Name____________________________________ Student #____________________________

Quiz 2
CHEM 3PA3; Fall 2018

This quiz has 6 problems worth 16 points each. There are 4 "free" bonus points.

Consider electron(s) confined to a cubic box with side *a*. I.e.,

$$V(x,y,z) = \begin{cases} 0 & 0 \le x,y,z \le a \\ +\infty & \text{otherwise} \end{cases}$$

1. **Write the expression for the ground-state energy of one electron in a cubic box.**

2. **Write the expression for the ground-state wavefunction of one electron in a cubic box.**

3. **Write the expression for energy of the first excited state of one electron in a cubic box.**

4. **What is the degeneracy of the first excited state of one electron in a cubic box.**

5. **What is the ground-state energy for four electrons in a cubic box, assuming that the electron-electron repulsion between the electrons can be entirely neglected.**

6. **Write a (Slater determinant) wavefunction for four electrons in a cubic box. You can use a shorthand like $\psi_{n_x n_y n_z}(x,y,z)$ to denote the orbitals.**

Bonus (5 pts) What is the degeneracy of the ground-state energy for four electrons in a cubic box, assuming that the electron-electron repulsion between the electrons can be entirely neglected.

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Quiz 2
CHEM 3PA3; Fall 2018

This quiz has 6 problems worth 17 points each. There are 2 "free" bonus points.

Consider electron(s) confined to a cubic box with side a. I.e.,

$$V(x,y,z) = \begin{cases} 0 & 0 \le x,y,z \le a \\ +\infty & \text{otherwise} \end{cases}$$

1. Write the expression for the ground-state energy of one electron in a cubic box.

By separation of variables, the energy eigenvalues are the sum of the energies in the three different directions,

$$E_{n_x n_y n_z} = \frac{h^2 n_x^2}{8ma^2} + \frac{h^2 n_y^2}{8ma^2} + \frac{h^2 n_z^2}{8ma^2} = \frac{h^2 \left(n_x^2 + n_y^2 + n_z^2\right)}{8ma^2}$$

The ground state is associated with the quantum numbers $n_x = n_y = n_z = 1$ and so, substituting into this expression, we have

$$E_0 = E_{111} = \frac{3h^2}{8ma^2}$$

2. Write the expression for the ground-state wavefunction of one electron in a cubic box.

By separation of variables, the eigenfunctions are the products of the eigenfunctions for the three different directions,

$$\Psi_{n_x n_y n_z}(x,y,z) = \left[\sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right)\right]\left[\sqrt{\frac{2}{a}} \sin\left(\frac{n_y \pi y}{a}\right)\right]\left[\sqrt{\frac{2}{a}} \sin\left(\frac{n_z \pi z}{a}\right)\right] = \frac{2\sqrt{2}}{a^{3/2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right)$$

The ground state is associated with the quantum numbers $n_x = n_y = n_z = 1$ and so, substituting into this expression, we have

$$\Psi_0(x,y,z) = \Psi_{111}(x,y,z) = \frac{2\sqrt{2}}{a^{3/2}} \sin\left(\frac{\pi x}{a}\right) \sin\left(\frac{\pi y}{a}\right) \sin\left(\frac{\pi z}{a}\right)$$

3. Write the expression for energy of the first excited state of one electron in a cubic box.

The first excited state can be formed by choosing $n_x = 2, n_y = n_z = 1$ or $n_y = 2, n_x = n_z = 1$ or $n_z = 2, n_x = n_y = 1$. The energy is thus,

$$E_1 = E_{211} = \frac{h^2 \left(2^2 + 1^1 + 1^2\right)}{8ma^2} = \frac{6h^2}{8ma^2} = \frac{3h^2}{4ma^2}$$

4. What is the degeneracy of the first excited state of one electron in a cubic box.

There are three choices of quantum numbers with the same energy for the first excited state, so it is a three-fold degeneracy. If you include the two choices of electron spin there are a total of six degenerate states.

5. What is the ground-state energy for four electrons in a cubic box, assuming that the electron-electron repulsion between the electrons can be entirely neglected.

We put 2 electrons in the $n_x = n_y = n_z = 1$ state and 2 electrons in any of the degenerate states with quantum numbers like $n_x = 2, n_y = n_z = 1$. The ground-state energy for four electrons is therefore

$$E_{\text{4-electrons}} = E_1 \cdot 2 + E_{211} \cdot 2 = \frac{3h^2}{8ma^2} \cdot 2 + \frac{6h^2}{8ma^2} \cdot 2 = \frac{18h^2}{8ma^2} = \frac{9h^2}{4ma^2}$$

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6. Write a (Slater determinant) wavefunction for four electrons in a cubic box.

$$\Psi = \frac{1}{\sqrt{4!}}\begin{vmatrix} \psi_{111}(\mathbf{r}_1)\alpha(1) & \psi_{111}(\mathbf{r}_1)\beta(1) & \psi_{211}(\mathbf{r}_1)\alpha(1) & \psi_{211}(\mathbf{r}_1)\beta(1) \\ \psi_{111}(\mathbf{r}_2)\alpha(2) & \psi_{111}(\mathbf{r}_2)\beta(2) & \psi_{211}(\mathbf{r}_2)\alpha(2) & \psi_{211}(\mathbf{r}_2)\beta(2) \\ \psi_{111}(\mathbf{r}_3)\alpha(3) & \psi_{111}(\mathbf{r}_3)\beta(3) & \psi_{211}(\mathbf{r}_3)\alpha(3) & \psi_{211}(\mathbf{r}_3)\beta(3) \\ \psi_{111}(\mathbf{r}_4)\alpha(4) & \psi_{111}(\mathbf{r}_4)\beta(4) & \psi_{211}(\mathbf{r}_4)\alpha(4) & \psi_{211}(\mathbf{r}_4)\beta(4) \end{vmatrix}$$

In general we would expect to occupy different spatial orbitals with the last two electrons, but that is an effect of electron-electron repulsion, which we are (by assumption) neglecting here.

Bonus (5 pts) What is the degeneracy of the ground-state energy for four electrons in a cubic box, assuming that the electron-electron repulsion between the electrons can be entirely neglected.

There are three degenerate spatial orbitals, $\psi_{211}(\mathbf{r}),\psi_{121}(\mathbf{r}),\psi_{211}(\mathbf{r})$ and each of these can hold up to two electrons. Said differently, there are six degenerate spin-orbitals, $\psi_{211}(\mathbf{r}_1)\alpha(1),\psi_{121}(\mathbf{r}_1)\alpha(1),\psi_{211}(\mathbf{r}_1)\alpha(1),\psi_{211}(\mathbf{r}_1)\beta(1),\psi_{121}(\mathbf{r}_1)\beta(1),\psi_{211}(\mathbf{r}_1)\beta(1)$. There are two electrons that we need to place in these orbitals (the other two electrons always occupying the $\psi_{111}(\mathbf{r})$ orbital). Since electron-electron repulsion is being neglected, all possible ways of placing the two electrons into the 6 spin-orbitals have the same energy. So there are 6 choose 2 ways to place the electrons, and the degeneracy is

$$\text{degeneracy} = \binom{6}{2} = \frac{6\cdot 5}{2} = 15$$