Chemistry 432
Problem Set 9
Spring 2020
Solutions

1. Give the electronic structures for all homonuclear diatomic molecules from H_2 to Ne_2 using molecular orbital theory. Which are predicted to be unbound?
Answer:

$$H_2 \qquad 1\sigma_g^2$$

$$He_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} \qquad \text{unbound}$$

$$Li_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2$$

$$Be_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} \qquad \text{unbound}$$

$$B_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^2$$

$$C_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4$$

$$N_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^2$$

$$O_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$$

$$F_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*4}$$

$$Ne_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*4} 3\sigma_u^{*2} \qquad \text{unbound}$$

2. On the basis of molecular orbital theory, explain the following: The binding energy of N_2^+ is 6.35 ev and the binding energy of N_2 is 7.38 ev, whereas the binding energy of O_2^+ is 6.48 ev and the binding energy of O_2 is 5.08 ev.
Answer:

$$N_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^2$$

$$N_2^+ \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^1$$

N_2^+ has 1 less bonding electron than N_2, and N_2 is more strongly bound than N_2^+.

$$O_2 \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*2}$$

$$O_2^+ \qquad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 3\sigma_g^2 1\pi_u^4 1\pi_g^{*1}$$

O_2^+ has 1 less anti-bonding electron than O_2, and O_2^+ is more strongly bound than O_2.

3. Give the Born-Oppenheimer Hamiltonian operator for the Be_2 molecule. Use molecular orbital theory to compare the binding strengths of Be_2^+, Be_2 and $\mathrm{Be}\ _2^-$ assuming the ordering of the molecular orbitals is the same for the ions as the ordering known to be correct for the neutral molecule.

   Answer:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{8}\nabla_i^2 - \sum_{i=1}^{8}\left(\frac{4e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_a|} + \frac{4e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_b|}\right) + \sum_{i<j}^{8}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} + \frac{16e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|}$$

Be
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(4 - 4) = 0$$

Unbound
Be$^-$
$\underline{\uparrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(5 - 4) = \frac{1}{2}$$

Bound
Be$^+$
$\underline{\uparrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(4 - 3) = \frac{1}{2}$$

Bound

4. Give the Born-Oppenheimer Hamiltonian operator for the C_2 molecule. Then use molecular orbital theory to determine the bond orders and relative binding strengths for the molecules C_2^+, C_2 and C_2^-.

   Answer

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{12}\nabla_i^2 - \sum_{i=1}^{12}\frac{6e^2}{4\pi\epsilon_0}\left(\frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{|\vec{r}_i - \vec{R}_b|}\right) + \frac{36e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|} + \sum_{i<j}^{12}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}$$

$$\mathrm{C}_2^+ : \quad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^3$$

$$BO = \frac{1}{2}(7-4) = \frac{3}{2}$$

$$\mathrm{C}_2 : \quad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4$$

$$BO = \frac{1}{2}(8-4) = 2$$

$$\mathrm{C}_2^- : \quad 1\sigma_g^2 1\sigma_u^{*2} 2\sigma_g^2 2\sigma_u^{*2} 1\pi_u^4 3\sigma_g^1$$

$$BO = \frac{1}{2}(9-4) = \frac{5}{2}$$

$$BE_{C_2^-} > BE_{C_2} > BE_{C_2^+}$$

5. Give the Born-Oppenheimer Hamiltonian operator for the F_2 molecule. Use molecular orbital theory to compare the binding strengths of F_2^+, F_2 and F_2^- assuming the ordering of the molecular orbitals is the same for the ions as the ordering known to be correct for the neutral molecule.
   Answer:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{18}\nabla_i^2 - \sum_{i=1}^{18}\frac{9e^2}{4\pi\epsilon_0}\left(\frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{|\vec{r}_i - \vec{R}_b|}\right) + \frac{81e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|} + \frac{1}{2}\sum_{i\neq j}^{18}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}$$

F_2
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_g^*$
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $3\sigma_g$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10-8) = 1$$

F_2^+
$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $1\pi_g^*$
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $3\sigma_g$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10-7) = 3/2$$

F_2^-
$\underline{\uparrow}$ $3\sigma_u^*$
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_g^*$
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $3\sigma_g$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 9) = 1/2$$

Binding energy order is $F_2^+ > F_2 > F_2^-$

6. Give the Born-Oppenheimer Hamiltonian operator for the O_2 molecule. Then use molecular orbital theory to determine the bond orders and relative binding strengths for the molecules O_2^+, O_2 and O_2^-.
Answer:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{16}\nabla_i^2 - \sum_{i=1}^{16}\frac{8e^2}{4\pi\epsilon_0}\left(\frac{1}{|\vec{r}_i - \vec{R}_a|} + \frac{1}{|\vec{r}_i - \vec{R}_b|}\right) + \frac{64e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|} + \frac{1}{2}\sum_{i\neq j}^{16}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}$$

O_2
$\underline{\uparrow}$ $\underline{\uparrow}$ $1\pi_g^*$
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $3\sigma_g$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 6) = 2$$

O_2^+
$\underline{\uparrow}$ $1\pi_g^*$
$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $3\sigma_g$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 5) = 5/2$$

O_2^-
$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $1\pi_g^*$

$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $3\sigma_g$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(10 - 7) = 3/2$$

Binding energy order is $O_2^+ > O_2 > O_2^-$

7. Give the Born-Oppenheimer Hamiltonian operator for the B_2^+ ion. Assuming the ordering of orbitals to be the same for neutral molecules as the ordering for ions, use molecular-orbital theory to compare the relative stabilities of B_2^+, B_2 and B_2^-.
Answer:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{9}\nabla_i^2 - \sum_{i=1}^{9}\left(\frac{5e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_a|} + \frac{5e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_b|}\right) + \sum_{i<j}^{9}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} + \frac{25e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|}$$

B_2^+
$\underline{\uparrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(5 - 4) = \frac{1}{2}$$

B_2
$\underline{\uparrow}$ $\underline{\uparrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(6 - 4) = 1$$

B_2^-
$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $1\pi_u$
$\underline{\uparrow\downarrow}$ $2\sigma_u^*$
$\underline{\uparrow\downarrow}$ $2\sigma_g$
$\underline{\uparrow\downarrow}$ $1\sigma_u^*$
$\underline{\uparrow\downarrow}$ $1\sigma_g$

$$BO = \frac{1}{2}(n - n^*) = \frac{1}{2}(7 - 4) = \frac{3}{2}$$

Relative stability

$$\mathrm{B}_2^+ < \mathrm{B}_2 < \mathrm{B}_2^-$$

8. The ungerade, antibonding molecular orbital of the H_2^+ molecule is given by

$$\psi_u = A[\phi_a - \phi_b]$$

with A the normalization and ϕ_a or ϕ_b the normalized 1s orbital centered respectively on nucleus a or b. Show that the expectation value of the Born-Oppenheimer Hamiltonian operator for the H_2^+ molecule with respect to ψ_u is given by

$$\langle \hat{H} \rangle = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

where

$$H_{aa} = \int \phi_a \hat{H} \phi_a d\tau, \quad H_{ab} = \int \phi_a \hat{H} \phi_b d\tau \quad \text{and} \quad S_{ab} = \int \phi_a \phi_b d\tau.$$

Answer:

First normalize

$$A^2 \int (\phi_a - \phi_b)^2 d\tau = A^2 [\int \phi_a^2 d\tau + \int \phi_b^2 d\tau - 2 \int \phi_a \phi_b d\tau]$$

$$= A^2 [2 - 2S_{ab}] = 1 \qquad A = \frac{1}{\sqrt{2(1 - S_{ab})}}$$

$$\langle \hat{H} \rangle = \frac{1}{2(1 - S_{ab})} \int (\phi_a - \phi_b) \hat{H} (\phi_a - \phi_b) d\tau$$

$$= \frac{1}{2(1 - S_{ab})} [\int \phi_a \hat{H} \phi_a d\tau + \int \phi_b \hat{H} \phi_b d\tau - 2 \int \phi_a \hat{H} \phi_b d\tau]$$

$$= \frac{1}{2(1 - S_{ab})} [H_{aa} + H_{bb} - 2H_{ab}] = \frac{1}{2(1 - S_{ab})} [H_{aa} + H_{aa} - 2H_{ab}] = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

9. Consider the gas phase NH molecule, and let ϕ_H be the 1s-orbital wavefunction centered on the hydrogen atom and ϕ_N be the $2\mathrm{p}_z$-orbital wavefunction centered on the nitrogen atom. Noting that all wavefunctions for this system are real numbers, let the Coulomb integral for the hydrogen atom be given by

$$\alpha_H = \int \phi_H \hat{H} \phi_H d\tau,$$

the Coulomb integral for the nitrogen atom be given by

$$\alpha_N = \int \phi_N \hat{H} \phi_N d\tau,$$

the overlap integral be

$$S = \int \phi_H \phi_N d\tau$$

and the resonance integral be given by

$$\beta = \beta_{H,N} = \beta_{N,H} = \int \phi_H \hat{H} \phi_N d\tau.$$

Derive the secular equation for the molecular-orbital energies for NH in terms of S, α_H, α_N and β.

Answer

$$\langle E \rangle = \frac{\displaystyle\int (c_H\phi_H + c_N\phi_N)\hat{H}(c_H\phi_H + c_N\phi_N)d\tau}{\displaystyle\int (c_H\phi_H + c_N\phi_N)(c_H\phi_H + c_N\phi_N)d\tau}$$

$$= \frac{c_H^2\alpha_H + c_N^2\alpha_N + 2c_Hc_N\beta}{c_H^2 + c_N^2 + 2Sc_Hc_N}$$

or

$$\langle E \rangle (c_H^2 + c_N^2 + 2Sc_Hc_N) = c_H^2\alpha_H + c_N^2\alpha_N + 2c_Nc_H\beta$$

Differentiating both sides with respect to c_H we obtain

$$2c_H\langle E \rangle + 2Sc_N\langle E \rangle = 2c_H\alpha_H + 2c_N\beta$$

or

$$(\alpha_H - \langle E \rangle)c_H + (\beta - \langle E \rangle S)c_N = 0. \tag{1}$$

Next we differentiate with respect to c_N to obtain

$$2c_N\langle E \rangle + 2Sc_H\langle E \rangle = 2c_N\alpha_N + 2c_H\beta$$

or

$$(\alpha_N - \langle E \rangle)c_N + (\beta - \langle E \rangle S)c_H = 0. \tag{2}$$

Equations (1) and (2) have non trivial solutions only if the secular determinant vanishes; i.e.

$$\begin{vmatrix} \alpha_H - \langle E \rangle & \beta - S\langle E \rangle \\ \beta - S\langle E \rangle & \alpha_N - \langle E \rangle \end{vmatrix} = 0$$

10. Consider the gas phase LiC molecule, and let ϕ_{Li} be the 2s-orbital wavefunction centered on the lithium atom and ϕ_C be the 2p$_z$-orbital wavefunction centered on the carbon atom. Noting that all wavefunctions for this system are real numbers, let the Coulomb integral for the lithium atom be given by

$$\alpha_{Li} = \int \phi_{Li}\hat{H}\phi_{Li}d\tau,$$

the Coulomb integral for the carbon atom be given by

$$\alpha_C = \int \phi_C \hat{H} \phi_C d\tau,$$

the overlap integral be

$$S = \int \phi_{Li} \phi_C d\tau$$

and the resonance integral be given by

$$\beta = \beta_{Li,C} = \beta_{C,Li} = \int \phi_{Li} \hat{H} \phi_C d\tau.$$

Using the expectation value of the Hamiltonian and the variational theorem, derive the secular equation for the molecular-orbital energies for LiC in terms of S, α_{Li}, α_C and β.

Answer:

$$\langle E \rangle = \frac{\int (c_{Li}\phi_{Li} + c_C\phi_C)\hat{H}(c_{Li}\phi_{Li} + c_C\phi_C)d\tau}{\int (c_{Li}\phi_{Li} + c_C\phi_C)(c_{Li}\phi_{Li} + c_C\phi_C)d\tau} \geq E_0$$

$$\langle E \rangle = \frac{c_{Li}^2\alpha_{Li} + c_C^2\alpha_C + 2c_{Li}c_C\beta}{c_{Li}^2 + c_C^2 + 2Sc_{Li}c_C}$$

or

$$\langle E \rangle(c_{Li}^2 + c_C^2 + 2Sc_{Li}c_C) = c_{Li}^2\alpha_{Li} + c_C^2\alpha_C + 2c_{Li}c_C\beta$$

Differentiating both sides with respect to c_{Li} we obtain

$$2c_{Li}\langle E \rangle + 2Sc_C\langle E \rangle = 2c_{Li}\alpha_{Li} + 2c_C\beta$$

or

$$(\alpha_{Li} - \langle E \rangle)c_{Li} + (\beta - \langle E \rangle S)c_C = 0. \tag{3}$$

Next we differentiate with respect to c_C to obtain

$$2c_C\langle E \rangle + 2Sc_{Li}\langle E \rangle = 2c_C\alpha_C + 2c_{Li}\beta$$

or

$$(\alpha_C - \langle E \rangle)c_C + (\beta - \langle E \rangle S)c_{Li} = 0. \tag{4}$$

Equations (1) and (2) have non trivial solutions only if the secular determinant vanishes; i.e.

$$\begin{vmatrix} \alpha_{Li} - \langle E \rangle & \beta - S\langle E \rangle \\ \beta - S\langle E \rangle & \alpha_C - \langle E \rangle \end{vmatrix} = 0$$

11. Recall that the anti-bonding, ungerade wavefunction of the H_2^+ molecule is given by

$$\psi_u = c_u(\phi_{1S_A} - \phi_{1S_B})$$

where ϕ_{1S_A} is the 1s, hydrogen atom orbital about center A, ϕ_{1S_B} is the 1s, hydrogen atom orbital about center B, and c_u is the normalization. Show that

$$c_u = \frac{1}{\sqrt{2(1 - S_{AB})}}$$

where S_{AB} is the overlap integral defined by

$$S_{AB} = \int \phi_{1s_A}\phi_{1s_B}\ d\tau.$$

Answer:

$$\int \psi_u^* \psi_u\ d\tau = 1$$

$$\int (c_u[\phi_{1S_A} - \phi_{1S_B}])^2\ d\tau = 1$$

$$c_u^2(\int \phi_{1S_A}^2\ d\tau + \int \phi_{1S_B}^2\ d\tau - 2\int \phi_{1S_A}\phi_{1S_B}\ d\tau)$$

$$= c_u^2(1 + 1 - 2S_{AB}) = c_u^2(2 - 2S_{AB}) = 1$$

$$c_u = \frac{1}{\sqrt{2(1 - S_{AB})}}$$

12. Consider the gas-phase lithium dimer Li_2. 1) Give the Born-Oppenheimer Hamiltonian operator for Li_2. 2) Assuming a good representation for the ground-state wavefunction for Li_2 is

$$\psi = A[\phi_{2sa} + \phi_{2sb}],$$

where A is the normalization, ϕ_{2sa} is a 2s orbital centered on atom "a" and ϕ_{2sb} is a 2s orbital centered on atom "b." Show that the expectation value of the Hamiltonian with respect to the approximate wavefunction ψ is given by

$$\langle \hat{H} \rangle = \frac{H_{aa} + H_{ab}}{1 + S}$$

where

$$H_{aa} = \int \phi_{2sa}\hat{H}\phi_{2sa}\ d\tau \quad H_{ab} = \int \phi_{2sa}\hat{H}\phi_{2sb}\ d\tau = \int \phi_{2sb}\hat{H}\phi_{2sa}\ d\tau$$

and the overlap integral is given by

$$S = \int \phi_{2sa}\phi_{2sb}\ d\tau.$$

Answer

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{6}\nabla_i^2 - \sum_{i=1}^{6}\left(\frac{3e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_a|} + \frac{3e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{R}_b|}\right)$$
$$+\frac{1}{2}\sum_{i\neq j}^{6}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|} + \frac{9e^2}{4\pi\epsilon_0|\vec{R}_a - \vec{R}_b|}$$

Normalize

$$A^2\int(\phi_{2a}^2 + \phi_{2b}^2 + 2\phi_{2a}\phi_{2b})d\tau = A^2(1+1+2S) = 1$$

$$A = \frac{1}{\sqrt{2(1+S)}}$$

$$\langle\hat{H}\rangle = \frac{1}{2(1+S)}\left(\int\phi_{2a}\hat{H}\phi_{2a}d\tau + \int\phi_{2b}\hat{H}\phi_{2b}d\tau + 2\int\phi_{2a}\hat{H}\phi_{2b}d\tau\right)$$
$$= \frac{1}{2(1+S)}(H_{aa} + H_{bb} + 2H_{ab}) = \frac{H_{aa} + H_{ab}}{1+S}$$