

## 1. 40 points.

- (a) Write the complex conjugate  $\psi^*$  of the wavefunction for the  $m_l = +2$  orbital of the  $3d$  subshell of  $C^{5+}$ . **Solution:** We need the wavefunction for  $n = 3$ ,  $l = 2$  (because this is a  $d$  orbital),  $m_l = -2$  (because this is the complex conjugate), and  $Z = 6$  (because the atom is carbon):

$$\psi_{322}(r, \theta, \phi)^* = R_{32}(r) Y_2^{-2}(\theta, \phi) = \left[ \frac{2\sqrt{2}}{81\sqrt{15}} \left(\frac{6}{a_0}\right)^{3/2} \left(\frac{6r}{a_0}\right)^2 e^{-2r/a_0} \right] \left[ \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\phi} \right].$$

- (b) Circle the number for each **allowed** transition of a one-electron atom in the following list (regardless of whether absorption or emission takes place). **Solution:** We are applying the selection rule  $\Delta l = \pm 1$ , so any transition where  $l$  changes by one unit is okay. There is no strict selection rule on  $n$ .

- i.  $2s \rightarrow 1s$  ( $\Delta l = 0$ )
- ii.  $2s \rightarrow 3s$  ( $\Delta l = 0$ )
- iii.  $2s \rightarrow 3p$  ( $\Delta l = 1$ )
- iv.  $2s \rightarrow 3d$  ( $\Delta l = 2$ )
- v.  $2s \rightarrow 4s$  ( $\Delta l = 0$ )
- vi.  $2s \rightarrow 4p$  ( $\Delta l = 1$ )
- vii.  $5s \rightarrow 4p$  ( $\Delta l = 1$ )
- viii.  $4f \rightarrow 3d$  ( $\Delta l = -1$ )

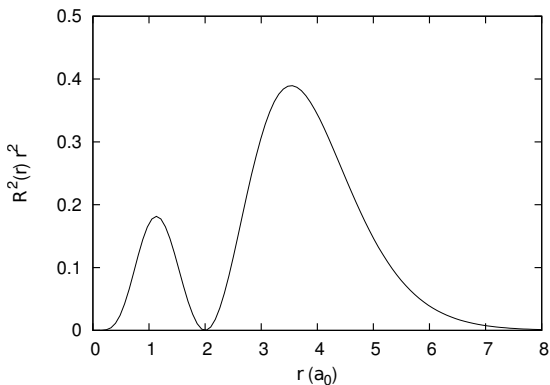
- (c) Write the Hamiltonian for  $B^{2+}$ . Use  $\nabla^2$  to represent the Laplacian operator. **Solution:** This is a three-electron system with  $Z = 5$ , so we'll have three electron kinetic energy terms, three terms for the electron-nucleus interaction, and three electron-electron repulsion terms (for  $r_{12}$ ,  $r_{23}$ , and  $r_{13}$ ):

$$\hat{H} = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{5e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} \right) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} + \frac{1}{r_{23}} + \frac{1}{r_{13}} \right).$$

- (d) Write the ground state electron configuration for the  $S^{2-}$  anion. **Solution:** This is an 18-electron system ( $Z = 16$  plus 2 for the  $-2$  charge), so we fill the orbitals in order until we've used up all the electrons:  $1s^2 2s^2 2p^6 3s^2 3p^6$ . You might also recognize this as the sulfide anion, relatively stable because its electron configuration fills the  $n = 3$  shell.

2. A the single electron in an atomic ion has orbital wavefunction  $\psi_{n,l,m_l}(r, \theta, \phi)$ . The unnormalized imaginary part of the angular wavefunction of  $\psi_{n,l,m_l}(r, \theta, \phi)$  is equal to  $-i \sin \theta \cos \theta \sin \phi$ . The radial probability density is graphed below. Give the following values, and show or briefly explain how you determined each:

- (a)  $n = 4$
- (b)  $l = 2$
- (c)  $m_l = -1$
- (d)  $Z = 6.$



**Solution:** The Legendre polynomial  $(\sin \theta \cos \theta)$  is second order, so  $l = 2$ . The imaginary part of  $e^{-m_l \phi}$  is  $i \sin(m_l \phi)$ . Here since we have the factor of  $-i \sin \phi$  indicates that  $m_l = -1$ . (If we're not sure, we can also just check the table of angular wavefunctions. Only the  $l = 2, |m_l| = 1$  functions have this  $\theta$ -dependence, but we'd still have to work out the sign of  $m_l$ .) Any nodes in the radial wavefunction are indicated by the positions between 0 and  $\infty$  at which the radial probability density is equal to zero. There is only one such point, at  $r = 2a_0$ , so the number of radial nodes is one, and  $n - l - 1 = 1$ . Therefore  $n = l + 2 = 4$ . Finally, the radial node in the  $4d$  subshell will appear where the Laguerre polynomial is equal to zero:

$$\left(1 - \frac{Zr}{12a_0}\right) = 1 - \frac{Z(2a_0)}{12a_0} = 1 - \frac{Z}{6} = 0 \quad Z = 6.$$

3. The Bohr model of the atom predicts that  $r_n = \frac{n^2}{Z}a_0$ .

- (a) Find the value of  $1/r$  for a  $4f$  electron, according to the Bohr model of the hydrogen atom. Leave the answer in terms of  $a_0$ . **Solution:**

$$\frac{1}{r_{n=4}} = \frac{Z}{n^2 a_0} = \boxed{\frac{1}{16a_0}}.$$

- (b) Now find the quantum mechanical expectation value  $\langle 1/r \rangle$  for the same  $4f$  electron. **Solution:** We use the average value theorem to solve this, using the radial

wavefunction for  $n = 4, l = 3$ :

$$\begin{aligned}
 \left\langle \frac{1}{r} \right\rangle &= \int_0^\infty R_{43}(r)^2 \left( \frac{1}{r} \right) r^2 dr = \int_0^\infty \left[ \frac{1}{768\sqrt{35}} \left( \frac{Z}{a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right)^3 e^{-r/(4a_0)} \right]^2 \left( \frac{1}{r} \right) r^2 dr \\
 &= \frac{1}{768^2 \cdot 35} \left( \frac{1}{a_0} \right)^3 \int_0^\infty \left[ \left( \frac{r}{a_0} \right)^6 e^{-2r/(4a_0)} \right] \left( \frac{1}{r} \right) r^2 dr \\
 &= \frac{1}{768^2 \cdot 35} \left( \frac{1}{a_0} \right)^3 \left( \frac{1}{a_0} \right)^6 \int_0^\infty r^7 e^{-r/(2a_0)} dr \\
 &= \frac{1}{768^2 \cdot 35} \left( \frac{1}{a_0} \right)^9 (7!)(2a_0)^8 = \frac{7! \cdot 2^8}{768^2 \cdot 35} \frac{1}{a_0} = \boxed{\frac{1}{16a_0}}.
 \end{aligned}$$

4. (a) Find  $L$  for an electron in the  $2p$  subshell.  $\hbar\sqrt{1(2)} = \boxed{\sqrt{2}\hbar}$ .  
 (b) Find  $L$  for an electron in the  $3d$  subshell.  $\hbar\sqrt{2(3)} = \boxed{\sqrt{6}\hbar}$ .  
 (c) Find  $\Delta L - \hbar$  for the  $2p \rightarrow 3d$  subshell. **Solution:**

$$\Delta L - \hbar = (\sqrt{6} - \sqrt{2} - 1) \hbar = (2.449 - 1.414 - 1) \hbar = \boxed{0.035\hbar}.$$

For  $l \geq 1$ , the error in setting the photon angular momentum equal to  $\hbar$  is less than 4%. This error decreases as  $l$  increases.

- (d) Explain the origin of this error. If you remember the explanation I offered in class, you can use that. Otherwise, a better explanation is available if you know: (i) the photon has a linear momentum  $p = h/\lambda$ , and (ii) like  $p$  and  $x$ , there is an uncertainty principle for  $p$  and  $L$ . **Solution:** My explanation was that the angular momentum for the interaction between two particles (such as the atom and the photon in this case) is conserved if we treat the system as a two-particle quantum system, rather than looking at each particle independently, and this is how we would properly treat the quantum mechanics of the problem. This is correct, but doesn't explain how the photon angular momentum seems to adjust itself to fit different atomic transitions. For example, the  $1s \rightarrow 2p$  transition requires the photon to contribute  $\sqrt{2}\hbar = 1.414\hbar$ , which is more than we need for the  $2p \rightarrow 3d$  transition in the problem.

The better answer is that the angular momentum  $L$  of the photon is intrinsically uncertain if the linear momentum  $p$  is known. The relationship is important because the linear momentum of the photon  $h/\lambda$  is directly related to the photon energy:  $E_{\text{photon}} = hc/\lambda = pc$ . If we know the transition energy, then  $E_{\text{photon}}$  is well-defined, and the angular momentum of the photon must be uncertain. That means that some photon-atom interactions will always be able to satisfy the angular momentum conservation, while others will not.