

## Section 3 Exercises, Problems, and Solutions

### 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.

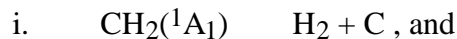
- a.) CH<sub>2</sub>      1a<sub>1</sub><sup>2</sup>2a<sub>1</sub><sup>2</sup>1b<sub>2</sub><sup>2</sup>3a<sub>1</sub><sup>1</sup>1b<sub>1</sub><sup>1</sup>
- b.) B<sub>2</sub> 1   g<sup>2</sup>1   u<sup>2</sup>2   g<sup>2</sup>2   u<sup>2</sup>1   u<sup>1</sup>2   u<sup>1</sup>
- c.) O<sub>2</sub> 1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

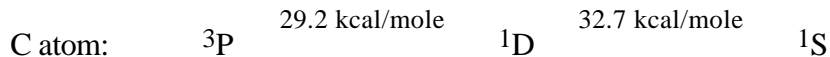
1. Show that the configuration (determinant) corresponding to the Li<sup>+</sup> 1s( )1s( ) state vanishes.
2. Construct the 3 triplet and 1 singlet wavefunctions for the Li<sup>+</sup> 1s<sup>1</sup>2s<sup>1</sup> configuration. Show that each state is a proper eigenfunction of S<sup>2</sup> and S<sub>z</sub> (use raising and lowering operators for S<sup>2</sup>)
3. Construct wavefunctions for each of the following states of CH<sub>2</sub>:
  - a.) <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>)
  - b.) <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>)
  - c.) <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>)
4. Construct wavefunctions for each state of the 1<sup>2</sup> 2<sup>2</sup> 3<sup>2</sup> 2<sup>1</sup> 2 configuration of NH.
5. Construct wavefunctions for each state of the 1s<sup>1</sup>2s<sup>1</sup>3s<sup>1</sup> configuration of Li.
6. 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.
7. Calculate the energy (using Slater Condon rules) associated with the 2p valence electrons for the following states of the C atom.
  - i. <sup>3</sup>P(M<sub>L</sub>=1, M<sub>S</sub>=1),
  - ii. <sup>3</sup>P(M<sub>L</sub>=0, M<sub>S</sub>=0),
  - iii. <sup>1</sup>S(M<sub>L</sub>=0, M<sub>S</sub>=0), and
  - iv. <sup>1</sup>D(M<sub>L</sub>=0, M<sub>S</sub>=0).
8. Calculate the energy (using Slater Condon rules) associated with the valence electrons for the following states of the NH molecule.
  - i. <sup>1</sup> (M<sub>L</sub>=2, M<sub>S</sub>=0),
  - ii. <sup>1</sup> (M<sub>L</sub>=0, M<sub>S</sub>=0), and
  - iii. <sup>3</sup> (M<sub>L</sub>=0, M<sub>S</sub>=0).

### Problems

1. Let us investigate the reactions:



under an assumed  $\text{C}_{2v}$  reaction pathway utilizing the following information:



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

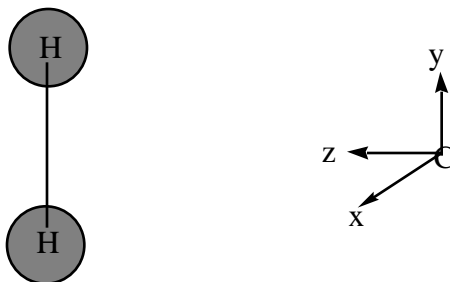
a. Write down (first in terms of  $2p_{1,0,-1}$  orbitals and then in terms of  $2p_{x,y,z}$  orbitals) the:

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  $^1D$  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:

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

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

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  $^1g^+$  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 ( $1_u^1 2_u^1$ ), we have  $M_L$  values of 1+1, 1-1, -1+1, and -1-1 (2, 0, 0, and -2). The term symbol  ${}^1\Sigma_g^+$  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  ${}^1\Sigma_g^-$  ( $M_L = 0$ ). 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:

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

- 1 ( $M_L=2$ ); one state ( $M_S=0$ ),
- 1 ( $M_L=-2$ ); one state ( $M_S=0$ ),
- 1 ( $M_L=0$ ); one state ( $M_S=0$ ),
- 3 ( $M_L=0$ ); 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:

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

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:

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

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

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

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

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

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

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

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

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



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

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

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  $(M_S=1, 0, \text{ and } -1)$ .

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

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

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 \ \rangle$
$\frac{1}{2}$		$ 1s \ 2s \ 3s \ \rangle,  1s \ 2s \ 3s \ \rangle,  1s \ 2s \ 3s \ \rangle$

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

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

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

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

$$\begin{aligned} S_- {}^4S(S=\frac{3}{2}, M_S=\frac{3}{2}) &= h \sqrt{\frac{3}{2}(\frac{3}{2} + 1) - \frac{3}{2}(\frac{3}{2} - 1)} \quad {}^4S(S=\frac{3}{2}, M_S=\frac{1}{2}) \\ &= h \sqrt{3} \quad {}^4S(S=\frac{3}{2}, M_S=\frac{1}{2}) \end{aligned}$$

$$S_- |1s \ 2s \ 3s \ | = h (|1s \ 2s \ 3s \ | + |1s \ 2s \ 3s \ | + |1s \ 2s \ 3s \ |)$$

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

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

$$\begin{aligned} S_+ {}^4S(S=\frac{3}{2}, M_S=-\frac{3}{2}) &= h \sqrt{\frac{3}{2}(\frac{3}{2} + 1) - -\frac{3}{2}(-\frac{3}{2} + 1)} \quad {}^4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) \\ &= h \sqrt{3} \quad {}^4S(S=\frac{3}{2}, M_S=-\frac{1}{2}) \end{aligned}$$

$$S_+ |1s \ 2s \ 3s \ | = h (|1s \ 2s \ 3s \ | + |1s \ 2s \ 3s \ | + |1s \ 2s \ 3s \ |)$$

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

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:

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

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

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

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

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;

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

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

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

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

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

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

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

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

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

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

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

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

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

Evaluating each matrix element gives:

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

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

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

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

Substitution of these expressions give:

$$\langle {}^3P(M_L=0, M_S=0) | H | {}^3P(M_L=0, M_S=0) \rangle$$

$$= \frac{1}{2} (f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11} - g_{1-1-11} \\ + f_{11} + f_{-1-1} + g_{1-11-1}) \\ = f_{11} + f_{-1-1} + g_{1-11-1} - g_{1-1-11}$$

7. iii.  ${}^1S(M_L=0, M_S=0); \frac{1}{\sqrt{3}}(|p_0 p_0 \rangle - |p_1 p_{-1} \rangle - |p_{-1} p_1 \rangle)$

$$\langle {}^1S(M_L=0, M_S=0) | H | {}^1S(M_L=0, M_S=0) \rangle$$

$$= \frac{1}{3} (\langle p_0 p_0 | H | p_0 p_0 \rangle - \langle p_0 p_0 | H | p_1 p_{-1} \rangle \\ - \langle p_0 p_0 | H | p_{-1} p_1 \rangle - \langle p_1 p_{-1} | H | p_0 p_0 \rangle \\ + \langle p_1 p_{-1} | H | p_1 p_{-1} \rangle + \langle p_1 p_{-1} | H | p_{-1} p_1 \rangle \\ - \langle p_{-1} p_1 | H | p_0 p_0 \rangle + \langle p_{-1} p_1 | H | p_1 p_{-1} \rangle \\ + \langle p_{-1} p_1 | H | p_{-1} p_1 \rangle )$$

Evaluating each matrix element gives:

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

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

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

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

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

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

Substitution of these expressions give:

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

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

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).

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

$$8. \quad \text{i. } |^1(M_L=2, M_S=0)\rangle = | \ 1 \ 1 \ 1 \ 1 \rangle$$

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

$$8. \quad \text{ii. } |^1(M_L=0, M_S=0)\rangle = \frac{1}{\sqrt{2}}(| \ 1 \ 1 \ -1 \ -1 \rangle - | \ 1 \ -1 \ 1 \ 1 \rangle)$$

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

Evaluating each matrix element gives:

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

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

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

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

Substitution of these expressions give:

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

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

Evaluating each matrix element gives:

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

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

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

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

Substitution of these expressions give:

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

### 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.

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

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

$${}^3P(M_L=-1, M_S=1) = |p_{-1} \ p_0 \ |$$

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

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,  $|p_x \quad p_z \quad |$  is  $xz$  ( $B_1$ ) and  $|p_y \quad p_z \quad |$  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.

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

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

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

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

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

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

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

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

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

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

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:

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

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

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

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

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

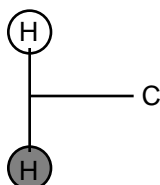
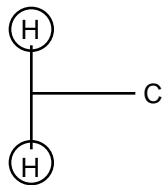
The only state left is the  $^1S$ :

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

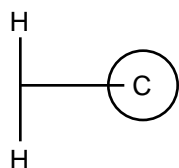
Each of the components of this state are  $A_1$  and hence this state has  $A_1$  symmetry.



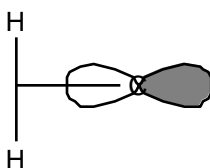
1. b. Forming SALC-AOs from the C and H atomic orbitals would generate the following:



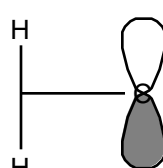
$$H_{1s} + H_{1s} = g = a_1 \quad H_{1s} - H_{1s} = u = b_2$$



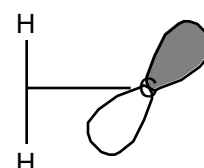
$$C_{2s} = a_1$$



$$C_{2p_z} = a_1$$

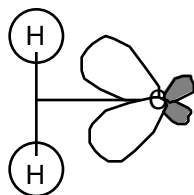


$$C_{2p_y} = b_2$$

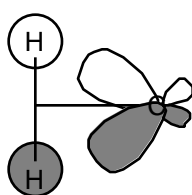


$$C_{2p_x} = b_1$$

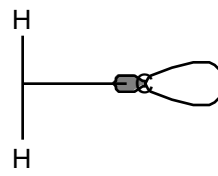
The bonding, nonbonding, and antibonding orbitals of CH<sub>2</sub> can be illustrated in the following manner:



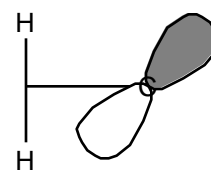
$$= a_1$$



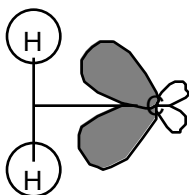
$$= b_2$$



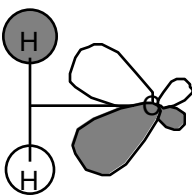
$$n = a_1$$



$$p = b_1$$



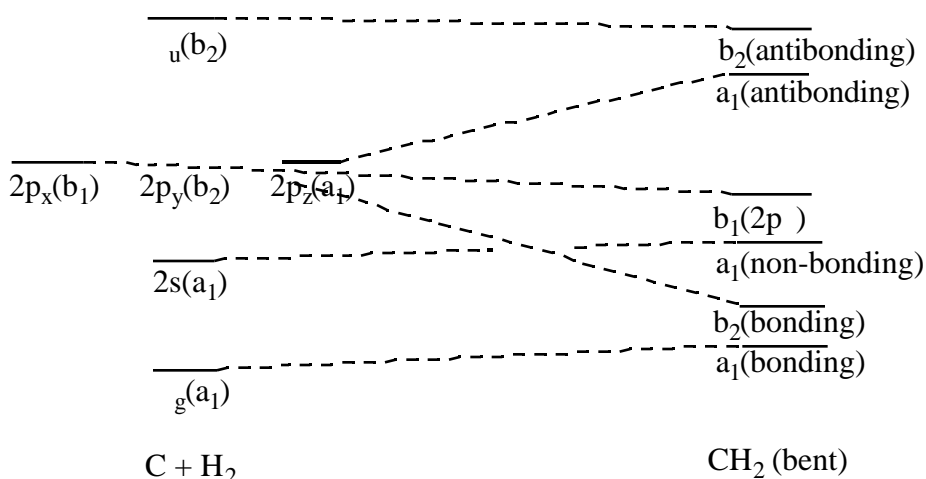
$$* = a_1$$



$$* = b_2$$

1. c.

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



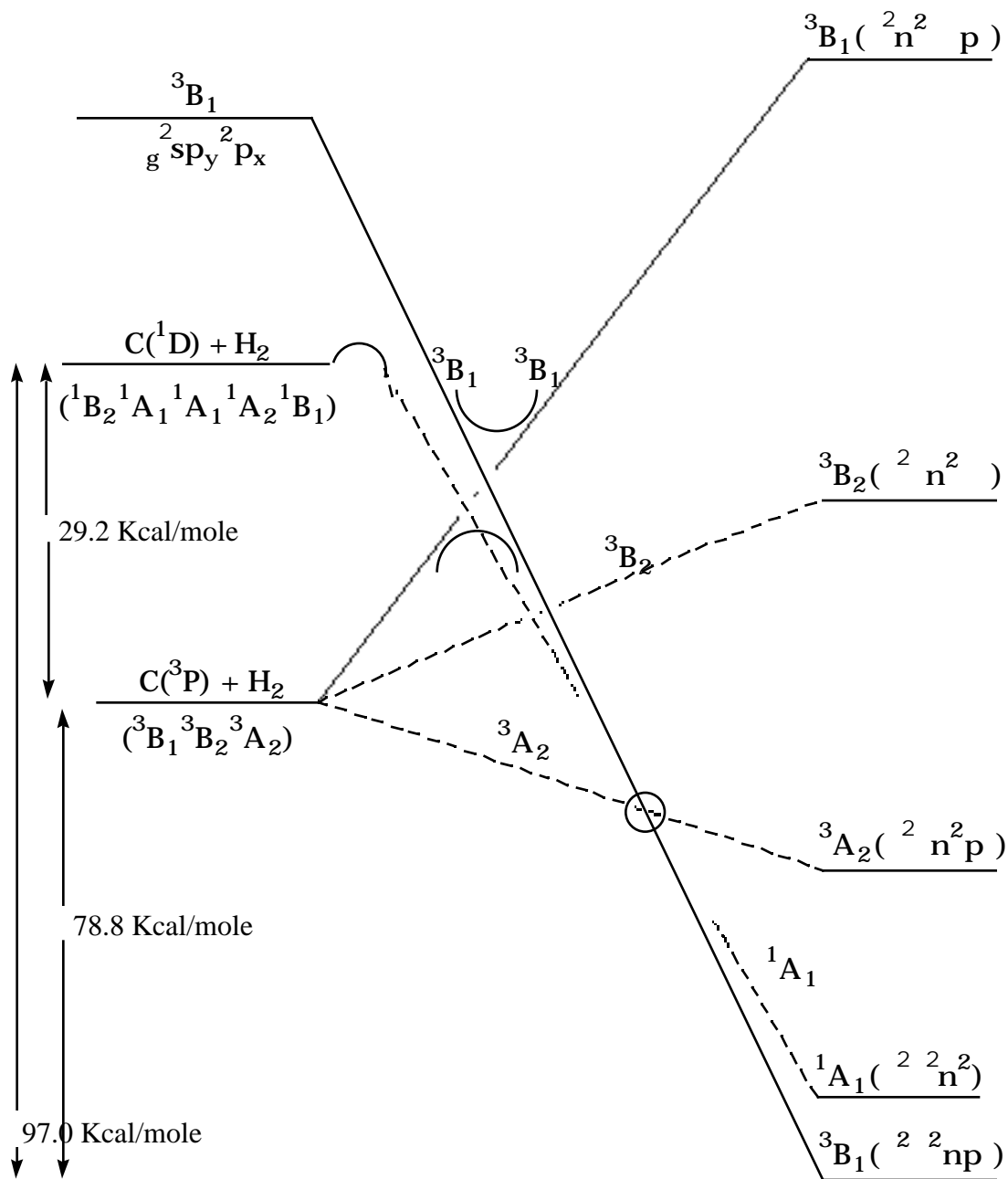
1. d. - e. It is necessary to determine how the wavefunctions found in part a. correlate with states of the  $CH_2$  molecule:

$$\begin{aligned}
 {}^3P(xz, M_S=1); {}^3B_1 &= g^2s^2p_xp_z & 2n^2p^* \\
 {}^3P(yx, M_S=1); {}^3A_2 &= g^2s^2p_xp_y & 2n^2p \\
 {}^3P(yz, M_S=1); {}^3B_2 &= g^2s^2p_y p_z & 2n^2^* \\
 {}^1D(xx-yy, M_S=0); {}^1A_1 & & 2n^2p^2 - 2n^2^2 \\
 {}^1D(yx, M_S=0); {}^1A_2 & & 2n^2p \\
 {}^1D(zx, M_S=0); {}^1B_1 & & 2n^2^*p \\
 {}^1D(zy, M_S=0); {}^1B_2 & & 2n^2^* \\
 {}^1D(2zz+xx+yy, M_S=0); {}^1A_1 & & 2^2n^2^*2 + 2n^2p^2 + 2n^2^2
 \end{aligned}$$

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,

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

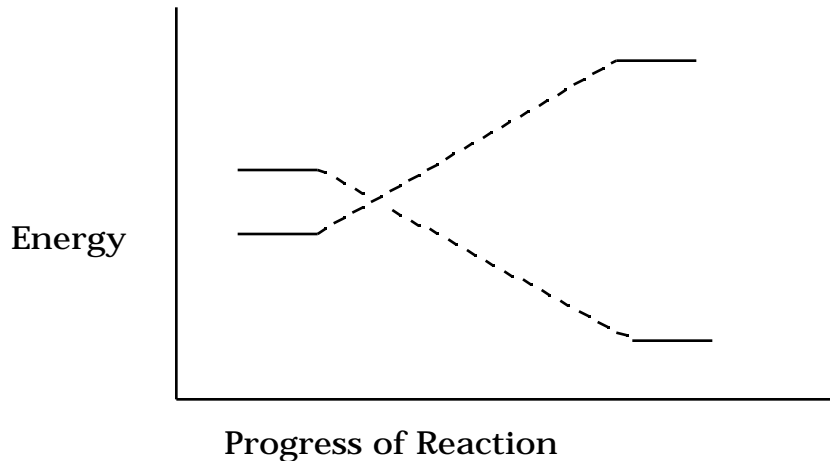
This indicates that a CCD must be drawn with a barrier near the  ${}^1D$  asymptote to represent the fact that  ${}^1A_1$   $CH_2$  correlates with a mixture of  ${}^1D$  and  ${}^1S$  carbon plus hydrogen. The  $C + H_2$  state to which the lowest  ${}^3B_1$  ( $2n^2p$ )  $CH_2$  state decomposes would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



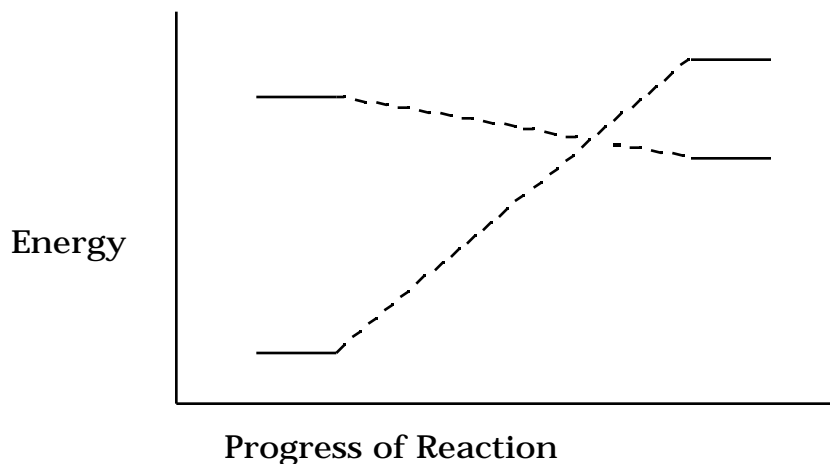
1. f. If you follow the  ${}^3B_1$  component of the  $C({}^3P) + H_2$  (since it leads to the ground-state products) to  ${}^3B_1 CH_2$  you must go over an approximately 20 Kcal/mole barrier. Of course this path produces  ${}^3B_1 CH_2$  product. Distortions away from  $C_{2v}$  symmetry, for example 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:

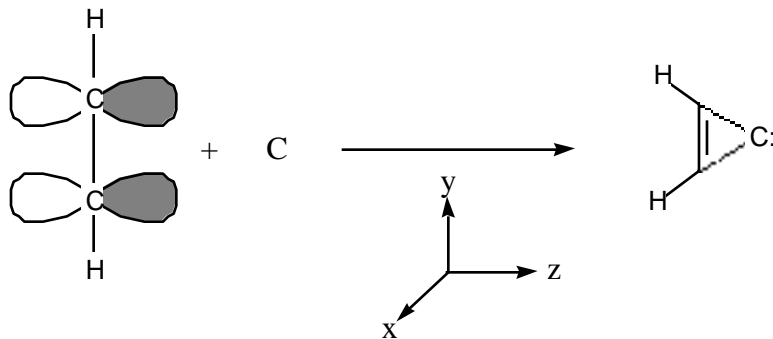


This relation between reaction endothermicity or exothermicity is known as the Hammond postulate. Note that the  $C(^3P_1) + H_2 \rightarrow CH_2$  reaction of interest here (see the CCD) has an early barrier.

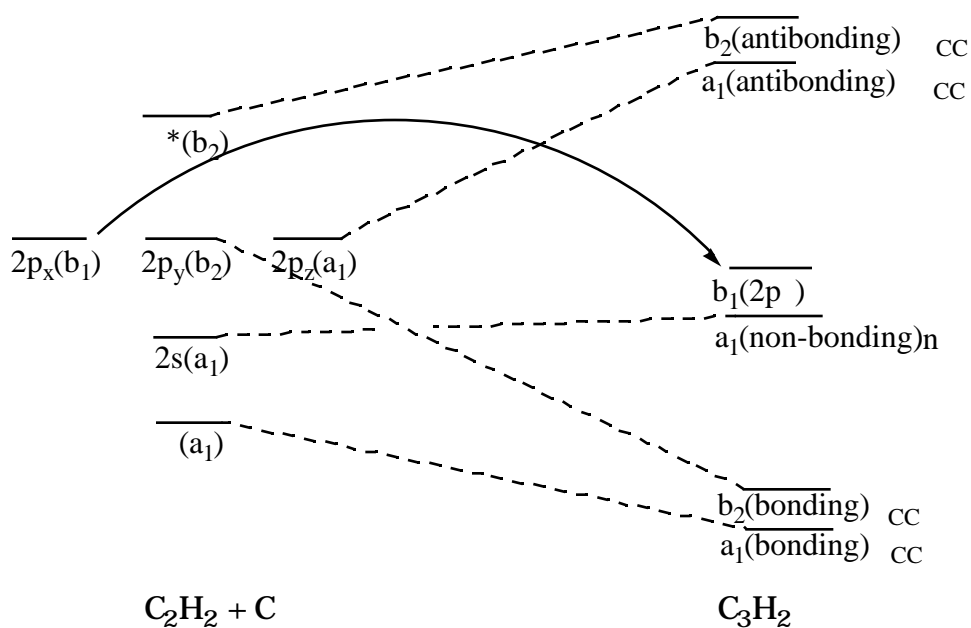
1. g. The reaction  $C(^1D) + H_2 \rightarrow CH_2 (^1A_1)$  should have no symmetry barrier (this can be recognized by following the  $^1A_1 (C(^1D) + H_2)$  reactants down to the  $^1A_1 (CH_2)$  products on the CCD).
2. This problem in many respects is analogous to problem 1.

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

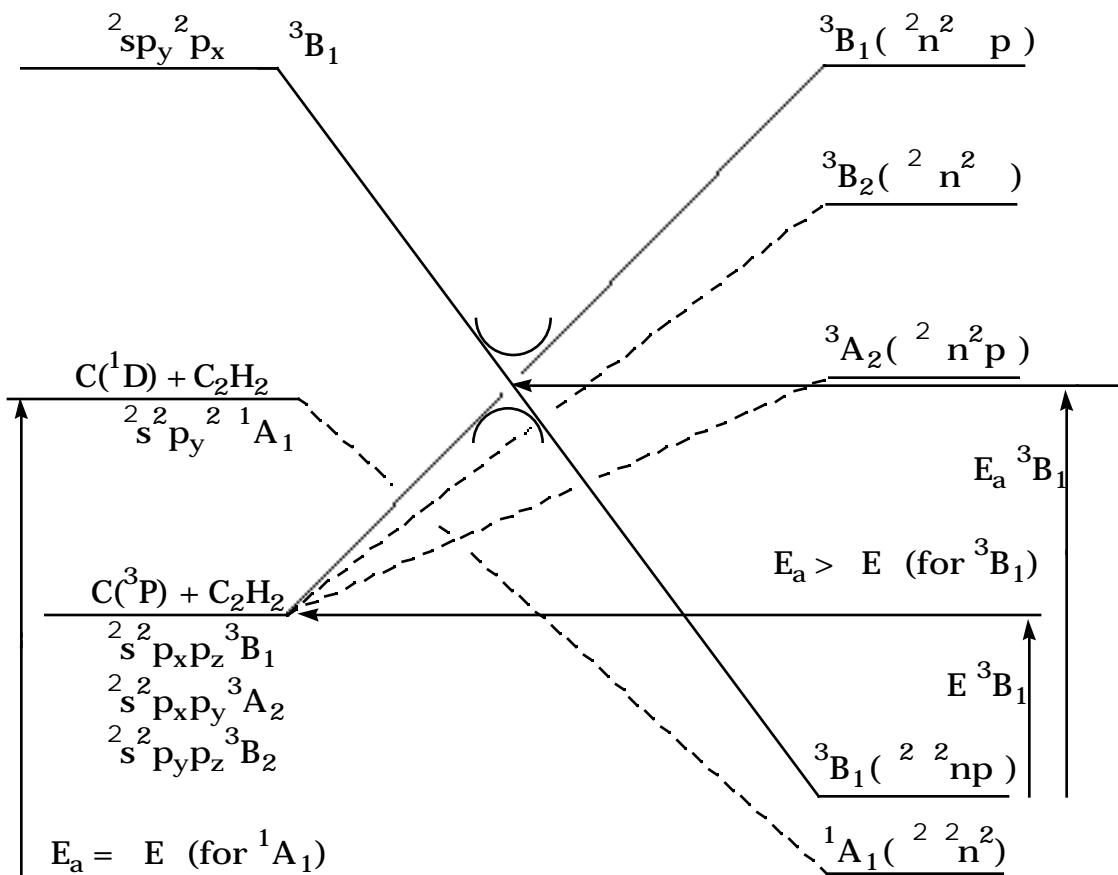
yield the required  $2s^2 2p_y^2$  configuration. Hence even the  $^1A_1$  surface would require a multiconfigurational wavefunction for adequate description.



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.

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

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

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

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

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

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

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

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.

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



$$= 2f_g + g_g$$

$$= 2(-1.184) + 0.564 = -1.804$$

$$H_{21} = H_{12} = \langle g | H | u \rangle$$

$$= \langle g | g | u \rangle$$

$$= 0.140$$

$$H_{22} = \langle u | H | u \rangle$$

$$= 2f_u + g_u$$

$$= 2(-0.575) + 0.582 = -0.568$$

3. d. Solving this eigenvalue problem:

$$\begin{vmatrix} -1.804 - \lambda & 0.140 \\ 0.140 & -0.568 - \lambda \end{vmatrix} = 0$$

$$(-1.804 - \lambda)(-0.568 - \lambda) - (0.140)^2 = 0$$

$$1.025 + 1.804\lambda + 0.568\lambda + \lambda^2 - 0.0196 = 0$$

$$\lambda^2 + 2.372\lambda + 1.005 = 0$$

$$= \frac{-2.372 \pm \sqrt{(2.372)^2 - 4(1)(1.005)}}{(2)(1)}$$

$$= -1.186 \pm 0.634$$

$$= -1.820, \text{ and } -0.552.$$

Solving for the coefficients:

$$\begin{vmatrix} -1.804 - \lambda & 0.140 \\ 0.140 & -0.568 - \lambda \end{vmatrix} \begin{matrix} C_1 \\ C_2 \end{matrix} = \begin{matrix} 0 \\ 0 \end{matrix}$$

For the first eigenvalue this becomes:

$$\begin{vmatrix} -1.804 + 1.820 & 0.140 \\ 0.140 & -0.568 + 1.820 \end{vmatrix} \begin{matrix} C_1 \\ C_2 \end{matrix} = \begin{matrix} 0 \\ 0 \end{matrix}$$

$$\begin{vmatrix} 0.016 & 0.140 \\ 0.140 & 1.252 \end{vmatrix} \begin{matrix} C_1 \\ C_2 \end{matrix} = \begin{matrix} 0 \\ 0 \end{matrix}$$

$$(0.140)(C_1) + (1.252)(C_2) = 0$$

$$C_1 = -8.943 C_2$$

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

$$(-8.943 C_2)^2 + C_2^2 = 1$$

$$80.975 C_2^2 = 1$$

$$C_2 = 0.111, C_1 = -0.994$$

For the second eigenvalue this becomes:

$$\begin{vmatrix} -1.804 + 0.552 & 0.140 \\ 0.140 & -0.568 + 0.552 \end{vmatrix} \begin{matrix} C_1 \\ C_2 \end{matrix} = \begin{matrix} 0 \\ 0 \end{matrix}$$

$$\begin{vmatrix} -1.252 & 0.140 \\ 0.140 & -0.016 \end{vmatrix} \begin{matrix} C_1 \\ C_2 \end{matrix} = \begin{matrix} 0 \\ 0 \end{matrix}$$

$$(-1.252)(C_1) + (0.140)(C_2) = 0$$

$$C_1 = 0.112 C_2$$

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

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

$$1.0125 C_2^2 = 1$$

$$C_2 = 0.994, C_1 = 0.111$$

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

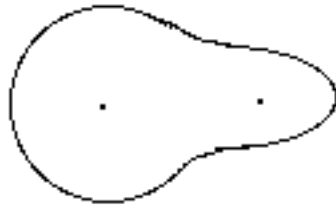
$$R_{\pm} = g \pm \sqrt{\frac{C_2}{C_1}} u$$

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

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

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

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



$R_+$  Left Polarized



$R_-$  Right Polarized