L. C. B. O.: An Easy Method to Predict Valence Ionization Energies. Application to Substituted Benzenes

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The linear combination bond orbitals (L.C.B. O.) MO treatment has been used to reproduce the π ionization energies of several ortho-, meta- and para-disubstituted benzenes. The Coulomb integral of the substituent π orbitals and their resonance integrals with the ring π orbitals have been obtained from the spectra of the corresponding monosubstituted benzenes, using the same procedure for all the compounds under examination. The ring Coulomb integrals have been chosen taking, as an internal standard, the experimental ionization energy value of the π (nπ) orbital, non interacting by symmetry in the monosubstituted and in the para-disubstituted compounds.

An application of this simple method to conformational analysis and to electron affinities is also shown.

Introduction

Photoelectron spectroscopy [1] provides the ionization energy values (IEs) related to atomic and molecular orbitals (AOs and MOs), measuring the kinetic energy of photoejected electrons: \( IE_i = \hbar v - KE_i \).

In the approximation of the validity of Koopmans' theorem [2], IEs are equal to the negative orbital energies, \( IE_i = -E_i \).

The development of this technique supplied a wealth of data on the electronic structure of molecular systems and also contributed to improve calculation methods providing empirical parameters and a test for their results. In turn, calculations provide a basis for the assignment of the bands of the photoelectron spectra to the corresponding MOs. Except for small molecules, even sophisticated calculation techniques often give energy values different from those experimentally determined. However, approximate MO methods of Hückel type can in many cases be employed successfully to predict valence ionization energies. Among these, the simplest is the L.C.B. O. method [3—6] (linear combination bond orbitals), which starts not from atomic orbitals but from the occupied group orbitals of the building blocks of a molecule, thus reducing the number of terms of the secular determinant. The agreement of the calculated energy levels with those experimentally determined is often as good as 0.1 eV. The MOs localization properties, with respect to the interacting group orbitals, are easily obtained as well, and the calculations can be performed with the only aid of a pocket calculator. For its simplicity, the L.C.B. O. method can easily be applied by experimentalists and can be useful in teaching the fundamentals of MO theory. In fact, it supplies a clear picture of the molecular orbital building-up.

The Hückel MO theory neglects the overlap integrals, so that \( S_{ij} = \int q_i q_j \, dv = 0 \) unless \( i = j \), and assumes that the integral \( H_{ij} = \int q_i H q_j \, dv \) is non zero only for adjacent atoms. The secular determinant for a linear system of interacting atomic orbitals, where the atomic orbitals are normalized and \( S_{ij} = 1 \), becomes

\[
\begin{bmatrix}
H_{11} - E & H_{12} - ES_{12} & H_{13} - ES_{13} & \cdots \\
H_{21} - ES_{21} & H_{22} - E & H_{23} - ES_{23} & \cdots \\
\vdots & \vdots & \vdots & \ddots \\
H_{n1} - E & H_{n2} - ES_{n2} & H_{n3} - ES_{n3} & \cdots \\
\end{bmatrix} = 0
\]

The Hückel MO theory neglects the overlap integrals, so that \( S_{ij} = \int q_i q_j \, dv = 0 \) unless \( i = j \), and assumes that the integral \( H_{ij} = \int q_i H q_j \, dv \) is non zero only for adjacent atoms. The secular determinant for a linear system of interacting atomic orbitals, where the atomic orbitals are normalized and \( S_{ij} = 1 \), becomes

\[
\begin{bmatrix}
H_{11} - E & H_{12} & 0 & \cdots \\
H_{21} & H_{22} - E & H_{23} & \cdots \\
\vdots & \vdots & \vdots & \ddots \\
H_{n1} & H_{n2} & H_{n3} & \cdots \\
\end{bmatrix} = 0
\]

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where the $H$ integrals are called Coulomb integrals when $i=j$ and resonance integrals when $i\neq j$. In the LCAO approximation, the MOs of a polyene with $N$ double bonds can be written as

$$\psi \equiv \sum_{\mu=1}^{2N} c_\mu \varphi_\mu$$

or, which is equivalent,

$$\psi \equiv \sum_{\mu=1}^{N} (c_\mu \pi_\mu + c_\mu^* \pi_\mu^*)$$

where $\pi_\mu$ and $\pi_\mu^*$ are the bonding and antibonding two centre orbitals of the double bond $\pi_\mu$. The neglection of the interaction with the empty $\pi_\mu^*$ orbitals ($c_\mu^* = 0$) leads to the L.C.B.O. model. The matrix elements are not mathematically evaluated but are empirical parameters which can compensate for the neglected integrals and the lack of empty orbitals. In particular, the numerical values, in units of energy, of the self energies ($A$) and of the interaction parameters ($B$) can be derived from the IEs of reference systems. Such a choice of the parameters takes therefore into partial account the non validity of Koopmans' theorem due to relaxation of the MOs under ionization and the correlation effects due to the mutually dependent electron motions.

**Application of the L.C.B.O. Method to Substituted Benzenes**

Let us consider first the $\pi$ MOs of a benzene ring monosubstituted by a group (X) bringing an orbital of $\pi$ symmetry ($\pi_x$): they derive from the interaction between the $\pi_\sigma$ and $\pi_0$ orbitals of the benzene fragment with the $\pi_x$ orbital (see Figure 1). The $\pi_A$ orbital does not mix with $\pi_x$, having a node on the carbon atom where X is attached. For the three interacting $\pi$ group orbitals, belonging to the $b_1$ symmetry species in the $C_{2v}$ point group,

the secular determinant is:

$$\begin{vmatrix} A_{\pi_\sigma} - E & B_{\pi_\sigma/\pi_x} & 0 \\ B_{\pi_\sigma/\pi_x} & A_{\pi_x} - E & B_{\pi_0/\pi_x} \\ 0 & B_{\pi_0/\pi_x} & A_{\pi_0} - E \end{vmatrix} = 0.$$
provides an internal standard for the self energies \( A_{n_e} \) and \( A_{n_0} \). This is done assuming that the three ring \( \pi \) orbitals are equally affected by the inductive effect of the substituent. \( A_{n_e} \) and \( B_{n_i/n_e} \) are still unknown but can be easily calculated from the secular determinant if two of the three energy levels, resulting from the interaction among \( \pi_\theta, \pi_x \) and \( \pi_0 \) are experimentally available.

For \( X=\text{NH}_2 \) [7], \( \text{N(CH}_3)_2 \) [7], \( \text{OCH}_3 \) [8], \( \text{SCH}_3 \) [8] and \( \text{C}=\text{CH} \) [9], the following values for the Coulomb and resonance integrals are obtained:

<table>
<thead>
<tr>
<th>( X )</th>
<th>( A_{n_x} )</th>
<th>( B_{n_i/n_x} )</th>
<th>( A_{n_0} )</th>
<th>( B_{n_i/n_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_2 )</td>
<td>(-10.29)</td>
<td>(-1.45)</td>
<td>(-12.8)</td>
<td>(-0.96/2/3)</td>
</tr>
<tr>
<td>( \text{N(CH}_3)_2 )</td>
<td>(-8.53)</td>
<td>(-1.19)</td>
<td>(-10.81)</td>
<td>(-1.33)</td>
</tr>
<tr>
<td>( \text{OCH}_3 )</td>
<td>(-10.81)</td>
<td>(-1.33)</td>
<td>(-9.12)</td>
<td>(-1.05)</td>
</tr>
<tr>
<td>( \text{SCH}_3 )</td>
<td>(-10.68)</td>
<td>(-1.065)</td>
<td>(-10.68)</td>
<td>(-1.065)</td>
</tr>
</tbody>
</table>

For benzonitrile \( (X=\text{CN}) \), \( A_{n_x} = -12.8 \) eV [10] and \( B_{n_i/n_x} = -0.96/2/3 \) eV [11] have been reported.

In the following, these parameters are used to predict the \( \pi \) energy values of disubstituted benzenes. The photoelectron spectra of p-benzonitriles \( \text{C}_6\text{H}_4—X \) \( (X=\text{OCH}_3, \text{NH}_2 \text{ and N(CH}_3)_2 \) [12]) are reported in Figure 2. The IE of the second band provides the energy value for the self energies \( A_{n_x} \) and \( A_{n_0} \), as described above.

The \( A_{n_x} \) values calculated for \( \text{C}_6\text{H}_5—X \) are shifted by 0.3 eV because of the strong electron withdrawing effect of the CN group (about 0.9 eV on the ring \( \pi_\text{A} \) orbital in \( \text{C}_6\text{H}_5\text{—CN} \) [10]). The following basis sets (values in eV) are obtained (\( Y=\text{CN} \)):

<table>
<thead>
<tr>
<th>( X )</th>
<th>( A_{n_x} )</th>
<th>( A_{n_0} )</th>
<th>( A_{n_x} )</th>
<th>( A_{n_0} )</th>
<th>( B_{n_i/n_x} )</th>
<th>( B_{n_i/n_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OCH}_3 )</td>
<td>(-9.97)</td>
<td>(-12.85)</td>
<td>(-11.1)</td>
<td>(-12.8)</td>
<td>(-1.33)</td>
<td>(-0.96/2/3)</td>
</tr>
<tr>
<td>( \text{NH}_2 )</td>
<td>(-9.85)</td>
<td>(-12.75)</td>
<td>(-10.6)</td>
<td>(-12.8)</td>
<td>(-1.45)</td>
<td>(-0.96/2/3)</td>
</tr>
<tr>
<td>( \text{N(CH}_3)_2 )</td>
<td>(-9.60)</td>
<td>(-12.50)</td>
<td>(-8.85)</td>
<td>(-12.8)</td>
<td>(-1.19)</td>
<td>(-0.96/2/3)</td>
</tr>
</tbody>
</table>

An analogous calculation can be performed on the series p-\( \text{X—C}_6\text{H}_4—\text{OCH}_3 \) \( (X=\text{NH}_2, \text{N(CH}_3)_2, \text{SCH}_3 \text{ and OCH}_3 \). The photoelectron spectra of these compounds [13] provide \( IE_{n_x} \), from which \( A_{n_x} \) and \( A_{n_0} \) are evaluated. With the \( A_{n_x}, A_{n_0}, B_{n_i/n_x} \) and \( B_{n_i/n_0} \) values previously calculated from the spectra of the corresponding monosubstituted benzenes \( \text{C}_6\text{H}_5—X \), the following basis sets (values in eV) are obtained (\( Y=\text{OCH}_3 \)):

<table>
<thead>
<tr>
<th>( X )</th>
<th>( A_{n_x} )</th>
<th>( A_{n_0} )</th>
<th>( A_{n_x} )</th>
<th>( A_{n_0} )</th>
<th>( B_{n_i/n_x} )</th>
<th>( B_{n_i/n_0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_2 )</td>
<td>(-9.15)</td>
<td>(-12.05)</td>
<td>(-10.29)</td>
<td>(-10.81)</td>
<td>(-1.45)</td>
<td>(-1.33)</td>
</tr>
<tr>
<td>( \text{N(CH}_3)_2 )</td>
<td>(-9.03)</td>
<td>(-11.95)</td>
<td>(-8.53)</td>
<td>(-10.81)</td>
<td>(-1.19)</td>
<td>(-1.33)</td>
</tr>
<tr>
<td>( \text{SCH}_3 )</td>
<td>(-9.26)</td>
<td>(-12.15)</td>
<td>(-9.12)</td>
<td>(-10.81)</td>
<td>(-1.05)</td>
<td>(-1.33)</td>
</tr>
<tr>
<td>( \text{OCH}_3 )</td>
<td>(-9.24)</td>
<td>(-12.15)</td>
<td>(-10.81)</td>
<td>(-10.81)</td>
<td>(-1.33)</td>
<td>(-1.33)</td>
</tr>
</tbody>
</table>
Table 1. Wave function coefficients of the $\pi(b_1)$ MOs of p-X—C₆H₄—CN, in order of increasing ionization energy, with respect to the building group orbitals.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\pi_X$</th>
<th>$\pi_S$</th>
<th>$\pi_O$</th>
<th>$\pi_{CN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCH₃</td>
<td>0.547</td>
<td>-0.815</td>
<td>-0.110</td>
<td>-0.155</td>
</tr>
<tr>
<td>NH₂</td>
<td>0.613</td>
<td>-0.768</td>
<td>-0.133</td>
<td>-0.131</td>
</tr>
<tr>
<td>N(CH₃)₂</td>
<td>0.613</td>
<td>-0.768</td>
<td>-0.133</td>
<td>-0.131</td>
</tr>
</tbody>
</table>

The secular determinants

\[
\begin{vmatrix}
A_{n^+} - E & B_{n^+}/n_s \\
B_{n^-}/n_s & A_{n^-} - E
\end{vmatrix} = 0
\]

and

\[
\begin{vmatrix}
A_{n^+} - E & B_{n^+}/n_o \\
B_{n^-}/n_o & A_{n^-} - E
\end{vmatrix} = 0
\]

Fig. 3. Interaction diagram showing the symmetry allowed $\pi$ interactions in p-CH₃O—C₆H₄—OCH₃.
X = NH₂
- 7.74
- 9.15
- 9.73
- 11.95
- 12.88
X = N(CH₃)₂
- 7.82
- 9.26
- 9.29
- 11.42
- 12.81
X = SCH₃
- 7.31
- 9.03
- 9.01
- 11.32
- 12.67
X = OCH₃
- 7.99
- 9.24
- 9.99
- 12.06
- 12.97

lead to the following energies and parentages*:

\[ E_4 = -7.99 \text{ eV} = 0.83 \pi_s - 0.55 \pi_n, \]
\[ E_3 = -9.99 \text{ eV} = 0.85 \pi_n - 0.52 \pi_s, \]
\[ E_2 = -12.06 \text{ eV} = 0.55 \pi_s + 0.83 \pi_n, \]
\[ E_1 = -12.79 \text{ eV} = 0.52 \pi_n + 0.85 \pi_0. \]

The energy values calculated

\[(IE_{exp} = -0.12 + 1.01 IE_{LCBO}; \ r^2 = 0.993)\]

for the \( \pi \) orbitals (including \( \pi_A \)) of the series p-X—C₆H₄—OCH₃ are reported together with the experimental IEs in Table 2.

According to the calculated wave function coefficients, the highest occupied MO mainly derives from \( \pi_s \) when \( X = OCH₃ \) and \( NH₂ \), but from \( \pi_n \) when \( X = N(CH₃)₂ \). For \( X = SCH₃ \), the localization of the HOMO at the ring and at the substituents is almost the same.

One of the two experimental energy values reported in brackets in Table 2 is related to ionization \( \sigma \) orbital. These L.C.B.O. calculations indicate that the band at higher IE is always associated to the forth \( \pi \) orbital, in contrast with the assignment based on more sophisticated (CNDO/2) calculations [13]. The present result is in agreement with the qualitative expectation that the larger \( \sigma \) framework of the substituted benzenes has a lower IE onset than benzene (11.5 eV).

For \( X = SCH₃ \), the second experimental IE value (8.72 eV) has no counterpart in the calculations. We think that this band is due to the presence of \( S(CH₃)₂ \) impurity \( (IE = 8.71 \text{ eV} [14]) \) or of conformational isomers and that the second and third ionizations of p-CH₃S—C₆H₄—OCH₃ both contribute to the band peaking at 9.26 eV.

The \( B_{\pi_s/\pi_n} \) and \( A_{\pi_n} \) values obtained from ethynylbenzene \( (C₆H₅—C≡CH) \) are now employed to perform L.C.B.O. calculations on the \( \pi \) system of ortho, meta and para-diethynylbenzenes, for which experimental IE values are available [14]. The five group orbitals, from which the \( \pi \) MOs of these compounds originate, would lead to a \( 5 \times 5 \) secular determinant. However, symmetry simplifications are possible. Scheme III shows the orientation of the substituents with respect to the nodal properties of the ring \( \pi \) orbitals.

* For the \( \pi_s/\pi_n \) interaction, for example, the secular equation \( c_n(A_{\pi_n} - E_i) + c_n(B_{\pi_n/\pi_n}) = 0 \), with the normalization condition \( c_{\pi_n}^2 + c_{\pi_n}^- = 1 \), gives: \( c_{\pi_n}^2 = 1/1 + ((A_{\pi_n} - E_i)/B_{\pi_n/\pi_n})^2 \) and \( c_{\pi_n}^- = -c_{\pi_n}(A_{\pi_n} - E_i)/B_{\pi_n/\pi_n} \).
In the para derivative, as seen for p-CH$_3$O—C$_6$H$_4$—OCH$_3$, two $2 \times 2$ determinants are to be solved to account for the $\pi_0/\pi_{cc}$ and $\pi_0/\pi_{cc}^+$ interactions, where the labels $\pi_{cc}$ and $\pi_{cc}^+$ are related to the out of phase and to the in phase combinations of the acetylene $\pi$ MOs, respectively. In the meta and ortho derivatives a $2 \times 2$ and a $3 \times 3$ determinant is needed, the symmetry allowed interactions being $\pi_0/\pi_{cc}^+/\pi_0$ and $\pi_0/\pi_{cc}^-$ in the former, and $\pi_0/\pi_{cc}^+/\pi_0$ and $\pi_0/\pi_{cc}$ in the latter. The experimental $IE$ value (9.54 eV) of the non interacting $\pi_A$ MO of p-diethynylbenzene leads to $A_{n_a} = A_{n_b} = -9.54$ eV and to $A_{n_b} = -12.45$ eV; with the previously calculated $A_{n_a} = -10.68$ eV and $B_{n_a/n_c} = -1.065$ eV, the following basis sets are obtained:

\[
A_{n_a} = A_{n_b} = -9.54 \text{ eV};
\]

\[
A_{n_a} = -12.45 \text{ eV};
\]

\[
A_{n_c} = A_{n_c}^* = -10.68 \text{ eV}
\]

for all the isomers.

p-diethynylbenzene:

\[
B_{n_a/n_c} = -1.065 \times \sqrt{2} \text{ eV},
\]

\[
B_{n_a/n_c}^* = B_{n_a/n_c} = 0,
\]

\[
B_{n_a/n_c} = -1.065 \text{ eV};
\]

m-diethynylbenzene:

\[
B_{n_a/n_c} = -1.065 \times \sqrt{3/12} \times \sqrt{2} \text{ eV},
\]

\[
B_{n_a/n_c}^* = -1.065 \times \sqrt{3/4} \times \sqrt{2} \text{ eV},
\]

\[
B_{n_a/n_c} = -1.065 \times \sqrt{3/6} \times \sqrt{2} \text{ eV};
\]

o-diethynylbenzene:

\[
B_{n_a/n_c} = -1.065 \times \sqrt{3/12} \times \sqrt{2} \text{ eV},
\]

\[
B_{n_a/n_c}^* = -1.065 \times \sqrt{3/4} \times \sqrt{2} \text{ eV},
\]

\[
B_{n_a/n_c} = -1.065 \times \sqrt{3/6} \times \sqrt{2} \text{ eV}.
\]

The calculated energy levels are reported in Table 3. They nicely fit the experimentally observed $IE$s and their trends

\[
(IE_{\text{exp}} = 0.59 + 0.95 IE_{\text{LCBO}}; \ r^2 = 0.997).
\]

The L.C.B.O. model, together with photoelectron spectroscopy data, can be employed also for conformational analysis. Within the framework of a HMO-type model, the dependence of the interaction term $B$ on the dihedral angle ($\theta$) between the axis of the two interacting orbitals (see Scheme IV) is of the form: $B_\theta = B_0 \cos \theta$ [4a, 4f, 6b].

As an example, we calculate the angle of rotation around the C—S bond in the sterically hindered C$_6$H$_5$—SB(n-Propyl)$_2$. The photoelectron spectrum of this molecule [15] gives the $IE$ values 8.77 eV and 10.55 eV for the two outer $\pi(b_1)$ MOs resulting from the interaction among $\pi_S$, $\pi_0$ and $\pi_X$, where $\pi_X$ refers to the sulphur lone pair, and 9.38 eV for $\pi_A$. From the $3 \times 3$ secular determinant, with $A_{n_a} = -9.38$ eV, $A_{n_b} = -12.29$ eV and the two above mentioned energy values, $A_{n_a} = -10.12$ eV and $B_{n_a/n_b} = -0.87$ eV are obtained.

The comparison of these data with those found for the coplanar thioanisole indicates that the higher ionization potential of the boron derivative is due to a) the stabilizing effect of boron, lowering the sulphur lone pair self energy and b) the reduced

<table>
<thead>
<tr>
<th>p-diethynylbenzene $E_{\text{LCBO}}$</th>
<th>$IE_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a$<em>2$ ($\pi_A$, $\pi</em>{cc}$)</td>
<td>8.50</td>
</tr>
<tr>
<td>1b$_1g$ ($\pi_a$)</td>
<td>9.54</td>
</tr>
<tr>
<td>2b$<em>{2g}$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>10.18</td>
</tr>
<tr>
<td>1b$<em>{2g}$ ($\pi</em>{ce}$, $\pi_{cc}$)</td>
<td>11.72</td>
</tr>
<tr>
<td>1b$<em>{2u}$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>12.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m-diethynylbenzene $E_{\text{LCBO}}$</th>
<th>$IE_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a$<em>2$ ($\pi_A$, $\pi</em>{cc}$)</td>
<td>8.69</td>
</tr>
<tr>
<td>3b$<em>1$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>9.09</td>
</tr>
<tr>
<td>2b$<em>1$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>10.60</td>
</tr>
<tr>
<td>1a$<em>2$ ($\pi</em>{ce}$, $\pi_{cc}$)</td>
<td>11.53</td>
</tr>
<tr>
<td>1b$<em>1$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>12.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>o-diethynylbenzene $E_{\text{LCBO}}$</th>
<th>$IE_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b$<em>1$ ($\pi_A$, $\pi</em>{ce}$, $\pi_0$)</td>
<td>8.59</td>
</tr>
<tr>
<td>2a$<em>2$ ($\pi_a$, $\pi</em>{cc}$)</td>
<td>9.17</td>
</tr>
<tr>
<td>2b$<em>1$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>11.03</td>
</tr>
<tr>
<td>1b$<em>1$ ($\pi</em>{ce}$, $\pi_0$)</td>
<td>13.05</td>
</tr>
</tbody>
</table>

Table 3. Calculated energies and experimental $IE$s for the $\pi$ MOs of para-(D$_{3h}$), meta- and ortho- (C$_{2v}$) diethynylbenzenes. $IE$s are taken from [4e].
mixing between the sulphur lone pair and the ring $\pi$ orbitals, due to rotation around the C—S bond. In particular, the ratio between the two resonance integrals gives

$$-0.87/1.05 = \cos \theta; \quad \theta = 34^\circ.$$  

This result is close to that indicated by CNDO/2 calculations [15] for the smaller molecule C$_6$H$_5$—SBH$_2$, ($\approx 40^\circ$). It has to be pointed out, however, that orbital interactions, not present in the coplanar conformer, can often arise in the rotated conformer. In the above example, we neglected the $\sigma$ ring/$\pi_\chi$ mixing which is non-zero when $\theta \neq 0^\circ$. In a better approximation, we should have solved a $4 \times 4$ secular determinant, including in the basis set $A_\sigma$ and $B_{n\sigma}/\cos (90^\circ - \theta)$. This subject is dealt more extensively by Klessinger and Rademacher in reference [6b].

Application of the Method to the Unfilled Orbitals

The increasing availability of electron affinity (EA) data, obtained by means of Electron Transmission Spectroscopy [16] (ETS), stimulated us to test the applicability of this simple type of MO treatment to the empty orbitals. In fact, its success in predicting IE values does not necessarily imply its adequacy in predicting the energies of the shorter lived anion states formed for electron capture into unfilled MOs.

In this case, for analogy with the LCBO method, only interactions among group orbitals normally unoccupied are considered, neglecting their interaction with the filled orbitals. The empirical parameters $A$ and $B$ can be derived from the EA values of reference systems.

As an example, we calculate the energies of the empty orbitals of stilbene using parameters obtained from the ETS spectrum of styrene [17]. The procedure employed is the same as previously described for the filled orbitals. The used experimental data are the first three EA values of styrene ($-0.25, -1.05$ and $-2.48$ eV) and those of benzene ($-1.12$, doubly degenerate, and $-4.82$ eV [18]). The parameters $A_{n\sigma}=1.90$ eV and $B_{n\sigma}/\cos (90^\circ-\theta)= -1.10$ eV are obtained. Stilbene has seven $\pi^*$ MOs. Three derive from the symmetry allowed interaction among $\pi_0^*$ with the out of phase combinations of the ring $\pi_0^*$ and $\pi_0^*$ MOs ($\pi_0^*$ and $\pi_0^*$). The remaining orbitals cannot interact by symmetry with the ethylene $\pi_0^*$ MO. Thus, the energy values of $\pi_0^+$, $\pi_0^+$, $\pi_0^-$ (nearly degenerate) and $\pi_0^+$ are expected close to those of benzene.

The EA values of trans-stilbene, determined with ETS, are $-0.97$, $-2.53$, $-4.4$ and $-5.0$ eV [19]. On the basis of the above discussion, the features at $0.97$ eV and $4.4$ eV are related to the degenerate $\pi_0^+, \pi_0^+$ and $\pi_0^-$ and to $\pi_0^+$ MOs, respectively **. These two values are taken as Coulomb integrals for the $\pi_0^+$ and $\pi_0^+$ orbitals. The basis set for the three orbital interaction is therefore

$$A_{n\sigma} = 0.97 \text{ eV}, \quad B_{n\sigma}/\cos (90^\circ-\theta) = -1.10/\sqrt{2} \text{ eV},$$

$$A_{n\sigma} = 1.90 \text{ eV}, \quad B_{n\sigma}/\cos (90^\circ-\theta) = -1.10 \text{ eV},$$

$$A_{n\sigma} = 4.4 \text{ eV},$$

The secular determinant leads to the following energy values (eV) for the three $\pi^*$ MOs arising from the interaction among $\pi_0^*, \pi_0^*$ and $\pi_0^*$: $-0.29$, $2.65$ and $4.91$.

The calculated energies are in good agreement with those experimentally determined. In particular, the lowest unoccupied orbital is predicted to be stable and therefore not detectable by means of the ETS technique.

A good reproducibility of the EA values with this approach has also been found for other aromatic compounds [18].

** It can be observed that the $\pi_0^*$ MO is stabilized with respect to the $\pi_0^*$ MO of benzene more than the $\pi^*$ MO with respect to the $\pi_0^*$ MO of benzene. This finding is in line with what is observed in pyridines [18], benzaldehyde [18] and styrene [18], where the uppermost anion state is stabilized with respect to that of benzene, despite the destabilization caused by the substituent $\pi^*$ orbital. It has been suggested [18] that this energy stabilization is due to the presence of doubly excited states at slightly higher energy.