Chemistry 410A **Exam 2** **Spring 2008**

Solutions

1. Write the normalized wavefunction for any state of an electron in a cubical box with length a on each side and total energy $E = 14\pi^2\hbar^2/(2m_e a^2)$. **Solution:** From Table 1.2 or Fig. 1.23, we can see that the states with energy $E = 14\pi^2\hbar^2/(2mV^{2/3})$ are those with values for the quantum numbers 3, 2, and 1 (because $3^2 + 2^2 + 1^2 = 14$). Or we could figure it out (all of the quantum numbers must be less than 4, or else the energy is too high, and at least one must be 3, or the energy is too low). One of the corresponding wavefunctions is

$$\psi_{3,2,1}(x, y, z) = \left(\frac{\sqrt{8}}{a^2}\right) \sin\left(\frac{3\pi x}{a}\right) \sin\left(\frac{2\pi y}{a}\right) \sin\left(\frac{\pi z}{a}\right),$$

2. Let the atomic nucleus, instead of being a point charge, be a hollow sphere of radius r_0, such that the potential of the electron is

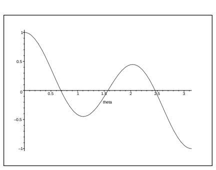
$$U(r) = -\frac{Ze^2}{4\pi\epsilon_0(r - r_0)}.$$

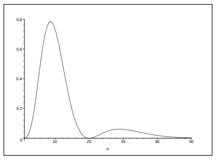
   (a) Do the wavefunctions for this new system have separable angular and radial coordinates? $\boxed{\text{yes}}$

   (b) Will the electron have any density at $r < r_0$? $\boxed{\text{yes}}$,

   (c) Sketch below what you think a graph of the r-dependent part of the lowest energy wavefunction will look like. **Solution:** No nodes, should peak in the middle (away from the tunnelling regions), and should tunnel into the wall(s).

3. Identify the n, l, m_l quantum numbers of the orbital represented below. The angular wavefunction is shown, as a *linear* plot (rather than a polar plot) of $Y(\theta, \phi)$ vs. θ. The radial probability density, not the radial waverfunction, is given. The function does not depend on ϕ.





Three angular nodes, so $l = 3$. No ϕ-dependence so $m_l = 0$. One radial node (where $R(r)^2$ goes to zero in the middle), so $n - l - 1 = 1$. $\boxed{n = 5,\, l = 3,\, m_l = 0}$

4. Write the expression necesary to calculate $\langle \phi^2 \rangle^{1/2}$, the root mean square ϕ value of the $2p_{m_l=1}$ state of Li^{2+}.

   Solution: We only need the angular part of the wavefunction, which is the $l = 1,\ m_l = 1$ spherical harmonic:

$$\left[\int_0^\pi \int_0^{2\pi} Y_1^{1*}(\theta,\phi)\, \phi^2\, Y_1^1(\theta,\phi)\, \sin\theta\, d\theta\, d\phi\right]^{1/2} = \left[\int_0^\pi \int_0^{2\pi} \left(\frac{3}{8\pi}\right) \sin^3\theta\, \phi^2\, d\theta\, d\phi\right]^{1/2}$$

5. The table below lists several operators. If our wavefunctions for the one-electron atom are eigenfunctions of that operator, write "yes" and give the eigenvalue. If not, write "no."

operator	**is $\psi_{n,l,m_l}(r,\theta,\phi)$ an eigenfunction?**	**eigenvalue**
$\hat{K}$	**no**	
U	**no**	
$\hat{H}$	**yes**	$E = -Z^2\ E_\mathrm{h}/(2n^2$
$\hat{L}^2$	**yes**	$\hbar^2 l(l+1)$
$\hat{L}_z^2$	**yes**	$\hbar^2 m_l^2$
r	**no**	