Physikalische Chemie III für Lehramt

Übungsblatt 8

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The following questions are from the book *Modern Physics* by Kenneth S. Krane.

1 Pauli exclusion principle

Simply stated, the Pauli exclusion principle is as follows:

No two electrons in a single atom can have the same set of quantum numbers (n, l, m_l, m_s).

Using this principle, answer the following questions.

a. A certain atom has six electrons in the $3d$ level.

- What is the *maximum* possible *total* m_l for the six electrons, and what is the *total* m_s in that configuration?
- What is the maximum possible total m_s for the six electrons, and what would be the largest possible total m_l in that configuration?

b. Copper has the electronic configuration $[\mathrm{Ar}]4s^1\,3d^{10}$ in its ground state. By adding a small amount of energy (about 1 eV) to a copper atom, it is possible to move one of the $3d$ electrons to the $4s$ level and change the configuration to $[\mathrm{Ar}]4s^2\,3d^9$. By adding still more energy (about 5 eV), one of the $3d$ electrons can be moved to the $4p$ level so that the configuration becomes $[\mathrm{Ar}]4s^1\,3d^9\,4p^1$.

- For each of these configurations, determine the *maximum* value of the *total* m_s of the electrons.

2 Addition of angular momenta

Suppose that we have an atom with two electrons outside of filled subshells. These electrons have quantum numbers $(n_1, l_1, m_{l1}, m_{s1})$ and $(n_2, l_2, m_{l2}, m_{s2})$. The total orbital angular momentum of the atom is determined by the vector sum of the orbital angular momenta of the two electrons: $\vec{L} = \vec{l}_1 + \vec{l}_2$. These vectors do not add like ordinary vectors, but have special addition rules associated with quantized angular momentum. These rules enable us to find L and its associated magnetic quantum number M_L.

1. The maximum value of the total orbital angular momentum quantum number is

$$L_{\max} = l_1 + l_2.$$

2. The minimum value of the total orbital angular momentum quantum number is

$$L_{\min} = |l_1 - l_2|.$$

3. The permitted values of L range from $L_{\min}$ to $L_{\max}$ in integer steps:

$$L = L_{\min}, L_{\min} + 1, L_{\min} + 2, \ldots, L_{\max}.$$

4. The z component of the total angular momentum vector is found from the sum of the z components of the individual vectors. Hence, in terms of the magnetic quantum numbers:

$$M_L = m_{l1} + m_{l2}.$$

   The permitted values of the total magnetic quantum number M_L range from $-L$ to $+L$ in integer steps:

$$M_L = -L, -L + 1, \ldots, -1, 0, 1, \ldots, L - 1, L.$$

An identical set of rules holds for coupling the spin angular momentum vectors to give the total spin angular momentum. For two electrons, each of which has $s = 1/2$, the total spin quantum number S can be 0 or 1.

All filled subshells have $L = 0$ and $S = 0$, so we don't need to consider filled subshells in analyzing the angular momentum of an atom.

- Find the possible values of the total orbital and spin quantum numbers for carbon.

3 Hund's rules

The two $2p$ electrons of carbon can combine to give $L = 0, 1,$ or 2 and $S = 0$ or 1. The ground state of carbon will be identified by only one particular choice of L and S. How do we know which of these combinations will be the ground state? The rules for finding the ground state quantum numbers are known as *Hund's rules*:

1. First find the maximum value of the total spin magnetic quantum number M_S consistent with the Pauli principle. Then

$$S = M_{S,\max}.$$

2. Next, for that M_S, find the maximum value of M_L consistent with the Pauli principle. Then

$$L = M_{L,\max}.$$

- Use Hund's rules to find the ground-state quantum numbers of carbon.