1310: Why are the energy levels of multi-electron atoms are separated by azimuthal and magnetic quantum numbers?

(The energy levels of hydrogen atom orbitals are determined only by the principal quantum number, but in multi-electron atoms, the azimuthal and magnetic quantum numbers also play a role. The reason is conceptually shown below.)

Key words: Differences in electron distribution between *s* and *p* orbitals; repulsion with inner shell *s* orbital electrons; relationship between force and energy

As mentioned in **1280**, the average distance from the nucleus to an electron ($\overline{r}$) is given by equation 1. The azimuthal quantum number (*l*) is involved. Even with the same principal quantum number, as the azimuthal quantum number increases, the distance from the nucleus decreases. For *s* orbitals, *l*=0, and for *p* orbitals, *l*=1, so if the principal quantum number is the same, an electron in a *p* orbital is closer to the nucleus than one in an *s* orbital. If this were the case, the energy level of the *p* orbital should be lower than that of an *s* orbital. However, the *s* orbital is lower. I will explain why.

$$\overline{r} = \frac{a_0 n^2}{z}\left\{\frac{3}{2} - \frac{l(l+1)}{2n^2}\right\} \tag{1}$$

Let's compare 2*s* electrons and 2*p* electrons (electrons in the 2*s* and 2*p* orbitals are called 2*s* and 2*p* electrons, respectively). First, we have already mentioned (**1300**) that when there is only one electron in a system, such as a hydrogen atom or He^+ or Li^{2+}, the 2*s* and 2*p* electron energies are equal. In other words, even if the average distance from the nucleus to the electron is different between the two, it does not affect the energy level (in the case of one electron).

However, when there are multiple electrons, there is repulsion between the electrons. Repulsion is the cause of raising the energy level. In this case, if there are inner shell electrons, the *s* electrons, which are less affected by the shielding effect, are lower than the *p* electrons. In general, the separation of energy levels is lower for the smaller azimuthal quantum number for the same principal quantum number. This fact can be understood qualitatively as follows.

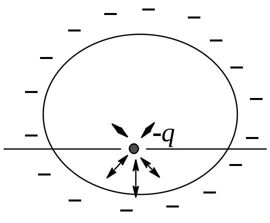

Figure 1. A charged particle covered with electric charges does not experience any force. The repulsion from below occurs because the distance between the charges is short, but the wall area is small, while the repulsion from above is small, but the wall area is large, so the two forces cancel each other out and become zero.

Let's say there is a particle with charge -*q* inside a sphere surrounded by a uniform charge, as shown in Figure 1. The question is what kind of force acts on that particle (forces are the source of energy!).

In conclusion, no force acts on the particle. The reason is that if we divide the particle's position into upper and lower parts, the charge on the upper part pushes the particle downward, and the charge on the lower part pushes the particle upward, and the sum of these forces is zero. Because no force acts, the Coulomb repulsion energy between the external charge and the particle's charge is also zero.

As shown in **1290**, some of the 2*s* atomic orbitals are inside the 1*s* orbitals. Electrons in these orbitals experience zero Coulomb repulsion energy from electrons in the 1*s* orbital. In contrast, there are fewer electrons in the 2*p* orbital inside the 1*s* orbital compared to the 2*s* orbital, so the Coulomb repulsion energy is greater. Therefore, the energy of the 2*s* orbital, which has less repulsion, is lower, and the energy of the 2*p*, which has more repulsion, is higher. For this reason, the larger the azimuthal quantum number, the greater the repulsion with inner *s* orbital electrons.