

# Chem 3060

Fall 2005

Mid-term Exam #2

November 22, 2005

Name: solutions

Uid# —

Signature: —

1.) (10 pts.) What would be a good approximation to an N-electron atom wave function? And why?

Slater determinant,

3 Pts  
↓  
Hartree-Fock:  
still uses Slater determin.  
but uses Hartree-Fock orbitals!  
A pett plays a role!

10 Pts  
→  $\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} 1s \alpha(1) & 1s \beta(1) & 2s \alpha(1) & 2s \beta(2) \\ 1s \alpha(2) & 1s \beta(2) & 2s \alpha(2) & \dots \\ 1s \alpha(3) & 1s \beta(3) & 2s \alpha(3) & \dots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix}$

2.) (5 pts.) Describe the Pauli exclusion principle.

Ⓢ All electronic wave functions must be antisymmetric under the interchange of any 2  $e^-$ .  
or No 2  $e^-$ 's can have the same set of quantum #'s

3.) a.) (10 pts.) State the variational principle and explain its significance.

$E_\phi \geq E_0$ , never reaches ~~and~~ below  $E_0$ .  
→ can use any trial wavefunction and start to approximate from there.

b.) (10 pts.) Describe a procedure for applying the variational principle to solve the  $\hat{H}\Psi = E\Psi$  equation.

- 2 Pts ① come up with <sup>trial</sup> wavefunction  $\phi = \sum_i c_i \psi_i$  (parameters known functions)
- 2 Pts ② solve for  $E_0 \leq \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$
- 2 Pts ③ set  $\frac{\partial E}{\partial c_1} = 0$   $\frac{\partial E}{\partial c_2} = 0 \dots$
- 2 Pts ④ solve for  $c_{1min}, c_{2min} \dots$  and plug in into eqn.
- 2 Pts ⑤ calculate E. if  $E_\phi \gg E_0$  then do step ①

- 4.) Given the Hamiltonian  $H = -\frac{1}{2}\nabla^2 + \lambda x$  (in au)  
 (15 pts.) (Where  $\lambda$  is a small constant.)

Describe in steps, (you don't have to solve them) how you would solve the  $\hat{H}\Psi = E\Psi$  equation. *Perturbation theory! (2)*

*Split  $\hat{H}$  into  $\hat{H}^0 + \hat{H}'$  since  $\hat{H}'$  is a small perturbation! (2)*  
 $\hat{H}^0\psi^0 = E^0\psi^0 \leftarrow$  solvable (2) then turn on perturbation smoothly (1)

- 5.) (5 pts.)

What is the physical meaning of the J quantum number in the term symbol  $^5F_5$ ?

*total angular momentum  $J = L + S$  spin  
 of 5 orbital angular m.*

- 6.) (25 pts.)

The ground configuration of the nitrogen is  $1s^2 2s^2 2p^3$ , which leads to atomic term symbols  $^4S$ ,  $^2P$ , and  $^2D$ .

- a.) How many states arise from the configuration of the nitrogen atom? (2)

$$\frac{6 \cdot 5 \cdot 4}{3!} = \frac{6 \cdot 5 \cdot 4}{6} = 20 \text{ states } (2)$$

- b.) What atomic levels (J-values) arise from the atomic term symbols? (10)

- c.) What does Hund's rule predict for the ground-state level of the nitrogen atom?

*$^4S: J = L + S \dots |L-S| \quad 0 + 3/2 \Rightarrow 4S_{3/2}$        $^2D: |1/2 + 2| = 5/2$   
 $^2P: J = 1 + 1/2 \dots |1 - 1/2| \quad 3/2, 1/2$        $= 3/2$*

- d.) Optical spectroscopy of atomic nitrogen has revealed atomic levels arising from the  $1s^2 2s^2 2p^3$  configuration at the energies listed below. The number of states observed when the atoms are placed in a magnetic field is also noted for each atomic level below. (3)

Energy	Number of States	Term symbols
$28842 \text{ cm}^{-1}$	splits into 2 states	$^2P_{1/2}$
$28838 \text{ cm}^{-1}$	splits into 4 states	$^2P_{3/2}$
$19231 \text{ cm}^{-1}$	splits into 4 states	$^2D_{3/2}$
$19223 \text{ cm}^{-1}$	splits into 6 states	$^2D_{5/2}$
$0 \text{ cm}^{-1}$	splits into 4 states	$^4S_{3/2}$

Identify the levels listed above with the atomic terms and levels which you derived in part(c) of this problem. (10)

7.)  
(10 pts.)

One of the excited configurations of atomic silicon is the  $[1s^2 2s^2 2p^6 3s^2] 3p^1 3d^1$  configuration. What atomic term symbols result from this configuration? (Be sure that your term symbol designates the values of L, S, and J in the appropriate way).

12 states  
adding idea  
4 P's  
6 P's  
-0.5

$$\begin{matrix} \frac{1}{-1} & \frac{1}{0} & \frac{1}{+1} \\ \frac{1}{-2} & \frac{1}{-1} & \frac{1}{0} & \frac{1}{+1} & \frac{1}{+2} \end{matrix}$$

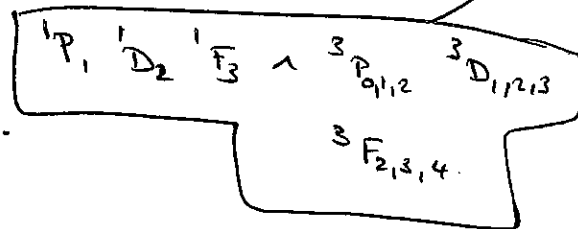
$L_1 = 1$   
 $S = 1/2$

Vector addition

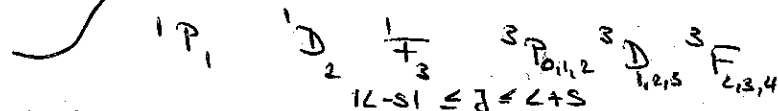
$L_2 = 2$   
 $S = 1/2$

$11-2 \quad 1 \leq L_1 + L_2 \leq 3$   
 $1 \leq L \leq 3; \quad L = 1, 2, 3$

$6 \times 10 = 60 \text{ states} //$



$0 \leq S \leq 1 \quad S = 0, 1$   
 $2S + 1 \Rightarrow 1, 3$



8.) Is  $CF_2$  a linear or bend molecule? If bend what is the value of the angle? Use the orbital energy diagram to explain your answer.  
(10 pts.)

bend, bond angle of less than  $120^\circ$  (2)  
due to free  $e^-$ -pair in the non bonding orbital

