1.a)i. The purpose of the Variation Principle is to provide a framework to find the best wavefunction to describe a molecule by finding the lowest energy.

ii. The coefficients used to weight the sum of atomic orbitals in their linear combination to form a molecular orbital are varied.

iii. The best we can do is to predict the exact wavefunction which will by definition have the lowest energy. Any less exact wavefunction will have higher energy because nature always selects the lowest energy (exact wavefunction).

\[ \begin{vmatrix} \alpha - E & \beta - E S \\ \beta - E S & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - E S)^2 = 0 \]

\[ \alpha^2 + E^2 - 2\alpha E - \beta^2 - E^2 S^2 + 2\beta E S = 0 \]

\[ (1-S^2)E^2 - (2\alpha - 2\beta S)E + \alpha^2 - \beta^2 = 0 \]

\[ E = \frac{(2\alpha - 2\beta S) \pm \sqrt{(2\alpha - 2\beta S)^2 - 4(1-S^2)(\alpha^2 - \beta^2)}}{2(1-S^2)} \]
working with the square root:

\[ \sqrt{4\alpha^2 + 4\beta^2 S^2 - 8\alpha \beta S} - 4(\alpha + \beta \pm \sqrt{\alpha^2 - \beta^2 - \alpha^2 S^2 + \beta^2 S^2}) \]

\[ \sqrt{4\beta^2 + 4\alpha^2 S^2 - 8\alpha \beta S} \]

\[ \sqrt{(2\alpha S - 2\beta)^2} \]

combining:

\[ E = \frac{(2\alpha - 2\beta S) \pm (2\alpha S - 2\beta)}{2(1+S)(1-S)} \]

\[ = \frac{2\alpha + 2\beta - 2\beta S - 2\alpha S}{2(1+S)(1-S)} \quad \text{or} \quad \frac{2\alpha - 2\beta - 2\beta S + 2\alpha S}{2(1+S)(1-S)} \]

\[ = \frac{(\alpha + \beta)(1-S)}{(1+S)(1-S)} \quad \text{or} \quad \frac{(\alpha - \beta)(1+S)}{(1-S)(1+S)} \]

\[ E = \frac{\alpha \pm \beta}{1 \pm S} \]
1.c) \[ S = 0.586 = \int |s_a - s_b|^2 dV \]

Normal expression for \( \Psi \)

\[ N_+^{-2} \int_{-\infty}^{\infty} |s_a - s_b|^2 dV = N_+^{-2} \left[ \int_{-\infty}^{\infty} |s_a|^2 dV + \int_{-\infty}^{\infty} |s_b|^2 dV - 2 \int_{-\infty}^{\infty} |s_a s_b| dV \right] = S \]

\[ N_-^{-2} \left[ 2 - 2S' \right] = 1 \]

\[ N_- = \frac{1}{\sqrt{2 - 2S}} = \frac{1}{\sqrt{2 - 2 \times 0.586}} = 1.10 \]

ii. \( N_- \) is larger than \( N_+ \) because of cancellation in the linear combination of atomic orbitals.

iii. Normal constant of \( \frac{1}{\sqrt{2}} \) is only valid for orbitals that have no overlap, \( S = 0 \). This is not the case here.

1.d) triplet means same spin \( \alpha(1)\alpha(2), \beta(1)\beta(2) \) or \( \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \)

excited state of \( H_2 \) has one \( e^- \) in \( \sigma_g \) and one in \( \sigma_u \). need antisymmetric space function.

\[ \Psi_{H_2^*} = \frac{1}{\sqrt{2}} \left( \sigma_g(1)\sigma_u(2) - \sigma_u(1)\sigma_g(2) \right) \begin{bmatrix} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \end{bmatrix} \]
\[ E_{\text{triplet}} = E_1 + E_2 + E_{\text{rep}} \]
\[ E = \frac{\alpha + \beta}{1 + S^2} + \frac{\alpha - \beta}{1 - S^2} + \frac{e^2}{4\pi \varepsilon_0 \sigma ab} \]

ii. \[ E_{ab} = \frac{-26.4 - 20.5}{1 + 0.656} + \frac{-26.4 + 20.5}{1 - 0.656} + \frac{(1.60 \cdot 10^{-19} \text{C})^2 (1.60 \cdot 10^{-19} \text{J})}{4\pi (8.85 \cdot 10^{-12} \text{C}^2 / \text{m})(1.5 \cdot 5.19 \cdot 10^{-10} \text{m})} \]
\[ E_{ab} = -28.3 - 17.2 + 18.5 \text{eV} = -27.0 \text{eV} \]

iii. \[ E_{\text{H-H}} = 2E_{1s} = 2(-13.6 \text{eV}) = -27.2 \text{eV} \]

\[ \text{B.D.E.} = E_{\text{diss.}} - E_{\text{bonded}} \]
\[ = E_{\text{H-H}} - E_{ab} = -27.2 \text{eV} + 27.0 \text{eV} \]
\[ \text{B.D.E.} = -0.2 \text{eV} \]

unstable, molecule will dissociate!

Yes, this is consistent because the bond order = 0

-1 = \sigma_u \text{ (antibonding)}

-1 = \sigma_g \text{ (bonding)}

\[ \text{B.O.} = \frac{1}{2} (N_{\text{bonding}} - N_{\text{antibond}}) = 0 \]
2.a) i. \[ c_a = \frac{c_b}{c_c} \quad x = \frac{\alpha - E}{\beta} \]

\[
\begin{vmatrix}
  x & 1 & 1 \\
  1 & x & 1 \\
  1 & 1 & x \\
\end{vmatrix} = x^3 + 2 - 3x = 0
\]

ii. \[ x^3 - 3x = -2 \]

occurs when \( x = 1 \)

\[
(x-1)(x^2+x-2) = 0
\]

\[
x = \frac{-1 \pm \sqrt{1^2 - 4(1)(-2)}}{2} = \frac{-1 \pm \frac{3}{2}}{2} = -2, 1
\]

roots occur at \( x = -2, 1, 1 \)

\[
\frac{\alpha - E}{\beta} = -2 \implies E_1 = \alpha + 2\beta
\]

\[
\frac{\alpha - E}{\beta} = 1 \implies E_{2,3} = \alpha - \beta
\]

2.b) i. \[ E_{2,3} = \alpha - \beta \]

\[ E_1 = \alpha + 2\beta \]

do not grade comments on symmetry as this has yet to be determined.
2.6 ii. use $E_1$:

need two secular eqn. and norm. cond.

$(\alpha - E)C_A + \beta C_B + \beta C_C = 0$

$\beta C_A + (\alpha - E)C_B + \beta C_C = 0$

$C_A^2 + C_B^2 + C_C^2 = 0$

Substitute $E = \alpha + 2\beta$

$-2\beta C_A + \beta C_B + \beta C_C = 0$

$C_A = \frac{1}{2}(C_B + C_C)$

Substitute into second sec. eqn.

$\frac{1}{2}\beta(C_B + C_C) - 2\beta C_B + \beta C_C = 0$

$\frac{3}{2}C_B = \frac{3}{2}C_C$

$C_B = C_C$ combining with the earlier eqn.

$C_A = C_B = C_C$ intuitive from symmetry

use normalization cond.

$3C_A^2 = 1$

$$C_A = \frac{1}{\sqrt{3}} = C_B = C_C$$
2.b) ii. (continued)

\[ \Phi_1 = \frac{1}{\sqrt{3}} (2\rho_a + 2\rho_b + 2\rho_c) \]

yes, the \( \pi^- e^- \) should be distributed evenly about the ring.

2.b) iii.

![Diagram]

2.c) i. benzene

\[
\begin{array}{cccccc}
\cdot a & \cdot b & 1 & 0 & 0 & 0 \\
\cdot c & 1 & 0 & 0 & 0 \\
\cdot d & 0 & 1 & 0 & 0 \\
\cdot e & 0 & 0 & 1 & 0 \\
\cdot f & 0 & 0 & 0 & 1 \\
\end{array}
\]

benzene (6 \( \pi^- e^- \))

ii. \[ \alpha - 2\beta \]

\[ \alpha - \beta \]

\[ \frac{1}{4} \]

\[ \frac{1}{4} \]

\[ \frac{1}{4} \]

\[ \alpha + 2\beta \]

\[ E_{tot} = 2(\alpha + 2\beta) + 4(\alpha + \beta) \]

\[ E_{tot} = 6\alpha + 8\beta \]

hexatriene \( a \to b \to c \to e \)

\[
\begin{array}{cccccc}
\cdot a & \cdot b & 1 & 0 & 0 & 0 \\
\cdot c & 1 & 0 & 0 & 0 \\
\cdot d & 0 & 1 & 0 & 0 \\
\cdot e & 0 & 0 & 1 & 0 \\
\cdot f & 0 & 0 & 0 & 1 \\
\end{array}
\]

cyclo-octatetraene (8 \( \pi^- e^- \))

\[ \alpha - 2\beta \]

\[ \alpha - 1.41\beta \]

\[ \frac{1}{4} \]

\[ \frac{1}{4} \]

\[ \frac{1}{4} \]

\[ \frac{1}{4} \]

\[ \alpha + 1.41\beta \]

\[ \alpha + 2\beta \]

\[ E_{tot} = 2(\alpha + 2\beta) + 4(\alpha + 1.41\beta) + 2\alpha \]

\[ E_{tot} = 8\alpha + 9.64\beta \]