Schroedinger's equation:

$$\underbrace{\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x,t)\,\psi(x,t)}_{\text{Hamiltonian } \hat{H}\psi} = i\hbar\frac{\partial}{\partial t}\psi(x,t)$$

w/ i imaginary number $i = \sqrt{-1}$

$\hbar = h/2\pi$

$\psi(x,t)$ wave function

$V(x,t)$ potential energy

The solution of this equation returns the wave function associated to the motion of the particle of mass m under the influence of a force defined by the potential, $V(x,t)$ $\left(\text{ie: } F = -\frac{\partial V(x,t)}{\partial x}\right)$

~~potential~~ energy

NOTE: This equation only applies for non-relativistic particles.
For relativistic particles → Dirac's equation.

In the case of free particle $\Rightarrow$ $V(x,t) = V_0 = \text{constant}$

$\Rightarrow$ $\psi(x,t) = \cos(kx - \omega t) + i\,\text{sen}(kx - \omega t)$, ie: the wave function is complex, w/ a real part & an imaginary part.

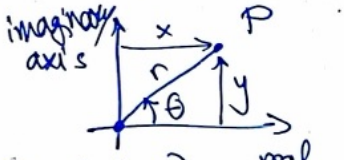
$k = p/\hbar = 2\pi/\lambda$ wave number
$\omega = 2\pi\nu$ angular frequency

NOTE: **Imaginary number** $i = \sqrt{-1}$ $\quad i^2 = -1$

$z \in \mathbb{C} \Rightarrow z = x + iy$, w/ $x, y \in \mathbb{R}$ $\quad z^* = x - iy$ complex conjugate of z

$z_1 = z_2 \Leftrightarrow x_1 = x_2 \cap y_1 = y_2$

$$zz^* = (x+iy)(x-iy) = x^2 + ixy - i^2y^2 - ixy = x^2 + y^2 \in \mathbb{R}$$



r modulus $\Rightarrow x = r\cos\theta$ $\quad \cos\theta = x/r$

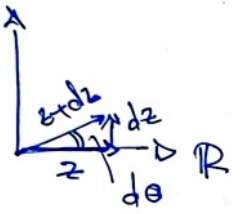
θ phase $\quad y = r\sin\theta$ $\quad \sin\theta = y/r$

$r^2 = x^2 + y^2$

$\Rightarrow z = r(\cos\theta + i\sin\theta)$

$zz^* = r^2$

II



If P rotates keeping r constant through a change of angle $d\theta$, the new complex number becomes

$z + dz \Rightarrow dz = iz\,d\theta \Rightarrow \frac{dz}{z} = i\,d\theta$

$\int_{z_i}^{z_f} \frac{dz}{z} = i\int_0^{\theta} d\theta \Rightarrow \ln\frac{z_f}{z_i} = i\theta \Rightarrow z_f = z_i e^{i\theta}$

If $r=1$, $z_i = 1 \Rightarrow z_f = \cos\theta + i\sin\theta = e^{i\theta}$

$\Rightarrow e^{-i\theta} = \cos\theta - i\sin\theta$

$\cos\theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$

$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$

$\Rightarrow (e^{i\theta})^* = e^{-i\theta}$

$r^2 = zz^* = (e^{i\theta})(e^{i\theta})^* = e^{i\theta}e^{-i\theta} = e^0 = 1$

The connection between the wave function and the behavior of the particle associated to the wave function is expressed in terms of probability density $P(x,t)$, probability per unit of length along the x axis, to find the particle near x at time t $\Rightarrow P(x,t) = \psi^*(x,t)\,\psi(x,t)$

the probability that the particle is at coordinates between x and $x+dx$ is $\psi^*(x,t)\,\psi(x,t)\,dx$

Quantum mechanics only tells us the probability to find the particle at different positions at a given time, ie: the predictions of quantum mechanics are statistical.

We have $\int_{-\infty}^{\infty} P\,dx = \int_{-\infty}^{\infty} dP(x,t) = \int_{-\infty}^{+\infty} \psi^*\psi\,dx = \int_{-\infty}^{\infty} |\psi(x,t)|^2 dx = 1$

the wave function is normalized

Expectation values: I define the expectation value of the x coordinate of a particle at time t (maintaining symmetry)

$$\bar{x} = \int_{-\infty}^{\infty} P(x,t)\, x\, dx = \int_{-\infty}^{+\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

$$\Leftrightarrow \quad \bar{x} = \frac{\int_{-\infty}^{+\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx}{\int_{-\infty}^{\infty} \psi^*(x,t)\, \psi(x,t)\, dx}$$

$$\overline{x^2} = \int_{-\infty}^{\infty} \psi^*(x,t)\, x^2\, \psi(x,t)\, dx$$

$$\overline{f(x)} = \int_{-\infty}^{\infty} \psi^*(x,t)\, f(x)\, \psi(x,t)\, dx$$

$$\overline{V(x,t)} = \int_{-\infty}^{\infty} \psi^*(x,t)\, V(x,t)\, \psi(x,t)\, dx$$

x, $V(x,t)$, p, E are dynamic quantities to characterise the behavior of the particle.

Momentum $\bar{p} = \int_{-\infty}^{\infty} \psi^*(x,t)\, p\, \psi(x,t)\, dx$

However, in quantum mechanics, for the Heisenberg principle, one cannot write p as a function of x & t

$$p[\psi(x,t)] = -i\hbar \frac{\partial}{\partial x}[\psi(x,t)] \quad \Rightarrow \text{operator } \hat{p} = -i\hbar \frac{\partial}{\partial x}$$ operator associated to momentum p

ie: the effect of multiplying p times $\psi(x,t)$ is the same as applying the operator $-i\hbar\frac{\partial}{\partial x}$ to $\psi(x,t)$

The same reasoning for energy E: $E[\psi(x,t)] = i\hbar \frac{\partial}{\partial t}[\psi(x,t)]$

Considering $E = \frac{p^2}{2m} + V(x,t)$ total energy

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t) = i\hbar \frac{\partial}{\partial t}$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

$$\Rightarrow \quad \bar{p} = \int_{-\infty}^{\infty} \psi^*(x,t)\, p\, \psi(x,t)\, dx = \int_{-\infty}^{\infty} \psi^*(x,t) \left(-i\hbar \frac{\partial}{\partial x}\right) \psi(x,t)\, dx$$

$$\Rightarrow \quad \boxed{\bar{p} = -i\hbar \int_{-\infty}^{\infty} \psi^*(x,t) \frac{\partial \psi(x,t)}{\partial x}\, dx}$$

$$\boxed{\bar{E} = i\hbar \int_{-\infty}^{\infty} \psi^*(x,t) \frac{\partial \psi(x,t)}{\partial t}\, dx}$$

Because $E = \frac{p^2}{2m} + V(x,t) \Rightarrow \boxed{\bar{E} = \int_{-\infty}^{\infty} \psi^*(x,t) \left(\frac{p^2}{2m} + V(x,t)\right) \psi(x,t)\, dx =}$

$$\boxed{= \int_{-\infty}^{+\infty} \psi^*(x,t) \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)\right) \psi(x,t)\, dx}$$

IF $f(x,p,t)$ is a dynamic quantity function of x, p, t useful to describe the state of motion of the particle associated w/ the wave function $\psi(x,t)$, then the expectation value

$$\overline{f(x,p,t)} = \int_{-\infty}^{+\infty} \psi^*(x,t)\, \underbrace{f_{op}\left(x, -i\hbar\frac{\partial}{\partial x}, t\right)}_{\text{operator replacing } p \text{ w/ } -i\hbar\frac{\partial}{\partial x}} \psi(x,t)\, dx$$

Time-independent Schroedinger's equation $\quad \psi(x,t) = \varphi(x)\,\varphi(t)$ (psi, phi)

If $V(x,t) = V(x)$ potential independent from t & replacing in Schroedinger's eq. $\Rightarrow$

$$-\frac{\hbar^2}{2m}\underbrace{\frac{\partial^2}{\partial x^2}\left[\varphi(x)\varphi(t)\right]}_{\varphi(t)\frac{d^2\varphi(x)}{dt^2}} + V(x)\varphi(x)\varphi(t) = i\hbar \underbrace{\frac{\partial}{\partial t}\left[\varphi(x)\varphi(t)\right]}_{\varphi(x)\frac{d\varphi(t)}{dt}}$$

Dividing by $\varphi(x)\varphi(t)$ on both sides

$$\frac{1}{\varphi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} + V(x)\varphi(x)\right] = \frac{1}{\varphi(t)}\, i\hbar\, \frac{d\varphi(t)}{dt}$$

The right side only depends on t, & the left side depends only on x, hence the common value must be equal to a constant G $\Rightarrow$ $\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)\right]=G$ G constant of separation

$i\hbar\frac{1}{\varphi(t)}\frac{d\varphi(t)}{dt}=G$

$\Rightarrow$ $\boxed{\varphi(t)=e^{-iGt/\hbar}=\cos\frac{Gt}{\hbar}-i\sin\frac{Gt}{\hbar}=\cos 2\pi\frac{Gt}{h}-i\sin\frac{2\pi G}{h}t}$

$\varphi(t)$ is an oscillating function that depends on t w/ frequency $\nu=G/h$

But $\nu=E/h$ $\Rightarrow$ $G=E$

Substituting $G=E$ in the other equation, & solving

$$\boxed{\psi(x,t)=\psi(x)\,e^{-iEt/\hbar}}$$

w/ E total energy of the particle

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x)}$$

is the time-independent Schroedinger's eq.

$\psi(x)$ is the characteristic function or eigenfunction

$\psi(x)$, $\frac{d\psi(x)}{dx}$ must be finite, single value, & continuous. Taking the $\psi(x)$ that satisfy these properties will result in the energy being quantized.

NOTE: when the relation between the total energy of the particle E & its potential energy is such that the particle is bound to a region of space because its potential energy is larger than the total energy outside of the region ⇒ total energy of the particle is quantized

If particle not bound to a limited region ⇒ the total energy is continuous

For time-independent Schroedinger's eq., the acceptable solutions exist only for certain values of energy $E_1, E_2, \dots, E_n$. These energies are eigen values of the potential $V(x)$. The first eigenvalues are discretized; then generally the eigenvalues are distributed continuously above a certain energy level. Corresponding to each eigenvalue there is an eigen function $\psi_1(x), \psi_2(x), \dots, \psi_n(x)$, solutions of the time-independent Schroedinger's eq. for the given potential $V(x)$.

⇒ corresponding wave function $\Psi_1(x,t), \dots, \Psi_n(x,t)$

w/ $\Psi_j(x,t) = \psi_j(x)\, e^{-iE_j t/\hbar}$ w/ $j = 1, \dots, n$

(n) is the principal quantum number, & the system is in the quantum state n.

The general solution is $\Psi(x,t) = c_1\Psi_1(x,t) + c_2\Psi_2(x,t) + \dots + c_n\Psi_n(x,t)$

EXAMPLE: 1) particle in a state such that single value of energy $\rightarrow \psi = \varphi(x)\, e^{-iEt/\hbar}$

The probability density function

$$\psi^*\psi = \varphi^*(x)\, e^{iEt/\hbar}\, \varphi(x)\, e^{-iEt/\hbar} = \varphi^*(x)\,\varphi(x)$$

independent of t (eg, the e^- is in the fundamental state of H atom)

2) particle in a state such that $E_1 \neq E_2$

$$\Rightarrow \psi = c_1 \varphi_1(x)\, e^{-iE_1 t/\hbar} + c_2 \varphi_2(x)\, e^{-iE_2 t/\hbar}$$

(eg, e^- transitioning from an excited state E_2 down to the fundamental state E_1)

$$\Rightarrow \psi^*\psi = c_1^* c_1 \varphi_1^* \varphi_1 + c_2^* c_2 \varphi_2^* \varphi_2 + c_2^* c_1 \varphi_2^* \varphi_1\, e^{\frac{i(E_2-E_1)t}{\hbar}} + c_1^* c_2 \varphi_1^* \varphi_2\, e^{-i(E_2-E_1)t/\hbar}$$

which depends on time, w/ the last two terms oscillating in time w/ frequency

$$\nu = \frac{E_2 - E_1}{2\pi\hbar} = \frac{E_2 - E_1}{h}$$

NOTE: If I consider an e^- of H in the fundamental state, since the e^- can be located anywhere the density distribution has a non-negligible value, then the transported charge is not localizable in a precise point $\Rightarrow$ charge distribution proportional to the density distribution. Since the e^- is its fundamental state, the charge distribution is independent of time $\Rightarrow$

a static distribution of charge does not emit electromagn. radiation ⇒ stability of the atom problem is resolved.

Excited atoms return to the fundamental state emitting radiation: the probability density (& the charge distribution) oscillates in time w/ frequency $\nu = \frac{E_2 - E_1}{h}$, which is also the frequency of the radiation emitted in the transition.

Atoms w/ one electron

Let's consider an e^- w/ reduced mass $\mu = \frac{Mm}{m+M}$, w/ m mass of the electron & M mass of the nucleus, moving under the influence of a Coulomb potential $V = V(x,y,z) = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$

where x,y,z are the e^- coordinates with respect to the nucleus, in the origin. $r = \sqrt{x^2+y^2+z^2}$ is the separation distance between e^- & nucleus.

$Z = 1$ H

$Z = 2$ He^+ ...

The classical expression for energy of the system

$$E = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + V(x,y,z)$$

⇒ equation operator $-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z) = i\hbar\frac{\partial}{\partial t}$

If $\psi(x,y,z,t) = \psi$ wave function

⇒ $-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi(x,y,z,t)}{\partial x^2} + \frac{\partial^2\psi(x,y,z,t)}{\partial y^2} + \frac{\partial^2\psi(x,y,z,t)}{\partial z^2}\right) + V(x,y,z)\psi(x,y,z,t) = i\hbar\frac{\partial\psi(x,y,z,t)}{\partial t}$

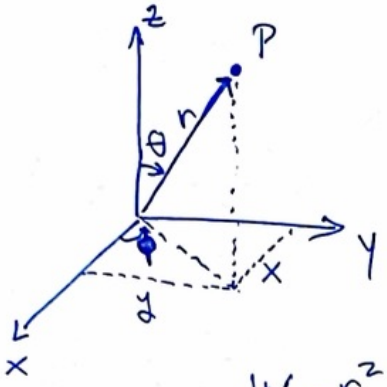
⇔ $-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$ is the Schroedinger eq. for the system.

w/ $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ laplacian operator

Since $V(x,y,z)$ does not depend on t $\Rightarrow \psi(x,y,z,t) = \psi(x,y,z)\, e^{-iEt/\hbar}$

q $-\frac{\hbar^2}{2\mu}\nabla^2\psi(x,y,z) + V(x,y,z)\,\psi(x,y,z) = E\,\psi(x,y,z)$

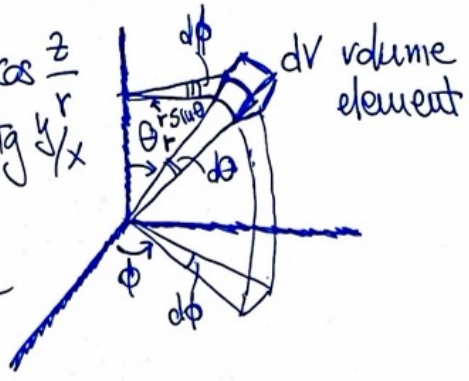
Let's change reference system from cartesian to polar spherical:



$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$
$r = \sqrt{x^2+y^2+z^2}$

$\theta = \arccos\frac{z}{r}$
$\phi = \text{arctg}\, y/x$

polar angle
azimuthal angle



$dV = r^2\sin\theta\, dr\, d\theta\, d\phi$

$$V = V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\Rightarrow\quad -\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi) + V(r)\,\psi(r,\theta,\phi) = E\,\psi(r,\theta,\phi)$$

w/ $$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

laplacian operator in coordinates spherical polar r, θ, ϕ.

W/ solution as $\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$.

- Replacing this into Schroedinger's eq.

$$\text{①}\quad \frac{d^2\Phi}{d\phi^2} = -m_\ell^2\,\Phi$$

$$\Rightarrow\quad \text{②}\quad -\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{m_\ell^2\,\Theta}{\sin^2\theta} = \ell(\ell+1)\,\Theta$$

$$\text{③}\quad \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu}{\hbar^2}\left[E - V(r)\right]R = \ell(\ell+1)\frac{R}{r^2}$$

$$\Phi_{m_e}(\phi) = e^{i m_e \phi} \quad , \quad |m_e| = 0, 1, 2, \ldots$$

$$\Theta_{\ell m_e}(\theta) = \sin^{|m_e|}\theta \; F_{\ell |m_e|}(\cos\theta) \quad , \quad \ell = |m_e|, |m_e|+1, |m_e|+2, \ldots$$

$$R_{n\ell}(r) = e^{-Zr/na_0} \left(\frac{Zr}{a_0}\right)^{\ell} G_{n\ell}\left(\frac{Zr}{a_0}\right) \quad , \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

$F_{\ell|m_e|}(\cos\theta)$ polynomia in $\cos\theta$ depending on ℓ & $|m_e|$

$G_{n\ell}\left(\frac{Zr}{a_0}\right)$ " " $\frac{Zr}{a_0}$ " " n & ℓ

a_0 radius of first orbit of Bohr

$$E_n = \frac{-\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \quad \text{w/} \quad n = \ell+1, \ell+2, \ell+3, \ldots$$

$$= -\frac{13.6\ eV}{n^2} \quad \text{(equal to Bohr's model)}$$

The total energies allowed of the particle are quantized w/ a non-zero value for the ground level.

E_n depends only on n, principal quantum number but the characteristic function $\psi(r,\theta,\phi) = R_{n\ell}(r)\,\Theta_{\ell m_e}(\theta)\,\Phi_{m_e}(\phi)$ depends on all three quantum numbers n, ℓ, m_e.

From $|m_e| = 0, 1, 2, \ldots$
$\ell = |m_e|, |m_e|+1, \ldots$
$n = \ell+1, \ell+2, \ldots$

$n = 1, 2, 3, \ldots$ principal quantum #
$\ell = 0, 1, 2, \ldots, n-1$ azimuthal quantum #
$m_e = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$ magnetic quantum #

NOTE: Two or more $\psi(r,\theta,\phi)$ can correspond to the same energy E_n
⇒ degenerate states (same energy but different behaviors)

ANALOGY w/ planetary motion: n is analog to total energy of the motion; ℓ is the type of orbit corresponding to same energy; m_e is orientation of the orbital plane.

NOTE: For every n, there are n possible values of ℓ
For every ℓ, " " $(2\ell+1)$ possible values of m_ℓ
$\Rightarrow$ for every n, there are n^2 possible $\psi(r,\theta,\phi)$

Probability density: $\psi^*\psi = \psi^*_{n\ell m_\ell} e^{iE_n t/\hbar} \psi_{n\ell m_\ell} e^{-iE_n t/\hbar} = \psi^*_{n\ell m_\ell} \psi_{n\ell m_\ell}$

$\Rightarrow \psi^*\psi = R^*_{n\ell}\, \Theta^*_{\ell m_\ell}\, \Phi^*_{m_\ell}\, R_{n\ell}\, \Theta_{\ell m_\ell}\, \Phi_{m_\ell}$

Let's consider the **radial probability density** $P(r)$, w/ $P(r)dr$ probability of finding the e^- between r & $r+dr$.

$$P_{n\ell}(r)\,dr = R^*_{n\ell}(r)\, R_{n\ell}(r)\, 4\pi r^2 dr$$

obtained integrating $\psi^*\psi$, probability per unit volume, over volume w/in two spheres of radius r & $r+dr$.

The radial probability density have non negligible values only in narrow intervals of $r \rightarrow$ shell

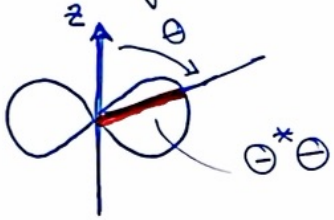
Expectation value of the radial coordinate $\bar{r}_{n\ell} = \int_0^\infty r\, P_{n\ell}(r)\,dr = \frac{n^2 a_0}{Z}\left\{1 + \frac{1}{2}\left[1 - \frac{\ell(\ell+1)}{n^2}\right]\right\}$

ie: $\bar{r}_{n\ell}$ depends most strongly on n & less so on ℓ.

Let's consider the angular probability density $\Phi_{m_\ell}(\phi)\,\Phi^*_{m_\ell}(\phi) = e^{-im_\ell\phi}\, e^{im_\ell\phi} = 1$

$\Rightarrow$ density probability $\psi^*_{n\ell m_\ell}\psi_{n\ell m_\ell}$ does not depend on ϕ
& the 3D behavior of $\psi^*\psi$ is completely determined by the product of $R^*_{n\ell}(r)\,R_{n\ell}(r) = P_{n\ell}(r)/4\pi r^2$
and $\Theta^*_{\ell m_\ell}(\theta)\,\Theta_{\ell m_\ell}(\theta)$.

The shape of $\Theta^*_{l m_e}(\theta)\,\Theta_{l m_e}(\theta)$ is presented in terms of polar diagrams: the origin of the diagram is at $r=0$; the diagram represents the directional dependence of $\psi^*\psi$ rotating the diagram around the z axis by 360° for angle ϕ.



To calculate the average probability density functions for the states corresponding to a given energy, one needs to sum & average the probability density functions of all states @ the same energy

Ex: $E_2 \longrightarrow \overline{\psi^*\psi} = \frac{1}{4}\left[\psi^*_{200}\psi_{200} + \psi^*_{21-1}\psi_{21-1} + \psi^*_{210}\psi_{210} + \psi^*_{211}\psi_{211}\right]$

When the behavior of the atom is cause by a potential that is spherical symmetric, as the Coulomb potential, no property of the atom can present preferable directions. However, if the atom is placed in an external electric or magnetic field, the spherical symmetry is destroyed.

→ figure

n	l	m_e		characteristic functions
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	2s	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	2p	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\theta$
2	1	±1	2p	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi}$
3	0	0	3s	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	3p	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\theta$
3	1	±1	3p	$\psi_{31\pm1} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\theta\, e^{\pm i\phi}$

$3\quad 2\quad 0\quad 3d \quad \psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2}e^{-Zr/3a_0}(3\cos^2\theta - 1)$

$3\quad 2\quad \pm 1\quad 3d \quad \psi_{32\pm1} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2}e^{-Zr/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$

$3\quad 2\quad \pm 2\quad 3d \quad \psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2}e^{-Zr/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$

Orbital angular momentum

The angular momentum of a particle is $\vec{L}$, such that $\vec{L} = \vec{r}\times\vec{p}$

w/ $\vec{r}$ position vector of the particle with respect to the origin

$\vec{p}$ momentum of the particle

$L_x = yp_z - zp_y$
$L_y = zp_x - xp_z$
$L_z = xp_y - yp_x$

⇒ angular momentum operators

$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$
$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$
$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

In polar spherical coordinates

$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$
$\hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$
$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$

$L^2 = L_x^2 + L_y^2 + L_z^2$

$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

⇒ Expectation value of z component of $\vec{L}$: $\overline{L_z} = \int \psi^*_{n\ell m_\ell}\hat{L}_z\psi_{n\ell m_\ell}\,d\tau$

w/ $d\tau = r^2\sin\theta\,dr\,d\theta\,d\phi$ volume element

Expectation value of L^2: $\overline{L^2} = \int \psi^*_{n\ell m_\ell}\hat{L}^2\psi_{n\ell m_\ell}\,d\tau$

$\hat{L}_z \psi_{n\ell m_\ell} = m_\ell \hbar \psi_{n\ell m_\ell}$

$\hat{L}^2 \psi_{n\ell m_\ell} = \ell(\ell+1)\hbar^2 \psi_{n\ell m_\ell}$

$\Rightarrow \bar{L}_z = m_\ell \hbar \underbrace{\int \psi^*_{n\ell m_\ell} \psi_{n\ell m_\ell} d\tau}_{=1} \Rightarrow \bar{L}_z = m_\ell \hbar$

$\bar{L}^2 = \ell(\ell+1)\hbar^2$

Since one can demonstrate that $\overline{L_z^2} = (m_\ell \hbar)^2$

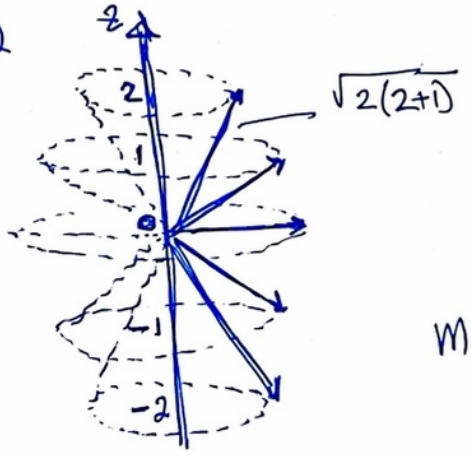
$\Rightarrow$ $L_z = m_\ell \hbar$

$L = \sqrt{\ell(\ell+1)}\,\hbar$

NOTE: Because of the uncertainty principle (Heisenberg's indeterminacy principle), it is not possible to know two components of the angular momentum. Although L_x & L_y are undefined, $\bar{L}_x = \bar{L}_y = 0$

If I consider a set of states w/ a common value of the quantum number ℓ, for each of these states, the length of the orbital angular momentum vector, in units of $\hbar$, is $\frac{L}{\hbar} = \sqrt{\ell(\ell+1)}$, while the z component is $L_z/\hbar = m_\ell$, w/ $m_\ell = -\ell, \dots, \ell$.

EX: $\ell = 2$



The angular momentum has equal probability to be w/in a cone symmetric around z, hence it has a defined value of L & L_z.

m_ℓ determines the spatial orientation of the orbital angular momentum vector of an atom w/ a single e^- $\Rightarrow$ orientation of the atom itself in space.

ℓ =	0	1	2	3
	s	p	d	f

Fig 9.1

[experiment of Stern-Gerlach + experiment of Phipps-Taylor]

The e^- has an intrinsic magnetic dipole momentum $\vec{\mu}_s$, due to the e^- having an intrinsic angular momentum $\vec{S}$, the spin. $\vec{S}$ is quantized as $\vec{L}$, w/ $S = \sqrt{s(s+1)}\,\hbar$

$S_z = m_s \hbar$

$s = \frac{1}{2}$

$m_s = -\frac{1}{2}, \frac{1}{2}$

If a magnetic dipole $\vec{\mu}$ is positioned in a magnetic field $\vec{B}$, a torque $\vec{\tau} = \vec{\mu} \times \vec{B}$ will apply on the dipole, trying to align the dipole to the magnetic field. Associated to the torque there is a potential energy of orientation $\Delta E = -\vec{\mu} \cdot \vec{B}$

For the intrinsic magnetic dipole momentum of the e^- $\vec{\mu}_s$

$$\Rightarrow \quad \Delta E = -\vec{\mu}_s \cdot \vec{B} = -\mu_{s_z} B = 2\mu_B m_s B = \pm 2 \frac{\mu_B B}{2}$$

($m_s = \pm \frac{1}{2}$)

ΔE is the separation of energy between the two components of the energy level which split due to the external magnetic field.

$\mu_{s_z} = -2\mu_B m_s$

$\mu_B = \frac{e\hbar}{2m} = 0.927 \times 10^{-23}\ Am^2$

Bohr's magneton, unit of atomic magnetic dipole.

NOTE: $\vec{\mu}_s$ & $\vec{S}$ are antiparallel.

NOTE: nella teoria di Schroedinger ottenuta con $E = \frac{p^2}{2m} + V$, the e^- spin is not predicted. But if I use $E = \sqrt{c^2 p^2 + m_0^2 c^4} + V$, the relativistic formula, one obtains Dirac's eq. & one naturally obtains that the e^- has to have an intrinsic spin $S = 1/2$: e^- spin is intimately connected w/ relativity.

Interaction spin - orbit (spin-orbit coupling)

Interaction between the e^- magnetic dipole spin $\vec{S}$ and the internal magnetic field of an atom w/ a single e^-, the latter connected to the orbital angular momentum $\vec{L}$ of the e^-. This weak interaction is partly responsible for the fine structure of the excited states of the atom w/ a single e^-. This is also present in atoms w/ multiple e^-s, but here it is stronger, because the internal magnetic field is more intense.

Let's consider the charged nucleus orbiting around the e^-
⇒ the e^- is within a ring flowing w/ a current producing a magnetic field.

The magnetic field at the position of the e^- is $\vec{B} = \frac{\mu_0}{4\pi}\frac{Ze}{r^3}\vec{r}\times\vec{v}$

If $\vec{E}$ is the electric field acting on the e^- $\vec{E} = \frac{Ze}{4\pi\epsilon_0}\frac{\vec{r}}{r^3}$,

substituting ⇒ $\boxed{\vec{B} = \epsilon_0\mu_0\vec{E}\times\vec{v} = \frac{1}{c^2}\vec{E}\times\vec{v}}$

$c = 1/\sqrt{\epsilon_0\mu_0}$

$\vec{B}$ magnetic field on the e^- when it moves w/ velocity $\vec{v}$ relative to the nucleus through the electric field $\vec{E}$ the nucleus exert on the e^-.

The potential energy of orientation of the magnetic dipole in this magnetic field is $\Delta E = -\vec{\mu}_s\cdot\vec{B}$

To go back to the reference system where the nucleus is at rest, I must divide by a factor of 2 (due to relativistic transformation of the velocities) → $\Delta E = -\frac{\vec{\mu}_s\cdot\vec{B}}{2} = \frac{\mu_B}{\hbar}\vec{S}\cdot\vec{B}$

Since $\vec{F} = -e\vec{E}$ is the force on the e^- due to the electric field

or $\vec{F} = -\frac{dV(r)}{dr}\frac{\vec{r}}{r}$ (vector defining the direction of the force)

⇒ $\vec{B} = \frac{1}{ec^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{r}\times\vec{v} = \frac{1}{c^2 em}\frac{1}{r}\frac{dV(r)}{dr}\vec{L}$

Replacing in ΔE & using $\mu_B = \frac{e\hbar}{2m}$ $\Rightarrow$ $\Delta E = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\vec{S}\cdot\vec{L}$

For H atom $\frac{1}{r}\frac{dV(r)}{dr} = \frac{1}{r}\frac{d}{dr}\left(\frac{e^2(-1)}{4\pi\epsilon_0 r}\right) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r^3}$

$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$

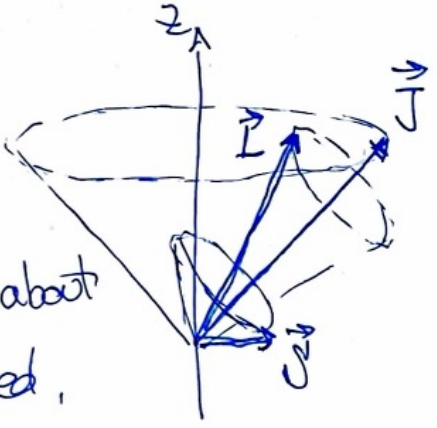
$$\Delta E = \frac{e^2}{4\pi\epsilon_0 2m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L}$$ potential energy of orientation for H

$$\Delta E = \frac{Ze^2}{4\pi\epsilon_0 2m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L}$$ for atoms w/ single $\bar{e}$

Total angular momentum: the spin-orbit interaction means that a strong internal magnetic field, whose orientation is determined by $\vec{L}$, acts on the e^-, & produces a torque on the e^- spin magnetic dipole, whose orientation is determined by $\vec{S}$. The torque does not alter $|\vec{S}|$. But the torque produces a coupling between $\vec{L}$ & $\vec{S}$ forcing them to precess w/ the direction of one depending on the direction of the other. They both precess about their sum, rather than precessing on symmetric cones about the z axis.

$\Rightarrow$ L_z & S_z don't have fixed values w/ a spin-orbit interaction

If the atom is in free space, no torque acts on $\vec{J} = \vec{L} + \vec{S}$ total angular momentum, & J_z & $|\vec{J}|$ remain fixed; $\vec{L}$ & $\vec{S}$ precess about $\vec{J}$ & their components abng $\vec{J}$ remain fixed.



$\Rightarrow$ $\boxed{J = \sqrt{j(j+1)}\,\hbar}$

$\boxed{J_z = m_j \hbar \quad , \quad m_j = -j, -j+1, \dots, \dots, j-1, j}$

$J_z = L_z + S_z$

If there is no spin-orbit interaction $\Rightarrow$ $L_z = m_\ell \hbar$, $S_z = m_s \hbar$

$\Rightarrow m_j \hbar = m_\ell \hbar + m_s \hbar \Rightarrow m_j = m_s + m_\ell \Rightarrow \boxed{(m_j)_{max} = \ell + \frac{1}{2}}$

$\Rightarrow j = \ell + \frac{1}{2}, \ell - \frac{1}{2}, \ell - \frac{3}{2}, \ell - \frac{5}{2} \dots$ which applies also w/ spin-orbit interaction

Since $|\vec{L} + \vec{S}| \geq \big||\vec{L}| - |\vec{S}|\big| \Rightarrow |\vec{J}| \geq \big||\vec{L}| - |\vec{S}|\big|$

$\Rightarrow \sqrt{j(j+1)}\,\hbar \geq \big|\sqrt{\ell(\ell+1)}\,\hbar - \sqrt{s(s+1)}\,\hbar\big|$

Since $s = \frac{1}{2}$ $\Rightarrow$ $\boxed{j = \ell + \frac{1}{2}, \ell - \frac{1}{2} \text{ if } \ell \neq 0 \quad ; \quad j = \frac{1}{2} \text{ if } \ell = 0}$

EX: $\ell = 2, s = \frac{1}{2} \Rightarrow j = \frac{5}{2}$, $m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$

$j = \frac{3}{2}$, $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

Spin-orbit interaction energy & H energy levels:

$$\Delta E = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \vec{S} \cdot \vec{L}$$

$\vec{J} \cdot \vec{J} = \vec{L} \cdot \vec{L} + \vec{S} \cdot \vec{S} + 2\vec{S} \cdot \vec{L} \rightarrow \vec{S} \cdot \vec{L} = \frac{\vec{J} \cdot \vec{J} - \vec{L} \cdot \vec{L} - \vec{S} \cdot \vec{S}}{2} =$

$= (J^2 - L^2 - S^2)/2$

$= \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$

$\Rightarrow \Delta E = \frac{\hbar^2}{4m^2c^2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right] \frac{1}{r} \frac{dV(r)}{dr}$

$$\Rightarrow \boxed{\Delta E = \begin{cases} a(n,\ell)\ \frac{\ell}{2} & \text{if } j = \ell + \frac{1}{2} \\ -a(n,\ell)\ \frac{\ell+1}{2} & \text{if } j = \ell - \frac{1}{2} \end{cases} \quad \text{w/} \quad a(n,\ell) = \frac{\hbar^2}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}}$$

Thomas' constant

For circular orbits $r_n = \frac{a_0 n^2}{Z}$ $\Rightarrow$ $\frac{1}{r}\frac{dV(r)}{dr} = \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r^3} = \frac{Z^4 e^2}{4\pi\epsilon_0}\frac{1}{a_0^3 n^6}$

$\Rightarrow$ the spin-orbit interaction
- increases for larger Z
- decreases w/ increasing n

The expectation value of the quantity ΔE is the spin-orbit energy

$$\overline{\Delta E} = \frac{\hbar^2}{4m^2c^2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right] \overline{\frac{1}{r}\frac{dV(r)}{dr}}$$

Without spin-orbit interaction $\Rightarrow$ Bohr's model energy levels.
With spin-orbit interaction $\Rightarrow$ energy shifted upward if $\vec{L} \parallel \vec{S}$, ie $j = \ell + \frac{1}{2}$, & shifted downward if $\vec{L}$ anti$\parallel \vec{S}$ ie; $j = \ell - \frac{1}{2}$. If $\ell = 0 \rightarrow j = \frac{1}{2} \rightarrow$ no shift.

From Dirac's theory $\Rightarrow$ $$\boxed{E = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]}$$

w/ $\mu = \frac{mM}{m+M}$ reduced mass of e^-

α fine structure constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \simeq \frac{1}{137}$$

The fine structure caused by the spin-orbit interaction, is independent of m_j; if an external magnetic field is not present.

Most energy levels depend on n & j. Since for each j, there are 2 values of ℓ → most energy levels are doublet.

Ex: H w/ $n=2$ $j=\frac{1}{2}$

This level is made of two levels $\ell=0$, $\ell=1$ that do not coincide perfectly.

$n=2\ \ell=0\ j=1/2$ ——— $2S_{1/2}$ } Lamb shift $2S_{1/2}$ is metastable
$n=2\ \ell=1\ j=1/2$ ——— $2P_{1/2}$ } $2P_{1/2}$ de-excites directly on the ground level.

Those in $2S_{1/2}$ do not de-excite spontaneously because of the selection rule $\Delta\ell=\pm1$

fine structure $\Delta E = 4.372\times10^{-6}$ eV

$$\overline{\frac{1}{r}\frac{dV(r)}{dr}} = \frac{Ze^2}{4\pi\epsilon_0}\overline{\left(\frac{1}{r^3}\right)} \quad \text{w/} \quad \overline{\frac{1}{r^3}} = \int \psi^*_{n\ell m_\ell}\frac{1}{r^3}\psi_{n\ell m_\ell}\,d\tau = \frac{Z^3}{n^3 a_0^3\,\ell(\ell+\frac{1}{2})(\ell+1)}$$

for single e⁻ atoms

$$\Rightarrow \overline{\Delta E} = \frac{\hbar^2}{4m^2c^2}\left[j(j+1)-\ell(\ell+1)-s(s+1)\right]\frac{e^2 Z}{4\pi\epsilon_0}\frac{Z^3}{n^3 a_0^3\,\ell(\ell+\frac{1}{2})(\ell+1)}$$

Using $a_0 = \frac{\hbar^2 4\pi\epsilon_0}{\mu e^2}$ $\quad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$ $\quad |E_n| = \frac{\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$, $m=\mu$

$$\Rightarrow \boxed{\Delta E = \frac{|E_n|\,Z^2\left[j(j+1)-\ell(\ell+1)-s(s+1)\right]\alpha^2}{2n\,\ell(\ell+1)(\ell+\frac{1}{2})}}$$

$$E = E_n + \Delta E$$

$$\Delta E = -\vec{\mu}_s\cdot\vec{B}_{loc}$$

Ex: H level $2p$: $n=2$, $\ell=1$ $\quad \Delta E = \frac{\alpha^2 |E_n|}{12}$

$\Rightarrow$ $2p$ ——— $2p_{3/2}$: $+\Delta E$ if $\vec{L} \parallel \vec{S}$ } 4.5×10^{-5} eV

$\Delta E = \frac{\alpha^2 |E_n|}{6}$ ——— $2p_{1/2}$: $-\Delta E$ if $\vec{L} \nparallel \vec{S}$ }

Since 4.5×10^{-5} eV $= 2 \vec{\mu}_s \cdot \vec{B}_{Bc} = 2\Delta E = 2\mu_B \cdot B_{Bc}$

& $\mu_B = 0{,}927 \times 10^{-23}$ Am^2

$\Rightarrow$ $B_{Bc} \simeq 0{,}4$ T this is why I do not observe any fine structure in H.

Selection rules (for transitions) : $\Delta \ell = \pm 1$

$\Delta j = 0, \pm 1$

$n \ell j \longleftrightarrow 2p_{1/2}$

ATOMS w/ MULTIPLE e^-s

A contains a nucleus w/ charge $+Ze$ surrounded by Z e^-s.
Each e^- feels attractive Coulomb force by the nucleus & repulsive Coulomb force by $(Z-1)$ e^-s

Exclusion principle – weak condition: in an atom w/ multiple e^-s, there are never two e^-s in the same quantum state.

→ **strong condition:** a system w/ several e^-s must be described by a total characteristic function that is anti-symmetric,

↳ eg: $\psi_A = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)\right]$ for two e^-s

particle 1 in state α ; particle 2 in state β ; $\alpha \equiv n, l, m_e, m_s$

Fermions, particles w/ spin half integer

NOTE: Switching $1 \to 2$, $2 \to 1$ $\quad \psi_A \to -\psi_A$

But expectation values do not change, as $\propto$ to $\psi_A^* \psi_A$.

He atom: Let's consider a pair of non-interacting e^-s

$\Rightarrow \psi_A = \frac{1}{\sqrt{2}}\left[\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)\right]$

Let's write ψ_A = (spatial characteristic function) (spin c.f.)
depending on $n l m_e$ depending on m_s

To have ψ_A antisymmetric, I can have s.c.f. symmetric & spin c.f. anti-symmetric, or viceversa.

$\Rightarrow$ spatial charact. function $\frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_b(1)\psi_a(2)\right]$ sym.

$\frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)\right]$ anti-sym.

w/ $a, b = n l m_e$

The spin variable is not continuum, but discrete, quantized

$S_z = \pm \frac{1}{2}\hbar$

$\Rightarrow$ spin c.f. antisymmetric : $\frac{1}{\sqrt{2}}\left[\left(\frac{1}{2},-\frac{1}{2}\right)-\left(-\frac{1}{2},\frac{1}{2}\right)\right]$ singulet

spin c.f. symmetric : $\left(\frac{1}{2},\frac{1}{2}\right)$

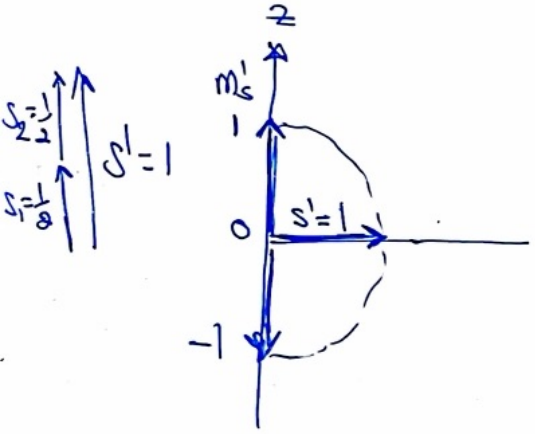
$\frac{1}{\sqrt{2}}\left[\left(\frac{1}{2},-\frac{1}{2}\right)+\left(-\frac{1}{2},\frac{1}{2}\right)\right]$ triplet

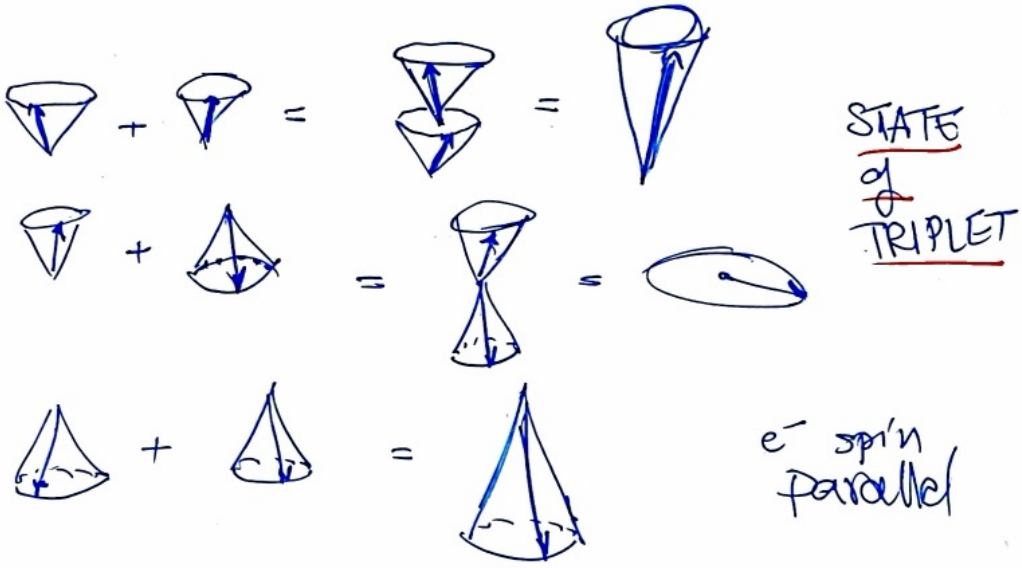
$\left(-\frac{1}{2},-\frac{1}{2}\right)$

NOTE: $\left(\frac{1}{2},-\frac{1}{2}\right)$ means
$m_s = \frac{1}{2}$ for e^-_1
$m_s = -\frac{1}{2}$ for e^-_2

IF $\vec{S}' = \vec{S}_1 + \vec{S}_2$ total spin angular momentum

$S' = \sqrt{s'(s'+1)}\,\hbar \qquad S'_z = m'_s \hbar$

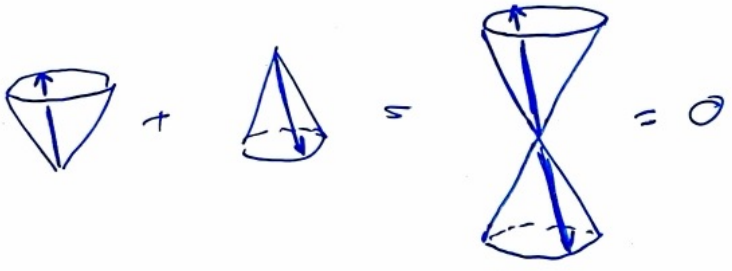




STATE of TRIPLET

e⁻ spin parallel

$\uparrow\downarrow$ $s'=0$, $m'_s=0$



STATE OF SINGULET

e⁻ spin anti-parallel

$$m'_s = -s', \ldots, s' \qquad s'=0,1$$

IF spins parallels & symmetric spin c.f. (triplet)
⇒ spatial c.f. is anti symmetric

In the case $\psi_a(1) \simeq \psi_a(2)$ ⇒ $\psi_a(1)\psi_b(2) \simeq \psi_b(1)\psi_a(2)$

similar spatial coordinates: $\psi_b(1) \simeq \psi_b(2)$

⇒ probability density ≃ 0 when e^-s are in a triplet state w/ similar spatial coordinates (when they are close)

the triplet state acts as repulsive, consequence of anti-symmetric spatial c.f.

Vicerversa IF spins anti-parallels & anti-symmetric spin c.f. (singulet) ⇒ spatial c.f. is symmetric,
the density probability is $2\psi_b^*(1)\psi_a^*(2)\psi_b(1)\psi_a(2)$
when e^-s are close together

⇒ e^-s in singulet state act as they attract one to the other.

⇒ e^-s move & behave as under the influence of a force whose sign depends on the relative orientation of the spins : exchange force

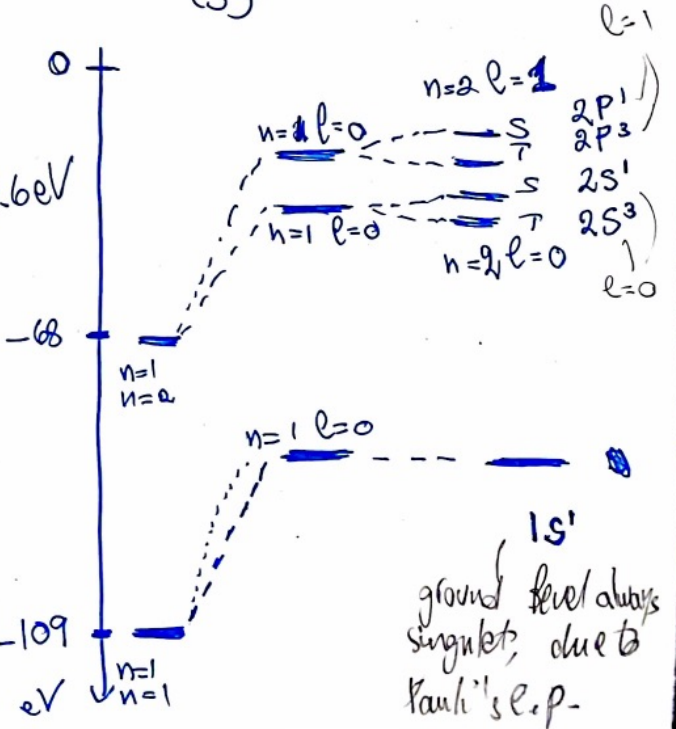
singulet (S) TRIPLET (T)

$$E_n = -13.6\,eV\,\frac{Z^2}{n^2}$$

Ground state $E_1 = E_{n=1} + E_{n=1} = -(4+4)\,13.6\,eV$ ($Z=2$)
$= -109\,eV$

($n=1$, $n=1$)

1st excited level $E_2 = E_{n=1} + E_{n=2} = -68\,eV$



ground level always singulet, due to Pauli's e.p.

Considering the repulsive Coulomb force between the two e^-s

$$\overline{V(1,2)} = \int \psi_a^*(1)\psi_b^*(2)\,V(1,2)\,\psi_a(1)\psi_b(2)\,d\tau$$

w/ $V(1,2) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}$ r_{12} distance between the two e^-s

$\Rightarrow \overline{V(1,2)} = \left(\frac{1}{r_{12}}\right)\frac{e^2}{4\pi\epsilon_0} \simeq 27\,eV$

Analogously for $n=2$

$\Rightarrow$ I obtain the values are the 2nd column; the levels are @ higher energy because the repulsive potential is positive

The values on the 3rd column show the effect of the exchange force; the ground level is a singulet, due to exclusion principle of Pauli.

Hartree's Theory:

Atom is treated considering the Coulomb interaction of the Z e^-s & the nucleus of charge Ze, and the Coulomb interaction between each e^- & the other $(Z-1)$ e^-s. I consider each e^- moving independently in a net potential $V(r)$, spherically symmetric, w/ r distance e^--nucleus. $V(r)$ is the sum of the spherical Coulomb attractive potential due to the nucleus & the " " repulsive " representing the average effect of the repulsive Coulomb interaction between the e^- & the other $Z-1$ e^-s.

Near the nucleus, $V(r) \simeq$ Coulomb potential caused by the nucleus

Away from the nucleus $V(r) \simeq$ " repulsive potential of a single e^- & nucleus $+Ze$ is shielded by $(Z-1)$ e^-s

$\Rightarrow$ time-independent Schroedinger's eq. can be separated in Z time-independent Schroedinger's eqs.; the total energy of the atom is the sum of Z energies E_i & $\psi_{Total} = \prod_{i=1}^{Z} \psi_i(r,\theta,\phi)$

... solving (numerically & w/ subsequent improvements of the net potential $V(r)$)

$$\psi_{n\ell m_\ell m_s}(r,\theta,\phi) = R_{n\ell}(r)\,\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\phi)\,(m_s)$$

$R_{n\ell}(r)$: different because $V(r)$ is different from atom w/ single e^-.

$\Theta_{\ell m_\ell}(\theta)\,\Phi_{m_\ell}(\phi)$: exactly the same for the atom w/ a single e^-

For each ℓ, there are $2\ell+1$ values of m_ℓ
" " m_ℓ, " " 2 " " m_s

$\Rightarrow$ $2(2\ell+1)\,P_{n\ell}(r)$ radial probability density for the quantum state n,ℓ multiplied by the # of e^-s that Pauli's exclusion principle allows in that state. Summing these over all state $\rightarrow$ $P(r)$ total radial probability density

$$P_{n\ell}(r) = 4\pi r^2 R^*_{n\ell}(r) R_{n\ell}(r)\,dr$$

$$\underline{V(r)} = -\frac{Z_i(r)\,e^2}{4\pi\epsilon_0 r} \quad \text{w/} \quad Z_i(r) \to Z \text{ for } r\to 0,\quad Z_i(r)\to 1 \text{ for } r\to\infty$$

$\underline{P_{n\ell}(r)}$: for all e^-s in states w/ the same n, $P_{n\ell}(r)$ are large only around similar radii $\rightarrow$ these e^-s belong to the same shell & $Z_i(r)$ is well defined w/in the shell.

$$\Rightarrow V_n(r) \simeq -\frac{Z_n e^2}{4\pi\epsilon_0 r} \quad \text{w/} \quad Z_n = Z_i(r_n)$$

r_n: average radius of the shell.

Z_n: effective Z of the shell

energy of atomic e^-s w/ n quantum #

$$E_n \simeq -\left(\frac{Z_n}{n}\right)^2 13.6\ \text{eV}$$

total energy of e^-s in the same shell (<20% errors)

NOTE: $Z_1 \simeq Z - 2$ for large multi-e^-s atoms
$Z_n \simeq n$ if n is the outer most populated shell.

1. In atoms w/ multiple e^-s, the inner most shells w/ small n have very small radii (they feel more the attraction of the nucleus) $r_1 \simeq \frac{r_H}{Z-2}$ r_H H radius
2. $E_1 \simeq (Z-2)^2 E_H$
3. For outer most shells, e^-s are almost entirely shielded so similar attraction of that felt by an e^- in the H nucleus. $r_n \simeq n a_0$
4. Total energy of the e^- in the outer most populated shell is the same as ground state energy of e^- in H
$E \simeq -13.6\,eV$, since $Z_n \simeq n$
5. Total energy of an e^- becomes rapidly less negative w/ increasing n if n is small, & less rapidly w/ n large.

For atoms w/ multiple e^-s, the total energy depends both on n & ℓ (only n for atoms w/ single e^-), but do not depend on m_ℓ & m_s, which determine only orientations of the orbit & spin. the spatial

$E_{n\ell}$ shell $\leftrightarrow n$ (n=1 2 3 4 5 6 7 = K, L, M, N, O, P, Q)
subshell $\leftrightarrow \ell$ (ℓ=0 1 2 3 = s p d f)

e^-s in the same subshell have the same quantum #s n & ℓ, same total energy, & same $P_{n\ell}(r)$.

$E_{n\ell}$ depends on ℓ because e^-s are not in a pure Coulomb potential w/ dependence $\propto \frac{1}{r}$.

GROUND STATES of atoms w/ multiple e⁻s & PERIODIC TABLE

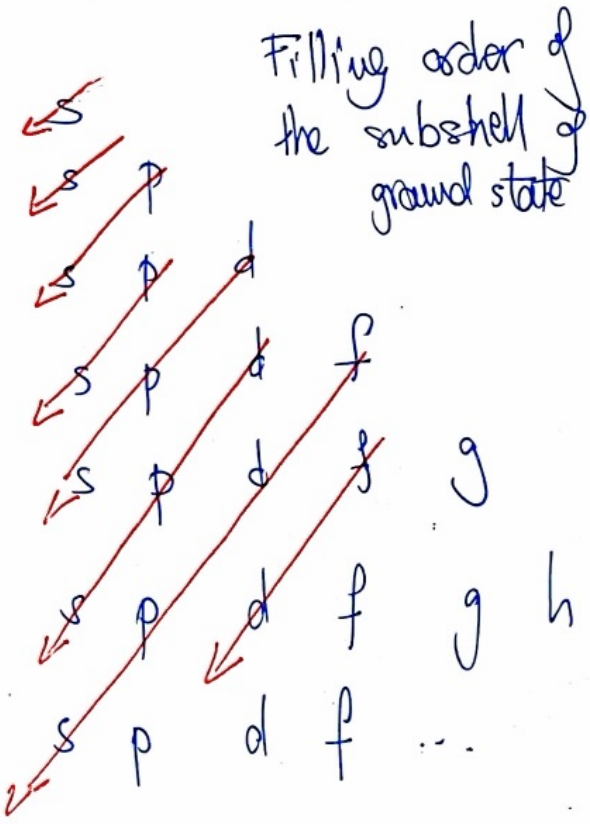
The elements of the periodic table & its interpretation is based on the information relative to the ~~order of filling~~ of successive subshells.

With growing n, in the form E_{nl}, the dependence on l can be larger than the n dependence, eg: the 4s subshell has more negative energy than 3d.

n,l	subshell	capacity of the subshell $(2(2l+1))$
1,0	1s	2
2,0	2s	2
2,1	2p	6
3,0	3s	2
3,1	3p	6
4,0	4s	2
3,2	3d	10
4,1	4p	6
5,0	5s	2
4,2	4d	10
5,1	5p	6
6,0	6s	2
4,3	4f	14
5,2	5d	10
6,1	6p	6
7,0	7s	2
5,3	5f	14
6,2	6d	10

↓ increase of energy (energy less negative)

↑ spectroscopic notation



Filling order of the subshell of ground state

Atom configuration: $nl^{\#\text{ of e}^-\text{s in subshell}}$

H $1s^1$
He $1s^2$ *
Li $1s^2\,2s^1$
Be $1s^2\,2s^2$
B $1s^2\,2s^2\,2p^1$
C $1s^2\,2s^2\,2p^2$
N
O
F
Ne $1s^2\,2s^2\,2p^6$ *

* subshell complete → noble gas very stable configuration inert

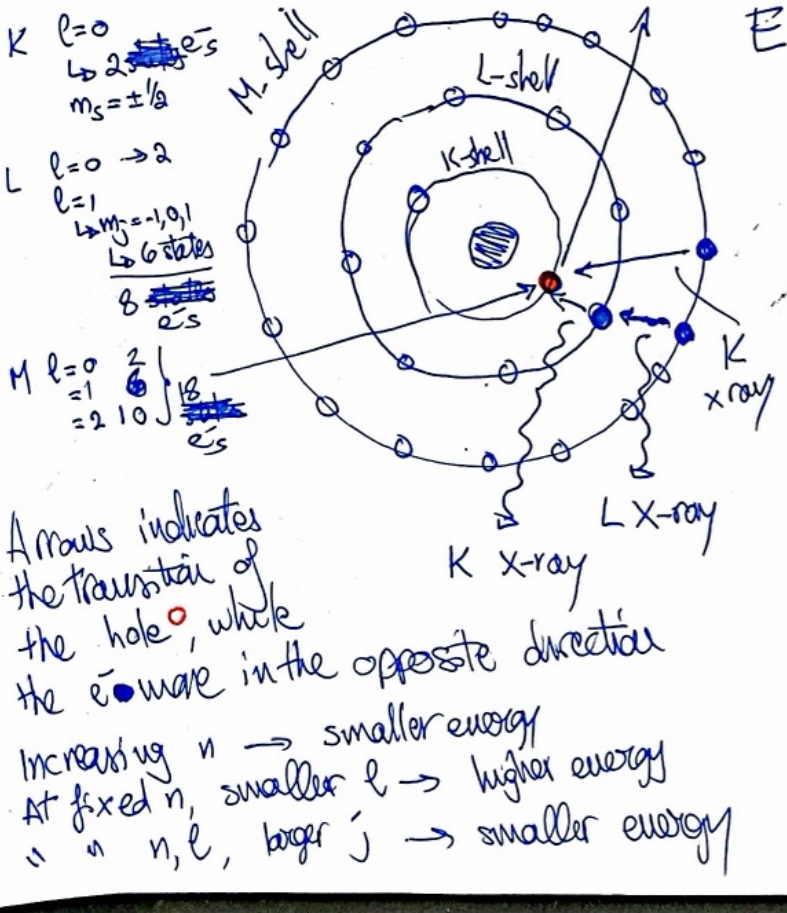
Alkali elements (H, Li, Na, ..) : single outermost e^- occupies a new shell → e^- weakly bound to atom
w/ low excitation / ionization energies
→ element extremely reactive (chemically)

Ionization energy : modulus of total energy of the e^- in the subshell w/ highest energy occupied.

Selection rules : Δn = free
$\Delta \ell = \pm 1$
$\Delta m = -1, 0, +1$
$\Delta s = 0$
$\Delta j = 0, \pm 1$ (spin orbit interaction (fine structure))

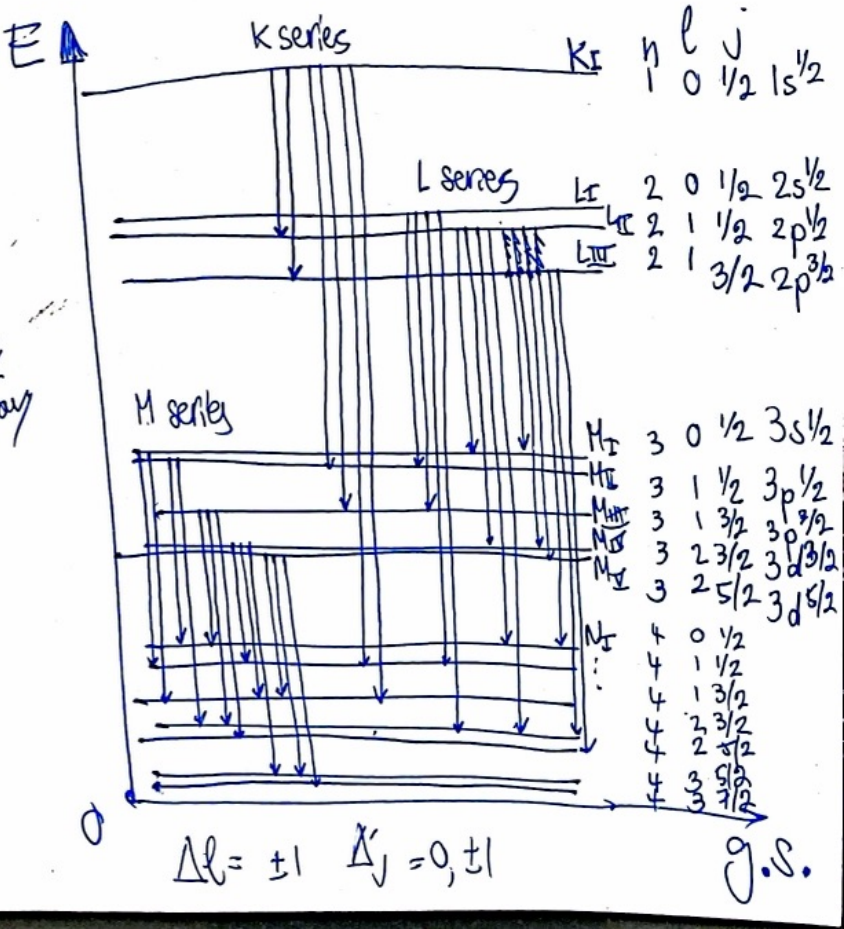
high-energy ($\sim 10^4$ eV)

X-ray spectral lines : in an X-ray tube, e^-s are bombarding a material. Occasionally, the e^-s will get close to an e^- in an internal subshell of the atoms in the material; through Coulomb interaction between the projectile e^- and the atomic e^-, the latter is removed, expelled from atom.



Arrows indicates the transition of the hole ○, while the e^-● move in the opposite direction

Increasing n → smaller energy
At fixed n, smaller ℓ → higher energy
" " n, ℓ, larger j → smaller energy



If I disregard the fine structure (ie, I don't consider the l-j coupling) → $K_\alpha, K_\beta, K_\gamma$ e^- ending on K shell from L, M, N respectively
L_α, L_β e^- " " L shell from M, N "
$M_\alpha, \ldots$ " " M shell from N shell

NOTE: j dependence of energy, strong for internal subshells in atoms w/ large Z, is caused by increasing spin-orbit interaction.

$E = h\nu = E_K - E_L$ in the X-ray region.

Sometimes, if a K-shell e^- is expelled, an e^- from the L shell can fill the hole, emitting photon w/ $h\nu = E_K - E_L$. This photon could be absorbed by another e^- in the L shell, expelled
⇒ Auger e^- w/ kinetic energy $h\nu - E_L = (E_K - E_L) - E_L$

⇒ Kinetic energy of Auger e^- $= E_K - 2E_L$

ATOMS W/ SEVERAL e^-s, OPTICAL EXCITATIONS

In the Hartree approximation, each e^- is treated as it moves independently in a potential that is spherically symmetric describing the average Coulomb interaction of the e^- w/ the nucleus & the other e^-s.
There are also other smaller interactions felt by the e^-s:
- coupling between the orbital angular momenta of the e^-s
- " " spin " " " " "
- spin-orbital angular momenta interactions due to the internal magnetic field
- external magnetic field → Zeeman effect.

optical line when the e^-, in an external subshell was excited to a small higher energy.

Alkali elements ground state has subshells fully occupied w/ external occupied shell w/ one e^- being s subshell,

eg, ^1H $1s^1$
^3Li $2s^1$
^{11}Na $3s^1$

The excited states can be completely described by the single e^- optically active, ignoring the rest of the atom.
The total energy of the atom is a constant (total energy of the central body) + total energy of the optically active e^-
$\Leftrightarrow$ total energy of the optically active e^- (w/ constant set to zero).
w/ fixed n, the e^- w/ smaller ℓ has more negative energy (as it spends more time close to the nucleus); the subshells w/ medium-large radii see the nucleus $+Ze$ almost completely shielded by the $-(Z-1)e$ negative e^- in the inner subshells $\Rightarrow$ energy levels of the optically active e^- $\approx$ H energy levels.

Fine structure: except the levels w/ $\ell=0$ (s), all others are doublet, because of the spin-orbit interaction

$\Rightarrow$ n, ℓ, j, m_j w/ $s = 1/2$

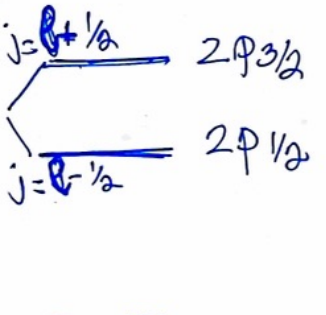
$\begin{cases} j = \ell - \frac{1}{2}, \ell + \frac{1}{2} & \text{if } \ell \neq 0 \rightarrow \text{DOUBLET} \\ j = \frac{1}{2} & \text{if } \ell = 0 \rightarrow \Delta E = 0 \end{cases}$

$j+\frac{1}{2}$ $\vec{L} \parallel \vec{S}$
$j-\frac{1}{2}$ $\vec{L} \nparallel \vec{S}$

$m_j = -j, -j+1, \dots, j-1, j$

selection rules
$\Delta \ell = \pm 1$
$\Delta j = 0, \pm 1$

eg: ^3Li



NOTE: If alkali element is NOT affected by external field, this is the only weak interaction acting on the optically active e^-. This is not the case for non-alkali elements.

Atoms w/ several optically active e^-s, ie there are several e^-s in the outermost sub-shell (not filled).

Hartree approximation ⇒ energy of each optically active e^- independently moving is E_{nl}; total energy is the total energy of the core (constant) plus sum of E_{nl} for each optically active e^-.

Two corrections:

1) residual Coulomb interaction: V(r) from Hartree only describe the mean effect of the Coulomb interaction between an e^- & the other optically active e^-s. No longer spherically sym

2) Spin-orbit interaction: coupling of spin angular momentum of each e^- w/ its own orbital angular momentum.

total spin angular momentum of optically active e^-s

$$\vec{S}' = \vec{S}_1 + \vec{S}_2 + \dots$$

$$S' = \sqrt{s'(s'+1)}\,\hbar$$

$$\vec{L}' = \vec{L}_1 + \dots + \vec{L}_i + \dots \qquad L' = \sqrt{l'(l'+1)}\,\hbar$$

1) ⇒ exchange force

↳ triplet states $[S'=1]$ $S' = \sqrt{s'(s'+1)}\,\hbar$

singulete state $S'=0$

1) & 2) produce opposite effects, but for atoms w/ Z small-medium, 1) is much large than 2)

⇒ $\vec{S}_i$ couple to form $\vec{S}'$ total spin angular momentum

$\vec{L}_i$ " " " $\vec{L}'$

Energy of atom depends on S' & L' ⇒ quantum states w/ same configuration but different S' & L' have different energies.

LS Coupling

Then, I consider $\vec{S}'$-$\vec{L}'$ coupling → $\vec{J}' = \vec{L}' + \vec{S}'$ $\quad J' = \sqrt{j'(j'+1)}\,\hbar$ = constant

↳ the energy of the atom also depends on J'!

IF Z large → spin-orbit interaction is larger

⇒ First I treat $\vec{J}_i = \vec{S}_i + \vec{L}_i$ of single electrons

↳ then the coupling of the individual $\vec{J}_i$

⇒ JJ coupling

LS coupling (or Russell-Saunder's coupling):

$J'_z = m'_j \hbar$ $\quad m'_j = -j', -j'+1, \dots, j'-1, j'$

Case w/ 2 e^-s: $s_1 = s_2 = \frac{1}{2}$ ⇒ $\boxed{S' = |s_1 - s_2|, |s_1 - s_2|+1, \dots, s_1 + s_2}$

↳ $S' = 0, 1$

W/o external magnetic field, atom energy does not depend on m_j

→ levels are $2j'+1$ degenerate.

$$\boxed{\begin{aligned} l' &= |l_1 - l_2|, |l_1 - l_2|+1, \dots, l_1 + l_2 \\ j' &= |s' - l'|, |s' - l'|+1, \dots, s' + l' \end{aligned}}$$

EX: $3d\,4p\ {}^3F_2$

configuration; quantum # $s'\,l'\,j'$

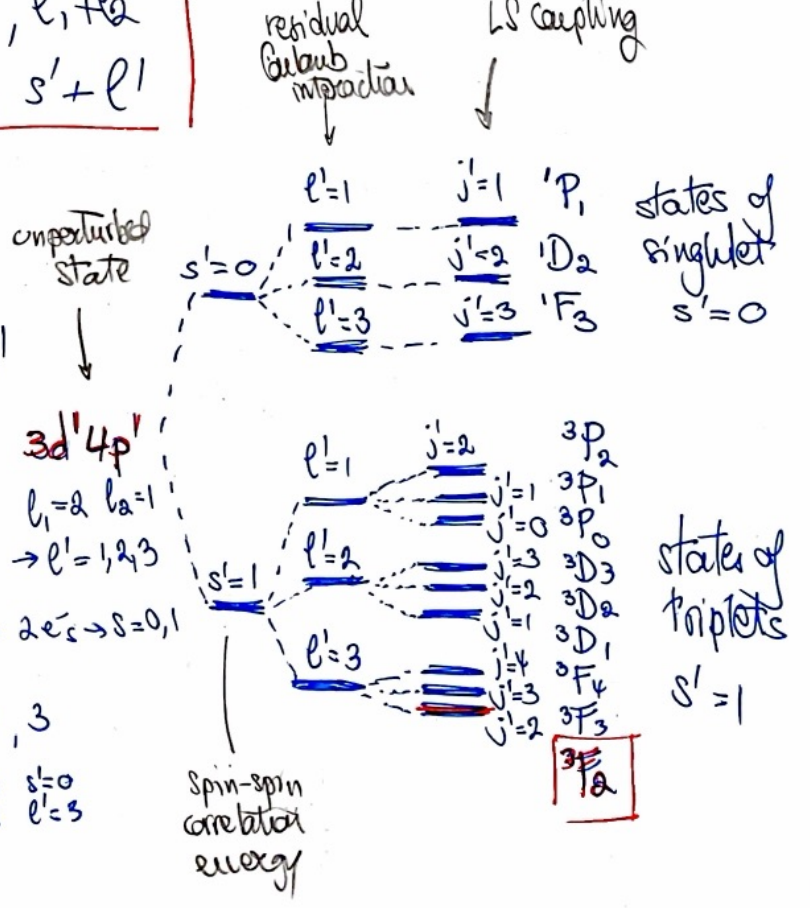
multiplet: $2s'+1\ l'_{j'}$

$2s'+1 = 3$ ↳ $\boxed{s'=1}$

* $s'=0, l'=1 \rightarrow j' = 0, 1, 2$

$s'=1, l'=2 \rightarrow j' = 1, 2, 3$

$s'=1, l'=3 \rightarrow j' = 2, 3, 4$



* $j' = 1, 2, 3$

$s'=0$ $s'=0$ $s'=0$

$l'=1$ $l'=2$ $l'=3$

If the energy of spin-orbit interaction is

$$\overline{\Delta E} = K\left[j'(j'+1) - \ell'(\ell'+1) - s'(s'+1)\right]$$

w/ K no longer proportional to $\overline{\frac{1}{r}\frac{dV(r)}{dr}}$

because $V(r)$ is more complicated.

However K only depends on j', ie K is the same for states w/ same s' & ℓ'.

$$\mathcal{E} := \overline{\Delta E}_{s',\ell',j'+1} - \overline{\Delta E}_{s',\ell',j'} = K\left[(j'+1)(j'+2) - j'(j'+1)\right]$$

level w/ larger energy — within same multiplet — level w/ lower energy

$\mathcal{E} = 2K(j'+1)$: the energy of separation between adjacent levels in a multiplet is proportional to j' of the energy level w/ larger energy

Selection rules for LS coupling:

1) transitions can occur only between states w/ different n, ℓ of a single e^-, ie: two or more e^-s cannot simultaneously make transitions between subshells.

2) $\Delta\ell = \pm 1$

3) $\Delta s' = 0$ $\quad \Delta\ell' = 0, \pm 1$ $\quad \Delta j' = 0, \pm 1$ (but not from $j'=0$ to $j'=0$)

↓

transitions between singlet ($s'=0$) & triplet ($s'=1$) states are forbidden.

Zeeman effect: when an atom is exposed to an external magnetic field, the energy levels split.

For weak $\vec{B}$, the separation is $\propto B$, & smaller than the split due to the fine structure (which is $\propto$ to internal magnetic field). Zeeman effect indicates that the energy levels of the atom split in different components due to the external magnetic field.

Zeeman effect
- normal (explained classically)
- ~~external~~ anomalous

Except in $^1S_0$, atom has total magnetic dipole momentum $\vec{\mu}$ due to $\vec{\mu}_\ell$ (orbital magnetic dipole) & $\vec{\mu}_s$ (spin) of the optically active e^-s (the other e^-s are in subshells filled) w/o a net magnetic dipole momentum.

Under the external magnetic field $\vec{B}_{ex}$ $\Rightarrow$ $\Delta E = -\vec{\mu}\cdot\vec{B}_{ex}$ potential energy of orientation

$\Rightarrow$ Each energy level of the atom splits in multiple components corresponding to the values of ΔE associated to the different orientations of $\vec{\mu}$ wrt the direction of $\vec{B}_{ex}$.

discrete

quantized

Since $\vec{\mu}_\ell = -\mu_B \vec{L}/\hbar$ $\Rightarrow$ $\vec{\mu} = -\frac{\mu_B}{\hbar}\sum_i \vec{L}_i - \frac{2\mu_B}{\hbar}\sum_i \vec{S}_i =$

$\vec{\mu}_s = -2\mu_B \vec{S}/\hbar$ $= -\frac{\mu_B}{\hbar}\left[\sum_i \vec{L}_i + 2\sum_i \vec{S}_i\right]$

If atom is such that LS coupling applies $\Rightarrow$ $\vec{\mu} = -\frac{\mu_B}{\hbar}\left[\vec{L}' + 2\vec{S}'\right]$

⇒ the total magnetic dipole momentum $\vec{\mu}$ of the atom is not anti-parallel wrt its total angular momentum $\vec{J}' = \vec{L}' + \vec{S}'$ ⇒ complex behaviour of $\vec{\mu}$.

IF $\boxed{\vec{S}' = 0}$, ie: the spins of the e^-s couples together canceling each other out, optically active

⇒ $\vec{\mu}$ anti-parallel to $\vec{J}'$ ⇒ normal Zeeman effect.

Otherwise, generally $\vec{S}' \neq 0$ → anomalous Zeeman effect.

See Fig: From $\vec{J}' = \vec{L}' + \vec{S}'$, the three vectors always lay in the same common plane, plane that precesses about $\vec{J}'$ due to the Larmor precession of $\vec{S}'$ in the internal magnetic field associated w/ $\vec{L}'$ (due to spin-orbit interaction).

From $\vec{\mu} = -\frac{\mu_B}{\hbar}\left[\vec{L}' + 2\vec{S}'\right]$, also $\vec{\mu}$ lays in the same precessing plane, but it is not generally anti-parallel to $\vec{J}'$ ⇒ $\vec{\mu}$ precesses about $\vec{J}'$ w/ a precessional frequency proportional to the internal magnetic field of the atom ($\omega = \mu_B \vec{B}/\hbar$ Larmor precessional frequency).

IF $\vec{B}_{ex}$ is applied → tendency of $\vec{\mu}$ to precess about $\vec{B}_{ex}$, w/ precessional frequency proportional to $\vec{B}_{ex}$. If $\vec{B}_{ex}$ weak compared to $\vec{B}$ ⇒ $\vec{\mu}$ precession about $\vec{B}_{ex}$ is slow compared to precession about $\vec{J}'$

since $|\vec{B}| \simeq 1$ Tesla → $|\vec{B}_{ex}| < 1$ Tesla

I need to evaluate $-\vec{\mu}\cdot\vec{B}_{ex} = -\mu_{\vec{B}} B_{ex}$

w/ $\mu_{\vec{B}}$ component of $\vec{\mu}$ along $\vec{B}_{ex}$ direction

Since $\vec{\mu}$ precesses about $\vec{J}'$ more rapidly than about $\vec{B}_{ex}$,
⇒ I calculate $\mu_{\vec{B}}$ finding first $\mu_{\vec{J}'}$, mean component of $\vec{\mu}$ along the $\vec{J}'$ direction.
$\mu_{\vec{J}'}$ is obtained multiplying μ times cosine angle between $\vec{\mu}$ e $\vec{J}'$; I obtain $\mu_{\vec{B}}$ multiplying $\mu_{\vec{J}'}$ times cosine of angle between $\vec{J}'$ e $\vec{B}_{ex}$.

$$\Rightarrow \mu_{\vec{J}'} = \mu \frac{\vec{\mu}\cdot\vec{J}'}{\mu J'} = -\frac{\mu_B}{\hbar}\frac{(\vec{L}' + 2\vec{S}')\cdot(\vec{L}' + \vec{S}')}{J'}$$

$$\mu_{\vec{B}} = \mu_{\vec{J}'}\frac{\vec{J}'\cdot\vec{B}_{ex}}{J' B_{ex}} = \mu_{\vec{J}'}\frac{J_z'}{J'} = -\frac{\mu_B}{\hbar}\frac{(\vec{L}'+2\vec{S}')\cdot(\vec{L}'+\vec{S}')J_z'}{J'^2}$$

$$\Rightarrow \mu_{\vec{B}} = -\frac{\mu_B}{\hbar}\left(L'^2 + 2S'^2 + 3\,\vec{L}'\cdot\vec{S}'\right)\frac{J_z'}{J'^2}$$

$$3\,\vec{L}'\cdot\vec{S}' = 3\left(J'^2 - L'^2 - S'^2\right)/2$$

$$\Rightarrow \mu_{\vec{B}} = -\frac{\mu_B}{\hbar}\left(L'^2 + 2S'^2 + \frac{3}{2}\left(J'^2 - L'^2 - S'^2\right)\right)\frac{J_z'}{J'^2}$$

$$\Rightarrow \mu_{\vec{B}} = -\frac{\mu_B}{\hbar}\frac{\left(3J'^2 + S'^2 - L'^2\right)}{2J'^2}J_z'$$

$$\Delta E = \frac{\mu_B B_{ex}}{\hbar}\frac{\left(3J'^2 + S'^2 - L'^2\right)}{2J'^2}J_z'$$

Since $S'^2 = s'(s'+1)\hbar^2$
$L'^2 = l'(l'+1)\hbar^2$
$J'^2 = j'(j'+1)\hbar^2$
$J_z' = m_j'\hbar$

$$\Rightarrow \Delta E = \mu_B B_{ex}\, g\, m_j'$$

w/ $g = 1 + \dfrac{j'(j'+1) + s'(s'+1) - l'(l'+1)}{2j'(j'+1)}$

Landé factor

For $s'=0$, $j'=l'$ → $g=1$ angular momentum purely orbital

For $l'=0$, $j'=s'$ → $g=2$ angular momentum purely spin.

Landé factor g is a variable determining the ratio between the total magnetic dipole momentum & the total angular momentum for states in which the angular momentum is partially spin & partial orbital.

Every energy level, under $\vec{B}_{ex}$, splits into $2j'+1$ components, one for each value of m'_j. The intensity of the energy split depends on g of the energy level.

Selection rule $\Delta m'_j = 0, \pm 1$ (excluded transition from $m'_j=0$ to $m'_j=0$ if $\Delta j' = 0$)

If $\vec{B}_{ex} > \vec{B}$, $\vec{B}_{ex}$ destroys the $\vec{S}'$ & $\vec{L}'$ coupling forming $\vec{J}'$
⇒ $\vec{S}'$ & $\vec{L}'$ precess independently about $\vec{B}_{ex}$

→ Paschen-Bach effect ($B_{ex} > 1$ tesla)

The total magnetic dipole momentum is still $\vec{\mu} = -\frac{\mu_B}{\hbar}[\vec{L}' + 2\vec{S}']$ since $\vec{B}_{ex}$ does not destroy the coupling of the individual spins & individual orbital angular momenta. But in this case.

⇒ $\vec{\mu}_B = -\frac{\mu_B}{\hbar}(L'_z + 2S'_z)$ ⇒ $\Delta E = \frac{\mu_B B_{ex}}{\hbar}(L'_z + 2S'_z) = \mu_B B_{ex}(m'_\ell + 2m'_s)$

w/ selection rule $\Delta m'_s = 0$ $\Delta m'_\ell = 0, \pm 1$

$\Delta m_{s'} = 0$ → total spin angular momentum & the magnetic dipole momentum do not change orientation in an atomic transition

All spectral lines are split into three components by the Paschen-Back effect, as in the normal Zeeman effect.

# e⁻s in outermost shell (valence e⁻s)	# of systems of spectral terms	Multiplicity
1	1	2 (doublets, except ground state)
2	2	1, 3
3	2	2, 4 (ie: 4 levels close to each other)
4	3	1, 3, 5
5	3	2, 4, 6

skip

If optically active e⁻s are more than half in the subshell, then the sign of the LS coupling is inverted ⇒ lower energy level is that w/ higher j & vice versa.

$\Delta m_{\ell'} = 0$ → transitions emitting e.l.m radiation that is polarized parallel to $\vec{B}ex$

$\Delta m'_{\ell} = \pm 1$ " " " perpendicularly to $\vec{B}ex$

HYPERFINE STRUCTURE

So far, we made the following simplifying assumptions:
- the nucleus is a point particle
- interaction of the nucleus w/ e^-s only through the Coulomb field of its total charge Ze

Their violations produce small effects on the atomic e^- states, aka hyperfine structure $\Rightarrow$ splitting of the states into several substates. Two groups:

1. Isotope effect: depending on the # of neutrons in the nucleus, different nucleus mass for the same species, isotops. $\Rightarrow$ slightly different set of atomic energy levels due to different $\mu = \frac{Mm}{M+m}$ & size.

2. Nuclear Spin: like e^-s, the nucleus also has a spin and an associated magnetic moment. Hence the nucleus has a total spin angular momentum $\vec{I}$, w/ eigenvalues

$$I^2 = i(i+1)\hbar \quad \& \quad I_z = m_i \hbar$$

$$\vec{\mu}_N = g \frac{e}{2Mc} \vec{I} \qquad \text{w/ } M \simeq 1840\, m_e, \quad g = 5.5855$$

magnetic moment of nucleus

NOTE: $\vec{\mu}_N \simeq 10^{-3 \div -4} \vec{\mu}_{e^-}$

The nuclear magnetic moment interacts w/ the magnetic moments of the atomic e^-s, & each previously described atomic state is split by this interaction.

Analogously to LS coupling, we introduce total angular momentum vector $\vec{F} = \vec{J} + \vec{I}$ & label the hyperfine states by the quantum number F.

For example, when $i = 2$ for a $^3D_3$ state, we have five splitting corresponding to $F = 1 \div 5$.

Ex: ground level of HI neutral Hydrogen

$^2S_{1/2}$ proton spin $1/2$

$\rightarrow$ two hyperfine states occur,

n/ ground state $F = 0$ & excited state $F = 1$. $\Delta E = 1420$ MHz

$\lambda = 21$ cm

Radiative transitions from $F = 1$ to $F = 0$ in a single atom are extremely rare, once in 10^7 yrs, but enormous HI abundance.

Primary selection rule $\Delta F = 0, \pm 1$

$\Delta F = 0$ & $\Delta M = 0$ is forbidden.

THERMAL EQUILIBRIUM: BOLTZMANN POPULATION of Levels

In thermal equilibrium, the populations of atomic levels only depends on T.

$$\frac{N_b}{N_a} = \frac{g_b}{g_a} e^{-(E_b - E_a)/KT}$$

BOLTZMANN's eq. for same species in given ionization state.

N_b = # density of atoms w/ energy E_b

N_a = " " " " " " E_a

g_b, g_a = statistical weights of energy levels E_b & E_a

For H (hydrogenic system) g_b = # of states w/ energy E_b

$g_n = 2n^2$

$$N_i = \frac{N}{\sum_i g_i e^{-E_i/KT}} g_i e^{-E_i/KT}$$

N total number density of atoms

N_i # density of atoms in the i-th energy level

$$N = \sum_i N_i$$

$\sum_i g_i e^{-E_i/KT}$ partition function

NOTE: In most cases of interest w/ $T < 10^4$ K,

$\sum_i g_i e^{-E_i/KT} \simeq g_0$ degeneracy of the ground level.

SAHA's Eq. provides the distribution of an atomic species among its various stages of ionization as a function of T.

If n_r # density of the r-times ionized species of an atom

n_{r+1} # = " " $(r+1)$-times " " " " "

n_e " " of free e^-s

χ_r ionization energy of species r

$$\Rightarrow \left(\frac{n_{r+1}}{n_r}\right) n_e = \frac{G_{r+1}}{G_r} g_e \frac{(2\pi m_e kT)^{3/2}}{h^3} e^{-\chi_r/kT} \quad (43)$$

$g_e = 2$

$\frac{G_{r+1}}{G_r}$ = partition functions $\quad G_r = \sum_{i=1}^{\infty} g_i e^{-E_i/kT}$

In term of pressure (ideal gas law) $P_e = n_e kT$

$$\left(\frac{n_{r+1}}{n_r}\right) P_e = \frac{G_{r+1}}{G_r} 2 \frac{(2\pi m_e)^{3/2}}{h^3} (kT)^{5/2} e^{-\chi_r/kT}$$

For H: $g_n = 2n^2$

or Hydrogenic system