

# Physics 471 – Fall 2008

## Homework #12, due Wednesday, December 3

1. [4] Griffiths problem 4.10.
2. [4] Griffiths problem 4.13.
3. [2] Griffiths problem 4.16
4. [2] a) A hydrogen atom emits a photon of energy  $1.89 \text{ eV} = \frac{5}{36} Ry$ , and ends up in a 2p state ( $n=2, l=1$ ). What are the possible states the atom could have been in before it emitted the photon? When an atom emits a photon, the value of  $l$  for the atomic state changes by  $\pm 1$ . You can use the traditional names for the states (such as 2p) or you can label them by their quantum numbers  $n$  and  $l$ . For each state on your list, state its degeneracy.  
  
b) A physicist measures the energy of the hydrogen atom in part (a) to confirm that the atom is in a 2p state with energy  $-Ry/4$ , then he measures the z-component of angular momentum,  $\hat{L}_z$ , and obtains the result  $-\hbar$ . After that his colleague measures the atom's energy again. What are the possible results she will get, and with what probabilities? Explain how you got your answer. You may assume that the atom does not emit or absorb a photon during the experiment.
5. [8] To understand Chemistry, we need to work with atomic orbitals that are neither eigenstates of  $\hat{L}_z$  nor of  $\hat{L}^2$ . For example, consider the three 2p states ( $n=2, l=1$ ):  $|2,1,1\rangle, |2,1,0\rangle, |2,1,-1\rangle$ .  
  
a) [1] Write down the three wavefunctions,  $\Psi_{211}, \Psi_{210}, \Psi_{21-1}$  in spherical coordinates, using Tables 4.3 and 4.7 in Griffiths.  
  
b) [2] Construct the following orthonormal linear combinations.
$$\Psi_{2px} \equiv \frac{1}{\sqrt{2}}(\Psi_{21-1} - \Psi_{211}), \quad \Psi_{2py} \equiv \frac{i}{\sqrt{2}}(\Psi_{21-1} + \Psi_{211}), \quad \Psi_{2pz} \equiv \Psi_{210}$$
Write the wavefunctions in rectangular coordinates, to see why I named them the way I did. (You may leave the exponentials in spherical coordinates.) Show that  $|\Psi_{2px}|^2 + |\Psi_{2py}|^2 + |\Psi_{2pz}|^2$  is spherically symmetric.  
  
c) [1] Carbon is a most amazing atom. In the form of graphite, each carbon atom is strongly bonded to 3 neighbors in a plane, and weakly bonded to the atoms above and below the plane. The atoms in the plane form a honeycomb lattice. We can create atomic orbitals that point in 3 directions separated by  $120^\circ$  in a plane by taking linear combinations of the 2s ( $l=0$ ) and any two of the 2p ( $l=1$ ) orbitals. The new orbitals are called “sp<sup>2</sup> hybrid” orbitals. We'll use the orbitals

$\Psi_{2s}, \Psi_{2px}, \Psi_{2py}$  to form  $sp^2$  orbitals in the x-y plane, while leaving  $\Psi_{2pz}$  as the orbital pointing out of the plane. Let's name the 3 new orbitals:  $\Psi_1, \Psi_2, \Psi_3$ . We'll construct them using the following principles:

- i) They must be orthonormal.
- ii) They must all contain the same "amount" of  $\Psi_{2s}$ , which is spherically symmetric.
- iii) Choose  $\Psi_a$  pointing along the +y axis. Then  $\Psi_b$  and  $\Psi_c$  will point into the 3<sup>rd</sup> and 4<sup>th</sup> quadrants, respectively, and are mirror images of each other reflected through the y-axis.

The constraints ii) and iii) can be represented by the following linear combinations:

$$\Psi_1 = a\Psi_{2s} + b\Psi_{2py}$$

$$\Psi_2 = a\Psi_{2s} + c\Psi_{2px} - d\Psi_{2py}$$

$$\Psi_3 = a\Psi_{2s} - c\Psi_{2px} - d\Psi_{2py}$$

Write down a system of four equations for the coefficients a, b, c, and d, based on the condition that the new set of states  $\Psi_1, \Psi_2, \Psi_3$  must be orthonormal.

d) [2] Assume that the coefficients a, b, c, and d are real. Solve your system of equations to find numerical values for a, b, c, and d. Make a rough sketch of the new orbitals in the x-y plane.

e) [2] In the form of diamond, each carbon atom is strongly bonded to 4 neighbors. The four bonds are all equally distant from each other, with an angle of  $109.5^\circ$  between any two bonds. The four orbitals used to make these bonds are called  $sp^3$  hybrid orbitals, because they are linear combinations of the s-state and three p-states. With a little knowledge of geometry, it is not hard to guess that the four  $sp^3$  orbitals are of the following form, where I have chosen the first one to point along the z-axis:

$$\Psi_1 = a\Psi_{2s} + b\Psi_{2pz}$$

$$\Psi_2 = a\Psi_{2s} - c\Psi_{2pz} + d\Psi_{2py}$$

$$\Psi_3 = a\Psi_{2s} - c\Psi_{2pz} - \frac{1}{2}d\Psi_{2py} + \frac{\sqrt{3}}{2}d\Psi_{2px}$$

$$\Psi_4 = a\Psi_{2s} - c\Psi_{2pz} - \frac{1}{2}d\Psi_{2py} - \frac{\sqrt{3}}{2}d\Psi_{2px}$$

Follow a similar procedure to what you did in parts b) and c), i.e. write down a set of four equations for the four unknown constants, a, b, c, and d. Then assume they are real, and solve your equations.

Some of you may have noticed that the coefficients b, c, and d you found in parts (d) and (e) look just like the components of the corresponding vectors in real space. But there is a difference, in that you can't find 3 orthogonal vectors in a plane, nor can you find 4 orthogonal vectors in 3-dimensional space. You were able to do it here because of the additional quantum state you used, namely the spherically symmetric s-state.