Chemistry 410A **Exam 2** **Fall 2011**

Solutions

1. **40 points.**

   (a) What is the degeneracy of the lowest excited energy level for a particle in a box with dimensions $a = b = 4.0\,\text{nm}$, $c = 2.0\,\text{nm}$? **Solution:** $\boxed{2}$

   (b) Write the wavefunction for an electron in the ground state of a cubical box, with each side of length a. **Solution:**

   $$\psi_{1,1,1}(x,y,z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{a}\right) \sin\left(\frac{\pi z}{a}\right)$$

   (c) For the $6p$ subshell,

   i. what are the values of n and l, and what are the possible values of m_l? $\boxed{n = 6, l = 1, m_l = -1, 0, 1}$

   ii. how many radial nodes does the wavefunction have? $n - l - 1 = \boxed{4}$

   iii. how many angular nodes does the wavefunction have? $l = \boxed{1}$

   iv. how many orbitals are there in the subshell? number of values of $m_l = \boxed{3}$

   v. what is the probability density at $r = 0$? If $l = 0$, then $\boxed{R_{n,l}(r = 0) = 0.}$

2. A particle in a three-dimensional cubical box of volume $8.0\,\text{Å}^3$ is in the (2,2,2) state with a total kinetic energy of $6.0 \cdot 10^{-20}\,\text{J}$. Give the following:

   (a) the zero-point energy (in J); **Solution:** For a cubical box, the energy of the (2,2,2) state is at $2^2 + 2^2 + 2^2 = 12$ times $\varepsilon_0 = \pi^2\hbar^2/(2ma^2)$, while the ground state is at $3\varepsilon_0$. The energy of the ground state is equal to the zero-point energy in this case (because the potential energy is a constant), 3/12 of the (2,2,2) energy is equal to $\boxed{1.5 \cdot 10^{-20}\,\text{J.}}$

   (b) λ_{dB} (in Å) of the particle along any axis; **Solution:** Each side of the box has length 2.0 Å. With $n = 2$ along each axis, the wavefunction undergoes one complete cycle from one end of the box to the other, so λ_{dB} is the length of the side: $\boxed{2.0\,\text{Å.}}$

   (c) the new energy in the (2,2,2) state if we double the length of each side of the box. **Solution:** Doubling the length a will decrease the value of $\varepsilon_0 = \pi^2\hbar^2/(2ma^2)$ by a factor of $2^2 = 4$, so the new energy is again $\boxed{1.5 \cdot 10^{-20}\,\text{J.}}$

   (d) the mass (in kg) of the particle; **Solution:** For this one, we actually need a calculator. Solve the energy $E_{2,2,2} = 12\varepsilon_0$ for m:

   $$m = \frac{12\pi^2\hbar^2}{2a^2 E_{2,2,2}} = \frac{12\pi^2(1.055 \cdot 10^{-34}\,\text{J s})^2}{2(2.0 \cdot 10^{-10}\,\text{m})^2(6.0 \cdot 10^{-20}\,\text{J})} = \boxed{2.7 \cdot 10^{-28}\,\text{kg.}}$$

3. For the $7d$ state of Li^{2+} with $m_l = -1$, calculate the following **in SI units**:

   (a) the energy; **Solution:** Set $n = 7$ and $Z = 3$ and use the general equation for the energy of the one-electron atom:

   $$E_n = -\frac{Z^2}{2n^2} E_\text{h} = -\frac{3^2}{2 \cdot 7^2} E_\text{h} = -\frac{9}{98} E_\text{h} = \boxed{-4.00 \cdot 10^{-19}\,\text{J.}}$$

   (b) the value of the orbital angular momentum; **Solution:** For a d orbital, $l = 2$. The eigenvalue of the $\hat{L}^2$ operator is $L^2 = \hbar^2 l(l+1)$, so the value of L is $\hbar\sqrt{l(l+1)} = \sqrt{6}\hbar$, or $\boxed{2.58 \cdot 10^{-34}\,\text{J s.}}$

(c) the projection of the orbital angular momentum onto the z axis. **Solution:** The eigenvalue of $\hat{L}_z$ is $m_l\hbar$, which for $m_l = -1$ is $-\hbar$ or $\boxed{-1.05 \cdot 10^{-34}\,\mathrm{J\,s.}}$

4. To convert from the Cartesian coordinate x to polar coordinates, we use the relation

$$x = r \sin\theta \cos\phi.$$

Write the expression we would need to solve in order to to find the root mean square value of x, equal to $\sqrt{\langle x^2 \rangle}$, of the electron in the $4f_{m_l=-3}$ state of atomic hydrogen. **Solution:** The atomic number is $Z = 1$ and the wavefunction is

$$\begin{aligned}\psi_{4,3,-3}(r,\theta,\phi) &= R_{4,3}(r)Y_3^{-3}(\theta,\phi)\\ &= \left[\frac{1}{768\sqrt{35}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^3 e^{-Zr/(4a_0)}\right]\left[\sqrt{\frac{35}{64\pi}}\,\sin^3\theta\; e^{-3i\phi}\right].\end{aligned}$$

The integrand in this case depends on r and on the angles, so we can't simplify by integrating over only radial or over only angular coordinates. However, the final integral is simplified by the fact that in evaluating $|\psi|^2$, the factors of $e^{-3i\phi}$ and $(e^{-3i\phi})^* = e^{+3i\phi}$ cancel to give a factor of 1. the rms value of x is therefore:

$$\begin{aligned}\sqrt{\langle x^2 \rangle} &= \left\{\int_0^\infty \int_0^\pi \int_0^{2\pi} |R_{4,3}Y_3^{-3}(\theta,\phi)|^2\,(r\sin\theta\cos\phi)^2\, r^2\,\sin\theta\, d\theta\, d\phi\right\}^{1/2}\\ &= \left\{\left[\int_0^\infty R_{4,3}^2\, r^4\, dr\right]\left[\int_0^\pi |Y_3^{-3}(\theta,\phi)|^2\,\sin^3\theta\, d\theta\right]\left[\int_0^{2\pi}\cos^2\phi d\phi\right]\right\}^{1/2}\\ &= \left\{\left[\frac{1}{768^2\cdot 35a_0^3}\int_0^\infty\left(\frac{r}{a_0}\right)^6 e^{-r/(2a_0)}\, r^4\, dr\right]\left[\frac{35}{64\pi}\int_0^\pi \sin^9\theta\, d\theta\right]\left[\int_0^{2\pi}\cos^2\phi\, d\phi\right]\right\}^{1/2}.\end{aligned}$$