Junior Sophister

Quantum Chemistry Course 3033 (Part)

Molecular Orbital Theory

$$\psi$$

D.A.Morton-Blake

Molecular orbital theory

We have seen how the atomic orbital wave function ψ provides a complete description of the distribution of an electron in an isolated atom. As the wave function (WF) $\psi(x,y,z)$ varies from one point in space to another, so does the electron density function $\rho(x,y,z) \equiv |\psi(x,y,z)|^2$. Remember too atomic orbital WFs come in several different shapes and sizes. The *s* are spherically symmetrical, while *p, d* etc. are directed in space. The *p* orbitals align along $\pm x$, $\pm y$, $\pm z$, while the *d* point along and between these axes.

Combination of orbitals

The function $f(x) = ax + b$ is *a linear function* of *x*. If it were not for the constant *b* it would be a simple proportionality $f(x) = ax$: the result of doubling *x* would be to double $f(x)$. (The constant *b* merely shifts the result by the same amount whatever the value of *x*.)

A *linear combination of functions* means adding them together under the control of mixing coefficients. If φ_1 and φ_2 are combined in this way,

$$\psi = c_1\varphi_1 + c_2\varphi_2$$

the resulting function ψ has characteristics derived from each of them. Their respective weighting factors are decided by the coefficients $c_1$and c_2. The function

$\psi = c_1(\varphi_1)^2 + c_2\varphi_2$ is *not* a linear function of φ_1 but it *is* a linear function of φ_2.

Let us first consider the combination of two atomic orbitals on the same atom. If both are *s* orbitals such as 1*s* and 2*s* the resulting ψ will obviously also have spherical symmetry, i.e. it will be another *s* obital. If we combine two *p* orbitals, say a p_x and a p_y the result is a *p* orbital that is directed intermediate between the *x* and *y* directions. Next, combine two different kinds of orbitals such as an *s* and a p_x. The result is an orbital which possesses characteristics of its component functions *s* and p_x.

This can be seen from the forms of the *s* and *p* orbital functions. First take the *s* orbital $s = e^{-r}$. This function is not directional: it depends solely on distance *r* from the nucleus, and is therefore spherically symmetrical. The exponential form means that the function is a maximum at the position of the nucleus and decays towards zero with increasing r without ever reaching zero. The p_x orbital function is $p = xe^{-r}$ This function too tends to zero at large distances from the nucleus, but the factor x multiplying the function means that p is proportional to x, and therefore directed along the x axis. It is positive for $x > 0$, negative for $x < 0$. The fact that it is zero at $r = 0$ means that the p function has a nodal plane running through the nucleus.

Next consider a mixing of the s and p_x orbitals in the 'hybrid' orbital *sp:*

$$\psi_{sp} = e^{-r} + xe^{-r}$$

This function also exponentially decays to zero with increasing r. Since the first term is always positive while the second is negative over a part of the x range ($x < 0$), it may be zero at some value of x when the two terms are equal and opposite. In other words it does have a node, but not at $r = 0$. The function *sp* is directed along the x axis, but the addition of the s to the positive lobe along $+x$ and to the negative lobe along $-x$ produces an *expanded* lobe along the $+x$ direction and a *contracted* one along $-x$. What we have just constructed is an *sp*-hybrid orbital that is used to describe the C–C sigma bond in the ethyne and N_2 molecules. (The other common hybrids, sp^2 and sp^3 can also be constructed by combining s and p orbital functions, but in these cases the mixing coefficients of the s and the p are unequal.)

Molecular orbitals

When a pair of atoms approach each other their electron distributions, initially spherical, become distorted because the electrons experience, not only the single nucleus they saw previously, but another nearby positively-charged nucleus and a negatively-charged electron cloud around it. The electrons respond to the new scenario by altering their original distribution so as to take in the new charged centre. The interatomic region takes on a cylindrical component that allows each electronic cloud increased access to both charged nuclei. In fact the electron distribution around such an atom — even one that has gone to the limit of forming a covalent bond — does not usually depart much from that in the free atom: the distortion from spherical symmetry is actually quite small.

If a function of a known form is slightly altered in this way, how can it then be described? The simplest method is to employ the original function, but to select a second one to be added to it, making a 'linear combination' as described above. Such a *linear combination of atomic orbitals* (LCAO) is central to molecular orbital theory. By adding a 1*s* function on hydrogen atom B to a 1*s* on hydrogen A, the result is a function which, close to either atom, is like a 1*s* (spherical). But in regions between the atoms there is a departure from spherical behaviour as the space comes under the effect of both functions.

The function $\psi = c_1\varphi_1 + c_2\varphi_2$ describes a *molecular orbital* (MO) and, like the atomic orbital functions φ_1 and φ_2, is a function of x, y and z. When plotted for example, along the H_2 molecule's interatomic axis, it shows the shape of the MO. But before this can be done we need to know what to write for the mixing coefficients (or 'LCAO' coefficients) c_1 and c_2

The significance of wave functions

Molecular orbital wave functions (MO-WFs) have the same properties as atomic orbital wave functions. They must be *normalized*, and any pair of them describing two states of the same molecule must be *orthogonal*. While a quantum state may have a well-defined energy (and other properties too) it is important to understand that although the state may be *defined* by a WF, the functions themselves have no direct physical reality. They possess a highly arbitrary nature. Sometimes you find that two rather different-looking functions describe the same physical state, and there is no point to take both of them. You cannot calculate a WF and then check it by conducting an experiment on a physical system to *measure* the wave function. The best you can do is to use the function to calculate some property that can be measured, such as

(1) electron density function $\rho(x,y,z) \equiv |\psi(x,y,z)|^2$

(2) energy (Schrödinger eqn.) $E = (\mathcal{H}\psi)/\psi$

if ψ is an eigenfunction of $\mathcal{H}$

(otherwise) $E_{approx} = \int \psi^* \mathcal{H} \psi \, d\tau$

and see if it correctly produces the correct electron density or energy.

Normalisation

It has been mentioned that when the WF is squared the resulting function $\rho(x,y,z) \equiv |\psi(x,y,z)|^2$ is the particle*'s density function*. This is a 'number density', expressing the number of particles per unit volume. When $\rho(x,y,z)$ is multiplied by the volume element $dx\,dy\,dz$ the result $|\psi(x,y,z)|^2\,dx\,dy\,dz$ (number density × volume) gives the probability of finding the particle in volume $dx\,dy\,dz$ around the point x, y, z. The probability of finding it in a *finite* volume $V \equiv V_2 - V_1$ around x, y, z is the integral $\int_{V_1}^{V_2} |\psi|^2 dV$. Now make V infinite. Then the integral $\int_0^{\infty} |\psi|^2 dV$ is the *probability of finding the particle somewhere in the whole of space*. And if our WF ψ actually really describes a particle (which is the case in our discussion so far), then this probability is just 1, so that we must have

$$\int_0^{\infty} |\psi|^2 dV = 1$$

This is the *normalisation condition* that must be obeyed by all WFs, as they describe particles that are *somewhere in space*.

A simple example of normalizing an AO wave function appears in the notes '*The quantum chemistry of atoms and small molecules*'.

Normalisation of a molecular orbital wave function

The condition that a wave function ψ is normalised is $\int_0^{\infty} |\psi|^2 d\tau = 1$. Substituting from $\psi = c_1\varphi_1 + c_2\varphi_2$ the condition is

$$1 = \int |c_1\phi_1 + c_2\phi_2|^2 d\tau = c_1^2 \int \phi_1^2 d\tau + c_2^2 \int \phi_2^2 d\tau + 2c_1c_2 \int \phi_1\phi_2 d\tau$$

where we now drop off the 0 and ∞ limits on the integrals. Since the AO WFs ϕ_1 and ϕ_2 are each normalized, the first two integrals are unity and the expression reduces to

$$1 = c_1^2 + c_2^2 + 2c_1c_2 \int \phi_1\phi_2 d\tau$$

The remaining integral depends on ϕ_1 and ϕ_2 and on the distance between the centres of the two atoms. In regions of space where both ϕ_1 and ϕ_2 are appreciable, the product $\phi_1\phi_2$ makes a large contribution to the integral $\int_0^\infty \phi_1\phi_2 d\tau$, which therefore depends on the *overlap* of functions ϕ_1 and ϕ_2. The integral

$$S = \int_0^\infty \phi_1\phi_2 d\tau$$

is thus called the **overlap integral** of AO-WFs ϕ_1 and ϕ_2. As it is a definite integral it is a numerical quantity (not a function).

The coefficients c_1 and c_2 are therefore related by the relation

$$1 = c_1^2 + c_2^2 + 2S$$

which shows that if c_1 is large, then c_2 is small and vice versa.

Molecular orbitals in the hydrogen molecule

A previous section has shown that these MOs can be written as

$$\psi = c_1\varphi_1 + c_2\varphi_2$$

The atomic orbitals φ_1 and φ_2 *could* be taken to be the 1*s* functions

$$\varphi_1 = N_1 e^{-Zr_1/a} \qquad \text{and} \qquad \varphi_2 = N_2 e^{-Zr_2/a}$$

taking account of the normalisation factors N_1 and N_2, the nuclear charge Z and scaling the distance r by dividing by the Bohr radius a. But for the present we don't need these explicit forms for φ_1 and φ_2.

Recalling that squaring a wave function produces a density function, the *squares of* the LCAO coefficients c_1 and c_2 can be interpreted as weighting factors of the respective atomic orbitals φ_1 and φ_2. But since the two sites are equivalent in the hydrogen molecule we must have that $c_1^2 = c_2^2$ and so there are two possible molecular orbital WFs for the hydrogen molecule:

$$\psi_+ = c(\varphi_1 + \varphi_2)$$

and $$\psi_- = c(\varphi_1 - \varphi_2)$$

Bearing in mind our remarks on the arbitrary nature of wave functions is there any significant difference between ψ_+ and ψ_-? Look at the plots of these functions on the next page. Although the ψ_+ function (*a*) is non-zero midway between the atomic centres, in (*b*) ψ_- does go to zero, indicating that here there is a *nodal plane* between the atoms. As the electron density $\rho_- \equiv |\psi_-|^2$ is zero on this plane, there is no negatively charged region to overcome the repulsion of the two positive nuclei. So ψ_- would be expected to describe a *high-energy condition* of the H_2 molecule. In (*a*) on the other hand the $\varphi_1\varphi_2$ term in the ρ_+ function has a maximum value half way between the nuclei. It indicates that in (*a*) the bonding MO ψ_+ is describing a negatively charged region in which the electrons provide a stabilising factor, binding the positively charged nuclei and resulting in a *low-energy condition*, i.e. stability.

We obtained the relationship $c_1 = \pm c_2$ becaue the AOs that were being combined in this example were c_1 and c_2 were chemically equivalent. What if they were not equivalent, or if there were more than just two coefficients to be calculated?

We shall write the energy of ψ as

$$E = \int \psi H \psi d\tau / \int \psi \psi d\tau$$

rather than the usual expression $E = \int \psi H \psi \, \mathrm{d}\tau$ so as to preserve the normalisation relationship between c_1 and c_2 that is implied by $\int \psi \psi d\tau = 1$.

Cross-multiplying gives

$$E \int (c_1\varphi_1 + c_2\varphi_2)^2 \, d\tau = \int (c_1\varphi_1 + c_2\varphi_2) H (c_1\varphi_1 + c_2\varphi_2) d\tau$$

$$E[c_1^2\int\varphi_1^2 \, d\tau + 2c_1c_2\int\varphi_1\varphi_2 \, d\tau + c_2^2\int\varphi_2^2 \, d\tau] = [c_1^2\int\varphi_1 H \varphi_1 \, d\tau + 2c_1c_2\int\varphi_1 H \varphi_2 \, d\tau + c_2^2\int\varphi_2 H \varphi_2 \, d\tau]$$

Recognising the normalisation of φ_1 and φ_2 and the definition of the overlap integral *S*, and using the familiar parameters α and β to denote the integrals on the right hand side of the last equation, we get

$$E(c_1^2 + 2c_1c_2S + c_2^2) = c_1^2\alpha_1 + 2c_1c_2\beta + c_2^2\alpha_2$$

Differentiate this equation partially with respect to c_1 and c_2 in turn:

$$(c_1^2 + 2c_1c_2S + c_2^2)(\partial E/\partial c_1) + 2E(c_1 + c_2S_{12}) = 2c_1\alpha_1 + 2c_2\beta$$

$$(c_1^2 + 2c_1c_2S + c_2^2)(\partial E/\partial c_2) + 2E(c_1S_{12} + c_2) = 2c_1\beta_1 + 2c_2\alpha_2$$

But since, for energy minimisation, $(\partial E/\partial c_1) = 0$ and $(\partial E/\partial c_2) = 0$, and neglecting the overlap integral *S* according to current practice, these equations become

$$c_1(\alpha_1 - E) \quad + \quad c_2\beta \quad = 0$$

$$c_1\beta \quad + \quad c_1(\alpha_2 - E) \quad = 0$$

where $\alpha_1 = \int \varphi_1 H \varphi_1 \, d\tau$, $\alpha_2 = \int \varphi_2 H \varphi_2 \, d\tau$ and $\beta = \int \varphi_1 H \varphi_2 \, d\tau$. The first two parameters have an obvious meaning: $\alpha = \int \varphi H \varphi \, d\tau$ is the *energy* of the AO φ. The last one β is the interaction energy between the AOs φ_1 and φ_2. The energy E and the coefficients c_1 and c_2 can be obtained by recognizing that the secular equations constitute linear equations whose solutions can be obtained by recognizing that the equations have a non-trivial solution only if the determinant

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{21} & \alpha_1 - E \end{vmatrix}$$

is zero. We therefore 'extract' the determinant to form an equation:

$$\begin{vmatrix} \alpha_1 - E & \beta \\ \beta & \alpha_2 - E \end{vmatrix} = 0$$

$$E^2 - E(\alpha_1 + \alpha_2) + (\alpha_1\alpha_2 - \beta^2) = 0$$

This quadratic equation in E has two roots describing the bonding (lower) and antibonding energy levels. Substituting these in turn into the secular equations provides the coefficients c_1 and c_2 of the bonding and antibonding MOs.

Back to the H_2 molecule

The variation principle provides a powerful tool for calculating the energies and wave functions of molecules. In preparation for Hückel theory (to come later) we'll suppose that the AOs φ_1 and φ_2 are chemically equivalent. Then their energies are equal and we can write $\alpha_1 = \alpha_2$ (= α). Divide all through by β, getting

$$c_1 \frac{\alpha - E}{\beta} \quad + \quad c_2 \quad = 0$$

$$c_1 \quad + \quad c_1 \frac{\alpha - E}{\beta} \quad = 0$$

and parameterize by writing $x \equiv \dfrac{\alpha - E}{\beta}$ so that the equations are

$$c_1 x \quad + \quad c_2 \quad = 0$$

$$c_1 \quad + \quad c_1 x \quad = 0$$

Then the determinantal equation is $\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$, leading to $x = \pm 1$,

$$\text{i.e.} \qquad E = \alpha + \beta \qquad \textit{lower}$$
$$E = \alpha - \beta \qquad \textit{higher}$$

Substituting for the x values in turn into the equations gives (for $x = -1$), $c_1 = c_2$ and (for $x = +1$), $c_1 = -c_2$. So the MOs and energies of the hydrogen molecule are

$$\psi_+ = c(\varphi_1 + \varphi_2) \qquad \text{and} \qquad \psi_- = c(\varphi_1 - \varphi_2)$$
$$E_+ = \alpha + \beta \qquad \text{and} \qquad E_- = \alpha - \beta$$

Normalization of the molecular orbital wave function

It's easy to do this for ψ_+ and ψ_- :

$$1 = \int \psi_+^2 \, d\tau = \int c(\varphi_1 + \varphi_2)\, c(\varphi_1 + \varphi_2)\, d\tau$$
$$1 = c^2 \left[\int \varphi_1^2 \, d\tau + \int \varphi_2^2 \, d\tau + 2\int \varphi_1 \varphi_2 \, d\tau \right]$$

Since all the wave functions like those of the AOs φ are already normalized, the first two terms are unity. The 3rd term is the overlap integral S that we neglect at this level of MO theory. So we have $1 = 2c^2$, and so $c = \frac{1}{\sqrt{2}}$. Try normalising ψ_- yourself (you'll find that the normalization factor is the same as that for ψ_+).

Final description of the molecular orbitals in the H_2 molecule

Antibonding $\quad \psi_- = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2) \qquad$ ———————— $E_- = \alpha - \beta$

Bonding $\quad \psi_+ = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2) \qquad$ ———↑↓——— $E_- = \alpha + \beta$

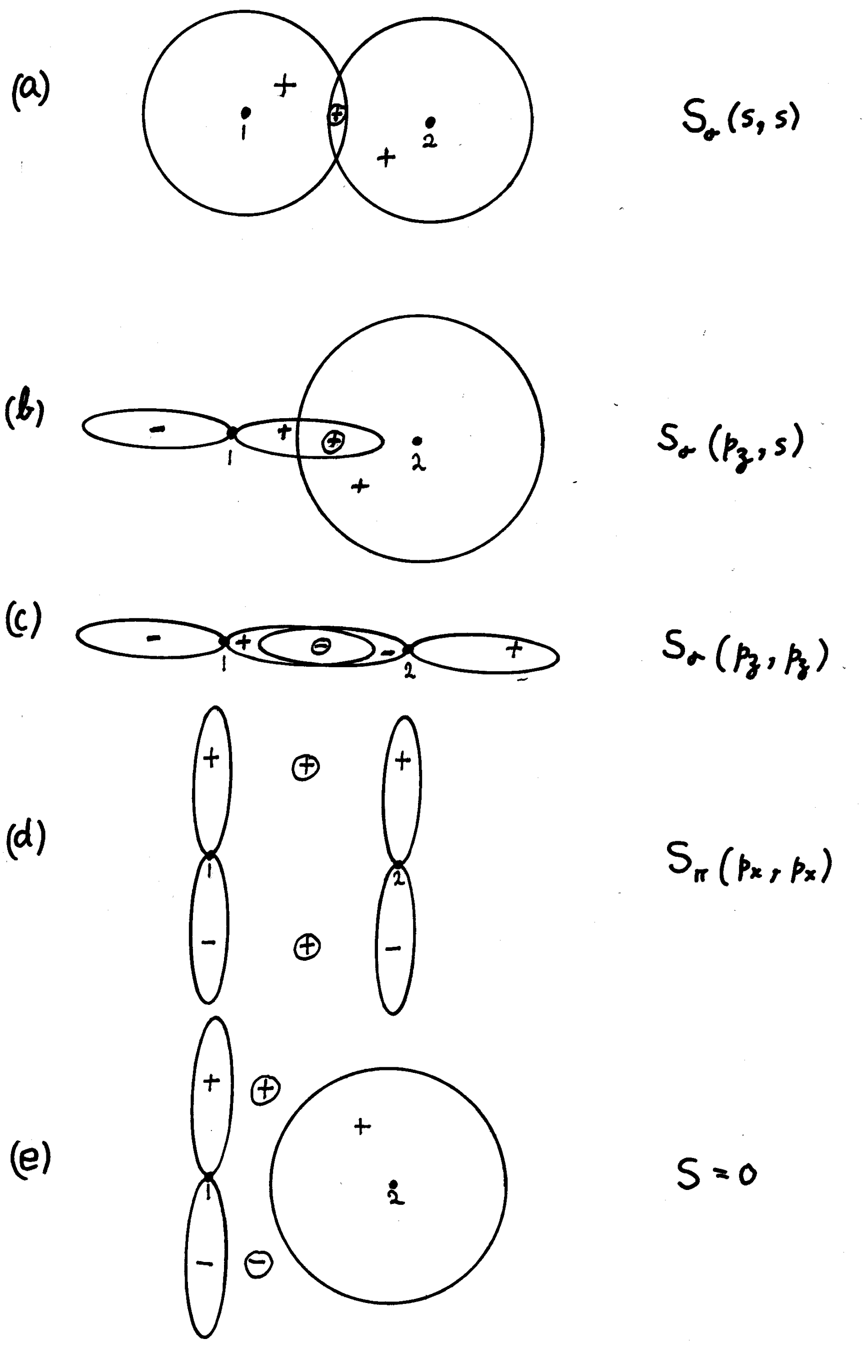
The two electrons in the H_2 molecule enter the bonding MO with paired spins.

The overlap integral – a subject of neglect

Although we neglect the overlap integral this is not because its value is negligible – it isn't – but because the results of simple MO theory are much the same whether or not S is included. And the calculations are simpler if S is neglected. So we neglect it. But having said that, it is an informative quantity because it's a measure of the degree to which the appropriate orbitals interact.

W have seen that the overlap integral for the AO functions φ_1 and φ_2 is

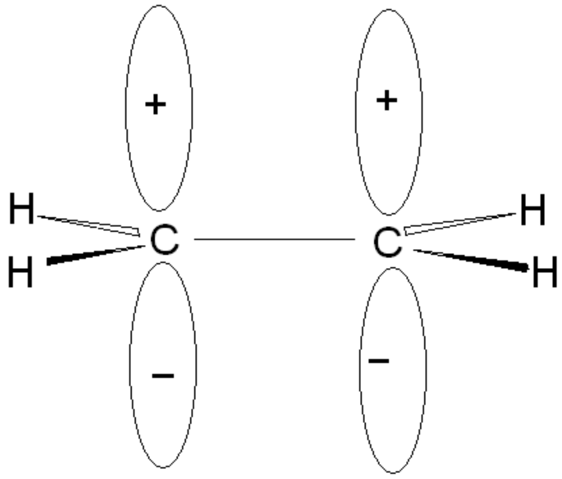
$$S_{12}=\int_0^\infty \varphi_1\varphi_2\,d\tau$$



In (a) the functions φ_1 and φ_2 are both 1*s* AO in the form $\varphi = Ne^{-Zr/a}$ as used before. Then since the integrand is everywhere positive, so also must the overlap integral S_σ be as it just sums these positive terms over the whole of space. In (b) the overlap integral is negative, but if the 2*s* were on the other 2*p* lobe it would be negative.

In (*c*) we have two p_z AOs in line with each other. The positive lobe of the one on the left overlaps with the negative lobe of the right hand AO, and so the product will be mainly negative. These contributions integrate to a negative overlap integral, $S < 0$. Sketch (*d*) shows two p_x AOs directed perpendicular to the line joining the φ_1 and φ_2 centres to form a π bond. The two positive lobes overlap as do the two negative lobes. The two terms therefore multiply to give positive products: hence $S > 0$. In the last case we have an all-positive function (an *s* AO) on the right overlapping the positive and negative lobes of p_x equally. So every positive product $\varphi_1\varphi_2$ in the integrand above the line will have a corresponding negative one below the line. The result is that these terms integrate to zero, i.e. in this case $S_{12} = 0$ and there is no interaction between these AOs.

We next introduce a method which treats only the π molecular orbitals in a molecule



Hückel π Molecular Orbital (HMO) theory

The principal effect of the computer revolution of modern times is that sophisticated calculation methods can now be performed on molecules to yield results which may compare favourably with those from experiment. So it is remarkable that an approach formulated by Erich Hückel in the 1930s still survives. Particularly when the method is based on approximations and simplifications that are so drastic that it is amazing that the method works at all! The results of the HMO are not accurate but they provide a useful description of a certain kind of molecule.

The HMO method is applied to π-electron systems. These may be aromatic hydrocarbons like benzene and naphthalene, or conjugated chains like polyenes. The molecule must be planar say in the *xy* plane, so that the principal atoms contribute electrons from their $2p_z$ AOs to the common π-electron pool.

Approximations and assumptions of the HMO theory

1. Only the π electrons and their orbitals are treated. The σ bonds are considered to be a structural framework to hold the molecule together with C–C and C–H bonds. The π molecular orbital WF is then regarded as a coating over the framework conferring the special properties associated with π delocalised molecules.

2. For interactions between pairs of carbon $2p_z$ AOs, only those between adjacent atoms are considered. There is thus only one β value — that between bonded atoms.

3. In common with many other simple molecular orbital methods, all overlap integrals $S_{ab}=\int_0^{\infty}\varphi_a\varphi_b\,d\tau$ between the $2p_z$ AOs pair φ_a and φ_b are neglected.

Examples of the applications of HMO

1. The allyl radical CH_2–CH–CH_2

As the carbon atom skeleton is $C^{(1)}$–$C^{(2)}$– $C^{(3)}$ there are three $2p$ AOs φ_1, φ_2 and φ_3 that combine to form MOs that have WFs of the form

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3$$

and we wish to determine the energies of the MOs and the coefficients c_1, c_2 and c_3.

The secular equations are

$$\begin{array}{lllllll}
c_1(\alpha - E) & + & c_2\beta & + & c_3 \times 0 & = 0 \\
c_1\beta & + & c_2(\alpha - E) & + & c_3\beta & = 0 \\
c_1 \times 0 & + & c_2\beta & + & c_3(\alpha - E) & = 0
\end{array}$$

The third term in the 1st equation iz zero. It is actually $c_3\beta_{13}$ but remember that because of the nearest-neighbour approximation the interaction parameter β_{13} between atoms 1 and 3 is zero. There is therefore only one species of interaction parameter — β_{12} and β_{23}, that we call just β. Dividing all through by β as before and parameterising $x \equiv (\alpha - E)/\beta$ we get

$$\begin{array}{lllllll}
c_1x & + & c_2 & & & = 0 \\
c_1 & + & c_2x & + & c_3 & = 0 \\
 & & c_2 & + & c_3x & = 0
\end{array}$$

which leads to the secular determinantal equation

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \qquad \text{i.e. } x(x^2 - 2) = 0$$

The three roots, $x = 0, \pm\sqrt{2}$, define the energies of the three MOs. Before examining them let us calculate the LCAO coefficients. These consist of three sets of c_1, c_2 and c_3 – one set for each MO. They can be got by substituting each x value in turn into the secular equations. Let's do it for $x = -\sqrt{2}$:

$$\begin{array}{ccccccc} -c_1\sqrt{2} & + & c_2 & & & = 0 \\ c_1 & - & c_2\sqrt{2} & + & c_3 & = 0 \\ & & c_2 & - & c_3\sqrt{2} & = 0 \end{array}$$

The first and third equation express c_1 and c_3 in terms of c_2. both are $c_2/\sqrt{2}$, which can be substituted in the second to give $c_2 - 2c_2 + c_2 = 0$, which doesn't tell us much. But from the MO WF expressed in terms of c_2 we have

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3$$

$$= \frac{c_2}{\sqrt{2}}\left(\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3\right)$$

where there is still a coefficient to determine. For this we can use the normalization condition $\int |\psi|^2 \, d\tau = 1$, giving

$$1 = \tfrac{1}{2} c_2^2 [\int\varphi_1^2 \, d\tau + 2\int\varphi_2^2 \, d\tau + \int\varphi_3^2 \, d\tau + \sqrt{2}\int\varphi_1\varphi_2 \, d\tau + \ldots]$$

But the AO-WFs φ_1, φ_2 and φ_3 are already normalized (we wouldn't use them otherwise) and cross-terms like $\int\varphi_1\varphi_2 \, d\tau$ are overlap integrals (S_{12}) that we agree to neglect. So the last equation becomes

$$1 = \tfrac{1}{2} c_2^2 [1 + 2 + 1]$$

which provides c_2. The final form of the MO-WF is therefore

$$\psi = \tfrac{1}{2}(\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3)$$

Calculate and normalize the other two MO-WFs yourself. Here are the collected results of the allyl problem:

$\psi_3 = \tfrac{1}{2}(\varphi_1 - \sqrt{2}\varphi_2 + \varphi_3)$ __________ $E_3 = \alpha - \sqrt{2}\,\beta$

$\psi_2 = ({}^{1}/_{\sqrt{2}})(\varphi_1 - \varphi_3)$ _____↑_____ $E_2 = \alpha$

$\psi_1 = \tfrac{1}{2}(\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3)$ _____↑↓____ $E_1 = \alpha + \sqrt{2}\,\beta$

The scheme shows the ground electronic state of allyl with the three π electrons occupy the three MO levels in accordance with the Pauli principle.

Example 2. Butadiene $CH_2{=}CH{-}CH{=}CH_2$

The secular equations may easily be written down by inspection in the same way as was done for the allyl radical. The secular determinantal equation is then

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

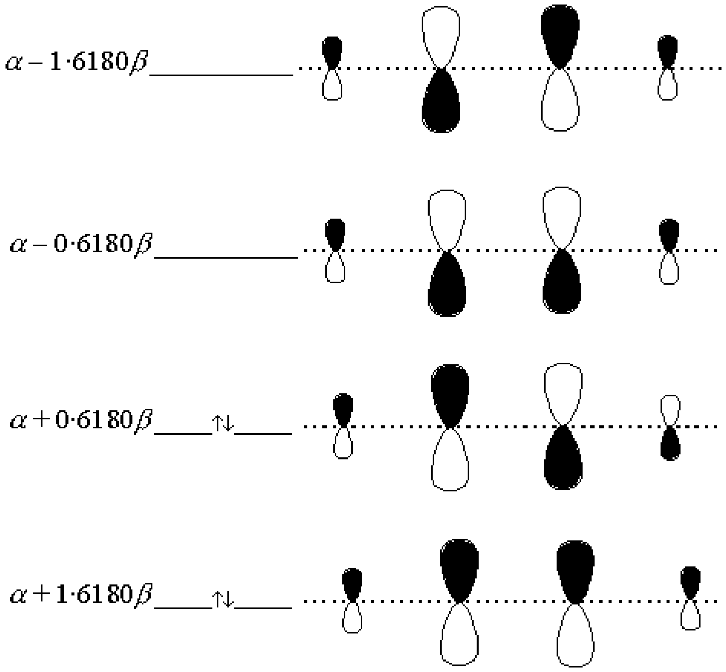
i.e. $x^4 - 3x^2 + 1 = 0$

Although it is a quartic equation it can be solved as a quadratic, yielding the four roots $x = \pm 1{\cdot}6180$ or $x = \pm 0{\cdot}6180$. Substituting these into the secular equations produces these four *sets* of the LCAO coefficients (c_1, c_2, c_3, c_4) – again, one *set* for each MO:

Energies E_i Coeffts:	c_{1i}	c_{2i}	c_{3i}	c_{4i}
$\alpha - 1{\cdot}6180\beta$	0.3717	–0.6015	0.6015	–0.3717
$\alpha - 0{\cdot}6180\beta$	0.6015	–0.3717	–0.3717	0.6015
$\alpha + 0{\cdot}6180\beta$	0.6015	0.3717	–0.3717	–0.6015
$\alpha + 1{\cdot}6180\beta$	0.3717	0.6015	0.6015	0.3717

The diagram below shows the structure of the ground electronic state butadiene with its four π electrons occupying the two lowest MOs. Referring to the amplitudes of the LCAO coefficients for the four MOs it also shows the nodal properties which are reminiscent of those for the particle confined to a line (or 1-

dimensional box). Both models agree that *the number of nodes increases with energy*.



Let us calculate the total π electron electron energy (TπEE). In the crude model that is the Hückel method you add the MO energies multiplying each with the number of electrons it contains. So for butadiene we get

$$\begin{aligned} T\pi EE &= 2(\alpha + 1{\cdot}6180\beta) + 2(\alpha + 0{\cdot}6180\beta) \\ &= 4\alpha + 4{\cdot}4720\beta \end{aligned}$$

'Resonance energy'

This brings us to another quantity that is sometimes referred to in chemistry. If the double bonds in butadiene were really localized in the 1-2 and 3-4 sites and connected by a pure single bond in 2-3 you would expect the TπEE to be just that of two ethene (C_2H_4) molecules, i.e. $2 \times (2\alpha + 2\beta)$. However rather than $4\alpha + 4\beta$ we have just seen that the energy is lower than this: it is $4\alpha + 4{\cdot}4720\beta$ (the parameter β is negative, remember). The extra stability predicted by the HMO method is a consequence of π electron delocalisation, and used to be referred to as 'resonance energy', a term that arose from resonating electron-pair structures (another theory, quite distinct from MO theory). It can be measured calorimetrically.

<u>Other examples e.g. benzene</u>

It would be nice to be able to tackle now the large number of π-conjugated molecules that we know including the aromatic hydrocarbons, and even things like DNA where the purine and pyrimidene bases in the double helix are aromatic rings. But you have seen that a molecule containing n carbon atoms leads to determinant of order *n* and therefore to a polynomial equation of order *n*. This would be too tedious to do here so I'll point out here two ways in which the problem is solved:

(a) the determinant can be input to a computer, which calculates the energies and LCAO coefficients (as well as several quantities derived from them).

(b) If the molecule possesses symmetry (chemically equivalent sites) then symmetry theory (e.g. Group Theory) can be applied.

(You'll have experience of both of these techniques in the Physical Chemistry Practical and Group Theory courses.)

It is easy to construct the secular determinant for benzene:

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

The six roots, $x = \pm 1$ (twice), ± 2 imply the following π electronic structure of benzene's ground state (the two doubly degenerate levels *could* accommodate up to four electrons):

Energy

$E_6 = \alpha - 2\beta$ ___________

$E_{5,4} = \alpha - \beta$ (2) =========

$E_{3,2} = \alpha + \beta$ (2) ==↑↓=↑↓===

$E_1 = \alpha + 2\beta$ ___↑↓_____

TπEE = $6\alpha + 8\beta$. Compared to benzene's 'non-resonating electronic structure' with three single and two double bonds [three ‘ethene molecules’ with TπEE = = $6\alpha + 6\beta$] benzene has an additional stability of $2|\beta|$. All aromatics enjoy large ‘resonance energies’.

π-electron populations at an atomic site

The condition required for the WF ψ to be normalized is that $\int_0^\infty |\psi|^2\, d\tau$ should be unity as we have seen that it corresponds to the probability that the particle described by ψ is *somewhere* in the whole of space. If ψ describes an LCAO-MO

$$\psi = c_1\varphi_1 + c_2\varphi_2 + c_3\varphi_3 + \ldots$$

this means

$$1 \equiv \int |\psi|^2\, d\tau = c_1^2\int\varphi_1^2\, d\tau + c_2^2\int\varphi_2^2\, d\tau + c_3^2\int\varphi_3^2\, d\tau + \ldots + 2c_1c_2\int\varphi_1\varphi_2\, d\tau$$

But since we are using normalized AO-WFs φ_r integrals like $\int \varphi_r^2 d\tau$ are equal to unity and as we are at the zero-overlap level terms like $2c_\mathrm{r}c_\mathrm{s}\int\varphi_\mathrm{r}\varphi_\mathrm{s}\, d\tau$ are zero. We are then left with

$$1 = c_1^2 + c_2^2 + c_3^2 + \ldots$$

which says that the probability of finding the electron in the whole of space (the left hand side) is the sum of the weighting factors $|c_r|^2$ over the various atomic sites r of the molecule. Therefore the factor $|c_r|^2$ measures the probability of finding the electron at sites r.

But this is for only one MO, whereas a molecule will have several (3 in allyl, 4 in butadiene, 6 in benzene . . .) and so we should write

$$\psi_i = c_{1i}\varphi_1 + c_{2i}\varphi_2 + c_{3i}\varphi_3 + \ldots$$

with a set of coefficients c_{1i}, c_{2i}, c_{3i}, . . . for *each* MO-WF like ψ_i. Moreover some

MOs ψ_i are occupied while others will be empty. The π-electron population ρ_r at atomic site r is proposed to be

$$\rho_r = \sum_{i=1}^{N} n_i \left|c_{ri}\right|^2$$

where n_i is the occupation number of the ith MO which is limited to the three values $n_i = 0, 1$ or 2. In order to get the net *charges* on the i^{th} atom which contributes N_i electrons to the π system, the π populations are subtracted from N_i:

$$q_i = N_i - \rho_r$$

Example: Calculate the π-electron populations and charges at the atomic sites of the allyl *anion* $[CH_2\text{-}CH\text{-}CH_2]^-$

Recall the π-electron structure of the allyl *radical*:

$\psi_3 = \frac{1}{2}(\varphi_1 - \sqrt{2}\varphi_2 + \varphi_3)$ __________ $E_3 = \alpha - \sqrt{2}\,\beta$

$\psi_2 = \sqrt{(\frac{1}{2})}(\varphi_1 - \varphi_3)$ _____↑_____ $E_2 = \alpha$

$\psi_1 = \frac{1}{2}(\varphi_1 + \sqrt{2}\varphi_2 + \varphi_3)$ _____↑↓____ $E_1 = \alpha + \sqrt{2}\,\beta$

Then for the allyl anion, in which there are two electrons in both the ψ_1 and ψ_2 MOs, the electron populations in the three atomic sites are

$$p_1 = 2 \times (\tfrac{1}{2})^2 + 2 \times (\tfrac{1}{2}) + 0 \times (\tfrac{1}{2})^2 = {}^3/_2$$

$$p_2 = 2 \times ({}^1/_{\sqrt{2}})^2 + 2 \times 0 + 0 \times ({}^1/_{\sqrt{2}})^2 \times 2 = 1$$

$$p_3 = 2 \times (\tfrac{1}{2})^2 + 2 \times (\tfrac{1}{2}) + 0 \times (\tfrac{1}{2})^2 = {}^3/_2$$

which as expected adds up to 4 — the number of π-electrons in $[CH_2\text{-}CH\text{-}CH_2]^-$. Since each C atom supplies one electron to the π system, the coulomb *charges* are obtained by subtracting these numbers from 1.0:

$$q_1 = -0{\cdot}5 \qquad q_2 = 0{\cdot}0 \qquad q_3 = -0{\cdot}5$$

These are the ‘partial atomic charges’ at the three carbon atoms, which correctly add up to −1 for the anion.

π-electron bond order

The π-bond order p_{rs} is the amount of 'double bond' character between atoms r and s. Like the π-electron population ρ_r it depends on the LCAO coefficients $\{c_{ri}\}$for the various MOs and the number of electrons populating these MOs. The π-bond order is thus defined as

$$p_{rs} = \sum_{i=1}^{N} n_i c_{ri} c_{si}$$

Example: Calculate the π-bond orders in butadiene $CH_2{=}CH{-}CH{=}CH_2$

In order to use the relation just given we recall the table of LCAO coefficients presented earlier:

Energies E_i Coeffts:	c_{1i}	c_{2i}	c_{3i}	c_{4i}
$\alpha - 1{\cdot}6180\beta$	0·3717	–0·6015	0·6015	–0·3717
$\alpha - 0{\cdot}6180\beta$	0·6015	–0·3717	–0·3717	0·6015
$\alpha + 0{\cdot}6180\beta$	0·6015	0·3717	–0·3717	–0·6015
$\alpha + 1{\cdot}6180\beta$	0·3717	0·6015	0·6015	0·3717

$\alpha - 1{\cdot}6180\beta$ __________

$\alpha - 0{\cdot}6180\beta$ __________

$\alpha + 0{\cdot}6180\beta$ _____↑↓_____

$\alpha + 1{\cdot}6180\beta$ _____↑↓_____

Then from the expression given,

$$p_{12} = 2 \times 0{\cdot}3717 \times 0{\cdot}6015 + 2 \times 0{\cdot}6015 \times 0{\cdot}3717 = 0{\cdot}8944$$

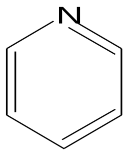
$$p_{23} = 2 \times 0{\cdot}6015 \times 0{\cdot}6015 + 2 \times 0{\cdot}3717 \times -0{\cdot}3717 = 0{\cdot}4473$$

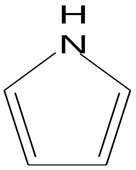
$$p_{34} = 2 \times 0{\cdot}6015 \times 0{\cdot}3717 + 2 \times -0{\cdot}3717 \times -0{\cdot}6015 = 0{\cdot}8944$$

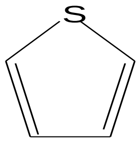
So the double bond characters of the inner and outer C–C bonds are respectively 89% and 45%.

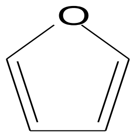
Hetero-conjugated systems

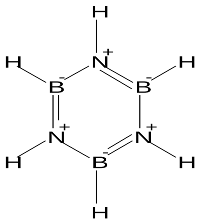
Atoms other than carbon may take part in conjugated π systems. All that is required is that the atom be a component of a planar part of the molecule and that it have an available *p* orbital directed perpendicular to the molecular plane. In


pyridine


pyrrole


thiophene


furan



molecules like pyridine, pyrrole, furan, thiophene, borazine and the carboxyl group, the atoms nitrogen, oxygen sulphur and boron fulfill these requirements, and therefore form conjugated π systems. Phosphorus may do the same. There are two ways in which these atoms may differ from carbon:

(1) whereas carbon nearly always contributes just one electron to the π system, the ‘hetero’ atoms may provide a different number — either 0, 1 or 2 depending on its number of valence electrons and on its bonding environment. For example while the nitrogen atom in pyridine contributes one π electron, in pyrrole it provides two (check it out from the Lewis bonding theory!).

(2) The electronegativity of the heteroatom will almost certainly be different from that of the carbon atom. (Oxygen and nitrogen for example are more electronegative than carbon.) Since hetero atoms would therefore be expected to influence greater (or less) attraction for the π-conjugated electrons some way is needed to describe the heteroatom’s electronegativity. This is done by assigning a different Hückel α parameter to the hetero atom compared with that of carbon. The reason for selecting α is that this quantity is defined as $\alpha = \int \varphi H \varphi \, d\tau$ which is the energy of an electron in the hetero atom’s $2p_z$ AO. If the hetero atom is more electronegative than carbon then the energy of its $2p_z$ AO (its α value) is *less* than the α of carbon. So if the hetero atom were nitrogen, for example, we *could* write something like $\alpha_N = \alpha - 0{\cdot}01$ where the first term on the right is the standard Hückel α (for carbon), showing that nitrogen α is 0·01eV lower than that of carbon. However this would require α to be expressed in eV, whereas the extraordinary beauty of Hückel theory is that it leads to

numbers without specifying any numerical values for the Hückel parameters α or β, and without having to bother with any units, either. Modifying the α parameter in a way consistent with the spirit of the theory is achieved by writing

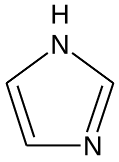
$$\alpha_X = \alpha + m_X\beta$$

where m_X is some parameter that is appropriate to the hetero atom X and α is the standard α for carbon. Since β is negative, this modification does reduce the energy of the $2p_z$ AO of the electronegative atom X as required.

Here is a brief table of *m* values culled from Lowe's *Quantum Chemistry*, where you'll find a more extensive list:

heteroatom X	m_X
N**:**	1·5
N**.**	0·5
O**:**	2·0
S	0

In order to see the procedure in action consider imidazole, which contains a nitrogen atom at position 1 that contributing one electron, and one at position 3 providing two electrons, to the π MOs:



1*H*-imidazole

Its secular determinant is

$$\begin{vmatrix} \alpha+1.5\beta-E & \beta & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 \\ 0 & \beta & \alpha+0.5\beta-E & \beta & 0 \\ 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & \beta & \alpha-E \end{vmatrix}$$

The equation for *E* is obtained by dividing throughout by β in the usual way and setting the result to zero:

$$\begin{vmatrix} x+1.5 & 1 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x+0.5 & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

which leads to 5 roots (*E* values) for the five MOs.

Some people also modify the β parameter of the bonds from X to take account of the different lengths of the C—X and C—C bonds. Other extensions specify parameters to bring CH_3 or halogen substituents into the π system. In this way it could be used to treat the nucleotide bases (these are heteroaromatic rings) in DNA. In fact the simple theory has been extended to perform calculations on molecules probably outside the scope of the method, and which would be better treated by other existing methods. Note, however, that unlike most quantum chemical techniques the method is not particularly size-limited: the π system can be quite large: if it involves *N* atoms all that is required is computational software that will solve a matrix (determinantal) equation of order *N*.