Chemistry 410A **Exam 2** **Fall 2008**

Solutions

1. **40 points.**

   (a) What are the quantum numbers for the wavefunction in a three-dimensional that has one node along x, three nodes along y, and no nodes along z? $\boxed{2, 4, 1}$

   (b) For the $4d$ subshell of an atom:

      i. what is the value of l? $\boxed{2}$

      ii. what are all the possible values of m_l? $\boxed{-2, -1, 0, 1, 2}$

      iii. what are all the possible values of m_s? $\boxed{-1/2, 1/2}$

      iv. how many orbitals are there? $\boxed{5}$

   (c) In the Hamiltonian for Be:

      i. how many electron kinetic energy terms appear? $\boxed{4}$ because there are 4 electrons.

      ii. how many electron-electron repulsion terms appear? $\boxed{6}$ because there are 6 distinct pairs of interacting electrons: 12,13,14,23,24,34.

   (d) For $2s$ electrons in the ground state atoms Be, B^+, and Li^-:

      i. which has the greatest amount of shielding? $\boxed{B^+}$ because the higher nuclear charge will bring the electrons closer together on average, and that will increase the electron-electron repulsion energy.

      ii. which has the lowest energy $2s$ electrons (having the highest ionization energy)? $\boxed{B^+}$ because the higher nuclear charge will stabilize the electrons more than the lower nuclear charges in Be and Li^-.

2. Find all (n_x, n_y, n_z) with $E = 7\pi^2\hbar^2/(ma^2)$ in a 3D box with sides a, $b = a$, and $c = 2a$. **Solution**: To start off, try writing the general expression for this energy, and then set it equal to the value in the problem and see what constraints appear:

$$
\begin{aligned}
E &= \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{a^2} + \frac{n_z^2}{(2a)^2}\right) = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{a^2} + \frac{n_z^2}{4a^2}\right) \\
&= \frac{\pi^2\hbar^2}{2m}\left(\frac{1}{4a^2}\right)\left(4n_x^2 + 4n_y^2 + n_z^2\right) = \frac{\pi^2\hbar^2}{8ma^2}\left(4n_x^2 + 4n_y^2 + n_z^2\right) \\
&= \frac{7\pi^2\hbar^2}{ma^2} \\
56 &= 4n_x^2 + 4n_y^2 + n_z^2
\end{aligned}
$$

So now we need to find all combinations of n_x, n_y, n_z such that the sum of the squares is 56, keeping in mind that the quantum numbers must all be integers. One way to do it is to recognize that $n_z < 8$ and to start checking the possible values of n_z and seeing if any values of n_x, n_y work out:

n_z	$4(n_x^2 + n_z^2)$	$n_x^2 + n_y^2$	n_x, n_y
7	7	7/4 not integer	
6	20	5	1, 2 2, 1
5	31	31/4 not integer	
4	40	10	1, 3 3, 1
3	47	47/4 not integer	
2	52	13	2, 3 3, 2
1	55	55/4 not integer	

The solutions are (1,2,6), (2,1,6) (1,3,4), (3,1,4), (2,3,2), (3,2,2).

3. Find n, l, m_l, and Z and the property being evaluated for the one-electron atom in the integral below,

$$-\frac{128\hbar^2}{3\pi a_0^5}\int_0^\infty\int_0^\pi\int_0^{2\pi} r\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}\,\sin\theta\,e^{-i\phi}\left\{\nabla^2\left[r\left(1-\frac{r}{a_0}\right)e^{-2r/a_0}\,\sin\theta\,e^{i\phi}\right]\right\}r^2\,dr\,\sin\theta\,d\theta\,d\phi$$

Solution: The integral has the form $\int \psi^* \hat{A}\psi\, d\tau$, where the integral is over all space and the operator $\hat{A}$ is $-\hbar^2\nabla^2$. This operator is the momentum squared operator $\hat{p}^2$, and the integral evaluates the $\boxed{\text{mean square momentum}}$. Examining the part of the integrand in square brackets, this is the original wavefunction (although the constants have been factored out). The ϕ-dependent term is $e^{i\phi}$, so $\boxed{m_l = 1}$. The angular part of the integral is first-order in $\sin\theta$, and the r^l term in the radial wavefunction is first-order, so $\boxed{l = 1}$. The Laguerre polynomial $1 - \frac{r}{a_0}$ in the radial wavefunction is first-order in r, so $n - l - 1 = 1$, and $\boxed{n = 3}$. Finally, to get the Z value, set the exponential e^{-2r/a_0} equal to $e^{-Zr/(na_0)}$. This gives $2 = Z/n$, so $\boxed{Z = 6}$.

4. Derive the r value of the maximum radial probability density when $l = n - 1$, as a function of Z and n. **Solution:** The $l = n - 1$ radial wavefunctions have no Laguerre polynomial ($n - l - 1 = 0$) so these have the relatively simple form

$$R_{n,n-1}(r) = A_{nl}\left(\frac{Zr}{a_0}\right)^{n-1} e^{-Zr/(na_0)}.$$

We take the general form for the radial probability density, $R(r)^2\, r^2$, plug in the expression above for $R_{n,n-1}(r)$, and then take the derivative to find the maximum:

$$R_{n,n-1}(r)^2\, r^2 = A_{nl}^2\left(\frac{Z}{a_0}\right)^{2(n-1)} r^{2(n-1)+2}\, e^{-2Zr/(na_0)} = A'\, r^{2n}\, e^{-2Zr/(na_0)} \qquad \text{combine constants}$$

$$\frac{d}{dr}\left[R_{n,n-1}(r)^2\, r^2\right] = A'\left[2nr^{2n-1}\, e^{-2Zr/(na_0)} - \left(\frac{2Z}{na_0}\right) r^{2n}\, e^{-2Zr/(na_0)}\right] = 0 \qquad d(uv) = udv - vdu$$

$$\left(\frac{2Z}{na_0}\right) r^{2n} = 2nr^{2n-1} \qquad \text{divide out } A',\ e^{-2Zr/(na_0)}$$

$$r = \frac{2n^2 a_0}{2Z} = \boxed{\frac{n^2}{Z} a_0}. \qquad \text{solve for } r$$