

1. (25 points) a. Determine the expectation value, or average value of  $r$  for an excited state of the hydrogen atom where the electron is in a  $2p_z$  orbital. You may leave your answer in symbolic form.

(wave function given below)

15 points

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$$

+5 setup

$$\langle r \rangle = \int \psi_{210}^* r \psi_{210} r^2 dr \sin\theta d\theta d\phi = \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{16 \cdot 2\pi a_0^3} \cdot \frac{r^2}{a_0^2} e^{-r/a_0} \cos^2\theta \cdot r^3 dr \sin\theta d\theta d\phi$$

$$= \frac{1}{32\pi a_0^5} \int_0^\infty r^5 e^{-r/a_0} dr \int_0^\pi \int_0^{2\pi} \cos^2\theta \sin\theta d\theta d\phi$$

$$2\pi \int_0^\pi \cos^2\theta \sin\theta d\theta = 2\pi \left( -\frac{\cos^3\theta}{3} \Big|_0^\pi \right) = 2\pi \left\{ \frac{1}{3} - \left(-\frac{1}{3}\right) \right\}$$

$$= \frac{2\pi}{3} \cdot \frac{1}{32\pi a_0^5} \int_0^\infty r^5 e^{-r/a_0} dr$$

$$= \frac{1}{24 a_0^5} \left( \frac{5! a_0^6}{(a_0)^6} \right) = 5 a_0$$

+5 math.

+5 answer

$$\langle r \rangle = 5 a_0$$

+10

1b. Use your result from part "a" to develop an expression for the portion of the hydrogen atom's kinetic energy that arises from the angular momentum of the electron in this excited state. You may take the reduced mass of the system to be the mass of the electron.

+5

$$\left\{ \begin{array}{l} K = \frac{L^2}{2I} \\ \langle K \rangle = \frac{2\hbar^2}{2 \cdot \mu \langle r \rangle^2} = \frac{\hbar^2}{m_e \cdot (5a_0)^2} = \frac{\hbar^2}{25 m_e a_0^2} \end{array} \right.$$

$$\hat{L}^2 \psi_{210} = 1(1+1)\hbar^2 \psi_{210} = (2\hbar^2) \psi_{210}$$

+3

+2



$$\langle E_{\text{rot}} \rangle = \frac{\hbar^2}{25 m_e a_0^2}$$

2. (20 points) The Hamiltonian operator that describes the energy of a three dimensional harmonic oscillator is given in spherical coordinates by,

$$\hat{H} = \frac{-\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{k}{2} r^2,$$

9-15pts

where  $k$  is the vibrational force constant,  $\mu$  is the reduced mass of the oscillator, and  $r$  varies over the interval from 0 to  $\infty$ . Using the trial function,  $\phi = e^{-\alpha r}$ , where  $\alpha$  is a variational parameter, estimate the ground state energy for the oscillator. The following integrals should be useful. The true ground state energy is  $3\hbar\omega/2$ .

$$\int_0^{\infty} \phi^* \hat{H} \phi r^2 dr = \frac{\hbar^2}{8\mu\alpha} + \frac{3k}{8\alpha^5}$$

$$E_{\phi} = \left\{ \frac{\hbar^2}{2\mu\alpha} + \frac{3k}{2\alpha^5} \right\} \cdot \left( \frac{4\alpha^3}{1} \right)$$

$$\int_0^{\infty} \phi^* \phi r^2 dr = \frac{1}{4\alpha^3}$$

$$= \frac{\hbar^2 \alpha^2}{2\mu} + \frac{3k}{2\alpha^2} \leftarrow +5 E_{\phi}$$

$$\frac{dE_{\phi}}{d\alpha} = 0 = \frac{2\hbar^2\alpha}{2\mu} - \frac{3k}{2\alpha^3}$$

$$\frac{3k}{\alpha^3} = \frac{\hbar^2\alpha}{\mu}$$

$$\frac{3k\mu}{\hbar^2} = \alpha^4$$

$$\alpha^2 = \frac{\sqrt{3}\sqrt{k\mu}}{\hbar}$$

+5 for determining optimal  $\alpha^2$  or  $\alpha$

$$E_{\phi}^{\min} = \frac{\hbar^2}{2\mu} \cdot \frac{\sqrt{3}\sqrt{k\mu}}{\hbar} + \frac{\sqrt{3}k \cdot \hbar}{2 \cdot \sqrt{3}\sqrt{k\mu}} = \frac{\sqrt{3}}{2} \hbar \sqrt{\frac{k}{\mu}} + \frac{\sqrt{3}}{2} \hbar \sqrt{\frac{k}{\mu}} = \sqrt{3} \hbar \omega \quad \left. \vphantom{E_{\phi}^{\min}} \right\} +5 \text{ algebra.}$$

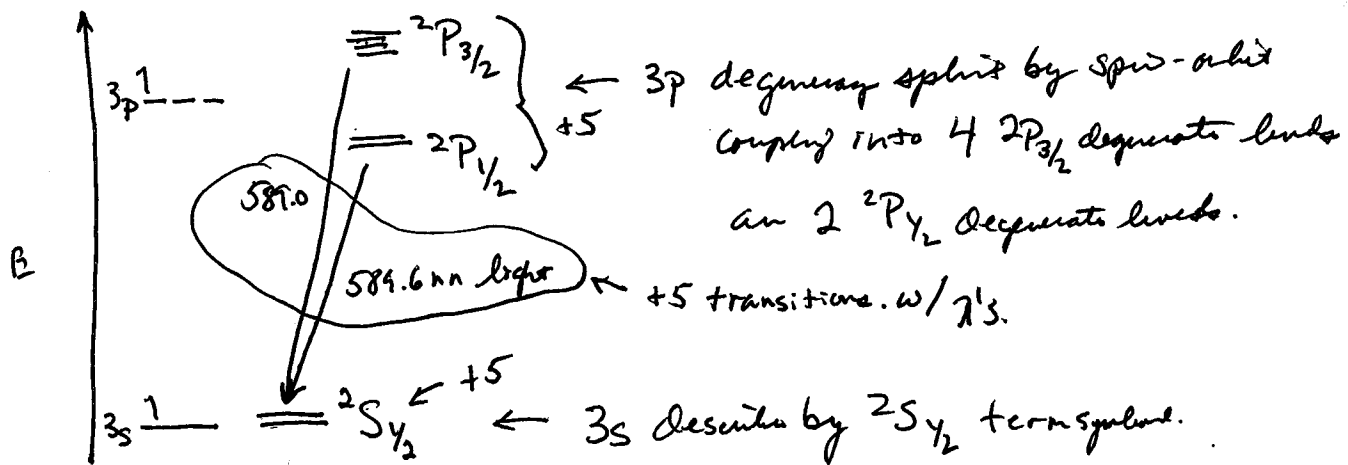
$$E = \sqrt{3} \hbar \omega$$

b) Does your answer conform to the variational principle?

Yes! Because  $\sqrt{3} \hbar \omega > 1.5 \cdot \hbar \omega$   
 $\uparrow$   $\uparrow$   $+4$   
 $+1$   $1.732$   
 +5

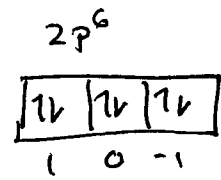
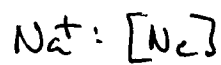
3. (20 points) a. A standard test that chemists use for the presence of  $\text{Na}^+$  in a mixture is a flame test. Specifically, when a small quantity of the mixture is burned,  $\text{Na}^+$  is detected by the emission of an intense yellow light. This emission comes from the decay of an excited Na valence electron from the  $3p \rightarrow 3s$  energy state and is often referred to as the sodium "doublet" because it consists of two groups of photons with wavelengths of 589.0 and 589.6 nm. Construct an energy level diagram that explains this emission of light. Label the energy levels with the appropriate term symbols and label the spectroscopic transitions with their emission wavelengths.

27  
1575



allowed emission line peaks:  $\Delta S = 0$   
 $\Delta L = \pm 1$   
 $\Delta J = 0, \pm 1$

b. What is the ground state term symbol of  $\text{Na}^+$ ?



$S=0, L=0$

$1S_0$  +5

4. (10 points) The orbital energies for Ne and Ar determined by the Hartree-Fock self consistent field method are given in the table below.

Ne:

Orbital	$\epsilon_i$ (kJ/mol)
1s	-86.0
2s	-5.06
2p	-1.94

Ar:

1s	-311.35
2s	-32.35
2p	-25.12
3s	-3.36
3p	-1.65

a. Estimate the first ionization energy for each element.

Using Koopman's Theorem. for Ne: I.E. =  $-\epsilon_{2p} = 1.94$  kJ/mole +3

for Ar: I.E. =  $-\epsilon_{3p} = 1.65$  kJ/mole +3

b. Explain the "trend" in ionization energy you obtained in part "a." (Which element is easier to ionize and why.)

(decrease)  
 I.E.'s go down as you move down a column of the periodic table because the valence electrons are further away from the nucleus. This makes the electrostatic attraction smaller so less energy needed for ionization. +4