

## Appendix 3 : Normalisation of MOs and Electron Density Distribution

### (a) Normalisation of Molecular Orbitals

You should recall the probability of finding a particle at a particular point in space is proportional to the value of  $\psi^2$  at that point, where  $\psi$  is the wavefunction used to describe the properties of that particle.

For a correctly normalised wavefunction, the integral of  $\psi^2$  over all space must therefore be unity since the particle must be located somewhere in this all-encompassing region (or, to put it another way, if we consider all possible outcomes then the total probability must be equal to one). This leads to the normalisation condition, namely that:

$$\int \psi^2 .d\tau = 1 \quad [1]$$

Within the LCAO approximation, where the molecular orbital is represented as a linear combination of atomic orbitals,  $\psi = \sum c_i \phi_i$ , it therefore follows that:

$$\int (\sum c_i \phi_i)^2 .d\tau = 1 \quad [2]$$

If we set

$$\begin{aligned} \int \phi_i \phi_j .d\tau &= 1 \text{ (if } i = j) && \text{i.e. assume the atomic orbitals are normalized.} \\ \int \phi_i \phi_j .d\tau &= 0 \text{ (if } i \neq j) && \text{i.e. neglect all overlap integrals} \end{aligned}$$

then equation [2] simplifies to

$$\sum c_i^2 = 1 \quad [3]$$

which is the normally-quoted *normalisation condition* for the coefficients of a molecular orbital.

### (b) Electron Density Distribution

To quantify the partial charges on the atoms in a molecule we need to have a procedure for allocating a fraction of the electrons in a particular MO to a particular atom (remember that MOs are typically delocalised across several, or indeed many, atoms).

For a molecular orbital,  $\psi = \sum c_i \phi_i$ , containing  $n$  electrons ( $n = 0, 1$  or  $2$ ), it follows from equation [3] by simple multiplication that:

$$n \sum c_i^2 = n$$

or, to write it the other way around,

$$\text{No. of valence electrons in the MO, } n = n \sum c_i^2$$

or

$$\text{No. of valence electrons in the MO, } n = \sum n c_i^2$$

The right hand side effectively consists of a sum over all the atoms of the amount of electron density associated with this MO in the vicinity of those atoms.

i.e. No. of valence electrons in the MO,  $n = \sum q_i$

where  $q_i$  is the electron density on atom,  $i$ , due to this particular MO .

It follows therefore that the electron density,  $q_i$ , on atom,  $i$ , due to one particular MO is given by:

$$q_i = n c_i^2$$

### (c) Bond Order

To quantify the bond order,  $p_{ij}$ , between two atoms ( $i$  and  $j$ ) arising as a result of occupancy of a molecular orbital, we need a model which must meet the basic requirement that a pair of electrons shared equally between the two atoms corresponds to a single bond (i.e. it yields a bond order of one).

It is clear that for an MO wavefunction of the form  $\psi = c_1\phi_1 + c_2\phi_2$

- if there are no electrons in the MO then the bond order must be zero,
- if either coefficient is zero, then the bond order must be zero

It also seems reasonable to assume that the bond order scales directly with the number,  $n$ , of electrons in the MO, i.e.  $p_{ij} \propto n$ .

The simplest formula for calculating a bond order that meets all these requirements is

$$p_{ij} = n c_i c_j$$

where :  
 $n$  = number of electrons in the MO (i.e. 0, 1 or 2)  
 $c_i$  = coefficient of the atomic orbital on atom,  $i$ , in the molecular orbital.  
 $c_j$  = coefficient of the atomic orbital on atom,  $j$ , in the molecular orbital.

*Exercise : check that the expression given for  $p_{ij}$  above does indeed give a bond order of one for the bonding in a homonuclear diatomic where a single, symmetrical bonding MO is occupied by a pair of electrons.*