

May 18, 2009
Chemistry 218, Molecular Structure
Second Examination- Spring 2009
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1 hour, 30 min

KEY

Name:

ID number:

Signature:

Useful information:

Permittivity of vacuum: $\epsilon_0 = 8.854187816 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$

$4\pi\epsilon_0 = 1.112650056 \times 10^{-10} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$

Bohr magneton: $\beta = 9.2740154 \times 10^{-24} \text{ J} \cdot \text{T}^{-1}$

Planck constant: $h = 6.6260755 \times 10^{-34} \text{ J} \cdot \text{s}$

Proton charge: $e = 1.60217733 \times 10^{-19} \text{ C}$

Speed of light in vacuum: $c = 2.99792458 \times 10^8 \text{ m} \cdot \text{s}^{-1}$

Electron rest mass: $m_e = 9.1093897 \times 10^{-31} \text{ kg}$

Bohr radius: $a_0 = 5.29177249 \times 10^{-11} \text{ m}$

A Hartree $E_h = \frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = 4.3597 \times 10^{-18} \text{ J}$

Potential energy V (nuclear charge Z and electron): $V = -\frac{Ze^2}{4\pi\epsilon_0 r}$ or $-\frac{Ze^2}{r}$

$$E_n = \frac{-m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = \frac{-e^2}{8\pi\epsilon_0 a_0 n^2} \text{ or } \frac{-e^2}{2a_0 n^2} \text{ for H atom}$$

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

$$d\tau = r^2 \sin \theta \, dr \, d\theta \, d\phi$$

$$\int_0^\infty x^n e^{-ax} \, dx = \frac{n!}{a^{n+1}}; n \text{ is a positive integer}$$

$$\int_0^\infty x^{2n} e^{-\alpha x^2} \, dx = \frac{1.3.5 \dots (2n-1)}{2^{n+1}} \sqrt{\frac{\pi}{\alpha^{2n+1}}}$$

Rayleigh Ratio: $\xi = \frac{\int \psi^* \hat{H} \psi d\tau}{\int \psi^* \psi d\tau}$

Rayleigh-Ritz method: $\det |H_{ij} - \xi S_{ij}| = 0$

Perturbation theory, 1st order correction to energy: $E^{(1)} = \int \psi^{(0)*} \hat{H}^{(1)} \psi^{(0)} d\tau$

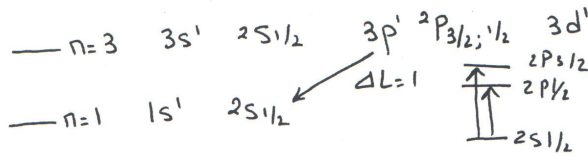
Electronic atomic transitions selection rules, absence of magnetic field:
 $\Delta S = 0; \Delta L = \pm 1; \Delta J = 0, \pm 1$ except $J = 0 \rightarrow J = 0$

Electronic atomic transitions selection rules, presence of magnetic field:
 $\Delta S = 0; \Delta L = \pm 1; \Delta J = 0, \pm 1$ except $J = 0 \rightarrow J = 0; \Delta M_j = 0, \pm 1$

Part I. Instructions: Circle one answer. No penalty. 5 points each. (25%)

• When considering spin/orbit coupling, in the *absence* of a magnetic field, the atomic absorption transition of the $n = 3$ to $n = 1$ of the hydrogen atom will consist of

- lines:
- a. 2
 - b. 3
 - c. 4
 - d. 7
 - e. 9
 - f. None of the above, the number of lines is _____



• Which of the following is the correct term symbol for the Ground State of Zr ($[\text{Kr}]5s^2 4d^2$) (hint: find ground state term symbol without finding all the term symbols).

- a. 3D_2
- b. 1D_2
- c. 3F_4
- d. 3F_2
- e. 1F_4
- f. None of the above, the term symbol for the ground state is _____

Handwritten notes for Zr ground state:
 $1 \uparrow \uparrow _ _ _$
 $m_l = 2 \ 1 \ 0 \ -1 \ -2$
 $\Rightarrow H_L = 3 \Rightarrow L = 3 \Rightarrow ^3F_2$
 1. maximum multiplicity: $S = 1$
 2. largest L
 3. lowest J ($< 1/2$ filled)
 $J: |L - S| = 3 - 1 = 2$

- Arrange the following term symbols for the C atom configuration $1s^2 2s^2 2p^2$: 1D_2 , 3P_0 , 3P_1 , 3P_2 , 1S_0 in the order of increasing energy according to Hund's rules for equivalent electrons.

- Hund's Rules: Largest S first
then largest L
then s - all at j (< 1/2 filled)
- $^1D_2 < ^3P_0 < ^3P_1 < ^3P_2 < ^1S_0$
 - $^3P_0 < ^3P_1 < ^3P_2 < ^1D_2 < ^1S_0$
 - $^3P_0 < ^3P_1 < ^3P_2 < ^1S_0 < ^1D_2$
 - $^3P_2 < ^3P_1 < ^3P_0 < ^1D_2 < ^1S_0$
 - $^3P_2 < ^3P_1 < ^3P_0 < ^1S_0 < ^1D_2$

- Which of the following wavefunctions is acceptable for a 2 electron system (He)

- $\Psi_n(1)\Psi_n(2)\alpha(1)\beta(2)$
- $\Psi_n(1)\Psi_n(2)[\alpha(2)\beta(1) - \alpha(1)\beta(2)]$
- $\Psi_n(1)\Psi_n(2)[\alpha(2)\alpha(1) - \beta(1)\beta(2)]$
- $\Psi_n(1)\Psi_n(2)[\alpha(2)\beta(1) + \alpha(1)\beta(2)]$
- $\Psi_n(1)\Psi_n(2)[\alpha(2)\alpha(1) + \beta(1)\beta(2)]$

must be antisymmetric for interchange of electrons
 \Rightarrow P12 $\Psi = -\Psi$

- Which of the following statements is false?

- The ground state energy for the He atom is $-2E_h$ *true*
- The atomic unit for distance is the Bohr radius a_0 , the atomic unit for energy is the Hartree E_h , and the atomic unit for angular momentum is \hbar *true*
- The spin-orbital wavefunction for the Li atom ($Z=3$) is separable into a spin part and a spatial part (i.e., it is a product of a spin function separated from a spatial function) *false. only 2-e system separable into spin and spatial*
- The Pauli exclusion principle postulates that electronic wavefunctions for multielectron atoms must be antisymmetric under the interchange of any two electrons *true*
- The determinantal wavefunction (Slater determinant) for the ground state of the He atom is an eigenfunction of the operator L^2 (the square of the orbital angular momentum operator) and the eigenvalue is 0. *true*
- c) and e) \rightarrow $\hbar^2 1s^2$ $L=0$
eigenvalue for L^2 is 0 \Rightarrow true

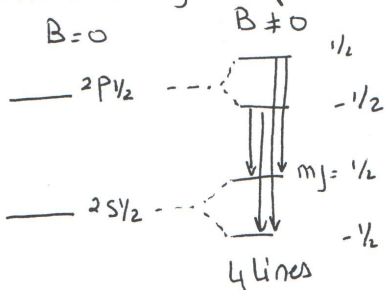
Part II. Answer the following and show your work (28 %)

II.1 Consider the H-atom electronic transitions from $n=2$ to $n=1$. Show into how many lines is this transition split in the presence of a magnetic field, while considering spin-orbit coupling. (8 %)

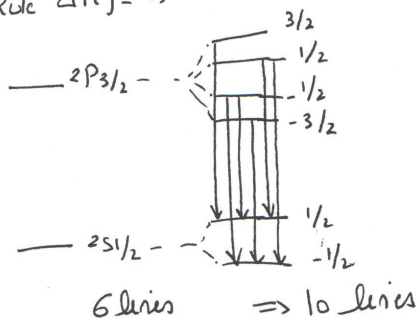
$n=2$ $2s'$: $2s'_{1/2}$ $2p'$: $2p'_{1/2}$ $2p'_{3/2}$

$n=1$ $1s'$: $2s'_{1/2}$

presence of a magnetic field:



Selectin Rule $\Delta M_j = 0, \pm 1$



II.2 Find all the term symbols for the He atom excited state $1s^1 2p^1$. (8 %)

12 microstates

$m_{l1} = 0$
 $m_{l2} = 1, 0, -1$
 $\Rightarrow M_L = 1, 0, -1$
 $m_{s1} = \pm 1/2$
 $m_{s2} = \pm 1/2$
 $\Rightarrow M_S = 1, 0, -1$

M _L	M _S		
	1	0	-1
1	\uparrow_0, \uparrow_1	$\uparrow_0, \uparrow_0; \bar{0}, \uparrow_1$	$\bar{0}, \uparrow_1$
0	\uparrow_0, \uparrow_0	$\uparrow_0, \uparrow_0; \bar{0}, \uparrow_0$	$\bar{0}, \uparrow_0$
-1	$\uparrow_0, \uparrow_{-1}$	$\uparrow_0, \uparrow_{-1}; \bar{0}, \uparrow_{-1}$	$\bar{0}, \uparrow_{-1}$

$M_L \text{ max} = 1 \Rightarrow L = 1 \Rightarrow P$
 $M_S \text{ max} = 1 \Rightarrow S = 1 \Rightarrow 3P$
 $J = 2, 1, 0$ ($L+S, \dots, |L-S$)
 $\Rightarrow 3P_2, 3P_1, 3P_0$

remains 3. $M_L \text{ max} = 1 \Rightarrow 1P \Rightarrow J = 1 \Rightarrow 1P_1$

II.3 (12%)

- (a) Write down the Hamiltonian operator for the Li atom ($Z=3$) in atomic units (a.u.) (6%)

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{\nabla_3^2}{2} - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}}$$

- (b) Write down a Slater determinant wavefunction (spin/orbital), without expanding it, for the ground state of the Lithium atom (6%)

$$\psi = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s \alpha(1) & 1s \beta(1) & 2s \alpha(1) \\ 1s \alpha(2) & 1s \beta(2) & 2s \alpha(2) \\ 1s \alpha(3) & 1s \beta(3) & 2s \alpha(3) \end{vmatrix}$$

Part III. (42%)

II.1 (14%) Consider a hydrogen atom in an electric field of strength ϵ . The Hamiltonian operator for this system is:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} + e\epsilon r \cos\theta$$

- Identify $H^{(1)}$, the perturbation to the Hamiltonian of the hydrogen atom as a result of the electric field.
- Using perturbation theory, calculate the first-order correction to the ground state energy for this system as a result of the electric field.

a. $H^{(1)} = e\epsilon r \cos\theta$

b. $E^{(1)} = \int \psi^{(0)*} H^{(1)} \psi^{(0)} d\tau$

$$= \int \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} e\epsilon r \cos\theta \cdot \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0} r^2 dr \sin\theta d\theta \cdot d\phi$$

$$= \frac{1}{\pi} \cdot \frac{1}{a_0^3} \cdot e\epsilon \int_0^\infty e^{-2r/a_0} r^3 dr \int_0^{2\pi} d\phi \int_0^\pi \underbrace{\sin\theta d\theta \cdot \cos\theta}_{\int_0^\pi \cos\theta d\cos\theta}$$

$$= \int_0^\pi \cos\theta d\cos\theta$$

$$= \left. \frac{\cos^2\theta}{2} \right|_0^\pi = \frac{1}{2} - \frac{1}{2} = 0$$

$$\Rightarrow E^{(1)} = 0$$

$$\text{and } E = E^{(0)}$$

II.2 (14%) Let $\phi(\alpha) = \left(\frac{\alpha^5}{3\pi}\right)^{1/2} r \cdot \exp(-\alpha r)$ be a trial function for the ground state of the hydrogen atom. Use the variation method to determine the lowest energy attainable from this function by variation of α , and compare to the true energy of the ground state of the hydrogen atom.

$$E = \frac{\int \phi(\alpha)^* \hat{H} \phi(\alpha) \cdot 4\pi r^2 dr}{\int \phi(\alpha)^* \phi(\alpha) \cdot 4\pi r^2 dr}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) - \frac{2e^2}{r} \quad Z=1$$

denominator:

$$\int_0^{\infty} \left(\frac{\alpha^5}{3\pi}\right) \cdot r^2 e^{-2\alpha r} \cdot 4\pi r^2 dr = 4\pi \cdot \frac{\alpha^5}{3\pi} \cdot \int_0^{\infty} r^4 e^{-2\alpha r} dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \cdot \frac{4!}{(2\alpha)^5}$$

Numerator:

$$4\pi \int_0^{\infty} \frac{\alpha^5}{3\pi} \cdot r \exp(-\alpha r) \left\{ \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} r e^{-\alpha r} \right) \right] - \frac{e^2}{r} \cdot r e^{-\alpha r} \right\} r^2 dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \int_0^{\infty} r \exp(-\alpha r) \left\{ \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left(r^2 (-\alpha r e^{-\alpha r} + e^{-\alpha r}) \right) \right] - e^2 e^{-\alpha r} \right\} r^2 dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \int_0^{\infty} r \exp(-\alpha r) \left\{ \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} (-\alpha r^3 e^{-\alpha r} + r^2 e^{-\alpha r}) \right] - e^2 e^{-\alpha r} \right\} r^2 dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \int_0^{\infty} r \exp(-\alpha r) \left\{ \left[-\frac{\hbar^2}{2m} \frac{1}{r^2} (-3\alpha r^2 e^{-\alpha r} + \alpha^2 r^3 e^{-\alpha r} + 2r e^{-\alpha r} - \alpha r^2 e^{-\alpha r}) \right] - e^2 e^{-\alpha r} \right\} r^2 dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \int_0^{\infty} r \exp(-\alpha r) \left\{ -\frac{\hbar^2}{2m} (-4\alpha r^2 e^{-\alpha r} + \alpha^2 r^3 e^{-\alpha r} + 2r e^{-\alpha r}) - e^2 e^{-\alpha r} \right\} r^2 dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \int_0^{\infty} \frac{-\hbar^2}{2m} \left(-4\alpha r^3 e^{-2\alpha r} + \alpha^2 r^4 e^{-2\alpha r} + 2r^2 e^{-2\alpha r} \right) \cdot e^2 r^3 e^{-2\alpha r} dr$$

$$= 4\pi \cdot \frac{\alpha^5}{3\pi} \left\{ \frac{-\hbar^2}{2m} \left[-4\alpha \cdot \frac{3!}{(2\alpha)^4} + \alpha^2 \cdot \frac{4!}{(2\alpha)^5} + 2 \cdot \frac{2!}{(2\alpha)^3} \right] - e^2 \cdot \frac{3!}{(2\alpha)^4} \right\}$$

$$\Rightarrow \mathcal{E} = \frac{-\frac{\hbar^2}{2m} \left[\frac{-4 \cdot 3!}{2^4 \alpha^3} + \frac{4!}{2^5 \alpha^3} + \frac{2 \cdot 2!}{2^3 \alpha^3} \right] - \frac{e^2 \cdot 3!}{(2\alpha)^4}}{\frac{4!}{(2\alpha)^5}}$$

$$= -\frac{\hbar^2}{m} \cdot \frac{2\alpha^2}{3} \left[-\frac{3}{2} + \frac{3}{4} + \frac{1}{2} \right] - \frac{\alpha e^2}{2}$$

$$= -\frac{\hbar^2}{m} \cdot \frac{2\alpha^2}{3} \cdot -\frac{1}{4} - \frac{\alpha e^2}{2}$$

$$= -\frac{\hbar^2 \alpha^2}{6m} - \frac{\alpha e^2}{2}$$

$$\frac{d\mathcal{E}}{d\alpha} = 0 \Rightarrow \frac{\hbar^2}{6m} \cdot 2\alpha - \frac{e^2}{2} = 0 \Rightarrow \alpha = \frac{3e^2 m}{2\hbar^2}$$

$$\mathcal{E}: E_{\min} = -\frac{\hbar^2}{6m} \cdot \left(\frac{3e^2 m}{2\hbar^2} \right)^2 - \left(\frac{3e^2 m}{2\hbar^2} \right) \left(\frac{\alpha e^2}{2} \right) = -\frac{3}{8} \left(\frac{e^2}{a_0} \right)$$

$$E_{true} = \frac{-e^2}{2a_0} < -\frac{3}{8} \frac{e^2}{a_0}$$

lower

III.3 (14%) ϕ_a and ϕ_b are chosen as the normalized basis (real) functions for a linear combination of atomic orbitals (LCAO) wavefunction Ψ for a one-electron, homonuclear, diatomic molecule:

$$\Psi = c_1\phi_a + c_2\phi_b$$

It is found that the values for some of the integrals (matrix elements) involving these functions are: (a.u. is atomic units).

$$H_{aa} = \int \phi_a^* \hat{H} \phi_a d\tau = -2 \text{ a.u.}$$

$$H_{ab} = \int \phi_a^* \hat{H} \phi_b d\tau = -1 \text{ a.u.}$$

$$H_{bb} = \int \phi_b^* \hat{H} \phi_b d\tau = -2 \text{ a.u.}$$

$$S_{ab} = \int \phi_a^* \phi_b d\tau = 1/4$$

where \hat{H} is the molecular Hamiltonian operator.

- Using the variation method, find the minimized energy using this trial function (the upper bound energy for the exact lowest electronic energy for this system).
- Find the corresponding values of c_1 and c_2 for the LCAO *normalized* approximate wavefunction Ψ having this energy.

$$\begin{vmatrix} H_{aa} - \epsilon S_{aa} & H_{ab} - \epsilon S_{ab} \\ H_{ba} - \epsilon S_{ba} & H_{bb} - \epsilon S_{bb} \end{vmatrix} = 0$$

$$\begin{vmatrix} -2 - \epsilon & -1 - \frac{\epsilon}{4} \\ -1 - \frac{\epsilon}{4} & -2 - \epsilon \end{vmatrix} = 0$$

$$\Rightarrow (-2 - \epsilon)(-2 - \epsilon) - (-1 - \frac{\epsilon}{4})(-1 - \frac{\epsilon}{4}) = 0$$

$$\Rightarrow (2 + \epsilon)^2 - (1 + \frac{\epsilon}{4})^2 = 0$$

$$\Rightarrow 2 + \epsilon = \pm 1 + \frac{\epsilon}{4}$$

$$2 + \epsilon = 1 + \frac{\epsilon}{4} \Rightarrow \epsilon = -\frac{4}{3} \text{ a.u.} \quad (-1.333 \text{ a.u.})$$

$$2 + \epsilon = -1 - \frac{\epsilon}{4} \Rightarrow \epsilon = -\frac{12}{5} \text{ a.u.} \quad (-2.4 \text{ a.u.})$$

$$E_{\min} = -\frac{12}{5} \text{ a.u.}$$

Continue Problem III.3. Do not detach.

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$$\begin{vmatrix} -2 + \frac{12}{5} & -1 + \frac{12}{20} \\ -1 + \frac{12}{20} & -2 + \frac{12}{5} \end{vmatrix} \begin{vmatrix} c_1 \\ c_2 \end{vmatrix} = 0$$

$$\Rightarrow \left(-2 + \frac{12}{5}\right)c_1 + \left(-1 + \frac{12}{20}\right)c_2 = 0 \quad (1)$$

$$\text{and } \Rightarrow \left(-1 + \frac{12}{20}\right)c_1 + \left(-2 + \frac{12}{5}\right)c_2 = 0 \quad (2)$$

$$(1) \Rightarrow \left(-\frac{10+12}{5}\right)c_1 + \left(-\frac{20+12}{20}\right)c_2 = 0 \Rightarrow \frac{2}{5}c_1 - \frac{8}{20}c_2 = 0$$

$$\Rightarrow c_1 = \frac{40}{40}c_2 \Rightarrow c_1 = c_2$$

Same with (2).

$$\phi = c_1\phi_a + c_1\phi_b = c_1(\phi_a + \phi_b)$$

$$\int \phi^* \phi = 1 \Rightarrow \int c_1(\phi_a + \phi_b) \cdot c_1(\phi_a + \phi_b) = 1$$

$$\Rightarrow c_1^2 \left[\int \phi_a \phi_a + 2 \int \phi_a \phi_b + \int \phi_b \phi_b \right] = 1$$

$$\Rightarrow c_1^2 [S_{aa} + 2S_{ab} + S_{bb}] = 1$$

$$\Rightarrow c_1^2 \cdot \left[1 + 2 \cdot \frac{1}{4} + 1\right] = 1$$

$$\Rightarrow c_1^2 \cdot \frac{5}{2} = 1 \Rightarrow c_1 = \pm \sqrt{\frac{2}{5}}$$

$$\Rightarrow \phi = \sqrt{\frac{2}{5}} (\phi_a + \phi_b)$$