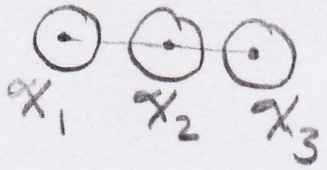
1 a) secular equations:



recall $S_{\mu\mu} = 1$
$S_{\mu\nu} = S_{\nu\mu}$
$H_{\mu\nu} = H_{\nu\mu}$

$$(H_{11} - e_i)c_{1i} + (H_{12} - e_i S_{12})c_{2i} + (H_{13} - e_i S_{13})c_{3i} = 0$$
$$(H_{12} - e_i S_{12})c_{1i} + (H_{22} - e_i)c_{2i} + (H_{23} - e_i S_{23})c_{3i} = 0$$
$$(H_{13} - e_i S_{13})c_{1i} + (H_{23} - e_i S_{23})c_{2i} + (H_{33} - e_i)c_{3i} = 0$$

since these are all hydrogen atoms $H_{11} = H_{22} = H_{33}$ therefore,

$$(H_{11} - e_i)c_{1i} + (H_{12} - e_i S_{12})c_{2i} + (H_{13} - e_i S_{13})c_{3i} = 0$$
$$(H_{12} - e_i S_{12})c_{1i} + (H_{11} - e_i)c_{2i} + (H_{23} - e_i S_{23})c_{3i} = 0$$
$$(H_{13} - e_i S_{13})c_{1i} + (H_{23} - e_i S_{23})c_{2i} + (H_{11} - e_i)c_{3i} = 0$$

secular determinant:

$$\begin{vmatrix} H_{11} - e_i & H_{12} - e_i S_{12} & H_{13} - e_i S_{13} \\ H_{12} - e_i S_{12} & H_{11} - e_i & H_{23} - e_i S_{23} \\ H_{13} - e_i S_{13} & H_{23} - e_i S_{23} & H_{11} - e_i \end{vmatrix} = 0$$

b) if $r_{12} = r_{23}$ then $H_{12} = H_{23}$ and $S_{12} = S_{23}$

and the secular determinant from a) becomes:

$$\begin{vmatrix} H_{11}-e_i & H_{12}-e_iS_{12} & H_{13}-e_iS_{13} \\ H_{12}-e_iS_{12} & H_{11}-e_i & H_{12}-e_iS_{12} \\ H_{13}-e_iS_{13} & H_{12}-e_iS_{12} & H_{11}-e_i \end{vmatrix} = 0$$

c) If r_{13} is very long then $S_{13} \to 0$ and $H_{13} \to 0$, therefore:

$$\begin{vmatrix} H_{11}-e_i & H_{12}-e_iS_{12} & 0 \\ H_{12}-e_iS_{12} & H_{11}-e_i & H_{12}-e_iS_{12} \\ 0 & H_{12}-e_iS_{12} & H_{11}-e_i \end{vmatrix} = 0$$

<u>note</u>: the form of this secular determinant can now be easily solved since it contains two 2×2 determinants.

d) $e_1 = -33.657$ eV
$e_2 = -13.600$ eV ← rigorously nonbonding!
$e_3 = 6.457$ eV

ψ_1: $c_{11} = c_{31} = 0.500$ $\quad c_{21} = 0.707$
ψ_2: $c_{12} = 0.707$ $\quad c_{32} = -0.707$ $\quad c_{22} = 0.000$
ψ_3: $c_{13} = c_{33} = -0.500$ $\quad c_{23} = 0.707$

The parameters, H_{12} and S_{12} come from using an STO for H and the Wolfsberg-Helmholtz approximation – Eq (1.19). The solution here is equivalent to doing a Hückel calculation (discussed in Section 12.2). Notice that the bonding MO, ψ_1, is stabilized as much as the antibonding MO, ψ_3, is destabilized using this approximation.

e). since $r_{12} = r_{23} = r_{13}$ then $H_{12} = H_{23} = H_{13}$ & $S_{12} = S_{23} = S_{13}$

secular equations:

$$(H_{11} - e_i)C_{1i} + (H_{12} - e_i S_{12})C_{2i} + (H_{12} - e_i S_{12})C_{3i} = 0$$
$$(H_{12} - e_i S_{12})C_{1i} + (H_{11} - e_i)C_{2i} + (H_{12} - e_i S_{12})C_{3i} = 0$$
$$(H_{12} - e_i S_{12})C_{1i} + (H_{12} - e_i S_{12})C_{1i} + (H_{11} - e_i)C_{3i} = 0$$

secular determinant

$$\begin{vmatrix} H_{11} - e_i & H_{12} - e_i S_{12} & H_{12} - e_i S_{12} \\ H_{12} - e_i S_{12} & H_{11} - e_i & H_{12} - e_i S_{12} \\ H_{12} - e_i S_{12} & H_{12} - e_i S_{12} & H_{11} - e_i \end{vmatrix} = 0$$

$e_1 = -41.964$ eV

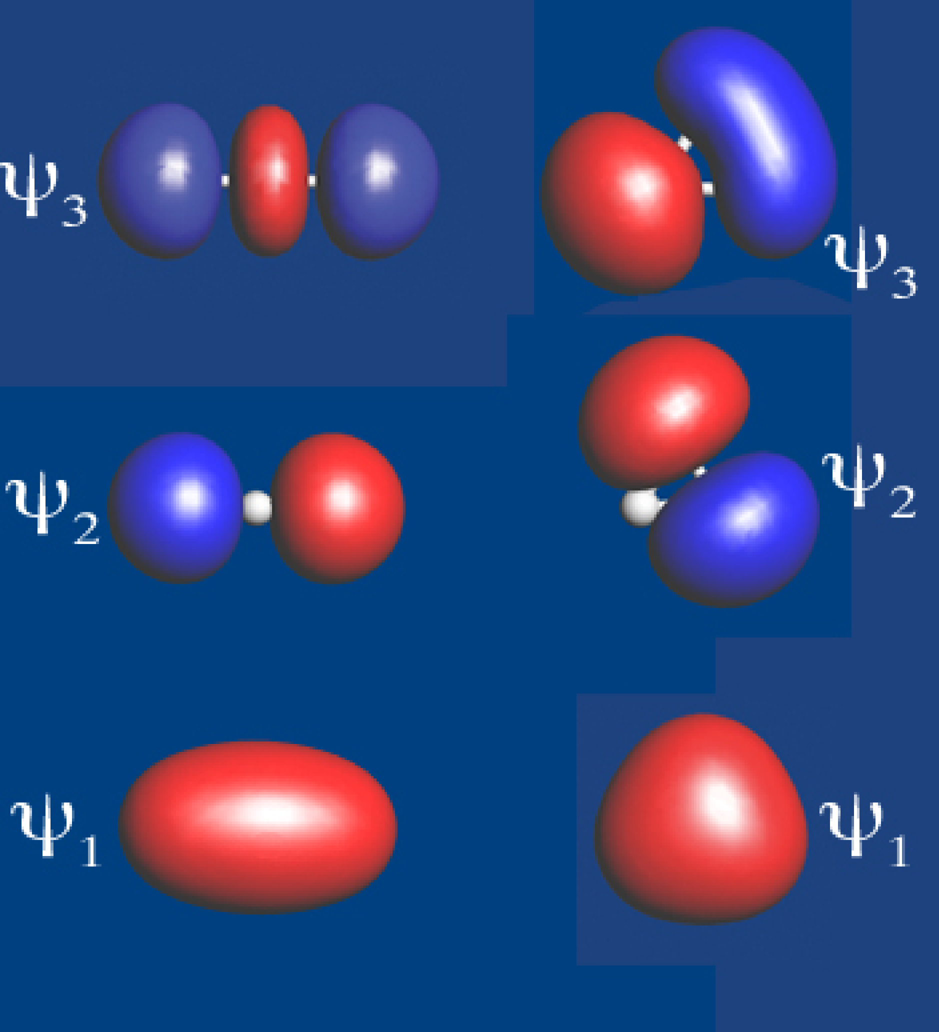
$e_2 = e_3 = 0.582$ eV

ψ_1: $c_{11} = c_{21} = c_{31} = 0.577$

ψ_2: $c_{12} = 0.707$ $c_{22} = -0.707$ $c_{32} = 0.000$

ψ_3: $c_{13} = c_{23} = -0.408$ $c_{33} = 0.817$

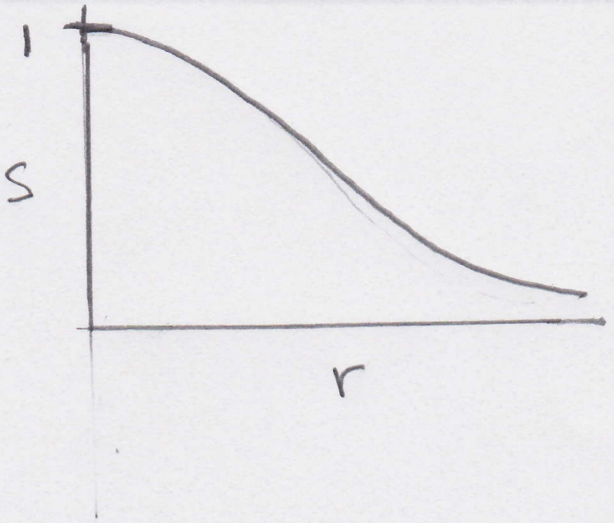
Notice that ψ_2 & ψ_3 are degenerate. We will see the pattern of fullybonding, nonbonding, antibonding for linear combinations and that just derived for many triangular combinations. A picture of both sets is shown at the end of the problem.



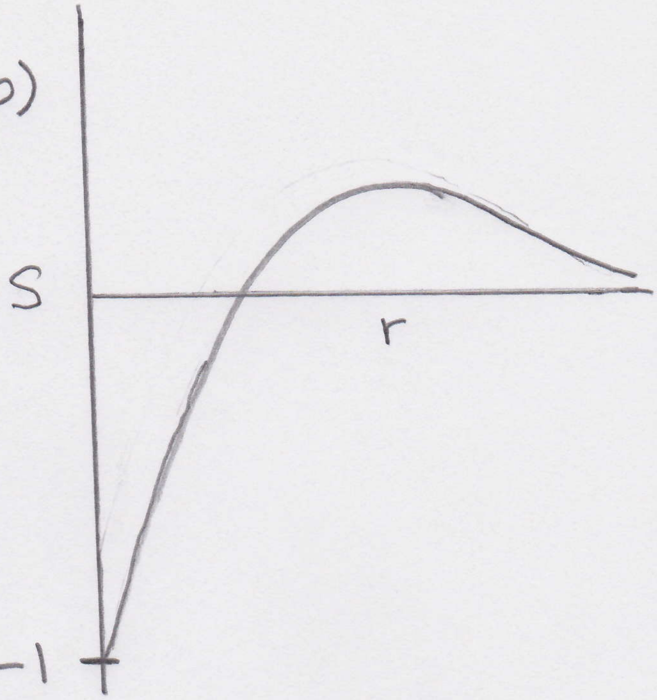
ψ_3
ψ_3
ψ_2
ψ_2
ψ_1
ψ_1

2.

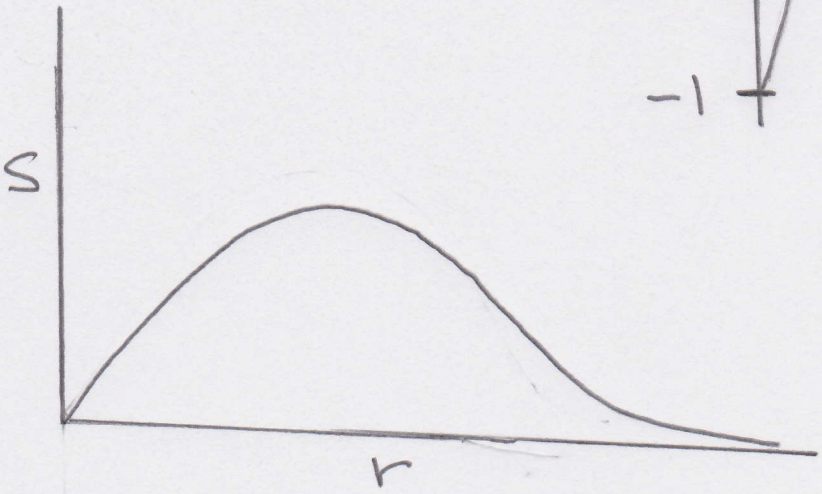
a)



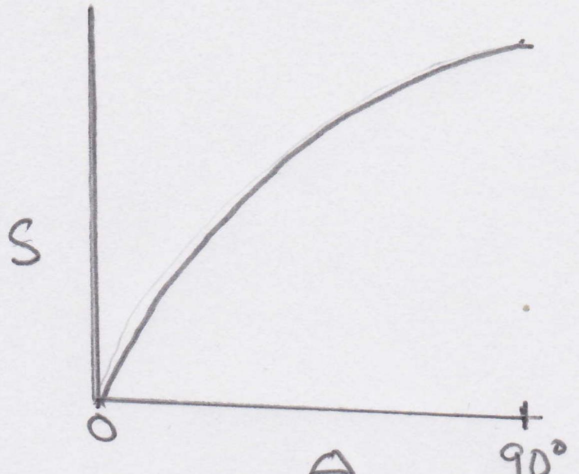
b)

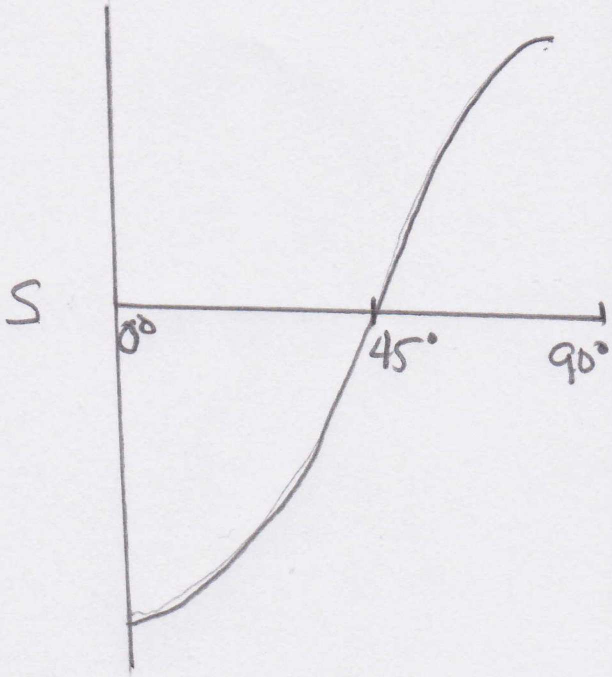


c)



d)





3. (a) **HC** = **SCe**

(b) $\widetilde{\mathbf{H}} = \begin{pmatrix} e_1 & 0 \\ 0 & e_2 \end{pmatrix}$, $\widetilde{\mathbf{S}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

(c) Diagonalization