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CHM 3411, Dr. Chatfield, March 9, 2009
Exam 2

Each problem is worth 20 points. You may a calculator, your text and notes but not a laptop. If you need extra room, you may use scratch paper, but ***put all final answers on the exam itself. Read all problems carefully***. Set up problems methodically, show your work, and be neat. Partial credit will be given when it is possible for me to follow your work. If you are having trouble with a problem, go on to the next and come back. GOOD LUCK!

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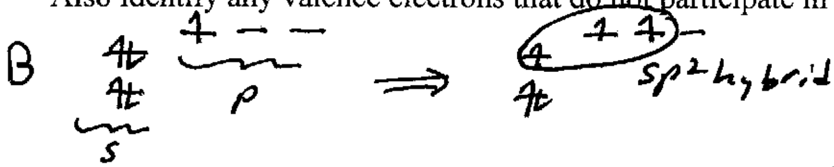
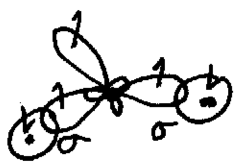
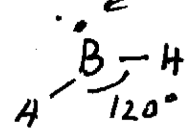
1. Short answer problems.

(a) Predict the hydridization of the boron atom in BH_2. Draw a picture of the molecule that shows all orbitals that overlap to form bonds and identify the type of bond (σ, π, etc). Also identify any valence electrons that do not participate in bonds.







single electron in boron sp^2 hybrid orbital

(b) Calculate the fundamental frequency (ν) and the zero point vibrational energy for the diatomic molecule $^1H^{19}F$.

(Table 13.2) 1.66×10^{-27} kg

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ k = force constant $= 965.7$ N/m

$= 1.244\times10^{14}\,s^{-1}$ μ = reduced mass $= \frac{m_H\, m_F}{m_H + m_F} = \frac{1\cdot19}{1+19}\cdot$ amu

$= 1.58\times10^{-27}$ kg

$E = (v+\frac{1}{2})h\nu$ $v = 0, 1, 2\ldots$

$E_{zp} = \frac{1}{2}h\nu = 4.122\times10^{-20}\,J = 2.573$ eV

(c) Consider the diatomic molecular ion LiH^{++}. Write the Hamiltonian for this ion in the Born-Oppenheimer approximation. (Hint: begin by considering how many electrons are present. Using atomic units is fine.)

1 2

LiH^{++} has 2 electrons, Label electrons "1", "2"

Label nuclei of Li, H "A", "B"

A B

B-O approximation: Nuclei effectively motionless.

Using a.u.: $\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{3}{r_{1A}} - \frac{3}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} + \frac{3}{r_{AB}} + \frac{1}{r_{12}}$

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2. Consider the following wavefunction for an electron in a hydrogen atom (in atomic units):

$$\psi = Nr^2 e^{-r/3}(3\cos^2\theta - 1)$$

(a) How many radial nodes and how many angular nodes are there?

radial nodes = 0 (the point r=0 is not a node)

angular " = 2

(b) What are the values of n and l?

$l = 2$ (because # angular nodes = 2)

$n = 3$ (n = total # nodes + 1)

(c) What is the energy in atomic units?

$E = -\frac{1}{2n^2} = -\frac{1}{18}$ (in a.u.)

(d) Name the orbital, being as specific as possible (e.g., 1s, 2p, $2p_x$ etc.).

$3d_{z^2}$

↑ z^2 from form of θ factor $(3\cos^2\theta - 1)$

↑ because $l = 2$

because $n = 3$

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3. Consider the possible electronic transitions between a ^2P and a ^2D term.

(a) What are the possible values of J for a ^2P term?

^2P: $M = 2 = 2S+1 \Rightarrow S = \frac{1}{2}$

$P \Rightarrow L = 1$

$J = L+S, \ldots, |L-S| = \frac{3}{2}, \frac{1}{2}$

$^2P_{3/2}$ $\quad$ $^2P_{1/2}$

(b) What are the possible vales of J for a ^2D term?

$D \Rightarrow L = 2$

$S = \frac{1}{2} \quad L = 2$

$J = L+S, \ldots, |L-S| = \frac{5}{2}, \frac{3}{2}$

$^2D_{5/2}$ $\quad$ $^2P_{3/2}$

(c) Whate are the possible allowed transitions that can occur between the various ^2P and ^2D terms above?

Selection rules: $\Delta S = 0$; $\Delta L = 0, \pm 1$; $\Delta J = 0, \pm 1$ but $J = 0 \not\leftrightarrow J = 1$

$^2P_{3/2} \leftrightarrow {}^2P_{1/2}$ $\qquad$ $^2P_{1/2} \leftrightarrow {}^2D_{3/2}$

$^2D_{5/2} \leftrightarrow {}^2D_{3/2}$ $\qquad$ $^2P_{3/2} \leftrightarrow {}^2D_{3/2}$

$^3P_{3/2} \leftrightarrow {}^2D_{5/2}$

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4. Determine the probability of finding a 1s electron in a He^+ cation beyond the classical turning radius. Hint: using atomic units will make this much simpler. The wavefunction for a 1s orbital is (you can convert this to SI units with one small simplification):

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

At classical turning radius, $E = V$

$$\left.\begin{aligned} E &= \frac{-Z^2}{2n^2} = -2 \quad (Z=2,\ n=1) \\ V &= -\frac{Z}{r} = -\frac{2}{r} \end{aligned}\right\} E = V \Rightarrow r_{ct} = 1$$

In a.u., $\psi_{1s} = \frac{1}{\sqrt{\pi}} Z^{3/2} e^{-Zr} = \frac{1}{\sqrt{\pi}} 2^{3/2} e^{-2r}$

$$P(r > r_{ct}) = \int_0^{2\pi}\int_0^{\pi}\int_{r_{ct}}^{\infty} \psi^* \psi\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$= 1 - \int_0^{2\pi}\int_0^{\pi}\int_0^{r_{ct}} \psi^* \psi\, r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$= 1 - 4\pi \int_0^1 \left[\frac{1}{\sqrt{\pi}} 2^{3/2} e^{-2r}\right]^2 r^2\, dr$$

$$= 1 - 32 \underbrace{\int_0^1 r^2 e^{-4r}\, dr}_{\substack{u = 4r \quad du = 4dr \\ r = \frac{1}{4}u \quad dr = \frac{1}{4}du}} = 1 - \frac{1}{2} \underbrace{\int_{u=0}^{4} u^2 e^{-u}\, du}$$

$\int_0^x u^2 e^{-u}\, du = 2 - (x^2 + 2x + 2)e^{-x}$

$\Downarrow$

$= 2 - (4^2 + 2\cdot 4 + 2)e^{-4}$

$= 1.524$

$P(r > r_{ct}) = 1 - \frac{1}{2}(1.524) = 0.238$

In other words, the electron will be found beyond the classical turning radius 23.8% of the time.

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5. Consider the following Schrödinger equation for a two dimensional system:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right]\psi = E\psi$$

Can the above equation be simplified by a separation of variable? If so, give the equations obtained after separating variables.

Multiply both sides by $-\frac{2mr^2}{\hbar^2}$

$$\left[\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{\partial^2}{\partial\phi^2}\right]\psi = \frac{-2mr^2E}{\hbar^2}\psi$$

$$\left[\underbrace{\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{2mr^2E}{\hbar^2}}_{\text{depends only on } r}+\underbrace{\frac{\partial^2}{\partial\phi^2}}_{\text{depends only on } \phi}\right]\psi = 0$$

substitute

$\Rightarrow$ separable operator

$\Rightarrow \psi(r,\phi) = R(r)\Phi(\phi)$

$$\Phi\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{2mr^2E}{\hbar^2}\right)R + R\frac{\partial^2}{\partial\phi^2}\Phi = 0$$

$\Downarrow$ divide by $R\Phi$

$$\underbrace{\frac{1}{R}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{2mr^2E}{\hbar^2}\right)R}_{=\text{constant}=K} + \underbrace{\frac{1}{\Phi}\frac{\partial^2}{\partial\phi^2}\Phi}_{=\text{constant}=-K} = 0$$

$$\boxed{\begin{aligned}&\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{2mr^2E}{\hbar^2}\right)R = KR\\ &\frac{\partial^2}{\partial\phi^2}\Phi = -K\Phi\end{aligned}}$$

Yes, they can be separated.