Chapter 5. Atomic Structure

§5.1. Atomic Structure Overview

(1) The main clue is to solve stationary-state Schrödinger equation of a single atom (i.e., the eigenvalue equation of $\hat{H}$) to derive energy eigenvalues and eigenstates:

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle .$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \hat{V} = \text{Kinetic Energy} + \text{Potential Energy}$$

All these operators in the eigenvalue equation are independent of time. (μ is the reduced mass $\mu = \frac{mM}{m+M}$)

(2) $\hat{V}$ is determined by interactions: inside an atom and interactions between atom and external field (Static, independent of time) if any.

* When $\hat{V}$ changes, the energy eigenvalues will change → the shift of energy levels or the removal of degeneracy of the energy levels.

(3) We have very limited ability to solve the stationary-state Schrödinger equation analytically. Only when $\hat{V}$ is in a simple format, e.g., $\hat{V} \propto \frac{1}{r}$, it is possible to solve the equation analytically, e.g. hydrogen atom when only consider Coulomb force between the nucleus and the single electron.

(4) For most of other cases, not only we can't solve the equation analytically, but also can't even numerically. Approximation methods have to be used to get an approximate solution. The most common approach

is the perturbation theory, in particular, time-independent perturbation theory for solving the $\hat{H}$ eigenvalue equation.

(5) The main idea of perturbation theory is to solve the equation for the major force, e.g., the Coulomb force between nucleus and electron, and produce the main energy levels, denoted by the principal quantum number n. And then consider the other minor force (e.g., spin-orbit coupling) as a perturbation to the main energy levels, so the equation can be simplied and approximated, and solutions approximate can be derived. The results are to place a correction to the main levels, depending on different states. Different states may experience different corrections, i.e., different shift of energy, thus, some degeneracy can be removed.

(6) Interactions to be considered in atomic structure theory:

Let's consider the simplest atom — ^1H.

① Electrostatic Interaction between the nucleus and the electron (Coulomb force) forming main energy levels with quantum number n, l, m_l (but l, m_l are degenerate)

degeneracy $= n^2$.

② Electron Spin and Angular momentum coupling

An electron orbiting around a nucleus → current in a circle ⇒ magnetic moment: orbital angular momentum

An electron has spin ⇒ spin magnetic moment ⇒ spin angular momentum

The electron's orbital and spin angular momentum can have magnetic interaction: the coupling between spin and orbit

⟹ main energy levels split, shift, partially remove degeneracy $\vec{L}+\vec{S}=\vec{J}$

⟹ fine structure of energy levels.

③ Nuclear influence:

a). Nuclear spin angular momentum coupling with electron total angular momentum $\vec{J}+\vec{I}=\vec{F}$

⟹ hyperfine structure

b). neutrons in nucleus affect mass and volume

⟹ isotope shift of energy levels.

e.g., ^1H, ^2D, ^3T (neutrons: 0, 1, 2)

④ External field: static electric and magnetic field

magnetic: Zeeman effect ⟹ energy levels split and shift

Electric: Stark effect → energy level split and shift.

Let's consider when an atom has more than one electron: (e.g., ^2He)

⑤ Electron–Electron Interactions:

a). Electrostatic interaction between electrons:

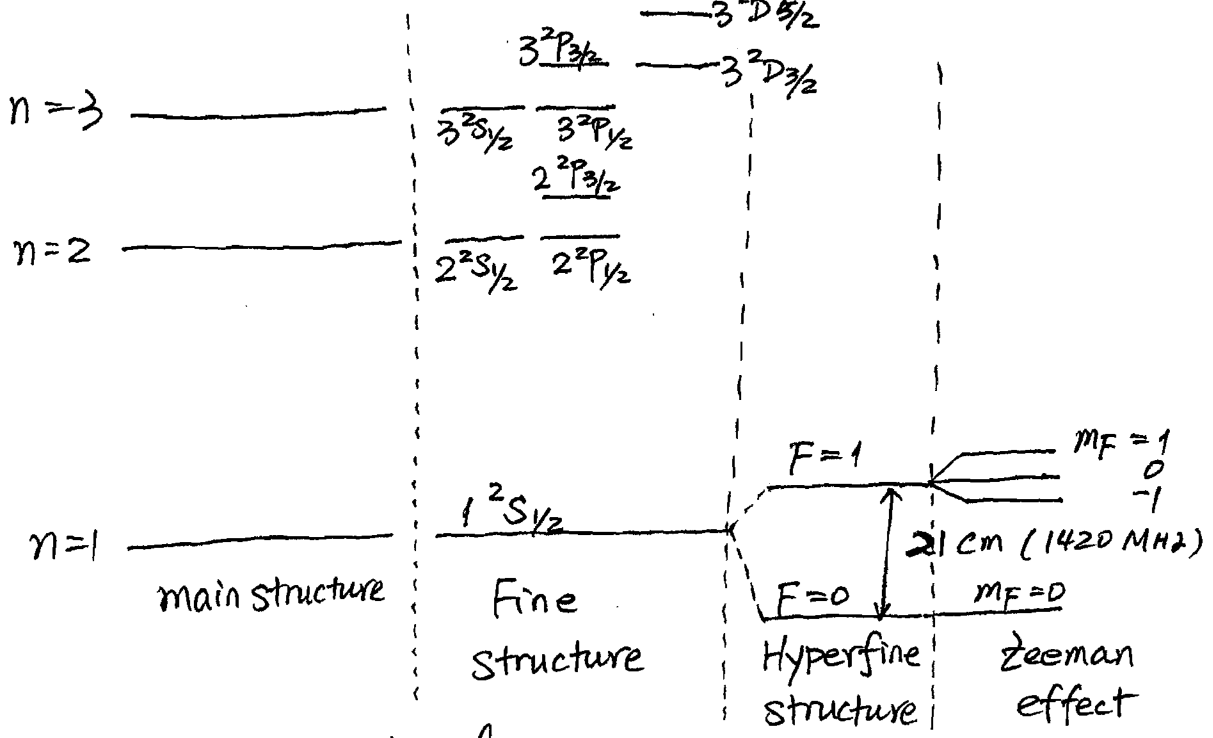
- Central Field part
- non-central Field part

b). Magnetic interaction between electron magnetic moments:

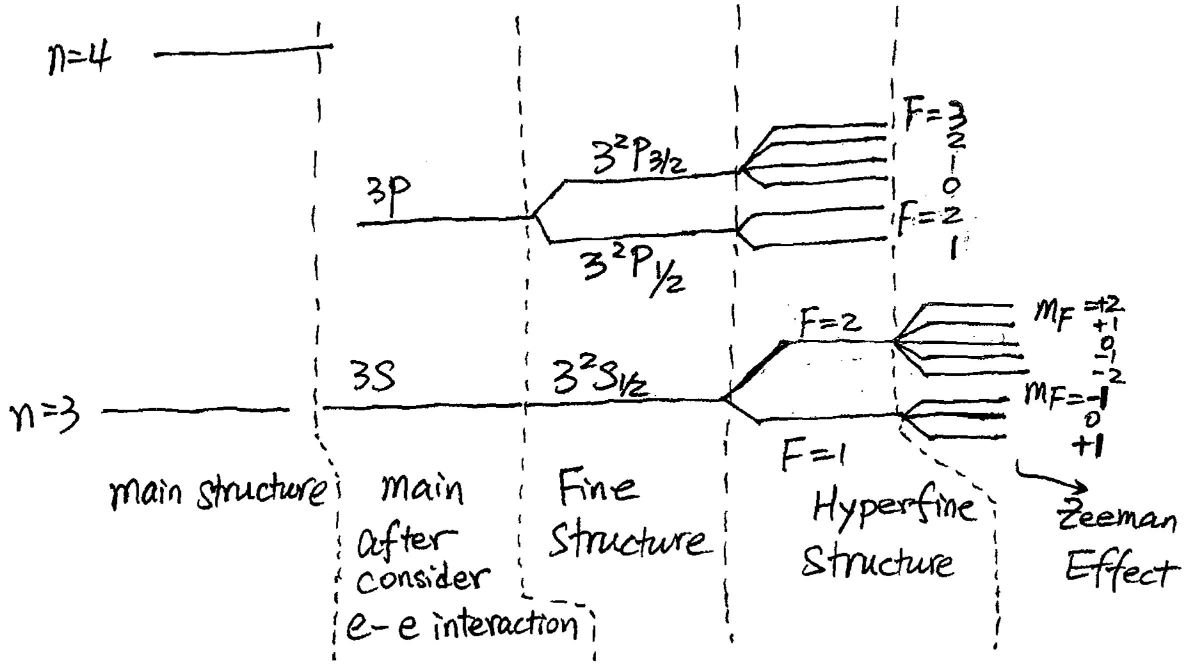
- one electron spin coupling with another electron orbital angular momentum
- Spin–spin electron angular momentum coupling.

The electron-electron interactions are much stronger than nuclear influence. So for multielectron atoms, we usually consider e-e interactions before considering nuclear influences.

Examples: ① Hydrogen atomic energy levels.



② Na atomic energy levels.



§5.2. Atomic Structure Inferred from Hydrogen Atom

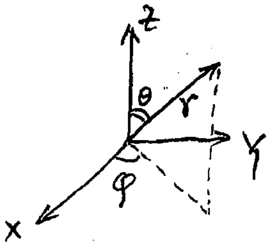
As explained in the last lecture, the atomic structure problems are to solve the energy eigenvalue equations, i.e., the stationary-state Schrödinger equation to derive energy eigenstates and eigenvalues.

Hydrogen atom is the only atomic structure that can be solved from the Schrödinger equation exactly. Therefore, it is representative to illustrate the approaches and fundamental principles in atomic structure study. We will use H to study the energy levels determined by the main force (electrostatic interaction between the nucleus and the electron), the spin-orbit angular momentum coupling, the nuclear spin and electron angular momentum coupling, the isotope shift, the external electric and magnetic field effects.

Then we will use Helium atom as an example to illustrate multielectron's interactions and how they complicate structures.

1. Hydrogen energy eigenvalues and eigenstate in Coulomb potential

* For this problem, we use the $\{|\vec{r}\rangle\}$ representation, and project the states and operators to a spherical coordinate system (r, θ, φ)



$$\hat{H}\psi = E\psi = \left(\frac{\hat{p}^2}{2\mu} + \hat{V}\right)\psi \qquad (1)$$

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\psi = E\psi. \qquad \hat{V} = -\frac{Ze^2}{4\pi\varepsilon_0 r}.$$

$$\mu = \frac{m_e M}{m_e + M}.$$

In the first step, we only consider the electrostatic force (Coulomb) between the nucleus and electron. Write ∇^2 in the spherical coordinates, then we have

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)\right] - \frac{\hbar^2}{2\mu}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right] + V(r)\psi = E\psi. \qquad (2)$$

Recall $\hat{\vec{l}}^2 = -\hbar^2 [\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}]$, (3)

then the second term on the left side of the hydrogen equation (2) is proportional to $\hat{\vec{l}}^2$. Thus,

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}(r^2\frac{\partial\psi}{\partial r}) + \frac{\hat{\vec{l}}^2}{2\mu r^2}\psi + V(r)\psi = E\psi. \quad (4)$$

On the left side, the 1st and 3rd term only concern r, while the 2nd term is only related to θ and φ. Therefore, we can solve the equation using separation of variables by assuming a solution of the form: $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$. (5)

Substitute this solution to the above equation, we get

$$\frac{1}{\hbar^2 Y}\hat{\vec{l}}^2 Y = \frac{1}{R}\frac{d}{dr}(r^2\frac{d}{dr}R) + \frac{2\mu r^2}{\hbar^2}[E - V(r)] = \alpha, \quad (6)$$

where α is a constant for the separation of variables.

Therefore, we get two equations from this:

$$\begin{cases} [-\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}(r^2\frac{d}{dr}) + \frac{\alpha\hbar^2}{2\mu r^2} + V(r)]\,R(r) = E\,R(r) & (7) \\ \hat{\vec{l}}^2\,Y(\theta,\varphi) = \alpha\hbar^2\,Y(\theta,\varphi) & (8) \end{cases}$$

Both are eigenvalue equations; the first is for the radial direction, an energy eigenvalue equation; the second is an eigenvalue equation for the square of angular momentum.

(1) * Let's solve the $\hat{\vec{l}}^2$ eigenvalue equation first. This equation is independent of $V(r)$, thus, a general equation for the central field potential case. We further separate variables:

$$Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\varphi) \quad (9)$$

Substitute this expression and $\hat{\vec{l}}^2$ expression (3) into the $\hat{\vec{l}}^2$ eigenvalue equation (8), we have

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) + \alpha\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = \nu \quad (10)$$

Where ν is another constant for the separation of variables. Thus, we get another two equations:

$$\begin{cases} \dfrac{d^2\Phi}{d\varphi^2} + \nu\Phi = 0 & (11) \\ \dfrac{\sin\theta}{\Theta}\dfrac{d}{d\theta}\left(\sin\theta\dfrac{d\Theta}{d\theta}\right) + \alpha\sin^2\theta = \nu. & (12) \end{cases}$$

The general solution for the first equation is given by

$$\begin{cases} \Phi = Ae^{i\sqrt{\nu}\varphi} + Be^{-i\sqrt{\nu}\varphi}, & \text{for } \nu \neq 0 & (13) \\ \Phi = C + D\varphi, & \text{for } \nu = 0 & (14) \end{cases}$$

A, B, C, D are constants.

As a wavefunction, $\Phi(\varphi) = \Phi(\varphi + 2\pi)$, i.e., single value in space. Thus, for $\nu = 0$, we must have $D = 0$; for $\nu \neq 0$, we must have $\sqrt{\nu} = m$, where m is an integer. This gives us a special solution to the first equation as:

$$\Phi_m = \frac{1}{\sqrt{2\pi}}e^{im\varphi}, \quad m = 0, \pm1, \pm2, \cdots \qquad (15)$$

Here, the coefficient $\frac{1}{\sqrt{2\pi}}$ is obtained by the normalization condition

$$\int_0^{2\pi}\Phi_m^*\Phi_m\, d\varphi = 1. \qquad (16)$$

Apparently, Φ_m is an eigenvalue function for $\hat{l}_z = -i\hbar\frac{\partial}{\partial\varphi}$:

$$\hat{l}_z\Phi_m = -i\hbar\frac{\partial}{\partial\varphi}\left(\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right) = m\hbar\left(\frac{1}{\sqrt{2\pi}}e^{im\varphi}\right) = m\hbar\Phi_m \quad (17)$$

∴ the eigenvalues of $\hat{l}_z$ is $\quad l_z = m\hbar, \quad m = 0, \pm1, \pm2, \cdots$ (18)

$\hat{l}_z$ is the z-component of the angular momentum vector.

* Substitute $\sqrt{\nu} = m$ into the second equation (12) above, we obtain

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \alpha\sin^2\theta = m^2 \qquad (19)$$

Let $u = \cos\theta$, then $\Theta(\theta) = P(u)$. The above equation (19) becomes

$$\frac{d}{du}\left[(1-u^2)\frac{dP}{du}\right] + \left(\alpha - \frac{m^2}{1-u^2}\right)P = 0 \qquad (20)$$

This equation can be solved analytically, but we only list the results here. The solution requires

$$\alpha = l(l+1), \quad l=0,1,2,\cdots \qquad (21)$$

$$|m| \leqslant l, \quad m=0,\pm 1,\pm 2,\cdots,\pm l. \qquad (22)$$

∴ From $\hat{\vec{l}}^2$ equation (8) we get

$$\hat{\vec{l}}^2 Y_{l,m} = l(l+1)\hbar^2 Y_{l,m} \qquad (23)$$

i.e; $Y_{l,m}$ is an eigen function of $\hat{\vec{l}}^2$, and the correspondig eigen-value is $l^2 = l(l+1)\hbar^2$. (24)

l is called the quantum number of angular momentum.

The solution to equation (20) is

$$P(u) = P_l^{|m|}(u) \qquad (25)$$

where

$$P_l^{|m|}(u) = (1-u^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{du^{|m|}} P_l(u) \qquad (26)$$

and

$$P_l(u) = \frac{1}{2^l l!} \frac{d^l}{du^l} (u^2-1)^l \qquad (27)$$

From above, we obtain the eigen function for $\hat{\vec{l}}^2$ as

$$Y_{l,m}(\theta,\varphi) = N_{lm} P_l^{|m|}(\cos\theta) e^{im\varphi} \qquad (28)$$

where N_{lm} is the normalization constant and obtained by

$$\int_0^{2\pi}\int_0^{\pi} Y_{l,m}^*(\theta,\varphi)\, Y_{l,m}(\theta,\varphi) \sin\theta\, d\theta\, d\varphi = 1. \qquad (29)$$

$$\Rightarrow \quad N_{lm} = \sqrt{\frac{(l-|m|)!\,(2l+1)}{4\pi\,(l+|m|)!}}\,. \qquad (30)$$

For $l=0,1,2$, the states are called s, p, d states.

$l=0$: $Y_{0,0} = \frac{1}{\sqrt{4\pi}}$; $l=1$: $Y_{1,0} = \sqrt{\frac{3}{4\pi}}\cos\theta$, $Y_{1,\pm1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$

$l=2$: $Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$, $Y_{2,\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{\pm i\varphi}$

and $Y_{2,\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm 2i\varphi}$

Notice that $|Y_{l,m}|^2$ is independent of φ, but only dependent on θ. This implies that the probability of electron appearance is rotational symmetric about the z-axis.

(2) * Parity of states: When making an operation of inversion transformation ($x \to -x$, $y \to -y$, $z \to -z$, i.e., $\vec{r} \to -\vec{r}$) on a state wave function $\psi(\vec{r})$, if $\psi(\vec{r})$ and $\psi(-\vec{r})$ have the following relations

$$\psi(-\vec{r}) = -\psi(\vec{r}) \qquad (31)$$

$$\text{or} \quad \psi(-\vec{r}) = +\psi(\vec{r}) \qquad (32)$$

then we say the state has parity: odd parity for (31) and even parity for (32).

"Parity is a measure of the symmetry of interactions under spatial inversion". In QM, parity is defined as an operator $\hat{\Pi}$, that

$$\left.\begin{aligned} &\hat{\Pi}\,|\vec{r}\rangle = |-\vec{r}\rangle \\ \text{or}\quad &\hat{\Pi}\,\psi(\vec{r}) = \psi(-\vec{r}) \end{aligned}\right\} \quad (33)$$

Apparently, $\hat{\Pi}^2\psi(\vec{r}) = \hat{\Pi}\,\psi(-\vec{r}) = \psi(\vec{r})$

$\therefore$ $\hat{\Pi}^2$ has an eigenvalue of 1, and $\hat{\Pi}$ has eigenvalues of ± 1.

For the $Y_{l,m}$ we obtained above, in spherical coordinates, under the spatial inversion ($r \to r$, $\theta \to \pi - \theta$, $\varphi \to \varphi + \pi$), we have

$$Y_{l,m}(\pi-\theta, \varphi+\pi) = (-1)^l\, Y_{l,m}(\theta, \varphi) \qquad (34).$$

So, when l is even number, $Y_{l,m}$ has even parity;
when l is odd number, $Y_{l,m}$ has odd parity.

In general, if there is no external force, Hamiltonian operator $\hat{H}$ remains unchanged under parity operator. Therefore, the parity of state wave function is constant, and does not change with time.

(3) * Now let's solve the energy eigenvalue equation (7).

Let $k^2 = -\frac{2\mu E}{\hbar^2}$, $\gamma = \frac{\mu e^2 Z}{4\pi\varepsilon_0 k\hbar^2}$, $\rho = 2kr$. (35)

then Equation (7) becomes

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[\frac{\gamma}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]R = 0 \quad (36)$$

This equation is solved under the boundary condition

$$R(r) \to \infty \text{ as } r \to \infty. \quad (37)$$

We skip the procedure of solving this equation, but list results as follows: the eigenvalues of energy are

$$E_n = -\frac{\mu e^4 Z^2}{32\pi^2\varepsilon_0^2\hbar^2 n^2}, \quad n = 1, 2, 3, \cdots \quad (38)$$

The normalized eigenvalue radial wave function $R_{n,l}(r)$ is

$$R_{n,l}(r) = -\left\{\left(\frac{2Z}{na_1}\right)^3 \frac{[n-(l+1))]!}{2n[(n+l)!]^3}\right\}^{1/2} \times \quad (39)$$

$$\exp\left(-\frac{Zr}{na_1}\right)\left(\frac{2Zr}{na_1}\right)^l L_{n+1}^{2l+1}\left(\frac{2Zr}{na_1}\right)$$

Where a_1 is the first Bohr radius, L is the associated Laguerre function. We also have

$$n \geqslant l+1 \quad (40).$$

Note: $a_1 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} \approx 0.053\,\text{nm}$.

Normalization condition for $R(r)$ is $\int |R|^2 \, dr = 1$.

Note: In this whole procedure, we used $V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$. This is for not only hydrogen atom itself, but also for other hydrogen-like ion, e.g., He^+, Li^{++}, Be^{+++}

In other words, the nucleus charge is Ze, and electron charge is $-e$. $Z = 1, 2, 3, 4, \cdots$ for H, He^+, Li^{++}, Be^{+++}, $\cdots$.

The reduced mass $\mu = \frac{m_e M}{m_e + M}$, where M will be different for different nucleus.

Thus, from the QM calculation, we obtain three quantum numbers (n, l, and m) and three eigenvaluation equations:

$$\begin{cases} \hat{H}\psi_{n,l,m} = +E_n \psi_{n,l,m} \\ \hat{\vec{L}}^2 \psi_{n,l,m} = l(l+1)\hbar^2 \psi_{n,l,m} \\ \hat{L}_z \psi_{n,l,m} = m\hbar\, \psi_{n,l,m} \end{cases}$$

where $\psi_{n,l,m} = R_{n,l}(r)\, Y_{l,m}(\theta,\varphi)$, $E_n = -\dfrac{\mu Z^2 e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2}$, $n = 1, 2, 3, \cdots$

Only under the central field Coulomb force, although the wave function depends on 3 quantum numbers (n, l, m), the energy eigenvalues are only dependent on n. This means that eigen value functions are degenerate, i.e., many different wave functions correspond to the same energy eigenvalue.

For each n, $\because\ n \geq l+1$, $\therefore\ l = 0, 1, 2, 3, \cdots, n-1$,

For each l, $\because\ l \geq |m|$ $\quad\therefore\ m = -l, -l+1, \cdots, 0, \cdots l-1, l$.

i.e., there are n of l, and $2l+1$ of m.

Thus, the degeneracy factor for each n is given by

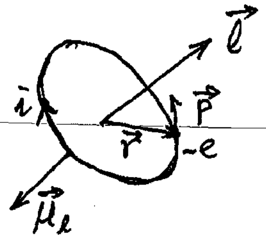
$$\sum_{l=0}^{n-1} (2l+1) = n^2.$$

i.e., the degeneracy for hydrogen atom and hydrogen-like ions is n^2 for the principal quantum number n.

2. Electron Spin-Orbit Interaction and Energy Fine Structure

An electron moves around a nucleus — what's going to happen?

(1) From Classical Physics, (see figure on the left)



If looking from mechanical aspect, there is angular momentum given by $\vec{l} = \vec{r} \times \vec{P}$,

where $\vec{l}$ is electron orbital angular moment

$\vec{r}$ is the position vector of the electron relative to the nucleus

$\vec{P}$ is the electron momentum.

($\vec{l}$ direction is given by the right-hand law)

When looking from electromagnetic theory, a current in circle will produce a magnetic dipole moment $\vec{\mu}_l$ given by

$$\vec{\mu}_l = i S \vec{n}_0$$

where i is the current, S is the area of the circle, and $\vec{n}_0$ is the unit vector perpendicular to the circle surface.

$\vec{\mu}_l$ direction is also given by the right-hand law, i.e., close your right hand in the current direction, then your thumb points to the direction of the magnetic field produced by the current. Since the electron has negative charge, the current is in opposite direction of electron movement. Thus, the magnetic moment μ_l points to the opposite direction of the angular momentum $\vec{l}$. In classical physics, we can get

$$\vec{\mu}_l = i S \vec{n}_0 = -ef \cdot \pi r^2 \cdot \vec{n}_0 = -\frac{ev}{2\pi r}\pi r^2 \vec{n}_0$$

$$= \frac{-e}{2} v r \vec{n}_0 = \frac{-e}{2m_e} \cdot \underbrace{m_e v r \vec{n}_0}_{\Rightarrow \vec{l}} = -\frac{e}{2m_e}\vec{l}$$

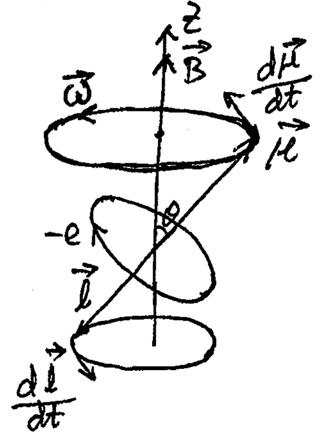
Let $\gamma = \frac{e}{2m_e}$, $\therefore \vec{\mu}_l = -\gamma \vec{l}$ (γ is called gyromagnetic ratio)

In a homogeneous magnetic field, a magnetic moment will experience a moment of force: $\vec{\tau} = \vec{\mu}_l \times \vec{B}$, (also called torque) where $\vec{\tau}$ is the moment of force, $\vec{B}$ is the magnetic field.

(See appendix), $\frac{d\vec{l}}{dt} = \vec{\tau} = \vec{\mu}_l \times \vec{B}$

$$\therefore \frac{d\vec{\mu}_l}{dt} = -\gamma \frac{d\vec{l}}{dt} = -\gamma\, \vec{\mu}_l \times \vec{B} = \vec{\omega} \times \vec{\mu}$$

where $\vec{\omega} \equiv \gamma \vec{B}$ is the angular speed of the magnetic moment's precession around $\vec{B}$.



The classical picture is that the electron moves around the nucleus, producing a magnetic moment $\vec{\mu}_l$, and then the $\vec{\mu}_l$ precesses around an external magnetic field $\vec{B}$ with an angle of θ and angular speed of ω.

(2) From Quantum mechanics: Similar to classical physics, the QM magnetic moment $\mu_l \propto l$, but its magnitude is quantized and given by $\sqrt{l^2} = \sqrt{l(l+1)}\,\hbar$.

Therefore, in QM, magnetic moment is given by

$$\left(\begin{matrix}\text{orbital} \\ \text{magnetic moment}\end{matrix}\right) \mu_l = -\gamma L = -\sqrt{l(l+1)}\,\hbar\gamma = -\sqrt{l(l+1)}\,\frac{e\hbar}{2m_e}.$$

Define Bohr magneton $\mu_B = \frac{e\hbar}{2m_e} = 0.9274 \times 10^{-23}\, J \cdot T^{-1}$

(Bohr magneton is the minimum unit of orbital magnetic moment — an important constant)

$$= 0.9274 \times 10^{-23}\, A \cdot m^2$$
$$= 0.009274\, mA \cdot (nm)^2$$
$$= 0.5788 \times 10^{-4}\, eV \cdot T^{-1}$$

$$\therefore \mu_l = -\sqrt{l(l+1)}\,\mu_B = -\sqrt{l(l+1)}\,g_l\,\mu_B$$

z-component: $\mu_z = -m_l\,\mu_B = -m_l\,g_l\,\mu_B$ $\quad (l_z = m_l\hbar)$

Here, g_l is call the g-factor for orbital magnetic moment

$$g = \frac{\text{measure } \mu_z \text{ in } \mu_B \text{ unit (component of } \mu \text{ in z-direction)}}{\text{projection of angular moment in z-direction (in } \hbar \text{ unit)}}$$

$g_l = 1.$

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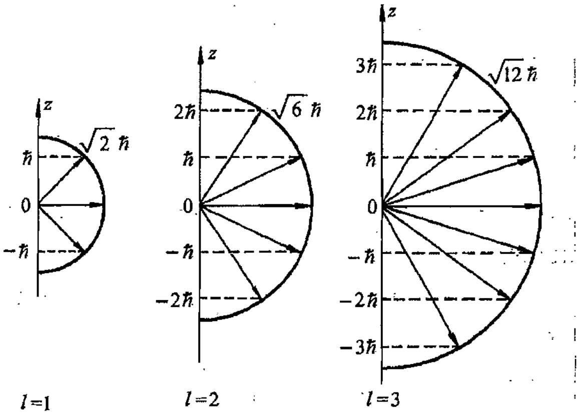
(3) Quantization of angular momentum / magnetic moment.

1). The magnitude of angular momentum is quantized

$$l^2 = l(l+1)\hbar^2$$

$$\mu_l = -\sqrt{l(l+1)}\,\mu_B\, g_l.$$

2). The spatial direction of angular momentum is also quantized



l=1 l=2 l=3

Orbital Angular momentum and its z-component (Both are quantized)

Since $l = 0, 1, 2, 3 \cdots$

$l = \sqrt{l^2} = \sqrt{l(l+1)}\,\hbar$ — quantized.

Since $m_l = l, l-1, \cdots, 0, \cdots, -l+1, -l$.

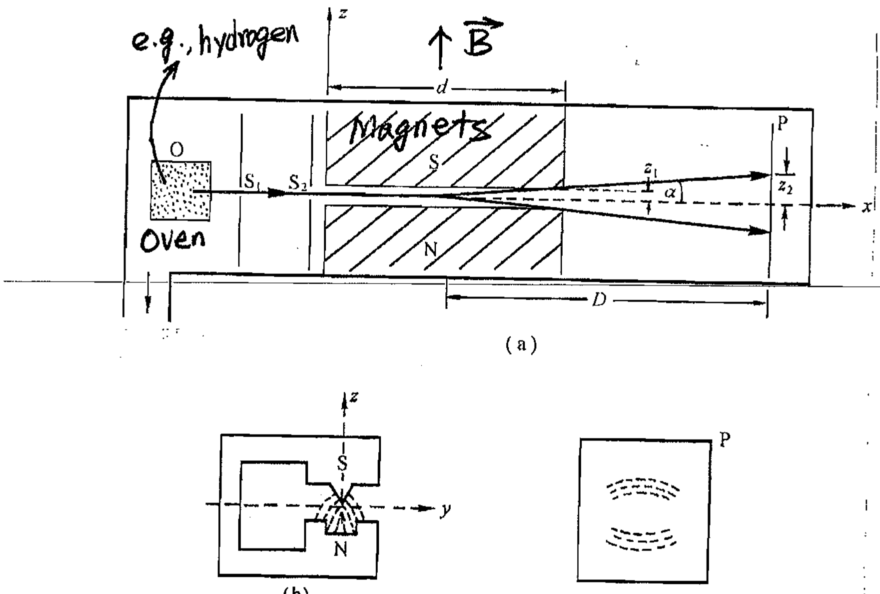
$\therefore l_z = m_l \hbar$ — quantized.

For $l=1$, $m_l = 1, 0, -1$

For $l=2$, $m_l = 2, 1, 0, -1, -2$

For $l=3$, $m_l = 3, 2, 1, 0, -1, -2, -3$.

(4) Stern-Gerlach Experiment. (1921)



(a)

(b)

(c)

Hydrogen atoms in container O is heated to become vapor. In thermal dynamic equilibrium, the atom velocity v is given by $\frac{1}{2}mv^2 = \frac{3}{2}k_BT$, where k_B is Boltzmann Constant, and T is the temperature.

Hydrogen atoms coming out of container O pass through slits S_1 and S_2, thus, we select the atoms going along x-direction. The magnetic field provided by two magnets are

$$\frac{\partial B_z}{\partial x} = \frac{\partial B_z}{\partial y} = 0, \quad \text{but } \frac{\partial B_z}{\partial z} \neq 0.$$

Thus, in inhomogeneous magnetic field, a magnetic moment will experience force: $F_z = \mu_z \frac{\partial B_z}{\partial z}$.

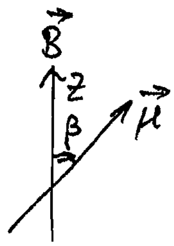
For atoms entering the magnetic field with x-direction velocity, they experience force in z-direction (perpendicular), thus,

$$\begin{cases} x = vt \\ z_1 = \frac{1}{2}at^2 = \frac{1}{2}\frac{F_z}{m}t^2 \end{cases}$$

$\Rightarrow$ tilted angle $\alpha = \arctan\left(\frac{dz}{dx}\right)_d = \arctan\left(\frac{F_z t}{mv}\right)_d = \arctan\left(\frac{F_z d}{mv^2}\right)$

After leaving magnets, atoms will go along straight line with α to the screen.

$$\Rightarrow z_2 = \mu_z \cdot \frac{\partial B_z}{\partial z} \cdot \frac{d \cdot D}{mv^2} = \mu_z \cdot \frac{\partial B_z}{\partial z} \cdot \frac{d \cdot D}{3k_BT}.$$



Since $\mu_z = \mu \cos\beta$, if $\cos\beta$ can be arbitrary, then μ_z is not quantized, and z_2 won't be quantized.

Only when $\cos\beta$ is quantized, i.e., the spatial direction of μ is quantized, then μ_z is quantized ⇒ Z_z is quantized.

Therefore, the experimental results will show whether μ_z is quantized. Indeed, Z_z is quantized — only two directions.

⇒ Conclusion: angular momentum / magnetic moment is quantized in magnetic field.

* However, until that point, the only two-direction cannot be explained by theory. Because for certain l, the spatial direction m_l has $2l+1$ directions. Since l is an integer, $2l+1$ has to be an odd number, not even!!!

⇒ This led to the electron spin hypothesis!

(5) Electron spin and magnetic moment.

- To explain the Stern-Gerlach experiement (even number of splitting), Uhlenbeck and Goudsmit proposed a hypothesis in 1925: an electron is not a point charge, but owns spin motion besides the orbital angular momentum.

- The intrinsic spin angular momentum ($\vec{s}$) $\vec{S}$ (of an electron) is given by

$$|\vec{S}| = \sqrt{s(s+1)}\,\hbar, \qquad s = \frac{1}{2}$$

Along z-direction, the component of spin angular momentum is

$$S_z = m_s \hbar, \qquad m_s = \pm\frac{1}{2}.$$

- The spin magnetic moment corresponding to the spin angular momentum is given by

$$\mu_s = -\sqrt{s(s+1)}\,\mu_B\, g_s$$

$$\mu_{s,z} = -m_s\,\mu_B\, g_s \qquad \boxed{g_s = 2}$$

This g_s can be derived from Dirac's relativity QM: $g_s \overset{\text{exact}}{\doteq} 2$

- Lande g-factor: for an arbitrary angular momentum j, the corresponding magnetic moment μ_j is given by

$$\begin{cases} \mu_j = -\sqrt{j(j+1)}\, g_j\, \mu_B \\ \mu_{j,z} = -m_j\, g_j\, \mu_B \end{cases}.$$

$$\therefore\ g_j = \frac{\text{Measured } \mu_z \text{ in } \mu_B \text{ unit}}{\text{angular momentum projection } l_z \text{ in } \hbar \text{ unit}}$$

(6) Spin-orbit coupling :

* To explain the Stern-Gerlach experiment, and the fine structure observed in hydrogen atomic spectra, we must an important interaction inside the atom, besides the major Coulomb force betwee the nucleus and the electron. This new force is the magnetic interaction between electron's orbit and electron spin, which is called the electron spin-orbit coupling.

* This coupling can be understood in the following three ways:

① The movement of electron around the nucleus can also be regarded as the nucleus moving around the electron (in the electron-rest coordinates). Therefore, it produces current

$$i_z = Zef = \frac{Zev}{2\pi r}$$

(v – speed,
e – electron charge
Z – nuclear number
r – orbit radius)

Therefore, the magnetic field produced by the current at the electron is

$$B = \frac{1}{4\pi\varepsilon_0}\frac{2\pi i}{c^2 r} = \frac{1}{4\pi\varepsilon_0}\frac{Zev}{c^2 r^2}$$

Written in vector: $\vec{B} = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{c^2 r^3}(-\vec{v})\times\vec{r} = \frac{1}{4\pi\varepsilon_0}\frac{Ze}{E_0 r^3}\vec{l}$

where $\vec{l} = m_e\vec{r}\times\vec{v}$, $E_0 = m_e c^2$ is the rest energy of electron.

Electron has spin magnetic moment $\vec{\mu}_s$, so it will interact with the magnetic field and have potential energy

$$U = -\vec{\mu}_s\cdot\vec{B}$$

Substituting $\mu_s = -\sqrt{s(s+1)}\, g_s\mu_B$, $|\vec{s}| = \sqrt{s(s+1)}\,\hbar$, and $\vec{B}$ into eq.,

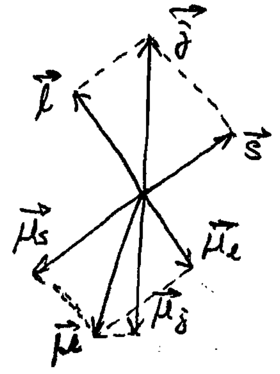
we obtain: $U = \frac{1}{4\pi\varepsilon_0}\frac{Z g_s\mu_B e}{E_0\hbar r^3}\vec{s}\cdot\vec{l}$ — This is the equation in the coordinates with the electron at rest.

When turn it into the coordinates with the nucleus at rest, there is a correction factor $\frac{1}{2}$. Therefore,

$$U = \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\frac{Z g_s \mu_B e}{m_e c^2 \hbar r^3}\vec{s}\cdot\vec{l}, \qquad \boxed{g_s = 2} \quad \boxed{\mu_B = \frac{e\hbar}{2m_e}}$$

② Another view is to say the spin-orbit coupling is the magnetic interaction between the orbital magnetic moment $\vec{\mu}_l$ and the spin magnetic moment $\vec{\mu}_s$ of the electron — analogy to the interaction between two small magnet bars.

③. More accurate explanation is from QM — the coupling of two angular momentums and cause the additional energy corrections:



$$\vec{j} = \vec{s} + \vec{l}$$

$$\therefore \quad \vec{j}^2 = \vec{s}^2 + \vec{l}^2 + 2\vec{s}\cdot\vec{l}$$

Eigenvalues of $\hat{\vec{j}}^2$ are $j(j+1)\hbar^2$,

where $j = |l+s|, |l+s|-1, \cdots, |l-s|$.

Eigenvalues of j_z are $m_j\hbar$, where $m_j = j, j-1, \cdots, -j$.

and $m_j = m_l + m_s$.

The interaction of the electron spin-orbit coupling can be expressed as an operator:

$$\Delta\hat{H}_{ls} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Z g_s \mu_B e}{2 m_e c^2 \hbar r^3}\hat{s}\cdot\hat{l}.$$

Thus, the total Hamiltonian operator: $\hat{H} = \hat{H}_0 + \Delta\hat{H}_{ls}$

where $\hat{H}_0 = \frac{\hat{p}^2}{2\mu} + \left(-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}\right)$.

Using time-independent perturbation theory (an approach), we can derive the energy shift ΔE_{ls} caused by this spin-orbit coupling interaction by deriving the mean value of $\Delta \hat{H}_{ls}$ in the state ψ_{nls} (i.e., small perturbation doesn't cause the change ~~of wave function ψ_{nls}) :~~

$$\Delta E_{ls} = \langle \Delta \hat{H}_{ls} \rangle = \int \psi^{*}_{nls} \, \Delta \hat{H}_{ls} \, \psi_{nls} \, d^3r .$$

The result is :

$$\begin{cases} \Delta E_{ls} = \dfrac{(\alpha Z)^4 m_e c^2}{4 n^3} \, \dfrac{[\,j(j+1) - l(l+1) - s(s+1)\,]}{l(l+1/2)(l+1)} , & l \neq 0 \\[2ex] \Delta E_{ls} = 0, & \text{when } l = 0 \end{cases}$$

Where $\alpha = \dfrac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \dfrac{1}{137}$ is the fine structure constant (dimensionless) important !

$$\boxed{\overline{\hat{S}\cdot\hat{l}} = \frac{1}{2}(\hat{j}^2 - \hat{s}^2 - \hat{l}^2) = \frac{1}{2}[\,j(j+1) - s(s+1) - l(l+1)\,]\hbar^2}$$

(7) As mentioned above, after the coupling of two angular momentums, the magnetic moment corresponding to the total angular momentum is given by $\mu_j = -\sqrt{j(j+1)}\, g_j \, \mu_B$, $\mu_{j,z} = -m_j g_j \mu_B$.

QM shows that g_j (the Lande g-factor) is given by

$$g_j = \frac{3}{2} + \frac{1}{2}\left(\frac{\hat{S}^2 - \hat{l}^2}{\hat{j}^2}\right) = \frac{3}{2} + \frac{1}{2}\left[\frac{S(S+1) - l(l+1)}{j(j+1)}\right].$$

This also stands true if an atom has many electrons, and electrons form an total spin S, total orbital L, and L-S Coupling is true, then

$$(\vec{J} = \vec{L} + \vec{S}) \longrightarrow g_J = \frac{3}{2} + \frac{1}{2}\left[\frac{S(S+1) - L(L+1)}{J(J+1)}\right].$$

(8) Rules for angular momentum coupling:

$$\vec{J} = \vec{L} + \vec{S}$$

Quantum number: $J = |L+S|, |L+S|-1, \cdots, |L-S|$

$$m_J = J, J-1, \cdots, -J$$

Different J will corresponding to different energy correction, so the originally degenerate energy levels may become non-degenerate, or partially non-degenerate.

* To express different energy states, we use the following terms: $^{2S+1}L_J$

spin quantum number

orbital angular momentum quantum number

total angular momentum quantum number.

Capitalized letters S, L, J are used to denote the overall electrons' effects. If it is a single electron, like in hydrogen-like atom or ions, we may use small letters: s, l, j.

For example, for H-atom ground state

$^2S_{1/2}$, $s = \frac{1}{2} \longrightarrow 2S+1 = 2 \Rightarrow S = 1/2$

$l = 0 \longrightarrow S \rightarrow l = 0$

$j = \frac{1}{2}$.

$l = 0, 1, 2, 3, 4 \ldots$

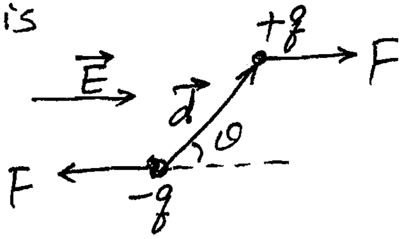
$\Rightarrow$ S, P, D, F, G$\cdots$

s, p, d, f, g, $\cdots$

Appendix Dipole moment:

(1) Electric Dipole Moment: definition is

$$\vec{D} = q\vec{d}$$



In homogeneous electric field,
the electric dipole will experience a moment of force (torque)

$$\vec{\tau} = \vec{d}\times\vec{F} = \vec{d}\times(q\vec{E}) = (q\vec{d})\times\vec{E}$$

$$\Rightarrow \quad \vec{\tau} = \vec{D}\times\vec{E}$$

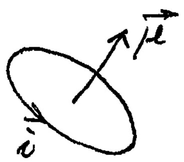
The potential energy of the electric dipole moment in the homogeneous electric field is given by the work done by this moment of force: $U_E = \int_{\pi/2}^{\theta} \tau\, d\theta = -DE\cos\theta$.

Here we define the potential energy $=0$ for $\theta = 90°$.

Thus, the potential energy $U_E = -\vec{D}\cdot\vec{E}$

(2) Magnetic dipole moment: defined as

$$\vec{\mu} = i S \vec{n}_0 = i\vec{S}.$$



In homogeneous magnetic field,
the magnetic dipole will experience a moment of force (torque),

$$\vec{\tau} = \vec{\mu}\times\vec{B}$$

Similar to the electric dipole moment case, the potential energy of the magnetic moment in the homogeneous magnetic field is given by $U_B = -\vec{\mu}\cdot\vec{B}$

Any force can be written as the gradiant of a potential energy:

$$\vec{F} = -\vec{\nabla}U = -\left(\frac{\partial U}{\partial x}\vec{i} + \frac{\partial U}{\partial y}\vec{j} + \frac{\partial U}{\partial z}\vec{k}\right).$$

∴ Z component of force acting on a magnetic moment is

$$F_z = -\frac{\partial U}{\partial z} = \mu_x\frac{\partial B_x}{\partial z} + \mu_y\frac{\partial B_y}{\partial z} + \mu_z\frac{\partial B_z}{\partial z}.$$

(3) Force, moment of Force, momentum, and angular momentum

① Force causes the change of momentum, i.e.,

$$\vec{F} = \frac{d}{dt}(m\vec{v}) = \frac{d\vec{P}}{dt}$$

In another format:

$$\vec{F} \cdot \Delta t = \Delta(m\vec{v}) = \Delta\vec{P} = \vec{P}_{Final} - \vec{P}_{initial}$$

i.e., impulse (force x time) is equal to the change amount of momentum.

② Moment of force causes the change of angular momentum,

i.e., $\vec{\tau} = \vec{r} \times \frac{d}{dt}(m\vec{v}) = \frac{d\vec{l}}{dt}$, $\vec{l} = \vec{r} \times \vec{p}$

$\because \vec{l} = \vec{r} \times \vec{p}$,

$$\therefore \frac{d\vec{l}}{dt} = \frac{d(\vec{r})}{dt} \times m\vec{v} + \vec{r} \times \frac{d(m\vec{v})}{dt} = \vec{r} \times \frac{d(m\vec{v})}{dt}$$

$$= \vec{r} \times \vec{F} = \vec{\tau}.$$

$\because \frac{d\vec{r}}{dt} = \vec{v}$, $\therefore \frac{d\vec{r}}{dt} \times m\vec{v} = 0$

In other format: $\vec{\tau} \cdot \Delta t = \Delta\vec{l} = \vec{l}_{Final} - \vec{l}_{initial}$

i.e., Moment of impulse (i.e., $\vec{\tau} \cdot \Delta t = \vec{r} \times (\vec{F}\Delta t)$) is equal to the change amount of angular momentum.

(9) Explanation of Stern-Garlach Experiment

* In the Stern-Gerlach experiment, the hydrogen atoms are in the ground state: $n=1$, $l=0$. For the single atom, it has a spin angular momentum $s = 1/2$.

The electron spin-orbit coupling: $\hat{\vec{j}} = \hat{\vec{s}} + \hat{\vec{l}} \Rightarrow j = l+s = 1/2$
i.e., for the H ground state, there is only $= |l-s| = 1/2$
one total angular momentum $j = 1/2$.

* According to the rules we described in last lecture, the ground state term is $^{2S+1}L_J \Rightarrow {}^{2\times\frac{1}{2}+1}S_{1/2} \Rightarrow {}^2S_{1/2}$

If we add n at the left side of this term, then the H ground state is: $1\,^2S_{1/2}$ (format: $\underline{\underline{n\,^{2S+1}L_J}}$)

* For the coupled total angular moment, the atom has an electron magnetic moment $\mu_j = -\sqrt{j(j+1)}\, g_j \mu_B$

and its z-component $\mu_{j,z} = m_j g_j \mu_B$

For H: $1\,^2S_{1/2}$, $s=1/2$, $l=0$, $j=1/2$, $n=1$, $m_j = \pm 1/2$

$$\therefore g_j = \frac{3}{2} + \frac{1}{2}\left[\frac{\frac{1}{2}\times(\frac{1}{2}+1) - 0(0+1)}{\frac{1}{2}\times(\frac{1}{2}+1)}\right] = \frac{3}{2}+\frac{1}{2} = 2.$$

$$\therefore \mu_j = -\frac{\sqrt{3}}{2}\times 2\mu_B = -\sqrt{3}\,\mu_B$$

$$\mu_{j,z} = \pm\frac{1}{2}\times 2\mu_B = \pm\mu_B.$$

i.e., μ_z has two distinct values: $+\mu_B$ and $-\mu_B$.

* In S-G experiment, $Z_2 = \mu_z \frac{\partial B_z}{\partial z}\cdot\frac{d\cdot D}{mv^2} = \pm\mu_B\frac{\partial B_z}{\partial z}\cdot\frac{d\cdot D}{3k_BT}$

$\therefore$ Hydrogen beam splits to two beams under inhomogeneous magnetic field: one goes up and another goes down.

* Some concrete experimental data in S-G experiment:

$\frac{\partial B_z}{\partial z} = 10\ T/m$, $d = 1m$, $D = 2m$, $T = 400k$, $k_B = 1.38\times10^{-23}\ J/k$

$\mu_B = 0.9274\times10^{-23}\ J/T$. We get:

$$Z_z = \pm \mu_B \frac{\partial B_z}{\partial z} \cdot \frac{d \cdot D}{3k_BT}$$

$$= \pm 0.9274\times10^{-23} \times 10 \times \frac{1\times2}{3\times1.38\times10^{-23}\times400}$$

$$= \pm 1.12\times10^{-2} m = \pm 1.12 cm.$$

* Tablized S-G experimental results for different atoms

Atoms	Ground State	g	m·g	Pattern
Zn, Cd, Hg, Pd	$^1S_0$	—	0	∣
Sn, Pb	$^3P_0$	—	0	∣
H, Li, Na, K, Cu, Ag, Au	$^2S_{1/2}$	2	±1	∣ ∣
Tl	$^2P_{1/2}$	2/3	±1/3	∣ ∣
O	$^3P_2$	3/2	$\pm3, \pm\frac{3}{2}, 0$	∣ ∣ ∣ ∣ ∣
	$^3P_1$	3/2	$\pm\frac{3}{2}, 0$	∣ ∣ ∣
	$^3P_0$	—	0	∣

* Stern-Gerlach experiment was a milestone experiment in atomic/Quantum physics, as it proved three things:

(1) Angular momentum is spatially quantized.

(2) an electron has spin angular momentum, and $S = 1/2$

(3) The electron spin magnetic moment $\mu_{s,z} = \pm\mu_B$, and $g_s = 2$.

(10) Fine Structure (Energy level splitting) of Hydrogen Atoms

- The electron spin-orbital angular momentum coupling causes the hydrogen energy levels to shift and/or split to form fine structure. At the same time, relativity also introduces two correction terms to the energy levels: correction due to mass correction in relativity and correction called Darwin term, also due to relativity.
- Relativity-corrected Schrödinger equation:
  We only consider this for hydrogen-like atom (ion) — the electron spin is ½, so the relativity-corrected Schrödinger equation is called the "Dirac equation". In absence of external field, the Hamiltonian operator is

$$\hat{H} = \hat{H}_0 + \Delta\hat{H}_m + \Delta\hat{H}_{ls} + \Delta\hat{H}_d$$

where $\hat{H}_0 = \frac{\hat{\vec{p}}^2}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$ is the Hamiltonian operator in the non-relativity case (only consider electrostatic interaction between the nucleus and the single electron).

$$\Delta\hat{H}_m = -\frac{\hat{\vec{p}}^4}{8\mu^3c^2} = \frac{1}{2\mu c^2}\left(H_0 + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2$$ is the operator corresponding to the correction caused by the kinetic energy change due to the mass change in relativity.

$$\Delta\hat{H}_{ls} = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{2\mu^2c^2r^3}\hat{\vec{s}}\cdot\hat{\vec{l}}$$ is the operator corresponding to the electron spin-orbit coupling interaction.

$$\Delta\hat{H}_d = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2\hbar^2}{4\mu^2c^2r^2}\frac{d}{dr}$$ is the operator corresponding to a relativity correction, called Darwin term (in memory of C. Darwin).

* The relativity correction can be viewed as below: when a particle is at rest, its energy in relativity theory corresponding to the rest mass m_0 is given by $E_0 = m_0 c^2$, where c is light speed.

When the particle moves with a velocity v, then its energy becomes:

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1-\frac{v^2}{c^2}}}$$

i.e., the particle's mass becomes larger than its rest mass m_0.

The gained energy of E compared to E_0 is defined as the particle's kinetic energy:

$$E_K = E - E_0 = mc^2 - m_0 c^2 = m_0 c^2 \left(\frac{1}{\sqrt{1-v^2/c^2}} - 1\right).$$

This relativitic E_K is different than classical $E_K^{Classic} = \frac{1}{2} m_0 v^2$.

If $v << c$, then $E_K = m_0 c^2 \left(1 + \frac{1}{2} v^2/c^2 - 1\right) = \frac{1}{2} m_0 v^2$, which turns into the classical expression.

In relativity, the momentum is

$$P = mv = \frac{m_0 v}{\sqrt{1-v^2/c^2}}.$$

$\therefore$ There exists such a relationship between E and P:

$$E = \sqrt{P^2 c^2 + m_0^2 c^4} = \frac{m_0 c^2}{\sqrt{1-v^2/c^2}} = mc^2.$$

Expanding E and take approximation, we obtain

$$E = \sqrt{P^2 c^2 + m_0^2 c^4} = m_0 c^2 \sqrt{1 + \frac{P^2 c^2}{m_0^2 c^4}} = m_0 c^2 \sqrt{1 + \left(\frac{P}{m_0 c}\right)^2}$$

$$= m_0 c^2 \left[1 + \frac{1}{2} \frac{P^2}{m_0^2 c^2} - \frac{1}{2} \times \frac{1}{4} \left(\frac{P^2}{m_0^2 c^2}\right)^2\right]$$

$$= m_0 c^2 + \frac{P^2}{2 m_0} \boxed{- \frac{P^4}{8 m_0^3 c^2}}$$

The third term is the correction ↑ caused by relativity mass change

* For energy eigenvalue equation (i.e., stationary-state Schrödinger equation),

$$\hat{H}\psi = E\psi$$

If $\hat{H} = \hat{H}_0 + \Delta H$, and $\hat{H}_0$ eigenvalue equation can be solved exactly: $\hat{H}_0 \psi^{(0)} = E^{(0)}\psi^{(0)}$.

and if $\Delta\hat{H} << \hat{H}_0$, then we can use perturbation theory to solve the $\hat{H}$ equation approximately. Usually, this is based on the $\psi^{(0)}$ and $E^{(0)}$, and then make the first order correction to wave functions, and make the first and second order correction to the energy eigenvalues.

After 1st order correction, the wave function is

$$\psi_k = \psi_k^{(0)} + \sum_n{}' \frac{\Delta H_{nk}}{E_k^{(0)} - E_n^{(0)}} \psi_n^{(0)}$$

After two orders of correction, the energy eigenvalue is

$$E_k = E_k^{(0)} + \Delta H_{kk} + \sum_n{}' \frac{|\Delta H_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}$$

where $\Delta H_{nk} = \int \psi_n^{(0)*} \Delta\hat{H} \psi_k^{(0)} d^3r \equiv \langle n|\Delta\hat{H}|k\rangle$

and $\sum_n{}'$ means to take sum but excluding $n=k$.

[If you are interested in the perturbation theory, you may check a QM book to learn it. We will just use its calculation results in our Spectroscopy class.]

* $\Delta\hat{H}_m$, $\Delta\hat{H}_{ls}$, and $\Delta\hat{H}_d$ terms of hydrogen atom are regarded as perturbations to $\hat{H}_0$ operator. The QM calculation results are:

$$\Delta E_m = \langle \Delta\hat{H}_m \rangle = -\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\left[\frac{1}{l+1/2} - \frac{3}{4n}\right]$$

for all possible l (in SI unit)

$$\Delta E_{ls} = \begin{cases} \dfrac{\alpha^4 Z^4 \mu c^2}{4n^3} \cdot \dfrac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, \quad l = 0 \end{cases} \quad \text{(in SI unit)}$$

$$\Delta E_d = \begin{cases} 0, & l \neq 0 \\ \dfrac{\alpha^4 Z^4 \mu c^2}{2n^3}, & l = 0 \end{cases} \quad \text{(in SI unit)}$$

* The sum of the relativity, $\hat{\vec{l}} \cdot \hat{\vec{s}}$ coupling, and Darwin terms are

$$\Delta E = \Delta E_m + \Delta E_{ls} + \Delta E_d$$
$$= -\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\left[\frac{1}{j+1/2} - \frac{3}{4n}\right],$$

where $j = l \pm s = l \pm \frac{1}{2}$, $s = 1/2$ for single electron.

This is the result from Dirac equation, i.e., the relativity-corrected Schrödinger equation for $S = 1/2$ (spin) particles. In other words, this is the result for hydrogen and hydrogen-like atoms (ions), whose electron spin angular momentum is $S = 1/2$.

* Example, Hydrogen atom $n=2$ energy level split:

		ΔE_m	ΔE_d	ΔE_{ls}	ΔE
$s=\frac{1}{2}$, $l=1$,	$j=3/2$	$-7/24$	0	$1/6$	$-1/8$
	$j=1/2$	$-7/24$	0	$-1/3$	$-5/8$
$s=\frac{1}{2}$, $l=0$,	$j=1/2$	$-13/8$	1	0	$-5/8$.

unit: $\left(\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\right)$.

Let's put in the real number to have an idea about the magnitude of energy splitting:

$\alpha \approx \frac{1}{137}$, $Z=1$, $\mu \approx m_e = 9.1\times10^{-31}\,kg$, $C=3\times10^8\,m/s$

$n=2$.

$$\therefore \frac{\alpha^4 Z^4 \mu c^2}{2n^3} = \frac{\left(\frac{1}{137}\right)^4 \times 1^4 \times 9.1\times10^{-31}\times(3\times10^8)^2}{2\times2^3} = 1.45\times10^{-23}\,J.$$

$\therefore$ The corresponding frequency is

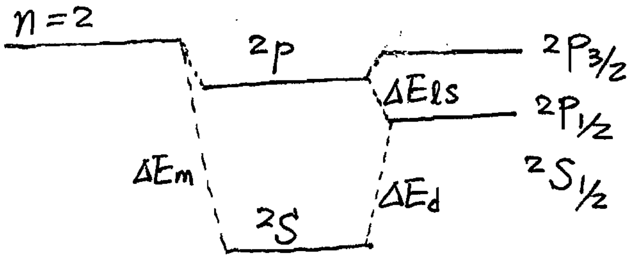
$$\Delta\nu = \frac{\Delta E}{h} = \frac{1.45\times10^{-23}}{6.626\times10^{-34}} = 2.19\times10^{10}\,Hz = 2.19\times10^4\,MHz.$$

For H-atom $n=2$ energy levels:

2P energy level: ${}^2P_{3/2}$ and ${}^2P_{1/2}$ have a split

$$\text{of } \left(-\frac{1}{8}\right)-\left(-\frac{5}{8}\right) = -\frac{1}{2}\cdot\frac{\alpha^4 Z^4 \mu c^2}{2n^3}$$

$$= -\frac{1}{2}\times 2.19\times10^4\,MHz = -1.09\times10^4\,MHz$$



Hydrogen $n=2$ energy level Fine Structure

3. Nucleus Influences and Hyperfine Structure

* In above atomic structure calculations, the nucleus has been treated as a point charge with certain mass. Only its electrostatic interaction with the electron is considered.

* However, in reality, the nucleus (even only consisting of one proton) is not a point mass or point charge. It has volume, charge distribution, spin angular momentum, magnetic moment. These properties cause the nucleus to interact with the magnetic and electric field produced by the electron, resulting in energy levels shift. splitting, and spectral lines to further splitting.

* Because the order of magnitude of these splittings is even smaller than the fine structure splitting, these splittings are called "Hyperfine Structure". The interactions that cause these hyperfine structures are called "hyperfine interaction".

* Table below lists a comparison of the order of magnitude of Coulomb potential, fine structure and hyperfine structure:

Interaction	Order of Magnitude of Energy Change		
	Hz	eV	cm^{-1}
Electrostatic Coulomb Force (Coarse Structure)	10^{15}	4	30,000
Fine Structure	$3\times10^{10} - 3\times10^{13}$	$10^{-4} - 10^{-1}$	1 – 1,000
Hyperfine Structure	$3\times10^{7} - 3\times10^{10}$	$10^{-7} - 10^{-4}$	$10^{-3} - 1$

* In general, the fine structure is about 10^4 times smaller than coarse structure ($\alpha^2 \approx 10^4$), and the hyperfine structure is about 10^3 times smaller than the fine structure.

* A nucleus can have magnetic multipole moments and electric multipole moments. The moments that have major influences on atomic energy levels are magnetic dipole moment and the electric quadrupole moment of the nucleus. Their influences form the hyperfine structure.

* In addition, isotopes have the same nuclear charge but different nuclear mass, different nuclear charge distribution, and different nuclear volume. These factors will also influence atomic energy levels and spectral lines. Their magnitudes are similar to hyperfine structure.

* Here we will consider the hyperfine structure caused by the nuclear magnetic dipole moment and electric quadrupole moment, and the isotope shifts.

(1) Magnetic hyperfine structure (magnetic dipole moment)

* A nucleus has intrinsic spin angular momentum $\hat{\vec{I}}$.

The eigenvalue of $\hat{\vec{I}}^2$ is (analogy to electron spin)

$$|\hat{\vec{I}}^2| = I(I+1)\hbar^2, \quad (I \text{ can be integer or half-integer})$$

The eigenvalue of z-component $\hat{I}_z$ is

$$|\hat{I}_z| = m_I \hbar, \quad m_I = I, I-1, \cdots, -I$$

Associated with the nuclear spin angular momentum, the nuclear magnetic dipole moment $\hat{\mu}_I$ is

$$\hat{\mu}_I = g_I \frac{e}{2M_p} \hat{I} = g_I \frac{e\hbar}{2M_p} \sqrt{I(I+1)}$$

$$\hat{\mu}_{I,z} = g_I \frac{e}{2M_p} \hat{I}_z = g_I m_I \frac{e\hbar}{2M_p}$$

where M_P is the proton mass, and e is the electron charge. Define a nuclear magneton μ_N as:

$$\mu_N \equiv \frac{e\hbar}{2M_P}$$

Since Bohr magneton $\mu_B \equiv \frac{e\hbar}{2m_e}$, the nuclear magneton is 3 order of magnitude smaller than the Bohr magneton:

$$\frac{\mu_N}{\mu_B} = \frac{m_e}{M_P} \approx \frac{1}{1836}$$

Using the nuclear magneton, the nuclear magnetic dipole moment and its z-component can be expressed as

$$\begin{cases} \mu_I = \sqrt{I(I+1)}\, g_I\, \mu_N \\ \mu_{I,z} = m_I\, g_I\, \mu_N . \end{cases}$$

Example: For proton (^1H): $I=\frac{1}{2}$, $\mu_I = 2.79\mu_N$, $g_I = 5.58$.

For (^2D): $I=1$, $\mu_I = 0.86\,\mu_N$, $g_I = 0.86$

For neutron (n): $I=\frac{1}{2}$, $\mu_I = -1.91\,\mu_N$, $g_I = -3.82$.

* The nuclear magnetic dipole moment will interact with the magnetic field produced by the electron at the nucleus' position. This magnetic dipole interaction is given by a Hamiltonian operator: $\Delta\hat{H}_M = -\hat{\vec{\mu}}_I \cdot \hat{\vec{B}}_e$

$\because$ $\hat{\mu}_I \propto \hat{\vec{I}}$, and $\hat{\vec{B}} \propto \hat{\vec{J}}$ (i.e., electron-produced magnetic field $\vec{B}_e$ is proportional to electron total angular momentum $\hat{\vec{J}}$), $\therefore$ We can have

$$\Delta\hat{H}_M = A\,\hat{\vec{I}} \cdot \hat{\vec{J}}$$

This is a general expression of magnetic hyperfine interaction. A is called the magnetic hyperfine interaction constant.

Note: A is very different from α. The fine structure constant α is a universal constant ($\alpha \approx \frac{1}{137}$). But A can be different for different atomic states.

Now consider single electron atoms (hydrogen atom or hydrogen-like ions),

* If $l \neq 0$, the electron-produced magnetic field is

$$\vec{\hat{B}}_e' = \frac{(-e\vec{\hat{v}})\times(-\vec{\hat{r}})}{c r^3} - \frac{1}{r^3}\left[\vec{\hat{\mu}}_s - \frac{3(\vec{\hat{\mu}}_s\cdot\vec{\hat{r}})\,\vec{\hat{r}}}{r^2}\right], \quad r \neq 0$$

where the first term is the magnetic field produced by electron orbital motion, $\vec{v}$ is electron orbital motion velocity, $\vec{r}$ is the electron coordinates regarding nucleus as the origin; the second term is the magnetic field produced by the electron spin magnetic moment $\vec{\mu}_s$.

Since $\vec{\hat{\mu}}_s = -2\mu_B\vec{\hat{s}}$, and $-e\vec{\hat{r}}\times\frac{\vec{\hat{v}}}{c} = 2\mu_B\vec{\hat{l}}$,

($\vec{\hat{s}}$ and $\vec{\hat{l}}$ are electron's spin and orbital angular momentum)

We have
$$\vec{\hat{B}}_e' = -2\frac{\mu_B}{r^3}\left[\vec{\hat{l}} - \vec{\hat{s}} + 3\frac{(\vec{\hat{s}}\cdot\vec{\hat{r}})\,\vec{\hat{r}}}{r^2}\right]$$
$$= -2\frac{\mu_B}{r^3}\vec{\hat{N}}$$

where $\vec{\hat{N}} = \vec{\hat{l}} - \vec{\hat{s}} + \frac{3(\vec{\hat{s}}\cdot\vec{\hat{r}})\,\vec{\hat{r}}}{r^2}$.

Since the angular momentum $\vec{\hat{N}}$ precesses around the electron total angular momentum $\vec{\hat{j}}$, the effective contribution is the projection of $\vec{\hat{N}}$ on the $\vec{\hat{j}}$ direction, Therefore, $\vec{\hat{B}}_e'$ should be
$$\vec{\hat{B}}_e = -\frac{2\mu_B}{r^3}\,\frac{\vec{\hat{N}}\cdot\vec{\hat{j}}}{j(j+1)}\,\vec{\hat{j}}$$

$\therefore$ the Hamiltonian operator is
$$\Delta\hat{H}_M = \left(2\mu_B\frac{\mu_I}{I}\right)\frac{1}{r^3}\cdot\frac{\vec{\hat{N}}\cdot\vec{\hat{j}}}{j(j+1)}\,\vec{\hat{I}}\cdot\vec{\hat{j}}.$$

The energy shift caused by this Hamiltonian operator can be derived by taking the mean of $\Delta\hat{H}_M$ in known electron wave function:

$$\Delta E_M = \langle \Delta\hat{H}_M \rangle = \frac{a_j}{2}\left[F(F+1) - j(j+1) - I(I+1)\right]$$

Here F is the quantum number for the total angular momentum $\hat{\vec{F}}$ of the entire atom. (note: $\hat{\vec{j}}$ is the total angular momentum of electron)

$$\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{J}}, \qquad F = I+J,\ I+J-1, \cdots, |I-J|.$$

$\hat{\vec{F}}$ is conservative as long as no external field presents.
$\hat{\vec{I}}$ is the nuclear angular momentum,
$\hat{\vec{J}}$ is the total angular momentum of the electrons.

where $\hat{\vec{I}}\cdot\hat{\vec{J}} = \frac{1}{2}\left(\hat{\vec{F}}^2 - \hat{\vec{J}}^2 - \hat{\vec{I}}^2\right) = \frac{1}{2}\left[F(F+1) - J(J+1) - I(I+1)\right].$

$$a_j = \left(2\mu_B\frac{\mu_I}{I}\right)\left\langle\frac{1}{r^3}\right\rangle\frac{l(l+1)}{j(j+1)}, \quad l \neq 0$$

* If $l=0$, then the magnetic hyperfine constant A is denoted as a_s which is given by

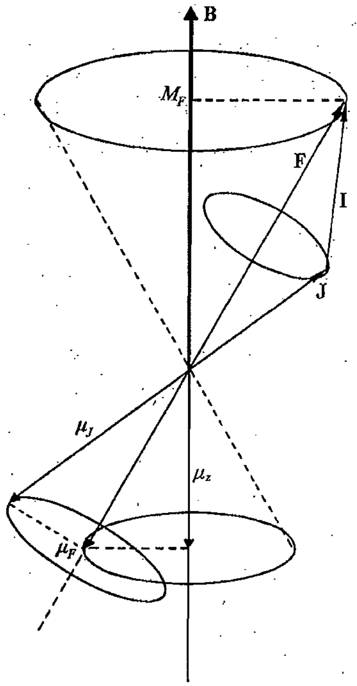
$$a_s = \left(2\mu_B\frac{\mu_I}{I}\right)\frac{8\pi}{3}|\psi(0)|^2, \quad l=0.$$

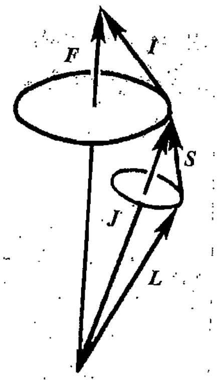
$$\therefore\ \Delta E_M = \langle\Delta\hat{H}_M\rangle = \frac{a_s}{2}\left[F(F+1) - j(j+1) - I(I+1)\right]$$

a_s is proportional to the probability density $|\psi(0)|^2$ at the nucleus' position $(r=0)$.

* Overall:

$$\Delta E_M = \begin{cases} \frac{a_s}{2}\left[F(F+1) - j(j+1) - I(I+1)\right], & l=0 \\ \quad \text{where } a_s = \left(2\mu_B\frac{\mu_I}{I}\right)\frac{8\pi}{3}|\psi(0)|^2 & \\ \frac{a_j}{2}\left[F(F+1) - J(J+1) - I(I+1)\right], & l\neq 0 \\ \quad \text{where } a_j = \left(2\mu_B\frac{\mu_I}{I}\right)\left\langle\frac{1}{r^3}\right\rangle\frac{l(l+1)}{j(j+1)}. & \end{cases}$$





Vector Model of Angular Momentum Coupling

$$\hat{\vec{\mu}}_F = \sqrt{F(F+1)}\, g_F\, \mu_N$$

$$\hat{\mu}_{F,z} = m_F\, g_F\, \mu_N \,, \quad m_F \doteq F, F-1, \cdots, -F.$$

Note: only when the electron wave function is known, we can calculate the hyperfine structure.

* Example: Hydrogen magnetic hyperfine structure (including hydrogen-like ions with nuclear charge Ze)

$$|\psi(0)|^2 = \frac{Z^3}{\pi a_1^3 n^3} \Rightarrow$$

$$a_s = \frac{1}{4\pi\varepsilon_0 c^2}\left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right)\frac{8}{3}\frac{Z^3}{a_1^3 n^3}, \quad l=0$$

For $l \neq 0$ $\quad \langle \frac{1}{r^3} \rangle = \frac{Z^3}{a_1^3 n^3 (l+\frac{1}{2}) l (l+1)} \Rightarrow$

$$a_j = \frac{1}{4\pi\varepsilon_0 c^2}(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}} \left(\frac{Z}{a_1 n}\right)^3 \frac{1}{(l+\frac{1}{2}) j(j+1)}, \quad l \neq 0$$

Let's consider the ground state of hydrogen: $1\,^2S_{1/2}$.

$n=1,\ l=0,\ s=\frac{1}{2},\ j=\frac{1}{2}.\quad I=\frac{1}{2}.\quad \hat{\vec{I}} + \hat{\vec{J}} \Rightarrow \hat{\vec{F}}$

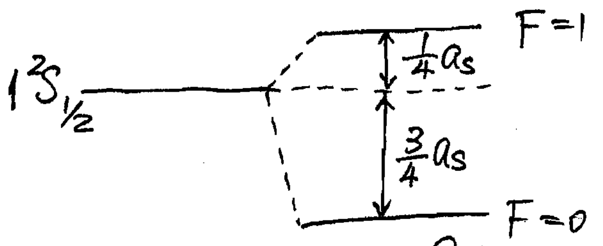
$\because \quad F = I+j,\ I+j-1,\ \cdots,\ |I-j|$

$\therefore \quad F = \frac{1}{2}+\frac{1}{2} = 1, \quad F = \frac{1}{2}-\frac{1}{2} = 0.$

i.e., $^2S_{1/2}$ ground state is split to two hyperfine levels.

For $F=1$, $\quad \Delta E_M = \frac{a_s}{2}[1\times 2 - \frac{1}{2}\times\frac{3}{2} - \frac{1}{2}\times\frac{3}{2}] = \frac{1}{4}a_s$

For $F=0$, $\quad \Delta E_M = \frac{a_s}{2}[0\times 1 - \frac{1}{2}\times\frac{3}{2} - \frac{1}{2}\times\frac{3}{2}] = -\frac{3}{4}a_s$



Hyperfine Splitting of hydrogen

The energy separation between these two hyperfine splittings of hydrogen ground state is

$$\Delta(\Delta E_M(F=1) - \Delta E_M(F=0)]$$
$$= \frac{1}{4}a_s - (-\frac{3}{4}a_s) = a_s$$
$$= h\nu_H.$$

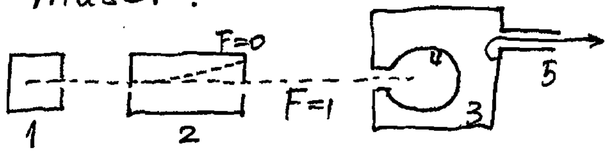
∴ The frequency corresponding to the transition between these two hyperfine splittings is

$$\nu_H = \frac{a_s}{h} = 1420.406 \text{ MHz} \approx 1.42 \text{ GHz}.$$

Corresponding wavelength $\lambda_H = \frac{c}{\nu_H} = 21$ cm.

— This is the most famous hyperfine wavelength in the universe !!! It was the first and also the most frequently used wavelength/frequency in radiofrequency astronomy to detect the distribution of hydrogen atoms in the universe. Remember this: 1420 MHz or 21 cm.

* Application of Hydrogen hyperfine transition 1420 MHz: the hydrogen — maser.



1: hydrogen atom source; 2: State-selector;
3: microwave harmonic oscillator; 4: Quartz cell
5: output of microwave

Working principle: hydrogen atoms coming from the sources are in the ground states F=0 and F=1. When they pass through the state selector, due to different magnetic moments, atoms on F=1 state will pass, while atoms on F=0 state will be kicked out of the beam. Thus, only F=1 atoms enter the quartz cell in the microwave harmonic oscillator. The oscillator is tuned to the hyperfine transition frequency ($F=1 \rightarrow F=0$) 1420 MHz. Thus, Self-oscillation will occur and output EM waves with very high stability. (1×10^{-13})

$$\nu_H = 1420405751.786 \pm 0.028\ Hz.$$

The H-maser has been used as secondary atomic clock to conduct many precise measurements. Unfortunately, the rep of H-master is not very good, so the H-maser is not primary atomic clock.

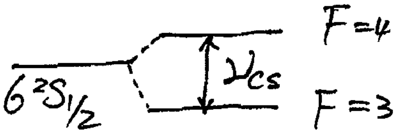
* ^{133}Cs hyperfine transition: (1967)

^{133}Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$

Ground state: $6\,^2S_{1/2}$, $I = 7/2$

$\Rightarrow$ $F = 4$

$F = 3$



$$\nu_{Cs} = 9192631770\ Hz.$$

This is the definition of a <u>second</u> in 1967.

(2) Electric Hyperfine Structure.

Here we consider the electric quadrupole interaction between the nuclear electric quadrupole moment and the electric field produced by the electrons.

* Note: not all atoms have electric quadrupole interaction, because it needs two conditions to have it:

1). nucleus has electric quadrupole moment Q

2). the electric field produced by electrons must have non-zero gradient of electric field.

* Assume electron total angular momentum $\hat{J}$ goes z-direction, electron motion is symmetric around z-axis. Then the electric field gradient $\phi_z = -\frac{\partial E_z}{\partial z} = \frac{\partial^2 V_e}{\partial z^2}$.

Where V_e is the potential produced by the electron.

* QM results give the energy shift caused by the electric quadrupole interaction as:

$$\Delta E_Q = \frac{B}{4} \frac{\frac{3}{2}K(K+1) - 2I(I+1)J(J+1)}{I(2I-1)J(2J-1)},$$

Where $K = F(F+1) - J(J+1) - I(I+1)$.

And $B = eQ\left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle$, is the electric quadrupole hyperfine constant. $\left\langle \frac{\partial^2 V_e}{\partial z^2} \right\rangle$ is the mean value of the electric field gradient produced by electron, and it is dependent on the wave function of electron motion.

* Hamiltonian operator for quadrupole interaction is

$$\Delta \hat{H}_Q = Q^{(2)} \cdot U^{(2)} \quad \Rightarrow \Delta E_Q = \langle \Delta \hat{H}_Q \rangle$$

* There is <u>no</u> electric quadrupole interaction in the following cases: 1). The electron is in S state, i.e., orbital angular momentum $L=0$. Because wavefunction is spherically symmetric, the electric field gradient $\langle \frac{\partial^2 V_e}{\partial z^2} \rangle = 0$.

2). The nuclear angular momentum $I=0$ or $1/2$, then the electric quadrupole $Q=0$.

3). If electron total angular momentum $J=1/2$ or $J=0$, then the electron wave function is spherically symmetric, the electric field gradient is zero at the nucleus.

* When consider the magnetic and the electric hyperfine interaction together, the sum of energy shift is

$$\Delta E = A \cdot \frac{K}{2} + B \cdot \frac{\frac{3}{2}K(K+1) - 2I(I+1)J(J+1)}{4I(2I-1)J(2J-1)}$$

where $K = F(F+1) - J(J+1) - I(I+1)$.

*. For hydrogen atom, because $I = 1/2$, for ${}^1H$, $Q=0$,
So there is no electric quadrupole interaction.

For alkali atoms, $I > \frac{1}{2}$, $\therefore Q \neq 0$.
However, ground state ${}^2S_{1/2} \Rightarrow \langle \frac{\partial^2 V_e}{\partial z^2} \rangle = 0$
excited state ${}^2P_{1/2} \Rightarrow \langle \frac{\partial^2 V_e}{\partial z^2} \rangle = 0$

$\therefore$ there is no electric quadrupole interaction for ${}^2S_{1/2}$. ${}^2P_{1/2}$.
The lowest energy level that can have quadrupole interaction is ${}^2P_{3/2}$: $J > \frac{1}{2}$, $l > 0$, $I > \frac{1}{2}$.

(3) Isotope Shift.

* For different isotopes of the same element, the nuclear magnetic moments and electric moments can be different, so the hyperfine structure can be different for different isotopes. This belongs to the contents we just discussed above.

* In addition, the nuclear mass, volume are different for isotopes, so it will also cause small energy shift. This energy shift is called the isotope shift.

* There are two main effects in isotope shift: mass effect and volume effect. → for heavy elements

for light elements

* Isotope shift caused by mass effect:

Reduced mass in an atom is given by

$$\mu = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + m_e/M}.$$

Using hydrogen as an example,

$$E_n = -\frac{\mu Z^2 e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2} = -\frac{\alpha^2 Z^2 \mu c^2}{2n^2}.$$

i.e., energy levels' energy is proportional to μ.

$$\therefore \quad \frac{\Delta E_n}{E_n} = \frac{\Delta\mu}{\mu} \approx \Delta\left(\frac{1}{1+m_e/M}\right) \approx -\Delta(m_e/M).$$

Consider Hydrogen, if we express E_0 as energy levels in infinit nuclear mass

$$E_0 = -\frac{\alpha^2 Z^2 m_e c^2}{2n^2} = -R_\infty hc\frac{Z^2}{n^2} = -\frac{R_\infty hc}{n^2}$$

$\therefore$ the isotope shift for each isotope of hydrogen is

$$\Delta E = -E_0\,\Delta(m_e/M) = -\frac{R_\infty hcZ^2}{n^2}\cdot\frac{m_e\,\delta M}{M(M+\delta M)}$$

* Isotope Shift caused by nuclear volume effect:

* A nucleus has certain charge distribution within finite volume. The electrostatic interaction between this distributed charge and electron will be different than when assuming the nucleus as a point charge. This is because for s state electrons, wave function is non-zero at the nucleus position, i.e., $\psi(0) \neq 0$. When the electron is in the internal potential of the nucleus, the potential energy is not $-1/r$. A simple explanation is as follows:

* Assume the electron potential at position r from the center of the nucleus:

$$V(r)=\begin{cases} V_0(r) = -\frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{r}, & r>R \\ \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{R}\left(-\frac{3}{2}+\frac{r^2}{2R^2}\right), & 0\le r\le R \end{cases}$$

where R is the radius of the nucleus.

The energy correction Hamiltonian operator is

$$\Delta\hat{H}_s = \hat{V}(r) - \hat{V}_0(r) = V(r) - V_0(r).$$

$\therefore$ The energy shift is

$$\Delta E_s = \langle \Delta\hat{H}_s \rangle = \int_0^\infty \psi^*[V(r)-V_0(r)]\psi\cdot 4\pi r^2 dr$$

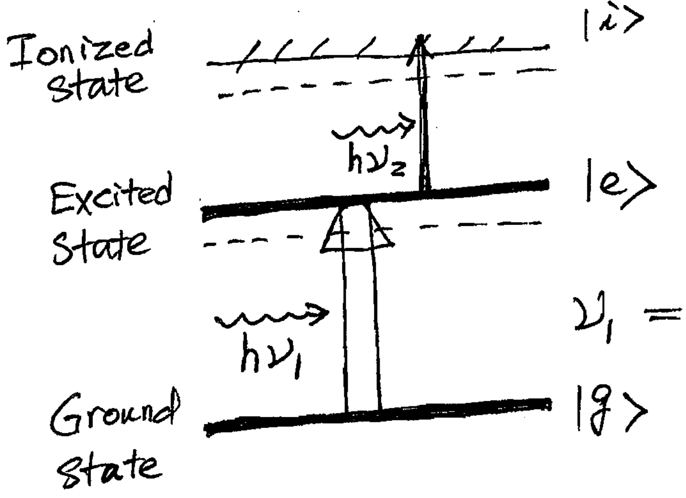
$$= |\psi(0)|^2 \int_0^R [V(r)-V_0(r)]\, 4\pi r^2 dr.$$

$$\therefore \quad \Delta E_s = \frac{2\pi}{5}|\psi(0)|^2 \frac{1}{4\pi\varepsilon_0} Ze^2R^2.$$

— This is the energy difference between a point charge and a charge sphere with radius of R. For different isotopes, R is different. So the energy shift between isotopes is

$$\delta(\Delta E_s) = \frac{4\pi}{5}|\psi(0)|^2 \frac{1}{4\pi\varepsilon_0} Ze^2R^2\frac{\delta R}{R}.$$

* Application of isotope shift — laser isotope separation



$$\nu_2 \geq \frac{E_i - E_e}{h}$$

$$\nu_1 = \frac{E_e - E_g}{h}$$

Workg principle: use single frequency, high power laser with $h\nu_1$ to excite one isotope to the excited state, and then use the 2nd laser beam to ionize it. Once ionized, the ionized isotopes can be separated from other non-ionized isotopes.

An example is Uranium enrichment by laser isotope separation

— laser excite ^{235}U, and then ionize it.

— Ionized ^{235}U is deflected by an electric field, while ^{238}U remain neutral and pass to a different collector.

Appendix: Conversion from Atomic Unit to the SI Unit

* In the atomic unit, the energy correction caused by mass change in relativity theory is

$$\Delta E_m = -\frac{\alpha^2 Z^4}{n^3}\left[\frac{1}{l+1/2} - \frac{3}{4n}\right] \text{ for all possible } l$$

Converting to the SI unit,

$$\Delta E_m = -\frac{\alpha^2 Z^4}{n^3} hc R_H \left[\frac{1}{l+1/2} - \frac{3}{4n}\right],$$

where $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c}$ is fine structure constant

$R_H = \frac{\mu e^4}{(4\pi\varepsilon_0)^2 4\pi \hbar^3 c}$ is Rydberg constant for the hydrogen-like atoms, and $\mu = \frac{m_e M_N}{m_e + M_N}$ is reduced mass.

$$\therefore \Delta E_m = -\frac{e^4 Z^4 hc}{(4\pi\varepsilon_0)^2 \hbar^2 c^2 n^3} \frac{\mu e^4}{(4\pi\varepsilon_0)^2 4\pi \hbar^3 c}\left[\frac{1}{l+1/2} - \frac{3}{4n}\right]$$

$$= -\frac{(e^2)^4 Z^4 \mu c^2}{(4\pi\varepsilon_0)^4 \hbar^4 c^4 2n^3}\left[\frac{1}{l+1/2} - \frac{3}{4n}\right]$$

$$= -\frac{\alpha^4 Z^4 \mu c^2}{2n^3}\left[\frac{1}{l+1/2} - \frac{3}{4n}\right]$$

* Similar derivation can be applied to ΔE_{ls} and ΔE_d:

$$\Delta E_{ls} = \frac{\alpha^2 Z^4}{n^3} \cdot \frac{1}{2} \frac{[j(j+1) - l(l+1) - s(s+1)]}{l(l+1/2)(l+1)} \quad (a.u.)$$

$$\Rightarrow \Delta E_{ls} = \begin{cases} \frac{\alpha^4 Z^4 \mu c^2}{4n^3} \cdot \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, \quad l = 0 \end{cases} \quad \text{(in SI unit)}$$

$$\Delta E_d = \begin{cases} 0, & l \neq 0 \\ \frac{\alpha^2 Z^4}{n^3}, & l = 0 \end{cases} \quad (a.u.)$$

$$\Rightarrow \Delta E_d = \begin{cases} 0, & l \neq 0 \\ \frac{\alpha^4 Z^4 \mu c^2}{2n^3}, & l = 0 \end{cases} \quad \text{(in SI unit)}$$

4. Influence of External (Static) Magnetic Field

(1) Zeeman Effect:

In 1896, Peter Zeeman found that when a light source was placed in a magnetic field, the emitted light spectral line was split into spectral lines. The splitting of spectral line indicates the splitting and shift of corresponding energy levels. This phenomenon is called the Zeeman effect. It is the influence result from the the interaction of atomic magnetic moments and the external static magnetic field.

(2) Interaction of static magnetic field with atoms:

The Hamiltonian operator $\Delta\hat{H}_{mag}$ corresponding to the interaction of a (homogeneous) static external magnetic field with an atom is give by:

$$\Delta\hat{H}_{mag} = -\hat{\vec{\mu}} \cdot \hat{\vec{B}}$$

Where $\hat{\vec{\mu}}$ is the total magnetic moments that an atom has, $\hat{\vec{B}}$ is the external magnetic field. In atomic dimension, $\vec{B}$ can be regarded as homogeneous.

The total magnetic moment $\hat{\vec{\mu}}$ can be regarded as

$$\hat{\vec{\mu}} = \hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s + \hat{\vec{\mu}}_I + \hat{\vec{\mu}}_{induced}$$

Where: $\hat{\vec{\mu}}_l = -g_l \mu_B \hat{\vec{l}}$ is the electron orbital magnetic moment,

$\hat{\vec{\mu}}_s = -g_s \mu_B \hat{\vec{S}}$ is the electron spin magnetic moment.

$\hat{\vec{\mu}}_I = g_I \mu_N \hat{\vec{I}} = g_I' \mu_B \hat{\vec{I}}$ is the nuclear spin magnetic momen

$\hat{\vec{\mu}}_{\text{induced}} = -\frac{\alpha^4}{2} \langle r^2 \sin^2\theta \rangle B$ is the induced magnetic moment under the external magnetic field.

Note that the nuclear magnetic moment is about 3 order of magnitude smaller than $\hat{\vec{\mu}}_l$ and $\hat{\vec{\mu}}_s$. In weak field, the induced magnetic moment is far smaller than the intrinsic magnetic moments ($\hat{\vec{\mu}}_l$ and $\hat{\vec{\mu}}_s$). But pay attention to the "–" sign in the $\hat{\vec{\mu}}_{\text{induced}}$ equation, which means the property of diamagnetism of any atoms. The induced magnetic moment will show effects in high excited states under very strong magnetic field. Here, we will ignore its influence.

$$
\begin{aligned}
\Delta \hat{H}_{mag} &= -\hat{\vec{\mu}} \cdot \hat{\vec{B}} \\
&\cong -(\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s + \hat{\vec{\mu}}_I) \cdot \hat{\vec{B}} \\
&= -(\mu_{lz} + \mu_{sz} + \mu_{Iz}) B \\
&= -\mu_B (g_l m_l + g_s m_s - g_I' m_I) B.
\end{aligned}
$$

(3) Zeeman Effect in Fine Structure

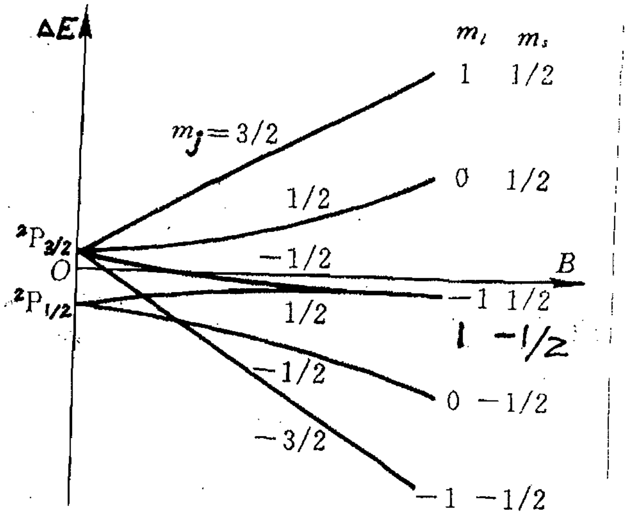
Consider single electron case (hydrogen atom or hydrogen-like ions), we analyze the influence of external magnetic field to the fine structure energy levels and spectral lines.

Here, the g_I' is too small to consider ($g_I' \sim \frac{m_e}{M_p} g_l$ (or g_s)).

Depending on the magnetic field strength, the Zeeman effect could be comparable to the electron spin-orbital coupling interaction. Therefore, these two interactions should be considered together. The corresponding Hamiltonian operator $\Delta\hat{H}$ is:

$$\Delta \hat{H} = a(r)\,\hat{\vec{l}}\cdot\hat{\vec{s}} - (\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\hat{\vec{B}}$$

This $\Delta\hat{H}$ can be treated as a perturbation to the main Hamiltonian operator, and then the energy shift caused by $\Delta\hat{H}$ can be derived from time-independent perturbation theory. This is the advantage of using QM to solve these problems. But the procedure is rather complicated, and we will only show the QM results below: for ^2p state ($s=\frac{1}{2}$, $l=1$).



(x-aix is magnetic field strength)

* In very weak magnetic field, l-s coupling (i.e., spin-orbit coupling) is dominant. So we have $j=\frac{1}{2}$ and $j=3/2$ two cases. That's on the far-most left side of the plot. Each j corresponds to $m_j=\pm\frac{1}{2}$ and $m_j=\pm\frac{3}{2}, \pm\frac{1}{2}$ magnetic sublevels. That's why we see the splitting of the sublevels when $\vec{B}$ gradually increases.

* These sublevels could cross with each other as $\vec{B}$ continues increasing (in the intermedium case).

* In very strong magnetic field, there is no longer l-s coupling, i.e; j and m_j are no longer good quantum numbers as they are not conservative. In this case, l, m_l, S, and m_s are approximately good quantum numbers.

$$m_l = 0, \pm 1, \quad m_s = \pm 1/2$$

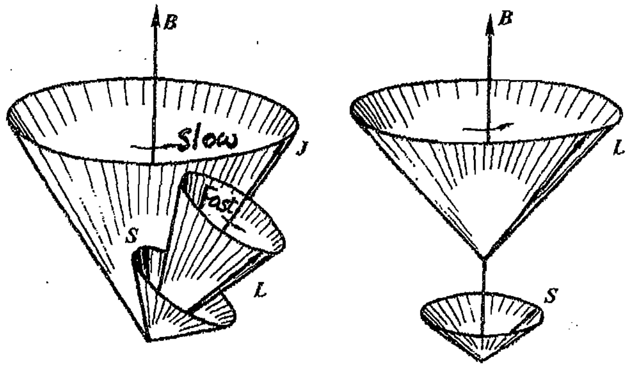
The combination of m_l and m_s is

m_l	1	0	-1	1	0	-1
m_s	½	½	½	-½	-½	-½

That's what is shown at the far-most right side of the plot

The intermedium case can only be solved by QM. But in the two extreme cases (very weak and very strong $\vec{B}$), we can simplify the problem and use vector model to help us to understand the Zeeman effect.

① In weak field approximation: Under weak field, l-S coupling is dominant, so they form fine structure energy levels. Use ^2P as an example, $^2P_{1/2}$ and $^2P_{3/2}$ states.



(a) Weak field (b) Strong Field

Figure. Vector model of spin-orbit coupling

We use the $|l s j m_j\rangle$ representation, regard the Hamiltonian operator $\Delta\hat{H}_{weak} = -(\vec{\mu}_l + \vec{\mu}_s)\cdot\vec{B}$ as perturbation to the $a(r)\,\hat{\vec{l}}\cdot\hat{\vec{s}}$ coupling term.

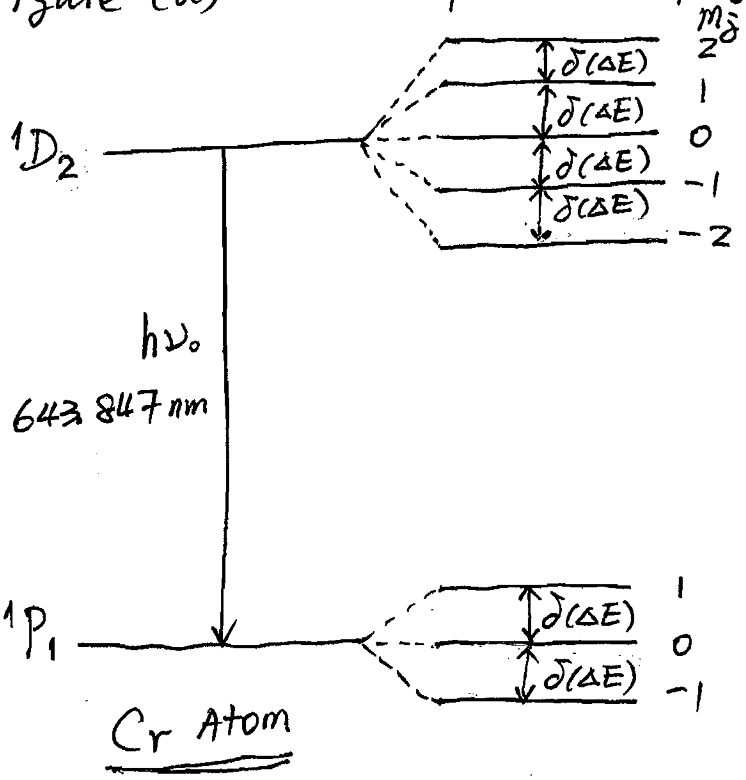
The energy shift caused by this perturbation (relative to the fine structure energy level) is given by

$$\begin{aligned}\Delta E_{mag} &= \langle \Delta \hat{H}_{weak} \rangle \\ &= \langle -(\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\vec{B} \rangle \qquad \left(\text{recall } \mu_{jz} = -g_j m_j \mu_B\right) \\ &= \langle -\mu_{jz} B \rangle \\ &= g_j\, m_j\, \mu_B\, B\end{aligned}$$

where $g_j = \frac{3}{2} + \frac{1}{2}\,\frac{s(s+1) - l(l+1)}{j(j+1)}$ (See appendix for the derivation of g_j)

The vector model for weak field is that angular momentum $\hat{\vec{L}}$ and $\hat{\vec{S}}$ do fast precession around $\hat{\vec{J}}$ direction and form the total angular momentum $\hat{\vec{J}}$, while the $\hat{\vec{J}}$ will process slowly around the external magnetic field $\vec{B}$ (See Figure (a) in the previous page).

Example:



$\left.\begin{array}{l} s=0 \\ l=2 \\ j=2,\end{array}\right\} \Rightarrow g_j = 1$, $m_j = 0, \pm1, \pm2$

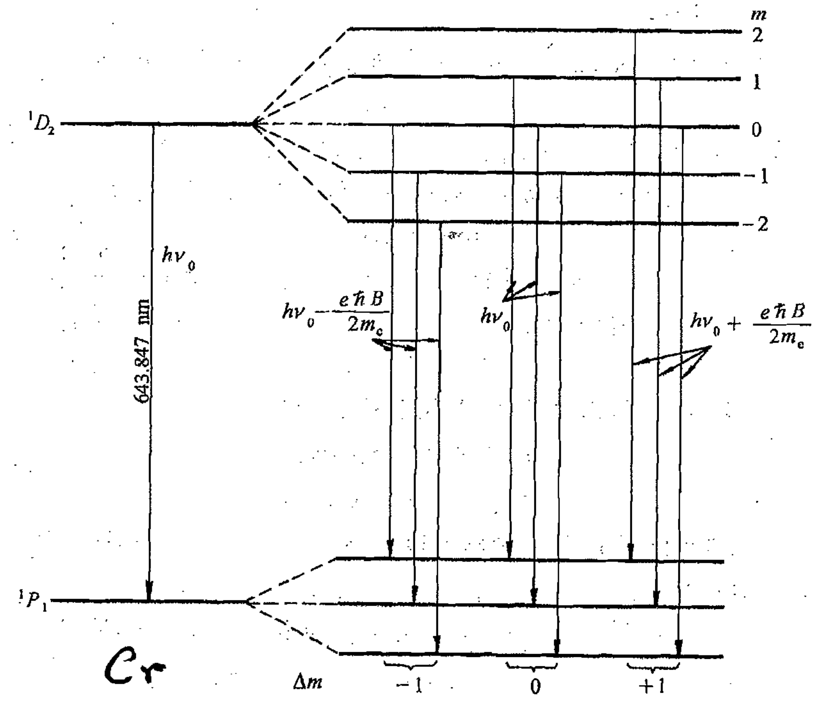
$$\begin{aligned}\delta(\Delta E) &= \Delta E(m_j=2) - \Delta E(m_j=1) \\ &= g_j\, \Delta m_j\, \mu_B\, B \\ &= 1 \times 1 \times \mu_B B \\ &= \mu_B B = \frac{e\hbar}{2m_e} B\end{aligned}$$

$s=0,\ l=1,\ j=1 \Rightarrow g_j = 1$

$m_j = 0, \pm1,$

$$\begin{aligned}\delta(\Delta E) &= \Delta E(m_j=1) - \Delta E(m_j=0) \\ &= g_j\, \Delta m_j\, \mu_B B \\ &= \mu_B B = \frac{e\hbar}{2m_e} B.\end{aligned}$$

Could you try to figure out the Zeeman splitting and spectral line splitting by yourself?



Selection rules $\Delta m_j = 0, \pm 1$.

If E_2 and E_1 are the energy for the upper and lower levels when there is no external magnetic field, then after adding external field, the energy levels become

$$\begin{cases} E_2' = E_2 + m_2 g_2 \mu_B B \\ E_1' = E_1 + m_1 g_1 \mu_B B \end{cases} \qquad (h\nu = E_2 - E_1)$$

∴ The transition frequency is changed to

$$h\nu' = E_2' - E_1' = (E_2 - E_1) + (m_2 g_2 - m_1 g_1)\mu_B B$$
$$= h\nu + (m_2 g_2 - m_1 g_1)\mu_B B,$$

∵ $g_2 = g_1 = 1$ in this case,

∴ $h\nu' = h\nu + (m_2 - m_1)\mu_B B = h\nu + \Delta m\, \mu_B B$.

Due to the selection rule $\Delta m_j = 0, \pm 1$, there will be three different wavelengths / frequencies:

$$h\nu' = h\nu + \begin{Bmatrix} +\mu_B B \\ 0 \\ -\mu_B B \end{Bmatrix}.$$

i.e., we will see 3 spectral lines, although there are 9 transitions.

② In strong field approximation:

Strong magnetic field prevents $l-s$ coupling. The result is that the spin and orbital angular momentums precess around the external magnetic field separatly (as shown in Figure (b)).

Use $|l s m_l m_s\rangle$ representation, the $\hat{\vec{l}}\cdot\hat{\vec{S}}$ coupling term is small so it is neglected.

$$\Delta \hat{H}_{strong} = a(r)\,\hat{\vec{l}}\cdot\hat{\vec{S}} - (\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\hat{\vec{B}}$$

$$\approx -(\hat{\vec{\mu}}_l + \hat{\vec{\mu}}_s)\cdot\hat{\vec{B}}$$

$$= \frac{e}{2m_e}(g_l\hat{\vec{l}} + g_s\hat{\vec{S}})\cdot\hat{\vec{B}}$$

The energy shift

$$\Delta E_{strong} = \langle \Delta\hat{H}_{strong}\rangle$$

$$= \langle \frac{e}{2m_e}(g_l\hat{\vec{l}} + g_s\hat{\vec{S}})\cdot\hat{\vec{B}}\rangle$$

$$= \frac{e\cdot B}{2m_e}(g_l l_z + g_s S_z)$$

$$= (g_l m_l + g_s m_s)\frac{e\hbar}{2m_e}B$$

$$= (g_l m_l + g_s m_s)\mu_B B$$

For ${}^2P$ energy level, $l=1$, $S=1/2$, $g_l=1$, $g_s=2$.

∴ for the combination of m_l, m_s,

m_l	1	0	-1	1	0	-1
m_s	½	½	½	-½	-½	-½
$g_l m_l + g_s m_s$	2	1	0	0	-1	-2

i.e; $(m_l=-1, m_s=1/2)$ and $(m_l=1, m_s=-1/2)$ two states have the same energy value under strong magnetic field.

That's why these two energy levels merge to one level at the far-most right side of ^2P figure.

The energy level splitting under very strong magnetic field is called Paschen-Back effect.

The selection rules are $\Delta m_s = 0$, $\Delta m_\ell = 0, \pm 1$.

(4) Zeeman Effect in Hyperfine Structure.

If an atom has hyperfine structure, its energy levels will further split in the magnetic field. For simplicity, in our class we assume the magnetic field is not strong so that Zeeman splitting is much smaller than fine structure. In this case, the hyperfine interaction and the interaction with magnetic field can be regarded as the perturbation to Fine structure. This perturbation Hamiltonian operator is

$$\Delta\hat{H} = \Delta\hat{H}_{hfs} + \Delta\hat{H}_{mag}.$$

where
$$\Delta\hat{H}_{hfs} = A(\vec{\hat{I}}\cdot\vec{\hat{J}}) + \frac{B}{I(2I-1)J(2J-1)}\times\left[3(\vec{\hat{I}}\cdot\vec{\hat{J}})^2 + \frac{3}{2}(\vec{\hat{I}}\cdot\vec{\hat{J}}) - \vec{\hat{I}}^2\vec{\hat{J}}^2\right]$$

$$\Delta\hat{H}_{mag} = -(\vec{\hat{\mu}}_J + \vec{\hat{\mu}}_I)\cdot\vec{\hat{B}}$$
$$= +g_J m_J \mu_B B - g_I' m_I \mu_B B$$

Since $g_I' \ll g_J$, the 2nd term in $\Delta\hat{H}_{mag}$ is usually ignored. Using QM perturbation theory, the energy shift caused by the $\Delta\hat{H}_{hfs}$ and $\Delta\hat{H}_{mag}$ can be derived. The equation of it is called Breit–Rabi equation. Let us consider $J = 1/2$ energy level (ground state of hydrogen and alkali atoms). Electric quadrupole $Q = 0$. So we do not consider the electric quadrupole interaction.

$$\Delta\hat{H} = A(\vec{\hat{I}}\cdot\vec{\hat{J}}) + g_J m_J \mu_B B - g_I' m_I \mu_B B.$$

We introduce a parameter x to express the strength of the magnetic field:

$$\begin{cases} x = \dfrac{(g_J + g_I')\mu_B B}{A(I+1/2)} = \dfrac{(g_J+g_I')\mu_B B}{\delta E} \\ \delta E = A(I+1/2) \text{ — hyperfine splitting in zero } \vec{B}. \end{cases}$$

$$\therefore \Delta E = \langle \Delta\hat{H} \rangle = -\frac{\delta E}{2(2I+1)} - m_F g_I' \mu_B B \pm \frac{\delta E}{2}\sqrt{1+\frac{4m_F}{2I+1}x + x^2},$$

— Breit–Rabi equation.

Where $m_F = \pm(I+1/2)$.

① When $B=0$, $\Delta E_{hfs} = \frac{I}{2I+1}\delta E$ (for $F=I+1/2$)

$\Delta E_{hfs} = -\frac{I+1}{2I+1}\delta E$ (for $F=I-1/2$)

$\Rightarrow \Delta E_{hfs}(F=I+1/2) - \Delta E_{hfs}(F=I-1/2) = \delta E.$

②. Under very weak magnetic field, F, m_F are good quantum numbers. $\sqrt{1+\frac{4m_F}{2I+1}x+x^2} \approx 1 + \frac{2m_F}{2I+1}x.$
$(x \ll 1)$

Neglect the g_I' term, we have

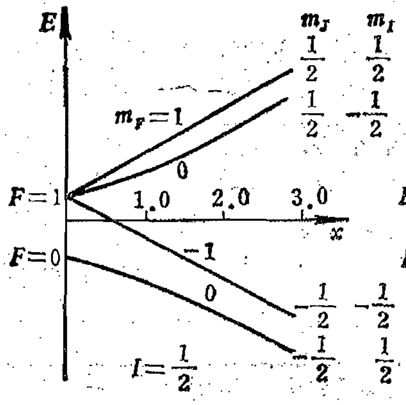
$$\Delta E = \Delta E_{hfs} \pm \frac{m_F}{2I+1}\delta E \cdot x. \quad \begin{cases} + \text{ for } F=I+1/2 \\ - \text{ for } F=I-1/2 \end{cases}$$

$$= \Delta E_{hfs} \pm \frac{1}{2I+1} g_J m_F \mu_B B$$

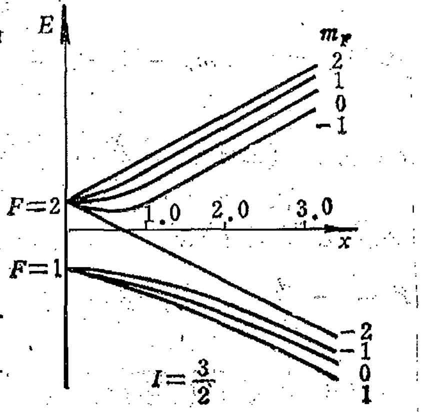
Each hyperfine energy level splits to sublevels with equal spacing.

③. When $\vec{B}$ is strong, m_J, m_I are good quantum numbers, $J=\frac{1}{2}$ energy level split as $m_J = \pm 1/2$, then further split according to m_I values.

④. If $\vec{B}$ is so large that magnetic interaction is larger or comparable to electron spin-orbit coupling, then we need to go back to consider fine structure with magnetic interaction and hyperfine interaction together.



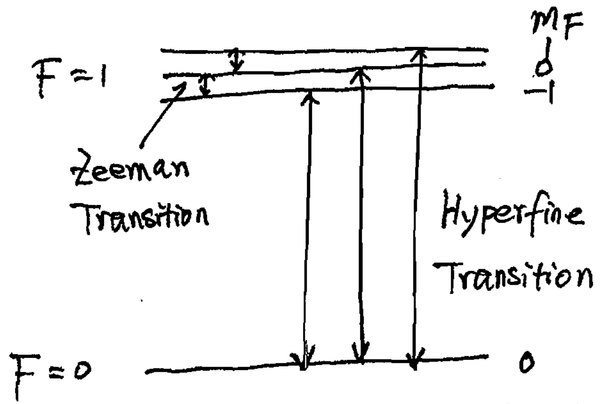
For $J=1/2$, $I=1/2$



For $J=1/2$, $I=3/2$

Could you figure out why in the 2nd case ($J=1/2$, $I=3/2$), the energy levels for $F=1$, $m_F = -1, 0, 1$ is in opposite order than the $F=2$, $m_F=2, 1, 0, -1, -2$ levels?

(5) Magnetic Resonance:



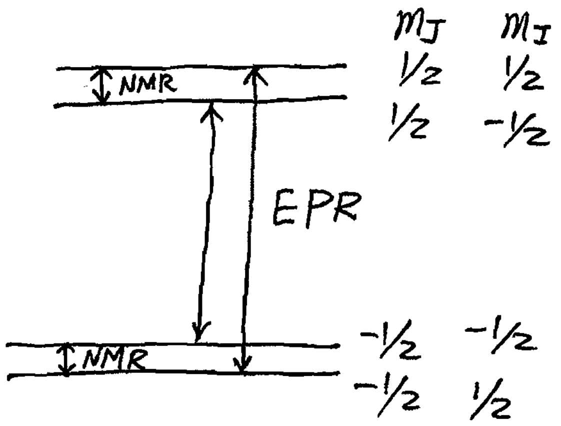
In weak magnetic field.

$\Delta F = \pm 1$, $\Delta m_F = 0, \pm 1$

(for hyperfine transition)

$\Delta F = 0$, $\Delta m_F = \pm 1$

(for Zeeman transition)



In strong magnetic field.

$\Delta m_J = \pm 1$, $\Delta m_I = 0$

(Electron Paramagnetic Resonance)

$\Delta m_J = 0$, $\Delta m_I = \pm 1$

(Nuclear Magnetic Resonance)

Magnetic Properties of matter:

① Diamagnetism ② Paramagnetism ③ Ferromagnetism

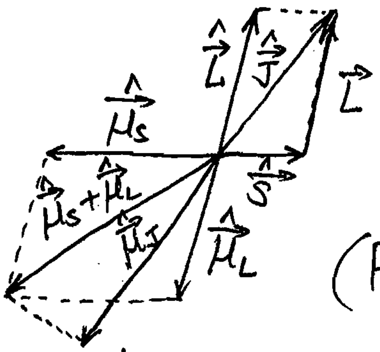
EPR and NMR and MRI:

These technologies have become very important approaches to study material structures, chemistry processes, medical diagnosis, etc.

You are encouraged to search on these topics and write a study report.

Appendix: Vector Model of Angular Momentum Coupling and Computation of g – Factor (Gyromagnetic Ratio)

(1) L – S Coupling of Electron:



(Figure 1)

As shown in Figure 1, the coupling of two angular momentum is given by

$$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$$

where $\hat{\vec{L}}$ is the orbital angular momentum,
$\hat{\vec{S}}$ is the electron spin angular momentum,
$\hat{\vec{J}}$ is the electron total angular momentum.

Corresponding magnetic moments are:

$$\begin{cases} \hat{\vec{\mu}}_L = -g_L \mu_B \hat{\vec{L}}, & g_L = 1 \quad \text{for single electron} \\ \hat{\vec{\mu}}_s = -g_S \mu_B \hat{\vec{S}}, & g_S = 1/2 \quad \text{for single electron} \\ \vec{\mu}_J = -g_J \mu_B \vec{J} \end{cases}$$

From the vector model, we want to derive g_J from known Parameters like g_L, g_s, L, S, and J.

Notice that the sum $\hat{\vec{\mu}}_S + \hat{\vec{\mu}}_L$ is <u>NOT</u> equal to μ_J, because $g_L \neq g_s$ and $\hat{\vec{\mu}}_s + \hat{\vec{\mu}}_L$ is <u>NOT</u> along the $\hat{\vec{J}}$ direction.

The projection of $\hat{\vec{\mu}}_s + \hat{\vec{\mu}}_L$ along $\hat{\vec{J}}$ direction is the $\hat{\vec{\mu}}_J$.

$$\therefore \hat{\vec{\mu}}_J = \frac{(\hat{\vec{\mu}}_L + \hat{\vec{\mu}}_s)\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}} = \frac{\hat{\vec{\mu}}_L\cdot\hat{\vec{J}} + \hat{\vec{\mu}}_s\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}}$$

$$\therefore \quad \hat{\vec{\mu}}_J = -\mu_B \frac{g_L \hat{\vec{L}} \cdot \hat{\vec{J}} + g_s \hat{\vec{S}} \cdot \hat{\vec{J}}}{\hat{\vec{J}}^2} \hat{\vec{J}}$$

According to the definition of g_J : $\hat{\vec{\mu}}_J = - g_J \mu_B \vec{J}$,

We have $$g_J = \frac{g_L \hat{\vec{L}} \cdot \hat{\vec{J}} + g_s \hat{\vec{S}} \cdot \hat{\vec{J}}}{\hat{\vec{J}}^2} .$$

From the Law of Cosines, considering the vector model,

We have : $$\hat{\vec{L}}^2 = \hat{\vec{J}}^2 + \hat{\vec{S}}^2 - 2\hat{\vec{S}} \cdot \hat{\vec{J}} \Rightarrow \hat{\vec{S}} \cdot \hat{\vec{J}} = \frac{\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2}{2}$$

$$\hat{\vec{S}}^2 = \hat{\vec{J}}^2 + \hat{\vec{L}}^2 - 2\hat{\vec{J}} \cdot \hat{\vec{L}} \Rightarrow \hat{\vec{L}} \cdot \hat{\vec{J}} = \frac{\hat{\vec{J}}^2 + \hat{\vec{L}}^2 - \hat{\vec{S}}^2}{2}$$

Substitute $\hat{\vec{S}} \cdot \hat{\vec{J}}$ and $\hat{\vec{L}} \cdot \hat{\vec{J}}$ into g_J equation, we get

$$g_J = \frac{g_L (\hat{\vec{J}}^2 + \hat{\vec{L}}^2 - \hat{\vec{S}}^2) + g_s (\hat{\vec{J}}^2 + \hat{\vec{S}}^2 - \hat{\vec{L}}^2)}{2 \hat{\vec{J}}^2}$$

The eigenvalues for $\hat{\vec{J}}^2$, $\hat{\vec{L}}^2$, $\hat{\vec{S}}^2$ are

$$\hat{\vec{J}}^2 \Rightarrow J(J+1), \quad \hat{\vec{L}}^2 \Rightarrow L(L+1), \quad \hat{\vec{S}}^2 \Rightarrow S(S+1)$$

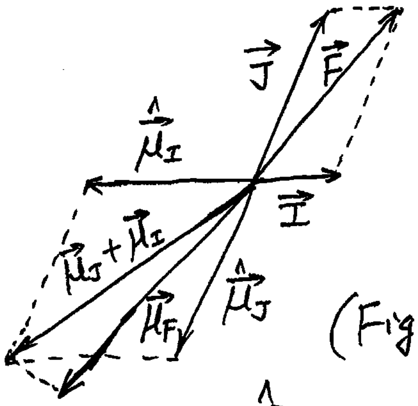
$$\therefore \quad g_J = \frac{\left\{ g_L [J(J+1) + L(L+1) - S(S+1)] + g_s [J(J+1) + S(S+1) - L(L+1)] \right\}}{2J(J+1)}$$

Substituting $g_L = 1$, $g_s = 2$ into the equation :

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$= \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

(2) Electron – Nucleus Coupling (I – J coupling)



(Figure 2)

Similar to L – S coupling, the I – J coupling is

$$\vec{\hat{F}} = \vec{\hat{J}} + \vec{\hat{I}}$$

where $\vec{\hat{J}}$ is the electron total angular momentum

$\vec{\hat{I}}$ is the nuclear spin angular momentum

$\vec{F}$ is the atomic total angular momentum

Corresponding magnetic moments are

$$\begin{cases} \vec{\hat{\mu}} = -g_J \mu_B \vec{\hat{J}} \\ \vec{\hat{\mu}}_I = g_I' \mu_N \vec{\hat{I}} = g_I \mu_B \hat{I}, \quad \left(\frac{g_I}{g_I'} = \frac{\mu_N}{\mu_B} = \frac{m_e}{M_P}\right) \\ \vec{\hat{\mu}}_F = -g_F \mu_B \vec{\hat{F}} \end{cases}$$

We want to derive g_F from g_J, g_I, J, I, F.

Again, $\vec{\hat{\mu}}_J + \vec{\hat{\mu}}_I$ is <u>NOT</u> equal to $\vec{\hat{\mu}}_F$. $\vec{\hat{\mu}}_F$ is the projection of $\vec{\hat{\mu}}_J + \vec{\hat{\mu}}_I$ along $\vec{\hat{F}}$ direction:

$$\vec{\hat{\mu}}_F = \frac{(\vec{\hat{\mu}}_J + \vec{\hat{\mu}}_I)\cdot\vec{\hat{F}}}{\vec{\hat{F}}^2}\vec{\hat{F}} = \frac{\vec{\hat{\mu}}_J\cdot\vec{\hat{F}} + \vec{\hat{\mu}}_I\cdot\vec{\hat{F}}}{\vec{\hat{F}}^2}\vec{\hat{F}}.$$

$$= -\mu_B \frac{g_J\vec{\hat{J}}\cdot\vec{\hat{F}} - g_I\vec{\hat{I}}\cdot\vec{\hat{F}}}{\vec{\hat{F}}^2}\vec{\hat{F}}$$

$$\therefore \quad g_F = \frac{g_J\vec{\hat{J}}\cdot\vec{\hat{F}} - g_I\vec{\hat{I}}\cdot\vec{\hat{F}}}{\vec{\hat{F}}^2}\vec{\hat{F}}.$$

From the law of cosines,

$$\hat{\vec{I}}^2 = \hat{\vec{F}}^2 + \hat{\vec{J}}^2 - 2\hat{\vec{F}}\cdot\hat{\vec{J}} \Rightarrow \hat{\vec{J}}\cdot\hat{\vec{F}} = \frac{\hat{\vec{F}}^2 + \hat{\vec{J}}^2 - \hat{\vec{I}}^2}{2}$$

$$\hat{\vec{J}}^2 = \hat{\vec{F}}^2 + \hat{\vec{I}}^2 - 2\hat{\vec{F}}\cdot\hat{\vec{I}} \Rightarrow \hat{\vec{I}}\cdot\hat{\vec{F}} = \frac{\hat{\vec{F}}^2 + \hat{\vec{I}}^2 - \hat{\vec{J}}^2}{2}$$

Also recall $\hat{\vec{J}}^2 = J(J+1)$, $\hat{\vec{I}}^2 = I(I+1)$, $\hat{\vec{F}}^2 = F(F+1)$.

We get
$$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g_I \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)} .$$

(3) In general, for any two angular momentum coupling:

$$\hat{\vec{J}} = \hat{\vec{J}}_1 + \hat{\vec{j}}_2 ,$$

$$\begin{cases} \hat{\vec{\mu}}_J = -g_J \mu_B \hat{\vec{J}} \\ \hat{\vec{\mu}}_{j_1} = -g_{j_1} \mu_B \hat{\vec{j}}_1 \\ \hat{\vec{\mu}}_{j_2} = -g_{j_2} \mu_B \hat{\vec{j}}_2 \end{cases}$$

We have
$$\hat{\vec{\mu}}_J = \frac{(\hat{\vec{\mu}}_{j_1} + \hat{\vec{\mu}}_{j_2})\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}}$$
$$= -\mu_B \frac{g_{j_1}\hat{\vec{j}}_1\cdot\hat{\vec{J}} + g_{j_2}\hat{\vec{j}}_2\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}\hat{\vec{J}}$$

$$\therefore\ g_J = g_{j_1}\frac{\hat{\vec{J}}_1\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2} + g_{j_2}\frac{\hat{\vec{j}}_2\cdot\hat{\vec{J}}}{\hat{\vec{J}}^2}$$

From the law of cosines, $\hat{\vec{j}}_1\cdot\hat{\vec{J}} = \frac{\hat{\vec{J}}^2 + \hat{\vec{j}}_1^2 - \hat{\vec{j}}_2^2}{2}$, $\hat{\vec{j}}_2\cdot\hat{\vec{J}} = \frac{\hat{\vec{J}}^2 + \hat{\vec{j}}_2^2 - \hat{\vec{j}}_1^2}{2}$

$$\therefore\ g_J = g_{j_1}\frac{J(J+1) + j_1(j_1+1) - j_2(j_2+1)}{2J(J+1)} - g_{j_2}\frac{J(J+1) + j_2(j_2+1) - j_1(j_1+1)}{2J(J+1)}$$

Another way to derive $\vec{I}\cdot\vec{F}$ and $\vec{J}\cdot\vec{F}$ is just to use the relationship $\hat{\vec{F}} = \hat{\vec{I}} + \hat{\vec{J}}$

$$\Rightarrow \hat{\vec{J}} = \hat{\vec{F}} - \hat{\vec{I}}$$

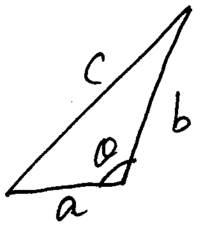
$$\therefore (\hat{\vec{J}})^2 = \hat{\vec{J}}\cdot\hat{\vec{J}} = (\hat{\vec{F}} - \hat{\vec{I}})\cdot(\hat{\vec{F}} - \hat{\vec{I}})$$

$$= (\hat{\vec{F}})^2 + (\hat{\vec{I}})^2 - 2\,\hat{\vec{I}}\cdot\hat{\vec{F}}$$

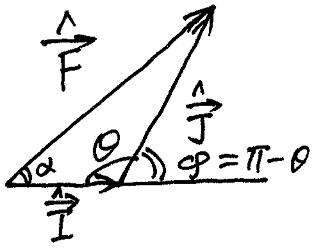
$$\Rightarrow \hat{\vec{I}}\cdot\hat{\vec{F}} = \frac{1}{2}(\hat{\vec{F}}^2 + \hat{\vec{I}}^2 - \hat{\vec{J}}^2)$$

Similarly, $\hat{\vec{J}}\cdot\hat{\vec{F}} = \frac{1}{2}(\hat{\vec{F}} + \hat{\vec{J}}^2 - \hat{\vec{I}}^2)$

<u>Note</u>: The law of cosines:



$c^2 = a^2 + b^2 - 2ab\cos\theta$ (in scalar)



$$\hat{\vec{F}}^2 = \hat{\vec{I}}^2 + \hat{\vec{J}}^2 - 2IJ\cos\theta$$

$$\because \hat{\vec{I}}\cdot\hat{\vec{J}} = IJ\cos\varphi = IJ\cos(\pi-\theta)$$

$$= -IJ\cos\theta$$

$$\therefore \vec{F}^2 = \vec{I}^2 + \vec{J}^2 + 2\vec{I}\cdot\vec{J}$$

$$\vec{J}^2 = \vec{F}^2 + \vec{I}^2 - 2FI\cos\alpha$$

$$\because \vec{F}\cdot\vec{I} = FI\cos\alpha$$

$$\therefore \vec{J}^2 = \vec{F}^2 + \vec{I}^2 - 2\vec{F}\cdot\vec{I}$$

$$\Rightarrow \vec{F}\cdot\vec{I} = \frac{1}{2}(\vec{F}^2 + \vec{I}^2 - \vec{J}^2)$$

5. Influence of External (Static) Electric Field

(1) Stark Effect: The influence of an external electric field on atomic spectra was discovered by J. Stark in 1913 and is known as the stark effect. Stark's discovery was made on the Balmer series of hydrogen. Before that in 1899, Voigt gave attention to the electric perturbation of atoms and came to the conclusion that the effects would be very small. This is because only hydrogen-like atoms/ions have significant linear stark effects, while other atoms usually have very small quadratic Stark effects, when the external electric field is small.

(2) Quadratic Stark Effect:

The Stark effect is the splitting and shifting of atomic levels under the interaction of an external electric field.

The energy of an atom in a homogeneous electric field is equal to the scalar product of the strength of the electric field $\vec{E}$ and the electric dipole moment of the atom $\vec{D}$ taken with negative sign. In other words, the Hamiltonian operator $\Delta\hat{H}e$ in a homogeneous static electric field is given by

$$\Delta\hat{H}e = -\hat{\vec{D}}\cdot\hat{\vec{E}} = e\sum_i \hat{\vec{r}_i}\cdot\hat{\vec{E}}$$

where $\hat{\vec{D}} = -e\sum_i \vec{r}_i$ is the electric dipole moment of the atomic system, and $\vec{E}$ is the electric field strength.

Change the SI unit to atomic unit, then

$$\Delta\hat{H}e = -\hat{\vec{D}}\cdot\hat{\vec{E}} = \sum_i \hat{\vec{r}_i}\cdot\hat{\vec{E}} \text{ (a.u.)}$$

One a.u. $\vec{E}$ is $\frac{e^2}{2a_0^2} = 8.576\times10^6$ (e.s.u) $= 2.572\times10^9$ V/cm

When the electric field $\vec{E}$ is weak, $\Delta\hat{H}_e$ is regarded as a perturbation to the original Hamiltonian operator. Thus, we can use perturbation theory to derive the energy correction.

Notice that the matrix elements of $\hat{\vec{D}}$ connecting states of the same parity, including the diagonal matrix elements, are zero: $\langle \psi_i | \Delta\hat{H}_e | \psi_i \rangle \equiv \langle \Delta\hat{H}_e \rangle = 0$.

This is because $\Delta\hat{H}_e$ has the following symmetry under spatial inversion: $\Delta\hat{H}_e(-\vec{r}) = -\Delta\hat{H}_e(\vec{r})$.

$$\therefore \langle \psi_i | \Delta\hat{H}_e | \psi_i \rangle = -\langle \psi_i | \Delta\hat{H}_e | \psi_i \rangle = 0.$$

Therefore, the first-order perturbation does not lead to any change in the atomic energy. The splitting of levels is determined by second-order corrections.

Let us choose the z-axis along the direction of the external field $\vec{E}$. $\Delta\hat{H}_e = -E\hat{D}_z$, where $\hat{D}_z$ is the projection of $\hat{\vec{D}}$ along z direction. For an energy state $|\alpha J M\rangle$ (where α represents the quantum numbers other than J, M, e.g., n, L, S), the 2nd order perturbation theory gives the energy correction as:

$$\Delta E_e = E^2 \sum_{\alpha' J'} \frac{|\langle \alpha J M | \hat{D}_z | \alpha' J' M' \rangle|^2}{E_{\alpha J} - E_{\alpha' J'}}$$

where the sum is taken for $\alpha' \neq \alpha$, $J' \neq J$.

Because $\hat{D}_z$ and $\hat{J}_z$ are commute, i.e., $[\hat{D}_z, \hat{J}_z] = 0$, only the $M' = M$ matrix elements are non-zero.

The nature of this second-order correction to the energy level is that the atom does not have intrinsic electric dipole moment, but the external field induced some electric dipole moment, i.e., induced electric dipole moment: $\vec{\hat{D}} \propto \vec{E}$

$\therefore$ the energy correction $\Delta E_e \propto E^2$.

i.e., proportional to the square of electric field strength.

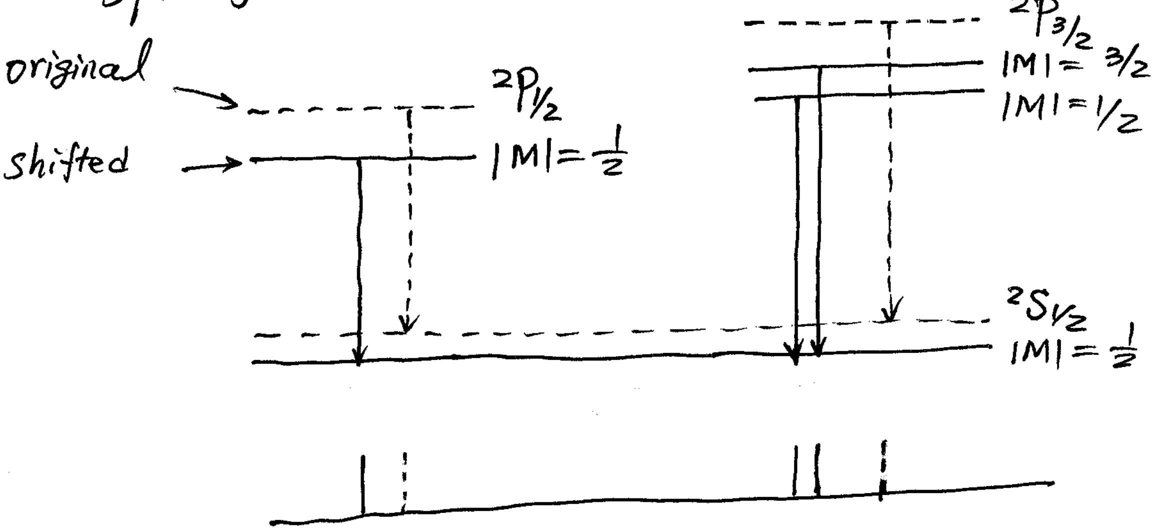
— So-called quadratic Stark effect.

Features of quadratic Stark effect:

① Energy levels with the same $|M|$ are degenerate.

— When reverse the $\vec{E}$ direction, the energy doesn't change.

② Energy shifts to one direction, instead of symmetric splitting on both sides:



(3) Linear Stark Effect.

The above quadratic Stark effect equations are valid as long as the corrections to the energy are small in comparison with the initial splitting $E_{\alpha J} - E_{\alpha' J'}$. In the general case it is necessary to treat, at the same time, the interaction with the field external $\Delta \hat{H}_e$ and the interaction $\hat{H}'$ that is responsible for the splitting of the levels αJ and $\alpha' J'$, like spin-orbital coupling.

Let us consider one pair of energy levels, they are separated by a splitting δ when $E=0$. Let

$$E_{\alpha J} = E_0 + \frac{1}{2}\delta, \quad E_{\alpha' J'} = E_0 - \frac{1}{2}\delta.$$

$$\frac{\delta}{2} = \langle \alpha J M | \hat{H}' | \alpha J M \rangle = - \langle \alpha' J' M | \hat{H}' | \alpha' J' M \rangle$$

Here, E_0 is the initial energy levels when J and J' are degenerate, and $\hat{H}'$ is the interaction that causes the splitting of J and J'.

With external electric field,

$$\Delta \hat{H} = \hat{H}' + \Delta \hat{H}_e$$

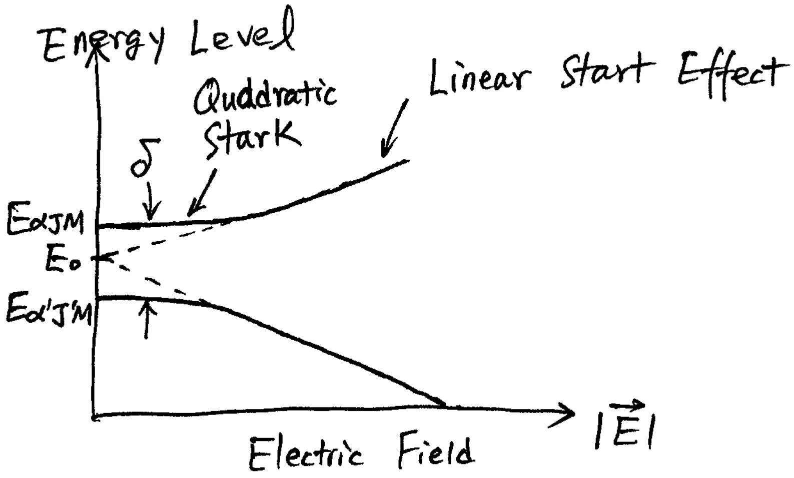
From perturbation theory, we have the energy correction

$$\Delta E = \pm \sqrt{\left(\frac{\delta}{2}\right)^2 + |\langle \alpha J M | \hat{D}_z | \alpha' J' M \rangle|^2 E^2}$$

When $|E|$ is very small, $\Delta E \simeq \pm \left[\frac{\delta}{2} + \frac{|\langle \alpha J M | \hat{D}_z | \alpha' J' M \rangle|^2 E^2}{\delta} \right]$

When $|E|$ is very large,

$$\Delta E \simeq \pm |\langle \alpha J M | \hat{D}_z | \alpha' J' M \rangle| \, \underline{\underline{|E|}}$$



If $\delta = 0$ from the beginning, i.e., two levels are degenerate, then only linear Stark effect will show up.

(4) Hydrogen's Stark effect.

It turns out that the Stark effect in H-atom is exceptionally large, especially in the Balmer series.

For $n=2$, $^2P_{1/2}$ and $^2S_{1/2}$ are nearly degenerate, except the small relativity fine structure correction.

Thus, its linear Stark effect is strong, which enabled Stark to observe the effect in 1913.

§5.3. Multielectron Atoms

For atoms containing more than one electron, the interactions that we need to consider, in addition to the considerations in hydrogen atom or hydrogen-like ions, are the electrostatic interactions between electrons and the magnetic interactions between electrons.

* The electrostatic interactions come from the Coulomb repulsion force between electrons (in contrast to the Coulomb attraction force between the nucleus and the electrons).

* The magnetic interactions come from the fact that each electron has orbital and spin angular momenta, so has corresponding magnetic moments. These angular momenta (magnetic moments) couple with each other, forming the magnetic interactions. For example, if an atom has two electrons with orbital and spin angular momenta quantum numbers l_1, s_1, l_2, s_2. Then there are six kinds of magnetic interactions:

$$G_1(s_1 s_2),\ G_2(l_1 l_2),\ G_3(l_1 s_1),\ G_4(l_2 s_2),\ G_5(l_1 s_2),\ G_6(l_2 s_1)$$

which means spin-spin, orbit-orbit coupling between two electrons (G_1, G_2)
spin-orbit coupling for each individual electron (G_3, G_4)
One electron orbit — another electron spin coupling (G_5, G_6).

Usually, G_5 and G_6 are weak, so can be ignored.

* When atoms contain more than one electron, even for the simplest ones, Helium (He), Schrödinger equation cannot be solved directly, either analytically or numerically. For this reason, the multielectron atomic structure must be based on some approximation model. Here it is necessary to estimate the magnitudes for different interactions so that we can treat the major interactions first, and then treat smaller forces as perturbations to the major interactions.

The electrostatic interactions between the nucleus and the electron and between electrons are on the order of magnitude of

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}|} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

$$\approx \frac{1}{4\pi\varepsilon_0}\frac{e^2}{a_1} \approx \frac{1.44\,nm \cdot eV}{0.053\ nm} \approx 28\,eV.$$

Where $a_1 \equiv r_1 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$ is the first Bohr radius.

The magnetic interactions between electrons or between the spin and orbit of the same electron are about 10^{-3} eV.

Therefore, the electrostatic interaction between electrons is much larger than magnetic interactions, and is in the same order of the electrostatic interaction between nucleus and electron. Thus, we must consider the electrons' electrostatic interaction with the nucleus and electron interaction together.

A suitable schematic treatment is one in which the concept of the individual state of an electron in an atom is accepted, and the state of an atom as a whole is determined by the set of the states of the electrons, taking into account their interaction. In the limit of this approximation, one succeeds in obtaining general information on the system of energy levels possible for a given atom, and on the relative position and grouping of the levels. Also in this limit of approximation, selection rules for radiative transitions are established, which enable one to predict the structure of the spectrum for each element.

1. Central Field Approximation.

Central Field Approximation is the starting point for treating multielectron atoms. The fundamental assumption is that each electron moves independently in a certain effective centrally symmetric field created by the nucleus and all the other electrons. Even without knowing the detailed form of this central field, many results can be obtained on the basis of the general theory of the motion of a particle in the centrally symmetric field.

A more detailed treatment requires a consideration of the noncentral part of the electrostatic interaction between electrons, and also of magnetic interactions, in particular spin-orbit interaction. These interactions are usually considered within perturbation theory as small corrections to the centrally symmetric field. As is known, a perturbation does not alter the number of possible states of a system.

For an atom with nucleus charge Ze and N electrons, the overall atom Hamiltonian operator $\hat{H}$ (only consider the electrostatic interaction) is given by

$$\hat{H} = + \sum_{i=1}^{N} \frac{\hat{\vec{P}}_i^2}{2\mu} - \sum_{i=1}^{N} \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i} + \sum_{i>j=1}^{N} \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{ij}}$$

where $\sum_{i=1}^{N}$ is to take sum for every electron, $\hat{\vec{P}}_i$ is the momentum for each electron, $\mu = \frac{m_e M}{m_e + M}$ is the reduced mass of electron (M is the nuclear mass), r_i is the distance of the ith electron from the nucleus, r_{ij} is the mutual distance of the ith and jth electrons.

The first term is the sum of all electrons kinetic energy; the second term is the electrostatic interaction between the nucleus and each electron. The third term is the electrostatic interaction between electrons. Notice that among electrons, the electrostatic interaction is Coulomb repulsion force, so the potential energy is positive, i.e., $+\sum_{i>j=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_{ij}}$. This is opposite to the Coulomb attraction interaction between the nucleus and the electrons: $-\sum_{i=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r_i}$.

The electrostatic interaction between electrons is usually noncentral field, and every electron motion is related with other electrons. Such complicated interactions and motions have no direct solution. We must simplify it using two assumptions. (1) Each electron moves independently in the mean field produced by nucleus and other electrons; (2) the mean field is a centrally symmetric electric field. Let the ith electron experience the central field $U_i(r_i)$, then the atomic Hamiltonian operator is simplified to

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{\vec{P}}_i^{\,2}}{2\mu} - \sum_{i=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r_i} + \sum_i U_i(r_i)$$

For each electron, the time-independent Schrödinger equation (i.e., the energy eigen-value equation) is

$$\left[\frac{\hat{\vec{P}}_i^{\,2}}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i} + U_i(r_i)\right]u_i = E_i u_i.$$

where u_i is the wave function for each electron.

The total wave function of an atom is

$$\Phi = u_1(\vec{r_1})\, u_2(\vec{r_2}) \cdots u_N(\vec{r_N}),$$

and the total energy of the atom is (under central field approximation)

$$E = \sum_{i=1}^{N} E_i .$$

The key step is to solve the equation for each individual electron. Since $U_i(r_i)$ is only dependent on r_i, but independent of θ_i, φ_i, we can apply the separation of variables to solve the equation. Let

$$u_i(\vec{r_i}) = R_i(r_i)\, Y_i(\theta_i, \varphi_i),$$

then we obtain two equations:

$$\begin{cases} \left[-\dfrac{\hbar^2}{2\mu r_i^2}\dfrac{d}{dr_i}\left(r_i^2\dfrac{d}{dr_i}\right) + \dfrac{\alpha_i \hbar^2}{2\mu r_i^2} - \dfrac{1}{4\pi\varepsilon_0}\dfrac{Ze^2}{r_i} + U_i(r_i)\right] R_i(r_i) \\ \qquad = E_i R_i(r_i) \\ \hat{l}_i^2\, Y_i(\theta_i, \varphi_i) = \alpha_i \hbar^2\, Y_i(\theta_i, \varphi_i) \end{cases}$$

Compared to hydrogen equation, we only add $U_i(r_i)$ in the first equation. Similar to hydrogen equation solutions, the solution is $u_i = R_{n_i l_i}(r_i)\, Y_{l_i m_i}(\theta_i, \varphi_i)$

where n_i, l_i, m_i are the principal quantum number, orbital angular momentum quantum number, and orbital magnetic quantum number of the ith electron. $Y_{l_i m_i}$ is universal for all atoms, and $\alpha_i = l_i(l_i+1)$, $l_i = 0, 1, 2, \cdots, n_i - 1$

$$|m_i| \le l_i \,, \qquad m_i = l_i, l_i - 1, \cdots, -l_i$$

* Similar to hydrogen, the quantum number l_i determines the orbital angular momentum of the electron, in the sense of

$$\hat{\vec{l}}_i^{\,2} u_i = l_i (l_i + 1) \hbar^2 u_i ,$$

i.e., the eigenvalue of the square of orbital angular momentum is $l_i(l_i+1)\hbar^2$.

* The magnetic quantum number m_i, as hydrogen, determines the component of angular momentum along the z-axis of coordinates, i.e., $l_z = m_i \hbar$. m_i represents the spatial orientation of the orbital angular momentum.

* Even with the central field potential, it is difficult to solve the $R_i(r_i)$ equation that also determines the energy eigenvalues E_i. In QM, approximation methods are used to solve the equation (mainly deriving the central field $V_i(r_i)$ and the individual electron wave function $u_i(\vec{r}_i) = R_i(r_i) Y_i(\theta_i, \varphi_i)$). A popular method is the so-called self-consistent-field approximation, or Hartree-Fock method. You may refer to the book "Quantum Theory of Atomic Structure" by John C. Slater (1960) for details. We will skip the details but introduce its results, mainly on the energy eigenvalues E_i.

* The main results for central field approximation include

① Similar to hydrogen, the energy eigenvalues are independent of m. The independence of m for the energy has a simple physical meaning: In a central field, all directions in space are equivalent, and therefore the energy cannot depend on the spatial orientation of the angular momentum.

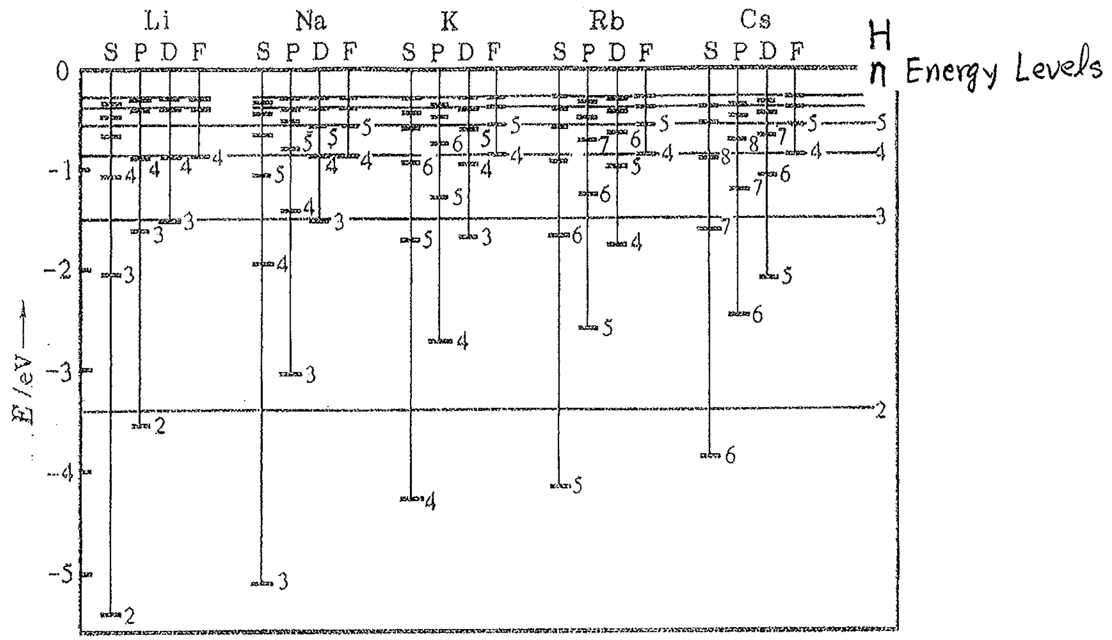
② Unlike the case of hydrogen, the energy from central field approximation depends on both n_i and l_i. FYI, the independence of l for the energy in hydrogen-like ions, is a specific property of the Coulomb field, and does not occur in the general case of a centrally symmetric field. In other words, Coulomb field potential ($\sim \frac{1}{r}$) is a special central field, and it leads to the energy eigenvalue E_n only depends on the principal quantum number n, but independent of l. However, central field does not have to be Coulomb form, i.e., it contains other forms, such as $U(r) \sim r$, or $U(r) \sim r^2$, or $U(r) \sim \frac{1}{r^2}$, etc, as long as $U(r)$ is spherically symmetric. Such non-Coulomb central field will cause the energy eigenvalues to depend on l. This comes from the eigenvalue equation of $R_i(r_i) \rightarrow R_{n_i l_i}(r_i)$ and the radial wave function.

③ For the same n_i, energy levels with larger l_i are higher. For the same l_i, energy levels with larger n_i are higher.

④ Each individual electron is characterized by three quantum numbers: n_i, l_i, and m_i.

(Please see an example in the next page)

Example:



Energy Levels of Alkali Atoms

As stated above, the central field approximation tells us that

① The energy levels depend on both n and l quantum numbers.

② For the same n, higher l corresponds to higher energy levels, e.g., for $n=3$ in the Li atom,

$$3s < 3p < 3d$$

③ For the same l, larger n corresponds to higher energy levels. e.g., for $l=0$ (S states),

$$2s < 3s < 4s < 5s$$

Plotted on the far rightmost column is the energy levels of hydrogen, as a comparison. For H, the $n=1$ level is not shown, but we recall the ground state of H ($n=1$, $l=0$), has energy of -13.6 eV, much lower than alkali atoms. This means H atom is much more stable because you need much more energy to reject the electron (ionization energy).

2. Electron Spin Quantum Number ⇒ Full Description of Electron States

Besides n_i, l_i, and m_i, we must consider the electron spin as we did in the hydrogen. Each electron has a spin angular momentum represented by spin quantum number $S_i = \frac{1}{2}$. Correspondig to s, we have the spin magnetic quantum number m_{si}, representig the component of spin angular momentum along the z-axis.

Thus, we have five quantum numbers to describe each electron state: n, l, S, m_l, m_s.

(Note: we remove i in the subscript, as we know we are talkig about each electron now; we use m_l to replace the m_i to represent the z-component of l)

Since electron's spin is alway $S = \frac{1}{2}$, the real distinguishable quantum numbers are the four quantum numbers

$$n, l, m_l, m_s,$$

We use these four quantum numbers to describe the state of an electron as $|n\, l\, m_l\, m_s\rangle$.

From these quantum numbers, let us derive the total stationary state number corresponding to each n:

① For each n, $l = 0, 1, 2, \cdots, n-1$ (i.e., n of l)

② For each l, $m_l = l, l-1, \cdots, -l$ (i.e., $2l+1$ of m_l)

③ For each m_l, $m_s = \pm\frac{1}{2}$, (i.e., 2 of m_s)

∴ The total number of possible stationary states is

$$N_n = \sum_{l=0}^{n-1} 2(2l+1) = 2n^2.$$

3. Pauli Exclusion Principle and Atomic Shell Structure

Pauli Exclusion Principle is a fundamental principle in atomic structure theory. The general statement of this principle is that for any system consisting of Fermions (particles with spin of $\frac{1}{2}\hbar$ or odd times of $\frac{1}{2}\hbar$, e.g., electrons, protons, and neutrons), there cannot be more than one Fermion in the same state of $|n\, l\, m_l\, m_s\rangle$. Therefore, each state $|n\, l\, m_l\, m_s\rangle$ can have a maximum of one electron or none.

For each n, the maximum number of possible stationary state is $2n^2$. So maximum $2n^2$ electrons can have the same principal quantum number n.

Example: For $n=1$, maximum ($2n^2 = 2\times 1^2 = 2$) 2 electrons can have $n=1$. This is because:

for $n=1$, we must have $l=0$ (because $l=0,1,\cdots,n-1$)

So $m_l=0$. Since $m_s=\pm\frac{1}{2}$, the possible states are

$$|n,l,m_l,m_s\rangle = |1,0,0,\tfrac{1}{2}\rangle \text{ and } |1,0,0,-\tfrac{1}{2}\rangle.$$

Therefore, only 2 electrons can be in these two states.

If an atom has more than 2 electrons, then the other electrons must go $n>1$, e.g., $n=2$ or 3. Let us calculate for the first a few n, the maximum allowable electron numbers:

$n=$	1	2	3	4	5	6	7
$2n^2=$	2	8	18	32	50	72	98

In atomic structure theory, we name the principal quantum number n corresponding to each main shell.

$n = 1, \ 2, \ 3, \ 4, \ 5, \ 6, \cdots$

Main Shell : K, L, M, N, O, P, ⋯

But please be aware that the shell is just a description to the principal quantum number n that mainly determines the majority part of energy, and roughly describes the distance of the electrons relative to the nucleus. Electrons do not really move on some shells within the atom, because we know for Quantum Mechanics, electrons have probability to occur in nearly every position inside the atom.

For each n, each $l = 0, 1, 2, \cdots, n-1$ forms a sub-shell. The maximum allowable electron number for a l sub-shell is $2(2l+1)$, because of the $(2l+1)$ of m_l, and 2 of m_s ($m_s = \pm\frac{1}{2}$).

$\therefore$ $l=0$, s shell, $2(2l+1) = 2$ (s)
$l=1$, p shell, $2(2l+1) = 6$ (p)
$l=2$, d shell, $2(2l+1) = 10$ (d)
$l=3$, f shell, $2(2l+1) = 14$ (f)
$l=4$, g shell, $2(2l+1) = 18$ (g)
$l=5$, h shell, $2(2l+1) = 22$ (h)

Note: please do not confuse these letters for denoting the orbital angular momentum with the main shell letters (K, L, M, N, ⋯).

4. Electron Configuration and Periodic Table of Elements

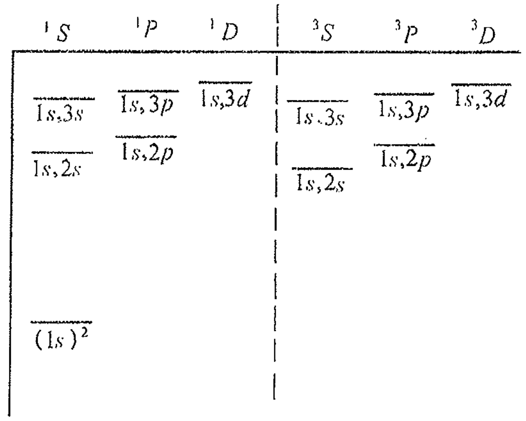
The results of energy eigenvalue E_i derived from the central field approximation are the energy eigenvalues of each individual electron. Recall our assumption of central field approximation: Each electron moves independently in the mean field. What we really care about is the total energy of the whole atom. Under the central field approximation, the atom total energy is the sum of each electron energy:

$$E = \sum_{i=1}^{N} E_i .$$

Since each electron energy E_i depends on n and l quantum numbers, the atom total energy will be determined by the arrangement (or combination or distribution) of multi-electrons' n and l values. We use $n_1 l_1$, $n_2 l_2$, $\cdots$, $n_N l_N$ to represent each electron (N of them) states. The combination of $n_1 l_1\, n_2 l_2 \cdots n_N l_N$ is called the electron configuration. In atomic structure theory, n is written as its number, while l is represented by a letter, e.g, $1s$ means $(n=1, l=0)$; $2p$ means $(n=2, l=1)$, etc. When we **have** more than one electrons, e.g., one is in $1s$, and another is $2p$, then the electron configuration is written as $1s\,2p$. If both electrons are in $1s$, we can write $1s\,1s$ as $1s^2$.

Since E_i depends on $n_i l_i$, the atom total energy E is mainly determined by the assignment of Electron Configuration

$n_1 l_1 n_2 l_2 \cdots n_N l_N$.



$$(1s)^2 \equiv 1s^2$$

He Electron configuration versus He energy levels.

The reason that we say the atom energy levels are <u>mainly</u> determined by the electron configuration (not totally), is that this is under central field approximation. When other interactions (e.g., noncentral electrostatic or magnetic interactions) are considered, there will be corrections to the $E = \sum_{i=1}^{N} E_i$ energy levels. These corrections may result in shift and splitting.

* You may notice in the figure of Helium shown above, there is alway one electron in 1s state. This is because it needs tremendous energy to excite both electrons out of ground states (1s). This is usually not achievable in experiments. For the spectroscopy we are interested, always 1s electron is in Helium with the 2nd electron in various states, which determines different energy levels of the entire atom.

With the electron configuration concept, let us now consider how to fill in the main shells and sub-shells of an atom when it has multi-electrons. Two principles we must follow:

① Pauli Exclusion Principle, no more than 1 electron in the same state

② Lowest Energy Principle: electrons fill in the levels with energy as low as possible.

According to these two principles,

			Electron Configuration
$Z = 1$,	H,	one electron,	so ground state is $1s$
$Z = 2$,	He,	2 electrons,	Ground state is $1s^2$
$Z = 3$,	Li,	3 " ,	Ground state $1s^2 2s$
$Z = 4$,	Be,	4 " ,	" $1s^2 2s^2$
$Z = 5$,	B,	5 " ,	" $1s^2 2s^2 2p$
$Z = 6$,	C,	6 " ,	" $1s^2 2s^2 2p^2$
$Z = 7$,	N,	7 " ,	" $1s^2 2s^2 2p^3$
$Z = 8$,	O,	8 " ,	" $1s^2 2s^2 2p^4$
$Z = 9$,	F,	9 " ,	" $1s^2 2s^2 2p^5$
$Z = 10$,	Ne,	10 " ,	" $1s^2 2s^2 2p^6$
$Z = 11$,	Na,	11 " ,	" $1s^2 2s^2 2p^6 3s$
$Z = 12$,	Mg,	12 " ,	" $1s^2 2s^2 2p^6 3s^2$.

Tables in the next page list the electron configurations for the ground states of all elements. Also shown in the next page is the order for filling in electrons in shells/subshells, according to energy levels.

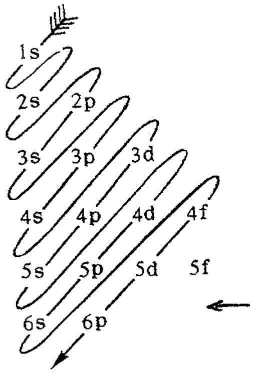
Electron Configurations for Elements

Z	Element	Electron Configuration	Atomic Ground State
1	H	1s	$^2S_{1/2}$
2	He	$(1s)^2$	$^1S_0$
3	Li	[He]2s	$^2S_{1/2}$
4	Be	$[He](2s)^2$	$^1S_0$
5	B	$[He](2s)^2 2p$	$^2P_{1/2}$
6	C	$[He](2s)^2(2p)^2$	$^3P_0$
7	N	$[He](2s)^2(2p)^3$	$^4S_{3/2}$
8	O	$[He](2s)^2(2p)^4$	$^3P_2$
9	F	$[He](2s)^2(2p)^5$	$^2P_{3/2}$
10	Ne	$[He](2s)^2(2p)^6$	$^1S_0$
11	Na	[Ne]3s	$^2S_{1/2}$
12	Mg	$[Ne](3s)^2$	$^1S_0$
13	Al	$[Ne](3s)^2 3p$	$^2P_{1/2}$
14	Si	$[Ne](3s)^2(3p)^2$	$^3P_0$
15	P	$[Ne](3s)^2(3p)^3$	$^4S_{3/2}$
16	S	$[Ne](3s)^2(3p)^4$	$^3P_2$
17	Cl	$[Ne](3s)^2(3p)^5$	$^2P_{3/2}$
18	Ar	$[Ne](3s)^2(3p)^6$	$^1S_0$
19	K	[Ar]4s	$^2S_{1/2}$
20	Ca	$[Ar](4s)^2$	$^1S_0$
21	Sc	$[Ar]3d(4s)^2$	$^2D_{3/2}$
22	Ti	$[Ar](3d)^2(4s)^2$	$^3F_2$
23	V	$[Ar](3d)^3(4s)^2$	$^4F_{3/2}$
24	Cr	$[Ar](3d)^5 4s$	$^7S_3$
25	Mn	$[Ar](3d)^5(4s)^2$	$^6S_{5/2}$
26	Fe	$[Ar](3d)^6(4s)^2$	$^5D_4$
27	Co	$[Ar](3d)^7(4s)^2$	$^4F_{9/2}$
28	Ni	$[Ar](3d)^8(4s)^2$	$^3F_4$
29	Cu	$[Ar](3d)^{10}4s$	$^2S_{1/2}$
30	Zn	$[Ar](3d)^{10}(4s)^2$	$^4S_{3/2}$
31	Ga	$[Ar](3d)^{10}(4s)^2 4p$	$^2P_{1/2}$
32	Ge	$[Ar](3d)^{10}(4s)^2(4p)^2$	$^3P_0$
33	As	$[Ar](3d)^{10}(4s)^2(4p)^3$	$^4S_{3/2}$
34	Se	$[Ar](3d)^{10}(4s)^2(4p)^4$	$^3P_2$

Z	Element	Electron Configuration	Atomic Ground State
35	Br	$[Ar](3d)^{10}(4s)^2(4p)^5$	$^2P_{3/2}$
36	Kr	$[Ar](3d)^{10}(4s)^2(4p)^6$	$^1S_0$
37	Rb	[Kr]5s	$^2S_{1/2}$
38	Sr	$[Kr](5s)^2$	$^1S_0$
39	Y	$[Kr]4d(5s)^2$	$^2D_{3/2}$
40	Zr	$[Kr](4d)^2(5s)^2$	$^3F_2$
41	Nb	$[Kr](4d)^4 5s$	$^6D_{1/2}$
42	Mo	$[Kr](4d)^5 5s$	$^7S_3$
43	Tc	$[Kr](4d)^5(5s)^2$	$^6S_{9/2}$
44	Rn	$[Kr](4d)^7 5s$	$^5F_5$
45	Rh	$[Kr](4d)^8 5s$	$^4F_{9/2}$
46	Pd	$[Kr](4d)^{10}$	$^1S_0$
47	Ag	$[Kr](4d)^{10}5s$	$^2S_{1/2}$
48	Cd	$[Kr](4d)^{10}(5s)^2$	$^1S_0$
49	In	$[Kr](4d)^{10}(5s)^2 5p$	$^2P_{1/2}$
50	Sn	$[Kr](4d)^{10}(5s)^2(5p)^2$	$^3P_0$
51	Sb	$[Kr](4d)^{10}(5s)^2(5p)^3$	$^4S_{3/2}$
52	Te	$[Kr](4d)^{10}(5s)^2(5p)^4$	$^3P_2$
53	I	$[Kr](4d)^{10}(5s)^2(5p)^5$	$^2P_{3/2}$
54	Xe	$[Kr](4d)^{10}(5s)^2(5p)^6$	$^1S_0$
55	Cs	[Xe]6s	$^2S_{1/2}$
56	Ba	$[Xe](6s)^2$	$^1S_0$
57	La	$[Xe]5d(6s)^2$	$^2D_{3/2}$
58	Ce	$[Xe]4f5d(6s)^2$	$^1G_4$
59	Pr	$[Xe](4f)^3(6s)^2$	$^4I_{9/2}$
60	Nd	$[Xe](4f)^4(6s)^2$	$^5I_4$
61	Pm	$[Xe](4f)^5(6s)^2$	$^6H_{5/2}$
62	Sm	$[Xe](4f)^6(6s)^2$	$^7F_0$
63	Eu	$[Xe](4f)^7(6s)^2$	$^8S_{7/2}$
64	Gd	$[Xe](4f)^7 5d(6s)^2$	$^9D_2$
65	Tb	$[Xe](4f)^9 5d(6s)^2$	$^6H_{15/2}$
66	Dy	$[Xe](4f)^{10}(6s)^2$	$^5I_8$
67	Ho	$[Xe](4f)^{11}(6s)^2$	$^4I_{15/2}$
68	Er	$[Xe](4f)^{12}(6s)^2$	$^3H_6$

Z	Element	Electron Configuration	Atomic Ground State
69	Tm	$[Xe](4f)^{13}(6s)^2$	$^2F_{7/2}$
70	Yb	$[Xe](4f)^{14}(6s)^2$	$^3D_3$
71	Lu	$[Xe](4f)^{14}5d(6s)^2$	$^2D_{3/2}$
72	Hf	$[Xe](4f)^{14}(5d)^2(6s)^2$	$^3F_2$
73	Ta	$[Xe](4f)^{14}(5d)^3(6s)^2$	$^4F_{3/2}$
74	W	$[Xe](4f)^{14}(5d)^4(6s)^2$	$^6D_0$
75	Re	$[Xe](4f)^{14}(5d)^5(6s)^2$	$^6S_{5/2}$
76	Os	$[Xe](4f)^{14}(5d)^6(6s)^2$	$^5D_4$
77	Ir	$[Xe](4f)^{14}(5d)^7(6s)^2$	$^4F_{9/2}$
78	Pt	$[Xe](4f)^{14}(5d)^9 6s$	$^3D_3$
79	Au	$[Xe](4f)^{14}(5d)^{10}6s$	$^2S_{1/2}$
80	Hg	$[Xe](4f)^{14}(5d)^{10}(6s)^2$	$^1S_0$
81	Tl	[Hg]6p	$^2P_{1/2}$
82	Pb	$[Hg](6p)^2$	$^3P_0$
83	Bi	$[Hg](6p)^3$	$^4S_{3/2}$
84	Po	$[Hg](6p)^4$	$^3P_2$
85	At	$[Hg](6p)^5$	$^2P_{3/2}$
86	Rn	$[Hg](6p)^6$	$^1S_0$
87	Fr	[Rn]7s	$^2S_{1/2}$
88	Ra	$[Rn](7s)^2$	$^1S_0$
89	Ac	$[Rn]6d(7s)^2$	$^3D_{3/2}$

Z	Element	Electron Configuration	Atomic Ground State
90	Th	$[Rn](6d)^2(7s)^2$	$^3F_2$
91	Pa	$[Rn](5f)^2 6d(7s)^2$	$^4K_{11/2}$
92	U	$[Rn](5f)^3 6d(7s)^2$	$^5L_6$
93	Np	$[Rn](5f)^4 6d(7s)^2$	$^6L_{11/2}$
94	Pu	$[Rn](5f)^6(7s)^2$	$^7F_0$
95	Am	$[Rn](5f)^7(7s)^2$	$^8S_{7/2}$
96	Cm	$[Rn](5f)^7 6d(7s)^2$	$^9D_2$
97	Bk	$[Rn](5f)^9(7s)^2$	$^8H_{17/2}$
98	Cf	$[Rn](5f)^{10}(7s)^2$	$^5I_8$
99	Es	$[Rn](5f)^{11}(7s)^2$	$^4I_{15/2}$
100	Fm	$[Rn](5f)^{12}(7s)^2$	$^3H_6$
101	Md	$[Rn](5f)^{13}(7s)^2$	$^2F_{7/2}$
102	No	$[Rn](5f)^{14}(7s)^2$	$^1S_0$
103	Lr	$[Rn](5f)^{14}6d(7s)^2$	$^2D_{5/2}$
104	Rf	$[Rn](5f)^{14}(6d)^2(7s)^2$?	$^3F_2$?
105	Db		
106	Sg		
107	Bh		
108	Hs		
109	Mt		



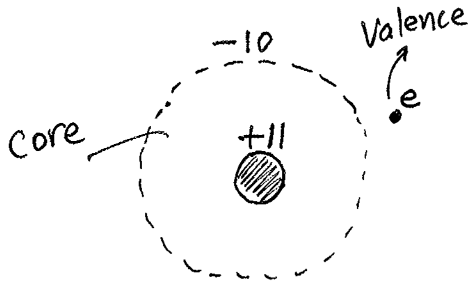
← Experimental experience of filliŋ orders.

$L = 0, 1, 2, 3, 4, 5, 6, 7, 8, \cdots$

$S, P, D, F, G, H, I, K, L, \cdots$

Let us introduce a few concepts regarding atomic shells and electron configurations: Atomic Core and Valence Electrons.

* Using Na ($Z=11$) as an example, the first 10 electrons fill in $1s^2 2s^2 2p^6$ shells, and the 11th electron in 3s or 3p or others.



The 10 electrons have strong interactions with the nucleus, and form a closed shell. (The maximum number of electrons determined by Pauli Exclusion Principle is $2+8=10$ for the first two main shells $n=1,2$)

Such a close shell (one nucleus with full shell electrons) is a stable structure, forming a core of the atom. We call this "Atomic Core".

* The electron outside the atomic core is called "Valence electron". Atomic chemical properties and spectrum are mainly determined by this Valence electron, Since the interaction between the valence electron and this atomic core is not strong, the valence electron is easy to be excited to excited states or be ionized.

* Since the smallest orbits have been occupied by core electrons (electrons of the atomic core are called core electrons), the valence electron cannot occupy the smallest orbits any more. So it has to go to larger orbits (usually with larger quantum numbers of n and/or l).

Example: For Li atom, 2 electrons occupy $n=1$, then the 3rd one (valence electron) has to be on $n \geq 2$. This is why the Li energy levels start with 2s, not 1s.

Similarly, Na energy levels start with $n=3$, i.e., 3s
K " " " " $n=4$, i.e., 4s
Rb " " " " $n=5$, i.e., 5s
Cs " " " " $n=6$, i.e. 6s

Only H and He can start with $n=1$ ($1s$ or $1s^2$).

* Atomic spectrum is mainly determined by the valence electrons. So elements with same number of valence electrons have similar spectra and also similar chemical properties.

* Periodic Table of elements:

The arrangements of elements are mainly determined by the number of valence electrons, along with electron configurations. To determine the quantity of valence electrons, we should look at the vertical column of the periodic table.

Group	Quantity of valence electrons
Group 1 (I) (Alkali metals)	1
Group 2 (II) (Alkaline Earth metals)	2
Group 3-12 (Transition metals)	1 or 2
Group 13 (III) (Boron Group)	3
Group 14 (IV) (Carbon Group)	4
Group 15 (V) (Nitrogen Group)	5
Group 16 (VI) (Chalcogens)	6
Group 17 (VII) (Halogens)	7
Group 18 (VIII) (Noble Gases)	8* → Except for He, only 2 valence electrons

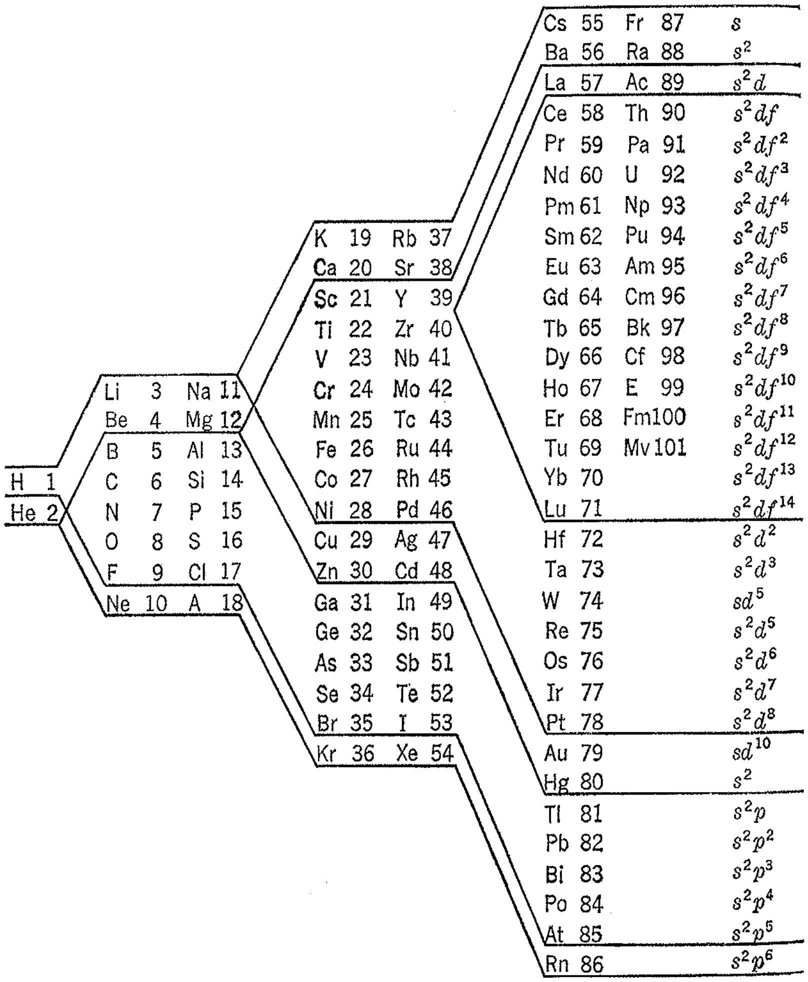


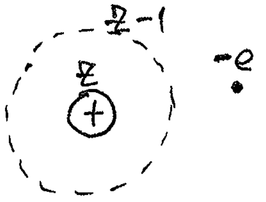
FIG. Periodic table of the elements, with electron configurations of the lowest states. The electron configurations do not in every case represent the absolutely lowest state, but in every case the state indicated at least is very close to the ground state. The lines are drawn to indicate chemically similar elements.

Shown here is a different form of periodic table, which is good at showing the valence electron numbers for elements. You may find normal periodic table from any Chemistry books.

* Note: though He and Be, Mg, Ca, etc all have 2 valence electrons, He has a closed shell, while the others are not. That's why He has very different chemical properties than others — He has ionization energy of ~ 24.5 eV, which is the most stable element!

5. Shielding, Penetration, Atomic Core Polarization Effects.

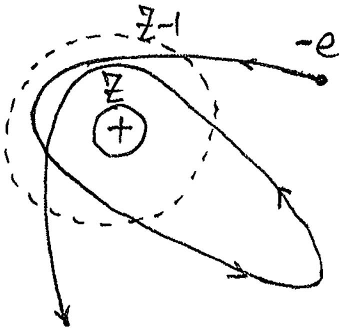
(1) Shielding :



Let us consider the case of one valence electron (alkali atoms). The inner electrons inside the atomic core will have shielding effect on the nucleus charge that the valence electron experienced.

Imaging this closed shell as a sphere with negative charges on the surface (e.g., 10 electrons of Na) and one positive charge at the center of the sphere (the nucleus with +11 charges). For the valence electron (the 11th) outside the sphere, the electron experiences a point charge at the center of the sphere with charge of +1, i.e., the atomic core charge $Z_a = 11 - 10 = +1$.

(2) Penetration :



However, the valence electron does not always stay outside the atomic core. As the calculation we made with QM in hydrogen atom, the valence electron does have probabilities to occur inside the atomic core. This phenomenon is called penetration.

When penetration occur, inside the "sphere", the valence electron will experience larger nucleus charges, because the shielding effect is partially removed. Thus, the charge that a valence electron can experience

Z^* is determined by the average effect of the sheeldG when outside the atomic and the penetration inside the core : $1 \leq Z^* \leq Z$.

The actual Z^* depends on how much time the valence electron spends inside and outside the atomic core. Obviously, Z^* values depend on both n and l quantum numbers, as different nl correspondg to different electron orbitals that strongly affect the penetration possibilities. Z^* is called the effective charge.

Besides the effective charge Z^*, the penetration also affects the effective quantum number n^* for multielectron atoms. Recall the principal quantum number n in energy level

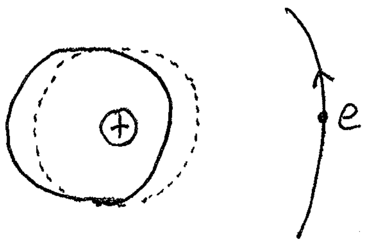
$$E_n = -Rhc\frac{Z^2}{n^2}$$ is defined in hydrogen atom, i.e.,

when electron has orbitals like hydrogen, it has full quantum number n. When penetration occurs, the valence electron's orbitals will be different from hydrogen electron orbitals. This causes the effective quantum number n^* to be smaller than n:

$$n^* = n - \delta_{nl},$$

where δ_{nl} is quantum defect and it varies with n and l for each element. Thus, for alkali atoms, the energy levels $E_{nl} = -Rhc\frac{(Z^*)^2}{(n^*)^2}$, where Z^* and n^* are determined from experiments.

(3) Atomic Core Polarization effect:



Because of the Coulomb field produced by the valence electron, the charge distribution center of the atomic core will have displacement.

This causes the negative electrons' charge center does not overlap with the positive nucleus anymore. Thus, the atomic core is polarized and forms an electric dipole. This atomic core electric dipole interacts on the valence electron and results in extra Coulomb attraction. This causes the valence electron (also the atom) energy decreases, i.e., n^* becomes smaller, so the E_{nl} becomes further negative.

Similarly, the reason that penetration causes n^* to be smaller than n is that the valence electron experiences extra Coulomb attraction, compared to full shielding, so resulting in lower energy $\Rightarrow$ smaller n^*.

In summary,

$$\left.\begin{array}{l}\text{Shielding}\\ \text{Penetration}\end{array}\right\} \Rightarrow 1 \le Z^* \le Z \quad \text{(effective charge)}$$

$$\left.\begin{array}{l}\text{Penetration}\\ \text{Atomic Core Polarization}\end{array}\right\} \Rightarrow 0 < n^* < n \quad \text{(effective quantum number)}$$

6. Alkali Atomic Structure

Since alkali atoms have one valence electron, just like the hydrogen atom, they have very similar atomic structure as the hydrogen atom. This is also because the atomic core has a closed or filled shell, resulting in zero total orbital angular momentum and corresponding magnetic moment, zero spin angular momentum and corresponding magnetic moment. Thus, the major magnetic interaction in an alkali atom is determined by the valence electron's spin-orbit coupling: $\hat{\vec{S}}+\hat{\vec{L}}=\hat{\vec{J}}$, forming fine structure. When considering nuclear spin, similar to hydrogen atom, alkali atoms will also have nuclear spin – electron total angular momentum coupling $\hat{\vec{I}}+\hat{\vec{J}}=\hat{\vec{F}}$, and form hyperfine structure.

But there are also two major differences between the alkali atomic structure and the hydrogen:

(1) Due to electrostatic interactions between electrons, though the mean electric field that the valence electron experiences is still a spherical symmetric field (central field) $V(r)$, it is not a Coulomb field $\left(-\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}\right)$, i.e., $V(r)$ does not have $-\frac{1}{r}$ format. Then as we pointed out earlier in the central field approximation, the energy levels depend on both n and l, i.e., different ls are now corresponding to different energy levels.

This is different from hydrogen atoms, where different ls under the same n are degenerate, i.e., they have the same energy eigenvalues. Thus, in the alkali atomic structure (e.g., Na), even before considering fine and hyperfine structures, the 3S and 3P levels are not degenerate.

(2) As just discussed above, shielding, penetration, and atomic core polarization effects cause alkali atoms to have effective charge Z^* and effective quantum number n^*. Both Z^* and n^* vary with elements and with n l numbers. They need to be determined from measurements.

When using measured Z^* and n^* to replace Z and n, the energy levels that we derived for hydrogen atoms can be used to calculate alkali atomic energy levels.

* Fine structure of Alkali atoms:

Recall hydrogen fine structure

$$\Delta E_{ls} = \begin{cases} \dfrac{\alpha^4 Z^4 \mu c^2}{4n^3} \cdot \dfrac{j(j+1)-l(l+1)-s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, \quad l=0 \end{cases}$$

Replace Z^4 with $Z_a^2 (Z^*)^2$ (where $Z_a = 1$), replace n^3 with $(n^*)^3$, and μ is the reduced mass for alkali atoms, then the alkali atoms fine struture

$$\Delta E_{ls} = \begin{cases} \dfrac{\alpha^4 Z_a^2 (Z^*)^2 \mu c^2}{4(n^*)^3} \cdot \dfrac{j(j+1)-l(l+1)-s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, \quad l=0 \end{cases}$$

* Hyperfine Structure of Alkali Atoms :

① For $\ell = 0$,

$$|\psi_s(0)|^2 = \frac{Z^* Z_a^2}{\pi a_1^3 (n^*)^3}\left(1 - \frac{d\delta}{dn}\right).$$

where $n^* = n - \delta$ (δ is quantum defect).

$$\therefore\ \Delta E_M = \frac{1}{4\pi\varepsilon_0 c^2}\left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right)\frac{8}{3}\,\frac{Z^* Z_a^2}{a_1^3 (n^*)^3}\left(1 - \frac{d\delta}{dn}\right)$$

$$* \frac{1}{2}\left[F(F+1) - j(j+1) - I(I+1)\right]$$

② For $\ell \neq 0$,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^* Z_a^2}{a_1^3 (n^*)^3 (\ell + \frac{1}{2})\,\ell(\ell+1)}$$

$$\therefore\ \Delta E_M = \frac{1}{4\pi\varepsilon_0 c^2}\left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right)\left(\frac{Z^* Z_a^2}{a_1^3 (n^*)^3}\right)\frac{1}{(\ell+\frac{1}{2})\,j(j+1)}$$

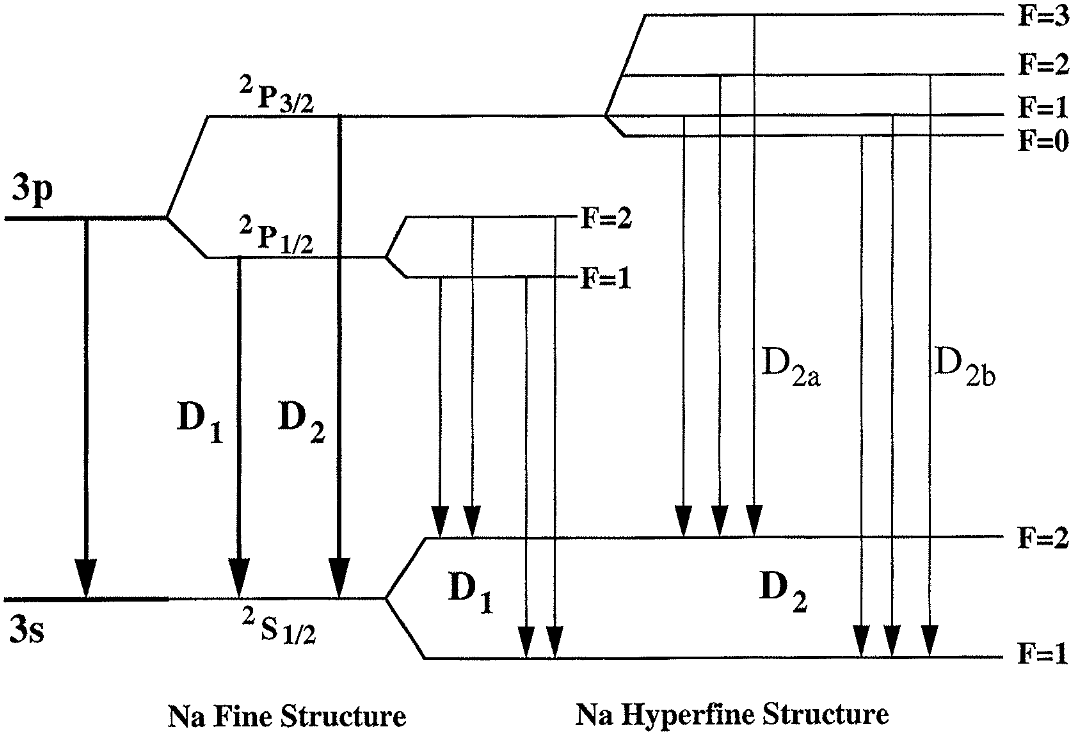
$$* \frac{1}{2}\left[F(F+1) - j(j+1) - I(I+1)\right]$$

* In magnetic field, alkali will also have Zeeman effect, similar to hydrogen situation.

Example : Quantum Defect of Na atom $\delta(n, \ell)$

ℓ \ n	3	4	5	6	7	8
0	1.373	1.357	1.352	1.349	1.348	1.351
1	0.883	0.867	0.862	0.859	0.858	0.857
2	0.010	0.011	0.013	0.011	0.009	0.013
3	—	0.000	-0.001	-0.008	-0.012	-0.015

		δ_{fs} (cm^{-1})	n^*	Z^*
Li	2P	0.34	1.966	2.060
Na	3P	17.20	2.116	3.531
K	4P	57.52	2.233	4.17
Rb	5P	237.60	2.286	5.83
Cs	6P	554.91	2.345	5.51



Energy Level Diagram of Atomic Na

Shown here is an example of Na atomic structure:

Ground State Electron Configuration: $1s^2 2s^2 2p^6 3s$

Ground state: 3s

$$n = 3,\ l = 0,\ s = \frac{1}{2} \Rightarrow j = l + s = \frac{1}{2} \Rightarrow {}^2S_{1/2}$$

$$\left.\begin{array}{l} \text{Na nuclear spin } I = 3/2 \\ \text{Total electron} \rightarrow j = \frac{1}{2} \end{array}\right\} \Rightarrow \begin{array}{l} F = I + j = 2 \\ F = I - j = 1 \end{array}$$

First excited state: 3p

$$n = 3,\ l = 1,\ s = \frac{1}{2} \Rightarrow j = \begin{cases} l + s = \frac{3}{2} \Rightarrow {}^2P_{3/2} \\ l - s = \frac{1}{2} \Rightarrow {}^2P_{1/2} \end{cases}$$

$$\left.\begin{array}{l} I = \frac{3}{2} \\ j = \frac{3}{2} \end{array}\right\} \Rightarrow F = 3, 2, 1, 0$$

$$\left.\begin{array}{l} I = 3/2 \\ j = 1/2 \end{array}\right\} \Rightarrow F = 2, 1.$$

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, $n_3 l_3$, $n_4 l_4$, $\cdots$ there correspond $2(2l_1+1)\ 2(2l_2+1)\ 2(2l_3+1) \cdots$ 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 $n_1 l_1$, $n_2 l_2$, $n_3 l_3$, $\ldots$ 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

$$\hat{H} = \left\{ \sum_{i=1}^{N} \frac{\hat{\vec{P}}_i^{\,2}}{2\mu} - \sum_{i=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r_i} + \sum_{i=1}^{N} U_i(r_i) \right\}$$

$$+ \underbrace{\left[\sum_{i>j=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} U_i(r_i) \right]}_{\Delta \hat{H}_{NCE}} + \underbrace{\sum_{i=1}^{N} a(r_i) \vec{l}_i \cdot \vec{s}_i}_{\Delta \hat{H}_m}$$

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

$$\hat{H}_1 = \sum_{i=1}^{N} \left[\frac{\hat{\vec{P}}_i^{\,2}}{2\mu} - \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r_i} + U_i(r_i) \right]$$

$$+ \left[\sum_{i>j=1}^{N} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} U_i(r_i) \right].$$

Every electron has an orbital angular momentum $\hat{\vec{l}}_i$, and spin angular momentum of $\hat{\vec{S}}_i$. Then the total orbital angular momentum for the atom is $\hat{\vec{L}} = \sum_{i=1}^{N} \hat{\vec{l}_i}$, and the total spin angular momentum $\hat{\vec{S}} = \sum_{i=1}^{N} \hat{\vec{S}_i}$.

* 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., $[\hat{H}_1, \hat{\vec{L}}] = 0$, $[\hat{H}_1, \hat{\vec{S}}] = 0$.

* 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.

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

L, S, M_L, and M_S are good quantum numbers, i.e., $\hat{\vec{L}}^2$, $\hat{\vec{S}}^2$, L_z, and S_z are conservative. Energy levels will go by ^{2S+1}L 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., $\hat{\vec{L}}$ and $\hat{\vec{S}}$ couple with each other to form $\hat{\vec{J}}$. Thus, the energy levels have fine splitting, i.e., form fine structure.

— 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_1,

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

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

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

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

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

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

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

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

Term $\quad {}^{2S+1}\boxed{\begin{array}{c}\text{The letter}\\ \text{representing}\\ L\end{array}}^{\circ \longrightarrow \text{odd parity}}_{J}$ is called multiplet under LS coupling.

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

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

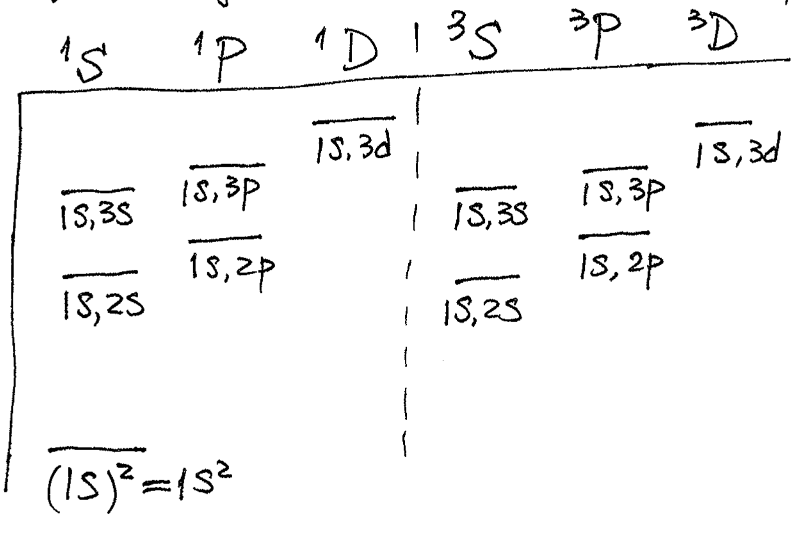
(M_L : $2L+1$, M_S : $2S+1$)

* 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

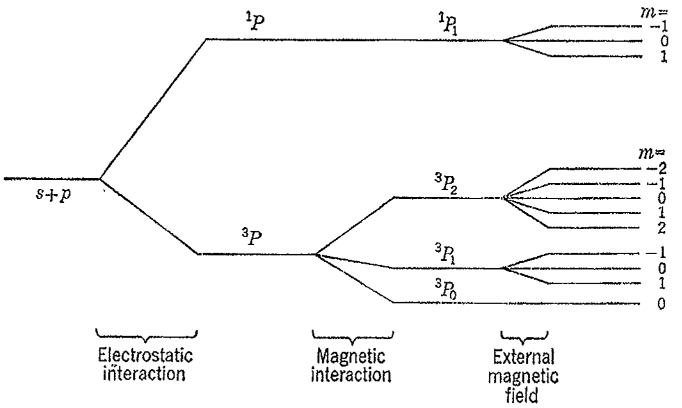


FIG. 13-1. Splitting of energy levels of multiplets arising from an s and a p electron, from electrostatic interaction, magnetic spin-orbit interaction, and a weak external magnetic field (schematic).

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.

<u>Example</u>: 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.

$$\left.\begin{array}{l} S_1 = \frac{1}{2},\ S_2 = \frac{1}{2} \Rightarrow S = 0,\ 1 \\ l_1 = 1,\ l_2 = 1 \Rightarrow L = 0, 1, 2 \Rightarrow S, P, D \end{array}\right\} \Rightarrow \begin{array}{l} {}^1S, {}^1P, {}^1D \\ {}^3S, {}^3P, {}^3D. \end{array}$$

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

8. jj 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

$$\hat{H}_2 = \sum_i \left[\frac{\hat{\vec{P}}_i^{\,2}}{2\mu} - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r_i} + U_i(r_i)\right] + \sum_i a(r_i)\,\hat{\vec{l}}_i\cdot\hat{\vec{s}}_i.$$

Under this case, $\hat{\vec{j}}_i = \hat{\vec{l}}_i + \hat{\vec{s}}_i$, i.e., each electron has l-s (spin-orbit) coupling and form j_i as good quantum number. Then these $\hat{\vec{j}}_i$ couple with each other to form a total angular momentum $\hat{\vec{J}} = \sum_{i=1}^{N}\hat{\vec{j}}_i$.

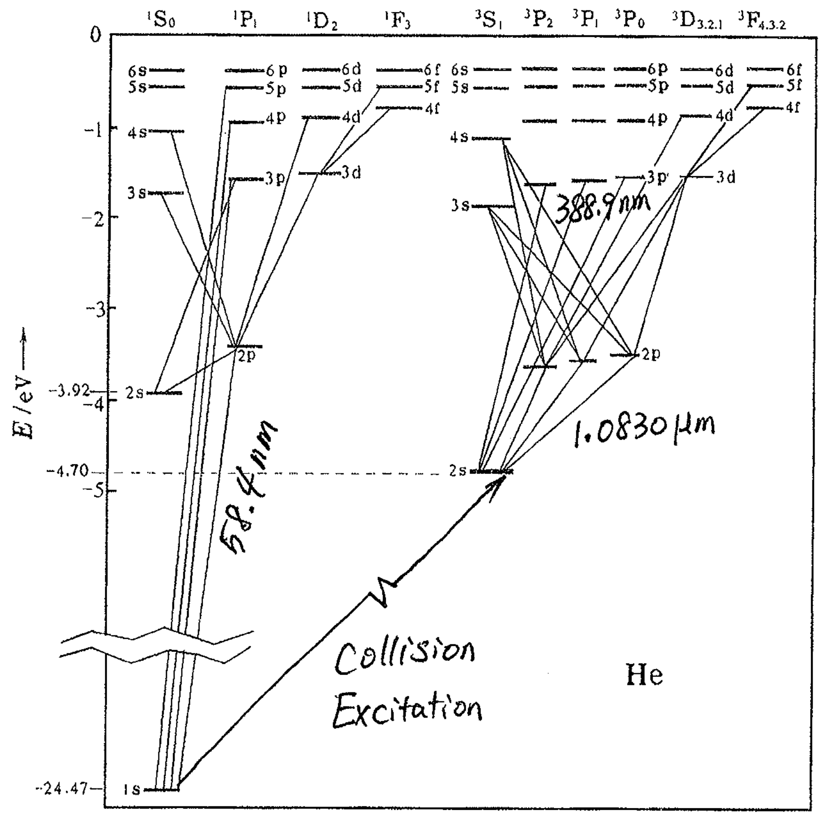
J and M_J are good quantum numbers (conservative). Eigenstate is $|j_1 j_2 \cdots J M_J\rangle$. The energy levels with same j_i but different J are degenerate. Now considering the weak noncentral electrostatic interaction, the degeneracy of different J will be removed.

— This is called jj coupling.

$$\left.\begin{array}{l} \left.\begin{array}{l} S_1=\frac{1}{2}\\ l_1=0\end{array}\right\}\Rightarrow j_1=\frac{1}{2} \\ \\ \left.\begin{array}{l} S_2=\frac{1}{2}\\ l_2=1\end{array}\right\}\Rightarrow j_2=\frac{3}{2},\frac{1}{2}\end{array}\right\}\Rightarrow \begin{array}{l} \left.\begin{array}{l} j_1=\frac{1}{2}\\ j_2=\frac{3}{2}\end{array}\right\}\Rightarrow J=2,1 \\ \\ \left.\begin{array}{l} j_1=\frac{1}{2}\\ j_2=\frac{1}{2}\end{array}\right\}\Rightarrow J=1,0\end{array}$$

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

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 $m_s = \pm\frac{1}{2}$, ∴ $|n\, l\, m_l\, m_s\rangle$ are $|1, 0, 0, \frac{1}{2}\rangle$ and $|1, 0, 0, -\frac{1}{2}\rangle$.

This configuration gives the lowest energy level → ground state

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

∴ $S = 0$, ⇒ 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, ⇒ single spectral line.

— This is called Singlet, or para-Helium.

* With two electron spins are parallel to each other, 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 $(l \geq 1)$ ⇒ triple spectral lines — This is called triplets or ortho-Helium.

④ LS coupling applied here:

$^1S_0$, $^3S_1$, $^3P_{2,1,0}$, ⋯ 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)

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

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

transition from $2\,{}^1S_0 \leftrightarrow 1\,{}^1S_0$ (because of $J=0 \not\rightarrow J'=0$).
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 twinlight or in the night. This is mainly caused by the transition from $2^3P — 2^3S_1$, which has wavelengths of ~1.083 μm.

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: ^4He and ^3He.

^4He $Z=2$, Neutron $=2$, $4.0026u$, 99.999%, $I=0$

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

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

But ^3He 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.