

### Review Exercises

1. For the given orbital occupations (configurations) of the following systems, determine all possible states (all possible allowed combinations of spin and space states). There is no need to form the determinantal wavefunctions simply label each state with its proper term symbol. One method commonly used is Harry Grays "box method" found in Electrons and Chemical Bonding.

- a.) CH<sub>2</sub>      1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>3a<sub>1</sub><sup>1</sup>1b<sub>1</sub><sup>1</sup>  
 b.) B<sub>2</sub> 1 g<sup>2</sup>1 u<sup>2</sup>2 g<sup>2</sup>2 u<sup>2</sup>1 u<sup>1</sup>2 u<sup>1</sup>  
 c.) O<sub>2</sub> 1 g<sup>2</sup>1 u<sup>2</sup>2 g<sup>2</sup>2 u<sup>2</sup>1 u<sup>4</sup>3 g<sup>2</sup>1 g<sup>2</sup>  
 d.) Ti 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>4s<sup>2</sup>3d<sup>1</sup>  
 e.) Ti 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>4s<sup>2</sup>3d<sup>2</sup>

### Exercises

- Show that the configuration (determinant) corresponding to the Li<sup>+</sup> 1s( )1s( ) state vanishes.
- Construct the 3 triplet and 1 singlet wavefunctions for the Li<sup>+</sup> 1s<sup>1</sup>2s<sup>1</sup> configuration. Show that each state is a proper eigenfunction of S<sup>2</sup> and S<sub>z</sub> (use raising and lowering operators for S<sup>2</sup>)
- Construct wavefunctions for each of the following states of CH<sub>2</sub>:
  - <sup>1</sup>B<sub>1</sub> (1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>3a<sub>1</sub><sup>1</sup>1b<sub>1</sub><sup>1</sup>)
  - <sup>3</sup>B<sub>1</sub> (1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>3a<sub>1</sub><sup>1</sup>1b<sub>1</sub><sup>1</sup>)
  - <sup>1</sup>A<sub>1</sub> (1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>3a<sub>1</sub><sup>2</sup>)
- Construct wavefunctions for each state of the 1 2<sub>2</sub> 2<sub>3</sub> 2<sub>1</sub> 2 configuration of NH.
- Construct wavefunctions for each state of the 1s<sup>1</sup>2s<sup>1</sup>3s<sup>1</sup> configuration of Li.
- Determine all term symbols that arise from the 1s<sup>2</sup>2s<sup>2</sup>2p<sup>2</sup>3d<sup>1</sup> configuration of the excited N atom.
- Calculate the energy (using Slater Condon rules) associated with the 2p valence electrons for the following states of the C atom.
  - <sup>3</sup>P(M<sub>L</sub>=1, M<sub>S</sub>=1),
  - <sup>3</sup>P(M<sub>L</sub>=0, M<sub>S</sub>=0),
  - <sup>1</sup>S(M<sub>L</sub>=0, M<sub>S</sub>=0), and
  - <sup>1</sup>D(M<sub>L</sub>=0, M<sub>S</sub>=0).
- Calculate the energy (using Slater Condon rules) associated with the valence electrons for the following states of the NH molecule.
  - <sup>1</sup> (M<sub>L</sub>=2, M<sub>S</sub>=0),
  - <sup>1</sup> (M<sub>L</sub>=0, M<sub>S</sub>=0), and
  - <sup>3</sup> (M<sub>L</sub>=0, M<sub>S</sub>=0).

### Problems

- Let us investigate the reactions:
  - CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>)      H<sub>2</sub> + C , and

ii.  $\text{CH}_2(^3\text{B}_1) \rightarrow \text{H}_2 + \text{C}$ ,  
under an assumed  $\text{C}_{2v}$  reaction pathway utilizing the following information:

C atom:  $^3\text{P}$   $29.2 \text{ kcal/mole}$   $^1\text{D}$   $32.7 \text{ kcal/mole}$   $^1\text{S}$

$\text{C}(^3\text{P}) + \text{H}_2 \rightarrow \text{CH}_2(^3\text{B}_1) \quad E = -78.8 \text{ kcal/mole}$

$\text{C}(^1\text{D}) + \text{H}_2 \rightarrow \text{CH}_2(^1\text{A}_1) \quad E = -97.0 \text{ kcal/mole}$

$\text{IP}(\text{H}_2) > \text{IP}(2s \text{ carbon})$ .

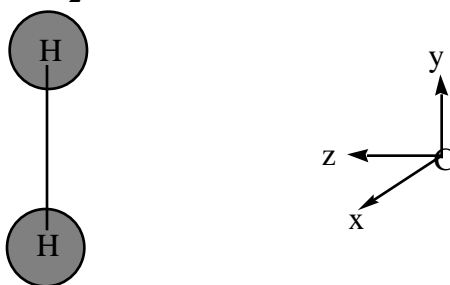
a. Write down (first in terms of  $2p_{1,0,-1}$  orbitals and then in terms of  $2p_{x,y,z}$  orbitals) the:

i. three Slater determinant (SD) wavefunctions belonging to the  $^3\text{P}$  state all of which have  $M_S = 1$ ,

ii. five  $^1\text{D}$  SD wavefunctions, and

iii. one  $^1\text{S}$  SD wavefunction.

b. Using the coordinate system shown below, label the hydrogen orbitals  $g$ ,  $u$  and the carbon  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ , orbitals as  $a_1$ ,  $b_1(x)$ ,  $b_2(y)$ , or  $a_2$ . Do the same for the  $s$ ,  $p$ ,  $d$ ,  $f$ ,  $g$ ,  $h$ , and  $i$  orbitals of  $\text{CH}_2$ .



c. Draw an orbital correlation diagram for the  $\text{CH}_2 \rightarrow \text{H}_2 + \text{C}$  reactions. Try to represent the relative energy orderings of the orbitals correctly.

d. Draw (on graph paper) a configuration correlation diagram for  $\text{CH}_2(^3\text{B}_1) \rightarrow \text{H}_2 + \text{C}$  showing all configurations which arise from the  $\text{C}(^3\text{P}) + \text{H}_2$  products. You can assume that doubly excited configurations lie much ( $\sim 100 \text{ kcal/mole}$ ) above their parent configurations.

e. Repeat step d. for  $\text{CH}_2(^1\text{A}_1) \rightarrow \text{H}_2 + \text{C}$  again showing all configurations which arise from the  $\text{C}(^1\text{D}) + \text{H}_2$  products.

f. Do you expect the reaction  $\text{C}(^3\text{P}) + \text{H}_2 \rightarrow \text{CH}_2$  to have a large activation barrier? About how large? What state of  $\text{CH}_2$  is produced in this reaction? Would distortions away from  $\text{C}_{2v}$  symmetry be expected to raise or lower the activation barrier? Show how one could estimate where along the reaction path the barrier top occurs.

g. Would  $\text{C}(^1\text{D}) + \text{H}_2 \rightarrow \text{CH}_2$  be expected to have a larger or smaller barrier than you found for the  $^3\text{P}$  C reaction?

2. The decomposition of the ground-state singlet carbene,



to produce acetylene and  $^1\text{D}$  carbon is known to occur with an activation energy equal to the reaction endothermicity. However, when triplet carbene decomposes to acetylene and ground-state (triplet) carbon, the activation energy exceeds this reaction's endothermicity.

Construct orbital, configuration, and state correlation diagrams which permit you to explain the above observations. Indicate whether single configuration or configuration interaction wavefunctions would be required to describe the above singlet and triplet decomposition processes.

3. We want to carry out a configuration interaction calculation on  $H_2$  at  $R=1.40$  au. A minimal basis consisting of normalized  $1s$  Slater orbitals with  $\alpha=1.0$  gives rise to the following overlap ( $S$ ), one-electron ( $h$ ), and two-electron atomic integrals:

$$\langle 1s_A | 1s_B \rangle = 0.753 \quad S,$$

$$\langle 1s_A | h | 1s_A \rangle = -1.110, \quad \langle 1s_B | h | 1s_A \rangle = -0.968,$$

$$\langle 1s_A 1s_A | h | 1s_A 1s_A \rangle = 0.625 \quad \langle AA | AA \rangle$$

$$\langle AA | BB \rangle = 0.323, \quad \langle AB | AB \rangle = 0.504, \text{ and}$$

$$\langle AA | AB \rangle = 0.426.$$

a. The normalized and orthogonal molecular orbitals we will use for this minimal basis will be determined purely by symmetry:

$$g = (2+2S)^{-\frac{1}{2}} (1s_A + 1s_B), \text{ and}$$

$$u = (2-2S)^{-\frac{1}{2}} (1s_A - 1s_B).$$

Show that these orbitals are indeed orthogonal.

b. Evaluate (using the one- and two- electron atomic integrals given above) the unique one- and two- electron integrals over this molecular orbital basis (this is called a transformation from the ao to the mo basis). For example, evaluate  $\langle u | h | u \rangle$ ,  $\langle uu | uu \rangle$ ,  $\langle gu | gu \rangle$ , etc.

c. Using the two  $1^+g$  configurations  $g^2$ , and  $u^2$ , show that the elements of the  $2 \times 2$  configuration interaction Hamiltonian matrix are  $-1.805$ ,  $0.140$ , and  $-0.568$ .

d. Using this configuration interaction matrix, find the configuration interaction (CI) approximation to the ground and excited state energies and wavefunctions.

e. Evaluate and make a rough sketch of the polarized orbitals which result from the above ground state  $g^2$  and  $u^2$  CI wavefunction.

## Solutions

### Review Exercises

1. a. For non-degenerate point groups one can simply multiply the representations (since only one representation will be obtained):

$$a_1 \otimes b_1 = b_1$$

Constructing a "box" in this case is unnecessary since it would only contain a single row. Two unpaired electrons will result in a singlet ( $S=0$ ,  $M_S=0$ ), and three triplets ( $S=1$ ,

$M_S=1$ ;  $S=1$ ,  $M_S=0$ ;  $S=1$ ,  $M_S=-1$ ). The states will be:  ${}^3B_1(M_S=1)$ ,  ${}^3B_1(M_S=0)$ ,  ${}^3B_1(M_S=-1)$ , and  ${}^1B_1(M_S=0)$ .

1. b. Remember that when coupling non-equivalent linear molecule angular momenta, one simply adds the individual  $L_z$  values and vector couples the electron spin. So, in this case ( $1 \otimes u^1 2 \otimes u^1$ ), we have  $M_L$  values of  $1+1$ ,  $1-1$ ,  $-1+1$ , and  $-1-1$  ( $2$ ,  $0$ ,  $0$ , and  $-2$ ). The

term symbol  $^1D$  is used to denote the spatially doubly degenerate level ( $M_L = \pm 2$ ) and there are two distinct spatially non-degenerate levels denoted by the term symbol  $^1D$  ( $M_L = 0$ ). Again, two unpaired electrons will result in a singlet ( $S=0, M_S=0$ ), and three triplets ( $S=1, M_S=1; S=1, M_S=0; S=1, M_S=-1$ ). The states generated are then:

- $^1D$  ( $M_L=2$ ); one state ( $M_S=0$ ),
- $^1D$  ( $M_L=-2$ ); one state ( $M_S=0$ ),
- $^3D$  ( $M_L=2$ ); three states ( $M_S=1, 0, \text{ and } -1$ ),
- $^3D$  ( $M_L=-2$ ); three states ( $M_S=1, 0, \text{ and } -1$ ),
- $^1D$  ( $M_L=0$ ); one state ( $M_S=0$ ),
- $^1D$  ( $M_L=0$ ); one state ( $M_S=0$ ),
- $^3D$  ( $M_L=0$ ); three states ( $M_S=1, 0, \text{ and } -1$ ), and
- $^3D$  ( $M_L=0$ ); three states ( $M_S=1, 0, \text{ and } -1$ ).

1. c. Constructing the "box" for two equivalent electrons one obtains:

$M_S$	$M_L$	2	1	0
1				1 -1
0		1 1		1 -1  ,   -1 1

From this "box" one obtains six states:

- $^1D$  ( $M_L=2$ ); one state ( $M_S=0$ ),
- $^1D$  ( $M_L=-2$ ); one state ( $M_S=0$ ),
- $^1D$  ( $M_L=0$ ); one state ( $M_S=0$ ),
- $^3D$  ( $M_L=0$ ); three states ( $M_S=1, 0, \text{ and } -1$ ).

1. d. It is not necessary to construct a "box" when coupling non-equivalent angular momenta since the vector coupling results in a range from the sum of the two individual angular momenta to the absolute value of their difference. In this case,  $3d^1 4d^1$ ,  $L=4, 3, 2, 1, 0$ , and  $S=1, 0$ . The term symbols are:  $^3G, ^1G, ^3F, ^1F, ^3D, ^1D, ^3P, ^1P, ^3S$ , and  $^1S$ . The L and S angular momenta can be vector coupled to produce further splitting into levels:

$$J = L + S \dots |L - S|$$

Denoting J as a term symbol subscript one can identify all the levels and subsequent ( $2J + 1$ ) states:

- $^3G_5$  (11 states),
- $^3G_4$  (9 states),
- $^3G_3$  (7 states),
- $^1G_4$  (9 states),
- $^3F_4$  (9 states),
- $^3F_3$  (7 states),

${}^3F_2$  (5 states),  
 ${}^1F_3$  (7 states),  
 ${}^3D_3$  (7 states),  
 ${}^3D_2$  (5 states),  
 ${}^3D_1$  (3 states),  
 ${}^1D_2$  (5 states),  
 ${}^3P_2$  (5 states),  
 ${}^3P_1$  (3 states),  
 ${}^3P_0$  (1 state),  
 ${}^1P_1$  (3 states),  
 ${}^3S_1$  (3 states), and  
 ${}^1S_0$  (1 state).

1. e. Construction of a "box" for the two equivalent d electrons generates (note the "box" has been turned side ways for convenience):

$M_L$	$M_S$	1	0
4			$ d_2 d_2  $
3		$ d_2 d_1  $	$ d_2 d_1  ,$ $ d_2 d_1  $
2		$ d_2 d_0  $	$ d_2 d_0  ,$ $ d_2 d_0  ,$ $ d_1 d_1  $
1		$ d_1 d_0  ,$ $ d_2 d_{-1}  $	$ d_1 d_0  ,$ $ d_1 d_0  ,$ $ d_2 d_{-1}  ,$ $ d_2 d_{-1}  $
0		$ d_2 d_{-2}  ,$ $ d_1 d_{-1}  $	$ d_2 d_{-2}  ,$ $ d_2 d_{-2}  ,$ $ d_1 d_{-1}  ,$ $ d_1 d_{-1}  ,$ $ d_0 d_0  $

The term symbols are:  ${}^1G$ ,  ${}^3F$ ,  ${}^1D$ ,  ${}^3P$ , and  ${}^1S$ . The L and S angular momenta can be vector coupled to produce further splitting into levels:

${}^1G_4$  (9 states),  
 ${}^3F_4$  (9 states),  
 ${}^3F_3$  (7 states),  
 ${}^3F_2$  (5 states),  
 ${}^1D_2$  (5 states),  
 ${}^3P_2$  (5 states),

${}^3P_1$  (3 states),  
 ${}^3P_0$  (1 state), and  
 ${}^1S_0$  (1 state).

### Exercises

1. Constructing the Slater determinant corresponding to the "state"  $1s( )1s( )$  with the rows labeling the orbitals and the columns labeling the electron gives:

$$\begin{aligned} |1s \ 1s| &= \frac{1}{\sqrt{2!}} \begin{vmatrix} 1s(1) & 1s(2) \\ 1s(1) & 1s(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (1s(1)1s(2) - 1s(1)1s(2)) \\ &= 0 \end{aligned}$$

2. Starting with the  $M_S=1$   ${}^3S$  state (which in a "box" for this  $M_L=0$ ,  $M_S=1$  case would contain only one product function;  $|1s \ 2s \uparrow \uparrow\rangle$ ) and applying  $S_-$  gives:

$$\begin{aligned} S_- {}^3S(S=1, M_S=1) &= \sqrt{1(1+1) - 1(1-1)} \hbar {}^3S(S=1, M_S=0) \\ &= \hbar \sqrt{2} {}^3S(S=1, M_S=0) \\ &= (S_-(1) + S_-(2)) |1s \ 2s \uparrow \uparrow\rangle \\ &= S_-(1) |1s \ 2s \uparrow \uparrow\rangle + S_-(2) |1s \ 2s \uparrow \uparrow\rangle \\ &= \hbar \sqrt{\frac{1}{2} \frac{1}{2} + 1} \left[ \frac{1}{2} |1s \ 2s \uparrow \downarrow\rangle - \frac{1}{2} |1s \ 2s \downarrow \uparrow\rangle \right] \\ &\quad + \hbar \sqrt{\frac{1}{2} \frac{1}{2} + 1} \left[ \frac{1}{2} |1s \ 2s \uparrow \downarrow\rangle - \frac{1}{2} |1s \ 2s \downarrow \uparrow\rangle \right] \\ &= \hbar (|1s \ 2s \uparrow \downarrow\rangle + |1s \ 2s \downarrow \uparrow\rangle) \end{aligned}$$

So,  $\hbar \sqrt{2} {}^3S(S=1, M_S=0) = \hbar (|1s \ 2s \uparrow \downarrow\rangle + |1s \ 2s \downarrow \uparrow\rangle)$

$${}^3S(S=1, M_S=0) = \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow \downarrow\rangle + |1s \ 2s \downarrow \uparrow\rangle)$$

The three triplet states are then:

$${}^3S(S=1, M_S=1) = |1s \ 2s \uparrow \uparrow\rangle,$$

$${}^3S(S=1, M_S=0) = \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow \downarrow\rangle + |1s \ 2s \downarrow \uparrow\rangle), \text{ and}$$

$${}^3S(S=1, M_S=-1) = |1s \ 2s \downarrow \downarrow\rangle.$$

The singlet state which must be constructed orthogonal to the three singlet states (and in particular to the  ${}^3S(S=1, M_S=0)$  state) can be seen to be:

$${}^1S(S=0, M_S=0) = \frac{1}{\sqrt{2}} (|1s \ 2s \uparrow \downarrow\rangle - |1s \ 2s \downarrow \uparrow\rangle).$$

Applying  $S^2$  and  $S_z$  to each of these states gives:

$$\begin{aligned} S_z |1s \ 2s \rangle &= (S_z(1) + S_z(2)) |1s \ 2s \rangle \\ &= S_z(1)|1s \ 2s \rangle + S_z(2)|1s \ 2s \rangle \\ &= \hbar \frac{1}{2} |1s \ 2s \rangle + \hbar \frac{1}{2} |1s \ 2s \rangle \\ &= \hbar |1s \ 2s \rangle \end{aligned}$$

$$\begin{aligned} S^2 |1s \ 2s \rangle &= (S \cdot S + S_z^2 + \hbar S_z) |1s \ 2s \rangle \\ &= S \cdot S |1s \ 2s \rangle + S_z^2 |1s \ 2s \rangle + \hbar S_z |1s \ 2s \rangle \\ &= 0 + \hbar^2 |1s \ 2s \rangle + \hbar^2 |1s \ 2s \rangle \\ &= 2\hbar^2 |1s \ 2s \rangle \end{aligned}$$

$$\begin{aligned} S_z \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) &= (S_z(1) + S_z(2)) \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) \\ &= \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \ 2s \rangle \\ &\quad + \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \ 2s \rangle \\ &= \frac{1}{\sqrt{2}} \hbar \left( \frac{1}{2} + \frac{1}{2} \right) |1s \ 2s \rangle \\ &\quad + \frac{1}{\sqrt{2}} \hbar \left( \frac{1}{2} + \frac{1}{2} \right) |1s \ 2s \rangle \\ &= 0\hbar \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) \end{aligned}$$

$$\begin{aligned} S^2 \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) &= (S \cdot S + S_z^2 + \hbar S_z) \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) \\ &= S \cdot S \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) \\ &= \frac{1}{\sqrt{2}} (S \cdot (S_+(1) + S_+(2)) |1s \ 2s \rangle + S \cdot (S_+(1) + S_+(2)) |1s \ 2s \rangle) \\ &= \frac{1}{\sqrt{2}} S \cdot \hbar (|1s \ 2s \rangle + |1s \ 2s \rangle) \\ &= 2\hbar \frac{1}{\sqrt{2}} (S \cdot (1) + S \cdot (2)) |1s \ 2s \rangle \\ &= 2\hbar \frac{1}{\sqrt{2}} \hbar |1s \ 2s \rangle + \hbar |1s \ 2s \rangle \\ &= 2\hbar^2 \frac{1}{\sqrt{2}} (|1s \ 2s \rangle + |1s \ 2s \rangle) \\ S_z |1s \ 2s \rangle &= (S_z(1) + S_z(2)) |1s \ 2s \rangle \\ &= S_z(1)|1s \ 2s \rangle + S_z(2)|1s \ 2s \rangle \\ &= \hbar \left( \frac{1}{2} \right) |1s \ 2s \rangle + \hbar \left( \frac{1}{2} \right) |1s \ 2s \rangle \end{aligned}$$

$$\begin{aligned}
&= -h |1s \ 2s \rangle \\
S^2 |1s \ 2s \rangle &= (S_+ S_- + S_z^2 - h S_z) |1s \ 2s \rangle \\
&= S_+ S_- |1s \ 2s \rangle + S_z^2 |1s \ 2s \rangle - h S_z |1s \ 2s \rangle \\
&= 0 + h^2 |1s \ 2s \rangle + h^2 |1s \ 2s \rangle \\
&= 2h^2 |1s \ 2s \rangle \\
S_z \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle) &= (S_z(1) + S_z(2)) \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle) \\
&= \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \ 2s \rangle \\
&\quad - \frac{1}{\sqrt{2}} (S_z(1) + S_z(2)) |1s \ 2s \rangle \\
&= \frac{1}{\sqrt{2}} h \left( -\frac{1}{2} + h \frac{1}{2} \right) |1s \ 2s \rangle \\
&\quad - \frac{1}{\sqrt{2}} h \left( \frac{1}{2} + h \left( -\frac{1}{2} \right) \right) |1s \ 2s \rangle \\
&= 0h \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle) \\
S^2 \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle) &= (S_- S_+ + S_z^2 + h S_z) \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle) \\
&= S_- S_+ \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle) \\
&= \frac{1}{\sqrt{2}} (S_- (S_+(1) + S_+(2)) |1s \ 2s \rangle - S_- (S_+(1) + S_+(2)) |1s \ 2s \rangle) \\
&= \frac{1}{\sqrt{2}} S_- h |1s \ 2s \rangle - S_- h |1s \ 2s \rangle \\
&= 0h \frac{1}{\sqrt{2}} (S_-(1) + S_-(2)) |1s \ 2s \rangle \\
&= 0h \frac{1}{\sqrt{2}} h |1s \ 2s \rangle - h |1s \ 2s \rangle \\
&= 0h^2 \frac{1}{\sqrt{2}} (|1s \ 2s \rangle - |1s \ 2s \rangle)
\end{aligned}$$

3. a. Once the spatial symmetry has been determined by multiplication of the irreducible representations, the spin coupling is identical to exercise 2 and gives the result:

$$\frac{1}{\sqrt{2}} (|3a_1 \ 1b_1 \rangle - |3a_1 \ 1b_1 \rangle)$$

3. b. There are three states here (again analogous to exercise 2):

1.)  $|3a_1 \ 1b_1 \rangle$ ,

2.)  $\frac{1}{\sqrt{2}} (|3a_1 \ 1b_1 \rangle + |3a_1 \ 1b_1 \rangle)$ , and

3.)  $|3a_1 \ 1b_1 \rangle$

3. c.  $|3a_1 \ 3a_1 \rangle$

4. As shown in review exercise 1c, for two equivalent electrons one obtains six states:



- 1 ( $M_L=2$ ); one state ( $M_S=0$ ),
- 1 ( $M_L=-2$ ); one state ( $M_S=0$ ),
- 1 ( $M_L=0$ ); one state ( $M_S=0$ ), and
- 3 ( $M_L=0$ ); three states ( $M_S=1, 0$ , and  $-1$ ).

By inspecting the "box" in review exercise 1c, it should be fairly straightforward to write down the wavefunctions for each of these:

- 1 ( $M_L=2$ );  $| 1 \ 1 \ |$
- 1 ( $M_L=-2$ );  $| -1 \ -1 \ |$
- 1 ( $M_L=0$ );  $\frac{1}{\sqrt{2}}(| 1 \ -1 \ | - | 1 \ -1 \ |)$
- 3 ( $M_L=0, M_S=1$ );  $| 1 \ -1 \ |$
- 3 ( $M_L=0, M_S=0$ );  $\frac{1}{\sqrt{2}}(| 1 \ -1 \ | + | 1 \ -1 \ |)$
- 3 ( $M_L=0, M_S=-1$ );  $| 1 \ -1 \ |$

5. We can conveniently couple another s electron to the states generated from the  $1s^1 2s^1$  configuration in exercise 2:

$^3S(L=0, S=1)$  with  $3s^1(L=0, S=\frac{1}{2})$  giving:

$L=0, S=\frac{3}{2}, \frac{1}{2}$ ;  $^4S$  (4 states) and  $^2S$  (2 states).

$^1S(L=0, S=0)$  with  $3s^1(L=0, S=\frac{1}{2})$  giving:

$L=0, S=\frac{1}{2}$ ;  $^2S$  (2 states).

Constructing a "box" for this case would yield:

$M_S$	$M_L$	0
$\frac{3}{2}$		$  1s \ 2s \ 3s \  $
$\frac{1}{2}$		$  1s \ 2s \ 3s \  ,   1s \ 2s \ 3s \  ,   1s \ 2s \ 3s \  $

One can immediately identify the wavefunctions for two of the quartets (they are single entries):

$^4S(S=\frac{3}{2}, M_S=\frac{3}{2})$ :  $| 1s \ 2s \ 3s \ |$

$^4S(S=\frac{3}{2}, M_S=-\frac{3}{2})$ :  $| 1s \ 2s \ 3s \ |$

Applying  $S_-$  to  $^4S(S=\frac{3}{2}, M_S=\frac{3}{2})$  yields:

$$S_- 4S(S=\frac{3}{2}, M_S=\frac{3}{2}) = h \sqrt{\frac{3}{2}(\frac{3}{2} + 1) - \frac{3}{2}(\frac{3}{2} - 1)} 4S(S=\frac{3}{2}, M_S=\frac{1}{2}) \\ = h \sqrt{3} 4S(S=\frac{3}{2}, M_S=\frac{1}{2})$$

$$S_- |1s \ 2s \ 3s \rangle = h (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle) \\ \text{So, } 4S(S=\frac{3}{2}, M_S=\frac{1}{2}) = \frac{1}{\sqrt{3}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle)$$

Applying  $S_+$  to  $4S(S=\frac{3}{2}, M_S=-\frac{3}{2})$  yields:

$$S_+ 4S(S=\frac{3}{2}, M_S=-\frac{3}{2}) = h \sqrt{\frac{3}{2}(\frac{3}{2} + 1) - -\frac{3}{2}(-\frac{3}{2} + 1)} 4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) \\ = h \sqrt{3} 4S(S=\frac{3}{2}, M_S=-\frac{1}{2})$$

$$S_+ |1s \ 2s \ 3s \rangle = h (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle) \\ \text{So, } 4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) = \frac{1}{\sqrt{3}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle)$$

It only remains to construct the doublet states which are orthogonal to these quartet states. Recall that the orthogonal combinations for systems having three equal components (for example when symmetry adapting the 3  $sp^2$  hybrids in  $C_{2v}$  or  $D_{3h}$  symmetry) give results of  $+++$ ,  $+2--$ , and  $0+-$ . Notice that the quartets are the  $+++$  combinations and therefore the doublets can be recognized as:

$$2S(S=\frac{1}{2}, M_S=\frac{1}{2}) = \frac{1}{\sqrt{6}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle - 2|1s \ 2s \ 3s \rangle)$$

$$2S(S=\frac{1}{2}, M_S=\frac{1}{2}) = \frac{1}{\sqrt{2}} (|1s \ 2s \ 3s \rangle - |1s \ 2s \ 3s \rangle + 0|1s \ 2s \ 3s \rangle)$$

$$2S(S=\frac{1}{2}, M_S=-\frac{1}{2}) = \frac{1}{\sqrt{6}} (|1s \ 2s \ 3s \rangle + |1s \ 2s \ 3s \rangle - 2|1s \ 2s \ 3s \rangle)$$

$$2S(S=\frac{1}{2}, M_S=-\frac{1}{2}) = \frac{1}{\sqrt{3}} (|1s \ 2s \ 3s \rangle - |1s \ 2s \ 3s \rangle + 0|1s \ 2s \ 3s \rangle)$$

6. As illustrated in this chapter a  $p^2$  configuration (two equivalent p electrons) gives rise to the term symbols:  $3P$ ,  $1D$ , and  $1S$ . Coupling an additional electron ( $3d^1$ ) to this  $p^2$  configuration will give the desired  $1s^2 2s^2 2p^2 3d^1$  term symbols:

$3P(L=1, S=1)$  with  $2D(L=2, S=\frac{1}{2})$  generates;

$L=3, 2, 1$ , and  $S=\frac{3}{2}, \frac{1}{2}$  with term symbols  $4F$ ,  $2F$ ,  $4D$ ,  $2D$ ,  $4P$ , and  $2P$ ,

$1D(L=2, S=0)$  with  $2D(L=2, S=\frac{1}{2})$  generates;

$L=4, 3, 2, 1, 0$ , and  $S=\frac{1}{2}$  with term symbols  $2G$ ,  $2F$ ,  $2D$ ,  $2P$ , and  $2S$ ,

$1S(L=0, S=0)$  with  $2D(L=2, S=\frac{1}{2})$  generates;

$L=2$  and  $S=\frac{1}{2}$  with term symbol  $2D$ .

7. The notation used for the Slater Condon rules will be the same as used in the text:

(a.) zero (spin orbital) difference;

$$\begin{aligned}\langle F + G \rangle &= \sum_i \langle i | f | i \rangle + \sum_{i>j} \langle i j | g | i j \rangle - \sum_{i>j} \langle i j | g | j i \rangle \\ &= \sum_i f_{ii} + \sum_{i>j} (g_{ijij} - g_{ijji})\end{aligned}$$

(b.) one (spin orbital) difference (  $p \quad p'$  );

$$\begin{aligned}\langle F + G \rangle &= \langle p | f | p' \rangle + \sum_{j \quad p;p'} \langle p j | g | p' j \rangle - \sum_{j \quad p;p'} \langle p j | g | j p' \rangle \\ &= f_{pp'} + \sum_{j \quad p;p'} (g_{pj p'j} - g_{pjj p'})\end{aligned}$$

(c.) two (spin orbital) differences (  $p \quad p'$  and  $q \quad q'$  );

$$\begin{aligned}\langle F + G \rangle &= \langle p q | g | p' q' \rangle - \langle p q | g | q' p' \rangle \\ &= g_{ppq'q'} - g_{ppqq'p'}\end{aligned}$$

(d.) three or more (spin orbital) differences;

$$\langle F + G \rangle = 0$$

7. i.  ${}^3P(M_L=1, M_S=1) = |p_1 \quad p_0 \quad |$

$$\langle |p_1 \quad p_0 \quad | H | p_1 \quad p_0 \quad | \rangle =$$

**Error!.** Using the Slater Condon rule (a.) above (SCa):

$$\langle |10 \rangle H | 10 \rangle = f_{11} + f_{00} + g_{1010} - g_{1001}$$

7. ii.  ${}^3P(M_L=0, M_S=0) = \frac{1}{\sqrt{2}} (|p_1 \quad p_{-1} \quad | + |p_1 \quad p_{-1} \quad |)$

$$\begin{aligned}\langle {}^3P(M_L=0, M_S=0) | H | {}^3P(M_L=0, M_S=0) \rangle \\ &= \frac{1}{2} ( \langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle + \langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle \\ &\quad + \langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle + \langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle )\end{aligned}$$

Evaluating each matrix element gives:

$$\begin{aligned}\langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle &= f_{1 \quad 1} + f_{-1 \quad -1} + g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCa}) \\ &= f_{11} + f_{-1-1} + g_{1-11-1} - 0\end{aligned}$$

$$\begin{aligned}\langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle &= g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCc}) \\ &= 0 - g_{1-1-11}\end{aligned}$$

$$\begin{aligned}\langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle &= g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCc}) \\ &= 0 - g_{1-1-11}\end{aligned}$$

$$\begin{aligned}\langle |p_1 \quad p_{-1} \quad | H | p_1 \quad p_{-1} \quad | \rangle &= f_{1 \quad 1} + f_{-1 \quad -1} + g_{1 \quad -1 \quad 1 \quad -1} - g_{1 \quad -1 \quad -1 \quad 1} \quad (\text{SCa}) \\ &= f_{11} + f_{-1-1} + g_{1-11-1} - 0\end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned}\langle {}^3P(M_L=0, M_S=0) | H | {}^3P(M_L=0, M_S=0) \rangle \\ &= \frac{1}{2} ( f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} - g_{1-1-11} \\ &\quad + f_{11} + f_{-1-1} + g_{1-11-1} )\end{aligned}$$

$$\begin{aligned}
&= f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} \\
7. \quad \text{iii. } &{}^1S(M_L=0, M_S=0); \frac{1}{\sqrt{3}}(|p_0 p_0 \rangle - |p_1 p_{-1} \rangle - |p_{-1} p_1 \rangle) \\
&\langle {}^1S(M_L=0, M_S=0) | H | {}^1S(M_L=0, M_S=0) \rangle \\
&= \frac{1}{3} ( \langle p_0 p_0 | H | p_0 p_0 \rangle - \langle p_0 p_0 | H | p_1 p_{-1} \rangle \\
&\quad - \langle p_0 p_0 | H | p_{-1} p_1 \rangle - \langle p_1 p_{-1} | H | p_0 p_0 \rangle \\
&\quad + \langle p_1 p_{-1} | H | p_1 p_{-1} \rangle + \langle p_1 p_{-1} | H | p_{-1} p_1 \rangle \\
&\quad - \langle p_{-1} p_1 | H | p_0 p_0 \rangle + \langle p_{-1} p_1 | H | p_1 p_{-1} \rangle \\
&\quad + \langle p_{-1} p_1 | H | p_{-1} p_1 \rangle )
\end{aligned}$$

Evaluating each matrix element gives:

$$\begin{aligned}
\langle p_0 p_0 | H | p_0 p_0 \rangle &= f_{00} + f_{00} + g_{0000} - g_{0000} \quad (\text{SCa}) \\
&= f_{00} + f_{00} + g_{0000} - 0
\end{aligned}$$

$$\begin{aligned}
\langle p_0 p_0 | H | p_1 p_{-1} \rangle &= \langle p_1 p_{-1} | H | p_0 p_0 \rangle \\
&= g_{001-1} - g_{00-11} \quad (\text{SCc}) \\
&= g_{001-1} - 0
\end{aligned}$$

$$\begin{aligned}
\langle p_0 p_0 | H | p_{-1} p_1 \rangle &= \langle p_{-1} p_1 | H | p_0 p_0 \rangle \\
&= g_{00-11} - g_{001-1} \quad (\text{SCc}) \\
&= g_{00-11} - 0
\end{aligned}$$

$$\begin{aligned}
\langle p_1 p_{-1} | H | p_1 p_{-1} \rangle &= f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} \quad (\text{SCa}) \\
&= f_{11} + f_{-1-1} + g_{1-11-1} - 0
\end{aligned}$$

$$\begin{aligned}
\langle p_1 p_{-1} | H | p_{-1} p_1 \rangle &= \langle p_{-1} p_1 | H | p_1 p_{-1} \rangle \\
&= g_{1-1-11} - g_{1-11-1} \quad (\text{SCc}) \\
&= g_{1-1-11} - 0
\end{aligned}$$

$$\begin{aligned}
\langle p_{-1} p_1 | H | p_{-1} p_1 \rangle &= f_{-1-1} + f_{11} + g_{-11-11} - g_{-11-1-1} \quad (\text{SCa}) \\
&= f_{-1-1} + f_{11} + g_{-11-11} - 0
\end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned}
&\langle {}^1S(M_L=0, M_S=0) | H | {}^1S(M_L=0, M_S=0) \rangle \\
&= \frac{1}{3} ( f_{00} + f_{00} + g_{0000} - g_{001-1} - g_{00-11} - g_{001-1} + f_{11} + f_{-1-1} \\
&\quad + g_{1-11-1} + g_{1-1-11} - g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} + g_{-11-11} ) \\
&= \frac{1}{3} ( 2f_{00} + 2f_{11} + 2f_{-1-1} + g_{0000} - 4g_{001-1} + 2g_{1-11-1} + 2g_{1-1-11} )
\end{aligned}$$

$$7. \quad \text{iv. } {}^1D(M_L=0, M_S=0) = \frac{1}{\sqrt{6}} ( 2|p_0 p_0 \rangle + |p_1 p_{-1} \rangle + |p_{-1} p_1 \rangle )$$

Evaluating  $\langle {}^1D(M_L=0, M_S=0) | H | {}^1D(M_L=0, M_S=0) \rangle$  we note that all the Slater Condon matrix elements generated are the same as those evaluated in part iii. (the signs for the

wavefunction components and the multiplicative factor of two for one of the components, however, are different).

$$\begin{aligned}
 & \langle {}^1D(M_L=0, M_S=0) | H | {}^1D(M_L=0, M_S=0) \rangle \\
 &= \frac{1}{6} (4f_{00} + 4f_{00} + 4g_{0000} + 2g_{001-1} + 2g_{00-11} + 2g_{001-1} + f_{11} \\
 &\quad + f_{-1-1} + g_{1-11-1} + g_{1-1-11} + 2g_{00-11} + g_{1-1-11} + f_{-1-1} + f_{11} \\
 &\quad + g_{-11-11}) \\
 &= \frac{1}{6} (8f_{00} + 2f_{11} + 2f_{-1-1} + 4g_{0000} + 8g_{001-1} + 2g_{1-11-1} + 2g_{1-1-11})
 \end{aligned}$$

$$\begin{aligned}
 8. \quad i. \quad & {}^1(M_L=2, M_S=0) = | \begin{matrix} 1 & 1 \\ 1 & 1 \end{matrix} | \\
 & \langle {}^1(M_L=2, M_S=0) | H | {}^1(M_L=2, M_S=0) \rangle \\
 &= \langle | \begin{matrix} 1 & 1 \\ 1 & 1 \end{matrix} | H | \begin{matrix} 1 & 1 \\ 1 & 1 \end{matrix} | \rangle \\
 &= f_{1 \ 1} + f_{1 \ 1} + g_{1 \ 1 \ 1 \ 1} - g_{1 \ 1 \ 1 \ 1} \quad (\text{SCa}) \\
 &= f_{11} + f_{11} + g_{1111} - 0 \\
 &= 2f_{11} + g_{1111}
 \end{aligned}$$

$$\begin{aligned}
 8. \quad ii. \quad & {}^1(M_L=0, M_S=0) = \frac{1}{\sqrt{2}} (| \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | - | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} |) \\
 & \langle {}^3(M_L=0, M_S=0) | H | {}^3(M_L=0, M_S=0) \rangle \\
 &= \frac{1}{2} ( \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle - \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle \\
 &\quad - \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle + \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle )
 \end{aligned}$$

Evaluating each matrix element gives:

$$\begin{aligned}
 \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle &= f_{1 \ 1} + f_{-1 \ -1} + g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCa}) \\
 &= f_{11} + f_{-1-1} + g_{1-11-1} - 0
 \end{aligned}$$

$$\begin{aligned}
 \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle &= g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCc}) \\
 &= 0 - g_{1-1-11}
 \end{aligned}$$

$$\begin{aligned}
 \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle &= g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCc}) \\
 &= 0 - g_{1-1-11}
 \end{aligned}$$

$$\begin{aligned}
 \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle &= f_{1 \ 1} + f_{-1 \ -1} + g_{1 \ -1 \ 1 \ -1} - g_{1 \ -1 \ -1 \ 1} \quad (\text{SCa}) \\
 &= f_{11} + f_{-1-1} + g_{1-11-1} - 0
 \end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned}
 & \langle {}^3(M_L=0, M_S=0) | H | {}^3(M_L=0, M_S=0) \rangle \\
 &= \frac{1}{2} (f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11} + g_{1-1-11} + f_{11} + f_{-1-1} + g_{1-11-1}) \\
 &= f_{11} + f_{-1-1} + g_{1-11-1} + g_{1-1-11}
 \end{aligned}$$

$$\begin{aligned}
 8. \quad iii. \quad & {}^3(M_L=0, M_S=0) = \frac{1}{\sqrt{2}} (| \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | + | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} |) \\
 & \langle {}^3(M_L=0, M_S=0) | H | {}^3(M_L=0, M_S=0) \rangle \\
 &= \frac{1}{2} ( \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle + \langle | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | H | \begin{matrix} 1 & -1 \\ 1 & -1 \end{matrix} | \rangle )
 \end{aligned}$$

$$+ \langle 1 \ -1 | H | 1 \ -1 \rangle + \langle 1 \ -1 | H | 1 \ -1 \rangle )$$

Evaluating each matrix element gives:

$$\begin{aligned} \langle 1 \ -1 | H | 1 \ -1 \rangle &= f_{11} + f_{-1-1} + g_{1-1} - g_{-1-1} \quad (\text{SCa}) \\ &= f_{11} + f_{-1-1} + g_{1-1-1} - 0 \end{aligned}$$

$$\begin{aligned} \langle 1 \ -1 | H | 1 \ -1 \rangle &= g_{1-1} - g_{-1-1} \quad (\text{SCc}) \\ &= 0 - g_{1-1-1} \end{aligned}$$

$$\begin{aligned} \langle 1 \ -1 | H | 1 \ -1 \rangle &= g_{1-1} - g_{-1-1} \quad (\text{SCc}) \\ &= 0 - g_{1-1-1} \end{aligned}$$

$$\begin{aligned} \langle 1 \ -1 | H | 1 \ -1 \rangle &= f_{11} + f_{-1-1} + g_{1-1} - g_{-1-1} \quad (\text{SCa}) \\ &= f_{11} + f_{-1-1} + g_{1-1-1} - 0 \end{aligned}$$

Substitution of these expressions give:

$$\begin{aligned} &\langle {}^3(M_L=0, M_S=0) | H | {}^3(M_L=0, M_S=0) \rangle \\ &= \frac{1}{2} (f_{11} + f_{-1-1} + g_{1-1-1} - g_{-1-1-1} - g_{1-1-1} + f_{11} + f_{-1-1} + g_{1-1-1}) \\ &= f_{11} + f_{-1-1} + g_{1-1-1} - g_{-1-1-1} \end{aligned}$$

### Problems

1. a. All the Slater determinants have in common the  $|1s \ 1s \ 2s \ 2s \rangle$  "core" and hence this component will not be written out explicitly for each case.

$$\begin{aligned} {}^3P(M_L=1, M_S=1) &= |p_1 \ p_0 \ | \\ &= \frac{1}{\sqrt{2}} (p_x + ip_y) \ (p_z) \ | \\ &= \frac{1}{\sqrt{2}} (|p_x \ p_z \ | + i|p_y \ p_z \ |) \end{aligned}$$

$$\begin{aligned} {}^3P(M_L=0, M_S=1) &= |p_1 \ p_{-1} \ | \\ &= \frac{1}{\sqrt{2}} (p_x + ip_y) \ \frac{1}{\sqrt{2}} (p_x - ip_y) \ | \\ &= \frac{1}{2} (|p_x \ p_x \ | - i|p_x \ p_y \ | + i|p_y \ p_x \ | + |p_y \ p_y \ |) \\ &= \frac{1}{2} (0 - i|p_x \ p_y \ | - i|p_x \ p_y \ | + 0) \\ &= \frac{1}{2} (-2i|p_x \ p_y \ |) \\ &= -i|p_x \ p_y \ | \end{aligned}$$

$$\begin{aligned} {}^3P(M_L=-1, M_S=1) &= |p_{-1} \ p_0 \ | \\ &= \frac{1}{\sqrt{2}} (p_x - ip_y) \ (p_z) \ | \\ &= \frac{1}{\sqrt{2}} (|p_x \ p_z \ | - i|p_y \ p_z \ |) \end{aligned}$$

As you can see, the symmetries of each of these states cannot be labeled with a single irreducible representation of the  $C_{2v}$  point group. For example,  $|p_x \ p_z \ |$  is  $xz$  ( $B_1$ ) and

$|p_y p_z \rangle$  is  $yz$  ( $B_2$ ) and hence the  ${}^3P(M_L=1, M_S=1)$  state is a combination of  $B_1$  and  $B_2$  symmetries. But, the three  ${}^3P(M_L, M_S=1)$  functions are degenerate for the C atom and any combination of these three functions would also be degenerate. Therefore we can choose new combinations which can be labeled with "pure"  $C_{2v}$  point group labels.

$$\begin{aligned} {}^3P(xz, M_S=1) &= |p_x p_z \rangle \\ &= \frac{1}{\sqrt{2}} ({}^3P(M_L=1, M_S=1) + {}^3P(M_L=-1, M_S=1)) = {}^3B_1 \end{aligned}$$

$$\begin{aligned} {}^3P(yx, M_S=1) &= |p_y p_x \rangle \\ &= \frac{1}{1} ({}^3P(M_L=0, M_S=1)) = {}^3A_2 \end{aligned}$$

$$\begin{aligned} {}^3P(yz, M_S=1) &= |p_y p_z \rangle \\ &= \frac{1}{i\sqrt{2}} ({}^3P(M_L=1, M_S=1) - {}^3P(M_L=-1, M_S=1)) = {}^3B_2 \end{aligned}$$

Now we can do likewise for the five degenerate  ${}^1D$  states:

$$\begin{aligned} {}^1D(M_L=2, M_S=0) &= |p_1 p_1 \rangle \\ &= \left| \frac{1}{\sqrt{2}}(p_x + ip_y) \frac{1}{\sqrt{2}}(p_x + ip_y) \right| \\ &= \frac{1}{2} (|p_x p_x \rangle + i|p_x p_y \rangle + i|p_y p_x \rangle - |p_y p_y \rangle) \end{aligned}$$

$$\begin{aligned} {}^1D(M_L=-2, M_S=0) &= |p_{-1} p_{-1} \rangle \\ &= \left| \frac{1}{\sqrt{2}}(p_x - ip_y) \frac{1}{\sqrt{2}}(p_x - ip_y) \right| \\ &= \frac{1}{2} (|p_x p_x \rangle - i|p_x p_y \rangle - i|p_y p_x \rangle - |p_y p_y \rangle) \end{aligned}$$

$$\begin{aligned} {}^1D(M_L=1, M_S=0) &= \frac{1}{\sqrt{2}} (|p_0 p_1 \rangle - |p_0 p_{-1} \rangle) \\ &= \frac{1}{\sqrt{2}} \left( |p_z \rangle \frac{1}{\sqrt{2}}(p_x + ip_y) \right| - \left( |p_z \rangle \frac{1}{\sqrt{2}}(p_x + ip_y) \right| \\ &= \frac{1}{2} (|p_z p_x \rangle + i|p_z p_y \rangle - |p_z p_x \rangle - i|p_z p_y \rangle) \end{aligned}$$

$$\begin{aligned} {}^1D(M_L=-1, M_S=0) &= \frac{1}{\sqrt{2}} (|p_0 p_{-1} \rangle - |p_0 p_1 \rangle) \\ &= \frac{1}{\sqrt{2}} \left( |p_z \rangle \frac{1}{\sqrt{2}}(p_x - ip_y) \right| - \left( |p_z \rangle \frac{1}{\sqrt{2}}(p_x - ip_y) \right| \\ &= \frac{1}{2} (|p_z p_x \rangle - i|p_z p_y \rangle - |p_z p_x \rangle + i|p_z p_y \rangle) \end{aligned}$$

$$\begin{aligned} {}^1D(M_L=0, M_S=0) &= \frac{1}{\sqrt{6}} (2|p_0 p_0 \rangle + |p_1 p_{-1} \rangle + |p_{-1} p_1 \rangle) \\ &= \frac{1}{\sqrt{6}} \left( 2|p_z p_z \rangle + \left| \frac{1}{\sqrt{2}}(p_x + ip_y) \frac{1}{\sqrt{2}}(p_x - ip_y) \right| \right. \\ &\quad \left. + \left| \frac{1}{\sqrt{2}}(p_x - ip_y) \frac{1}{\sqrt{2}}(p_x + ip_y) \right| \right) \\ &= \frac{1}{\sqrt{6}} (2|p_z p_z \rangle \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2}(|p_x p_x \rangle - i|p_x p_y \rangle + i|p_y p_x \rangle + |p_y p_y \rangle) \\
& + \frac{1}{2}(|p_x p_x \rangle + i|p_x p_y \rangle - i|p_y p_x \rangle + |p_y p_y \rangle) \\
& = \frac{1}{\sqrt{6}}(2|p_z p_z \rangle + |p_x p_x \rangle + |p_y p_y \rangle)
\end{aligned}$$

Analogous to the three  $^3P$  states we can also choose combinations of the five degenerate  $^1D$  states which can be labeled with "pure"  $C_{2v}$  point group labels:

$$\begin{aligned}
^1D_{(xx-yy, M_S=0)} &= |p_x p_x \rangle - |p_y p_y \rangle \\
&= (^1D_{(M_L=2, M_S=0)} + ^1D_{(M_L=-2, M_S=0)}) = ^1A_1
\end{aligned}$$

$$\begin{aligned}
^1D_{(yx, M_S=0)} &= |p_x p_y \rangle + |p_y p_x \rangle \\
&= \frac{1}{i} (^1D_{(M_L=2, M_S=0)} - ^1D_{(M_L=-2, M_S=0)}) = ^1A_2
\end{aligned}$$

$$\begin{aligned}
^1D_{(zx, M_S=0)} &= |p_z p_x \rangle - |p_z p_x \rangle \\
&= (^1D_{(M_L=1, M_S=0)} + ^1D_{(M_L=-1, M_S=0)}) = ^1B_1
\end{aligned}$$

$$\begin{aligned}
^1D_{(zy, M_S=0)} &= |p_z p_y \rangle - |p_z p_y \rangle \\
&= \frac{1}{i} (^1D_{(M_L=1, M_S=0)} - ^1D_{(M_L=-1, M_S=0)}) = ^1B_2
\end{aligned}$$

$$\begin{aligned}
^1D_{(2zz+xx+yy, M_S=0)} &= \frac{1}{\sqrt{6}}(2|p_z p_z \rangle + |p_x p_x \rangle + |p_y p_y \rangle) \\
&= ^1D_{(M_L=0, M_S=0)} = ^1A_1
\end{aligned}$$

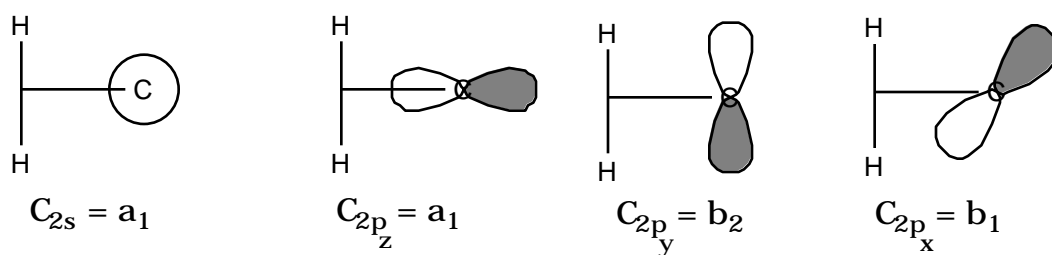
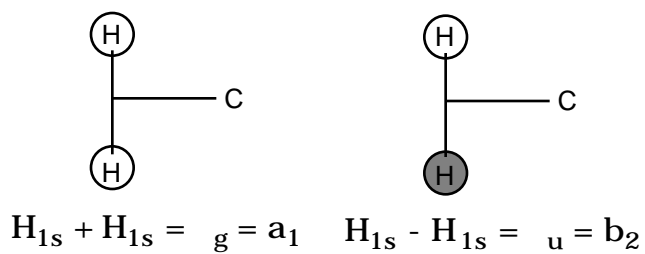
The only state left is the  $^1S$ :

$$\begin{aligned}
^1S_{(M_L=0, M_S=0)} &= \frac{1}{\sqrt{3}}(|p_0 p_0 \rangle - |p_1 p_{-1} \rangle - |p_{-1} p_1 \rangle) \\
&= \frac{1}{\sqrt{3}}(|p_z p_z \rangle - \frac{1}{\sqrt{2}}(p_x + ip_y) \frac{1}{\sqrt{2}}(p_x - ip_y) \\
&\quad - \frac{1}{\sqrt{2}}(p_x - ip_y) \frac{1}{\sqrt{2}}(p_x + ip_y) \rangle) \\
&= \frac{1}{\sqrt{3}}(|p_z p_z \rangle \\
&\quad - \frac{1}{2}(|p_x p_x \rangle - i|p_x p_y \rangle + i|p_y p_x \rangle + |p_y p_y \rangle) \\
&\quad - \frac{1}{2}(|p_x p_x \rangle + i|p_x p_y \rangle - i|p_y p_x \rangle + |p_y p_y \rangle) \rangle) \\
&= \frac{1}{\sqrt{3}}(|p_z p_z \rangle - |p_x p_x \rangle - |p_y p_y \rangle)
\end{aligned}$$

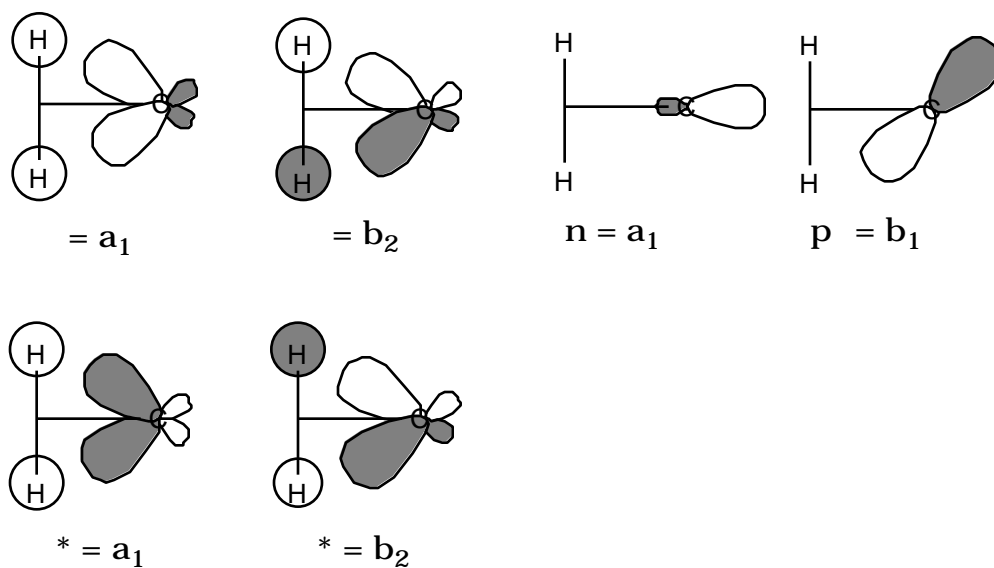
Each of the components of this state are  $A_1$  and hence this state has  $A_1$  symmetry.

1. b. Forming SALC-AOs from the C and H atomic orbitals would generate the following:



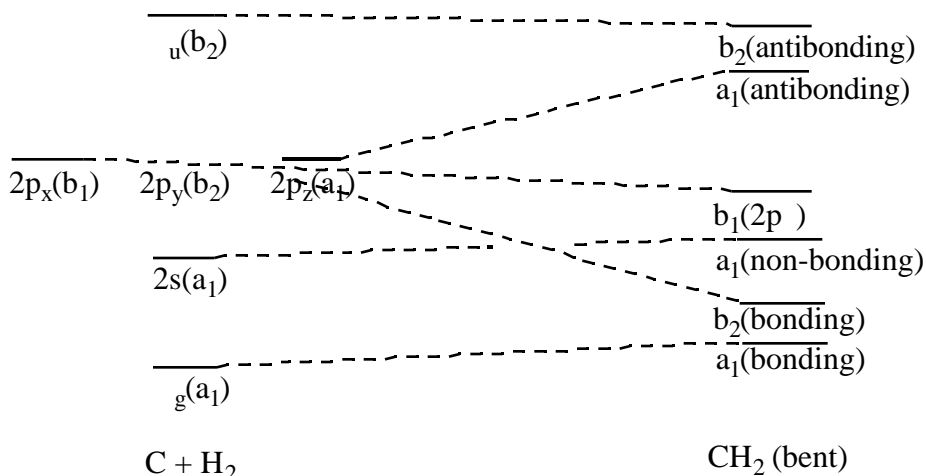


The bonding, nonbonding, and antibonding orbitals of  $CH_2$  can be illustrated in the following manner:



1. c.

Orbital-correlation diagram for the reaction  $C + H_2 \rightarrow CH_2$  (bent)



1. d. - e. It is necessary to determine how the wavefunctions found in part a. correlate with states of the  $CH_2$  molecule:

$${}^3P(xz, M_S=1); {}^3B_1 = g^2s^2p_xp_z \quad 2n^2p^*$$

$${}^3P(yx, M_S=1); {}^3A_2 = g^2s^2p_xp_y \quad 2n^2p$$

$${}^3P(yz, M_S=1); {}^3B_2 = g^2s^2p_y p_z \quad 2n^2^*$$

$${}^1D(xx-yy, M_S=0); {}^1A_1 \quad 2n^2p^2 - 2n^2^2$$

$${}^1D(yx, M_S=0); {}^1A_2 \quad 2n^2p$$

$${}^1D(zx, M_S=0); {}^1B_1 \quad 2n^2^*p$$

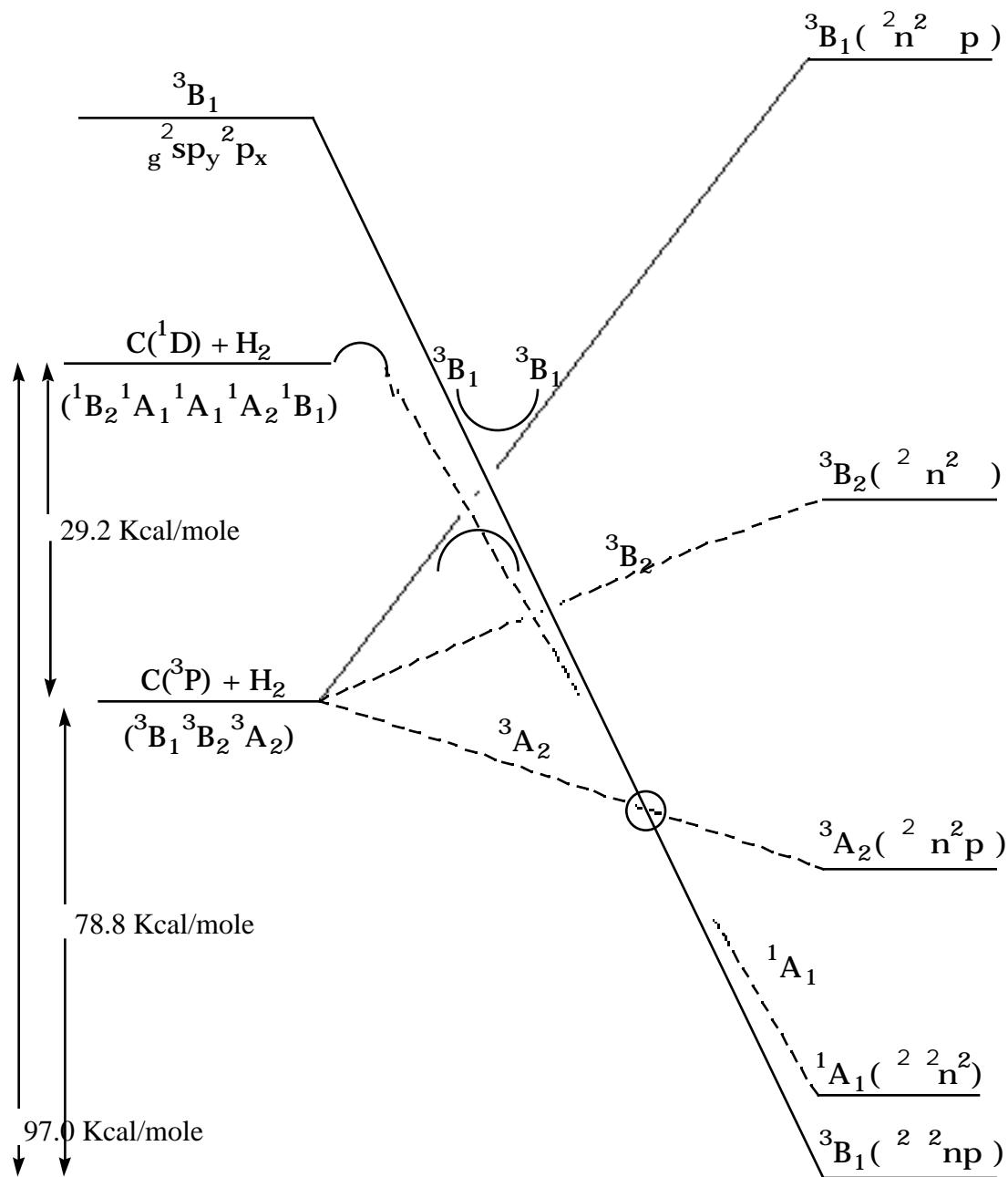
$${}^1D(zy, M_S=0); {}^1B_2 \quad 2n^2^*$$

$${}^1D(2zz+xx+yy, M_S=0); {}^1A_1 \quad 2^2n^2^*2 + 2n^2p^2 + 2n^2^2$$

Note, the  $C + H_2$  state to which the lowest  ${}^1A_1$  ( $2n^2^2$ )  $CH_2$  state decomposes would be  $g^2s^2p_y^2$ . This state ( $g^2s^2p_y^2$ ) cannot be obtained by a simple combination of the  ${}^1D$  states. In order to obtain pure  $g^2s^2p_y^2$  it is necessary to combine  ${}^1S$  with  ${}^1D$ . For example,

$$g^2s^2p_y^2 = \frac{1}{6}(\sqrt{6} {}^1D(0,0) - 2\sqrt{3} {}^1S(0,0)) - \frac{1}{2}({}^1D(2,0) + {}^1D(-2,0)) .$$

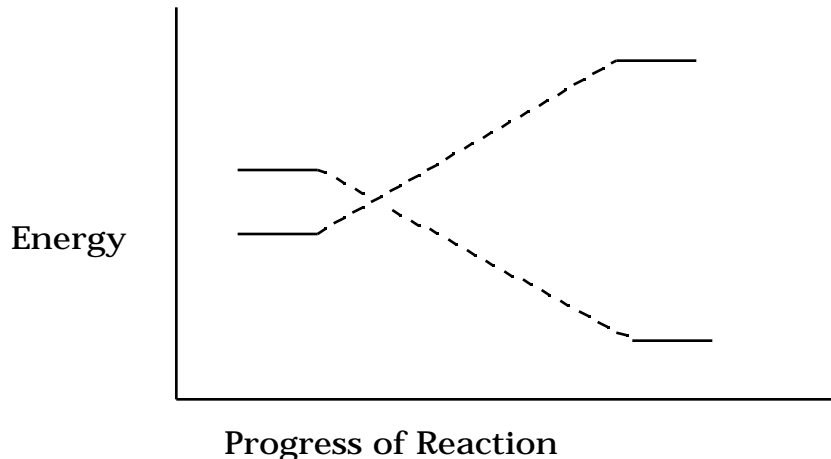
This indicates that a CCD must be drawn with a barrier near the  ${}^1D$  asymptote to represent the fact that  ${}^1A_1$   $CH_2$  correlates with a mixture of  ${}^1D$  and  ${}^1S$  carbon plus hydrogen. The  $C + H_2$  state to which the lowest  ${}^3B_1$  ( $2n^2p$ )  $CH_2$  state decomposes would be  $g^2sp_y^2p_x$ .



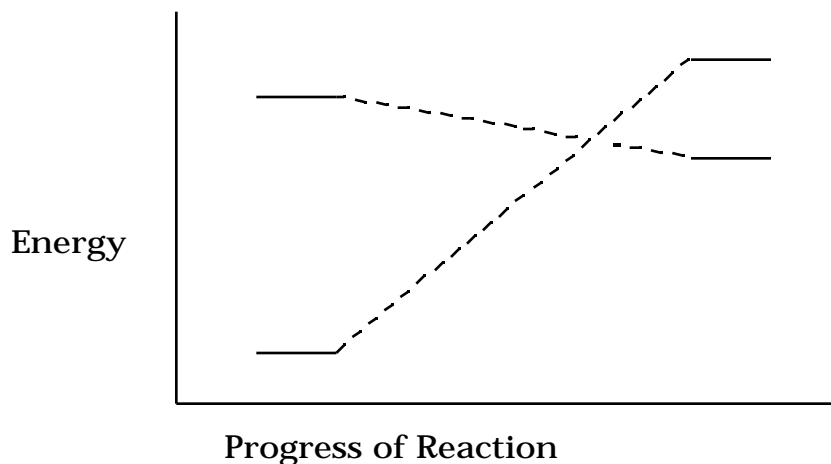
1. f. If you follow the  ${}^3B_1$  component of the  $C({}^3P) + H_2$  (since it leads to the ground-state products) to  ${}^3B_1$   $CH_2$  you must go over an approximately 20 Kcal/mole barrier. Of course this path produces  ${}^3B_1$   $CH_2$  product. Distortions away from  $C_{2v}$  symmetry, for example to  $C_s$  symmetry, would make the  $a_1$  and  $b_2$  orbitals identical in symmetry ( $a'$ ). The  $b_1$  orbitals would maintain their identity going to  $a''$  symmetry. Thus  ${}^3B_1$  and  ${}^3A_2$  (both  ${}^3A''$  in  $C_s$  symmetry and odd under reflection through the molecular plane) can mix. The system could thus follow the  ${}^3A_2$  component of the  $C({}^3P) + H_2$  surface to the place

(marked with a circle on the CCD) where it crosses the  $^3B_1$  surface upon which it then moves and continues to products. As a result, the barrier would be lowered.

You can estimate when the barrier occurs (late or early) using thermodynamic information for the reaction (i.e. slopes and asymptotic energies). For example, an early barrier would be obtained for a reaction with the characteristics:



and a late barrier would be obtained for a reaction with the characteristics:

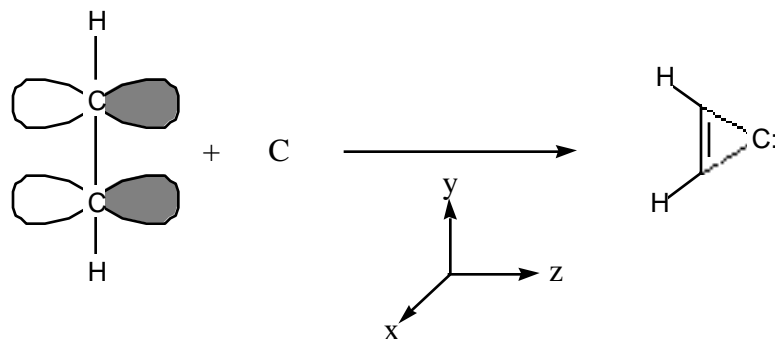


This relation between reaction endothermicity or exothermicity is known as the Hammond postulate. Note that the  $C(^3P_1) + H_2 \rightarrow CH_2$  reaction of interest here (see the CCD) has an early barrier.

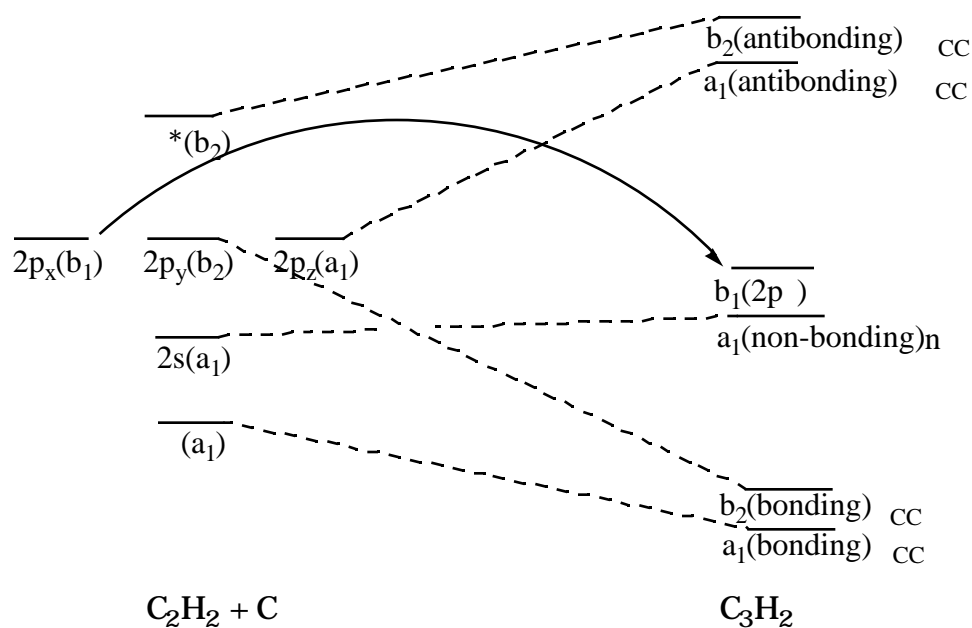
1. g. The reaction  $C(^1D) + H_2 \rightarrow CH_2 (^1A_1)$  should have no symmetry barrier (this can be recognized by following the  $^1A_1 (C(^1D) + H_2)$  reactants down to the  $^1A_1 (CH_2)$  products on the CCD).
2. This problem in many respects is analogous to problem 1.

The  $^3B_1$  surface certainly requires a two configuration CI wavefunction; the  $^2 2np_x$  ( $^2 p_y^2 sp_x$ ) and the  $^2 n^2 p_x * (^2 s^2 p_x p_z)$ . The  $^1A_1$  surface could use the  $^2 2n^2$  ( $^2 s^2 p_y^2$ ) only but once again there is no combination of  $^1D$  determinants which gives purely this configuration ( $^2 s^2 p_y^2$ ). Thus mixing of both  $^1D$  and  $^1S$  determinants are necessary to

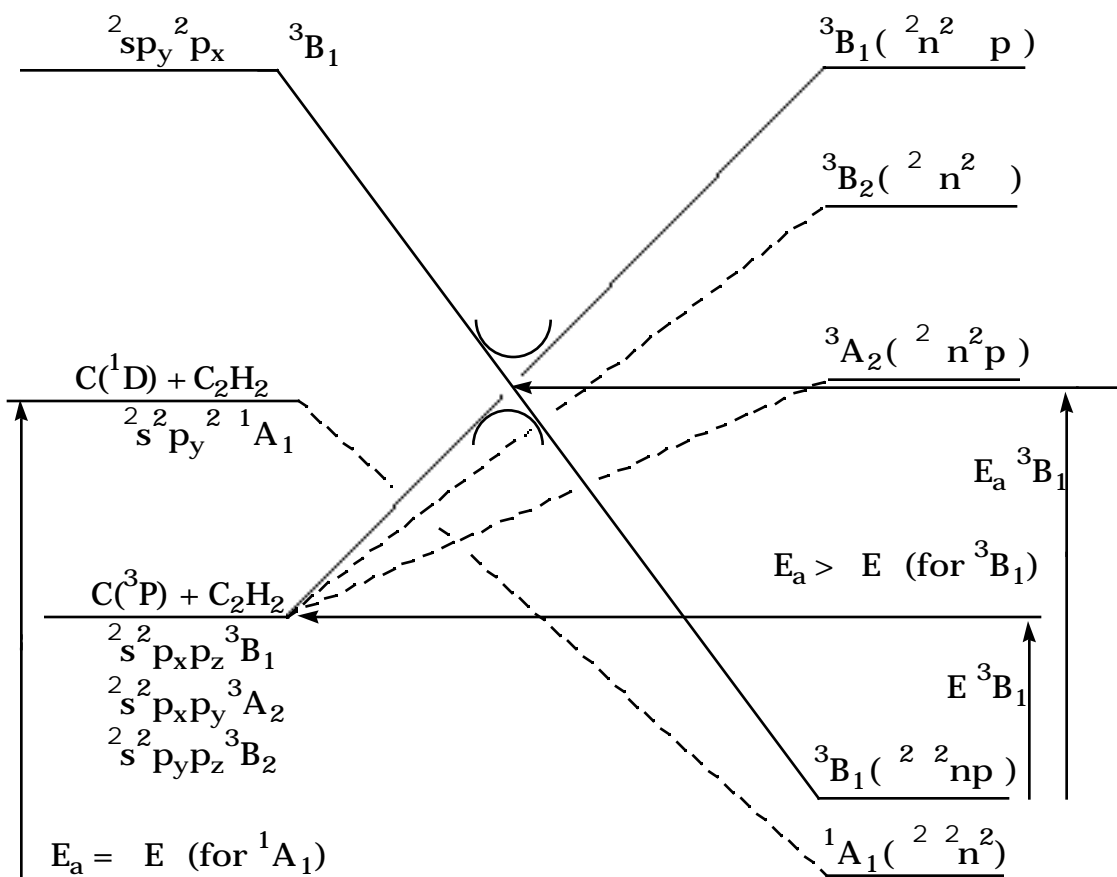
yield the required  $2s^2 2p_y^2$  configuration. Hence even the  $^1A_1$  surface would require a multiconfigurational wavefunction for adequate description.



Orbital-correlation diagram for the reaction  $C_2H_2 + C \rightarrow C_3H_2$



Configuration correlation diagram for the reaction  $C_2H_2 + C \rightarrow C_3H_2$ .



3. a.

$$\begin{aligned}
 \langle g | g \rangle &= \left\langle (2+2S)^{-\frac{1}{2}}(1s_A + 1s_B) \left| (2+2S)^{-\frac{1}{2}}(1s_A + 1s_B) \right. \right\rangle \\
 &= (2+2S)^{-1} (\langle 1s_A | 1s_A \rangle + \langle 1s_A | 1s_B \rangle + \langle 1s_B | 1s_A \rangle + \langle 1s_B | 1s_B \rangle) \\
 &= (0.285)((1.000) + (0.753) + (0.753) + (1.000)) \\
 &= 0.999 \quad 1
 \end{aligned}$$

$$\begin{aligned}
 \langle g | u \rangle &= \left\langle (2+2S)^{-\frac{1}{2}}(1s_A + 1s_B) \left| (2-2S)^{-\frac{1}{2}}(1s_A - 1s_B) \right. \right\rangle \\
 &= (2+2S)^{-\frac{1}{2}}(2-2S)^{-\frac{1}{2}} (\langle 1s_A | 1s_A \rangle + \langle 1s_A | 1s_B \rangle \\
 &\quad + \langle 1s_B | 1s_A \rangle + \langle 1s_B | 1s_B \rangle) \\
 &= (1.423)(0.534)((1.000) - (0.753) + (0.753) - (1.000)) \\
 &= 0
 \end{aligned}$$

$$\begin{aligned}
 \langle u | u \rangle &= \left\langle (2-2S)^{-\frac{1}{2}}(1s_A - 1s_B) \left| (2-2S)^{-\frac{1}{2}}(1s_A - 1s_B) \right. \right\rangle \\
 &= (2-2S)^{-1} (\langle 1s_A | 1s_A \rangle - \langle 1s_A | 1s_B \rangle - \langle 1s_B | 1s_A \rangle + \langle 1s_B | 1s_B \rangle) \\
 &= (2.024)((1.000) - (0.753) - (0.753) + (1.000)) \\
 &= 1.000
 \end{aligned}$$

3. b.

$$\begin{aligned}
\langle g|h|g\rangle &= \langle (2+2S)^{-\frac{1}{2}}(1s_A + 1s_B) |h|(2+2S)^{-\frac{1}{2}}(1s_A + 1s_B) \rangle \\
&= (2+2S)^{-1} (\langle 1s_A|h|1s_A\rangle + \langle 1s_A|h|1s_B\rangle \\
&\quad + \langle 1s_B|h|1s_A\rangle + \langle 1s_B|h|1s_B\rangle) \\
&= (0.285)((-1.110) + (-0.968) + (-0.968) + (-1.110)) \\
&= -1.184
\end{aligned}$$

$$\begin{aligned}
\langle u|h|u\rangle &= \langle (2-2S)^{-\frac{1}{2}}(1s_A - 1s_B) |h|(2-2S)^{-\frac{1}{2}}(1s_A - 1s_B) \rangle \\
&= (2-2S)^{-1} (\langle 1s_A|h|1s_A\rangle - \langle 1s_A|h|1s_B\rangle \\
&\quad - \langle 1s_B|h|1s_A\rangle + \langle 1s_B|h|1s_B\rangle) \\
&= (2.024)((-1.110) + (0.968) + (0.968) + (-1.110)) \\
&= -0.575
\end{aligned}$$

$$\begin{aligned}
\langle g|g|h|g\rangle \quad \langle gg|gg\rangle &= (2+2S)^{-1}(2+2S)^{-1} \cdot \\
&\langle (1s_A + 1s_B)(1s_A + 1s_B) | (1s_A + 1s_B)(1s_A + 1s_B) \rangle \\
&= (2+2S)^{-2} \cdot (\langle AA|AA\rangle + \langle AA|AB\rangle + \langle AA|BA\rangle + \langle AA|BB\rangle + \\
&\quad \langle AB|AA\rangle + \langle AB|AB\rangle + \langle AB|BA\rangle + \langle AB|BB\rangle + \\
&\quad \langle BA|AA\rangle + \langle BA|AB\rangle + \langle BA|BA\rangle + \langle BA|BB\rangle + \\
&\quad \langle BB|AA\rangle + \langle BB|AB\rangle + \langle BB|BA\rangle + \langle BB|BB\rangle) \\
&= (0.081) ( (0.625) + (0.426) + (0.426) + (0.323) + \\
&\quad (0.426) + (0.504) + (0.323) + (0.426) + \\
&\quad (0.426) + (0.323) + (0.504) + (0.426) + \\
&\quad (0.323) + (0.426) + (0.426) + (0.625) ) \\
&= 0.564
\end{aligned}$$

$$\begin{aligned}
\langle uu|uu\rangle &= (2-2S)^{-1}(2-2S)^{-1} \cdot \\
&\langle (1s_A - 1s_B)(1s_A - 1s_B) | (1s_A - 1s_B)(1s_A - 1s_B) \rangle \\
&= (2-2S)^{-2} \cdot (\langle AA|AA\rangle - \langle AA|AB\rangle - \langle AA|BA\rangle + \langle AA|BB\rangle - \\
&\quad \langle AB|AA\rangle + \langle AB|AB\rangle + \langle AB|BA\rangle - \langle AB|BB\rangle - \\
&\quad \langle BA|AA\rangle + \langle BA|AB\rangle + \langle BA|BA\rangle - \langle BA|BB\rangle + \\
&\quad \langle BB|AA\rangle - \langle BB|AB\rangle - \langle BB|BA\rangle + \langle BB|BB\rangle) \\
&= (4.100) ( (0.625) - (0.426) - (0.426) + (0.323) - \\
&\quad (0.426) + (0.504) + (0.323) - (0.426) - \\
&\quad (0.426) + (0.323) + (0.504) - (0.426) + \\
&\quad (0.323) - (0.426) - (0.426) + (0.625) ) \\
&= 0.582
\end{aligned}$$

$$\begin{aligned}
\langle gg|uu\rangle &= (2+2S)^{-1}(2-2S)^{-1} \cdot \\
&\langle (1s_A + 1s_B)(1s_A + 1s_B) | (1s_A - 1s_B)(1s_A - 1s_B) \rangle
\end{aligned}$$

$$\begin{aligned}
&= (2+2S)^{-1}(2-2S)^{-1} \cdot \\
&\quad (\langle AA|AA \rangle - \langle AA|AB \rangle - \langle AA|BA \rangle + \langle AA|BB \rangle + \\
&\quad \langle AB|AA \rangle - \langle AB|AB \rangle - \langle AB|BA \rangle + \langle AB|BB \rangle + \\
&\quad \langle BA|AA \rangle - \langle BA|AB \rangle - \langle BA|BA \rangle + \langle BA|BB \rangle + \\
&\quad \langle BB|AA \rangle - \langle BB|AB \rangle - \langle BB|BA \rangle + \langle BB|BB \rangle ) \\
&= (0.285)(2.024) ((0.625) - (0.426) - (0.426) + (0.323) + \\
&\quad (0.426) - (0.504) - (0.323) + (0.426) + \\
&\quad (0.426) - (0.323) - (0.504) + (0.426) + \\
&\quad (0.323) - (0.426) - (0.426) + (0.625)) \\
&= 0.140
\end{aligned}$$

$$\begin{aligned}
\langle gu|gu \rangle &= (2+2S)^{-1}(2-2S)^{-1} \cdot \\
&\quad \langle (1s_A + 1s_B)(1s_A - 1s_B) | (1s_A + 1s_B)(1s_A - 1s_B) \rangle \\
&= (2+2S)^{-1}(2-2S)^{-1} \cdot \\
&\quad (\langle AA|AA \rangle - \langle AA|AB \rangle + \langle AA|BA \rangle - \langle AA|BB \rangle - \\
&\quad \langle AB|AA \rangle + \langle AB|AB \rangle - \langle AB|BA \rangle + \langle AB|BB \rangle + \\
&\quad \langle BA|AA \rangle - \langle BA|AB \rangle + \langle BA|BA \rangle - \langle BA|BB \rangle - \\
&\quad \langle BB|AA \rangle + \langle BB|AB \rangle - \langle BB|BA \rangle + \langle BB|BB \rangle ) \\
&= (0.285)(2.024) ((0.625) - (0.426) + (0.426) - (0.323) - \\
&\quad (0.426) + (0.504) - (0.323) + (0.426) + \\
&\quad (0.426) - (0.323) + (0.504) - (0.426) - \\
&\quad (0.323) + (0.426) - (0.426) + (0.625)) \\
&= 0.557
\end{aligned}$$

Note, that  $\langle gg|gu \rangle = \langle uu|ug \rangle = 0$  from symmetry considerations, but this can be easily verified. For example,

$$\begin{aligned}
\langle gg|gu \rangle &= (2+2S)^{-\frac{1}{2}}(2-2S)^{-\frac{3}{2}} \cdot \\
&\quad \langle (1s_A + 1s_B)(1s_A + 1s_B) | (1s_A + 1s_B)(1s_A - 1s_B) \rangle \\
&= (2+2S)^{-\frac{1}{2}}(2-2S)^{-\frac{3}{2}} \cdot \\
&\quad (\langle AA|AA \rangle - \langle AA|AB \rangle + \langle AA|BA \rangle - \langle AA|BB \rangle + \\
&\quad \langle AB|AA \rangle - \langle AB|AB \rangle + \langle AB|BA \rangle - \langle AB|BB \rangle + \\
&\quad \langle BA|AA \rangle - \langle BA|AB \rangle + \langle BA|BA \rangle - \langle BA|BB \rangle + \\
&\quad \langle BB|AA \rangle - \langle BB|AB \rangle + \langle BB|BA \rangle - \langle BB|BB \rangle ) \\
&= (0.534)(2.880) ((0.625) - (0.426) + (0.426) - (0.323) + \\
&\quad (0.426) - (0.504) + (0.323) - (0.426) + \\
&\quad (0.426) - (0.323) + (0.504) - (0.426) + \\
&\quad (0.323) - (0.426) + (0.426) - (0.625)) \\
&= 0.000
\end{aligned}$$

3. c. We can now set up the configuration interaction Hamiltonian matrix. The elements are evaluated by using the Slater-Condon rules as shown in the text.

$$H_{11} = \langle g \quad g | H | g \quad g \rangle$$



$$= 2f_{gg} + g_{gg} \\ = 2(-1.184) + 0.564 = -1.804$$

$$H_{21} = H_{12} = \langle g \quad g | H | u \quad u \rangle \\ = g_{gu} \\ = 0.140$$

$$H_{22} = \langle u \quad u | H | u \quad u \rangle \\ = 2f_{uu} + g_{uu} \\ = 2(-0.575) + 0.582 = -0.568$$

3. d. Solving this eigenvalue problem:

$$\begin{array}{cc} -1.804 & - & 0.140 \\ & & \\ & 0.140 & -0.568 & - \end{array} = 0$$

$$\begin{aligned} (-1.804 - \lambda)(-0.568 - \lambda) - (0.140)^2 &= 0 \\ 1.025 + 1.804\lambda + 0.568\lambda + \lambda^2 - 0.0196 &= 0 \\ \lambda^2 + 2.372\lambda + 1.005 &= 0 \\ &= \frac{-2.372 \pm \sqrt{(2.372)^2 - 4(1)(1.005)}}{(2)(1)} \\ &= -1.186 \pm 0.634 \\ &= -1.820, \text{ and } -0.552. \end{aligned}$$

Solving for the coefficients:

$$\begin{array}{ccc} -1.804 & - & 0.140 & C_1 & = & 0 \\ & & & & & \\ & 0.140 & -0.568 & - & C_2 & = & 0 \end{array}$$

For the first eigenvalue this becomes:

$$\begin{array}{ccc} -1.804 + 1.820 & & 0.140 & C_1 & = & 0 \\ & 0.140 & -0.568 + 1.820 & C_2 & = & 0 \\ 0.016 & 0.140 & C_1 & & & 0 \\ & & & & & \\ 0.140 & 1.252 & C_2 & & & 0 \\ (0.140)(C_1) + (1.252)(C_2) & & & & & = 0 \\ C_1 = -8.943 C_2 & & & & & \\ C_1^2 + C_2^2 = 1 & & & & & \text{(from normalization)} \\ (-8.943 C_2)^2 + C_2^2 = 1 & & & & & \\ 80.975 C_2^2 = 1 & & & & & \\ C_2 = 0.111, C_1 = -0.994 & & & & & \end{array}$$

For the second eigenvalue this becomes:

$$\begin{array}{ccc} -1.804 + 0.552 & & 0.140 & C_1 & = & 0 \\ & & & & & \\ & 0.140 & -0.568 + 0.552 & C_2 & = & 0 \\ -1.252 & 0.140 & C_1 & & & 0 \\ & & & & & \\ 0.140 & -0.016 & C_2 & & & 0 \\ (-1.252)(C_1) + (0.140)(C_2) & & & & & = 0 \end{array}$$

$$C_1 = 0.112 C_2$$

$$C_1^2 + C_2^2 = 1 \text{ (from normalization)}$$

$$(0.112 C_2)^2 + C_2^2 = 1$$

$$1.0125 C_2^2 = 1$$

$$C_2 = 0.994, C_1 = 0.111$$

3. e. The polarized orbitals,  $R_{\pm}$ , are given by:

$$R_{\pm} = g \pm \sqrt{\frac{C_2}{C_1}} u$$

$$R_{\pm} = g \pm \sqrt{\frac{0.111}{0.994}} u$$

$$R_{\pm} = g \pm 0.334 u$$

$$R_+ = g + 0.334 u \text{ (left polarized)}$$

$$R_- = g - 0.334 u \text{ (right polarized)}$$



$R_+$  Left Polarized



$R_-$  Right Polarized

### Section 4 Exercises, Problems, and Solutions

#### Exercises:

1. Consider the molecules  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ .

a. What kind of rotor are they (symmetric top, etc; do not bother with oblate, or near-prolate, etc.)

b. Will they show pure rotational spectra?

c. Assume that ammonia shows a pure rotational spectrum. If the rotational constants are  $9.44$  and  $6.20 \text{ cm}^{-1}$ , use the energy expression:

$$E = (A - B) K^2 + B J(J + 1),$$

to calculate the energies (in  $\text{cm}^{-1}$ ) of the first three lines (i.e., those with lowest  $K$ ,  $J$  quantum number for the absorbing level) in the absorption spectrum (ignoring higher order terms in the energy expression).

2. The molecule  $^{11}\text{B } ^{16}\text{O}$  has a vibrational frequency  $\nu_e = 1885 \text{ cm}^{-1}$ , a rotational constant  $B_e = 1.78 \text{ cm}^{-1}$ , and a bond energy from the bottom of the potential well of  $D_e^0 = 8.28 \text{ eV}$ . Use integral atomic masses in the following:

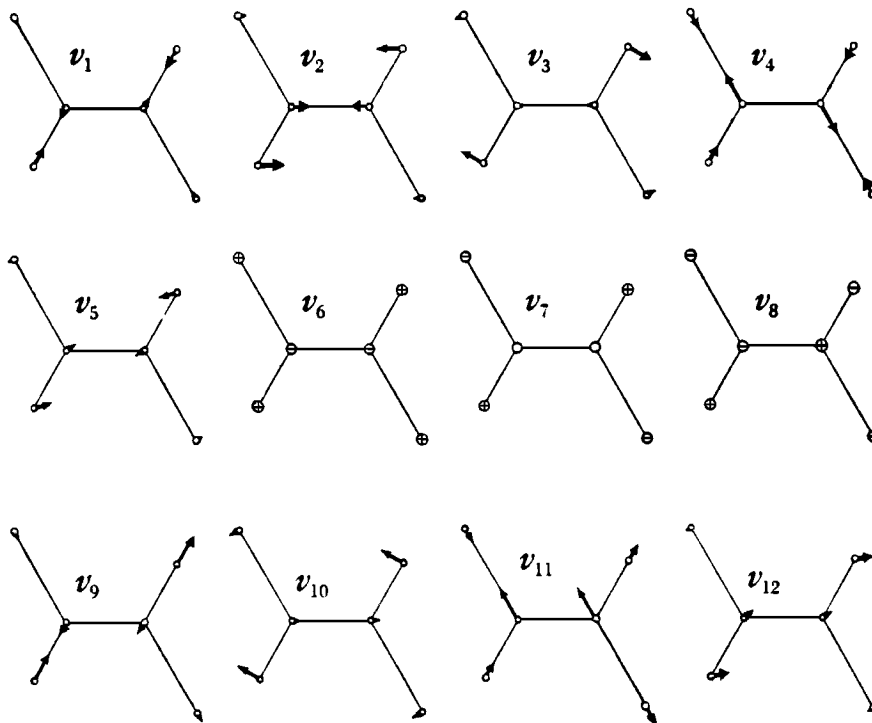
a. In the approximation that the molecule can be represented as a Morse oscillator, calculate the bond length,  $R_e$  in angstroms, the centrifugal distortion constant,  $D_e$  in  $\text{cm}^{-1}$ , the anharmonicity constant,  $x_e$  in  $\text{cm}^{-1}$ , the zero-point corrected bond energy,  $D_0^0$  in eV, the vibration rotation interaction constant,  $B_v$  in  $\text{cm}^{-1}$ , and the vibrational state specific rotation constants,  $B_0$  and  $B_1$  in  $\text{cm}^{-1}$ . Use the vibration-rotation energy expression for a Morse oscillator:

$E = \hbar \nu_e (v + 1/2) - \hbar \nu_e x_e (v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2$ , where

$$B_v = B_e - \nu_e (v + 1/2), \quad x_e = \frac{-6B_e^2}{\hbar \nu_e} + \frac{6\sqrt{B_e^3 \hbar \nu_e}}{\hbar \nu_e}, \quad \text{and } D_e = \frac{4B_e^3}{\hbar \nu_e^2}.$$

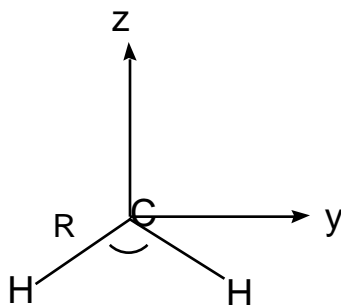
b. Will this molecule show a pure rotation spectrum? A vibration-rotation spectrum? Assume that it does, what are the energies (in  $\text{cm}^{-1}$ ) of the first three lines in the P branch ( $v = +1$ ,  $J = -1$ ) of the fundamental absorption?

3. Consider  $\text{trans-C}_2\text{H}_2\text{Cl}_2$ . The vibrational normal modes of this molecule are shown below. What is the symmetry of the molecule? Label each of the modes with the appropriate irreducible representation.



Problems:

1. Suppose you are given two molecules (one is  $\text{CH}_2$  and the other is  $\text{CH}_2^-$  but you don't know which is which). Both molecules have  $C_{2v}$  symmetry. The CH bond length of molecule I is 1.121 Å and for molecule II it is 1.076 Å. The bond angle of molecule I is  $104^\circ$  and for molecule II it is  $136^\circ$ .



a. Using a coordinate system centered on the C nucleus as shown above (the molecule is in the YZ plane), compute the moment of inertia tensors of both species (I and II). The definitions of the components of the tensor are, for example:

$$I_{xx} = \sum_j m_j (y_j^2 + z_j^2) - M(Y^2 + Z^2)$$

$$I_{xy} = - \sum_j m_j x_j y_j - MXY$$

Here,  $m_j$  is the mass of the nucleus  $j$ ,  $M$  is the mass of the entire molecule, and  $X, Y, Z$  are the coordinates of the center of mass of the molecule. Use Å for distances and amu's for masses.

b. Find the principal moments of inertia  $I_a < I_b < I_c$  for both compounds (in amu Å<sup>2</sup> units) and convert these values into rotational constants  $A, B,$  and  $C$  in  $\text{cm}^{-1}$  using, for example,

$$A = h(8 \pi^2 c I_a)^{-1}$$

c. Both compounds are "nearly prolate tops" whose energy levels can be well approximated using the prolate top formula:

$$E = (A - B) K^2 + B J(J + 1),$$

if one uses for the  $B$  constant the average of the  $B$  and  $C$  values determined earlier. Thus, take  $B$  and  $C$  values (for each compound) and average them to produce an effective  $B$  constant to use in the above energy formula. Write down (in  $\text{cm}^{-1}$  units) the energy formula for both species. What values are  $J$  and  $K$  allowed to assume? What is the degeneracy of the level labeled by a given  $J$  and  $K$ ?

d. Draw a picture of both compounds and show the directions of the three principle axes (a,b,c). On these pictures show the kind of rotational motion associated with the quantum number  $K$ .

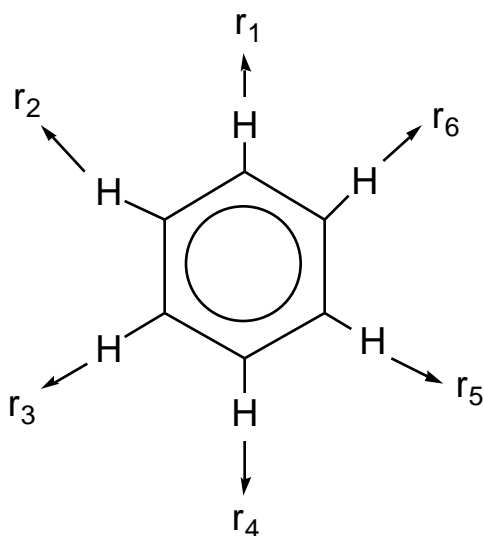
e. Given that the electronic transition moment vector  $\mu$  connecting species I and II is directed along the  $Y$  axis, what are the selection rules  $J$  and  $K$ ?

f. Suppose you are given the photoelectron spectrum of  $\text{CH}_2^-$ . In this spectrum  $J_j = J_i + 1$  transitions are called R-branch absorptions and those obeying  $J_j = J_i - 1$  are called P-branch transitions. The spacing between lines can increase or decrease as functions of  $J_i$  depending on the changes in the moment of inertia for the transition. If spacings grow closer and closer, we say that the spectrum exhibits a so-called band head formation. In the photoelectron spectrum that you are given, a rotational analysis of the vibrational lines in this spectrum is carried out and it is found that the R-branches show band head formation but the P-branches do not. Based on this information, determine which compound I or II is the  $\text{CH}_2^-$  anion. Explain your reasoning.

g. At what  $J$  value (of the absorbing species) does the band head occur and at what rotational energy difference?

2. Let us consider the vibrational motions of benzene. To consider all of the vibrational modes of benzene we should attach a set of displacement vectors in the x, y, and z directions to each atom in the molecule (giving 36 vectors in all), and evaluate how these transform under the symmetry operations of  $D_{6h}$ . For this problem, however, let's only inquire about the C-H stretching vibrations.

a. Represent the C-H stretching motion on each C-H bond by an outward-directed vector on each H atom, designated  $r_i$ :



These vectors form the basis for a reducible representation. Evaluate the characters for this reducible representation under the symmetry operations of the  $D_{6h}$  group.

b. Decompose the reducible representation you obtained in part a. into its irreducible components. These are the symmetries of the various C-H stretching vibrational modes in benzene.

c. The vibrational state with zero quanta in each of the vibrational modes (the ground vibrational state) of any molecule always belongs to the totally symmetric representation. For benzene the ground vibrational state is therefore of  $A_{1g}$  symmetry. An excited state which has one quantum of vibrational excitation in a mode which is of a given symmetry species has the same symmetry species as the mode which is excited (because the vibrational wave functions are given as Hermite polynomials in the stretching coordinate). Thus, for example, excitation (by one quantum) of a vibrational mode of  $A_{2u}$  symmetry gives a wavefunction of  $A_{2u}$  symmetry. To resolve the question of what vibrational modes may be excited by the absorption of infrared radiation we must examine

the x, y, and z components of the transition dipole integral for initial and final state wave functions  $\psi_i$  and  $\psi_f$ , respectively:

$$|\langle \psi_f | x | \psi_i \rangle|, |\langle \psi_f | y | \psi_i \rangle|, \text{ and } |\langle \psi_f | z | \psi_i \rangle|.$$

Using the information provided above, which of the C-H vibrational modes of benzene will be infrared-active, and how will the transitions be polarized? How many C-H vibrations will you observe in the infrared spectrum of benzene?

d. A vibrational mode will be active in Raman spectroscopy only if one of the following integrals is nonzero:

$$|\langle \psi_f | xy | \psi_i \rangle|, |\langle \psi_f | xz | \psi_i \rangle|, |\langle \psi_f | yz | \psi_i \rangle|, \\ |\langle \psi_f | x^2 | \psi_i \rangle|, |\langle \psi_f | y^2 | \psi_i \rangle|, \text{ and } |\langle \psi_f | z^2 | \psi_i \rangle|.$$

Using the fact that the quadratic operators transform according to the irreducible representations:

$$(x^2 + y^2, z^2) \quad A_{1g}$$

$$(xz, yz) \quad E_{1g}$$

$$(x^2 - y^2, xy) \quad E_{2g}$$

Determine which of the C-H vibrational modes will be Raman-active.

e. Are there any of the C-H stretching vibrational motions of benzene which cannot be observed in either infrared or Raman spectroscopy? Give the irreducible representation label for these unobservable modes.

3. In treating the vibrational and rotational motion of a diatomic molecule having reduced mass  $\mu$ , equilibrium bond length  $r_e$  and harmonic force constant  $k$ , we are faced with the following radial Schrödinger equation:

$$\frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{J(J+1)\hbar^2}{2\mu r^2} R + \frac{1}{2} k(r - r_e)^2 R = E R$$

a. Show that the substitution  $R = r^{-1}F$  leads to:

$$\frac{-\hbar^2}{2\mu} F'' + \frac{J(J+1)\hbar^2}{2\mu r^2} F + \frac{1}{2} k(r - r_e)^2 F = E F$$

b. Taking  $r = r_e + \rho$  and expanding  $(1 + x)^{-2} = 1 - 2x + 3x^2 + \dots$ ,

show that the so-called vibration-rotation coupling term  $\frac{J(J+1)\hbar^2}{2\mu r^2}$  can be approximated

(for small  $\rho$ ) by  $\frac{J(J+1)\hbar^2}{2\mu r_e^2} \left( 1 - \frac{2\rho}{r_e} + \frac{3\rho^2}{r_e^2} \right)$ . Keep terms only through order  $\rho^2$ .

c. Show that, through terms of order  $\rho^2$ , the above equation for  $F$  can be rearranged to yield a new equation of the form:

$$\frac{-\hbar^2}{2\mu} F'' + \frac{1}{2} k(r - r_e)^2 F = \left( E - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \right) F$$

Give explicit expressions for how the modified force constant  $\tilde{k}$ , bond length  $\tilde{r}_e$ , and energy shift  $\tilde{E}$  depend on  $J$ ,  $k$ ,  $r_e$ , and  $\mu$ .

d. Given the above modified vibrational problem, we can now conclude that the modified energy levels are:

$$E = \hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right) + \frac{J(J+1)\hbar^2}{2\mu r_e^2} .$$

Explain how the conclusion is "obvious", how for  $J = 0$ ,  $k = k$ , and  $r_e = r_e$ , we obtain the usual harmonic oscillator energy levels. Describe how the energy levels would be expected to vary as  $J$  increases from zero and explain how these changes arise from changes in  $k$  and  $r_e$ . Explain in terms of physical forces involved in the rotating-vibrating molecule why  $r_e$  and  $k$  are changed by rotation.

## Solutions

### Exercises:

1. a.  $\text{CCl}_4$  is tetrahedral and therefore is a spherical top.  $\text{CHCl}_3$  has  $C_{3v}$  symmetry and therefore is a symmetric top.  $\text{CH}_2\text{Cl}_2$  has  $C_{2v}$  symmetry and therefore is an asymmetric top.
- b.  $\text{CCl}_4$  has such high symmetry that it will not exhibit pure rotational spectra.  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  will both exhibit pure rotation spectra.
- c.  $\text{NH}_3$  is a symmetric top (oblate). Use the given energy expression,

$$E = (A - B) K^2 + B J(J + 1),$$

$A = 6.20 \text{ cm}^{-1}$ ,  $B = 9.44 \text{ cm}^{-1}$ , selection rules  $J = \pm 1$ , and the fact that  $\mu_0$  lies along the figure axis such that  $K = 0$ , to give:

$$E = 2B (J + 1) = 2B, 4B, \text{ and } 6B \text{ (} J = 0, 1, \text{ and } 2\text{)}.$$

So, lines are at  $18.88 \text{ cm}^{-1}$ ,  $37.76 \text{ cm}^{-1}$ , and  $56.64 \text{ cm}^{-1}$ .

2. To convert between  $\text{cm}^{-1}$  and energy, multiply by  $hc = (6.62618 \times 10^{-34} \text{ J sec})(2.997925 \times 10^{10} \text{ cm sec}^{-1}) = 1.9865 \times 10^{23} \text{ J cm}$ .

Let all quantities in  $\text{cm}^{-1}$  be designated with a bar,

e.g.  $B_e = 1.78 \text{ cm}^{-1}$ .

$$\text{a. } hcB_e = \frac{\hbar^2}{2\mu R_e^2}$$

$$R_e = \frac{\hbar}{\sqrt{2\mu hcB_e}}$$

$$\mu = \frac{m_B m_O}{m_B + m_O} = \frac{(11)(16)}{(11 + 16)} \times 1.66056 \times 10^{-27} \text{ kg} \\ = 1.0824 \times 10^{-26} \text{ kg}.$$

$$hcB_e = hc(1.78 \text{ cm}^{-1}) = 3.5359 \times 10^{-23} \text{ J}$$

$$R_e = \frac{1.05459 \times 10^{-34} \text{ J sec}}{\sqrt{(2)(1.0824 \times 10^{-26} \text{ kg})(3.5359 \times 10^{-23} \text{ J})}}$$

$$R_e = 1.205 \times 10^{-10} \text{ m} = 1.205 \text{ \AA}$$

$$D_e = \frac{4B_e^3}{\hbar e^2}, D_e = \frac{4B_e^3}{e^2} = \frac{(4)(1.78 \text{ cm}^{-1})^3}{(1885 \text{ cm}^{-1})^2} = 6.35 \times 10^{-6} \text{ cm}^{-1}$$

$$e^{x_e} = \frac{\hbar e^2}{4D_e^0}, e^{x_e} = \frac{e^2}{4D_e^0} = \frac{(1885 \text{ cm}^{-1})^2}{(4)(66782.2 \text{ cm}^{-1})} = 13.30 \text{ cm}^{-1}.$$

$$D_0^0 = D_e^0 - \frac{\hbar e}{2} + \frac{\hbar e^{x_e}}{4}, D_0^0 = D_e^0 - \frac{e}{2} + \frac{e^{x_e}}{4}$$

$$= 66782.2 - \frac{1885}{2} + \frac{13.3}{4}$$

$$= 65843.0 \text{ cm}^{-1} = 8.16 \text{ eV}.$$

$$e = \frac{-6B_e^2}{\hbar e} + \frac{6\sqrt{B_e^3 \hbar e^{x_e}}}{\hbar e}$$

$$e = \frac{-6B_e^2}{e} + \frac{6\sqrt{B_e^3 e^{x_e}}}{e}$$

$$e = \frac{(-6)(1.78)^2}{(1885)} + \frac{6\sqrt{(1.78)^3(13.3)}}{(1885)} = 0.0175 \text{ cm}^{-1}.$$

$$B_0 = B_e - e(1/2), B_0 = B_e - e(1/2) = 1.78 - 0.0175/2$$

$$= 1.77 \text{ cm}^{-1}$$

$$B_1 = B_e - e(3/2), B_1 = B_e - e(3/2) = 1.78 - 0.0175(1.5)$$

$$= 1.75 \text{ cm}^{-1}$$

b. The molecule has a dipole moment and so it should have a pure rotational spectrum. In addition, the dipole moment should change with R and so it should have a vibration rotation spectrum.

The first three lines correspond to  $J = 1 \rightarrow 0$ ,  $J = 2 \rightarrow 1$ ,  $J = 3 \rightarrow 2$

$$E = \hbar e(v + 1/2) - \hbar e^{x_e}(v + 1/2)^2 + B_v J(J + 1) - D_e J^2(J + 1)^2$$

$$E = \hbar e - 2\hbar e^{x_e} - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

$$E = e - 2 e^{x_e} - B_0 J(J + 1) + B_1 J(J - 1) - 4D_e J^3$$

$$E = 1885 - 2(13.3) - 1.77J(J + 1) + 1.75J(J - 1) - 4(6.35 \times 10^{-6})J^3$$

$$= 1858.4 - 1.77J(J + 1) + 1.75J(J - 1) - 2.54 \times 10^{-5} J^3$$

$$E(J = 1) = 1854.9 \text{ cm}^{-1}$$

$$E(J = 2) = 1851.3 \text{ cm}^{-1}$$

$$E(J = 3) = 1847.7 \text{ cm}^{-1}$$

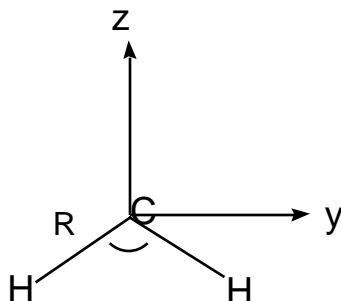
3. The  $\text{C}_2\text{H}_2\text{Cl}_2$  molecule has a  $\sigma_h$  plane of symmetry (plane of molecule), a  $\text{C}_2$  axis (to plane), and inversion symmetry, this results in  $\text{C}_{2h}$  symmetry. Using  $\text{C}_{2h}$  symmetry labels



the modes can be labeled as follows: 1, 2, 3, 4, and 5 are  $a_g$ , 6 and 7 are  $a_u$ , 8 is  $b_g$ , and 9, 10, 11, and 12 are  $b_u$ .

Problems:

1.



Molecule I  
 $R_{CH} = 1.121 \text{ \AA}$

$$\text{HCH} = 104^\circ$$

$$y_H = R \sin(\theta/2) = \pm 0.8834$$

$$z_H = R \cos(\theta/2) = -0.6902$$

Center of Mass(COM):

clearly,  $X = Y = 0$ ,

$$Z = \frac{12(0) - 2R \cos(\theta/2)}{14} = -0.0986$$

Molecule II  
 $R_{CH} = 1.076 \text{ \AA}$

$$\text{HCH} = 136^\circ$$

$$y_H = \pm 0.9976$$

$$z_H = -0.4031$$

$$Z = -0.0576$$

$$a. \quad I_{xx} = \sum_j m_j(y_j^2 + z_j^2) - M(Y^2 + Z^2)$$

$$I_{xy} = - \sum_j m_j x_j y_j - MXY$$

$$I_{xx} = 2(1.121)^2 - 14(-0.0986)^2$$

$$= 2.377$$

$$I_{xx} = 2(1.076)^2 - 14(-0.0576)^2$$

$$= 2.269$$

$$I_{yy} = 2(0.6902)^2 - 14(-0.0986)^2$$

$$= 0.8167$$

$$I_{yy} = 2(0.4031)^2 - 14(-0.0576)^2$$

$$= 0.2786$$

$$I_{zz} = 2(0.8834)^2$$

$$= 1.561$$

$$I_{zz} = 2(0.9976)^2$$

$$= 1.990$$

$$I_{xz} = I_{yz} = I_{xy} = 0$$

b. Since the moment of inertia tensor is already diagonal, the principal moments of inertia have already been determined to be

( $I_a < I_b < I_c$ ):

$$I_{yy} < I_{zz} < I_{xx}$$

$$0.8167 < 1.561 < 2.377$$

$$I_{yy} < I_{zz} < I_{xx}$$

$$0.2786 < 1.990 < 2.269$$

$$\text{Using the formula: } A = \frac{h}{8 \sqrt{2cI_a}} = \frac{6.626 \times 10^{-27}}{8 \sqrt{(3 \times 10^{10})I_a}} \times \frac{6.02 \times 10^{23}}{(1 \times 10^{-8})^2}$$

$$A = \frac{16.84}{I_a} \text{ cm}^{-1}$$

similarly,  $B = \frac{16.84}{I_b} \text{ cm}^{-1}$ , and  $C = \frac{16.84}{I_c} \text{ cm}^{-1}$ .

So,

Molecule I

$$y \quad A = 20.62$$

$$z \quad B = 10.79$$

$$x \quad C = 7.08$$

c. Averaging B + C:

$$B = (B + C)/2 = 8.94$$

$$A - B = 11.68$$

Using the prolate top formula:

$$E = (A - B) K^2 + B J(J + 1),$$

Molecule I

$$E = 11.68K^2 + 8.94J(J + 1)$$

Levels:  $J = 0, 1, 2, \dots$  and  $K = 0, 1, \dots, J$

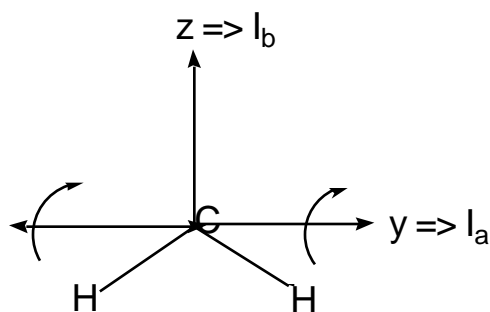
For a given level defined by J and K, there are  $M_J$  degeneracies given by:  $(2J + 1) \times$

$$1 \text{ for } K = 0$$

$$2 \text{ for } K = 1$$

d.

Molecule I



Molecule II

$$y \quad A = 60.45$$

$$z \quad B = 8.46$$

$$x \quad C = 7.42$$

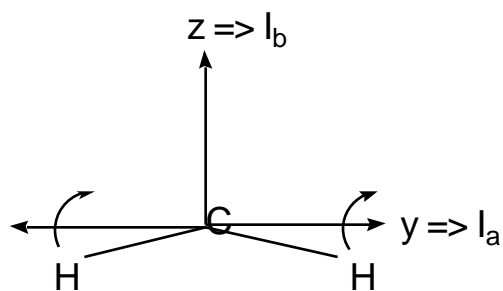
$$B = (B + C)/2 = 7.94$$

$$A - B = 52.51$$

Molecule II

$$E = 52.51K^2 + 7.94J(J + 1)$$

Molecule II



e. Since  $\mu$  is along Y,  $K = 0$  since K describes rotation about the y axis.

Therefore  $J = \pm 1$

f. Assume molecule I is  $\text{CH}_2^-$  and molecule II is  $\text{CH}_2$ . Then,

$$E = E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-), \text{ where:}$$

$$E(\text{CH}_2) = 52.51K^2 + 7.94J(J + 1), \text{ and } E(\text{CH}_2^-) = 11.68K^2 + 8.94J(J + 1)$$

For R-branches:  $J_j = J_i + 1, \quad K = 0:$

$$\begin{aligned} E_R &= E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-) \\ &= 7.94(J_i + 1)(J_i + 1 + 1) - 8.94J_i(J_i + 1) \\ &= (J_i + 1)\{7.94(J_i + 1 + 1) - 8.94J_i\} \\ &= (J_i + 1)\{(7.94 - 8.94)J_i + 2(7.94)\} \\ &= (J_i + 1)\{-J_i + 15.88\} \end{aligned}$$

For P-branches:  $J_j = J_i - 1, \quad K = 0:$

$$E_P = E_{J_j}(\text{CH}_2) - E_{J_i}(\text{CH}_2^-)$$

$$\begin{aligned}
&= 7.94(J_i - 1)(J_i - 1 + 1) - 8.94J_i(J_i + 1) \\
&= J_i\{7.94(J_i - 1) - 8.94(J_i + 1)\} \\
&= J_i\{(7.94 - 8.94)J_i - 7.94 - 8.94\} \\
&= J_i\{-J_i - 16.88\}
\end{aligned}$$

This indicates that the R branch lines occur at energies which grow closer and closer together as J increases (since the  $15.88 - J_i$  term will cancel). The P branch lines occur at energies which lie more and more negative (i.e. to the left of the origin). So, you can

predict that if molecule I is  $\text{CH}_2^-$  and molecule II is  $\text{CH}_2$  then the R-branch has a band head and the P-branch does not. This is observed therefore our assumption was correct:

molecule I is  $\text{CH}_2^-$  and molecule II is  $\text{CH}_2$ .

g. The band head occurs when  $\frac{d(E_R)}{dJ} = 0$ .

$$\begin{aligned}
\frac{d(E_R)}{dJ} &= \frac{d}{dJ} [(J_i + 1)\{-J_i + 15.88\}] = 0 \\
&= \frac{d}{dJ} (-J_i^2 - J_i + 15.88J_i + 15.88) = 0 \\
&= -2J_i + 14.88 = 0
\end{aligned}$$

$$J_i = 7.44, \text{ so } J = 7 \text{ or } 8.$$

At  $J = 7.44$ :

$$E_R = (J + 1)\{-J + 15.88\}$$

$$E_R = (7.44 + 1)\{-7.44 + 15.88\} = (8.44)(8.44) = 71.2 \text{ cm}^{-1} \text{ above the origin.}$$

2. a.

$D_{6h}$	E	$2C_6$	$2C_3$	$C_2$	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	h	3	d	3	v		
$A_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	$R_z$	$x^2+y^2, z^2$
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	-1	-1		
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	1	-1	-1		
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	-1	1	1		
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	0	0	$(R_x, R_y)$	$(xz, yz)$ $(x^2 - y^2, xy)$
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0	0	0		
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	z	
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1		
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	-1	1	1		
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	1	-1	-1		
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	0	0	$(x, y)$	
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0	0	0		
$C-H$	6	0	0	0	0	2	0	0	0	6	2	0	0	0		

b. The number of irreducible representations may be found by using the following formula:

$$n_{\text{irrep}} = \frac{1}{g} \sum_{\mathbf{R}} \text{red}(\mathbf{R}) \text{ irrep}(\mathbf{R}),$$

where  $g$  = the order of the point group (24 for  $D_{6h}$ ).

$$\begin{aligned} n_{A_{1g}} &= \frac{1}{24} \sum_{\mathbf{R}} \text{C-H}(\mathbf{R}) \cdot A_{1g}(\mathbf{R}) \\ &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\ &\quad + (3)(0)(1) + (3)(2)(1) + (1)(0)(1) + (2)(0)(1) \\ &\quad + (2)(0)(1) + (1)(6)(1) + (3)(2)(1) + (3)(0)(1) \} \\ &= 1 \\ n_{A_{2g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\ &\quad + (3)(0)(-1) + (3)(2)(-1) + (1)(0)(1) + (2)(0)(1) \\ &\quad + (2)(0)(1) + (1)(6)(1) + (3)(2)(-1) + (3)(0)(-1) \} \\ &= 0 \\ n_{B_{1g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\ &\quad + (3)(0)(1) + (3)(2)(-1) + (1)(0)(1) + (2)(0)(-1) \\ &\quad + (2)(0)(1) + (1)(6)(-1) + (3)(2)(1) + (3)(0)(-1) \} \\ &= 0 \\ n_{B_{2g}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\ &\quad + (3)(0)(-1) + (3)(2)(1) + (1)(0)(1) + (2)(0)(-1) \\ &\quad + (2)(0)(1) + (1)(6)(-1) + (3)(2)(-1) + (3)(0)(1) \} \\ &= 0 \\ n_{E_{1g}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) \\ &\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(2) + (2)(0)(1) \\ &\quad + (2)(0)(-1) + (1)(6)(-2) + (3)(2)(0) + (3)(0)(0) \} \\ &= 0 \\ n_{E_{2g}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) \\ &\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(2) + (2)(0)(-1) \\ &\quad + (2)(0)(-1) + (1)(6)(2) + (3)(2)(0) + (3)(0)(0) \} \\ &= 1 \\ n_{A_{1u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\ &\quad + (3)(0)(1) + (3)(2)(1) + (1)(0)(-1) + (2)(0)(-1) \\ &\quad + (2)(0)(-1) + (1)(6)(-1) + (3)(2)(-1) + (3)(0)(-1) \} \\ &= 0 \\ n_{A_{2u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) \\ &\quad + (3)(0)(-1) + (3)(2)(-1) + (1)(0)(-1) + (2)(0)(-1) \\ &\quad + (2)(0)(-1) + (1)(6)(-1) + (3)(2)(1) + (3)(0)(1) \} \\ &= 0 \\ n_{B_{1u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\ &\quad + (3)(0)(1) + (3)(2)(-1) + (1)(0)(-1) + (2)(0)(1) \\ &\quad + (2)(0)(-1) + (1)(6)(1) + (3)(2)(-1) + (3)(0)(1) \} \\ &= 0 \end{aligned}$$

$$\begin{aligned}
n_{B_{2u}} &= \frac{1}{24} \{ (1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) \\
&\quad + (3)(0)(-1) + (3)(2)(1) + (1)(0)(-1) + (2)(0)(1) \\
&\quad + (2)(0)(-1) + (1)(6)(1) + (3)(2)(1) + (3)(0)(-1) \} \\
&= 1 \\
n_{E_{1u}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(-2) + (2)(0)(-1) \\
&\quad + (2)(0)(1) + (1)(6)(2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 1 \\
n_{E_{2u}} &= \frac{1}{24} \{ (1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) \\
&\quad + (3)(0)(0) + (3)(2)(0) + (1)(0)(-2) + (2)(0)(1) \\
&\quad + (2)(0)(1) + (1)(6)(-2) + (3)(2)(0) + (3)(0)(0) \} \\
&= 0
\end{aligned}$$

We see that  $\chi_{c-H} = A_{1g} \quad E_{2g} \quad B_{2u} \quad E_{1u}$

c. x and y  $E_{1u}$ , z  $A_{2u}$ , so, the ground state  $A_{1g}$  level can be excited to the degenerate  $E_{1u}$  level by coupling through the x or y transition dipoles. Therefore  $E_{1u}$  is infrared active and polarized.

d.  $(x^2 + y^2, z^2)$   $A_{1g}$ ,  $(xz, yz)$   $E_{1g}$ ,  $(x^2 - y^2, xy)$   $E_{2g}$ , so, the ground state  $A_{1g}$  level can be excited to the degenerate  $E_{2g}$  level by coupling through the  $x^2 - y^2$  or  $xy$  transitions or be excited to the degenerate  $A_{1g}$  level by coupling through the  $xz$  or  $yz$  transitions. Therefore  $A_{1g}$  and  $E_{2g}$  are Raman active..

e. The  $B_{2u}$  mode is not IR or Raman active.

$$\begin{aligned}
3. \quad a. \quad \frac{d}{dr} (F r^{-1}) &= F' r^{-1} - r^{-2} F \\
r^2 \frac{d}{dr} (F r^{-1}) &= r F' - F \\
\frac{d}{dr} r^2 \frac{d}{dr} (F r^{-1}) &= F' - F' + r F''
\end{aligned}$$

So,

$$\frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} r^2 \frac{d}{dr} (F r^{-1}) = \frac{-\hbar^2}{2\mu} \frac{F''}{r}$$

Rewriting the radial Schrödinger equation with the substitution:  $R = r^{-1}F$  gives:

$$\frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} r^2 \frac{d(Fr^{-1})}{dr} + \frac{J(J+1)\hbar^2}{2\mu r^2} (Fr^{-1}) + \frac{1}{2} k(r - r_e)^2 (Fr^{-1}) = E (Fr^{-1})$$

Using the above derived identity gives:

$$\frac{-\hbar^2}{2\mu} \frac{F''}{r} + \frac{J(J+1)\hbar^2}{2\mu r^2} (Fr^{-1}) + \frac{1}{2} k(r - r_e)^2 (Fr^{-1}) = E (Fr^{-1})$$

Cancelling out an  $r^{-1}$ :

$$\frac{-\hbar^2}{2\mu} F'' + \frac{J(J+1)\hbar^2}{2\mu r^2} F + \frac{1}{2} k(r - r_e)^2 F = E F$$

$$b. \quad \frac{1}{r^2} = \frac{1}{(r_e + r)^2} = \frac{1}{r_e^2 \left(1 + \frac{r}{r_e}\right)^2} = \frac{1}{r_e^2} \left(1 - \frac{2r}{r_e} + \frac{3r^2}{r_e^2}\right)$$

So,

$$\frac{J(J+1)\hbar^2}{2\mu r^2} = \frac{J(J+1)\hbar^2}{2\mu r_e^2} \left(1 - \frac{2r}{r_e} + \frac{3r^2}{r_e^2}\right)$$

c. Using this substitution we now have:

$$\frac{-\hbar^2}{2\mu} F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \left(1 - \frac{2r}{r_e} + \frac{3r^2}{r_e^2}\right) F + \frac{1}{2} k(r - r_e)^2 F = E F$$

Now, regroup the terms which are linear and quadratic in  $r = r - r_e$ :

$$\begin{aligned} & \frac{1}{2} k r^2 + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{3}{r_e^2} r^2 - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{2}{r_e} r \\ &= \frac{1}{2} k + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{3}{r_e^2} r^2 - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{2}{r_e} r \end{aligned}$$

Now, we must complete the square:

$$a r^2 - b r = a \left( r - \frac{b}{2a} \right)^2 - \frac{b^2}{4a}$$

So,

$$\begin{aligned} & \frac{1}{2} k + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{3}{r_e^2} r^2 - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{2}{r_e} r \\ &= \frac{1}{2} k + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{3}{r_e^2} \left( r - \frac{r_e}{3} \right)^2 - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{2}{r_e} r \\ &= \frac{1}{2} k + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{3}{r_e^2} \left( r - \frac{r_e}{3} \right)^2 - \frac{J(J+1)\hbar^2}{2\mu r_e^2} \frac{2}{r_e} r \end{aligned}$$

Now, redefine the first term as  $\frac{1}{2} k$ , second term as  $(r - r_e)^2$ , and the third term as - giving:

$$\frac{1}{2} k (r - r_e)^2 -$$

From:

$$\frac{-\hbar^2}{2\mu} F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \left(1 - \frac{2r}{r_e} + \frac{3r^2}{r_e^2}\right) F + \frac{1}{2} k(r - r_e)^2 F = E F,$$

$$\frac{-\hbar^2}{2\mu} F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2} F + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \left(-\frac{2r}{r_e} + \frac{3r^2}{r_e^2}\right) F + \frac{1}{2} k r^2 F = E F,$$

and making the above substitution results in:

$$\frac{-\hbar^2}{2\mu} F'' + \frac{J(J+1)\hbar^2}{2\mu r_e^2} F + \frac{1}{2}k(r - r_e)^2 F = E F,$$

or,

$$\frac{-\hbar^2}{2\mu} F'' + \frac{1}{2}k(r - r_e)^2 F = E - \frac{J(J+1)\hbar^2}{2\mu r_e^2} + F.$$

d. Since the above is nothing but a harmonic oscillator differential equation in  $x$  with force constant  $k$  and equilibrium bond length  $r_e$ , we know that:

$$\begin{aligned} \frac{-\hbar^2}{2\mu} F'' + \frac{1}{2}k(r - r_e)^2 F &= F, \text{ has energy levels:} \\ &= \hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right), v = 0, 1, 2, \dots \end{aligned}$$

So,

$$E + \dots - \frac{J(J+1)\hbar^2}{2\mu r_e^2} =$$

tells us that:

$$E = \hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right) + \frac{J(J+1)\hbar^2}{2\mu r_e^2} \dots$$

As  $J$  increases,  $r_e$  increases because of the centrifugal force pushing the two atoms apart.

On the other hand  $k$  increases which indicates that the molecule finds it more difficult to stretch against both the centrifugal and Hooke's law (spring) Harmonic force field. The

total energy level (labeled by  $J$  and  $v$ ) will equal a rigid rotor component  $\frac{J(J+1)\hbar^2}{2\mu r_e^2}$  plus a

Harmonic oscillator part  $\hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right)$  (which has a force constant  $k$  which increases with  $J$ ).

## Section 5 Exercises, Problems, and Solutions

### Exercises:

1. Time dependent perturbation theory provides an expression for the radiative lifetime of an excited electronic state, given by  $\tau_R$ :

$$\tau_R = \frac{3\hbar^4 c^3}{4(E_i - E_f)^3 |\mu_{fi}|^2},$$

where  $i$  refers to the excited state,  $f$  refers to the lower state, and  $\mu_{fi}$  is the transition dipole.

a. Evaluate the  $z$ -component of the transition dipole for the  $2p_z$   $1s$  transition in a hydrogenic atom of nuclear charge  $Z$ , given:

$$1s = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}, \text{ and } 2p_z = \frac{1}{4\sqrt{2}} \left( \frac{Z}{a_0} \right)^{5/2} r \cos \theta e^{-Zr/2a_0}.$$

Express your answer in units of  $ea_0$ .

b. Use symmetry to demonstrate that the x- and y-components of  $\mu_{fi}$  are zero, i.e.

$$\langle 2p_z | e x | 1s \rangle = \langle 2p_z | e y | 1s \rangle = 0.$$

c. Calculate the radiative lifetime  $\tau_R$  of a hydrogenlike atom in its  $2p_z$  state. Use the

relation  $e^2 = \frac{\hbar^2}{m_e a_0}$  to simplify your results.

2. Consider a case in which the complete set of states  $\{ |k\rangle \}$  for a Hamiltonian is known.

a. If the system is initially in the state  $m$  at time  $t=0$  when a constant perturbation  $V$  is suddenly turned on, find the probability amplitudes  $C_k^{(2)}(t)$  and  $C_m^{(2)}(t)$ , to second order in  $V$ , that describe the system being in a different state  $k$  or the same state  $m$  at time  $t$ .

b. If the perturbation is turned on adiabatically, what are  $C_k^{(2)}(t)$  and  $C_m^{(2)}(t)$ ?

Here, consider that the initial time is  $t_0 = -\tau$ , and the potential is  $V e^{-t/\tau}$ , where the positive parameter  $\tau$  is allowed to approach zero  $\tau \rightarrow 0$  in order to describe the adiabatically (i.e., slowly) turned on perturbation.

c. Compare the results of parts a. and b. and explain any differences.

d. Ignore first order contributions (assume they vanish) and evaluate the transition rates  $\frac{d}{dt} |C_k^{(2)}(t)|^2$  for the results of part b. by taking the limit  $\tau \rightarrow 0^+$ , to obtain the adiabatic results.

3. If a system is initially in a state  $m$ , conservation of probability requires that the total probability of transitions out of state  $m$  be obtainable from the decrease in the probability of being in state  $m$ . Prove this to the lowest order by using the results of exercise 2, i.e.

show that:  $|C_m|^2 = 1 - \sum_{k \neq m} |C_k|^2$ .

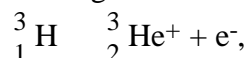
$$\sum_{k \neq m}$$

### Problems:

1. Consider an interaction or perturbation which is carried out suddenly (instantaneously, e.g., within an interval of time  $\tau$  which is small compared to the natural period  $\tau_{nm}^{-1}$  corresponding to the transition from state  $m$  to state  $n$ ), and after that is turned off adiabatically (i.e., extremely slowly as  $V e^{-t/\tau}$ ). The transition probability in this case is given as:

$$T_{nm} = \frac{|\langle n | V | m \rangle|^2}{\hbar^2 \tau_{nm}^2}$$

where  $V$  corresponds to the maximum value of the interaction when it is turned on. This formula allows one to calculate the transition probabilities under the action of sudden perturbations which are small in absolute value whenever perturbation theory is applicable. Let's use this "sudden approximation" to calculate the probability of excitation of an electron under a sudden change of the charge of the nucleus. Consider the reaction:





and assume the tritium atom has its electron initially in a 1s orbital. a. Calculate the transition probability for the transition 1s → 2s for this reaction using the above formula for the transition probability.

b. Suppose that at time  $t = 0$  the system is in a state which corresponds to the wavefunction  $\psi_m$ , which is an eigenfunction of the operator  $H_0$ . At  $t = 0$ , the sudden change of the Hamiltonian occurs (now denoted as  $H$  and remains unchanged). Calculate the same 1s → 2s transition probability as in part a., only this time as the square of the magnitude of the coefficient,  $A_{1s,2s}$  using the expansion:

$$\psi(r,0) = \psi_m(r) = \sum_n A_{nm} \psi_n(r), \text{ where } A_{nm} = \int \psi_m(r) \psi_n(r) d^3r$$

Note, that the eigenfunctions of  $H$  are  $\psi_n$  with eigenvalues  $E_n$ . Compare this "exact" value with that obtained by perturbation theory in part a.

2. The methyl iodide molecule is studied using microwave (pure rotational) spectroscopy. The following integral governs the rotational selection rules for transitions labeled  $J, M, K$  →  $J', M', K'$ :

$$I = \langle D_{M'K'}^{J'} | \cdot \mu | D_{MK}^J \rangle.$$

The dipole moment  $\mu$  lies along the molecule's  $C_3$  symmetry axis. Let the electric field of the light define the lab-fixed Z-direction.

a. Using the fact that  $\cos \theta = D_{00}^{1*}$ , show that

$$I = 8 \mu^2 (-1)^{M+K} \begin{matrix} J' & 1 & J \\ M & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ K & 0 & K \end{matrix} \begin{matrix} M'M & K'K \end{matrix}$$

b. What restrictions does this result place on  $J = J' - J$ ? Explain physically why the  $K$  quantum number can not change.

3. Consider the molecule BO.

a. What are the total number of possible electronic states which can be formed by combination of ground state B and O atoms?

b. What electron configurations of the molecule are likely to be low in energy? Consider all reasonable orderings of the molecular orbitals. What are the states corresponding to these configurations?

c. What are the bond orders in each of these states?

d. The true ground state of BO is  $^2 \Sigma^-$ . Specify the +/- and u/g symmetries for this state.

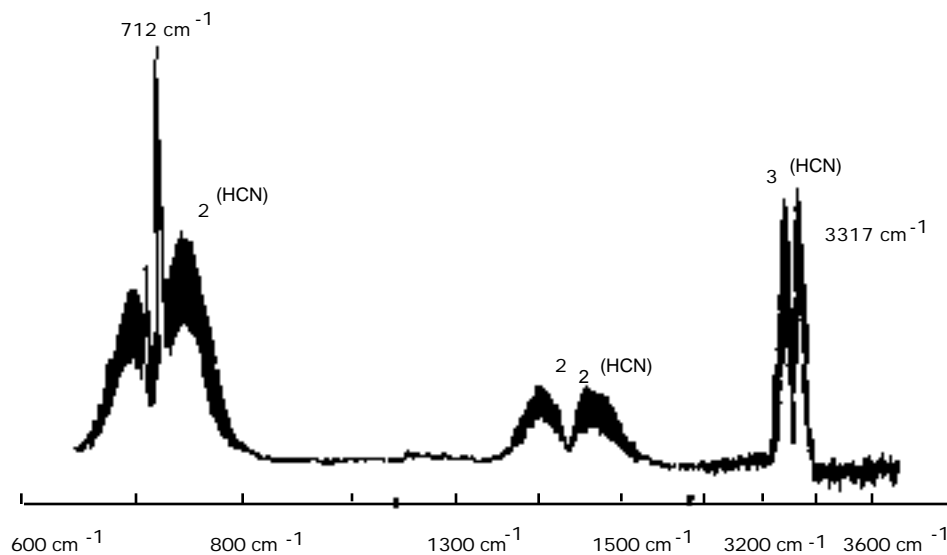
e. Which of the excited states you derived above will radiate to the  $^2 \Sigma^-$  ground state? Consider electric dipole, magnetic dipole, and electric quadrupole radiation.

f. Does ionization of the molecule to form a cation lead to a stronger, weaker, or equivalent bond strength?

g. Assuming that the energies of the molecular orbitals do not change upon ionization, what are the ground state, the first excited state, and the second excited state of the positive ion?

h. Considering only these states, predict the structure of the photoelectron spectrum you would obtain for ionization of BO.

4.



The above figure shows part of the infrared absorption spectrum of HCN gas. The molecule has a CH stretching vibration, a bending vibration, and a CN stretching vibration.

- a. Are any of the vibrations of linear HCN degenerate?
- b. To which vibration does the group of peaks between 600  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$  belong?
- c. To which vibration does the group of peaks between 3200  $\text{cm}^{-1}$  and 3400  $\text{cm}^{-1}$  belong?
- d. What are the symmetries ( , , ) of the CH stretch, CN stretch, and bending vibrational motions?
- e. Starting with HCN in its 0,0,0 vibrational level, which fundamental transitions would be infrared active under parallel polarized light (i.e., z-axis polarization):
  - i. 000 001?
  - ii. 000 100?
  - iii. 000 010?
- f. Which transitions would be active when perpendicular polarized light is used?
- g. Why does the 712  $\text{cm}^{-1}$  transition have a Q-branch, whereas that near 3317  $\text{cm}^{-1}$  has only P- and R-branches?

## Solutions

Exercises:

1. a. Evaluate the z-component of  $\mu_{fi}$ :

$$\mu_{fi} = \langle 2p_z | e^{-Zr/a_0} | 1s \rangle, \text{ where } |1s\rangle = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}, \text{ and } |2p_z\rangle = \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^{5/2} r \cos \theta e^{-Zr/2a_0}.$$

$$\begin{aligned} \mu_{fi} &= \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^{5/2} \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \langle r \cos \theta e^{-Zr/2a_0} | e^{-Zr/a_0} | r \cos \theta e^{-Zr/a_0} \rangle \\ &= \frac{1}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^4 \langle r \cos \theta e^{-Zr/2a_0} | e^{-Zr/a_0} \rangle \\ &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^4 \int_0^\pi \sin \theta d\theta \int_0^\infty r^2 dr e^{-Zr/2a_0} e^{-Zr/a_0} \cos^2 \theta \\ &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^4 \int_0^\pi \sin \theta \cos^2 \theta d\theta \int_0^\infty r^4 e^{-3Zr/2a_0} dr \end{aligned}$$

Using integral equation 4 to integrate over  $r$  and equation 17 to integrate over  $\theta$  we obtain:

$$\begin{aligned} &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^4 \frac{4!}{3Z^5} \frac{-1}{3} \int_0^\pi \cos^3 \theta d\theta \\ &= \frac{e}{4\sqrt{2}} \left(\frac{Z}{a_0}\right)^4 \frac{2^5 a_0^5 4!}{3^5 Z^5} \frac{-1}{3} ((-1)^3 - (1)^3) \\ &= \frac{e}{\sqrt{2}} \frac{2^8 a_0}{3^5 Z} = \frac{ea_0}{Z} \frac{2^8}{\sqrt{2} 3^5} = 0.7449 \frac{ea_0}{Z} \end{aligned}$$

b. Examine the symmetry of the integrands for  $\langle 2p_z | e^{-Zr/a_0} | 1s \rangle$  and  $\langle 2p_z | e^{-Zr/a_0} | 1s \rangle$ . Consider reflection in the  $xy$  plane:

Function	Symmetry
$2p_z$	-1
$x$	+1
$1s$	+1
$y$	+1

Under this operation the integrand of  $\langle 2p_z | e^{-Zr/a_0} | 1s \rangle$  is  $(-1)(1)(1) = -1$  (it is antisymmetric) and hence  $\langle 2p_z | e^{-Zr/a_0} | 1s \rangle = 0$ .

Similarly, under this operation the integrand of  $\langle 2p_z | e^{-Zr/a_0} | 1s \rangle$  is

$(-1)(1)(1) = -1$  (it is also antisymmetric) and hence  $\langle 2p_z | e y | 1s \rangle = 0$ .

$$c. \quad R = \frac{3\hbar^4 c^3}{4(E_i - E_f)^3 |\mu_{fi}|^2},$$

$$E_i = E_{2p_z} = -\frac{1}{4} Z^2 \frac{e^2}{2a_0}$$

$$E_f = E_{1s} = -Z^2 \frac{e^2}{2a_0}$$

$$E_i - E_f = \frac{3}{8} \frac{e^2}{a_0} Z^2$$

Making the substitutions for  $E_i - E_f$  and  $|\mu_{fi}|$  in the expression for  $R$  we obtain:

$$R = \frac{3\hbar^4 c^3}{4 \left( \frac{3}{8} \frac{e^2}{a_0} Z^2 \right)^3 \left( \frac{ea_0}{Z} \frac{2^8}{\sqrt{2} 3^5} \right)^2},$$

$$= \frac{3\hbar^4 c^3}{4 \frac{3^3}{8^3} \frac{e^6}{a_0^3} Z^6 \frac{e^2 a_0^2}{Z^2} \frac{2^{16}}{(2)3^{10}}},$$

$$= \frac{\hbar^4 c^3 3^8 a_0}{e^8 Z^4 2^8},$$

Inserting  $e^2 = \frac{\hbar^2}{m_e a_0}$  we obtain:

$$R = \frac{\hbar^4 c^3 3^8 a_0 m_e^4 a_0^4}{\hbar^8 Z^4 2^8} = \frac{3^8 c^3 a_0^5 m_e^4}{2^8 \hbar^4 Z^4}$$

$$= 25.6289 \frac{c^3 a_0^5 m_e^4}{\hbar^4 Z^4}$$

$$= 25,6289 \frac{1}{Z^4} \times$$

$$\frac{(2.998 \times 10^{10} \text{ cm sec}^{-1})^3 (0.529177 \times 10^{-8} \text{ cm})^5 (9.109 \times 10^{-28} \text{ g})^4}{(1.0546 \times 10^{-27} \text{ g cm}^2 \text{ sec}^{-1})^4}$$

$$= 1.595 \times 10^{-9} \text{ sec} \times \frac{1}{Z^4}$$

So, for example:

Atom	R
H	1.595 ns
He <sup>+</sup>	99.7 ps
Li <sup>+2</sup>	19.7 ps
Be <sup>+3</sup>	6.23 ps
Ne <sup>+9</sup>	159 fs

2. a.  $H = H_0 + H'(t)$ ,  $H'(t) = V(t)$ ,  $H_0 |k\rangle = E_k |k\rangle$ ,  $E_k = E_k/\hbar$

$$i\hbar \frac{d}{dt} = H$$

let  $|\psi(t)\rangle = \sum_j c_j(t) e^{-i E_j t/\hbar}$  and insert into the above expression:

$$i\hbar \sum_j \dot{c}_j e^{-i E_j t/\hbar} - \sum_j c_j E_j e^{-i E_j t/\hbar} = i\hbar \sum_j \dot{c}_j e^{-i E_j t/\hbar} (H_0 + H'(t)) |j\rangle$$

$$i\hbar \sum_j \dot{c}_j e^{-i E_j t/\hbar} + \sum_j c_j E_j e^{-i E_j t/\hbar} - \sum_j c_j E_j e^{-i E_j t/\hbar} - \sum_j c_j H' e^{-i E_j t/\hbar} = 0$$

$$i\hbar \sum_j \dot{c}_j \langle m|j\rangle e^{-i E_j t/\hbar} - \sum_j c_j \langle m|H'|j\rangle e^{-i E_j t/\hbar} = 0$$

$$i\hbar \dot{c}_m e^{-i E_m t/\hbar} = \sum_j c_j H'_{mj} e^{-i E_j t/\hbar}$$

So,

$$c_m = \frac{1}{i\hbar} \sum_j c_j H'_{mj} e^{-i(E_j - E_m)t/\hbar}$$

Going back a few equations and multiplying from the left by  $\langle k|$  instead of  $\langle m|$  we obtain:

$$i\hbar \sum_j \dot{c}_j \langle k|j\rangle e^{-i E_j t/\hbar} - \sum_j c_j \langle k|H'|j\rangle e^{-i E_j t/\hbar} = 0$$

$$i\hbar \dot{c}_k e^{-i E_k t/\hbar} = \sum_j c_j H'_{kj} e^{-i E_j t/\hbar}$$

So,

$$c_k = \frac{1}{i\hbar} \sum_j c_j H'_{kj} e^{-i(E_j - E_k)t/\hbar}$$

Now, let:

$$c_m = c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots$$

$$c_k = c_k^{(0)} + c_k^{(1)} + c_k^{(2)} + \dots$$

and substituting into above we obtain:

$$c_m^{(0)} + c_m^{(1)} + c_m^{(2)} + \dots = \frac{1}{i\hbar} \sum_j [c_j^{(0)} + c_j^{(1)} + c_j^{(2)} + \dots] H'_{mj} e^{-i(E_j - E_m)t/\hbar}$$

first order:

$$c_m^{(0)} = 0 \quad c_m^{(0)} = 1$$

second order:

$$c_m^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{mj} e^{-i(E_j - E_m)t/\hbar}$$

(n+1)<sup>st</sup> order:

$$c_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(\omega_j - \omega_m)t}$$

Similarly:

first order:

$$c_k^{(0)} = 0 \quad c_m^{(0)} = 0$$

second order:

$$c_k^{(1)} = \frac{1}{i\hbar} \sum_j c_j^{(0)} H'_{kj} e^{-i(\omega_j - \omega_k)t}$$

(n+1)<sup>st</sup> order:

$$c_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(\omega_j - \omega_k)t}$$

So,

$$c_m^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{mm} e^{-i(\omega_m - \omega_m)t} = \frac{1}{i\hbar} H'_{mm}$$

$$c_m^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' V_{mm} = \frac{V_{mm}t}{i\hbar}$$

and similarly,

$$c_k^{(1)} = \frac{1}{i\hbar} c_m^{(0)} H'_{km} e^{-i(\omega_m - \omega_k)t} = \frac{1}{i\hbar} H'_{km} e^{-i(\omega_m - \omega_k)t}$$

$$c_k^{(1)}(t) = \frac{1}{i\hbar} V_{km} \int_0^t dt' e^{-i(\omega_m - \omega_k)t'} = \frac{V_{km}}{\hbar(\omega_m - \omega_k)} [e^{-i(\omega_m - \omega_k)t} - 1]$$

$$c_m^{(2)} = \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{mj} e^{-i(\omega_j - \omega_m)t}$$

$$c_m^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}}{\hbar(\omega_j - \omega_m)} [e^{-i(\omega_j - \omega_m)t} - 1] H'_{mj} e^{-i(\omega_j - \omega_m)t} + \frac{1}{i\hbar} \frac{V_{mm}t}{i\hbar} H'_{mm}$$

$$c_m^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}V_{mj}}{\hbar(\omega_j - \omega_m)} \int_0^t dt' e^{-i(\omega_j - \omega_m)t'} [e^{-i(\omega_j - \omega_m)t'} - 1] - \frac{V_{mm}V_{mm}}{\hbar^2} \int_0^t t' dt'$$

$$= \sum_j \frac{V_{jm}V_{mj}}{\hbar^2(\omega_j - \omega_m)} \int_0^t dt' [1 - e^{-i(\omega_j - \omega_m)t'}] - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2}$$

$$= \sum_j \frac{V_{jm}V_{mj}}{\hbar^2(\omega_j - \omega_m)} t - \frac{e^{-i(\omega_j - \omega_m)t} - 1}{-i(\omega_j - \omega_m)} - \frac{|V_{mm}|^2}{\hbar^2} \frac{t^2}{2}$$

$$\begin{aligned}
&= \sum_j \frac{V_{jm}V_{mj}}{\hbar^2 m_j^2} (e^{-i(jm)t} - 1) + \sum_j \frac{V_{jm}V_{mj}}{i\hbar^2 m_j} t - \frac{|V_{mm}|^2 t^2}{2\hbar^2} \\
\text{Similarly,} \\
c_k^{(2)} &= \frac{1}{i\hbar} \sum_j c_j^{(1)} H'_{kj} e^{-i(jk)t} \\
&= \sum_j \frac{1}{i\hbar} \frac{V_{jm}}{\hbar m_j} [e^{-i(mj)t} - 1] H'_{kj} e^{-i(jk)t} + \\
&\quad \frac{1}{i\hbar} \frac{V_{mm}t}{i\hbar} H'_{km} e^{-i(mk)t} \\
c_k^{(2)}(t) &= \sum_j \frac{V_{jm}V_{kj}}{i\hbar^2 m_j} \int_0^t dt' e^{-i(jk)t'} [e^{-i(mj)t'} - 1] \\
&\quad - \frac{V_{mm}V_{km}}{\hbar^2} \int_0^t dt' dt' e^{-i(mk)t'} \\
&= \sum_j \frac{V_{jm}V_{kj}}{i\hbar^2 m_j} \frac{e^{-i(mj+jk)t} - 1}{-i(mk)} - \frac{e^{-i(jk)t} - 1}{-i(jk)} \\
&\quad - \frac{V_{mm}V_{km}}{\hbar^2} e^{-i(mk)t} \frac{t'}{-i(mk)} - \frac{1}{-(i(mk))^2} t \\
&= \sum_j \frac{V_{jm}V_{kj}}{\hbar^2 m_j} \frac{e^{-i(mk)t} - 1}{mk} - \frac{e^{-i(jk)t} - 1}{jk} \\
&\quad + \frac{V_{mm}V_{km}}{\hbar^2 mk} e^{-i(mk)t} \frac{t'}{i} - \frac{1}{mk} t \\
&= \sum_j \frac{V_{jm}V_{kj}}{E_m - E_j} \frac{e^{-i(mk)t} - 1}{E_m - E_k} - \frac{e^{-i(jk)t} - 1}{E_j - E_k} \\
&\quad + \frac{V_{mm}V_{km}}{\hbar(E_m - E_k)} e^{-i(mk)t} \frac{t}{i} - \frac{1}{mk} t + \frac{1}{mk}
\end{aligned}$$

So, the overall amplitudes  $c_m$ , and  $c_k$ , to second order are:

$$\begin{aligned}
c_m(t) &= 1 + \frac{V_{mm}t}{i\hbar} + \sum_j \frac{V_{jm}V_{mj}}{i\hbar(E_m - E_j)} t + \\
&\quad \sum_j \frac{V_{jm}V_{mj}}{\hbar^2(E_m - E_j)^2} (e^{-i(jm)t} - 1) - \frac{|V_{mm}|^2 t^2}{2\hbar^2} \\
c_k(t) &= \frac{V_{km}}{(E_m - E_k)} [e^{-i(mk)t} - 1] +
\end{aligned}$$

$$\frac{V_{mm}V_{km}}{(E_m - E_k)^2} [1 - e^{-i(mk)t}] + \frac{V_{mm}V_{km}}{(E_m - E_k)} \frac{t}{\hbar} e^{-i(mk)t} +$$

$$\frac{V_{jm}V_{kj}}{E_m - E_j} \frac{e^{-i(mk)t} - 1}{E_m - E_k} - \frac{e^{-i(jk)t} - 1}{E_j - E_k}$$

b. The perturbation equations still hold:

$$c_m^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{mj} e^{-i(jm)t} ; c_k^{(n)} = \frac{1}{i\hbar} \sum_j c_j^{(n-1)} H'_{kj} e^{-i(jk)t}$$

So,  $c_m^{(0)} = 1$  and  $c_k^{(0)} = 0$

$$c_m^{(1)} = \frac{1}{i\hbar} H'_{mm} t$$

$$c_m^{(1)} = \frac{1}{i\hbar} \int_0^t V_{mm} dt' e^{-i(mm)t'} = \frac{V_{mm} e^{-i(mm)t}}{i\hbar}$$

$$c_k^{(1)} = \frac{1}{i\hbar} H'_{km} e^{-i(mk)t}$$

$$c_k^{(1)} = \frac{1}{i\hbar} \int_0^t V_{km} dt' e^{-i(mk)t'} = \frac{V_{km}}{i\hbar(-i(mk))} [e^{-i(mk)t} - 1]$$

$$= \frac{V_{km}}{E_m - E_k + i\hbar} [e^{-i(mk)t} - 1]$$

$$c_m^{(2)} = \frac{1}{i\hbar} \sum_j \frac{V_{jm}}{E_m - E_j + i\hbar} e^{-i(jm)t} V_{mj} e^{-i(jm)t} +$$

$$\frac{1}{i\hbar} \frac{V_{mm} e^{-i(mm)t}}{i\hbar} V_{mm} e^{-i(mm)t}$$

$$c_m^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}V_{mj}}{E_m - E_j + i\hbar} e^{-i(jm)t} - \frac{|V_{mm}|^2}{\hbar^2} e^{-i(mm)t}$$

$$= \sum_j \frac{V_{jm}V_{mj}}{i\hbar^2 (E_m - E_j + i\hbar)} e^{-i(jm)t} - \frac{|V_{mm}|^2}{2\hbar^2} e^{-i(mm)t}$$

$$c_k^{(2)} = \sum_j \frac{1}{i\hbar} \frac{V_{jm}}{E_m - E_j + i\hbar} e^{-i(jm)t} H'_{kj} e^{-i(jk)t} +$$

$$\frac{1}{i\hbar} \frac{V_{mm} e^{-i(mm)t}}{i\hbar} H'_{km} e^{-i(mk)t}$$



$$c_k^{(2)} = \int_0^t \frac{1}{i\hbar} \frac{V_{jm}V_{kj}}{E_m - E_j + i\hbar} e^{-i(E_m - E_k + 2\hbar) t'} dt' - \frac{V_{mm}V_{km}}{\hbar^2} \int_0^t e^{-i(E_m - E_k + 2\hbar) t'} dt'$$

$$= \int_0^t \frac{V_{jm}V_{kj} e^{-i(E_m - E_k + 2\hbar) t'}}{(E_m - E_j + i\hbar)(E_m - E_k + 2i\hbar)} - \frac{V_{mm}V_{km} e^{-i(E_m - E_k + 2i\hbar) t}}{i\hbar (E_m - E_k + 2i\hbar)}$$

Therefore, to second order:

$$c_m(t) = 1 + \frac{V_{mm}e^{-iEt}}{i\hbar} + \int_0^t \frac{V_{jm}V_{mj}}{i\hbar^2 (E_m - E_j + i\hbar)} e^{-iEt} dt$$

$$c_k(t) = \frac{V_{km}}{i\hbar(-i(E_m - E_k + 2\hbar))} [e^{-i(E_m - E_k + 2\hbar)t}] + \int_0^t \frac{V_{jm}V_{kj} e^{-i(E_m - E_k + 2\hbar) t'}}{(E_m - E_j + i\hbar)(E_m - E_k + 2i\hbar)}$$

c. In part a. the  $c^{(2)}(t)$  grow linearly with time (for  $V_{mm} = 0$ ) while in part b. they remain finite for  $t > 0$ . The result in part a. is due to the sudden turning on of the field.

$$d. |c_k(t)|^2 = \frac{V_{jm}V_{kj} e^{-i(E_m - E_k + 2\hbar)t}}{(E_m - E_j + i\hbar)(E_m - E_k + 2i\hbar)}^2$$

$$= \frac{V_{kj}V_{kj}'V_{jm}V_{j'm} e^{-i(E_m - E_k + 2\hbar)t} e^{i(E_m - E_k + 2\hbar)t}}{jj' [(E_m - E_j + i\hbar)(E_m - E_j' - i\hbar)(E_m - E_k + 2i\hbar)(E_m - E_k - 2i\hbar)]}$$

$$= \frac{V_{kj}V_{kj}'V_{jm}V_{j'm} e^{4\hbar t}}{jj' [(E_m - E_j)(E_m - E_j') + i\hbar(E_j - E_j') + \hbar^2] [(E_m - E_k)^2 + 4\hbar^2]}$$

$$\frac{d}{dt} |c_k(t)|^2 = \frac{4 V_{kj}V_{kj}'V_{jm}V_{j'm}}{jj' [(E_m - E_j)(E_m - E_j') + i\hbar(E_j - E_j') + \hbar^2] [(E_m - E_k)^2 + 4\hbar^2]}$$

Now, look at the limit as  $\hbar \rightarrow 0^+$ :

$$\frac{d}{dt} |c_k(t)|^2 \rightarrow 0 \text{ when } E_m = E_k$$

$$\lim_{\hbar \rightarrow 0^+} \frac{4}{((E_m - E_k)^2 + 4\hbar^2)} (E_m - E_k)$$

So, the final result is the 2<sup>nd</sup> order golden rule expression:

$$\frac{d}{dt} |c_k(t)|^2 \frac{2}{\hbar} (E_m - E_k) \lim_{\hbar \rightarrow 0^+} \int_0^t \frac{V_{jm}V_{kj}}{(E_j - E_m - i\hbar)}$$

3. For the sudden perturbation case:

$$|c_m(t)|^2 = 1 + \sum_j \frac{V_{jm}V_{mj}}{(E_m - E_j)^2} [e^{-i(E_j - E_m)t} - 1 + e^{i(E_j - E_m)t} - 1] + O(V^3)$$

$$|c_m(t)|^2 = 1 + \sum_j \frac{V_{jm}V_{mj}}{(E_m - E_j)^2} [e^{-i(E_j - E_m)t} + e^{i(E_j - E_m)t} - 2] + O(V^3)$$

$$|c_k(t)|^2 = \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [-e^{-i(E_k - E_m)t} - e^{i(E_k - E_m)t} + 2] + O(V^3)$$

$$1 - \sum_k |c_k(t)|^2 = 1 - \sum_k \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [-e^{-i(E_k - E_m)t} - e^{i(E_k - E_m)t} + 2] + O(V^3)$$

$$= 1 + \sum_k \frac{V_{km}V_{mk}}{(E_m - E_k)^2} [e^{-i(E_k - E_m)t} + e^{i(E_k - E_m)t} - 2] + O(V^3)$$

to order  $V^2$ ,  $|c_m(t)|^2 = 1 - \sum_k |c_k(t)|^2$ , with no assumptions made regarding  $V_{mm}$ .

For the adiabatic perturbation case:

$$|c_m(t)|^2 = 1 + \sum_j \frac{V_{jm}V_{mj}e^{2t}}{i\hbar^2 (E_m - E_j + i\hbar)} + \frac{V_{jm}V_{mj}e^{2t}}{-i\hbar^2 (E_m - E_j - i\hbar)} + O(V^3)$$

$$= 1 + \sum_j \frac{1}{i\hbar^2} \frac{1}{(E_m - E_j + i\hbar)} - \frac{1}{(E_m - E_j - i\hbar)} V_{jm}V_{mj}e^{2t} + O(V^3)$$

$$= 1 + \sum_j \frac{1}{i\hbar^2} \frac{-2i\hbar}{(E_m - E_j)^2 + \hbar^2} V_{jm}V_{mj}e^{2t} + O(V^3)$$

$$= 1 - \sum_j \frac{V_{jm}V_{mj}e^{2t}}{(E_m - E_j)^2 + \hbar^2} + O(V^3)$$

$$|c_k(t)|^2 = \frac{V_{km}V_{mk}}{(E_m - E_k)^2 + \hbar^2} e^{2t} + O(V^3)$$

to order  $V^2$ ,  $|c_m(t)|^2 = 1 - \sum_k |c_k(t)|^2$ , with no assumptions made regarding  $V_{mm}$  for this

case as well.

### Problems:

$$1. \quad a. \quad T_{nm} = \frac{|\langle n|V|m\rangle|^2}{\hbar^2 \omega_{nm}^2}$$

evaluating  $\langle 1s|V|2s\rangle$  (using only the radial portions of the 1s and 2s wavefunctions since the spherical harmonics will integrate to unity) where  $V = (e^2/r)$ :

$$\langle 1s|V|2s\rangle = 2 \frac{Z}{a_0} \frac{3}{2} e^{-\frac{Zr}{a_0}} \frac{1}{r} \frac{1}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}} r^2 dr$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \int_0^\infty r e^{-\frac{3Zr}{2a_0}} dr - \frac{Zr^2}{2a_0} e^{-\frac{3Zr}{2a_0}} dr$$

Using integral equation 4 for the two integrations we obtain:

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \left[ \frac{1}{\frac{3Z}{2a_0}} - \frac{Z}{2a_0} \frac{2}{\frac{3Z}{2a_0}} \right]$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \left[ \frac{2^2 a_0^2}{3^2 Z^2} - \frac{2^3 a_0^2}{3^3 Z^2} \right]$$

$$\langle 1s|V|2s\rangle = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{(3)2^2 a_0^2 - 2^3 a_0^2}{3^3 Z^2} = \frac{8Z}{\sqrt{2} 27 a_0}$$

Now,

$$E_n = -\frac{Z^2 e^2}{n^2 2a_0}, E_{1s} = -\frac{Z^2 e^2}{2a_0}, E_{2s} = -\frac{Z^2 e^2}{8a_0}, E_{2s} - E_{1s} = \frac{3Z^2 e^2}{8a_0}$$

So,

$$T_{nm} = \frac{\frac{8Z}{\sqrt{2} 27 a_0}^2}{\frac{3Z^2}{8a_0}} = \frac{2^6 Z^2 2^6 a_0^2}{(2) 3^8 a_0^2 Z^4} = \frac{2^{11}}{3^8 Z^2} = 0.312 \text{ (for } Z = 1)$$

$$b. \quad m(r) = {}_{1s} = 2 \frac{Z}{a_0} \frac{3}{2} e^{-\frac{Zr}{a_0}} Y_{00}$$

The orthogonality of the spherical harmonics results in only s-states having non-zero values for  $A_{nm}$ . We can then drop the  $Y_{00}$  (integrating this term will only result in unity) in determining the value of  $A_{1s,2s}$ .

$$n(r) = {}_{2s} = \frac{1}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}$$

Remember for  ${}_{1s} Z = 1$  and for  ${}_{2s} Z = 2$

$$A_{nm} = 2 \frac{Z}{a_0} \frac{3}{2} e^{-\frac{Zr}{a_0}} \frac{1}{\sqrt{2}} \frac{Z+1}{a_0} \frac{3}{2} \left(1 - \frac{(Z+1)r}{2a_0}\right) e^{-\frac{(Z+1)r}{2a_0}} r^2 dr$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} e^{-\frac{(3Z+1)r}{2a_0}} \left(1 - \frac{(Z+1)r}{2a_0}\right) r^2 dr$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \int_0^\infty r^2 e^{-\frac{(3Z+1)r}{2a_0}} dr - \frac{(Z+1)r^3}{2a_0} e^{-\frac{(3Z+1)r}{2a_0}} dr$$

Evaluating these integrals using integral equation 4 we obtain:

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \frac{2}{\frac{3Z+1}{2a_0}} - \frac{Z+1}{2a_0} \frac{(3)(2)}{\frac{3Z+1}{2a_0}}$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \frac{2^4 a_0^3}{(3Z+1)^3} - (Z+1) \frac{(3)2^4 a_0^3}{(3Z+1)^4}$$

$$A_{nm} = \frac{2}{\sqrt{2}} \frac{Z}{a_0} \frac{3}{2} \frac{Z+1}{a_0} \frac{3}{2} \frac{-2^5 a_0^3}{(3Z+1)^4}$$

$$A_{nm} = -2 \frac{[2^3 Z(Z+1)]^{\frac{3}{2}}}{(3Z+1)^4}$$

The transition probability is the square of this amplitude:

$$T_{nm} = -2 \frac{[2^3 Z(Z+1)]^{\frac{3}{2}}}{(3Z+1)^4} = \frac{2^{11} Z^3 (Z+1)^3}{(3Z+1)^8} = 0.25 \text{ (for } Z = 1\text{)}.$$

The difference in these two results (parts a. and b.) will become negligible at large values of  $Z$  when the perturbation becomes less significant as in the case of  $Z = 1$ .

2.  $\hat{z}$  is along  $Z$  (lab fixed), and  $\hat{\mu}$  is along  $z$  (the C-I molecule fixed bond). The angle between  $Z$  and  $z$  is  $\theta$ :

$$\hat{z} \cdot \hat{\mu} = \mu \cos \theta = \mu D_{00}^{1*}(\theta)$$

So,

$$I = \langle D_{M'K'}^{J'} | \hat{z} \cdot \hat{\mu} | D_{MK}^J \rangle = \langle D_{M'K'}^{J'} | \mu D_{MK}^J \sin \theta | D_{MK}^J \rangle \\ = \mu \langle D_{M'K'}^{J'} | D_{00}^{1*} | D_{MK}^J \rangle \sin \theta$$

Now use:

$$D_{M'n'}^{J'*} D_{00}^{1*} = \sum_{jmn} \langle J'M'10 | jm \rangle^* D_{mn}^{j*} \langle jn | J'K'10 \rangle^*$$

to obtain:

$$I = \mu \sum_{jmn} \langle J'M'10 | jm \rangle^* \langle jn | J'K'10 \rangle^* D_{mn}^{j*} D_{MK}^J \sin \theta$$

Now use:

$$D_{mn}^{j*} D_{MK}^J \sin \theta = \frac{8}{2J+1} \langle J'M'10 | jm \rangle^* \langle jn | J'K'10 \rangle^* \langle J'M'10 | jm \rangle \langle jn | J'K'10 \rangle$$

to obtain:

$$I = \mu \frac{8}{2J+1} \sum_{jmn} \langle J'M'10 | jm \rangle^* \langle jn | J'K'10 \rangle^* \langle J'M'10 | jm \rangle \langle jn | J'K'10 \rangle$$

$$= \mu \frac{8}{2J+1} \langle J'M'10|JM\rangle \langle JK|J'K'10\rangle.$$

We use:

$$\langle JK|J'K'10\rangle = \sqrt{2J+1}(-i)^{(J'-1+K)} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix}$$

and,

$$\langle J'M'10|JM\rangle = \sqrt{2J+1}(-i)^{(J'-1+M)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix}$$

to give:

$$\begin{aligned} I &= \mu \frac{8}{2J+1} \sqrt{2J+1}(-i)^{(J'-1+M)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix} \sqrt{2J+1}(-i)^{(J'-1+K)} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix} \\ &= \mu 8 \sqrt{2}(-i)^{(J'-1+M+J'-1+K)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix} \\ &= \mu 8 \sqrt{2}(-i)^{(M+K)} \begin{matrix} J' & 1 & J \\ & M' & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ & K' & 0 & K \end{matrix} \end{aligned}$$

The 3-J symbols vanish unless:  $K' + 0 = K$  and  $M' + 0 = M$ .

So,

$$I = \mu 8 \sqrt{2}(-i)^{(M+K)} \begin{matrix} J' & 1 & J \\ & M & 0 & M \end{matrix} \begin{matrix} J' & 1 & J \\ & K & 0 & K \end{matrix} \quad M'M \quad K'K.$$

b.  $\begin{matrix} J' & 1 & J \\ & M & 0 & M \end{matrix}$  and  $\begin{matrix} J' & 1 & J \\ & K & 0 & K \end{matrix}$  vanish unless  $J' = J + 1, J, J - 1$   
 $J = \pm 1, 0$

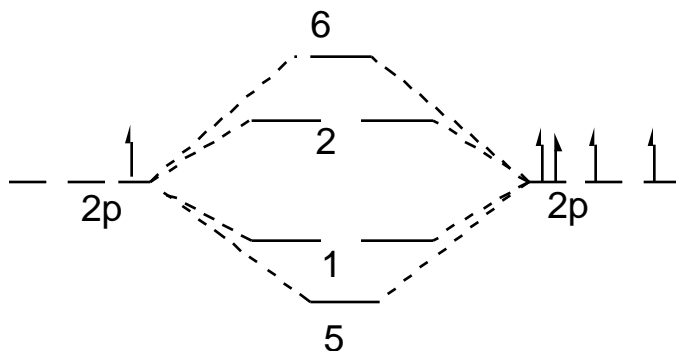
The K quantum number can not change because the dipole moment lies along the molecule's  $C_3$  axis and the light's electric field thus can exert no torque that twists the molecule about this axis. As a result, the light can not induce transitions that excite the molecule's spinning motion about this axis.

3. a. B atom:  $1s^2 2s^2 2p^1$ ,  $^2P$  ground state  $L = 1, S = \frac{1}{2}$ , gives a degeneracy  $((2L+1)(2S+1))$  of 6.

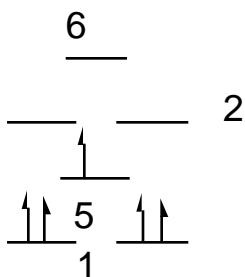
O atom:  $1s^2 2s^2 2p^4$ ,  $^3P$  ground state  $L = 1, S = 1$ , gives a degeneracy  $((2L+1)(2S+1))$  of 9.

The total number of states formed is then  $(6)(9) = 54$ .

b. We need only consider the p orbitals to find the low lying molecular states:



Which, in reality look like this:



This is the correct ordering to give a  $2^+$  ground state. The only low-lying electron configurations are  $1^3 5^2$  or  $1^4 5^1$ . These lead to  $2^-$  and  $2^+$  states, respectively.

c. The bond orders in both states are  $2\frac{1}{2}$ .

d. The  $2^-$  is + and g/u cannot be specified since this is a heteronuclear molecule.

e. Only one excited state, the  $2^-$ , is spin-allowed to radiate to the  $2^+$ . Consider symmetries of transition moment operators that arise in the E1, E2 and M1 contributions to the transition rate

Electric dipole allowed:  $z^+$ ,  $x, y^-$ , the  $2^- \rightarrow 2^+$  is electric dipole allowed via a perpendicular band.

Magnetic dipole allowed:  $R_z^-$ ,  $R_{x,y}^+$ , the  $2^- \rightarrow 2^+$  is magnetic dipole allowed.

Electric quadrupole allowed:  $x^2+y^2, z^2^+$ ,  $xy, yz^-$ ,  $x^2-y^2, xy^-$  the  $2^- \rightarrow 2^+$  is electric quadrupole allowed as well.

f. Since ionization will remove a bonding electron, the  $BO^+$  bond is weaker than the BO bond.

g. The ground state  $BO^+$  is  $1^+$  corresponding to a  $1^4$  electron configuration. An electron configuration of  $1^3 5^1$  leads to a  $3^-$  and a  $1^-$  state. The  $3^-$  will be lower in energy. A  $1^2 5^2$  configuration will lead to higher lying states of  $3^-$ ,  $1^-$ , and  $1^+$ .

h. There should be 3 bands corresponding to formation of  $BO^+$  in the  $1^+$ ,  $3^-$ , and  $1^-$  states. Since each of these involves removing a bonding electron, the Franck-Condon integrals will be appreciable for several vibrational levels, and thus a vibrational progression should be observed.

4. a. The bending ( $\nu_2$ ) vibration is degenerate.

b. H---C N

bending fundamental

c. H---C N

stretching fundamental

d. CH stretch ( $\nu_3$  in figure) is  $\nu_3$ , CN stretch is  $\nu_4$ , and HCN ( $\nu_2$  in figure) bend is  $\nu_2$ .

e. Under  $z$  ( ) light the CN stretch and the CH stretch can be excited, since  $\nu_0 =$  ,  $\nu_1 =$  and  $z =$  provides coupling.

f. Under  $x,y$  ( ) light the HCN bend can be excited, since  $\nu_0 =$  ,  $\nu_1 =$  and  $x,y =$  provides coupling.

g. The bending vibration is active under  $(x,y)$  perpendicular polarized light.  $J = 0, \pm 1$  are the selection rules for  $\perp$  transitions. The CH stretching vibration is active under  $(z) \parallel$  polarized light.  $J = \pm 1$  are the selection rules for  $\parallel$  transitions.

## Section 6 Exercises, Problems, and Solutions

### Review Exercises:

1. Contrast Slater type orbitals (STOs) with Gaussian type orbitals (GTOs).

### Exercises:

1. By expanding the molecular orbitals  $\{ \psi_k \}$  as linear combinations of atomic orbitals  $\{ \chi_\mu \}$ ,

$$\psi_k = \sum_{\mu} c_{\mu k} \chi_{\mu}$$

show how the canonical Hartree-Fock (HF) equations:

$$F_{ij} = \int \chi_i^* (h + \sum_j \chi_j^* \chi_j) \chi_j$$

reduce to the matrix eigenvalue-type equation of the form given in the text:

$$F_{\mu} C_i = \epsilon_i S_{\mu} C_i$$

where:

$$F_{\mu} = \langle \chi_{\mu} | h | \chi_{\mu} \rangle + \sum_{\nu} P_{\nu} \langle \chi_{\mu} | g | \chi_{\nu} \rangle - \frac{1}{2} \sum_{\nu}^{\text{ex}} \langle \chi_{\mu} | g | \chi_{\nu} \rangle ,$$

$$S_{\mu} = \langle \chi_{\mu} | \chi_{\mu} \rangle , \quad P_{\nu} = \sum_{i=\text{occ}} C_i C_i ,$$

$$\text{and } \sum_{\nu}^{\text{ex}} = \sum_{i=\text{occ and same spin}} C_i C_i .$$

Note that the sum over  $i$  in  $P_{\nu}$  and  $\sum_{\nu}^{\text{ex}}$  is a sum over spin orbitals. In addition, show that this Fock matrix can be further reduced for the closed shell case to:

$$F_{\mu} = \langle \chi_{\mu} | h | \chi_{\mu} \rangle + P \langle \chi_{\mu} | g | \chi_{\mu} \rangle - \frac{1}{2} \langle \chi_{\mu} | g | \chi_{\mu} \rangle ,$$

where the charge bond order matrix,  $P$ , is defined to be:

$$P = \sum_{i=occ} 2C_i C_i^T,$$

where the sum over  $i$  here is a sum over orbitals not spin orbitals.

2. Show that the HF total energy for a closed-shell system may be written in terms of integrals over the orthonormal HF orbitals as:

$$E(SCF) = 2 \sum_k^{occ} \langle k|h|k \rangle + \sum_{kl}^{occ} [2\langle kl|g|kl \rangle - \langle kl|g|lk \rangle] + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}}.$$

3. Show that the HF total energy may alternatively be expressed as:

$$E(SCF) = \sum_k^{occ} \epsilon_k + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}},$$

where the  $\epsilon_k$  refer to the HF orbital energies.

### Problems:

1. This problem will be concerned with carrying out an SCF calculation for the  $\text{HeH}^+$  molecule in the  $1^1_g+(1^2_g)$  ground state. The one- and two-electron integrals (in atomic units) needed to carry out this SCF calculation at  $R = 1.4$  a.u. using Slater type orbitals with orbital exponents of 1.6875 and 1.0 for the He and H, respectively are:

$$\begin{aligned} S_{11} &= 1.0, & S_{22} &= 1.0, & S_{12} &= 0.5784, \\ h_{11} &= -2.6442, & h_{22} &= -1.7201, & h_{12} &= -1.5113, \\ g_{1111} &= 1.0547, & g_{1121} &= 0.4744, & g_{1212} &= 0.5664, \\ g_{2211} &= 0.2469, & g_{2221} &= 0.3504, & g_{2222} &= 0.6250, \end{aligned}$$

where 1 refers to  $1s_{\text{He}}$  and 2 to  $1s_{\text{H}}$ . Note that the two-electron integrals are given in Dirac notation. Parts a. - d. should be done by hand. Any subsequent parts can make use of the QMIC software provided.

a. Using  $\psi_1 = 1s_{\text{He}}$  for the initial guess of the occupied molecular orbital, form a  $2 \times 2$  Fock matrix. Use the equation derived above in question 1 for  $F_{\mu}$ .

b. Solve the Fock matrix eigenvalue equations given above to obtain the orbital energies and an improved occupied molecular orbital. In so doing, note that  $\langle \psi_1 | \psi_1 \rangle = 1 = C_1^T S C_1$  gives the needed normalization condition for the expansion coefficients of the  $\psi_1$  in the atomic orbital basis.

c. Determine the total SCF energy using the result of exercise 3 above at this step of the iterative procedure. When will this energy agree with that obtained by using the alternative expression for  $E(SCF)$  given in exercise 2?

d. Obtain the new molecular orbital,  $\psi_1$ , from the solution of the matrix eigenvalue problem (part b).



e. A new Fock matrix and related total energy can be obtained with this improved choice of molecular orbital,  $\psi_1$ . This process can be continued until a convergence criterion has been satisfied. Typical convergence criteria include: no significant change in the molecular orbitals or the total energy (or both) from one iteration to the next. Perform this iterative procedure for the  $\text{HeH}^+$  system until the difference in total energy between two successive iterations is less than  $10^{-5}$  a.u.

f. Show, by comparing the difference between the SCF total energy at one iteration and the converged SCF total energy, that the convergence of the above SCF approach is primarily linear (or first order).

g. Is the SCF total energy calculated at each iteration of the above SCF procedure (via exercise 3) an upper bound to the exact ground-state total energy?

h. Using the converged self-consistent set of molecular orbitals,  $\psi_1$  and  $\psi_2$ , calculate the one- and two-electron integrals in the molecular orbital basis. Using the equations for  $E(\text{SCF})$  in exercises 2 and 3 calculate the converged values of the orbital energies making use of these integrals in the mo basis.

i. Does this SCF wavefunction give rise (at  $R = 1.0$  a.u.) to proper dissociation products?

2. This problem will continue to address the same  $\text{HeH}^+$  molecular system as above, extending the analysis to include "correlation effects." We will use the one- and two-electron integrals (same geometry) in the converged (to  $10^{-5}$  au) SCF molecular orbital basis which we would have obtained after 7 iterations above. The converged mos you would have obtained in problem 1 are:

$$\begin{array}{r} \psi_1 = \\ \psi_2 = \end{array} \begin{array}{r} -0.89997792 \\ -0.15843012 \end{array} \quad \begin{array}{r} -0.83233180 \\ 1.21558030 \end{array}$$

a. Carry out a two configuration CI calculation using the  $\psi_1^2$  and  $\psi_2^2$  configurations first by obtaining an expression for the CI matrix elements  $H_{ij}$  ( $i, j = \psi_1^2, \psi_2^2$ ) in terms of one- and two-electron integrals, and secondly by showing that the resultant CI matrix is (ignoring the nuclear repulsion term):

$$\begin{pmatrix} -4.2720 & 0.1261 \\ 0.1261 & -2.0149 \end{pmatrix}$$

b. Obtain the two CI energies and eigenvectors for the matrix found in part a.

c. Show that the lowest energy CI wavefunction is equivalent to the following two-determinant (single configuration) wavefunction:

$$\frac{1}{2} \left( \frac{1}{a^2} \psi_1 + \frac{1}{b^2} \psi_2 \right) \left( \frac{1}{a^2} \psi_1 - \frac{1}{b^2} \psi_2 \right) + \frac{1}{a^2} \psi_1 - \frac{1}{b^2} \psi_2 \left( \frac{1}{a^2} \psi_1 + \frac{1}{b^2} \psi_2 \right)$$

involving the polarized orbitals:  $\frac{1}{a^2} \psi_1 \pm \frac{1}{b^2} \psi_2$ , where  $a = 0.9984$  and  $b = 0.0556$ .

d. Expand the CI list to 3 configurations by adding the  $\psi_1 \psi_2$  to the original  $\psi_1^2$  and  $\psi_2^2$  configurations of part a above. First, express the proper singlet spin-coupled  $\psi_1 \psi_2$  configuration as a combination of Slater determinants and then compute all elements of this 3x3 matrix.

e. Obtain all eigenenergies and corresponding normalized eigenvectors for this CI problem.

f. Determine the excitation energies and transition moments for  $\text{HeH}^+$  using the full CI result of part e above. The nonvanishing matrix elements of the dipole operator  $\mathbf{r}(x,y,z)$  in the atomic basis are:

$$\langle 1s_{\text{H}}|z|1s_{\text{He}}\rangle = 0.2854 \text{ and } \langle 1s_{\text{H}}|z|1s_{\text{H}}\rangle = 1.4.$$

First determine the matrix elements of  $\mathbf{r}$  in the SCF orbital basis then determine the excitation energies and transition moments from the ground state to the two excited singlet states of  $\text{HeH}^+$ .

g. Now turning to perturbation theory, carry out a RSPT calculation of the first-order wavefunction  $|1^2\rangle^{(1)}$  for the case in which the zeroth-order wavefunction is taken to be the  $1^2$  Slater determinant. Show that the first-order wavefunction is given by:

$$|1^2\rangle^{(1)} = -0.0442|2^2\rangle.$$

h. Why does the  $|1^2\rangle$  configuration not enter into the first-order wavefunction?

i. Normalize the resultant wavefunction that contains zeroth- plus first-order parts and compare it to the wavefunction obtained in the two-configuration CI study of part b.

j. Show that the second-order RSPT correlation energy,  $E^{(2)}$ , of  $\text{HeH}^+$  is  $-0.0056$  a.u. How does this compare with the correlation energy obtained from the two-configuration CI study of part b?

3. Using the QMIC programs, calculate the SCF energy of  $\text{HeH}^+$  using the same geometry as in problem 1 and the STO3G basis set provided in the QMIC basis set library. How does this energy compare to that found in problem 1? Run the calculation again with the 3-21G basis set provided. How does this energy compare to the STO3G and the energy found using STOs in problem 1?

4. Generate SCF potential energy surfaces for  $\text{HeH}^+$  and  $\text{H}_2$  using the QMIC software provided. Use the 3-21G basis set and generate points for geometries of  $R = 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5,$  and  $10.0$ . Plot the energies vs. geometry for each system. Which system dissociates properly?

5. Generate CI potential energy surfaces for the 4 states of  $\text{H}_2$  resulting from a CAS calculation with 2 electrons in the lowest 2 SCF orbitals ( $1_g$  and  $1_u$ ). Use the same geometries and basis set as in problem 4. Plot the energies vs. geometry for each system. Properly label and characterize each of the states (e.g., repulsive, dissociate properly, etc.).

## Solutions

### Review Exercises:

1. Slater type orbitals (STOs) are "hydrogen-like" in that they have a normalized form of:

$$\frac{2}{a_0} \left(\frac{r}{a_0}\right)^{n+\frac{1}{2}} \frac{1}{(2n)!} \frac{1}{2} r^{n-1} e^{-\frac{r}{a_0}} Y_{l,m}(\theta, \phi),$$

whereas gaussian type orbitals GTOs have the form:

$$N r^l e^{-\alpha r^2} Y_{l,m}(\theta, \phi),$$

although in most quantum chemistry computer programs they are specified in so-called "cartesian" form as:

$$N^{\frac{1}{2}} x^a y^b z^c e^{-r^2}$$

where a, b, and c are quantum numbers each ranging from zero upward in unit steps. So, STOs give "better" overall energies and properties that depend on the shape of the wavefunction near the nuclei (e.g., Fermi contact ESR hyperfine constants) but they are more difficult to use (two-electron integrals are more difficult to evaluate; especially the 4-center variety which have to be integrated numerically). GTOs on the other hand are easier to use (more easily integrable) but improperly describe the wavefunction near the nuclear centers because of the so-called cusp condition (they have zero slope at  $R = 0$ , whereas 1s STOs have non-zero slopes there).

### Exercises:

$$1. \quad F_{ij} = \langle i | j \rangle = h_{ij} + \sum_j [J_j - K_j]_{ij}$$

Let the closed shell Fock potential be written as:

$$V_{ij} = \sum_k (2\langle ik|jk \rangle - \langle ik|kj \rangle), \text{ and the } 1e^- \text{ component as:}$$

$$h_{ij} = \left\langle i \left| -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r - R_A|} \right| j \right\rangle, \text{ and the delta as:}$$

$$\delta_{ij} = \langle i | j \rangle, \text{ so that: } h_{ij} + V_{ij} = \delta_{ij}$$

using:  $i = \sum_{\mu} C_{\mu i} \mu$ ,  $j = \sum_{\nu} C_{\nu j}$ , and  $k = \sum_{\kappa} C_{\kappa k}$ , and transforming from the mo to ao

basis we obtain:

$$\begin{aligned} V_{ij} &= \sum_{k\mu} C_{\mu i} C_{\kappa k} C_{\nu j} C_{\kappa k} 2\langle \mu | \nu \rangle - \langle \mu | \nu \rangle \\ &= \sum_{k\mu} (C_{\kappa k} C_{\nu j}) (C_{\mu i} C_{\kappa k}) 2\langle \mu | \nu \rangle - \langle \mu | \nu \rangle \\ &= \sum_{\mu} (C_{\mu i} C_{\nu j}) V_{\mu} \text{ where,} \end{aligned}$$

$$V_{\mu} = \sum_{\kappa} P_{\mu\kappa} 2\langle \mu | \nu \rangle - \langle \mu | \nu \rangle, \text{ and } P_{\mu\kappa} = \sum_k (C_{\kappa k} C_{\nu j})$$

$$h_{ij} = \sum_{\mu} (C_{\mu i} C_{\nu j}) h_{\mu}, \text{ where}$$

$$h_{\mu} = \left\langle \mu \left| -\frac{1}{2} \nabla^2 - \sum_A \frac{Z_A}{|r - R_A|} \right| \right\rangle, \text{ and}$$

$$ij = \langle ij | \rangle = \sum_{\mu} (C_{\mu i} S_{\mu} C_{\mu j}) .$$

So,  $h_{ij} + V_{ij} = ij$  becomes:

$$\begin{aligned} \sum_{\mu} (C_{\mu i} C_{\mu j}) h_{\mu} + \sum_{\mu} (C_{\mu i} C_{\mu j}) V_{\mu} &= \sum_{\mu} (C_{\mu i} S_{\mu} C_{\mu j}) , \\ \sum_{\mu} (C_{\mu i} S_{\mu} C_{\mu j}) - \sum_{\mu} (C_{\mu i} C_{\mu j}) h_{\mu} - \sum_{\mu} (C_{\mu i} C_{\mu j}) V_{\mu} &= 0 \text{ for all } i, j \\ \sum_{\mu} C_{\mu i} S_{\mu} - \sum_{\mu} h_{\mu} - \sum_{\mu} V_{\mu} C_{\mu j} &= 0 \text{ for all } i, j \end{aligned}$$

Therefore,

$$\sum_{\mu} h_{\mu} + \sum_{\mu} V_{\mu} - \sum_{\mu} S_{\mu} - C_{\mu j} = 0$$

This is FC = SCE.

2. The Slater Condon rule for zero (spin orbital) difference with N electrons in N spin orbitals is:

$$\begin{aligned} E = \langle H + G | \rangle &= \sum_i^N \langle i | h | i \rangle + \sum_{i > j}^N \langle i j | g | i j \rangle - \sum_{i > j}^N \langle i j | g | j i \rangle \\ &= \sum_i h_{ii} + \sum_{i > j} (g_{ijij} - g_{ijji}) \\ &= \sum_i h_{ii} + \frac{1}{2} \sum_{ij} (g_{ijij} - g_{ijji}) \end{aligned}$$

If all orbitals are doubly occupied and we carry out the spin integration we obtain:

$$E = 2 \sum_i^{\text{occ}} h_{ii} + \sum_{ij}^{\text{occ}} (2g_{ijij} - g_{ijji}) ,$$

where i and j now refer to orbitals (not spin-orbitals).

3. If the occupied orbitals obey  $F_k = k k$ , then the expression for E in problem 2 above can be rewritten as.

$$E = \sum_i^{\text{occ}} h_{ii} + \sum_j^{\text{occ}} (2g_{ijij} - g_{ijji}) + \sum_i^{\text{occ}} h_{ii}$$

We recognize the closed shell Fock operator expression and rewrite this as:

$$E = \sum_i^{\text{occ}} F_{ii} + \sum_i^{\text{occ}} h_{ii} = \sum_i^{\text{occ}} (F_{ii} + h_{ii})$$

Problems:

1. We will use the QMIC software to do this problem. Lets just start from the beginning. Get the starting "guess" mo coefficients on disk. Using the program MOCOEFs it asks us for the first and second mo vectors. We input 1, 0 for the first mo (this means that the first mo is 1.0 times the He 1s orbital plus 0.0 times the H 1s orbital; this bonding mo is more likely to be heavily weighted on the atom having the higher nuclear charge) and 0, 1 for the

second. Our beginning mo-ao array looks like:  $\begin{matrix} 1.0 & 0.0 \\ 0.0 & 1.0 \end{matrix}$  and is placed on disk in a file we

choose to call "mocoefs.dat". We also put the ao integrals on disk using the program RW\_INTS. It asks for the unique one- and two- electron integrals and places a canonical list of these on disk in a file we choose to call "ao\_integrals.dat". At this point it is useful for us to step back and look at the set of equations which we wish to solve:  $FC = SCE$ . The QMIC software does not provide us with a so-called generalized eigenvalue solver (one that contains an overlap matrix; or metric), so in order to use the diagonalization program that is provided we must transform this equation ( $FC = SCE$ ) to one that looks like ( $F'C' = C'E$ ). We do that in the following manner:

Since  $S$  is symmetric and positive definite we can find an  $S^{-\frac{1}{2}}$  such that  $S^{-\frac{1}{2}} S^{+\frac{1}{2}} = 1$ ,  $S^{-\frac{1}{2}} S^{+\frac{1}{2}} = S^{+\frac{1}{2}} S^{-\frac{1}{2}}$ , etc.

rewrite  $FC = SCE$  by inserting unity between  $FC$  and multiplying the whole equation on the left by  $S^{-\frac{1}{2}}$ . This gives:

$$S^{-\frac{1}{2}} FS^{-\frac{1}{2}} S^{+\frac{1}{2}} C = S^{-\frac{1}{2}} SCE = S^{+\frac{1}{2}} CE.$$

Letting:  $F' = S^{-\frac{1}{2}} FS^{-\frac{1}{2}}$

$$C' = S^{+\frac{1}{2}} C, \text{ and inserting these expressions above give:}$$

$$F'C' = C'E$$

Note, that to get the next iterations mo coefficients we must calculate  $C$  from  $C'$ :

$C' = S^{+\frac{1}{2}} C$ , so, multiplying through on the left by  $S^{-\frac{1}{2}}$  gives:

$$S^{-\frac{1}{2}} C' = S^{-\frac{1}{2}} S^{+\frac{1}{2}} C = C$$

This will be the method we will use to solve our fock equations.

Find  $S^{-\frac{1}{2}}$  by using the program FUNCT\_MAT (this program generates a function of a matrix). This program will ask for the elements of the  $S$  array and write to disk a file

(name of your choice ... a good name might be "shalf") containing the  $S^{-\frac{1}{2}}$  array. Now we are ready to begin the iterative Fock procedure.

a. Calculate the Fock matrix,  $F$ , using program FOCK which reads in the mo coefficients from "mocoefs.dat" and the integrals from "ao\_integrals.dat" and writes the resulting Fock matrix to a user specified file (a good filename to use might be something like "fock1").

b. Calculate  $F' = S^{-\frac{1}{2}} FS^{-\frac{1}{2}}$  using the program UTMATU which reads in  $F$  and  $S^{-\frac{1}{2}}$  from files on the disk and writes  $F'$  to a user specified file (a good filename to use might be something like "fock1p"). Diagonalize  $F'$  using the program DIAG. This program reads

in the matrix to be diagonalized from a user specified filename and writes the resulting eigenvectors to disk using a user specified filename (a good filename to use might be something like "coef1p"). You may wish to choose the option to write the eigenvalues (Fock orbital energies) to disk in order to use them at a later time in program FENERGY.

Calculate C by back transforming e.g.  $C = S^{-\frac{1}{2}} C'$ . This is accomplished by using the program MATXMAT which reads in two matrices to be multiplied from user specified files and writes the product to disk using a user specified filename (a good filename to use might be something like "mocoefs.dat").

c. The QMIC program FENERGY calculates the total energy, using the result of exercises 2 and 3;

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}}, \quad \text{and}$$

$$\epsilon_k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}}.$$

This is the conclusion of one iteration of the Fock procedure ... you may continue by going back to part a. and proceeding onward.

d. and e. Results for the successful convergence of this system using the supplied QMIC software is as follows (this is a lot of bloody detail but will give the user assurance that they are on the right track; alternatively one could switch to the QMIC program SCF and allow that program to iteratively converge the Fock equations):

The one-electron AO integrals:

-2.644200	-1.511300
-1.511300	-1.720100

The two-electron AO integrals:

1	1	1	1	1.054700
2	1	1	1	0.4744000
2	1	2	1	0.5664000
2	2	1	1	0.2469000
2	2	2	1	0.3504000
2	2	2	2	0.6250000

The "initial" MO-AO coefficients:

1.000000	0.000000
0.000000	1.000000

AO overlap matrix (S):

1.000000	0.578400
0.578400	1.000000

$S^{-\frac{1}{2}}$

1.168032	-0.3720709
-0.3720709	1.168031

\*\*\*\*\*  
 ITERATION 1  
 \*\*\*\*\*

The charge bond order matrix:

1.000000	0.000000
0.000000	0.000000

The Fock matrix (F):

-1.589500	-1.036900
-1.036900	-0.8342001

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.382781	-0.5048679
-0.5048678	-0.4568883

The eigenvalues of this matrix (Fock orbital energies) are:

[ -1.604825   -0.2348450 ]

Their corresponding eigenvectors ( $C' = S^{+\frac{1}{2}} * C$ ) are:

-0.9153809	-0.4025888
-0.4025888	0.9153810

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

-0.9194022	-0.8108231
-0.1296498	1.218985

The one-electron MO integrals:

-2.624352	-0.1644336
-0.1644336	-1.306845

The two-electron MO integrals:

1	1	1	1	0.9779331
2	1	1	1	0.1924623
2	1	2	1	0.5972075
2	2	1	1	0.1170838
2	2	2	1	-0.0007945194
2	2	2	2	0.6157323

The closed shell Fock energy from formula:

$$2\sum_{kl} \langle k|h|k\rangle + 2\sum_{kl} \langle kl|kl\rangle - \sum_{\mu} \langle kl|lk\rangle + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}} = -2.84219933$$

from formula:

$$\epsilon_k + \langle k|h|k\rangle + \frac{Z_\mu Z}{R_\mu} = -2.80060530$$

the difference is: -0.04159403

\*\*\*\*\*

ITERATION 2

\*\*\*\*\*

The charge bond order matrix:

0.8453005	0.1192003
0.1192003	0.01680906

The Fock matrix:

-1.624673	-1.083623
-1.083623	-0.8772071

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.396111	-0.5411037
-0.5411037	-0.4798213

The eigenvalues of this matrix (Fock orbital energies) are:

[ -1.646972   -0.2289599 ]

Their corresponding eigenvectors ( $C' = S^{+\frac{1}{2}} * C$ ) are:

-0.9072427	-0.4206074
-0.4206074	0.9072427

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

-0.9031923	-0.8288413
-0.1537240	1.216184

The one-electron MO integrals:

-2.617336	-0.1903475
-0.1903475	-1.313861

The two-electron MO integrals:

1	1	1	1	0.9626070
2	1	1	1	0.1949828
2	1	2	1	0.6048143



2 2 1 1 0.1246907  
 2 2 2 1 0.003694540  
 2 2 2 2 0.6158437

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84349298$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.83573675$$

the difference is: -0.00775623

\*\*\*\*\*  
 ITERATION 3  
 \*\*\*\*\*

The charge bond order matrix:

0.8157563	0.1388423
0.1388423	0.02363107

The Fock matrix:

-1.631153	-1.091825
-1.091825	-0.8853514

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.398951	-0.5470731
-0.5470730	-0.4847007

The eigenvalues of this matrix (Fock orbital energies) are:

[ -1.654745   -0.2289078 ]

Their corresponding eigenvectors ( $C' = S^{-\frac{1}{2}} * C$ ) are:

-0.9058709	-0.4235546
-0.4235545	0.9058706

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

-0.9004935	-0.8317733
-0.1576767	1.215678

The one-electron MO integrals:

$$\begin{array}{cc} -2.616086 & -0.1945811 \\ -0.1945811 & -1.315112 \end{array}$$

The two-electron MO integrals:

$$\begin{array}{cc} 1 & 1 & 1 & 1 & 0.9600707 \\ 2 & 1 & 1 & 1 & 0.1953255 \\ 2 & 1 & 2 & 1 & 0.6060572 \\ 2 & 2 & 1 & 1 & 0.1259332 \\ 2 & 2 & 2 & 1 & 0.004475587 \\ 2 & 2 & 2 & 2 & 0.6158972 \end{array}$$

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84353018$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84225941$$

the difference is: -0.00127077

\*\*\*\*\*  
 ITERATION 4  
 \*\*\*\*\*

The charge bond order matrix:  $\begin{array}{cc} 0.8108885 & 0.1419869 \\ 0.1419869 & 0.02486194 \end{array}$

The Fock matrix:  $\begin{array}{cc} -1.632213 & -1.093155 \\ -1.093155 & -0.8866909 \end{array}$

$S \frac{1}{2} F S \frac{1}{2}$   $\begin{array}{cc} -1.399426 & -0.5480287 \\ -0.5480287 & -0.4855191 \end{array}$

The eigenvalues of this matrix (Fock orbital energies) are:

$$[ -1.656015 \quad -0.2289308 ]$$

Their corresponding eigenvectors ( $C' = S^{+\frac{1}{2}} * C$ ) are:

$$\begin{array}{cc} -0.9056494 & -0.4240271 \\ -0.4240271 & 0.9056495 \end{array}$$

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

$$\begin{array}{cc} -0.9000589 & -0.8322428 \\ -0.1583111 & 1.215595 \end{array}$$

The one-electron MO integrals:

$$\begin{array}{cc} -2.615881 & -0.1952594 \\ -0.1952594 & -1.315315 \end{array}$$

The two-electron MO integrals:

$$\begin{array}{cccc} 1 & 1 & 1 & 1 & 0.9596615 \\ 2 & 1 & 1 & 1 & 0.1953781 \\ 2 & 1 & 2 & 1 & 0.6062557 \\ 2 & 2 & 1 & 1 & 0.1261321 \\ 2 & 2 & 2 & 1 & 0.004601604 \\ 2 & 2 & 2 & 2 & 0.6159065 \end{array}$$

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352922$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84332418$$

the difference is: -0.00020504

\*\*\*\*\*  
 ITERATION 5  
 \*\*\*\*\*

The charge bond order matrix:  $\begin{array}{cc} 0.8101060 & 0.1424893 \\ 0.1424893 & 0.02506241 \end{array}$

The Fock matrix:  $\begin{array}{cc} -1.632385 & -1.093368 \\ -1.093368 & -0.8869066 \end{array}$

$$\begin{array}{cc}
 S \frac{1}{2} & F S \frac{1}{2} \\
 -1.399504 & -0.5481812 \\
 -0.5481813 & -0.4856516
 \end{array}$$

The eigenvalues of this matrix (Fock orbital energies) are:

$$[ -1.656219 \quad -0.2289360 ]$$

Their corresponding eigenvectors ( $C' = S^{-\frac{1}{2}} * C$ ) are:

$$\begin{array}{cc}
 -0.9056138 & -0.4241026 \\
 -0.4241028 & 0.9056141
 \end{array}$$

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

$$\begin{array}{cc}
 -0.8999892 & -0.8323179 \\
 -0.1584127 & 1.215582
 \end{array}$$

The one-electron MO integrals:

$$\begin{array}{cc}
 -2.615847 & -0.1953674 \\
 -0.1953674 & -1.315348
 \end{array}$$

The two-electron MO integrals:

$$\begin{array}{cc}
 1 & 1 & 1 & 1 & 0.9595956 \\
 2 & 1 & 1 & 1 & 0.1953862 \\
 2 & 1 & 2 & 1 & 0.6062872 \\
 2 & 2 & 1 & 1 & 0.1261639 \\
 2 & 2 & 2 & 1 & 0.004621811 \\
 2 & 2 & 2 & 2 & 0.6159078
 \end{array}$$

The closed shell Fock energy from formula:

$$\sum_{kl} 2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352779$$

from formula:

$$\sum_k \langle k|h|k\rangle + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}} = -2.84349489$$

the difference is:

$$-0.00003290$$

\*\*\*\*\*

ITERATION 6

\*\*\*\*\*

The charge bond order matrix:

0.8099805	0.1425698
0.1425698	0.02509460

The Fock matrix:

-1.632412	-1.093402
-1.093402	-0.8869413

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.399517	-0.5482056
-0.5482056	-0.4856730

The eigenvalues of this matrix (Fock orbital energies) are:

[ -1.656253   -0.2289375 ]

Their corresponding eigenvectors ( $C' = S^{+\frac{1}{2}} * C$ ) are:

-0.9056085	-0.4241144
-0.4241144	0.9056086

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

-0.8999786	-0.8323296
-0.1584283	1.215580

The one-electron MO integrals:

-2.615843	-0.1953846
-0.1953846	-1.315353

The two-electron MO integrals:

1	1	1	1	0.9595859
2	1	1	1	0.1953878
2	1	2	1	0.6062925
2	2	1	1	0.1261690
2	2	2	1	0.004625196
2	2	2	2	0.6159083

The closed shell Fock energy from formula:

$$2\sum_{kl} \langle k|h|k\rangle + 2\sum_{kl} \langle kl|kl\rangle - \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352827$$

from formula:

$$\epsilon_k + \frac{\langle k|h|k\rangle}{R_\mu} = -2.84352398$$

the difference is: -0.00000429

\*\*\*\*\*

ITERATION 7

\*\*\*\*\*

The charge bond order matrix:

0.8099616	0.1425821
0.1425821	0.02509952

The Fock matrix:

-1.632416	-1.093407
-1.093407	-0.8869464

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.399519	-0.5482093
-0.5482092	-0.4856761

The eigenvalues of this matrix (Fock orbital energies) are:

[ -1.656257   -0.2289374 ]

Their corresponding eigenvectors ( $C' = S^{+\frac{1}{2}} * C$ ) are:

-0.9056076	-0.4241164
-0.4241164	0.9056077

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

-0.8999770	-0.8323317
-0.1584310	1.215580

The one-electron MO integrals:

-2.615843	-0.1953876
-0.1953876	-1.315354

The two-electron MO integrals:

1	1	1	1	0.9595849
2	1	1	1	0.1953881
2	1	2	1	0.6062936

2 2 1 1 0.1261697  
 2 2 2 1 0.004625696  
 2 2 2 2 0.6159083

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352922$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352827$$

the difference is: -0.00000095

\*\*\*\*\*  
 ITERATION 8  
 \*\*\*\*\*

The charge bond order matrix:

0.8099585	0.1425842
0.1425842	0.02510037

The Fock matrix:

-1.632416	-1.093408
-1.093408	-0.8869470

$S^{-\frac{1}{2}} F S^{-\frac{1}{2}}$

-1.399518	-0.5482103
-0.5482102	-0.4856761

The eigenvalues of this matrix (Fock orbital energies) are:

[ -1.656258 -0.2289368 ]

Their corresponding eigenvectors ( $C' = S^{-\frac{1}{2}} * C$ ) are:

-0.9056074	-0.4241168
-0.4241168	0.9056075

The "new" MO-AO coefficients ( $C = S^{-\frac{1}{2}} * C'$ ):

-0.8999765	-0.8323320
-0.1584315	1.215579

The one-electron MO integrals:

$$\begin{array}{cc} -2.615842 & -0.1953882 \\ -0.1953882 & -1.315354 \end{array}$$

The two-electron MO integrals:

$$\begin{array}{cc} 1 & 1 & 1 & 1 & 0.9595841 \\ 2 & 1 & 1 & 1 & 0.1953881 \\ 2 & 1 & 2 & 1 & 0.6062934 \\ 2 & 2 & 1 & 1 & 0.1261700 \\ 2 & 2 & 2 & 1 & 0.004625901 \\ 2 & 2 & 2 & 2 & 0.6159081 \end{array}$$

The closed shell Fock energy from formula:

$$2\langle k|h|k\rangle + 2\langle kl|kl\rangle - \langle kl|lk\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352827$$

from formula:

$$k + \langle k|h|k\rangle + \frac{Z_{\mu}Z}{R_{\mu}} = -2.84352827$$

the difference is: 0.00000000

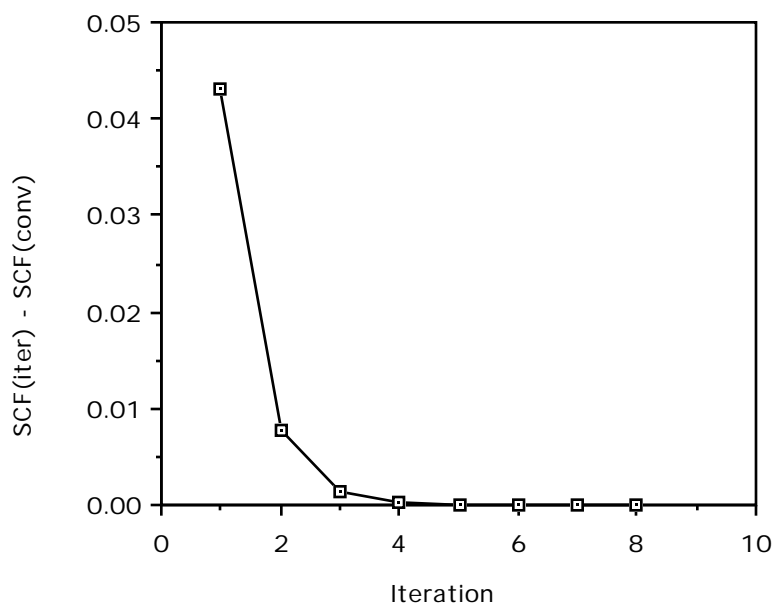
f. In looking at the energy convergence we see the following:

Iter	Formula 1	Formula 2
1	-2.84219933	-2.80060530
2	-2.84349298	-2.83573675
3	-2.84353018	-2.84225941
4	-2.84352922	-2.84332418
5	-2.84352779	-2.84349489
6	-2.84352827	-2.84352398
7	-2.84352922	-2.84352827
8	-2.84352827	-2.84352827

f. If you look at the energy differences (SCF at iteration n - SCF converged) and plot this data versus iteration number, and do a 5th order polynomial fit, we see the following:



$$y = 0.144 - 0.153x + 0.063x^2 - 0.013x^3 + 0.001x^4 \quad R = 1.00$$



In looking at the polynomial fit we see that the convergence is primarily linear since the coefficient of the linear term is much larger than those of the cubic and higher terms.

g. The converged SCF total energy calculated using the result of exercise 3 is an upper bound to the ground state energy, but, during the iterative procedure it is not. At convergence, the expectation value of the Hamiltonian for the Hartree Fock determinant is given by the equation in exercise 3.

h. The one- and two- electron integrals in the MO basis are given above (see part e iteration 8). The orbital energies are found using the result of exercise 2 and 3 to be:

$$E(\text{SCF}) = \sum_k \epsilon_k + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}}$$

$$E(\text{SCF}) = \sum_{kl} 2\langle k|h|k\rangle + 2\sum_{kl}^{\text{occ}} \langle kl|kl\rangle - \sum_{kl} \langle kl|lk\rangle + \sum_{\mu} \frac{Z_{\mu}Z}{R_{\mu}}$$

so,  $\epsilon_k = \langle k|h|k\rangle + \sum_l^{\text{occ}} (2\langle kl|kl\rangle - \langle kl|lk\rangle)$

$$\begin{aligned} \epsilon_1 &= h_{11} + 2\langle 11|11\rangle - \langle 11|11\rangle \\ &= -2.615842 + 0.9595841 \\ &= -1.656258 \end{aligned}$$

$$\begin{aligned} \epsilon_2 &= h_{22} + 2\langle 21|21\rangle - \langle 21|12\rangle \\ &= -1.315354 + 2*0.6062934 - 0.1261700 \\ &= -0.2289372 \end{aligned}$$

i. Yes, the  $1^2$  configuration does dissociate properly because at  $R \rightarrow \infty$  the lowest energy state is  $\text{He} + \text{H}^+$ , which also has a  $1^2$  orbital occupancy (i.e.,  $1s^2$  on He and  $1s^0$  on  $\text{H}^+$ ).

2. At convergence the mo coefficients are:

$$1 = \begin{matrix} -0.8999765 \\ -0.1584315 \end{matrix} \quad 2 = \begin{matrix} -0.8323320 \\ 1.215579 \end{matrix}$$

and the integrals in this MO basis are:

$$\begin{aligned} h_{11} &= -2.615842 & h_{21} &= -0.1953882 & h_{22} &= -1.315354 \\ g_{1111} &= 0.9595841 & g_{2111} &= 0.1953881 & g_{2121} &= 0.6062934 \\ g_{2211} &= 0.1261700 & g_{2221} &= 0.04625901 & g_{2222} &= 0.6159081 \end{aligned}$$

$$\begin{aligned} \text{a. } H &= \begin{matrix} \langle 1 | H | 1 \rangle & \langle 1 | H | 2 \rangle \\ \langle 2 | H | 1 \rangle & \langle 2 | H | 2 \rangle \end{matrix} = \begin{matrix} 2h_{11} + g_{1111} & g_{1122} \\ g_{1122} & 2h_{22} + g_{2222} \end{matrix} \\ &= \begin{matrix} 2 \cdot -2.615842 + 0.9595841 & 0.1261700 \\ 0.1261700 & 2 \cdot -1.315354 + 0.6159081 \end{matrix} \\ &= \begin{matrix} -4.272100 & 0.126170 \\ 0.126170 & -2.014800 \end{matrix} \end{aligned}$$

b. The eigenvalues are  $E_1 = -4.279131$  and  $E_2 = -2.007770$ . The corresponding eigenvectors are:

$$C_1 = \begin{matrix} -0.99845123 \\ 0.05563439 \end{matrix}, \quad C_2 = \begin{matrix} 0.05563438 \\ 0.99845140 \end{matrix}$$

c.

$$\begin{aligned} &\frac{1}{2} \begin{pmatrix} \frac{1}{a^2} & \frac{1}{b^2} \\ \frac{1}{a^2} & \frac{1}{b^2} \end{pmatrix} + \begin{pmatrix} \frac{1}{a^2} & \frac{1}{b^2} \\ \frac{1}{a^2} & \frac{1}{b^2} \end{pmatrix} \\ &= \frac{1}{2\sqrt{2}} \begin{pmatrix} \frac{1}{a^2} & \frac{1}{b^2} \\ \frac{1}{a^2} & \frac{1}{b^2} \end{pmatrix} + \frac{1}{2\sqrt{2}} \begin{pmatrix} \frac{1}{a^2} & \frac{1}{b^2} \\ \frac{1}{a^2} & \frac{1}{b^2} \end{pmatrix} \quad \left( \begin{matrix} - \\ - \end{matrix} \right) \\ &= \frac{1}{\sqrt{2}} (a \quad 1 \quad 1 - b \quad 2 \quad 2) \quad \left( \begin{matrix} - \\ - \end{matrix} \right) \end{aligned}$$

(note from part b.  $a = 0.9984$  and  $b = 0.0556$ )

d. The third configuration  $|1 \ 2 \rangle = \frac{1}{\sqrt{2}} [ |1 \ 2 \rangle - |1 \ 2 \rangle ]$ ,

Adding this configuration to the previous 2x2 CI results in the following 3x3 'full' CI:

$$\begin{aligned} H &= \begin{matrix} \langle 1 | H | 1 \rangle & \langle 1 | H | 2 \rangle & \langle 1 | H | 1 \ 2 \rangle \\ \langle 2 | H | 1 \rangle & \langle 2 | H | 2 \rangle & \langle 2 | H | 1 \ 2 \rangle \\ \langle 1 \ 2 | H | 1 \rangle & \langle 1 \ 2 | H | 2 \rangle & \langle 1 \ 2 | H | 1 \ 2 \rangle \end{matrix} \\ &= \begin{matrix} 2h_{11} + g_{1111} & g_{1122} & \frac{1}{\sqrt{2}} [2h_{12} + 2g_{2111}] \\ g_{1122} & 2h_{22} + g_{2222} & \frac{1}{\sqrt{2}} [2h_{12} + 2g_{2221}] \\ \frac{1}{\sqrt{2}} [2h_{12} + 2g_{2111}] & \frac{1}{\sqrt{2}} [2h_{12} + 2g_{2221}] & h_{11} + h_{22} + g_{2121} + g_{2211} \end{matrix} \end{aligned}$$

Evaluating the new matrix elements:

$$\begin{aligned}
 H_{13} = H_{31} &= \sqrt{2} * (-0.1953882 + 0.1953881) = 0.0 \\
 H_{23} = H_{32} &= \sqrt{2} * (-0.1953882 + 0.004626) = -0.269778 \\
 H_{33} &= -2.615842 - 1.315354 + 0.606293 + 0.126170 \\
 &= -3.198733 \\
 &= \begin{matrix} -4.272100 & 0.126170 & 0.0 \\ 0.126170 & -2.014800 & -0.269778 \\ 0.0 & -0.269778 & -3.198733 \end{matrix}
 \end{aligned}$$

e. The eigenvalues are  $E_1 = -4.279345$ ,  $E_2 = -3.256612$  and  $E_3 = -1.949678$ . The corresponding eigenvectors are:

$$\begin{aligned}
 C_1 &= \begin{matrix} -0.99825280 & -0.02605343 & -0.05302767 \\ 0.05732290 & -0.20969283 & -0.97608540 \\ 0.01431085 & -0.97742000 & 0.21082004 \end{matrix}, C_2 = \begin{matrix} -0.02605343 & -0.97608540 & 0.21082004 \end{matrix}, C_3 = \begin{matrix} -0.05302767 & -0.97608540 & 0.21082004 \end{matrix}
 \end{aligned}$$

f. We need the non-vanishing matrix elements of the dipole operator in the mo basis. These can be obtained by calculating them by hand. They are more easily obtained by using the TRANS program. Put the  $1e^-$  ao integrals on disk by running the program RW\_INTS. In this case you are inserting  $z_{11} = 0.0$ ,  $z_{21} = 0.2854$ , and  $z_{22} = 1.4$  (insert 0.0 for all the  $2e^-$  integrals) ... call the output file "ao\_dipole.ints" for example. The converged MO-AO coefficients should be in a file ("mocoefs.dat" is fine). The transformed integrals can be written to a file (name of your choice) for example "mo\_dipole.ints". These matrix elements are:

$$\begin{aligned}
 z_{11} &= 0.11652690, z_{21} = -0.54420990, z_{22} = 1.49117320 \\
 \text{The excitation energies are } E_2 - E_1 &= -3.256612 - -4.279345 = 1.022733, \text{ and } E_3 - E_1 = - \\
 &= 1.949678 - -4.279345 = 2.329667.
 \end{aligned}$$

Using the Slater-Condon rules to obtain the matrix elements between configurations we get:

$$\begin{aligned}
 &\langle 1^2 | z | 1^2 \rangle \quad \langle 1^2 | z | 2^2 \rangle \quad \langle 1^2 | z | 1^2 2 \rangle \\
 H_z &= \begin{matrix} \langle 2^2 | z | 1^2 \rangle & \langle 2^2 | z | 2^2 \rangle & \langle 2^2 | z | 1^2 2 \rangle \\ \langle 1^2 2 | z | 1^2 2 \rangle & \langle 2^2 | z | 1^2 2 \rangle & \langle 1^2 2 | z | 1^2 2 \rangle \\ 2z_{11} & 0 & \frac{1}{\sqrt{2}} [2z_{12}] \\ = & 0 & 2z_{22} & \frac{1}{\sqrt{2}} [2z_{12}] \\ \frac{1}{\sqrt{2}} [2z_{12}] & \frac{1}{\sqrt{2}} [2z_{12}] & z_{11} + z_{22} \\ 0.233054 & 0 & -0.769629 \\ = & 0 & 2.982346 & -0.769629 \\ -0.769629 & -0.769629 & 1.607700 \end{matrix}
 \end{aligned}$$

Now,  $\langle 1|z|2\rangle = C_1^T H_z C_2$ , (this can be accomplished with the program UTMATU)

$$\begin{aligned} & \begin{matrix} -0.99825280 & T & 0.233054 & 0 & -0.769629 & -0.02605343 \\ 0.05732290 & & 0 & 2.982346 & -0.769629 & -0.20969283 \\ 0.01431085 & & -0.769629 & -0.769629 & 1.607700 & -0.97742000 \end{matrix} \\ & = -0.757494 \end{aligned}$$

and,  $\langle 1|z|3\rangle = C_1^T H_z C_3$

$$\begin{aligned} & \begin{matrix} -0.99825280 & T & 0.233054 & 0 & -0.769629 & -0.05302767 \\ 0.05732290 & & 0 & 2.982346 & -0.769629 & -0.97608540 \\ 0.01431085 & & -0.769629 & -0.769629 & 1.607700 & 0.21082004 \end{matrix} \\ & = 0.014322 \end{aligned}$$

g. Using the converged coefficients the orbital energies obtained from solving the Fock equations are  $\epsilon_1 = -1.656258$  and  $\epsilon_2 = -0.228938$ . The resulting expression for the RSPT first-order wavefunction becomes:

$$\begin{aligned} |1\ 2\rangle^{(1)} &= -\frac{g_{2211}}{2(\epsilon_2 - \epsilon_1)} |2\ 2\rangle \\ |1\ 2\rangle^{(1)} &= -\frac{0.126170}{2(-0.228938 + 1.656258)} |2\ 2\rangle \\ |1\ 2\rangle^{(1)} &= -0.0441982 |2\ 2\rangle \end{aligned}$$

h. As you can see from part c., the matrix element  $\langle 1\ 2|H|1\ 2\rangle = 0$  (this is also a result of the Brillouin theorem) and hence this configuration does not enter into the first-order wavefunction.

i.  $|0\rangle = |1\ 2\rangle - 0.0441982 |2\ 2\rangle$ . To normalize we divide by:

$$\sqrt{[1 + (0.0441982)^2]} = 1.0009762$$

$$|0\rangle = 0.999025 |1\ 2\rangle - 0.044155 |2\ 2\rangle$$

In the 2x2 CI we obtained:

$$|0\rangle = 0.99845123 |1\ 2\rangle - 0.05563439 |2\ 2\rangle$$

j. The expression for the 2<sup>nd</sup> order RSPT is:

$$\begin{aligned} E^{(2)} &= -\frac{|g_{2211}|^2}{2(\epsilon_2 - \epsilon_1)} = -\frac{0.126170^2}{2(-0.228938 + 1.656258)} \\ &= -0.005576 \text{ au} \end{aligned}$$

Comparing the 2x2 CI energy obtained to the SCF result we have:

$$-4.279131 - (-4.272102) = -0.007029 \text{ au}$$

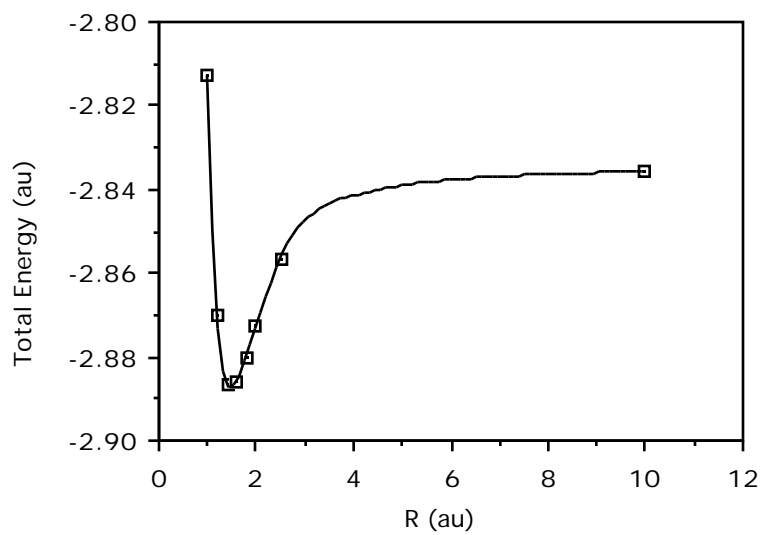
3. STO total energy: -2.8435283
- STO3G total energy -2.8340561
- 3-21G total energy -2.8864405

The STO3G orbitals were generated as a best fit of 3 primitive gaussians (giving 1 CGTO) to the STO. So, STO3G can at best reproduce the STO result. The 3-21G orbitals are more flexible since there are 2 CGTOs per atom. This gives 4 orbitals (more parameters to optimize) and a lower total energy.

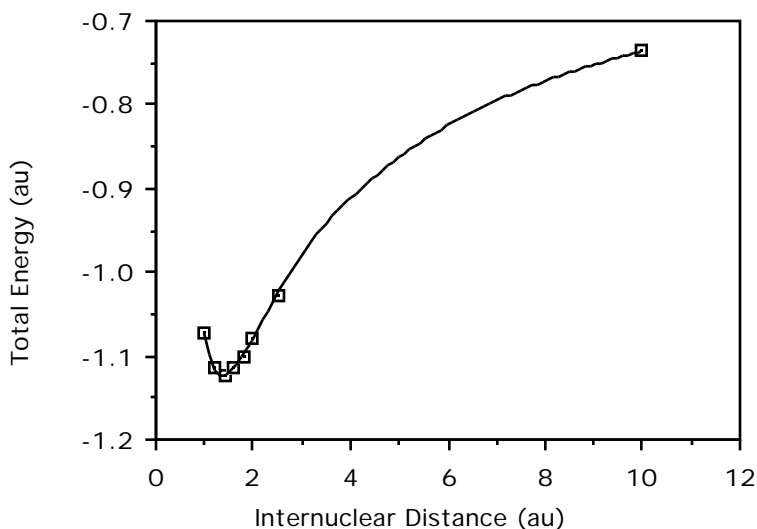
4.

R	HeH <sup>+</sup> Energy	H <sub>2</sub> Energy
1.0	-2.812787056	-1.071953297
1.2	-2.870357513	-1.113775015
1.4	-2.886440516	-1.122933507
1.6	-2.886063576	-1.115567684
1.8	-2.880080938	-1.099872589
2.0	-2.872805595	-1.080269098
2.5	-2.856760263	-1.026927710
10.0	-2.835679293	-0.7361705303

Plotting total energy vs. geometry for HeH<sup>+</sup>:



Plotting total energy vs. geometry for H<sub>2</sub>:



For  $\text{HeH}^+$  at  $R = 10.0$  au, the eigenvalues of the converged Fock matrix and the corresponding converged MO-AO coefficients are:

-.1003571E+01	-.4961988E+00	.5864846E+00	.1981702E+01
.4579189E+00	-.8245406E-05	.1532163E-04	.1157140E+01
.6572777E+00	-.4580946E-05	-.6822942E-05	-.1056716E+01
-.1415438E-05	.3734069E+00	.1255539E+01	-.1669342E-04
.1112778E-04	.7173244E+00	-.1096019E+01	.2031348E-04

Notice that this indicates that orbital 1 is a combination of the s functions on He only (dissociating properly to  $\text{He} + \text{H}^+$ ).

For  $\text{H}_2$  at  $R = 10.0$  au, the eigenvalues of the converged Fock matrix and the corresponding converged MO-AO coefficients are:

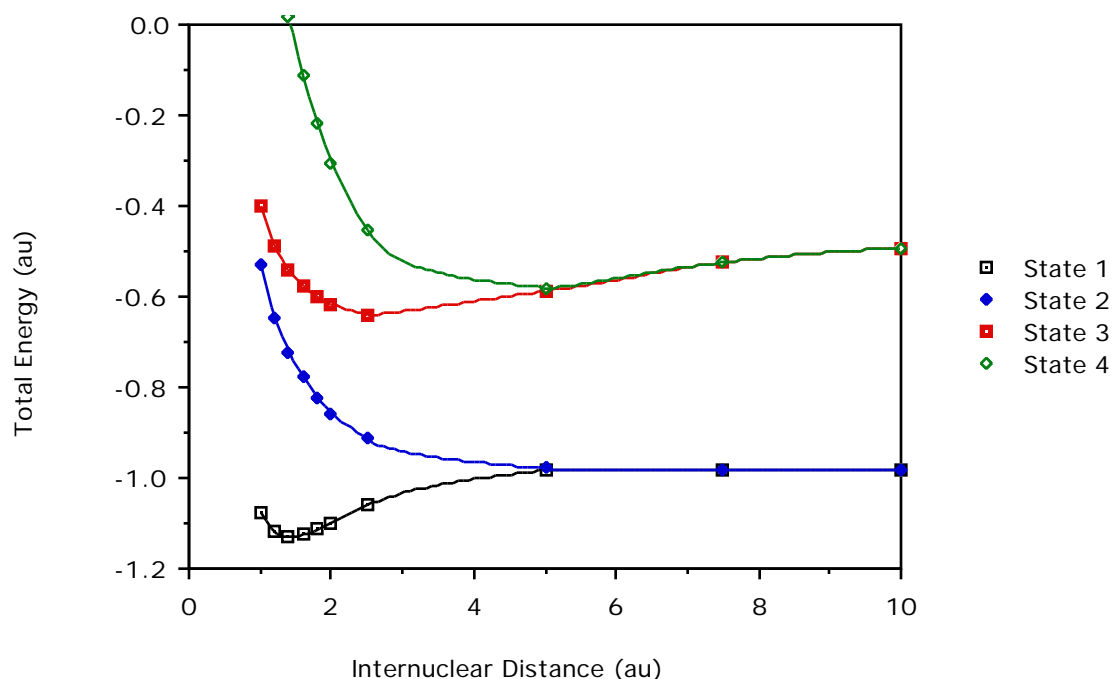
-.2458041E+00	-.1456223E+00	.1137235E+01	.1137825E+01
.1977649E+00	-.1978204E+00	.1006458E+01	-.7903225E+00
.5632566E+00	-.5628273E+00	-.8179120E+00	.6424941E+00
.1976312E+00	.1979216E+00	.7902887E+00	.1006491E+01
.5629326E+00	.5631776E+00	-.6421731E+00	-.8181460E+00

Notice that this indicates that orbital 1 is a combination of the s functions on both H atoms (dissociating improperly; equal probabilities of  $\text{H}_2$  dissociating to two neutral atoms or to a proton plus hydride ion).

5. The  $\text{H}_2$  CI result:

R	$1_{g^+}$	$3_{u^+}$	$1_{u^+}$	$1_{g^+}$
1.0	-1.074970	-0.5323429	-0.3997412	0.3841676
1.2	-1.118442	-0.6450778	-0.4898805	0.1763018
1.4	-1.129904	-0.7221781	-0.5440346	0.0151913
1.6	-1.125582	-0.7787328	-0.5784428	-0.1140074

1.8	-1.113702	-0.8221166	-0.6013855	-0.2190144
2.0	-1.098676	-0.8562555	-0.6172761	-0.3044956
2.5	-1.060052	-0.9141968	-0.6384557	-0.4530645
5.0	-0.9835886	-0.9790545	-0.5879662	-0.5802447
7.5	-0.9806238	-0.9805795	-0.5247415	-0.5246646
10.0	-0.980598	-0.9805982	-0.4914058	-0.4913532



For  $H_2$  at  $R = 1.4$  au, the eigenvalues of the Hamiltonian matrix and the corresponding determinant amplitudes are:

determinant	-1.129904	-0.722178	-0.544035	0.015191
$ 1_g 1_g $	0.99695	0.00000	0.00000	0.07802
$ 1_g 1_u $	0.00000	0.70711	0.70711	0.00000
$ 1_g 1_u $	0.00000	0.70711	-0.70711	0.00000
$ 1_u 1_u $	-0.07802	0.00000	0.00000	0.99695

This shows, as expected, the mixing of the first  $1_g^+$  ( $1_g^2$ ) and the 2nd  $1_g^+$  ( $1_u^2$ ) determinants, the

$$3_u^+ = \left( \frac{1}{\sqrt{2}} (|1_g 1_u| + |1_g 1_u|) \right),$$

$$\text{and the } 1_u^+ = \left( \frac{1}{\sqrt{2}} (|1_g 1_u| - |1_g 1_u|) \right).$$

Also notice that the first  $1_g^+$  state is the bonding ( $0.99695 - 0.07802$ ) combination (note specifically the  $+$  combination) and the second  $1_g^+$  state is the antibonding combination

(note specifically the ++ combination). The ++ combination always gives a higher energy than the +- combination. Also notice that the 1st and 2nd states ( $^1g^+$  and  $^3u^+$ ) are dissociating to two neutral atoms and the 3rd and 4th states ( $^1g^+$  and  $^3u^+$ ) are dissociating to proton/anion combinations. The difference in these energies is the ionization potential of H minus the electron affinity of H.