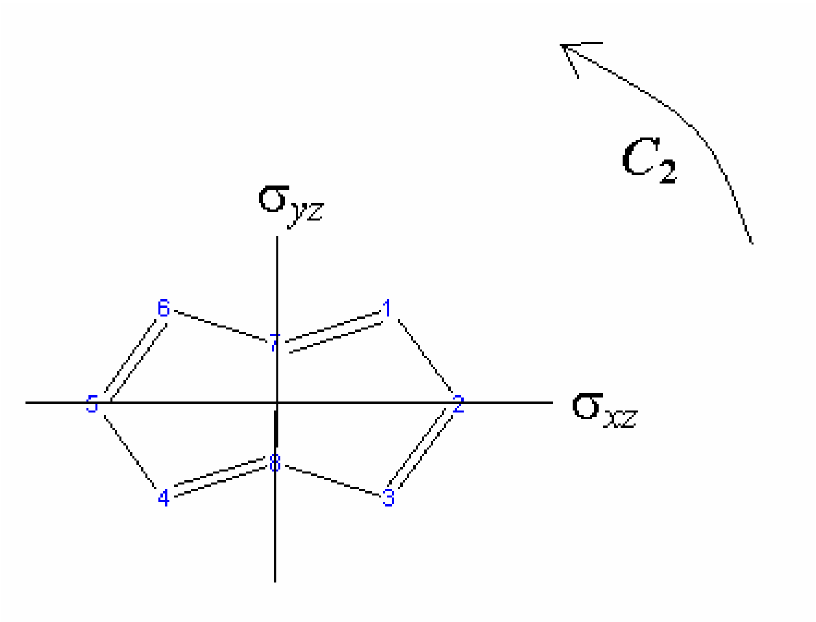
Junior Sophister Quantum Chemistry course

Symmetry in π Molecular Orbitals



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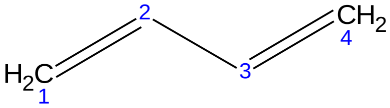
The application of symmetry principles to π MO theory

Hückel molecular orbital (HMO) theory is a simple and versatile method that provides important features for any π conjugated molecule. However since the method leads to an $n \times n$ energy matrix (determinant) the solution of the consequent polynomial equation of order n constitutes a 'bottleneck' in the calculation. So unless a computer is deployed to assist with the numerical solution of the secular equations, 'pencil and paper' calculations are necessarily limited to rather small molecules. Fortunately, if the molecule contains atoms which are symmetrically 'equivalent', this limitation may not be necessary, and the exploitation of symmetry can lead to other benefits, as we shall see.



Our treatment of butadiene $H_2C{=}CH{-}CH{=}CH_2$ in the introducton to Hückel theory did not recognise the equivalence of carbon atoms 1 and 4 in the terminal methylene groups or of atoms 2 and 3 forming the central bond. The π MO was written as

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + c_4\varphi_4 \qquad (1)$$

and in order to evaluate the LCAO coefficients $\{c_r\}$ we applied the Variation Method which led to four secular equations, a determinantal equation in x^4 and to four MOs and four enegy levels. Even a simple consideration can show that this entailed unnecessary labour. We have seen that in eqn. (1) the quantity $|c_r|^2$ measures the electron population in the π MO ψ. But these populations are the same for atoms 1 and 4 and also for 2 and 3. So we write

$$|c_1|^2 = |c_4|^2 \qquad \text{and} \qquad |c_2|^2 = |c_3|^2$$

and immediately deduce that $c_1 = \pm\, c_4$ and $c_2 = \pm\, c_3$. The LCAO coefficients in eqn. (1) have therefore been reduced to two, and reduces to

$$\psi = c_1(\varphi_1 \pm \varphi_4) + c_2(\varphi_2 \pm \varphi_3) \qquad (2)$$

which is a linear combination of two **symmetry orbitals**, and for any + or – sign would lead to *two* secular equations (not 4) and therefore to a *quadratic* (not quartic) equation.

Before proceeding there are three things to point out.

(1) Remember that while $\psi(x,y,z)$ is a function that describes the whole of space (x, y and z may be given any values) $\psi(x_p,y_p,z_p)$ is not a function – it specifies the numerical value of ψ at the point (x_p,y_p,z_p) in space.

(2) If ψ in eqn. (2) is really to be expressed as a combination of symmetry orbitals these should be normalised. So replace (2) by

$$\psi = c_1 \frac{1}{\sqrt{2}}(\varphi_1 \pm \varphi_4) + c_2 \frac{1}{\sqrt{2}}(\varphi_2 \pm \varphi_3) \qquad (2a)$$

(3) Could the ± signs in eqn. (2a) be independently '+' and '–', leading to *four* possible WFs, or should they be taken in tandem i.e. '+' with '+', and '–' with '–', resulting in *two* WFs?

Let's address point (2) immediately. Consider a symmetry element that transforms atom 1 into atom 4 and atom 2 into atom 3. This symmetry operation will be denoted R; for butadiene R could be a 180° rotation (C_2) about the molecular centre. Mathematically the action of R on the wave function $\psi \equiv \psi(x,y,z)$ at point $(x_1\, y_1\, z_1)$ is a transformation to some other (symmetrically related) point e.g. $(x_4\, y_4\, z_4)$, i.e.

$$R\ \psi(x_1\, y_1\, z_1) = \psi(x_4\, y_4\, z_4) \qquad (3)$$

Similarly $$R\ \psi(x_2\, y_2\, z_2) = \psi(x_3\, y_3\, z_3).$$

Now if we were to apply R to $|\psi|^2$ the result would leave $|\psi|^2$ unchanged. This is because R transforms $|\psi(x_1\, y_1\, z_1)|^2$ to the symmetrically equivalent point $|\psi(x_2\, y_2\, z_2)|^2$, and since the electron densities are the same at these two points,

$$|\psi(x_1\, y_1\, z_1)|^2 = |\psi(x_4\, y_4\, z_4)|^2,$$

so $$R\ [|\psi(x_1\, y_1\, z_1)|^2] = |\psi(x_4\, y_4\, z_4)|^2. \qquad (4)$$

Since R on the left hand side of eqn. (4) operates on the whole of $\psi \times \psi$ the equation means

$$[R\ \psi(x_1\, y_1\, z_1)][R\ \psi(x_1\, y_1\, z_1)] = |\psi(x_4\, y_4\, z_4)|^2.$$

This equation is obeyed if the following conditions hold for the two chemical sites:

$$R\ \psi(x_1\, y_1\, z_1) = \pm\psi(x_4\, y_4\, z_4)$$

$$(5)$$

$$R\ \psi(x_2\, y_2\, z_2) = \pm\psi(x_3\, y_3\, z_3)$$

In other words, the application of a symmetry operation to the wave function either leaves it unchanged or else multiplies it by –1. (Actually 'multiplies it by a factor of modulus unity', which means that it could alternatively be multiplied it by i or by $-i$, but as we shall at present use only real wave functions this alternative will not arise.)

Let's see if the MO wave functions in eqn. (2a) satisfy the condition in eqn. (5).

(a) Consider first the case where all the signs in eqn. (2) are positive. As R interchanges atoms 1 and 4 and also 2 and 3, its result on ψ is:

$$R\psi_+ = c_1\frac{1}{\sqrt{2}}(\varphi_4+\varphi_1)+c_2\frac{1}{\sqrt{2}}(\varphi_3+\varphi_2)$$

i.e. $R\psi_+ = \psi_+$

and so condition (5) is obeyed.

(b) Take the negative signs in eqn. (2) and get

$$R\psi_- = c_1\frac{1}{\sqrt{2}}(\varphi_4-\varphi_1)+c_2\frac{1}{\sqrt{2}}(\varphi_3-\varphi_2)$$

i.e. $R\psi_- = -\psi_-$

Again condition (5) is obeyed, and so ψ_+ and ψ_- are acceptable. Each is of the form

$$\psi = c_1\Phi_1 + c_2\Phi_2$$

where the Φs are symmetry orbitals, and so *each* of them will provide two MOs and two energy levels, making a total of four as is expected for butadiene.

What about a 'mixed' function such as

$$\psi = c_1\frac{1}{\sqrt{2}}(\varphi_1+\varphi_4)+c_2\frac{1}{\sqrt{2}}(\varphi_2-\varphi_3)$$

where the first symmetry orbital is symmetric and the second is antisymmetric? In such a case it is easy to see that $R\psi \neq \pm\psi$, i.e. our required condition (5) is not obeyed (try it!), and so this ψ is *not an acceptable MO*. Indeed it would be disturbing if this were not the case because we have seen that ψ_+ and ψ_- between them have already provided the four MOs required for butadiene! In short, for a MO wave function to be acceptable *all parts of it must transform in the same way* when it is subjected to a symmetry operation.

Example

Let us take one of these symmetry adapted MO-WFs (ψ_-, say) see how we can use them to calculate the energy levels.

$$\psi_- = c_1\frac{1}{\sqrt{2}}(\varphi_1-\varphi_4)+c_2\frac{1}{\sqrt{2}}(\varphi_2-\varphi_3) = c_1\Phi_1^- + c_2\Phi_2^-$$

where the symmetry functions are denoted by Φ symbols. We proceed in the standard way in the Hückel method and calculate the secular determinant:

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{21} & H_{22}-E \end{vmatrix} = 0$$

where the elements are defined in the usual manner (i.e. $H_{11} = \int \Phi_1^- \mathrm{H} \Phi_1^- \, d\tau$ etc.) and where

$$\Phi_1^- = \sqrt{\frac{1}{2}}(\varphi_1 - \varphi_4) \qquad \text{and} \qquad \Phi_2^- = \sqrt{\frac{1}{2}}(\varphi_2 - \varphi_3)$$

Evaluating the H_{ij}, we have

$$\begin{aligned}
H_{11} &= \tfrac{1}{2}\int(\varphi_1 - \varphi_4)\mathrm{H}(\varphi_1 - \varphi_4)\, d\tau \\
&= \tfrac{1}{2}\left[\int\varphi_1\mathrm{H}\varphi_1\, d\tau + \int\varphi_2\mathrm{H}\varphi_2\, d\tau - \int\varphi_1\mathrm{H}\varphi_2\, d\tau - \int\varphi_2\mathrm{H}\varphi_1\, d\tau\right] \\
&= \tfrac{1}{2}[\alpha + \alpha - 0 - 0] \\
&= \alpha \\
H_{22} &= \tfrac{1}{2}\int(\varphi_2 - \varphi_3)\mathrm{H}(\varphi_2 - \varphi_3)\, d\tau \\
&= \tfrac{1}{2}\left[\int\varphi_2\mathrm{H}\varphi_2\, d\tau + \int\varphi_3\mathrm{H}\varphi_3\, d\tau - \int\varphi_2\mathrm{H}\varphi_3\, d\tau - \int\varphi_3\mathrm{H}\varphi_2\, d\tau\right] \\
&= \tfrac{1}{2}[\alpha + \alpha - \beta - \beta] \\
&= \alpha - \beta \\
H_{12} &= \tfrac{1}{2}\int(\varphi_1 - \varphi_4)\mathrm{H}(\varphi_2 - \varphi_3)\, d\tau \\
&= \tfrac{1}{2}\left[\int\varphi_1\mathrm{H}\varphi_2\, d\tau - \int\varphi_1\mathrm{H}\varphi_3\, d\tau - \int\varphi_4\mathrm{H}\varphi_2\, d\tau + \int\varphi_4\mathrm{H}\varphi_3\, d\tau\right] \\
&= \tfrac{1}{2}[\beta - 0 - 0 + \beta] \\
H_{12} &= \beta
\end{aligned}$$

The secular determinant al equation is therefore

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - \beta - E \end{vmatrix} = 0$$

i.e. $$\begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = x(x-1) - 1 = 0$$

so

$x = 0{\cdot}618034$ or $x = -1{\cdot}618034$

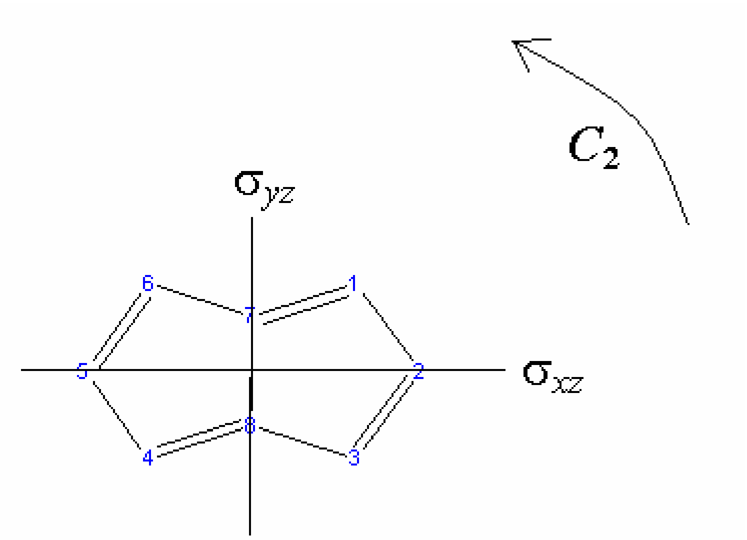
which were two of butadiene's four roots obtained previously. The other two (–0·618034 and +1·618034) are obtained from the ψ_+ function.

Other symmetries

If the molecule has only *one* symmetry element e.g. a C_2 rotation or a mirror plane it is easy to construct the MO wave functions — we ensure that they are either symmetric or antisymmetric to that symmetry element. But naphthalene for example has, in addition to C_2, mirror planes σ_{xz} and σ_{yz}. If the symmetry orbitals were chosen so as to be symmetric and antisymmetric to *each* symmetry element, there would be 2 × 2 × 2 of them, which would lead to far too many MO-WFs.

We have derived the rule requiring that the symmetry functions of all *species* of atoms for butadiene these are either *symmetric* or *antisymmetric* to symmetry operation $\hat{R}$. What do we do when the molecular symmetry contains several symmetry elements? The answer is that we must create **symmetry functions Φ^i that transform according to an 'irreducible representation' or symmetry type** (labelled *i*) **of the molecular point group**. This will be discussed in the next section.

The use of Group Theory to calculate MOs in pentalene



The π molecular orbital wave function in pentalene (refer to the atomic numbering below on this page) are

$$\psi = c_1\,\tfrac{1}{2}(\varphi_1 \ast \varphi_3 \ast \varphi_4 \ast \varphi_6) + c_2\sqrt{\tfrac{1}{2}}(\varphi_2 \ast \varphi_5) + c_7\sqrt{\tfrac{1}{2}}(\varphi_7 \ast \varphi_8) \qquad (6a)$$

or

$$\psi = c_1\Phi_1 + c_2\Phi_2 + c_7\Phi_7 \qquad (6b)$$

where Φ_1, Φ_2 and Φ_7 are symmetry orbitals for atoms of type 1, 2 and 7, and where the five symbols '$\ast$' stand for some set of '+' and '–' signs.

We find the combinations of signs ‘*’ in the first equation using the projection operator method. Although the molecule’s full point group is D_{2h}, the C_{2v} (sub)group is the most convenient one to describe the ψ molecular orbitals in a planar molecule. (D_{2h} would give the same results, but with greater labour because it includes unnecessary elements like σ_{xy}, i.e. reflection in the molecular plane.)

Symmetry functions $\Phi_r^{(i)}$ transforming according to symmetry i (where i is A_1, A_2, B_1 or B_2, can be formed by ‘projecting’ them out of the total wave function as follows:

$$\Phi_r^i = N \sum_R^{E,C_2,\sigma_{xz},\sigma_{yz}} \chi_R^{(i)} R\varphi_r \qquad (7)$$

where $\chi_R^{(i)}$ is the character of symmetry element R in the ith irreducible representation and N the normalisation constant, which is determined at the end of the calculation. The summation is taken over all the elements R of the group. These are given on the top line of the C_{2v} character table:

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	+1	+1	+1	+1	z
A_2	+1	+1	–1	–1	
B_1	+1	–1	+1	–1	x
B_2	+1	–1	–1	+1	y

As an example of the method, let’s calculate the molecular orbital that has symmetry B_1. Application of eq. (7) to calculate the symmetry orbital of atom type 1 gives

$$\Phi_1^{B_1} = N[\chi_E^{B_1} E\varphi_1 + \chi_{C_2}^{B_1} C_2\varphi_1 + \chi_{\sigma_{xz}}^{B_1} \sigma_{xz}\varphi_1 + \chi_{\sigma_{yz}}^{B_1} \sigma_{yz}\varphi_1] \qquad (8)$$

Application of E, C_2, σ_{xz} and σ_{yz} to φ_1 generates φ_1, φ_4, φ_3 and φ_6. So eq. (8) produces $N(\varphi_1 + \varphi_3 - \varphi_4 - \varphi_6)$, and since four symmetrically equivalent functions are being combined the normalization factor is 1/√4:

$$\Phi_1^{B_1} = ½(\varphi_1 + \varphi_3 - \varphi_4 - \varphi_6)$$

the factor ½ being obtained from normalisation. A similar application to ϕ_2 produces $N(\varphi_2 + \varphi_2 - \varphi_5 - \varphi_5)$ which is a combination of two functions, φ_2 and φ_5. So the symmetry orbital is

$$\Phi_2^{B_1} = \sqrt{½}(\phi_2 - \phi_5),$$

while the symmetry orbital for atoms 7 and 8 turns out to be zero:

$$\Phi_7^{B_1} = 0.$$

The molecular orbital with B_1 symmetry is therefore

$$\psi^{B_1} = c_1 ½(\varphi_1 + \varphi_3 - \varphi_4 - \varphi_6) + c_2 \sqrt{½}(\phi_2 - \phi_5)$$

The complete set of MOs, classified according to the four symmetries of C_{2v} are:

$$\begin{array}{lll}
\psi^{A_1} = c_1 ½(\varphi_1 + \varphi_3 + \varphi_4 + \varphi_6) & + c_2 \sqrt{½}(\phi_2 + \phi_5) & + c_7 \sqrt{½}(\phi_7 + \phi_8) \\
\psi^{A_2} = c_1 ½(\varphi_1 - \varphi_3 + \varphi_4 - \varphi_6) & & \\
\psi^{B_1} = c_1 ½(\varphi_1 + \varphi_3 - \varphi_4 - \varphi_6) & + c_2 \sqrt{½}(\phi_2 - \phi_5) & \\
\psi^{B_2} = c_1 ½(\varphi_1 - \varphi_3 + \varphi_4 - \varphi_6) & & + c_7 \sqrt{½}(\phi_7 - \phi_8)
\end{array}$$

Because of the numbers of symmetry orbitals that are being combined to form ψ^{A_1}, ψ^{A_2}, ψ^{B_1} and ψ^{B_2}, there will be respectively 3, 1, 2 and 2 molecular orbitals transforming according to the symmetries A_1, A_2, B_1 and B_2. So there are

three A_1 molecular orbitals and energy levels,
one A_2 molecular orbital and energy level,
two B_1 molecular orbitals and energy levels,
two B_2 molecular orbitals and energy levels.

Secular equations

We shall consider the A_1 orbitals, and let you do the rest (which are easier!).

$$\begin{array}{lllll}
c_1(H_{11} - E) & + c_2 H_{12} & + & c_7 H_{17} & = 0 \\
c_1 H_{21} & + c_2 (H_{22} - E) & + & c_7 H_{27} & = 0 \\
c_1 H_{71} & + c_2 H_{72} & + & c_7 (H_{77} - E) & = 0
\end{array}$$

Secular-determinantal equation:

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{17} \\ H_{21} & H_{22} - E & H_{27} \\ H_{71} & H_{72} & H_{77} - E \end{vmatrix} = 0$$

The matrix elements $H_{rs} = \int \Phi_r^* H \Phi_s \, d\tau$ are calculated as follows:

$$H_{11} = \int \Phi_1 H \Phi_1 \, d\tau = ¼\int(\varphi_1 + \varphi_3 + \varphi_4 + \varphi_6) H (\varphi_1 + \varphi_3 + \varphi_4 + \varphi_6) \, d\tau = ¼ \times 4\alpha = \alpha$$

$$H_{22} = \int \Phi_2 H \Phi_2 \, d\tau = ½\int(\varphi_2 + \varphi_5) H (\varphi_2 + \varphi_5) \, d\tau = ½ \times 2\alpha = \alpha$$

$$H_{77} = \int \Phi_7 H\, \Phi_7\, d\tau = \tfrac{1}{2}\int(\varphi_7 + \varphi_8)H(\varphi_7 + \varphi_8)\, d\tau = \tfrac{1}{2} \times 2\alpha \qquad = \alpha$$

$$H_{12} = \int \Phi_1 H\, \Phi_2\, d\tau = {}^{1}/_{2\sqrt{2}} \int(\varphi_1+\varphi_3+\varphi_4+ \varphi_6)H\,(\varphi_2 + \varphi_5)\, d\tau \qquad = {}^{\sqrt{2}}/_{4} \times 4\beta \qquad = \beta\sqrt{2}$$

$$H_{17} = \int \Phi_1 H\, \Phi_7\, d\tau = {}^{1}/_{2\sqrt{2}} \int(\varphi_1+\varphi_3+\varphi_4+ \varphi_6)H(\varphi_7 + \varphi_8)\, d\tau \qquad = \beta\sqrt{2}$$

$$H_{27} = \int \Phi_2 H\, \Phi_7\, d\tau = \tfrac{1}{2}\int(\varphi_2 + \varphi_5)H(\varphi_7 + \varphi_8)\, d\tau \qquad = 0$$

The secular equations are now

$$\begin{aligned} c_1(\alpha - E) &+ c_2\,\beta\sqrt{2} &+\quad & c_7\,\beta\sqrt{2} &= 0 \\ c_1\,\beta\sqrt{2} &+ c_2(\alpha - E) & & &= 0 \\ c_1\,\beta\sqrt{2} & &+\quad & c_7\,(\alpha+\beta - E) &= 0, \end{aligned} \qquad (9)$$

giving

$$\begin{vmatrix} x & \sqrt{2} & \sqrt{2} \\ \sqrt{2} & x & 0 \\ \sqrt{2} & 0 & x+1 \end{vmatrix} = 0$$

where $x = (\alpha - E)/\beta$. Expanding the determinant, we get the cubic equation

$$x^3 + x^2 - 4x - 2 = 0$$

whose solutions are $x = -2{\cdot}3429$, $x = -0{\cdot}4707$ or $x = +1{\cdot}8136$. Substituting these values in turn into the secular eqns (9) gives the LCAO coefficients.

x	c_1	c_2	c_7
1·8136	0·7332	–0·5716	–0·3685
–0·4707	–0·2414	–0·7252	0·6449
–2·3429	0·6358	0·3838	0·6696

Taking account of the normalisation factors ½ and √½ in eq. (6a), the lowest-energy molecular obital (that for $E = \alpha + 2{\cdot}3429\,\beta$) can be written

$$\psi = 0{\cdot}3179(\varphi_1+\varphi_3+\varphi_4+ \varphi_6) + 0{\cdot}2714(\varphi_2 + \varphi_5) + 0{\cdot}4735(\varphi_7 + \varphi_8),$$

and the other two similarly.

Final results

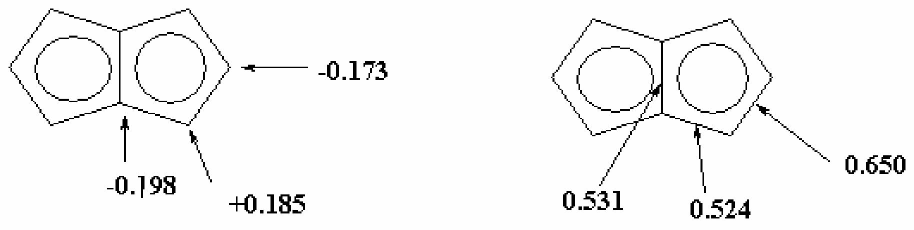
The same procedure is followed to obtain the MOs characterised by the remaining symmetries, A_2, B_1 and B_2. The results are displayed in the following table, which lists the MOs and their energies from $E_1 = \alpha + 2.3429\,\beta$ (lowest) to $E_8 = \alpha - 2.0000\,\beta$ (highest). The eight π electrons occupy the lowest available energy levels, E_1 to E_4.

Energy	Sym.	c_1	c_2	c_7

$\alpha - 2.0000\,\beta$	______	B_2	–0.5774	0.0000	0.8166
$\alpha - 1.8136\beta$	______	A_1	0.7332	–0.5716	–0.3685
$\alpha - 1.4142\,\beta$	______	B_1	–0.7072	0.7071	0.0000
$\alpha + 0.0000\beta$	______	A_2	1.0000	0.0000	0.0000
$\alpha + 0.4707\,\beta$	–↑–↓–	A_1	–0.2414	–0.7252	0.6449
$\alpha + 1.0000\beta$	–↑–↓–	B_2	0.8166	0.0000	0.5774
$\alpha + 1.4142\,\beta$	–↑–↓–	B_1	0.7072	0.7071	0.0000
$\alpha + 2.3429\,\beta$	–↑–↓–	A_1	0.6358	0.3838	0.6696

The coefficients not listed in the table (c_3, c_4, c_5, c_6 and c_8) can be obtained from the functions ψ^{A_1}, ψ^{A_2}, ψ^{B_1} and ψ^{B_2} that were derived above.

The LCAO coefficients may be used to calculate the net atomic charges on the carbon atoms and the bond orders:



Net atomic charges **π bond orders**

Notes on the results of the calculation

1. The application of Group Theory to pentalene replaces the secular determinant of order 8 when symmetry is not applied, by *four* determinants, of orders 1, 2, 2 and 3. The theory identifies the respective symmetries of the molecular orbitals in these cases as A_2, B_1, B_2 and A_1.
2. In the lowest-energy molecular orbital all the LCAO coefficients possess the same sign; i.e. this MO possesses no nodes perpendicular to the molecule.
3. The molecule possesses a non-bonding MO (energy $E = \alpha$, and symmetry A_2), although it is unoccupied. The reason for its existence should be clear from the form of the function ψ^{A_2} on p. 6: it is simply that none of the atomic orbitals involved in ψ^{A_2} are nearest neighbours. In accordance with the nearest-neighbour approximation inherent in the Hückel method, there are therefore no interactions between the atomic orbitals. Consequently the molecular orbital consists of a set of isolated C(2*p*) orbitals, with energy α.

Electronic transitions involving π molecular orbitals

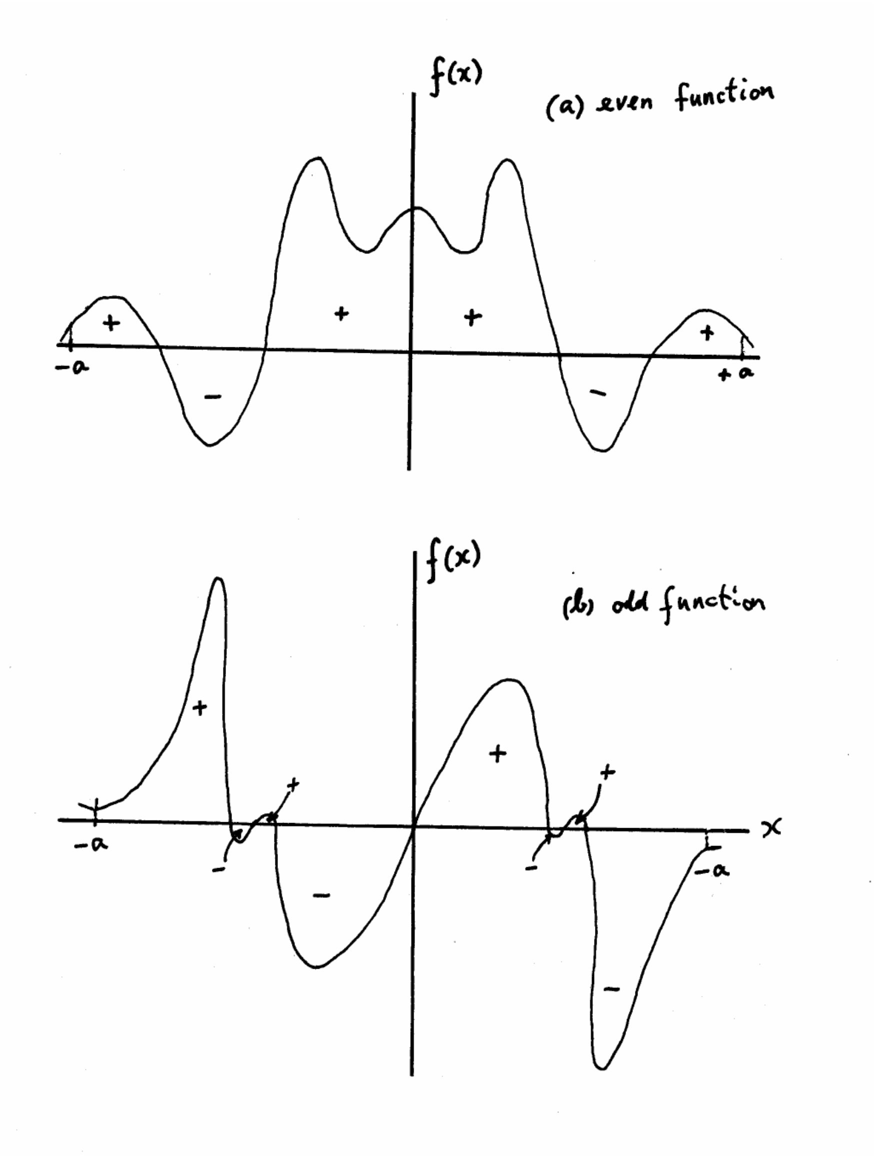
We consider 'electric dipole transitions' which occur as a result of the coupling between the electric field component of the electromagnetic radiation (which oscillates with the frequency of the radiation) and the electric dipole moment which the electric field induces in the molecule*. An electric dipole moment $\boldsymbol{\mu}$ interacts with an electric field **E**, shifting its energy by an amount $E = -\boldsymbol{\mu}\cdot\mathbf{E}$. If a dipole were just a pair of charges (q, $-q$) connected by a vector $\boldsymbol{x}$ the dipole moment would be $\boldsymbol{\mu} = q\boldsymbol{x}$ and the energy coupling with the field **E** would be given by $E = -q\boldsymbol{x}\cdot\mathbf{E}$. However in atoms and molecules the electric effects giving rise to dipoles are not *point* charges, but must be described by an electron density function $\rho(x,y,z)$, which is the *square* of some electronic wave function $\psi(x,y,z)$. As a result the coupling energy will involve the factor $-q\mathbf{E}\,\boldsymbol{x}|\psi|^2$ which must be integrated over space to explore the different charges over the different regions of space.

In short a photon may be absorbed from the radiation field provided the photon's energy just matches the coupling between the dipole moment $\boldsymbol{\mu}$ and the electric field **E**. If it does, a transition will occur between the initial state Ψ_0 of the molecule and its final state Ψ_1 and energy is absorbed from the radiation field at a *rate* proportional to

$$M_{01}^{x} = \int \Psi_0 x \Psi_1 d\tau \qquad (10)$$

which is called the **transition moment integral** (TMI) between the states Ψ_0 and Ψ_1 when the electric field is polarized along the x direction. The TMIs M_{01}^{y} and M_{01}^{z} are defined analagously to eqn. (10) for polarizations along the other two directions. Since the TMI is a measure of the rate of energy absorption it is also measures the *probability of a transition* between the specified states Ψ_0 and Ψ_1. Using q to symbolise x or y or z, the explanation of the TMI implies that if M_{01}^{q} is large the transition is 'highly allowed' and **if it is zero, the transition is forbidden**. For our purpose it will never be necessary to evaluate the TMI: we shall be interested only in ascertaining whether or not a proposed transition is allowed. It will then be sufficient to test whether or not the TMI has a non-zero value.

In order to carry out this test symmetry considerations come to our aid. Some mathematical functions have parity properties: for example cos (x) is an *even* function while sin (x) is an *odd* function. This is because of the behaviour of the functions when the sign of the argument is changed: cos (x) = cos ($-x$) whereas sin (x) = $-$sin ($-x$). As a result, the integral $\int_{-a}^{+a} f(x)\,dx$ of an *odd* $f(x)$ is zero, since it is the sum of pairs of mutually annihilating integrand contributions as shown in the sketch, while this is not (necessarily) so if $f(x)$ is an *even* function*.



Electronic state

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* The radiation of course also has a *magnetic* field component, which oscillates perpendicular to the *electric* field and with the same frequency. But as the magnetic susceptibility of diamagnetic molecules is low, we do not consider magnetic effects.

* It has to be put like that. An even function might 'accidentally' have $\int_{-a}^{+a} f(x)dx = 0$ as we would have for the integral $\int_{-\pi}^{+\pi} \cos x\,dx$. If such an integral occurred in eqn. (10) then the transition would be forbidden. All we're saying is that if the integrand is *odd* then the integral will *definitely* be zero. The approach could *not* be used to prove that an integral with an *even* integrand is definitely non-zero.

Before proceeding further we should ensure that we agree on the meaning of an *electronic state*. It describes the result of assigning electrons to the available molecular orbitals. If all the electrons in our pentalene example above occupy the lowest-energy MOs in accordance with the Pauli principle the resulting electronic structure $(\psi_1)^2$, $(\psi_2)^2$, $(\psi_3)^2$, $(\psi_4)^2$, $(\psi_5)^0$, $(\psi_6)^0$, $(\psi_7)^0$, $(\psi_8)^0$ is referred to as the *ground electronic state* and it will be described by an overall wave function Ψ_0. Any other electron assignments to the MOs will define *excited electronic states* Ψ_{45}, Ψ_{46}, . . .

MO	sym				
ψ_8	B_2				
ψ_7	A_1				↑
ψ_6	B_1			↑	
ψ_5	A_2		↑		
ψ_4	A_1	↑↓	↓	↓	↓
ψ_3	B_2	↑↓	↑↓	↑↓	↑↓
ψ_2	B_1	↑↓	↑↓	↑↓	↑↓
ψ_1	A_1	↑↓	↑↓	↑↓	↑↓
		Ψ_0 Ground state	Ψ_{45} 1st excited state	Ψ_{46} 2nd excited state	Ψ_{47}

Electronic states will be described by upper-case symbols Ψ_0, Ψ_{45}, Ψ_{46}, . . . (whereas lower-case symbols ψ_1, ψ_2, ψ_3, ψ_4, . . . as usual denote the MO-WFs).

The transitions

Whether or not the transition from the ground state to the 1st excited state with x polarization is allowed or forbidden depends on the TMI $M_{0,45}^{x} = \int \Psi_0 \, x \Psi_{45} \, d\tau$. And whether or not it is zero just depends on the symmetry of the *integrand* $\Psi_0 x \Psi_{45}$: if the transition is to be allowed **the integrand must be totally symmetric, i.e. it must have representation A_1**. How this is ascertained will now be shown.

We know the symmetries of the component MOs ψ_1, ψ_2, ψ_3, . . . In fact the MOs are often denoted by their symmetry labels so that the electronic states would be described as

$$\Psi_0 \equiv a_1^2 \, b_1^2 \, b_2^2 \, a_1^2 \, a_2^0 \, b_1^0 \, a_1^0 \, b_2^0$$

$$\Psi_{45} \equiv a_1^2 \, b_1^2 \, b_2^2 \, a_1^1 \, a_2^1 \, b_1^0 \, a_1^0 \, b_2^0$$

$$\Psi_{46} \equiv a_1^2 \, b_1^2 \, b_2^2 \, a_1^1 \, a_2^0 \, b_1^1 \, a_1^0 \, b_2^0$$

But what are the symmetries of these electronic states Ψ_0, Ψ_1, Ψ_2, . . .? This is provided by the **direct products** of the symmetries of each of the occupied one-electron MOs: Using the symbol Γ to mean 'the symmetry of' we write

$$\Gamma(\Psi_0) = (A_1\times A_1) \times (B_1\times B_1) \times (B_2\times B_2) \times (A_1\times A_1)$$

which consists of multiplied product pairs associated with the 1st to 4th MOs, which are doubly occupied. There are no contributions from the unoccupied MOs (nos. 5 to 8). The direct product of a pair of symmetries is obtained by multiplying the characters of each of them in turn, and then using the result to identifying the symmetry. Suppose for example we wanted to know the symmetry of $A_2 \times B_1$. From the character table of $\mathbf{C_{2v}}$ (p. 6) we have

$$\Gamma(A_2 \times B_1) = (+1\ +1\ –1\ –1) \times (+1\ –1\ +1\ –1) = (+1\ –1\ –1\ +1)$$

But as the same character table shows that these characters are those that describe symmetry B_2, we conclude that $A_2 \times B_1 = B_2$.

Now let's take the electronic states that we wish to consider for pentalene. The symmetries of doubly-occupied MOs are always A_1 because for example

$$\Gamma(A_2 \times A_2) = (+1\ +1\ –1\ –1) \times (+1\ +1\ –1\ –1) = (+1\ +1\ +1\ +1) \qquad = A_1.$$

So,

$$\Gamma(\Psi_0) = (A_1\times A_1) \times (B_1\times B_1) \times (B_2\times B_2) \times (A_1\times A_1) \qquad = A_1.$$

$$\Gamma(\Psi_{45}) = (A_1\times A_1) \times (B_1\times B_1) \times (B_2\times B_2) \times (A_1\times A_2) = A_1 \times A_2 \qquad = A_2$$

$$\Gamma(\Psi_{46}) = (A_1\times A_1) \times (B_1\times B_1) \times (B_2\times B_2) \times (A_1\times B_1) = A_1 \times B_1 \qquad = B_1$$

We now have the symmetries of the required states. It only remains now to get the overall symmetries of the TMI integrands for the various cases. For example the possibility of a transition between the ground and first excited states depends on the symmetry of the integrand in $M^x_{0,45} = \int \Psi_0\, x\, \Psi_{45}\, d\tau$. Now,

$$\begin{aligned} \Gamma(\Psi_0\, x\, \Psi_{45}) &= \Gamma(\Psi_0) \times \Gamma(x) \times \Gamma(\Psi_{45}) = A_1 \times B_1 \times A_2 \ = B_1 \times A_2 \\ &= (+1\ –1\ +1\ –1) \times (+1\ +1\ –1\ –1) \\ &= (+1\ –1\ –1\ +1) \\ &= B_2. \end{aligned}$$

We have just determined the symmetry of the integrand in $M^x_{0,45}$, and it is *not* A_1! *Therefore the transition is not allowed with x polarization*. What about the polarizations along the other directions?

$$\Gamma(\Psi_0\, y\, \Psi_{45}) \qquad = \Gamma(\Psi_0) \times \Gamma(y) \times \Gamma(\Psi_{45}) = A_1 \times B_2 \times A_2 \ = B_2 \times A_2 = B_1.$$

$$\Gamma(\Psi_0\, z\, \Psi_{45}) \qquad = \Gamma(\Psi_0) \times \Gamma(z) \times \Gamma(\Psi_{45}) = A_1 \times A_1 \times A_2 \ = A_1 \times A_2 = A_2.$$

We therefore conclude that as the transition is not allowed with polarizations *x* or *y* or *z*, **the transition from the ground state to the first excited state ($\Psi_0 \rightarrow \Psi_{45}$) is symmetry-forbidden**.

What about a transition from ground to the second excited state Ψ_{46}?

$\Gamma(\Psi_0\, x\, \Psi_{46}) = \Gamma(\Psi_0)\, \Gamma(x)\, \Gamma(\Psi_{45}) = A_1 \times B_1 \times B_1 = A_1 \times A_1 = A_1$

$\Gamma(\Psi_0\, y\, \Psi_{46}) = \Gamma(\Psi_0)\, \Gamma(y)\, \Gamma(\Psi_{45}) = A_1 \times B_2 \times B_1 = B_2 \times B_1 = A_2$

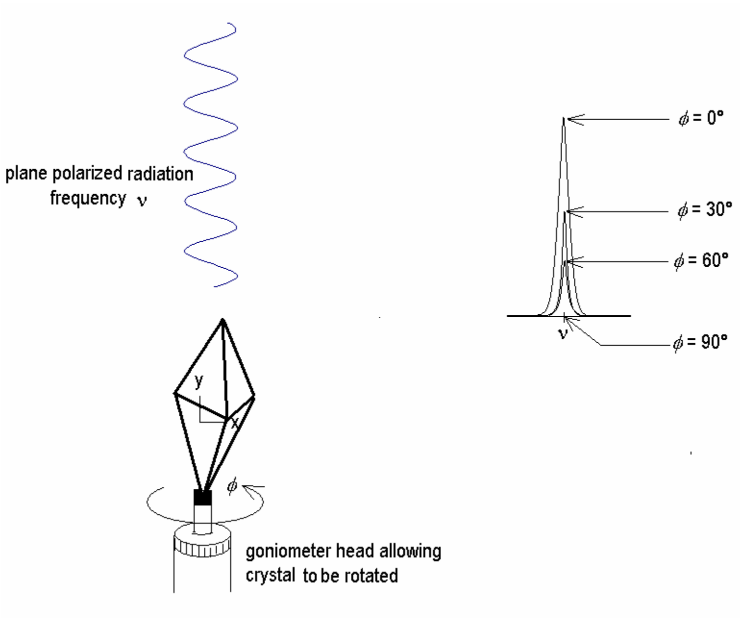
$\Gamma(\Psi_0\, z\, \Psi_{46}) = \Gamma(\Psi_0)\, \Gamma(z)\, \Gamma(\Psi_{45}) = A_1 \times A_1 \times B_1 = A_1 \times B_1 = B_1$.

Of the three TMIs, $M^x_{0,46}$, $M^y_{0,46}$ and $M^z_{0,46}$ only the integrand in $M^x_{0,46}$ has A_1 symmetry. So **a transition from the ground state to the second excited state ($\Psi_0 \rightarrow \Psi_{46}$) is symmetry-allowed with *x* polarization.**

The polarization of a spectroscopic transition

Recall our discussion at the start of this section in which a picture was presented of a molecule's electrons being polarized by the oscillating electric field of the incident radiation. The resulting induced electric dipole moment may couple with the field, absorbing a photon of the appropriate frequency so as to bring about a spectroscopic transition. But the last calculation showed that in order for a transition to occur several conditions must be fulfilled, involving the symmetries of the states and the direction in which the radiation's electric field vector oscillates. The results of some of the $\Psi_0 \rightarrow \Psi_{46}$ calculation are summarised in the diagram below.

If the pentalene were in a fixed position such as in a crystal lattice and irradiated with polarized light the $\Psi_0 \rightarrow \Psi_{46}$ transition would occur only if the electric field comes in oscillating parallel to the molecule's *x* axis. There are several ways in which this could happen, and the sketch shows one of them, in which the light beam is directed along the *y* axis so that the light is *xy* plane polarized. If now the light beam were rotated around the *z* axis (which is perpendicular to the molecular plane) the absorption should decrease because the component of the molecule's x axis with the electric field is diminishing. When the beam reaches the *x* axis there is no absorption because the electric field is now parallel to *y* and, as demonstrated in the calculation, the transition is



forbidden. Further rotation around z would restore the field to an alignment in which the transition is allowed again. This is shown in the Figure, where the crystal is initially held with the molecule’s x axis parallel with the direction of the polarization of the radiation (ϕ = 0°). As the crystal is rotated through 90° the signal diminishes until it vanishes, and would start to reappear at $\phi > 90°$. It is an example of single-crystal spectroscopy, in which the spectrum depends on the relative positions of the crystal sample and the incident beam.

Instead of rotating the polarized radiation, the beam could be kept fixed and the *crystal* realigned, which for technical reasons is much easier. But what happens if the molecule were not fixed in a lattice site but is continuously re-orientating as it would if it were a liquid, e.g. in solution? In such a state the re-orientation motion means that the molecule presents different ‘postures’ to the radiation’s electric field vector. At any instant there are molecules whose y axes make a range of orientations with the electric field of the radiation. So there will always be enough of them for the $\Psi_0 \rightarrow \Psi_{46}$ to be observed and the transition is simply *allowed* (without any reference to polarization). For a molecule in the liquid state, therefore, in order for an electric dipole transition to be allowed it is necessary only for *at least one* of the three TMIs, $M^{x}_{0,46}$, $M^{y}_{0,46}$ and $M^{z}_{0,46}$ to be non-zero.