1320: Rules for how electrons fit into atomic orbitals of multi-electron atoms

(There is a simple rule for how the electrons of an atom in the ground state are arranged. We will explain the rule and the reason.)

Key words: Electron spin; α spin; β spin; Pauli principle; Hund's rule; Bose particles, fermions; spin quantum number; total spin quantum number; magnetic moment; degeneracy; spin multiplicity; electron arrangement

First, we need to explain electron spin, Pauli's (Wolfgang Pauli (1900-1958), Austria) exclusion principle, and Hund's rule (details about Hund are unknown) (this explanation will be long).

If we consider electrons as simple particles in classical mechanics, it seems possible to pack several electrons into the same state (for example, one of the atomic orbitals), but in the microscopic world, this is not always the case. It is known that there are two types.

[Bose particles and fermions]

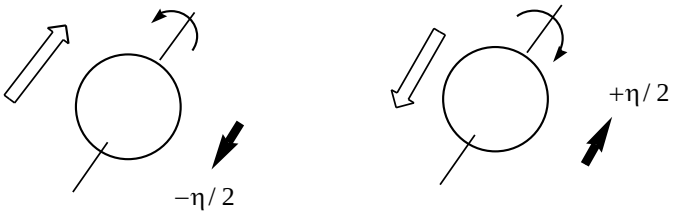
There are two types of particles: one type in which multiple particles can occupy the same state and is called a boson particle. Examples of boson particles include photons, pions, and helium atoms. The other type is called a fermion, in which more than one of the same particles cannot exist in the same state. Bosons and fermions are properties inherent to particles.

Electrons belong to fermions and are particles that avoid having more than one in the same state (we don't know why electrons are fermions). The state here includes not only the spatial state (the orbital χ that the electron occupies) but also the state of the electron itself. In addition to electrons, protons and neutrons are also fermions..

[Electron spin and spin quantum number]

It is known that there are two types of states (internal states) of an electron itself. In the classical model, this corresponds to the rotation of the electron, so it is called spin. Since the concept is easy to grasp, we will explain it using the classical model.

Let's assume that an electron is a "sphere" for the time being (Figure 1). The magnitude of the rotational moment has been measured and it is known to have values of $+\hbar/2$ and $-\hbar/2$. One of these is called an α spin electron and the other is called a β spin electron. $\hbar$ is the value of Planck's constant divided by 2π, and has a quantity of 1.054572×10^{-34}J·s. The coefficients 1/2 and -1/2 of $\hbar$ are called the spin quantum numbers.



α spin electron β spinelectron

Figure 1. Direction of the rotational moment (black arrow) and magnetic moment (white arrow) of an electron

[Pauli's principle]

When including spin states, a single orbital can have up to two fermion electrons with different spins. This is called Pauli's exclusion principle.

Atomic orbitals χ have spatial coordinates (*x*, *y*, *z* in Cartesian coordinates; *r*, *θ*, *ϕ* in polar coordinates), and spin has spin coordinates that represent the spin state of the electron. Since these phenomena are independent, the state of the electron can be expressed as the product of their functions. For example, when electron 1 has a α spin and occupies χ, it is expressed as χ (1) α (1), and when electron 2 has a β spin and occupies □, it is expressed as χ (2) β (2).

[Magnetic moment of electron spin]

As shown in Figure 1, a charged sphere generates magnetic field lines (magnetic momentum) as it rotates. Therefore, when a magnetic field is applied, an energy difference occurs.

In Figure 2, **a** and **b** show the orbits as horizontal bars or circles, and the electron spin as up and down arrows. The up arrows are usually used to represent α spin electrons. On the other hand, the expressions **c** and **d** are used when electron spin is not discussed.

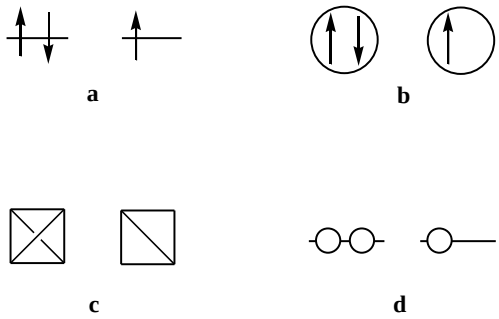


Figure 2. How electrons are depicted when occupying orbitals.

[Hund's rule]

Let's consider how multiple electrons enter degenerate (degeneration: multiple states with the same energy level) atomic orbitals. Taking Pauli's principle into account, Figure 3 shows the possible

combinations for two electrons entering two degenerate orbitals (χ_a, χ_b).

States **A**, **A'** and **B**, **B'** are all considered to have equal energy (because electrons are indistinguishable). Similarly, the energies of **C** and **D** are equal.

E and **F** will have equal energy unless a magnetic field is applied to these systems. When there is no magnetic field, the question becomes which of states **A**, **C**, and **E** has the lowest energy.

It is easy to guess that state **A** has the highest energy. This is because two electrons occupy the same orbital, and therefore the probability that electrons 1 and 2 are close to each other is high, resulting in a large repulsive energy (positive value) between the electrons.

Comparing **C** and **E**, the only difference between them is the spin of the electrons. The shape and size of the orbital are not clearly defined, and strictly speaking, the size of the orbital is infinite. For this reason, "a little" of the electrons in orbital χ_a is near orbital χ_b. If an electron in an χ_a orbital and an electron in an χ_b orbital are close to each other, the repulsive energy between the electrons will naturally be greater, and the energy will be higher accordingly. This possibility is large in state **C**, but small in state **E**. Because the two electrons have the same spin, Pauli's principle makes it difficult for electrons to move from χ_a to χ_b, or from χ_b to χ_a. This reduces the repulsion between electrons, and the orbital energy is lower. Therefore, the **E** electron configuration has the lowest energy.

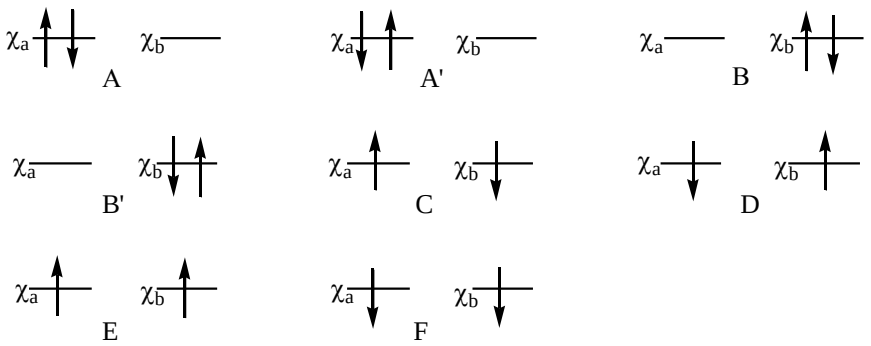


Figure 3. Possibilities when two electrons enter two degenerate orbitals.

[Total spin quantum number]

Each electron has a quantum number of +1/2 or -1/2. Consider the sum of the spin quantum numbers of the individual electrons. If two electrons both have α spin, then 1/2 + 1/2 = 1. If one is α and the other is β spin, then 1/2 - 1/2 = 0. If both have β spin, then -1/2 - 1/2 = -1. The absolute value of the sum of the spin quantum numbers of the individual electrons is called the total spin quantum number.

$$S = |s_1 + s_2 + \cdots + s_n| \equiv |\sum_{i=1}^{n} s_i|$$

The way electrons enter degenerate orbitals generally takes an electronic configuration that maximizes the total spin quantum number. This is called the Hund rule.

[Spin multiplicity]

In **1260**, there are 2*l*+1 magnetic states for azimuthal quantum number *l*, and these are represented by magnetic quantum number m. Similarly, there are 2*S*+1 magnetic states for total spin quantum number *S* (when a magnetic field is applied, it separates into 2*S*+1 different energy states). This number is called spin multiplicity. The numbers 1, 2, 3, ... are called singlet state, doublet state, triplet state, ... respectively. For example, a hydrogen atom has one electron, so *S*=1/2, and the spin multiplicity is 2×(1/2)+1=2, which is a doublet state. In the lowest energy state (called the ground state), He has two electrons with reversed spins, so *S*=-1/2+1/2=0, and 2*S*+1 is 1, so it is in a singlet state.

[How electrons enter atomic orbitals]

Based on the above rules, the way electrons enter atomic orbitals in the ground state can be summarized as follows: (1) electrons occupy orbitals with lower energy levels, (2) up to two electrons can enter one atomic orbital, and (3) if there are multiple atomic orbitals with the same energy level, they will be entered so that the total spin quantum number is maximized. Following these rules, the electron configurations of H to Na in the periodic table are shown in Figure 4.

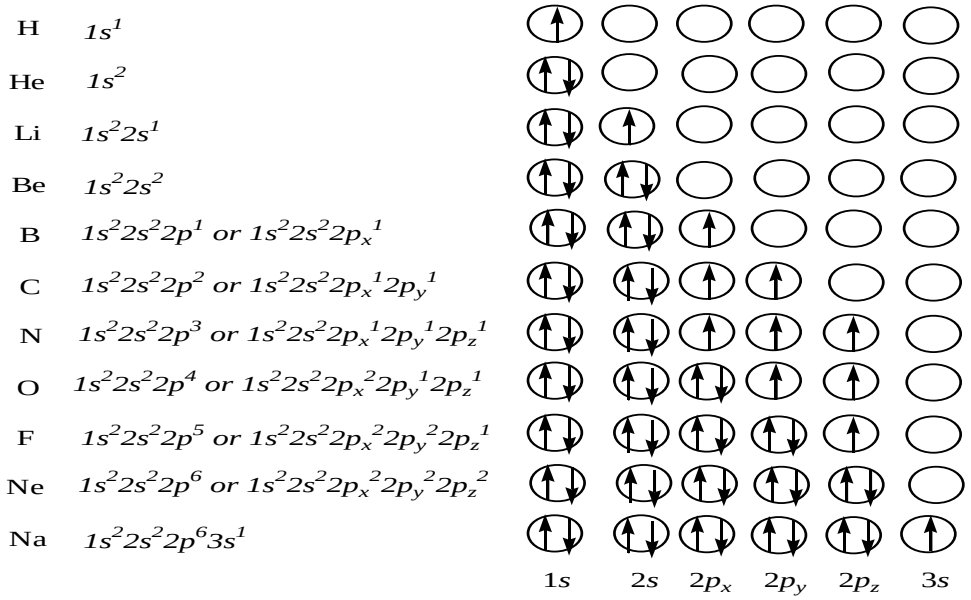


Figure 4. Electron configuration of a multi-electron atom.

As shown in the diagram above, when there is one electron in the 1*s* orbital it is represented by the symbol $1s^1$, and when there are two electrons it is represented by the symbol $1s^2$. The Li atom is $1s^2 2s^1$.