Matrices (the rules of the game!)

A Matrix is simply and array of elements… eg:

$$\mathbf{A}=\begin{pmatrix}1 & -2 & 4\\ 3 & 10 & 6\\ 1 & -9 & 41\end{pmatrix}$$

Elements can be labelled as we did for determinants..

$$\mathbf{A}=\begin{pmatrix}a_{11} & a_{12} & a_{13}\\ a_{21} & a_{22} & a_{23}\\ a_{31} & a_{32} & a_{33}\end{pmatrix}$$

To Add or Subtract Matrices

$$\mathbf{A}=\begin{pmatrix}a_{11} & a_{12} & a_{13}\\ a_{21} & a_{22} & a_{23}\\ a_{31} & a_{32} & a_{33}\end{pmatrix} \qquad \mathbf{B}=\begin{pmatrix}b_{11} & b_{12} & b_{13}\\ b_{21} & b_{22} & b_{23}\\ b_{31} & b_{32} & b_{33}\end{pmatrix}$$

$$\mathbf{C}=\mathbf{A}+\mathbf{B}=\begin{pmatrix}a_{11}+b_{11} & a_{12}+b_{12} & a_{13}+b_{13}\\ a_{21}+b_{21} & a_{22}+b_{22} & a_{23}+b_{23}\\ a_{31}+b_{31} & a_{32}+b_{32} & a_{33}+b_{33}\end{pmatrix}$$

For example

$$\begin{pmatrix}2 & 1\\ 3 & 4\end{pmatrix}+\begin{pmatrix}-3 & 1\\ 10 & -8\end{pmatrix}=\begin{pmatrix}2-3 & 1+1\\ 3+10 & 4-8\end{pmatrix}=\begin{pmatrix}-1 & 2\\ 13 & -4\end{pmatrix}$$

To Multiply Matrices (2x2)

$$\begin{pmatrix}a_{11} & a_{12}\\ a_{21} & a_{22}\end{pmatrix}\times\begin{pmatrix}b_{11} & b_{12}\\ b_{21} & b_{22}\end{pmatrix}=\begin{pmatrix}(a_{11}b_{11}+a_{12}b_{21}) & (a_{11}b_{12}+a_{12}b_{22})\\ (a_{21}b_{11}+a_{22}b_{21}) & (a_{21}b_{12}+a_{22}b_{22})\end{pmatrix}$$

For example:

$$\begin{pmatrix}2 & 3\\ -1 & 6\end{pmatrix}\times\begin{pmatrix}4 & 1\\ 3 & -2\end{pmatrix}=\begin{pmatrix}(2\times4)+(3\times3) & (2\times1)+(3\times-2)\\ (-1\times4)+(6\times3) & (-1\times1)+(6\times-2)\end{pmatrix}$$

$$=\begin{pmatrix}17 & -4\\ 14 & -19\end{pmatrix}$$

Multiply by a Number

$$3\times\begin{pmatrix}a_{11} & a_{12}\\ a_{21} & a_{22}\end{pmatrix}=\begin{pmatrix}3a_{11} & 3a_{12}\\ 3a_{21} & 3a_{22}\end{pmatrix}$$

Non Square Matrices

Eg: (2x2) x (2x1) to produce a 2x1 matrix

$$\begin{pmatrix}a_{11} & a_{12}\\ a_{21} & a_{22}\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=\begin{pmatrix}a_{11}x+a_{12}y\\ a_{21}x+a_{22}y\end{pmatrix}$$

In general you multiply an NxM by an MxL to produce an NxL result.

H_2 In Matrix Notation

$$\alpha c_A+\beta c_B=Ec_A$$
$$\beta c_A+\alpha c_B=Ec_B$$

Rewrite as:

$$\begin{pmatrix}\alpha & \beta\\ \beta & \alpha\end{pmatrix}\begin{pmatrix}c_A\\ c_B\end{pmatrix}=E\begin{pmatrix}c_A\\ c_B\end{pmatrix}$$

Or:

$$\begin{pmatrix}\alpha-E & \beta\\ \beta & \alpha-E\end{pmatrix}\begin{pmatrix}c_A\\ c_B\end{pmatrix}=0$$

Has Solutions When:

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

For a bigger molecule

4 identical atoms generates a 4x4 problem

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

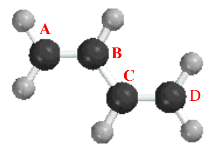
This terms computational labs will involve calculations of atoms based on these ideas.

(also: 3rd year QM lectures)

Butadiene (s-trans 1,3-)

Consider the π-system only

$$\alpha = \int \chi_A H \chi_A dr = \int \chi_B H \chi_B dr = \int \chi_C H \chi_C dr = \int \chi_D H \chi_D dr$$
$$\beta = \int \chi_A H \chi_B dr = \int \chi_B H \chi_C dr = \int \chi_C H \chi_D dr$$



$$\begin{array}{c} \\ A \\ B \\ C \\ D \end{array}\begin{array}{c} \begin{array}{cccc} A & B & C & D \end{array} \\ \begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \end{array}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

$$\begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

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

Simplify the notation…

Divide by β

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 1 & 0 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - E}{\beta} & 1 \\ 0 & 0 & 1 & \frac{\alpha - E}{\beta} \end{vmatrix} = 0$$

Let x = (α-E)/β

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

Compute the determinant

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

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

$$= x\{x(x^2 - 1) - 1(x - 0)\} - 1\{1(x^2 - 1) - 1(0 - 0\}$$

$$= x(x^3 - x - x) - 1(x^2 - 1)$$

$$= x^4 - 3x^2 + 1 = 0$$

Solve the root finding problem…

$$x^4 - 3x^2 + 1 = 0$$

Which is, in effect, a quadratic equ; let $z = x^2$

$$z^2 - 3z + 1 = 0$$

The solutions of which are;

$$z = \frac{3 \pm \sqrt{3^2 - 4(1 \times 1)}}{2 \times 1} = \frac{3 \pm \sqrt{5}}{2}$$
$$= 2.62 \text{ or } 0.38$$

Four solutions for x

$x = \pm\sqrt{z}$

Therefore

$x = \pm\sqrt{2.62} = \pm 1.62$ or

$x = \pm\sqrt{0.38} = \pm 0.62$

and

$$x = \frac{(\alpha - E)}{\beta}$$

so....

Four energy levels

Remember that both α and β are negative energies so the four energy levels in order of increasing energy are;

$$E_1 = \alpha + 1.62\beta$$
$$E_2 = \alpha + 0.62\beta$$
$$E_3 = \alpha - 0.62\beta$$
$$E_4 = \alpha - 1.62\beta$$

The Wavefunction Coefficients

Substitute each of the energies back into our original equ. to find c_1,c_2,c_3,c_4 for each MO

$$\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}$$

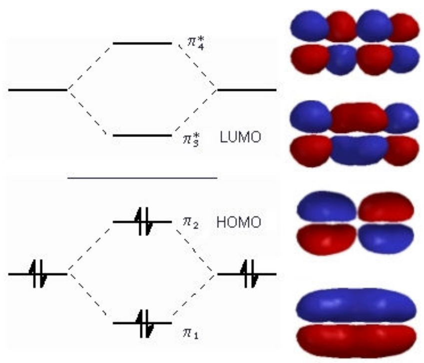
$\pi_1 = 0.37 p_z^A + 0.60 p_z^B + 0.60 p_z^C + 0.37 p_z^D$ $E_1 = \alpha + 1.62\beta$

$\pi_2 = 0.60 p_z^A + 0.37 p_z^B - 0.37 p_z^C - 0.60 p_z^D$ $E_2 = \alpha + 0.62\beta$

$\pi_3^* = 0.60 p_z^A - 0.37 p_z^B - 0.37 p_z^C + 0.60 p_z^D$ $E_3 = \alpha - 0.62\beta$

$\pi_4^* = 0.37 p_z^A - 0.60 p_z^B + 0.60 p_z^C - 0.37 p_z^D$ $E_4 = \alpha - 1.62\beta$

The Energy Levels and Wavefunctions



Delocalisation Energy

The bonding energy is simply the sum of energies of the four electrons in π_1 and π_2.

$$E_{but} = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta)$$

Ethylene: just like H_2 and E_1= (α+β)

$$E_{ethylene} = 2(\alpha + \beta)$$

$$E_{delocalisation} = E_{but} - 2 \times E_{ethylene} = 0.47\beta$$

β ~ -75kJ/mol :

Delocalisation energy ~ -35 kJ/mol