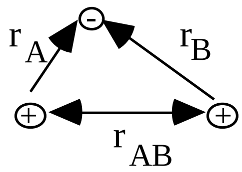
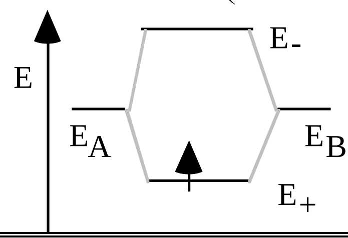
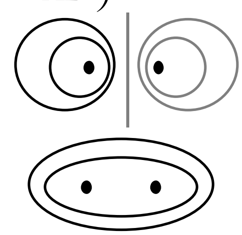
Hydrogen Molecule Ion- Variation Theory



$$\frac{-\hbar^2}{2m}\nabla^2\Psi + \frac{e^2}{4\pi\varepsilon_o}\left(-\frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{r_{AB}}\right)\Psi = E\,\Psi$$





$\Psi_{MO} = c_A\Psi_A + c_B\Psi_B$ ground state: $\Psi_A = 1s_A$, $\Psi_B = 1s_B$

$$E = \frac{\int \Psi_{MO}^* \, H \, \Psi_{MO} \, d\tau}{\int \Psi_{MO}^2 \, d\tau}$$

$$E = \frac{\int (c_A\Psi_A + c_B\Psi_B)^* \, H \, (c_A\Psi_A + c_B\Psi_B) \, d\tau}{\int (c_A\Psi_A + c_B\Psi_B)^2 \, d\tau}$$

$$E = \frac{c_A^2 \int \Psi_A^* \, H \, \Psi_A \, d\tau + c_B^2 \int \Psi_B^* \, H \, \Psi_B \, d\tau + 2\, c_A c_B \int \Psi_A^* \, H \, \Psi_B \, d\tau}{c_A^2 \int \Psi_A^2 \, d\tau + c_B^2 \int \Psi_B^2 \, d\tau + 2\, c_A c_B \int \Psi_A \Psi_B d\tau}$$

$H_{AA} = \int \Psi_A^* \, H \, \Psi_A \, d\tau$ Coulomb Integral $\approx E_A$ (single electron atom A)

$H_{AB} = \int \Psi_A^* \, H \, \Psi_B \, d\tau$ Resonance Integral

$S_{AA} = \int \Psi_A^2 \, d\tau$ Atomic Normalization

$S_{AB} = \int \Psi_A \Psi_B d\tau$ Overlap Integral

$$E = \frac{c_A^2 H_{AA} + c_B^2 H_{BB} + 2\, c_A c_B H_{AB}}{c_A^2 S_{AA} + c_B^2 S_{BB} + 2\, c_A c_B S_{AB}} = \frac{N}{D}$$

$$\left(\frac{\partial E}{\partial C_A}\right)_{C_B} = 0 = [2c_A H_{AA} + 2c_B H_{AB}]D - [2c_A S_{AA} + 2c_B S_{AB}]N$$

$$0 = 2c_A H_{AA} + 2c_B H_{AB} - E\,[2c_A S_{AA} + 2c_B S_{AB}]$$

$$0 = c_A H_{AA} + c_B H_{AB} - E\,[c_A S_{AA} + c_B S_{AB}]$$

$$\left(\frac{\partial E}{\partial C_A}\right)_{C_B} = 0 = c_A H_{AA} + c_B H_{AB} - E\,[c_A S_{AA} + c_B S_{AB}]$$

$$\left(\frac{\partial E}{\partial C_B}\right)_{C_A} = 0 = c_B H_{BB} + c_A H_{AB} - E\,[c_B S_{BB} + c_A S_{AB}]$$

$$c_A(H_{AA} - E\,S_{AA}) + c_B(H_{AB} - E\,S_{AB}) = 0$$
$$c_A(H_{AB} - E\,S_{AB}) + c_B(H_{BB} - E\,S_{BB}) = 0$$

$$\begin{vmatrix} H_{AA} - E\,S_{AA} & H_{AB} - E\,S_{AB} \\ H_{AB} - E\,S_{AB} & H_{BB} - E\,S_{BB} \end{vmatrix} = 0$$

$Ax + By = 0$
$Cx + Dy = 0$

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} = AD - BC = 0$$

Example: $4x + 8y = 0$, $2x + 4y = 0$

$$\begin{vmatrix} 4 & 8 \\ 2 & 4 \end{vmatrix} = 4*4 - 2*8 = 0$$

$$(H_{AA} - E\,S_{AA})(H_{BB} - E\,S_{BB}) - (H_{AB} - E\,S_{AB})^2 = 0$$

<u>Homonuclear:</u> $H_{AA} = H_{BB}$ $\qquad H_{AA} - E = \pm(H_{AB} - E\,S)$

$$E_+ = \frac{H_{AA} + H_{AB}}{1 + S} \qquad E_- = \frac{H_{AA} - H_{AB}}{1 - S}$$

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prove for next homework by substituting E_+ and secondly E_- into Secular Equations:

$c_A = c_B$ for E_+ and $c_A = -c_B$ for E_-

$c_A = c_B = c_+$ $\qquad \Psi_+ = c_+(\Psi_A + \Psi_B)$

$c_A = -c_B = c_-$ $\qquad \Psi_- = c_-(\Psi_A - \Psi_B)$

$$\int \Psi_+^2\, d\tau = 1 = c_+^2 \left[\int \Psi_A^2\, d\tau + 2 \int \Psi_A \Psi_B\, d\tau + \int \Psi_B^2\, d\tau \right]$$
$$1 = c_+^2 \left[1 + 2S + 1 \right]$$

$$c_+ = \frac{1}{\sqrt{2+2\,S}} \qquad c_- = \frac{1}{\sqrt{2-2\,S}}$$