V25.0109: General Chemistry I (Honors)

Problem set #5 Due 10/23

Practice problems from Chapter 3: 7,9,10,11,12,17,21

Graded problems

1. Recall that the appropriate quantum state for two identical particles in a one-dimensional box that spans the range $x = 0$ to $x = L$ is

$$\Psi_{n_1 n_2}(x_1, x_2) = \frac{1}{\sqrt{2}}\left[\psi_{n_1}(x_1)\psi_{n_2}(x_2) - \psi_{n_1}(x_2)\psi_{n_2}(x_1)\right]$$

where n_1 and n_2 are the two quantum numbers needed to characterize the energy levels $E_{n_1 n_2}$ and $\psi_{n_1}(x)$ and $\psi_{n_2}(x)$ are properly normalized particle-in-a-box wave functions. This state arises because if the particles are identical, then we cannot tell apart the state in which particle 1 is in the state with quantum number n_1 and particle 2 is in the state with quantum number n_2 and the state in which we interchange the particles and place particle 2 in the state with quantum number n_1 and particle 1 in the state with quantum number n_2. Note that only two states can be constructed by particle interchanges. In constructing the second term above, note that we only interchanged the coordinates x_1 and x_2 but kept the single-particle wave functions in the same order $\psi_{n_1}\psi_{n_2}$.

In this problem, you will construct the analogous three-particle wave function $\Psi_{n_1 n_2 n_3}(x_1, x_2, x_3)$. The wave function must be a sum of terms containing products of three single-particle wave functions, e.g. $\psi_{n_1}(x_1)\psi_{n_2}(x_2)\psi_{n_3}(x_3)$,...

   a. How many states can be constructed by particle interchanges?

   b. The sign of each term in the wave function is determined from the following rule: Start with the term $\psi_{n_1}(x_1)\psi_{n_2}(x_2)\psi_{n_3}(x_3)$ in which the coordinates appear in the order x_1, x_2, x_3. A new term in the wave function is obtained by interchanging the coordinates but not the order in which the single-particle wave functions are multiplied. That is, ψ_{n_1} is first, followed by ψ_{n_2} and then ψ_{n_3}, however, the arguments of the functions are different in each term according to the above rule. Each time such an interchange of coordinates is made, we have to change the sign of that term. For example, to generate a term of the form $\psi_{n_1}(x_2)\psi_{n_2}(x_1)\psi_{n_3}(x_3)$, we need just one exchange of x_1 and x_2 so this term would be added to the total wave function with a minus sign. Using this rule, determine the complete three-particle wave function. Make sure that your wave function is properly normalized!

   c. Show that your wave function vanishes if any two of the coordinates x_1, x_2 or x_3 are equal to each other.

   d. Show that your wave function vanishes if any two of the quantum numbers n_1, n_2 or n_3 are equal to each other.

   e. Determine the ground-state wave function and ground-state energy for the system.

   f. How many terms would you expect a four-particle wave function to have?

   g. How many terms would you expect an N-particle wave function to have?

2. a. For an electron in a three-dimensional box $x \in [0, L]$, $y \in [0, L]$, $z \in [0, L]$, what is the probability that a measurement of the particle's position yields $x \in [0, L/4]$, $y \in [0, L/4]$, $z \in [0, L/4]$ when the electron is in a state with $n_x = 2$, $n_y = 1$, and $n_z = 1$? Provide a rationalization for your answer.

b. For an electron in a two-dimensional box $x \in [0, L]$ and $y \in [0, L]$, what is the probability that a measurement of the particle's position yields $x \in [0, L/4]$ and $y \in [0, L/4]$ when the electron is in a state with $n_x = 2$ and $n_y = 1$? Provide a rationalization for your answer.

c. Now consider two electrons in a one-dimensional box between 0 and L. What is the probability that a simultaneous measurement of the positions of both particles yields values $x_1 \in [0, L/4]$ and $x_2 \in [0, L/4]$ when the electron is in a state with $n_1 = 2$ and $n_2 = 1$? Compare your answer to that of part b and explain any differences.

d. Suppose we place two *different* particles in the box of part c. Let one particle have a mass m and the other a mass M. Write down expressions for the allowed wave functions and energies of this system and explain your answer.

3. When more then one allowed wave function exists for a given allowed energy level, that energy level is said to be a *degenerate* energy level. If there are p allowed wave functions, then the energy level is referred to as p-fold degenerate. Determine the value of p for the following casees:

   a. A particle in a two-dimensional box with energy $\hbar^2\pi^2/(mL^2)$.
   b. A particle in a two-dimensional box with energy $5\hbar^2\pi^2/(2mL^2)$.
   c. A particle in a two-dimensional box with energy $4\hbar^2\pi^2/(mL^2)$.
   d. A particle in a three-dimensional box with energy $3\hbar^2\pi^2/(mL^2)$.
   e. Two particles in a one-dimensional box with energy $5\hbar^2\pi^2/(2mL^2)$.
   f. The electron in a hydrogen atom with energy $E_n = -1/n^2$ Ry (determine a general formula in terms of n).

4. *How far away from the nucleus is the electron?* For an electron in the $n = 2$, $l = 1$, $m = 0$ state of a hydrogen atom, what is the probability that measurement of the electron's distance from the nucleus will yield a value $r \geq ka_0$, where a_0 is the Bohr radius and k is an integer, $k = 0, 1, 2, \ldots.$ Determine the probability for each set of quantum numbers as a function of k and sketch a plot of each probability as a function of increasing k. What should the probability be when $k = 0$ in both cases?