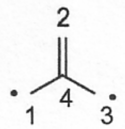
level of expectation for exam

Sols to

Chem 131/231A // problem set 14

not for exam purposes, just to learn how.

1. Set up and solve the secular determinant for trimethylenemethane; it's illustrated below. Use the atom numbering system indicated by the drawing.



2. For the allyl anion:
   Set up and solve the secular determinant for the eigenvalues.
   Set up the secular equations. Use the eigenvalues to determine the relationships between the AO-coefficients for each MO.
   Normalize each MO eigenfunction. [Normalized functions satisfy the condition: $<\psi_i|\psi_i> = 1$]

1.

$$0 = \begin{array}{c|cccc|} & 1 & 2 & 3 & 4 \\ 1 & x & 0 & 0 & 1 \\ 2 & 0 & x & 0 & 1 \\ 3 & 0 & 0 & x & 1 \\ 4 & 1 & 1 & 1 & x \end{array} = 0$$

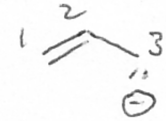
$$= x\begin{vmatrix} x & 0 & 1 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} - 1\begin{vmatrix} 0 & x & 0 \\ 0 & 0 & x \\ 1 & 1 & 1 \end{vmatrix}$$

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

$$= x^4 - 3x^2 = x^2(x^2 - 3) = 0$$

$$\boxed{\begin{aligned} &\therefore x = 0; 0 \Rightarrow E' = \alpha = E'' \text{ (NBMO's)} \\ &\text{\& } x = \pm\sqrt{3} \Rightarrow E''' = \alpha + \sqrt{3}\beta \text{ (BMO)} \\ &\qquad \text{\& } E'''' \ \alpha - \sqrt{3}\beta \text{ (ABMO)} \end{aligned}}$$

2.



$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = x^3 - 2x$$

$$= x(x^2 - 2) = 0$$

$\therefore$ $x = 0 \Rightarrow E = \alpha$ (NBMO)

& $x = \pm\sqrt{2}$

$\Rightarrow$ eigenvalues of

$\alpha + \sqrt{2}\beta$ (BMO)

& $\alpha - \sqrt{2}\beta$ (ABMO)

$$\left.\begin{aligned} c_1x + c_2 &= 0 \\ c_1 + c_2x + c_3 &= 0 \\ c_3x + c_2 &= 0 \end{aligned}\right\} \text{Sec. eqs.}$$

For: $\underline{x = 0}$

$c_2 = 0$

$c_1 = -c_3$

$\underline{x = -\sqrt{2}}$

$-\sqrt{2}c_1 = -c_2$

or $\sqrt{2}c_1 = c_2$

Also, $-\sqrt{2}c_3 = \cancel{x}\ c_2$

or $\sqrt{2}c_3 = c_2$

$\therefore$ $c_2 = \sqrt{2}c_1 = \sqrt{2}c_3$. $\therefore$ $c_1 = c_3$

Similarly, $\underline{\text{when } x = \sqrt{2}}$

$c_1 = c_3$ & $c_2 = -\sqrt{2}c_1 = -\sqrt{2}c_3$

(Cont'd)

Thus, when $x = 0$ (the NBMO) $c_1 = -c_3$. Let $c_1 = 1$. Then $c_3 = -1$ & $\psi_2 = \chi_1 - \chi_3$ ← un normalized

when $x = -\sqrt{2}$ (the BMO)

$c_1 = c_3$; $c_2 = \sqrt{2}\, c_1$. Let $c_1 = 1$.

Then $c_3 = c_1 = 1$ & $c_2 = \sqrt{2}$

$$\therefore \psi_1^u = (\chi_1 + \sqrt{2}\,\chi_2 + \chi_3)$$

Finally, when $x = \sqrt{2}$ (the ABMO)

$$\psi_3^u = (\chi_1 - \sqrt{2}\,\chi_2 + \chi_3)$$

Each ψ is un normalized. The normalized functions are:

$$\psi_1 = \frac{1}{2}(\chi_1 + \sqrt{2}\,\chi_2 + \chi_3)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_3)$$

and $$\psi_3 = \frac{1}{2}(\chi_1 - \sqrt{2}\,\chi_2 + \chi_3)$$