



NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
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Lecture 12: Variational Method in Chemical Bonding - I

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\hat{H} = \sum_{A=1}^2 -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^2 \left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^2 \frac{1}{r_{iA}} \right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

Overlap Integrals

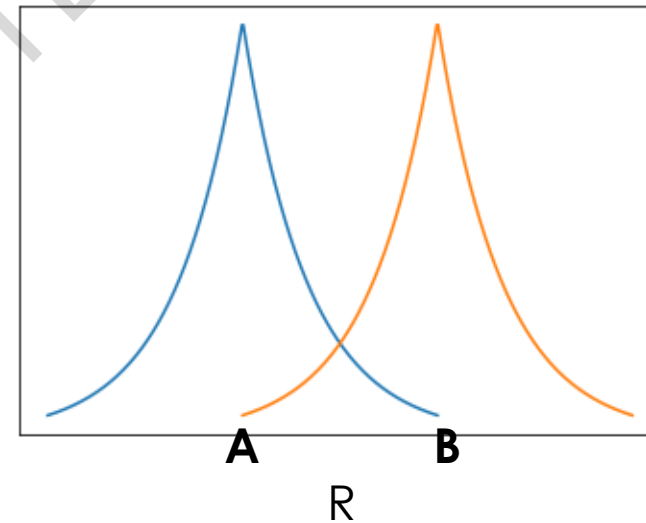
$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{aligned} S_{11} &= \langle 1s_A(1)1s_B(2) | 1s_A(1)1s_B(2) \rangle \\ &= \int 1s_A^*(1)1s_A(1) dr_1 \int 1s_B^*(2)1s_B(2) dr_2 \\ &= 1 = S_{22} \end{aligned}$$

$$\begin{aligned} S_{12} &= \langle 1s_A(1)1s_B(2) | 1s_A(2)1s_B(1) \rangle \\ &= \int 1s_A^*(1)1s_B(1) dr_1 \int 1s_B^*(2)1s_A(2) dr_2 \\ &= S^2 = S_{21} \end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\begin{aligned}\phi_1 &= 1s_A(1)1s_B(2) \\ \phi_2 &= 1s_A(2)1s_B(1) \\ \phi &= c_1\phi_1 + c_2\phi_2\end{aligned}$$

Energy Integrals

$$\begin{aligned}\hat{H} &= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \\ &= \hat{h}_1 + \hat{h}_2 + \hat{h}'\end{aligned}$$

$$\hat{h}_1 1s_A(1) = -0.5 1s_A(1)$$

$$\hat{h}_2 1s_B(2) = -0.5 1s_B(2)$$

$$\begin{aligned}H_{11} &= \left\langle 1s_A(1)1s_B(2) \left| \hat{h}_1 + \hat{h}_2 + \hat{h}' \right| 1s_A(1)1s_B(2) \right\rangle \\ &= -0.5 \langle 1s_B(2) | 1s_B(2) \rangle - 0.5 \langle 1s_A(1) | 1s_A(1) \rangle \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(1)1s_B(2) dr_1 dr_2 \\ &= -1 + \int 1s_A^*(1) \left(-\frac{1}{r_{1B}} \right) 1s_A(1) dr_1 + \int 1s_B^*(2) \left(-\frac{1}{r_{2A}} \right) 1s_B(2) dr_2 \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} \right) 1s_A(1)1s_B(2) dr_1 dr_2 + \left(\frac{1}{R_{AB}} \right) = -1 + J = H_{22}\end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\begin{aligned}\phi_1 &= 1s_A(1)1s_B(2) \\ \phi_2 &= 1s_A(2)1s_B(1) \\ \phi &= c_1\phi_1 + c_2\phi_2\end{aligned}$$

Energy Integrals

$$\begin{aligned}\hat{H} &= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \\ &= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1B}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2A}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \\ &= \hat{h}_1 + \hat{h}_2 + \hat{h}'\end{aligned}$$

$$\begin{aligned}\hat{h}_1 1s_B(1) &= -0.5 1s_B(1) \\ \hat{h}_2 1s_A(2) &= -0.5 1s_A(2)\end{aligned}$$

$$\begin{aligned}H_{12} &= \left\langle 1s_A(1)1s_B(2) \left| \hat{h}_1 + \hat{h}_2 + \hat{h}' \right| 1s_A(2)1s_B(1) \right\rangle \\ &= -0.5 \langle 1s_A(1) | 1s_B(1) \rangle \langle 1s_B(2) | 1s_A(2) \rangle - 0.5 \langle 1s_B(2) | 1s_A(2) \rangle \langle 1s_A(1) | 1s_B(1) \rangle \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(2)1s_B(1) dr_1 dr_2 \\ &= -S^2 + \int 1s_A^*(1) \left(-\frac{1}{r_{1A}} \right) 1s_B(1) dr_1 \int 1s_B^*(2)1s_A(2) dr_2 \\ &\quad + \int 1s_B^*(2) \left(-\frac{1}{r_{2B}} \right) 1s_A(2) dr_2 \int 1s_A^*(1)1s_B(1) dr_1 \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(2)1s_B(1) dr_1 dr_2 = -S^2 + K = H_{21}\end{aligned}$$





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Approximate Methods in Quantum Chemistry

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Lecture 13: Variational Method in Chemical Bonding - II

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

$$\hat{H} = \sum_{A=1}^2 -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^2 \left(-\frac{\nabla_i^2}{2} - \sum_{A=1}^2 \frac{1}{r_{iA}} \right) + \frac{1}{r_{12}} + \frac{1}{R_{AB}}$$

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2

Overlap Integrals

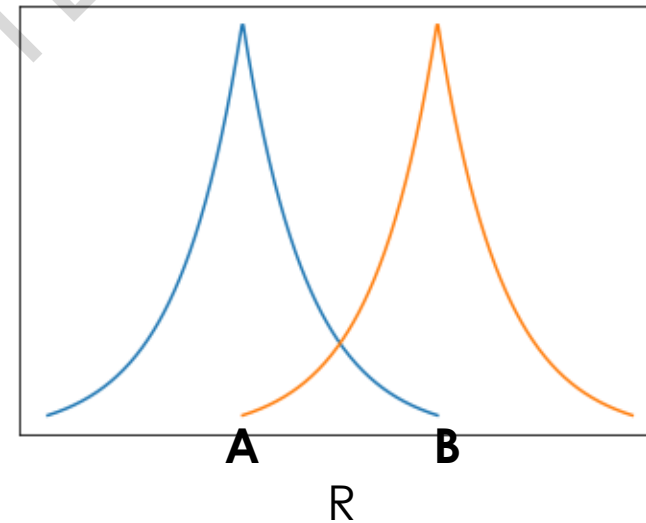
$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{aligned} S_{11} &= \langle 1s_A(1)1s_B(2) | 1s_A(1)1s_B(2) \rangle \\ &= \int 1s_A^*(1)1s_A(1) dr_1 \int 1s_B^*(2)1s_B(2) dr_2 \\ &= 1 = S_{22} \end{aligned}$$

$$\begin{aligned} S_{12} &= \langle 1s_A(1)1s_B(2) | 1s_A(2)1s_B(1) \rangle \\ &= \int 1s_A^*(1)1s_B(1) dr_1 \int 1s_B^*(2)1s_A(2) dr_2 \\ &= S^2 = S_{21} \end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\begin{aligned}\phi_1 &= 1s_A(1)1s_B(2) \\ \phi_2 &= 1s_A(2)1s_B(1) \\ \phi &= c_1\phi_1 + c_2\phi_2\end{aligned}$$

Energy Integrals

$$\begin{aligned}\hat{H} &= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \\ &= \hat{h}_1 + \hat{h}_2 + \hat{h}'\end{aligned}$$

$$\hat{h}_1 1s_A(1) = -0.5 1s_A(1)$$

$$\hat{h}_2 1s_B(2) = -0.5 1s_B(2)$$

$$\begin{aligned}H_{11} &= \left\langle 1s_A(1)1s_B(2) \left| \hat{h}_1 + \hat{h}_2 + \hat{h}' \right| 1s_A(1)1s_B(2) \right\rangle \\ &= -0.5 \langle 1s_B(2) | 1s_B(2) \rangle - 0.5 \langle 1s_A(1) | 1s_A(1) \rangle \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(1)1s_B(2) dr_1 dr_2 \\ &= -1 + \int 1s_A^*(1) \left(-\frac{1}{r_{1B}} \right) 1s_A(1) dr_1 + \int 1s_B^*(2) \left(-\frac{1}{r_{2A}} \right) 1s_B(2) dr_2 \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} \right) 1s_A(1)1s_B(2) dr_1 dr_2 + \left(\frac{1}{R_{AB}} \right) = -1 + J = H_{22}\end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\begin{aligned}\phi_1 &= 1s_A(1)1s_B(2) \\ \phi_2 &= 1s_A(2)1s_B(1) \\ \phi &= c_1\phi_1 + c_2\phi_2\end{aligned}$$

Energy Integrals

$$\begin{aligned}\hat{H} &= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1A}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2B}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \\ &= -\frac{\nabla_1^2}{2} - \frac{1}{r_{1B}} - \frac{\nabla_2^2}{2} - \frac{1}{r_{2A}} - \frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \\ &= \hat{h}_1 + \hat{h}_2 + \hat{h}'\end{aligned}$$

$$\begin{aligned}\hat{h}_1 1s_B(1) &= -0.5 1s_B(1) \\ \hat{h}_2 1s_A(2) &= -0.5 1s_A(2)\end{aligned}$$

$$\begin{aligned}H_{12} &= \left\langle 1s_A(1)1s_B(2) \left| \hat{h}_1 + \hat{h}_2 + \hat{h}' \right| 1s_A(2)1s_B(1) \right\rangle \\ &= -0.5 \langle 1s_A(1) | 1s_B(1) \rangle \langle 1s_B(2) | 1s_A(2) \rangle - 0.5 \langle 1s_B(2) | 1s_A(2) \rangle \langle 1s_A(1) | 1s_B(1) \rangle \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(2)1s_B(1) dr_1 dr_2 \\ &= -S^2 + \int 1s_A^*(1) \left(-\frac{1}{r_{1A}} \right) 1s_B(1) dr_1 \int 1s_B^*(2)1s_A(2) dr_2 \\ &\quad + \int 1s_B^*(2) \left(-\frac{1}{r_{2B}} \right) 1s_A(2) dr_2 \int 1s_A^*(1)1s_B(1) dr_1 \\ &\quad + \int 1s_A^*(1)1s_B^*(2) \left(\frac{1}{r_{12}} + \frac{1}{R_{AB}} \right) 1s_A(2)1s_B(1) dr_1 dr_2 = -S^2 + K = H_{21}\end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

$$\phi = c_1\phi_1 + c_2\phi_2$$

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} = 0$$

$$H_{11} = -1 + J = H_{22}$$

$$H_{12} = -S^2 + K = H_{21}$$

$$S_{11} = S_{22} = 1$$

$$S_{12} = S_{21} = S^2$$

$$\begin{pmatrix} -1 + J - E & -S^2 + K - ES^2 \\ -S^2 + K - ES^2 & -1 + J - E \end{pmatrix} = 0$$

$$E_{\pm} = -1 + \frac{J \pm K}{1 \pm S^2}$$

$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}} (\phi_1 \pm \phi_2)$$

$$E_+ \Rightarrow c_1 = c_2; \quad c_1 = \frac{1}{\sqrt{2(1 + S^2)}} \Rightarrow \phi_+$$

$$E_- \Rightarrow c_1 = -c_2; \quad c_1 = \frac{1}{\sqrt{2(1 - S^2)}} \Rightarrow \phi_-$$



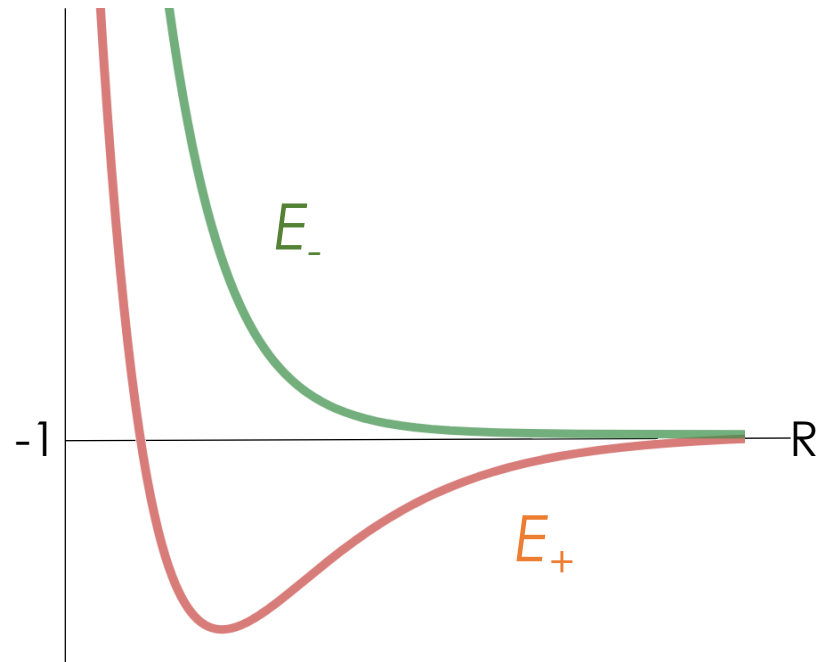
Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂

$$\begin{aligned}\phi_1 &= 1s_A(1)1s_B(2) \\ \phi_2 &= 1s_A(2)1s_B(1) \\ \phi &= c_1\phi_1 + c_2\phi_2\end{aligned}$$

$$E_{\pm} = -1 + \frac{J \pm K}{1 \pm S^2}$$

$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}} (\phi_1 \pm \phi_2)$$



Is this wave function well-behaved?

Linear Variational Principle in Chemical Bonding

Spin-Statistics Theorem

- 5** Wave function of a system of identical particles
- must be antisymmetric wrt interchange of any two particles if the particles have half-integer spin (fermions)
 - must be symmetric wrt interchange of any two particles if the particles have integer spin (bosons)

$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}} (\phi_1 \pm \phi_2)$$

$$\begin{aligned}\phi_1 &= 1s_A(1)1s_B(2) \\ \phi_2 &= 1s_A(2)1s_B(1)\end{aligned}$$

$$\begin{aligned}\hat{\mathcal{P}}_{12}\phi_+ &= \hat{\mathcal{P}}_{12}(1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)) \\ &= (1s_A(2)1s_B(1) + 1s_A(1)1s_B(2)) \\ &= \phi_+\end{aligned}$$

$$\begin{aligned}\hat{\mathcal{P}}_{12}\phi_- &= \hat{\mathcal{P}}_{12}(1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)) \\ &= (1s_A(2)1s_B(1) - 1s_A(1)1s_B(2)) \\ &= -\phi_-\end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂: electron spin

$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S^2)}} (\phi_1 \pm \phi_2)$$

$$\phi_1 = 1s_A(1)1s_B(2)$$

$$\phi_2 = 1s_A(2)1s_B(1)$$

For one electron system:

$$\hat{S}^2|\alpha\rangle = s(s+1)\hbar^2|\alpha\rangle$$

$$\hat{S}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle$$

$$\hat{S}^2|\beta\rangle = s(s+1)\hbar^2|\beta\rangle$$

$$\hat{S}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$$

For two electron system:

$$\hat{S} = \hat{S}_1 + \hat{S}_2$$

$$|\alpha_1 \alpha_2\rangle$$

$$s = s_1 + s_2, \dots, |s_1 - s_2|$$

$$|\beta_1 \beta_2\rangle$$

$$m_s = -s, -s+1, \dots, s-1, s$$

$$|s, m_s\rangle \equiv |0, 0\rangle, |1, 0\rangle, |1, \pm 1\rangle$$

$$\left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 + \alpha_2 \beta_1) \right\rangle$$

$$\left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \alpha_2 \beta_1) \right\rangle$$

Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H₂: electron spin

$$\begin{array}{ll}
 \phi_+ & |\alpha_1 \alpha_2\rangle \\
 \phi_- & |\beta_1 \beta_2\rangle \\
 & \left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 + \alpha_2 \beta_1) \right\rangle \quad \left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \alpha_2 \beta_1) \right\rangle
 \end{array}$$

well-behaved wave function:

$$\begin{aligned}
 & |\phi_+\rangle \left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \alpha_2 \beta_1) \right\rangle \\
 & |1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)\rangle \left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \alpha_2 \beta_1) \right\rangle
 \end{aligned}$$



Linear Variational Principle in Chemical Bonding

Valence Bond Treatment of H_2 : electron spin
well-behaved wave function:

$$\begin{aligned} & |1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)\rangle \left| \frac{1}{\sqrt{2}}(\alpha_1 \beta_2 - \alpha_2 \beta_1) \right\rangle \\ &= \frac{1}{\sqrt{2}} |1s_A(1)1s_B(2)\alpha_1 \beta_2 - 1s_A(1)1s_B(2)\alpha_2 \beta_1 + 1s_A(2)1s_B(1)\alpha_1 \beta_2 - 1s_A(2)1s_B(1)\alpha_2 \beta_1\rangle \\ &= \frac{1}{\sqrt{2}} \left| 1s_A(1)\overline{1s_B(2)} - 1s_A(2)\overline{1s_B(1)} + \overline{1s_A(2)}1s_B(1) - \overline{1s_A(1)}1s_B(2) \right\rangle \\ &= \frac{1}{\sqrt{2}} \left[\begin{vmatrix} 1s_A(1) & \overline{1s_B(1)} \\ 1s_A(2) & \overline{1s_B(2)} \end{vmatrix} + \begin{vmatrix} 1s_B(1) & \overline{1s_A(1)} \\ 1s_B(2) & \overline{1s_A(2)} \end{vmatrix} \right] \end{aligned}$$





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Department of Chemistry, IIT Kharagpur

Lecture 14: Variational Method in Chemical Bonding - III

Linear Variational Principle in Chemical Bonding

Molecular Orbital Treatment of H_2^+

Hamiltonian

$$\hat{H} = -\frac{\nabla^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R_{AB}}$$

$$\left(-\frac{\nabla^2}{2} - \frac{1}{r_A}\right) 1s_A = -0.5 1s_A$$

$$\left(-\frac{\nabla^2}{2} - \frac{1}{r_B}\right) 1s_B = -0.5 1s_B$$

Overlap integrals

$$S_{11} = \langle 1s_A | 1s_A \rangle = 1$$

$$S_{12} = \langle 1s_A | 1s_B \rangle = S$$

Trial wave function

$$\phi_1 = 1s_A$$

$$\phi_2 = 1s_B$$

$$\phi = c_1 \phi_1 + c_2 \phi_2$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

Energy integrals

$$\begin{aligned} H_{11} &= \langle 1s_A | \hat{H} | 1s_A \rangle \\ &= \left\langle 1s_A \left| \left(-\frac{\nabla^2}{2} - \frac{1}{r_A} \right) \right| 1s_A \right\rangle + \left\langle 1s_A \left| \left(-\frac{1}{r_B} + \frac{1}{R_{AB}} \right) \right| 1s_A \right\rangle \\ &= -0.5 + J = H_{22} \end{aligned}$$

$$\begin{aligned} H_{12} &= \langle 1s_A | \hat{H} | 1s_B \rangle \\ &= \left\langle 1s_A \left| \left(-\frac{\nabla^2}{2} - \frac{1}{r_B} \right) \right| 1s_B \right\rangle + \left\langle 1s_A \left| \left(-\frac{1}{r_A} + \frac{1}{R_{AB}} \right) \right| 1s_B \right\rangle \\ &= -0.5S + K = H_{21} \end{aligned}$$

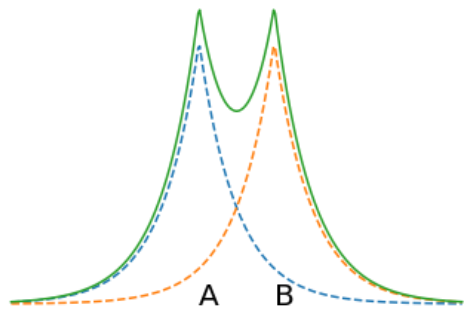


Linear Variational Principle in Chemical Bonding

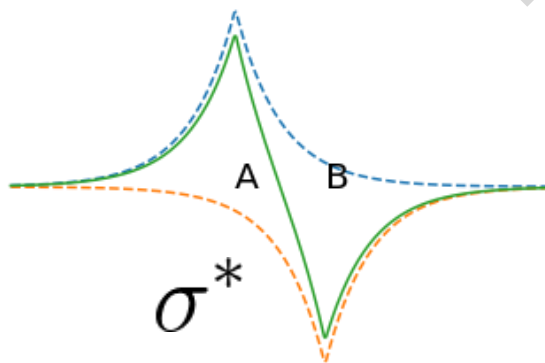
Molecular Orbital Treatment of H_2^+

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0 \quad E_{\pm} = -0.5 + \frac{J \pm K}{1 \pm S}$$

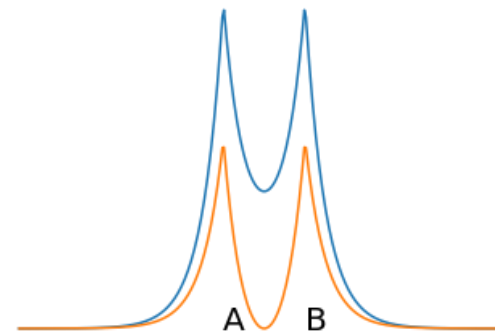
$$\phi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (1s_A \pm 1s_B)$$



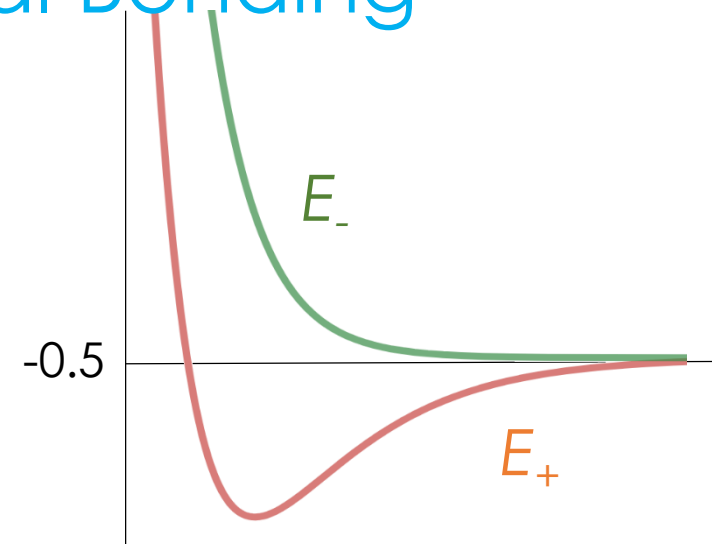
σ



σ^*



A B



Linear Variational Principle in Chemical Bonding

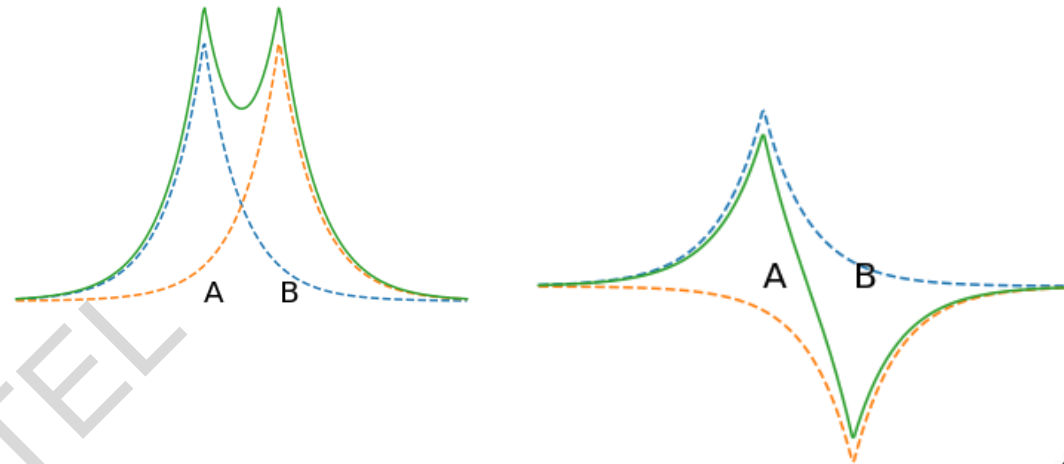
Molecular Orbital Treatment of H₂

$$\phi_{\pm} = (1s_A \pm 1s_B)$$

$$\phi_{\text{MO}} = (1s_A(1) + 1s_B(1)) (\textcolor{red}{1s_A(2)} + \textcolor{red}{1s_B(2)})$$

$$= 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)$$

$$= \phi_{\text{ionic}} + \phi_{\text{VB}}$$





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Lecture 15: Molecular Orbital Treatment of Diatomics and Polyatomics

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Diatomics

O: $1s^2 2s^2 2p^4$

$$\phi = \sum_{i=1}^n c_i \psi_i$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

- core orbitals are too compact and virtual orbitals are too diffused for significant overlap (constructive/destructive) between neighbouring atoms.

	E	2 C _∞ [∞]	...	∞ σ _v		
A ₁ =Σ ⁺	1	1	...	1	z	x ² + y ² , z ²
A ₂ =Σ ⁻	1	1	...	-1	R _z	
E ₁ =Π	2	2 cos(Φ)	...	0	(x, y), (R _x , R _y)	(xz, yz)
E ₂ =Δ	2	2 cos(2Φ)	...	0		(x ² - y ² , xy)
E ₃ =Φ	2	2 cos(3Φ)	...	0		
...	...	...	...	...		

$$\begin{aligned} \langle \psi_i | \hat{H} | \psi_j \rangle &= H_{ij} \neq 0 \\ \langle \psi_i | \psi_j \rangle &= S_{ij} \neq 0 \end{aligned}$$

Only when the atomic orbitals have same symmetry species in the point group of the molecule

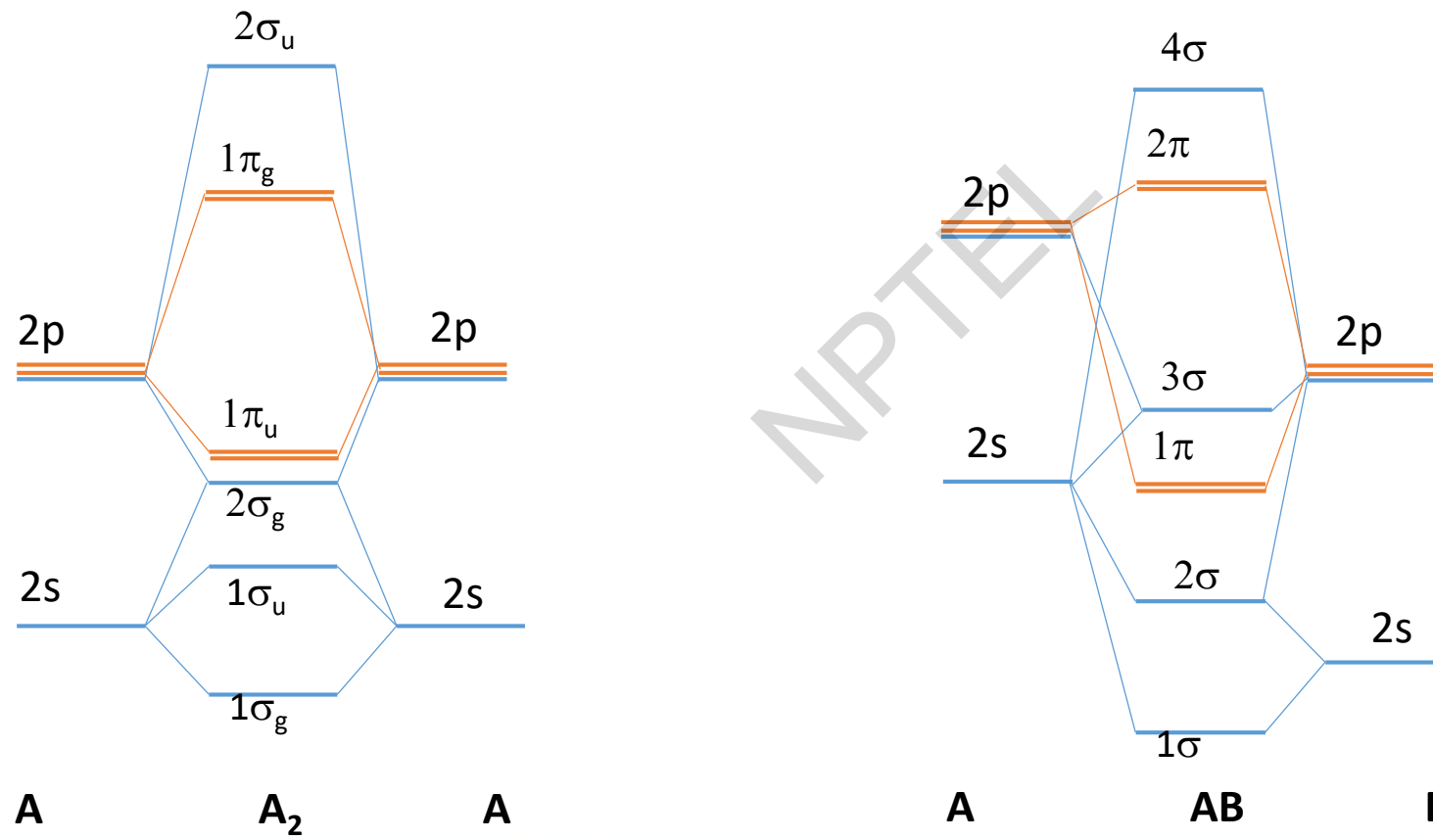
Σ : 2s 2p_z

Π : 2p_{x,y}

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Diatomics





NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

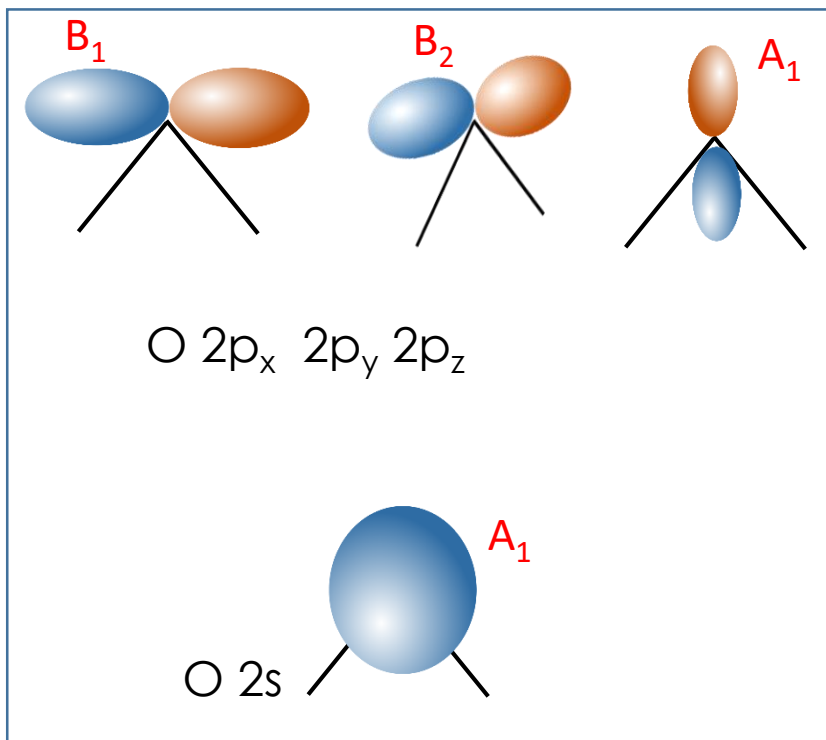
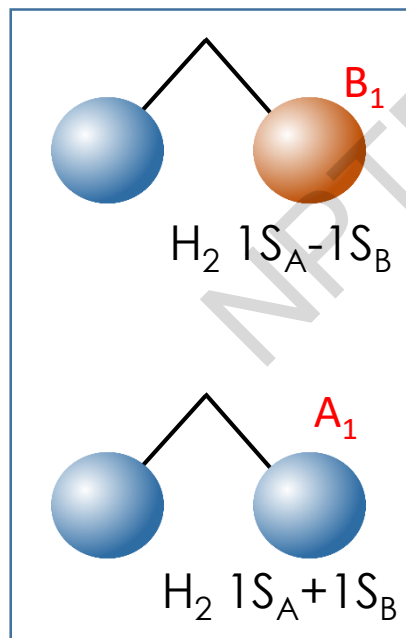
Sabyashachi Mishra
Department of Chemistry, IIT Kharagpur

Lecture 16: Molecular Orbital Treatment of Polyatomics

Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2



$$\psi(A_1) = c_1\phi(\text{O}, 2s) + c_2\phi(\text{O}, 2p_z) + c_3\phi(\text{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\text{O}, 2p_x) + c_2\phi(\text{H}_2, 1s_A - 1s_B)$$

$$\psi(B_2) = \phi(\text{O}, 2p_y)$$

z
x

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Linear Variational Principle in Chemical Bonding

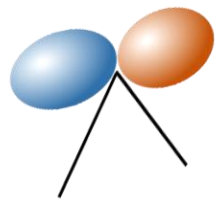
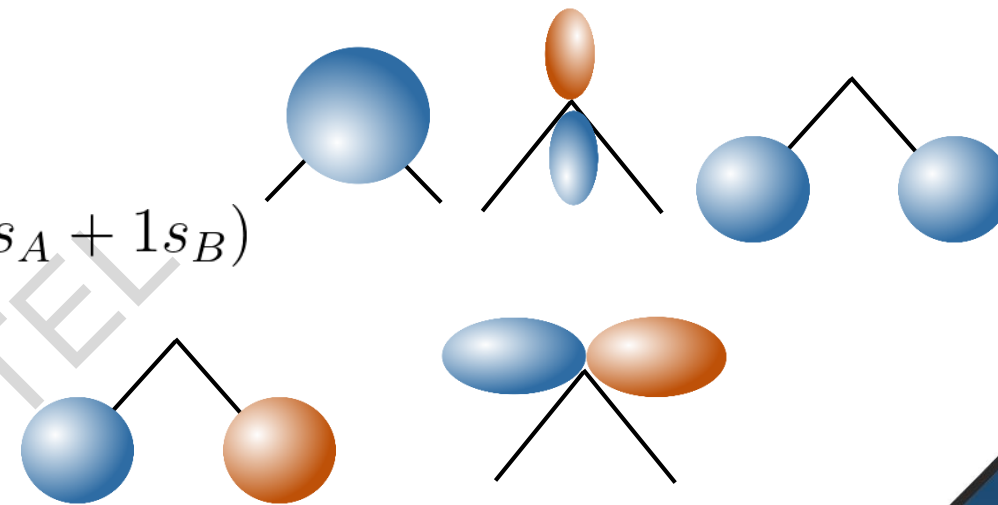
Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2

$$\psi(A_1) = c_1\phi(\text{O}, 2s) + c_2\phi(\text{O}, 2p_z) + c_3\phi(\text{H}_2, 1s_A + 1s_B)$$

$$\psi(B_1) = c_1\phi(\text{O}, 2p_x) + c_2\phi(\text{H}_2, 1s_A - 1s_B)$$

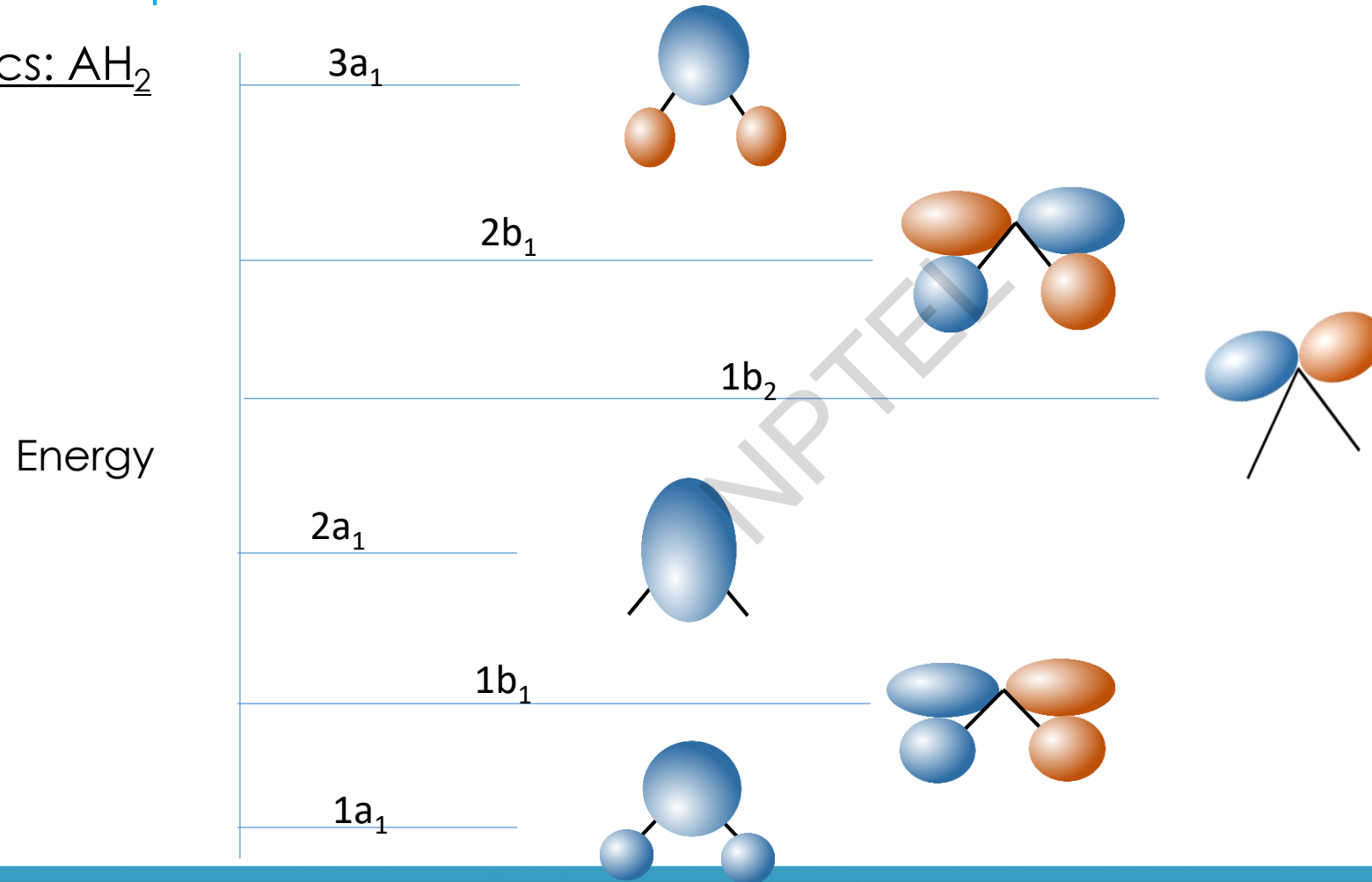
$$\psi(B_2) = \phi(\text{O}, 2p_y)$$



Linear Variational Principle in Chemical Bonding

Symmetry Adapted Linear Combination of Atomic Orbitals

Polyatomics: AH_2



Hückel's Molecular Orbital Method: An empirical treatment of pi electrons

$$\hat{H}_{\pi} = \sum_{i=1}^{n_{\pi}} \hat{H}(i)$$

$$\hat{H}_{\pi} \psi_{\pi} = E_{\pi} \psi_{\pi}$$

$$\psi_{\pi} = \prod_{i=1}^{n_{\pi}} \phi_i$$

$$\hat{H}(i) \phi_i = e_i \phi_i$$

$$\phi_i = \sum_{r=1}^{n_C} c_{ri} f_r$$

Secular Equations

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & H_{nn} - ES_{nn} \end{vmatrix} \cdot \begin{vmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{vmatrix} = 0$$

Overlap integrals $S_{ij} = \delta_{ij}$

Energy integrals

$$H_{ii} = \alpha$$

$$H_{ij} = \beta \quad \text{If } i \text{ and } j \text{ are connected}$$

$$H_{ij} = 0 \quad \text{If } i \text{ and } j \text{ are NOT connected}$$



Hückel's Molecular Orbital Method for butadiene

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

$$e_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right), \quad k = 1, \dots, N$$

$$e_1 = \alpha + 1.618\beta$$

$$e_2 = \alpha + 0.618\beta$$

$$e_3 = \alpha - 0.618\beta$$

$$e_4 = \alpha - 1.618\beta$$

$$\phi_1 = 0.372f_1 + 0.602f_2 + 0.602f_3 + 0.372f_4$$

$$\phi_2 = 0.602f_1 + 0.372f_2 - 0.372f_3 - 0.602f_4$$

$$\phi_3 = 0.602f_1 - 0.372f_2 - 0.372f_3 + 0.602f_4$$

$$\phi_4 = 0.372f_1 - 0.602f_2 + 0.602f_3 - 0.372f_4$$

