

7. Noncentral Electrostatic Interaction and Spin-Orbit Splitting in the LS coupling Approximation.

* In the central field approximation, the energy of an atom is completely determined by the assignment of the electron configuration, i.e., by the assignment of the values of n and l for all the electrons. To each electron configuration $n_1, l_1, n_2, l_2, n_3, l_3, \dots$ there correspond $2(2l_1+1) 2(2l_2+1) 2(2l_3+1) \dots$ states, differing by the values of the quantum numbers m_l and m_s , or in other words, by the mutual orientation of the orbital angular momenta and spins of the electrons.

* Attributing all these states to one and the same energy level of an atom is possible as long as we neglect that part of the electrostatic interaction between electrons which is not taken into account in a centrally symmetric approximation, and also spin-orbit magnetic interaction. In reality, both types of interaction always occur, which leads to splitting of the level $n_1, l_1, n_2, l_2, n_3, l_3, \dots$ into a number of sublevels. Joint consideration of both interactions is an extremely complex task. As a rule, therefore, one uses a considerably simplified approach in which one of the interactions is considered small in comparison with the other.

* When considering the noncentral electrostatic interaction and the magnetic interaction, the atomic Hamiltonian operator is given by

$$\hat{H} = \left\{ \sum_{i=1}^N \frac{\hat{p}_i^2}{2\mu} - \sum_{i=1}^N \frac{1}{4\pi\epsilon_0} \frac{ze^2}{r_i} + \sum_{i=1}^N U_i(r_i) \right\} \\ + \underbrace{\left[\sum_{i>j=1}^N \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_{i=1}^N U_i(r_i) \right]}_{\Delta \hat{H}_{ncE}} + \underbrace{\sum_{i=1}^N a(r_i) \vec{l}_i \cdot \vec{s}_i}_{\Delta \hat{H}_m}$$

where the first term is the Hamiltonian operator for the centrally symmetric field;

the second term is the non-central electrostatic interaction;

the third term is the electron magnetic interaction.

The 2nd and 3rd terms are usually the perturbation to the 1st term. Depending on the relative magnitude of the 2nd term and the 3rd term, different methods will be used to derive equations. If the 2nd and 3rd terms are comparable, we have to treat these two interactions together, which is very complicated. But we will consider two extreme cases.

The first one is the noncentral electrostatic interaction is much stronger than the magnetic interaction

$$\Delta \hat{H}_{ncE} \gg \Delta \hat{H}_m$$

In this case, neglect $\Delta \hat{H}_m$, but leave

$$\hat{H}_1 = \sum_{i=1}^N \left[\frac{\hat{p}_i^2}{2\mu} - \frac{1}{4\pi\epsilon_0} \frac{ze^2}{r_i} + U_i(r_i) \right] \\ + \left[\sum_{i>j=1}^N \frac{1}{4\pi\epsilon_0} \frac{e^2}{r_{ij}} - \sum_{i=1}^N U_i(r_i) \right].$$

Every electron has an orbital angular momentum \vec{l}_i , and spin angular momentum of \vec{s}_i . Then the total orbital

Angular momentum for the atom is $\vec{L} = \sum_{i=1}^N \vec{l}_i$, and the total spin angular momentum $\vec{S} = \sum_{i=1}^N \vec{s}_i$. II96.

* This can be understood as: in classical physics, each electron experiences noncentral force, so its orbital angular momentum is no longer conservative. But the whole atom does not experience external force, so the total orbital angular momentum is conservative. In QM, the relationship is similar, and the total spin angular momentum is also conservative, i.e., $[\hat{H}_1, \vec{L}] = 0$, $[\hat{H}_1, \vec{S}] = 0$.

* Thus, the noncentral electrostatic interaction between electrons leads to a splitting of the level corresponding to a given electron configuration into a number of levels, characterized by different values of the total orbital angular momentum of the electrons L and the total spin angular momentum of the electrons S .

$$\begin{cases} [\hat{H}_1, \vec{L}^2] = 0, & [\hat{H}_1, \vec{S}^2] = 0 \\ [\hat{H}_1, \hat{L}_z] = 0, & [\hat{H}_1, \hat{S}_z] = 0 \end{cases}$$

L , S , M_L , and M_S are good quantum numbers, i.e., \vec{L}^2 , \vec{S}^2 , L_z , and S_z are conservative. Energy levels will go by $2S+1L$ to different eigenvalues, and the eigenstate can be expressed as $|L S M_L M_S\rangle$. Based on this, we further consider spin-orbit coupling, i.e., \vec{L} and \vec{S} couple with each other to form \vec{J} . Thus, the

energy levels have fine splitting, i.e., form fine structure. II 97

— This is the LS coupling approximation.

Let us consider Helium atom: He has two electrons.

Assume the electrons have l_1 and l_2 , S_1 and S_2 ,

$$\vec{L} = \vec{L}_1 + \vec{L}_2 \Rightarrow L = |l_1 + l_2|, l_1 + l_2 - 1, \dots, |l_1 - l_2|$$

$$\vec{S} = \vec{S}_1 + \vec{S}_2 \Rightarrow S = S_1 + S_2, S_1 + S_2 - 1, \dots, |S_1 - S_2|$$

$$M_L = m_{l_1} + m_{l_2}$$

$$M_S = m_{s_1} + m_{s_2}$$

$$L = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12$$

$$S, P, D, F, G, H, I, K, L, M, N, O, Q.$$

$$S_1 = S_2 = \frac{1}{2}, l_1 = 0, l_2 = 1,$$

$$\begin{aligned} \rightarrow S = 0, 1, \\ L = 1 \end{aligned} \left. \vphantom{\begin{aligned} \rightarrow S = 0, 1, \\ L = 1 \end{aligned}} \right\} \Rightarrow \begin{aligned} S = 0, J = 1 &\Rightarrow {}^1P_1 \\ S = 1, J = 2, 1, 0 &\Rightarrow {}^3P_2, {}^3P_1, {}^3P_0 \end{aligned}$$

Term $2S+1$ The letter representing L J 0 \rightarrow odd parity is called multiplet under LS coupling.

The Multiplicity of the energy level is $2S+1$ ($L \geq S$)

The energy level degeneracy is $(2L+1)(2S+1)$.

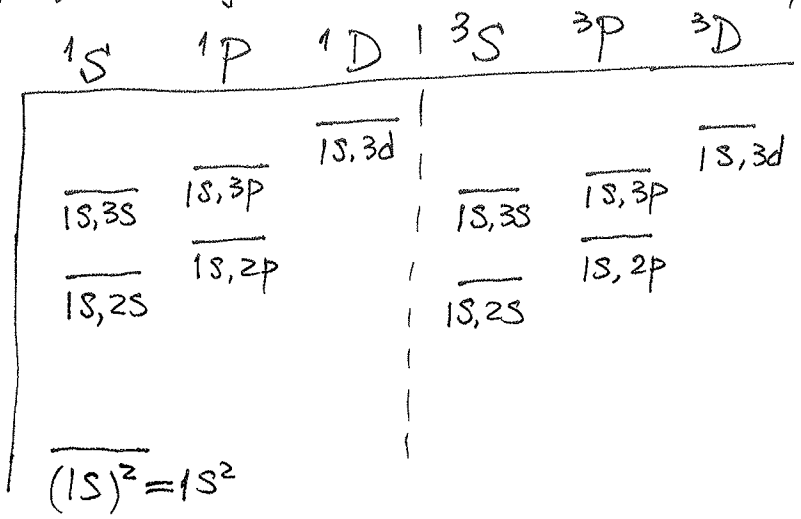
$$(M_L: 2L+1, M_S: 2S+1)$$

* The dependence of the energy of splitting on L has a simple physical meaning: to the different values of L , there corresponds a different mutual orientation of the orbital angular momenta of the electrons, or roughly speaking, a different orientation of

electron orbits. Therefore in states with different values of L , the electrons, on the average, are at different distances from each other, which also leads to a difference in the electrostatic energy of repulsion.

* The Coulomb force between the nucleus and the electrons has different signs than the Coulomb force between electrons. Therefore, the electrostatic interaction of electrons with each other leads to a shift of the energy levels upwards (the absolute magnitude of the coupling energy is decreased).

* It has been established empirically that, for ground configurations and for configurations containing equivalent electrons (electrons with the same n and l are called equivalent electrons), electrostatic splitting obeys a definite rule — so-called Hund's rule. According to the Hund's rule, the level with the greatest possible value of S for the given electron configuration and the greatest (possible for this S) value of L has the lowest energy.



He energy levels

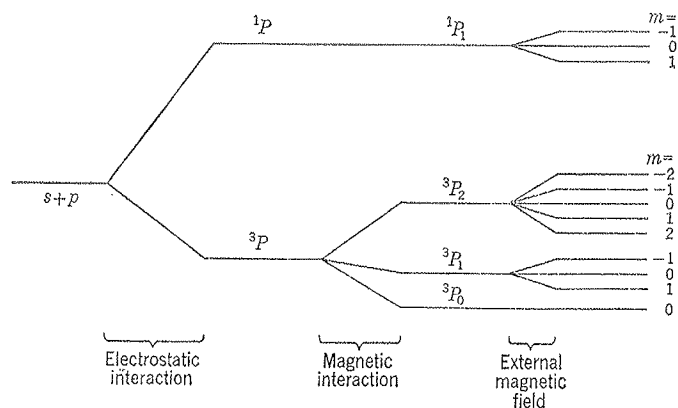


FIG. 13-1. Splitting of energy levels of multiplets arising from an s and a p electron, from electrostatic interaction, magnetic spin-orbit interaction, and a weak external magnetic field (schematic).

Here is a schematic of the Coupling (LS) between a s electron and a p electron as we discussed above.

* In external magnetic field, the energy levels also experience Zeeman splitting.

* When finding atomic states from electron configuration, if these are equivalent electrons (with same n and l), then Pauli Exclusion principle will prohibit many atomic states, compared to nonequivalent electrons.

Example: for 2 electrons in p state, if they are nonequivalent, i.e., they have different n , then vector model tells us that LS coupling results in $1D, 1P, 1S$ and $3D, 3P, 3S$ terms.

$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2} \Rightarrow S = 0, 1$$

$$l_1 = 1, l_2 = 1 \Rightarrow L = 0, 1, 2 \Rightarrow S, P, D \left. \begin{array}{l} \Rightarrow 1S, 1P, 1D \\ \Rightarrow 3S, 3P, 3D \end{array} \right\}$$

But if they are equivalent, then they can only form $1S, 1D$ and $3P$ terms.

8. $\hat{j}\hat{j}$ coupling

In the second extreme case, the magnetic interaction is much larger than the noncentral electrostatic interaction:

$$\Delta \hat{H}_m \gg \Delta \hat{H}_{nce}$$

In this case, we ignore the $\Delta \hat{H}_{nce}$ first, and get

$$\hat{H}_2 = \sum_i \left[\frac{\hat{P}_i^2}{2\mu} - \frac{1}{4\pi\epsilon_0} \frac{ze^2}{r_i} + U_i(r_i) \right] + \sum_i a(r_i) \hat{l}_i \cdot \hat{s}_i$$

Under this case, $\hat{j}_i = \hat{l}_i + \hat{s}_i$, i.e., each electron has l-s (spin-orbit) coupling and form \hat{j}_i as good quantum number.

Then these \hat{j}_i couple with each other to form a total angular momentum $\hat{J} = \sum_{i=1}^N \hat{j}_i$.

J and M_J are good quantum numbers (conservative).

Eigenstate is $|\hat{j}_1 \hat{j}_2 \dots J M_J\rangle$. The energy levels with

same \hat{j}_i but different J are degenerate. Now considering the weak noncentral electrostatic interaction, the degeneracy of different J will be removed.

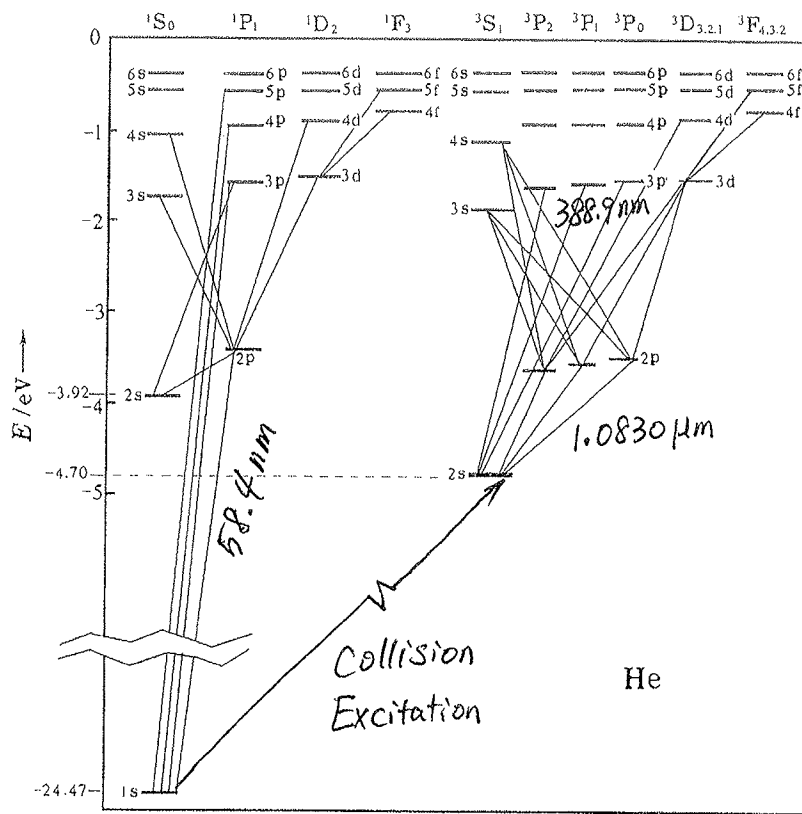
— This is called $\hat{j}\hat{j}$ coupling.

$$\left. \begin{array}{l} S_1 = \frac{1}{2} \\ l_1 = 0 \end{array} \right\} \Rightarrow \hat{j}_1 = \frac{1}{2} \quad \left. \begin{array}{l} \hat{j}_1 = \frac{1}{2} \\ \hat{j}_2 = \frac{3}{2} \end{array} \right\} \Rightarrow J = 2, 1$$

$$\left. \begin{array}{l} S_2 = \frac{1}{2} \\ l_2 = 1 \end{array} \right\} \Rightarrow \hat{j}_2 = \frac{3}{2}, \frac{1}{2} \quad \left. \begin{array}{l} \hat{j}_1 = \frac{1}{2} \\ \hat{j}_2 = \frac{1}{2} \end{array} \right\} \Rightarrow J = 1, 0$$

$$\therefore \left(\frac{1}{2}, \frac{3}{2}\right)_2, \left(\frac{1}{2}, \frac{3}{2}\right)_1, \left(\frac{1}{2}, \frac{1}{2}\right)_1, \left(\frac{1}{2}, \frac{1}{2}\right)_0$$

9. He Energy Levels and Applications in Remote Sensing



Let us use He as an example to illustrate the principles that we just learned.

① Ground state: $1S^2$

Two electrons have opposite $m_s = \pm \frac{1}{2}$, $\therefore |n \ell m_\ell m_s\rangle$ are $|1, 0, 0, \frac{1}{2}\rangle$ and $|1, 0, 0, -\frac{1}{2}\rangle$.

This configuration gives the lowest energy level \rightarrow ground state

$\therefore m_s = \pm \frac{1}{2}$, antiparallel

$\therefore S = 0$, \Rightarrow atomic state for the ground state is $1S_0$.

② 3S_0 does NOT exist, because Pauli exclusion principle exhibits it: $|1, 0, 0, \frac{1}{2}\rangle$ cannot hold more than one electrons.

③ Singlets vs Triplets:

* With two electrons having spin antiparallel, we have

$$S = S_1 - S_2 = \frac{1}{2} - \frac{1}{2} = 0.$$

This is for terms on the left half of the diagram.

Since $S=0$, for each l , we have $j = l + 0 = l$,

so single j for each nl , \Rightarrow single spectral line.

— This is called singlet, or para-Helium.

* With two electron spins are parallel to each other,

$$\text{We have } S = S_1 + S_2 = \frac{1}{2} + \frac{1}{2} = 1.$$

This is for the terms on the right half.

Since $S=1$, for $L \geq 1$, $J = L+1, L, L-1$,

so triple j for each nl ($l \geq 1$) \Rightarrow triple spectral

lines — This is called triplets or ortho-Helium.

④ LS coupling applied here:

$1S_0, 3S_1, 3P_{2,1,0}, \dots$ are all formed under LS coupling.

⑤ Metastable states:

As we will discuss in later lectures, the selection rules for radiative transitions require (LS coupling)

$$\left\{ \begin{array}{l} \Delta S = 0 \\ \Delta L = 0, \pm 1 \\ \Delta J = 0, \pm 1 \text{ (except } J=0 \rightarrow J'=0) \\ \Delta n \text{ is arbitrary.} \end{array} \right.$$

According to these rules, there is no radiative transition from $2^3S_1 \leftrightarrow 1^1S_0$ (because of $\Delta S \neq 0$); also no radiative

transition from $2^1S_0 \leftrightarrow 1^1S_0$ (because of $J=0 \rightarrow J'=0$).

Therefore, once Helium atoms are excited by collision to 2^3S_1 state or 2^1S_0 state, they will stay there for long time unless collisionally (non-radiative transition) decay to the ground state 1^1S_0 . These two states are called metastable states. They enable many applications in remote sensing field.

⑥ Hund's rules:

The diagram indicates that 2^3S_1 energy is lower than 2^1S_0 , which is determined by the Hund's rule — greater S corresponds to lower energy, if n, l are the same.

⑦ Helium has very large ionization energy ~ 24.5 eV, nearly double of Hydrogen. This reflects the closed shell structure of Helium atom — Very stable structure.

Applications of Helium

Helium atoms distribute in the Earth's atmosphere from about 100 km to +1500 km. Due to the very low ground state energy, any transitions to the ground state are less than 60 nm, far far UV. This is impossible to detect on the ground (due to atmosphere absorption).

However, since 2^3S_1 is a metastable state, there can be appreciable population of Helium on this state.

Helium atoms on this metastable state can be excited by sunlight, then giving out airglow during twilight or in the night. This is mainly caused by the transition from $2^3p - 2^3S_1$, which has wavelengths of $\sim 1.083 \mu m$.

Using Fabry-Perot interferometer, Kerr et al. [1996] could measure Helium density distribution in a large range of the atmosphere.

Moreover, it has been suggested that a lidar may be possible to detect Helium using the 1083 nm lines or other two lines: 388.9 nm from $2^3S_1 \rightarrow 3p$ and 318.8 nm from $2^3S_1 \rightarrow 4^3p$.

The attractive point is that the Helium is somehow in thermal equilibrium with the surrounding atmosphere. So if we can measure the Doppler width and shift of the Helium transition lines, we can measure the temperature and wind in a large thermosphere range!

This is why we are now so interested in Helium atomic structure and spectrum.

* In addition, Helium was observed from the Sun and other stars. By measuring the Doppler shifts of various lines of Helium, astronomers were able to measure star velocities, temperatures, and compositions, etc.

* Isotopes of Helium:

Helium has two stable isotopes: ${}^4\text{He}$ and ${}^3\text{He}$.

${}^4\text{He}$ $Z=2$, Neutron = 2, 4.0026 u, 99.999%, $I=0$

${}^3\text{He}$ $Z=2$, Neutron = 1, 3.0160 u, 0.0001%, $I=\frac{1}{2}$.

Since ${}^4\text{He}$ has even $Z=2$, even $A=4$, its nuclear spin $I=0$, so no hyperfine structure from magnetic hyperfine interaction.

But ${}^3\text{He}$ has $I=\frac{1}{2}$, so it has hyperfine structure.

Appendix :

Names for numbers and symbols used in atomic spectroscopy:

Z — Atomic number

A — Mass number

n — Principal quantum number

l — Orbital quantum number angular momentum

s — Spin angular momentum quantum number

m_l — Orbital magnetic quantum number

m_s — Spin magnetic quantum number

n^* — Effective quantum number

δ — quantum defect

Z^* — effective charge

j — electron total angular momentum

I — Nuclear spin angular momentum

F — Total angular momentum of atom.