approach, unlike the H–S scheme, suffers from the drawback that the net TB interaction energies can not be uniquely partitioned into contributions from the various SLMOs because the energies of the SLMOs calculated from the model 'cluster', need not be equal to the energies of the respective SLMOs in the actual molecule. This is, indeed, the case for cyclohexa-1,4-diene in which the $^{CM}\pi_-$ and $^{CM}\pi^*_-$ levels of this molecule lie 0.19 and 0.34 eV, respectively, below the $^{SL}\pi_-$ and $^{SL}\pi^*_-$ levels of the dimer (**2**). For cyclohexa-1,4-diene, symmetry requires that the $^{CM}\pi_-$ and $^{SL}\pi_-$ levels should be the same, as should the $^{CM}\pi^*_-$ and $^{SL}\pi^*_-$ levels.

## Conclusions

The use of orthogonal LMOs for such an analysis (*e.g.*, FBLMOs, WNBOs, and WNLMOs), as pioneered by Heilbronner and Schmelzer,[5] and subsequently by Imamura *et al.*,[14] has the particular advantage of simplicity (use of orthogonal LMOs leads to a simple Hückel-type treatment) and transferability (Fock matrix elements in the basis of the LMOs are transferable from one molecule to another). This approach also has the important advantage of allowing one to dissect quantitatively TB interactions into contributions from various σ (and σ*) relays. This facility is not available using the 'cluster' approach. Unfortunately, the necessary presence of orthogonalization tails in the LMOs can lead to substantial incorporation of TB effects into the so-called pure TS interaction energies. The TB effects incorporated in the tails can, in some cases, outweigh the TS interaction energies, thereby resulting in inverted sequences of SLMOs, contrary to the Hoffmann model. This was found to be the case for so-called TS interactions between the π* LMOs in cyclohexa-1,4-diene.

Two different ways of avoiding the above problem were suggested. The first is to utilize only the $T_{12}(T^*_{12})$ terms in the definition of $\Delta_{TS}(\Delta^*_{TS})$ as the measure of the TS interaction. The second is the 'cluster' approach. The 'cluster' approach appears to be quite satisfactory if the only information required is the *net* TS and TB interaction energies, for the latter is simply obtained by subtraction of the former from the final CMO level splitting energy.

With regard to the orthogonal LMO approach of Heilbronner and Schmelzer, we note that the problems of incorporating TB effects *via* the orthogonalization tails are less severe in the dienes (**3**) and (**4**) than in cyclohexa-1,4-diene.[20,21] Even for dienes, such as (**5**), in which TS interaction energies are very small, the possibility of obtaining an inverted sequence of SLMOs using orthogonal LMOs does not present a serious conundrum. In such cases, one can reasonably assume that the TS interaction energy is negligible, and then use the orthogonal LMO scheme to analyse the TB interactions. Thus the orthogonal LMO approach remains a useful procedure for estimating TB and TS contributions between remote functional groups in many classes of molecules although we do advise prudence in its use. The orthogonalization tail problem in the H–S scheme can be ameliorated by choosing a localization procedure that produces the most localized LMOs. Recently, Pipek and Mezey have described a localization procedure which seems to generate LMOs that are more localized than those produced by the Foster–Boys procedure.[22,‡] The suitability of using the Pipek–Mezey LMOs in the H–S scheme will be investigated in the near future.

Finally it should be noted that the present investigation of orbital interactions in cyclohexa-1,4-diene should be viewed purely as a model study to illustrate some possible difficulties that may be encountered using LMOs to analyse TS interactions. Conclusions about the final sequence of the π* CMOs in particular should not be made since the results of Table 1 refer to a minimal basis set. In fact, calculations with more flexible basis sets (*e.g.*, 3-21G) place the $\pi^*_-$ CMO below the $\pi^*_+$ CMO level, a result which is supported by recent experimental work.[23]

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