QM 2

Graduate 3

Degenerate Perturbation Theory

$\{|m^{(0)}\rangle\}$ is a set of linearly independent eigenkets of g

$\dim\{|m^{(0)}\rangle\} = g$. They are all degenerate

$$H_0|m^{(0)}\rangle = E_D^{(0)}|m^{(0)}\rangle, \quad m = 1, 2, \cdots, g.$$

Under perturbation λV, $(H = H_0 + \lambda V)$ $D = \{1, 2, \cdots, g\}$.

$$(H_0 + \lambda V)|l\rangle = (E_D^{(0)} + \Delta_l)|l\rangle.$$

Note that $|l^{(0)}\rangle$ must be within the space spanned by $\{|m^{(0)}\rangle\}$. However, it does not have to be identical to a single state $|m^{(0)}\rangle$. Instead, it ~~may b~~ is, in general, a linear combination: $|l^{(0)}\rangle = \sum_{m\in D} |m^{(0)}\rangle\langle m^{(0)}|l^{(0)}\rangle$, where $\lim_{\lambda\to 0}|l\rangle = |l^{(0)}\rangle$.

$$(E_D^{(0)} - H_0)|l\rangle = (\lambda V - \Delta_l)|l\rangle$$

$|l\rangle$ can be expanded as

$$|l\rangle = |l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \lambda^2|l^{(2)}\rangle + \cdots$$

$$(E_D^{(0)} - H_0)(|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \cdots)$$
$$= [\lambda(V - \Delta_l^{(1)}) - \lambda^2\Delta_l^{(2)} \cdots](|l^{(0)}\rangle + \lambda|l^{(1)}\rangle + \cdots)$$

order $\lambda^{(0)}$: $(E_D^{(0)} - H_0)|l^{(0)}\rangle = 0$

order $\lambda^{(1)}$: $(E_D^{(0)} - H_0)|l^{(1)}\rangle = (V - \Delta_l^{(1)})|l^{(0)}\rangle$

multiplying $\langle m^{(0)}|$ to the left, we find that

$$\langle m^{(0)}|V|l^{(0)}\rangle = \Delta_l^{(1)}\langle m^{(0)}|l^{(0)}\rangle$$

$$\langle m^{(0)}| V |\ell^{(0)}\rangle = \Delta_\ell^{(1)} \langle m^{(0)}|\ell^{(0)}\rangle$$

$$\mathbb{1} = \sum_{m'\in D} |m'^{(0)}\rangle\langle m'^{(0)}|$$

$$\langle m^{(0)}| V |m'^{(0)}\rangle\langle m'^{(0)}|\ell^{(0)}\rangle = \Delta_\ell^{(1)} \langle m^{(0)}|\ell^{(0)}\rangle$$

$$V_{mm'}\, \ell_{m'} = \Delta_\ell^{(1)} \ell_m$$

$$\Rightarrow \; VL = \Delta_\ell^{(1)} L \qquad L = \begin{pmatrix} \langle 1^{(0)}|\ell^{(0)}\rangle \\ \vdots \\ \langle g^{(0)}|\ell^{(0)}\rangle \end{pmatrix}$$

is a colum vector

It is an eigenvalue equation!

$$(V - \Delta_\ell^{(1)}\mathbb{1})L = 0.$$

In order to have a non-trivial ($L \neq 0$) solution, we must have

$$\det(V - \Delta_\ell^{(1)}\mathbb{1}) = 0.$$

We return to order-λ equation

$$(E_D^{(0)} - H_0)|\ell^{(1)}\rangle = (V - \Delta_\ell^{(1)})|\ell^{(0)}\rangle$$

We define the projection operator

$$\phi_D = 1 - \sum_{m\in D} |m^{(0)}\rangle\langle m^{(0)}| = \sum_{k\notin D} |k^{(0)}\rangle\langle k^{(0)}|$$

that removes the components in the vector space generated by $\{|m^{(0)}\rangle\}$.

$$\phi_D(E_D^{(0)}-H_0)\,|l^{(1)}\rangle = \phi_D(V-\Delta_l^{(1)})\,|l^{(0)}\rangle$$

Because $\langle m^{(0)}|(E_D^{(0)}-H_0)|l^{(1)}\rangle = 0$, $\left(\langle m^{(0)}|H_0 = \langle m^{(0)}|E_D^{(0)}\right)$

$(V-\Delta_l^{(1)})|l^{(0)}\rangle$ does not have any component $|m^{(0)}\rangle$, $m \in D$.

Therefore,

$$(V-\Delta_l^{(1)})|l^{(0)}\rangle = \phi_D(V-\Delta_l^{(1)})|l^{(0)}\rangle.$$

In addition, because $|l^{(0)}\rangle$ is a linear combination of $\{|m^{(0)}\rangle\}$,

$$\phi_D|l^{(0)}\rangle = 0 \rightarrow \phi_D\Delta_l^{(1)}|l^{(0)}\rangle = 0.$$

Therefore,

$$= \phi_D V|l^{(0)}\rangle.$$

$$\Rightarrow \quad \phi_D(E_D^{(0)}-H_0)|l^{(1)}\rangle = \phi_D V|l^{(0)}\rangle$$

$$\Rightarrow \quad |l^{(1)}\rangle = \phi_D \frac{1}{E_D^{(0)}-H_0}\phi_D V|l^{(0)}\rangle$$

$$\boxed{|l^{(1)}\rangle = \phi_D \frac{1}{E_D^{(0)}-H_0} V|l^{(0)}\rangle}$$

$$\boxed{= \sum_{k\notin D} \frac{|k^{(0)}\rangle}{E_D^{(0)}-E_k^{(0)}}\langle k^{(0)}|V|l^{(0)}\rangle}$$

Order-λ^2 equation is

$$(E_D^{(0)}-H_0)|l^{(2)}\rangle = -\Delta_l^{(2)}|l^{(0)}\rangle + (V-\Delta_l^{(1)})|l^{(1)}\rangle$$

$$\Rightarrow \quad \underbrace{\langle l^{(0)}|(E_D^{(0)}-H_0)|l^{(2)}\rangle}_{=0} = -\Delta_l^{(2)}$$

$$\boxed{\begin{aligned}\Delta_l^{(2)} &= \langle l^{(0)}|(V-\Delta_l^{(1)})|l^{(1)}\rangle \\ &= \langle l^{(0)}|V\frac{\phi_D}{E_D^{(0)}-H_0}V|l^{(0)}\rangle\end{aligned}}$$

$$\Delta_\ell^{(2)} = \sum_{k\notin D} \frac{\langle \ell^{(0)}|V|k^{(0)}\rangle\langle k^{(0)}|V|\ell^{(0)}\rangle}{E_D^{(0)}-E_k^{(0)}} = \sum_{k\notin D} \frac{|V_{k\ell}|^2}{E_D^{(0)}-E_k^{(0)}}$$

We return to the all-order expression:

$$(E_D^{(0)}-H_0)|\ell\rangle = (\lambda V - \Delta_\ell)|\ell\rangle$$

Because $\langle m^{(0)}|(E_D^{(0)}-H_0)|\ell\rangle = 0$
to any order in λ,

$$\langle m^{(0)}|(\lambda V - \Delta_\ell)|\ell\rangle = 0$$

$$\Rightarrow \Delta_\ell \langle m^{(0)}|\ell\rangle = \lambda \langle m^{(0)}|V|\ell\rangle$$

to all orders in λ.

As in the non-~~perturbative~~ degenerate case, it is convenient to choose the normalization

$$\langle \ell^{(0)}|\ell\rangle = 1$$

$$\therefore \quad \Delta_\ell = \lambda \langle \ell^{(0)}|V|\ell\rangle$$

Linear stark effect.

Hydrogen atom states

$|n l m\rangle$

If $n=1$, then $l=0$ and $m=0$.

$\therefore$ $|100\rangle$ is the only state whose energy is $E_n = E_1 = -\frac{1}{2}\mu c^2 (Z\alpha)^2$.

If $n=2$, then $l = \begin{cases} 1 \\ 0 \end{cases}$ $m = -1, 0, 1$.

($\therefore$ $|200\rangle$

$|21{-1}\rangle, |210\rangle, |211\rangle$)

There are 4 states with the energy eigenvalue

$E_n = E_2 = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{2^2}$

Note that

$E_n = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2}$ and $\alpha = \frac{e^2 k_1}{\hbar c} \approx \frac{1}{137}$

where $k_1 = \begin{cases} \frac{1}{4\pi\varepsilon_0} & \text{MKSA unit system} \\ \frac{1}{4\pi} & \text{Heaviside-Lorentz unit} \\ 1 & \text{Gaussian unit.} \end{cases}$

$\therefore \alpha = \begin{cases} \frac{e^2}{4\pi\varepsilon_0 \hbar c} & \text{MKSA} \\ \frac{e^2}{4\pi\hbar c} & \text{HL} \\ e^2/(\hbar c) & \text{G.} \end{cases}$

We introduce the Bohr radius

$$a_0 = \frac{\hbar}{\mu c \alpha} = \begin{cases} \dfrac{4\pi\varepsilon_0 \hbar^2}{\mu e^2} & \text{MKSA} \\ 4\pi\hbar^2/(\mu e^2) & \text{HL} \\ \dfrac{\hbar^2}{\mu e^2} & \text{G} \end{cases}$$

Note that

$$E_n = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2} = -\frac{1}{2}(\mu c \alpha)\,\frac{(c Z^2 \alpha)}{n^2}$$

$$\mu c \alpha = \frac{\hbar}{a_0} \qquad = -\frac{1}{2}\,\frac{\hbar}{a_0}\,\frac{c Z^2 \alpha}{n^2}$$

$$\alpha = \frac{k_1 e^2}{\hbar c} \qquad = -\frac{1}{2}\,\frac{\cancel{\hbar c}}{a_0}\cdot\frac{Z^2}{n^2}\cdot\frac{k_1 e^2}{\cancel{\hbar c}}$$

$$= -\frac{1}{2}\left(\frac{k_1 e^2}{a_0}\right)\frac{Z^2}{n^2}$$

$$\therefore E_n = \begin{cases} -\dfrac{1}{2}\left(\dfrac{e^2}{4\pi\varepsilon_0 a_0}\right)\dfrac{Z^2}{n^2} & \text{MKSA} \\ -\dfrac{1}{2}\left(\dfrac{e^2}{4\pi a_0}\right)\dfrac{Z^2}{n^2} & \text{HL} \\ -\dfrac{1}{2}\left(\dfrac{e^2}{a_0}\right)\dfrac{Z^2}{n^2} & \text{G} \end{cases}$$

5.3 Hydrogenlike atoms: Fine structure and the Zeeman effect.

Spin-orbit Interaction and Fine structure

Hydrogenlike atoms are those which have only one valence electron outside the closed she[ll]. For example, Alkali atoms such as sodium (Na) and potassium (K) belong to this catagory.

At the CM frame of p-e system, the electron moves fast and the proton is at rest.

$$\textcircled{p} \longrightarrow \vec{E} \qquad \textcircled{e}$$

The electric field felt by the electron is

$$\vec{E} = -\vec{\nabla}\phi, \quad \phi = k_1 \frac{e}{r}, \quad e > 0$$

where e is the charge of the proton.

Because the proton is at rest, there is no current and therefore, the electron does not feel the magnetic force in this frame.

The field strength tensor $F^{\mu\nu}$ in the CM frame (proton-rest) is, then,

$$F^{\mu\nu} = \begin{pmatrix} 0 & -E & 0 & 0 \\ E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad \begin{cases} \vec{E} = E\hat{x} \\ \vec{B} = \vec{0} \end{cases}$$

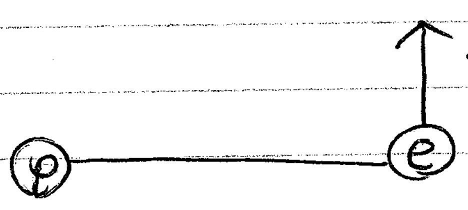
where we have chosen the x axis along the straight line from p to e.

$$(p) \xrightarrow{x} (e).$$

Note that, in general,

$$F^{\mu\nu} = \begin{pmatrix} 0 & -E^1 & -E^2 & -E^3 \\ E^1 & 0 & B & B \\ E^2 & B & 0 & B \\ E^3 & B & B & 0 \end{pmatrix}$$

$$\vec{v} = (0, v, 0) = v\hat{y}$$



In the rest frame of the electron, $\vec{v}_e = \vec{0}$. Therefore, the boost matrix from the CM to the electron rest frame is

$$\Lambda^{\mu}{}_{\nu} = \begin{pmatrix} \gamma & 0 & -\gamma\beta & 0 \\ 0 & 1 & 0 & 0 \\ -\gamma\beta & 0 & \gamma & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}.$$

Then the field-strength tensor in the electron rest frame is

$$F^{\mu\nu}\Big|_{e\text{-rest}} = \Lambda^{\mu}{}_{\alpha}\,\Lambda^{\nu}{}_{\beta}\,F^{\alpha\beta}\Big|_{CM}$$

$$= \Lambda^{\mu}{}_{\alpha}\,F^{\alpha\beta}\Big|_{CM}\left(\Lambda^{\nu}{}_{\beta}\right)^{T}$$

$$= \begin{pmatrix} \gamma & 0 & -\gamma\beta & 0 \\ 0 & 1 & 0 & 0 \\ -\gamma\beta & 0 & \gamma & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & -E & 0 & 0 \\ E & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \gamma & 0 & -\gamma\beta & 0 \\ 0 & 1 & 0 & 0 \\ -\gamma\beta & 0 & \gamma & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & -\gamma E & 0 & 0 \\ E & 0 & 0 & 0 \\ 0 & \gamma\beta E & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \gamma & 0 & -\gamma\beta & 0 \\ 0 & 1 & 0 & 0 \\ -\gamma\beta & 0 & \gamma & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & -\gamma E & 0 & 0 \\ \gamma E & 0 & -\gamma\beta E & 0 \\ 0 & \gamma\beta E & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & -E^1 & -E^2 & -E^3 \\ E^1 & 0 & -\frac{c}{\alpha}B^3 & \frac{c}{\alpha}B^2 \\ E^2 & \frac{c}{\alpha}B^3 & 0 & -\frac{c}{\alpha}B^1 \\ E^3 & -\frac{c}{\alpha}B^2 & \frac{c}{\alpha}B^1 & 0 \end{pmatrix}$$

Therefore,

$$\vec{E} = -\gamma E\,\hat{x}$$

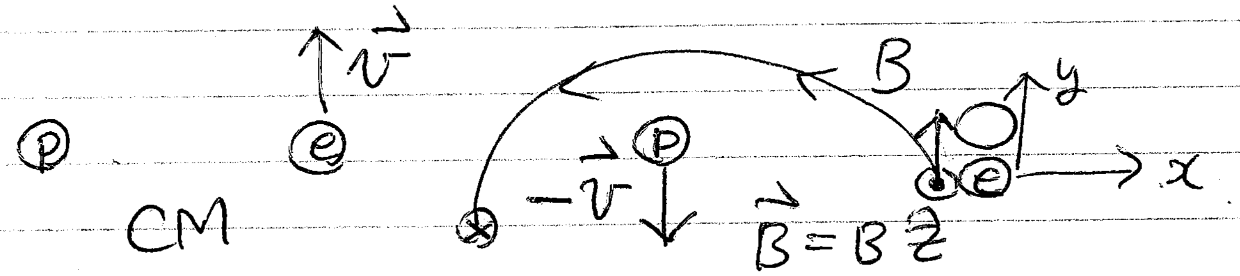
$$\vec{B} = \frac{\alpha}{c}\gamma\beta E\,\hat{z} = \begin{cases} \frac{v}{c}\gamma E\,\hat{z} & (\text{HL G} \\ \frac{v}{c^2}\gamma E\,\hat{z} & (\text{MKS} \end{cases}$$

$$\vec{v} = v\hat{y}, \quad \vec{E} = \gamma E \hat{x} \quad \Big\} \quad \vec{v}\times\vec{E} = -c\gamma\beta E\hat{z}$$

$$\vec{B} = \frac{\alpha}{c}\gamma\beta E\hat{z} = -\frac{\alpha}{c^2}\vec{v}\times\vec{E}$$

Therefore, in the electron's rest frame, the electron feels the magnetic field

$$\vec{B} = -\frac{\alpha}{c^2}\vec{v}\times\vec{E} = \begin{cases} -\dfrac{\vec{v}}{c}\times\vec{E} & (\text{HL \& G}) \\ -\dfrac{\vec{v}}{c^2}\times\vec{E} & (\text{MKSA}) \end{cases}$$



$$\boxed{\vec{B} = -\frac{\alpha}{c^2}\vec{v}\times\vec{E},}$$ where $\vec{E}$ is the electric field generated by the proton in the CM frame

We recall that

$$\vec{E} = -\vec{\nabla}\phi, \quad \text{where } \phi = k_1\frac{e}{r}, \quad e > 0.$$

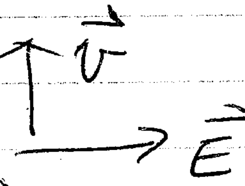
$$\left(k_1 = \underset{\text{MKSA}}{\frac{1}{4\pi\varepsilon_0}} \quad \underset{\text{HL}}{\frac{1}{4\pi}} \quad \underset{\text{G}}{1} \right)$$

$$\vec{B} = -\frac{\alpha}{c^2}\vec{v}\times(-\vec{\nabla}\phi)$$
$$= \frac{\alpha}{c^2}\vec{v}\times\vec{\nabla}\phi$$
$$= \frac{\alpha}{c^2}\vec{v}\times\hat{r}\frac{\partial\phi}{\partial r}$$

$$\vec{\nabla}\phi = \hat{r}\frac{\partial\phi}{\partial r}$$

because $\phi = \phi(r)$ is a function of r.

$$\vec{B} = \frac{\alpha}{c^2}\left(\vec{v}\times\vec{r}\right)\left(\frac{1}{r}\frac{\partial\phi}{\partial r}\right)$$



$$\vec{v}\times\vec{r} = \frac{m\vec{v}\times\vec{r}}{m} = -\frac{\vec{r}\times\vec{p}}{m} = -\frac{\vec{L}}{m}$$

$$= \frac{\alpha}{c^2}\left(-\frac{\vec{L}}{m}\right)\left(\frac{1}{r}\frac{\partial\phi}{\partial r}\right)$$

$$= \begin{cases} -\dfrac{\vec{L}}{mc}\dfrac{1}{r}\dfrac{\partial\phi}{\partial r} & (\text{HL \& G}) \\ -\dfrac{\vec{L}}{mc^2}\dfrac{1}{r}\dfrac{\partial\phi}{\partial r} & (\text{MKSA}) \end{cases}$$

We know that the potential energy of a magnetic dipole $\vec{\mu}$ under the magnetic field $\vec{B}$ is

$$V = -\vec{\mu}\cdot\vec{B}.$$

Next we find the expression for the intrinsic magnetic diple of an electron due to its spin.

The magnetic dipole $\vec{\mu}$ ~~of~~ ~~due~~ ~~an orbital~~ ~~mo~~ of an electron due to its orbital motion is first reviewed.

electron's charge

$$\vec{\mu} = \frac{i}{\alpha}\vec{A} \qquad \alpha = \begin{cases} c & \text{HL\&G} \\ 1 & \end{cases}$$

area, unit vector.

$$= \frac{1}{\alpha}\frac{(-e)}{T}(\pi r^2)\,\hat{n}$$

i'' period, area of the orbit

Note that $T = \frac{2\pi r}{v}$ $\therefore$ $\pi r^2 = 2\pi r \frac{r}{2} = T\frac{rv}{2}$

$$= \frac{1}{\alpha}\frac{(-e)}{\cancel{T}}\cancel{T}\frac{rv}{2}\hat{n}$$

electron's mass

$$= \frac{(-e)\,r\,mv}{2\alpha m}\hat{n} \qquad m\vec{v}$$

$$\vec{r}\times m\vec{v} = \vec{L} = rmv\hat{n}$$

$$= -\frac{e}{2m\alpha}\vec{L}$$

$$= -\frac{e\hbar}{2m\alpha}\left(\frac{\vec{L}}{\hbar}\right)$$

We call

$$\mu_B = \frac{e\hbar}{2m\alpha} = \begin{cases} \frac{e\hbar}{2m} & : \text{MKSA} \\ \frac{e\hbar}{2mc} & : \text{HL\&G} \end{cases}$$

Bohr magneton

In general, the magnetic moment of

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S$$

$\vec{\mu}_L$ is that due to the orbital motion

$\vec{\mu}_S$ is that due to the intrinsic spin angular momentum $\vec{S}$ that is independent of the orbital motion.

$$\vec{\mu}_L = -\mu_B\left(\frac{\vec{L}}{\hbar}\right), \quad \mu_B = \frac{e\hbar}{2m\alpha} > 0 \quad (e > 0)$$

$$\vec{\mu}_S = -g\mu_B\left(\frac{\vec{S}}{\hbar}\right).$$

For an orbital angular momentum eigenket $|l\,m\rangle$, $\langle l\,m|\vec{\mu}_L|l\,m\rangle = -\mu_B m$, $m = -l \cdots$

For a spin angular momentum eigenket,

$$\langle s\,s_z|\vec{\mu}_S|s\,s_z\rangle = -g\mu_B\left(\frac{\pm 1}{2}\right) \quad \text{for } m = \pm\frac{1}{2}$$

Phenomenologically,

they have found that

the factor g is $\gtrsim 2$.

This factor g is called the electron g-factor.

$\gamma = g\frac{\mu_B}{\hbar}$ is the electron's gyromagnetic ratio.

The factor g is calculable if we use the relativistic spin $\frac{1}{2}$ particle theory (Dirac Eq

As a result, the potential

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

due to the electron's intrinsic spin magnetic moment that interacts with the magnetic field generated by the proton in the electron's rest frame is

$$V = -\vec{\mu}_s\cdot\vec{B} \leftarrow \begin{cases} \vec{\mu}_s = -g\mu_B\left(\dfrac{\vec{S}}{\hbar}\right), \quad \mu_B = \dfrac{e\hbar}{2mc} \\ \vec{B} = -\dfrac{\alpha\hbar}{mc^2}\left(\dfrac{\vec{L}}{\hbar}\right)\dfrac{1}{r}\dfrac{d\phi}{dr} \end{cases}$$

$$= -\frac{g\mu_B\alpha\hbar}{mc^2}\left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right)\frac{1}{r}\frac{d\phi}{dr}$$

Note that $\alpha = \begin{cases} 1 & \text{MKSA} \\ c & \text{HL\&G.} \end{cases}$

$$\phi = k_1\frac{Ze}{r}$$

$$\frac{d\phi}{dr} = k_1\left(-\frac{Ze}{r^2}\right)$$

$$= \frac{\alpha k_1 g\mu_B\hbar}{mc^2}\left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right)\frac{Ze}{r^3}, \quad (e>0) \text{ proton's Charge.}$$

$$\frac{\alpha k_1 g\mu_B\hbar}{mc^2} = \frac{\alpha k_1 g\hbar}{mc^2}\times\frac{e\hbar}{2m\cancel{c}}$$

$$= \cancel{\frac{k_1 g}{2m^2c^2}}\left(\frac{g}{2}\right)\frac{k_1 e\hbar^2}{m^2c^2}$$

$$= \frac{\hbar^2}{m^2c^2}\left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right)\left(\frac{k_1 Ze^2}{r^3}\right)\left(\frac{g}{2}\right)$$

$$V_{LS} = \frac{\hbar^2}{m^2c^2}\left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right)\left(k_1\frac{Ze^2}{r^3}\right)\left(\frac{g}{2}\right)$$

This interaction is called the Spin-orbit potential.

Because the full Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{k_1 Ze^2}{r} + V_{LS}$$

and V_{LS} is not proportional to the Coulomb potential, we have to solve the problem again.

We had better apply the perturbation theory to compute the corrections in the energy levels.

Because the interaction potential V_{LS} is proportional to $\vec{L}\cdot\vec{S}$, we should ~~take~~ be carful ~~with~~ choosing the state kets.

We define the total angular momentum operator $\vec{J} = \vec{L} + \vec{S}$.

Then We find that all of the following operators $\vec{L}^2$, $\vec{S}^2$, $\vec{J}^2$ and J_z commute.

Note that

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left[2\vec{L}\cdot\vec{S}\right]$$
$$= \frac{1}{2}\left[(\vec{L}+\vec{S})^2 - \vec{L}^2 - \vec{S}^2\right]$$
$$= \frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]$$

$$|n\, l\, m_l\rangle \otimes |S\, m_s\rangle = |J = l + \tfrac{1}{2}, \overset{m_s + m_l}{m}\rangle \oplus |J = l - \tfrac{1}{2}, m\rangle .$$

In chapter 3, we have derived that

$$\mathcal{Y}_l^{j = l \pm \frac{1}{2}, m} = \pm\sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}}\, Y_l^{m-\frac{1}{2}} \chi_+ + \sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}}\, Y_l^{m+\frac{1}{2}} \chi_-$$
$$= \frac{1}{\sqrt{2l+1}} \begin{pmatrix} \pm\sqrt{l \pm m + \frac{1}{2}} \\ \sqrt{l \mp m + \frac{1}{2}} \end{pmatrix},$$

where $Y_l^m(\theta, \phi)$ is the spherical harmonics and $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ are spin up and down kets, respectively.

Let us now compute the expectation value for $\vec{L}\cdot\vec{S}$ for the $|l, s, J, J_z\rangle$ statket.

For the state

$$\mathcal{Y}_l^{j=l\pm\frac{1}{2},m} = \frac{1}{\sqrt{2l+1}}\begin{pmatrix} \pm\sqrt{l\pm m+\frac{1}{2}}\, Y_{l m-\frac{1}{2}}(\theta,\phi) \\ \sqrt{l\mp m+\frac{1}{2}}\, Y_{l m+\frac{1}{2}}(\theta,\phi)\end{pmatrix}$$

$$\vec{L}\cdot\vec{S} = \frac{1}{2}\left[\vec{J}^2-\vec{S}^2-\vec{L}^2\right] = \frac{1}{2}\left[J(J+1)-S(S+1)-l(l+1)\right]$$

$$\int \mathcal{Y}^\dagger \vec{L}\cdot\vec{S}\,\mathcal{Y}\,d\Omega = \frac{\hbar^2}{2}\begin{cases}(l+\frac{1}{2})(l+\frac{3}{2})-\frac{1}{2}\cdot\frac{3}{2}-l(l+1) : & l+\frac{1}{2} \\ (l-\frac{1}{2})(l+\frac{1}{2})-\frac{1}{2}\cdot\frac{3}{2}-l(l+1) : & l-\frac{1}{2}\end{cases}$$

$$= \frac{\hbar^2}{2}\begin{cases}2l-l=l \\ \cancel{l^2}-\frac{1}{4}-\frac{3}{4}-\cancel{l^2}-l=-(l+1)\end{cases}$$

$$= \begin{cases}\frac{l\hbar^2}{2} & \text{for } J=l+\frac{1}{2} \\ -\frac{(l+1)}{2}\hbar^2 & \text{for } J=l-\frac{1}{2}\end{cases}$$

This equation is called <u>Lande's</u> interval rule.

We recall that the $\vec{L}\cdot\vec{S}$ coupling potential is of the form

$$V_{LS} = \frac{\hbar^2}{m^2c^2}\left(\frac{\vec{L}\cdot\vec{S}}{\hbar^2}\right)\left(k_1\frac{Ze^2}{r^3}\right)\left(\frac{g}{2}\right)$$

$$\langle n\,l s; J J_z | V_{LS} | n\,l s; J J_z\rangle$$

$$= \frac{\hbar^2}{m^2c^2}\begin{pmatrix} \frac{l}{2} \\ -\frac{(l+1)}{2} \end{pmatrix}\underbrace{(k_1 Z)\left(\frac{g}{2}\right)}_{\text{pure numbers.}}\langle \underset{J J_z}{n l s} | \frac{e^2}{r^3} | \underset{J J_z}{n l s}\rangle$$

for $\begin{pmatrix} J = l+\frac{1}{2} \\ J = l-\frac{1}{2} \end{pmatrix}$ states, respectively.

Without any explicit calculation, we can still carry out a dimensional analysis.

$$\left\langle \frac{e^2}{r^3}\right\rangle_{nl} \sim \frac{e^2}{a_0^3}$$

because $a_0 = \frac{\hbar}{\mu c \alpha} \rightarrow \alpha = \frac{\hbar}{a_0 mc} \rightarrow \alpha^2 = \frac{\hbar^2}{a_0^2 m^2 c^2}$

(fine-structure constant)

$$\Delta_{nl} \sim \frac{\hbar^2}{m^2c^2}\,\#\,\frac{e^2}{a_0^3} = \frac{e^2}{a_0} \times \frac{\hbar^2}{a_0^2 m^2 c^2} \times \#$$

$$E_n = -\frac{1}{2}\left(\frac{e^2}{a_0}\right)\frac{Z^2}{n^2} \qquad \sim E_n \times \frac{\hbar^2}{a_0^2 m^2 c^2}\,\#$$

$$\Rightarrow E_n \times \alpha^2 \times \#$$

fine structure co.

Therefore,

$$\frac{\Delta_{n\ell}}{E_n} \sim \alpha^2 \sim \left(\frac{1}{137}\right)^2$$

and the splitting is of order α^2 up to an overal dimensionless constant.

This splitting is called the fine-structure splitting which is due to the spin-orbit coupling!.

For a later use, we had better verify the following identities:

$$\left\langle \frac{1}{r} \right\rangle_{n\ell} = \frac{Z}{n^2 a_0}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{n\ell} = \frac{Z^2}{a_0^2} \frac{1}{n^3(\ell+\frac{1}{2})}$$

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{Z^3}{a_0^3} \frac{1}{n^3 \ell(\ell+\frac{1}{2})(\ell+1)}$$

An explicit derivation of these identities can be found in

H.S. Song, Quantum Mechanics 2nd edition PP.500-5

Relativistic Correction

The relativistic correction to the kinetic energy of the electron is

$$V_{rel} = \underbrace{\sqrt{(mc^2)^2+(pc)^2}-mc^2}_{\text{relativistic kinetic energy}} - \underbrace{\frac{p^2}{2m}}_{\text{non-relativistic kinetic energy}}$$

$$= \left[\sqrt{1+\left(\frac{p}{mc}\right)^2}-1\right]mc^2 - \frac{p^2}{2m}$$

$$= \left[1+\frac{1}{2}\left(\frac{p}{mc}\right)^2+\frac{\frac{1}{2}\left(-\frac{1}{2}\right)}{2}\left(\frac{p}{mc}\right)^4+\cdots-1\right]mc^2-\frac{p^2}{2m}$$

$$= \cancel{\frac{p^2}{2m}} - \frac{p^4}{8m^3c^2} - \cancel{\frac{p^2}{2m}} + O(v^6)$$

$$= -\frac{p^4}{8m^3c^2}+O\left[\left(\frac{p}{m}\right)^6\right].$$

We can rewrite this term as

$$= -\frac{1}{2mc^2}\left(\frac{p^2}{2m}\right)\left(\frac{p^2}{2m}\right)$$

Because $H_0 = \frac{p^2}{2m} - k_1\frac{Ze^2}{r}$, MKSA, HL, G

$$\frac{p^2}{2m} = H_0 + k_1\frac{Ze^2}{r}, \quad k_1 = \frac{1}{4\pi\varepsilon_0}, \frac{1}{4\pi}, 1$$

Therefore,

$$V_{rel} = -\frac{1}{2mc^2}\left(H_0+k_1\frac{Ze^2}{r}\right)\left(H_0+k_1\frac{Ze^2}{r}\right)$$

The energy shift of the state $|nlm\rangle$ can be computed as

$$\Delta_{nlm} = \langle nlm | \left(-\frac{1}{2mc^2}\right)\left(H_0 + k_1 \frac{Ze^2}{r}\right)\left(H_0 + k_1 \frac{Ze^2}{r}\right) | nl$$

Because $\langle nlm | H_0 = E_n \langle nlm |$

$H_0 | nlm\rangle = E_n | nlm\rangle$,

$$E_n = -\frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2},$$

$$\Delta_{nlm} = \left(-\frac{1}{2mc^2}\right)\left(E_n^2 + 2k_1 E_n Ze^2 \left\langle \frac{1}{r}\right\rangle_{nl} + k_1^2 (Ze^2)^2 \left\langle \frac{1}{r^2}\right\rangle_{n}\right.$$

Recall that

$$\left\langle \frac{1}{r}\right\rangle_{nl} = \frac{Z}{n^2 a_0}$$

$$\left\langle \frac{1}{r^2}\right\rangle_{nl} = \frac{Z^2}{a_0^2}\frac{1}{n^3(l+\frac{1}{2})}$$

$$= -\frac{1}{2mc^2}\left(E_n^2 + 2k_1 E_n \frac{Z^2 e^2}{n^2 a_0} + k_1^2 \frac{Z^4 e^4}{n^3 a_0^2 (l+\frac{1}{2})}\right)$$

Because $E_n = -\frac{1}{2}\left(\frac{k_1 e^2}{a_0}\right)\frac{Z^2}{n^2}$

$$= -\frac{1}{2mc^2}\left(E_n^2 - 4E_n^2 + 4E_n^2\left(\frac{n}{l+\frac{1}{2}}\right)\right)]$$

$$= -\frac{E_n^2}{2mc^2}\left(-3 + 4\left(\frac{n}{l+\frac{1}{2}}\right)\right)]$$

$$= -\frac{2E_n^2 n}{mc^2}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right).$$

$$\Delta_{nlm} = -\frac{2E_n^2 n}{mc^2}\left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n}\right)$$

$$-\frac{2E_n^2 n}{mc^2} = -2\,\frac{\left(-\frac{1}{2}mc^2\frac{(Z\alpha)^2}{n^2}\right)^2 n}{mc^2}$$

$$= -\frac{1}{2}mc^2\,\frac{(Z\alpha)^4}{n^3}$$

$$= -\frac{1}{2}mc^2(Z\alpha)^2\left[\frac{(Z\alpha)^2}{n^3(l+\frac{1}{2})} - \frac{3(Z\alpha)^2}{4n^4}\right]$$

The Zeeman effect

Let us consider the magnetic dipole moment of the hydrogenlike atom under an external magnetic field $\vec{B}$.

The additional potential energy is then

$$V = -\vec{\mu}\cdot\vec{B},$$

where
$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_s = -\mu_B\left(\frac{\vec{L}+g\vec{S}}{\hbar}\right), \quad \mu_B = \frac{e\hbar}{2m\alpha} = \begin{cases} \dfrac{e\hbar}{2m} & \text{M} \\ \dfrac{e\hbar}{2mc} & \text{H \& G} \end{cases}$$

$g \approx 2$ is the electron's g-factor.

The magnetic field $\vec{B} = \vec{\nabla}\times\vec{A}$ can be obtained by choosing the constant vector potential $\vec{A} = \frac{1}{2}\vec{B}\times\vec{r}$:

$$(\vec{\nabla}\times\vec{A})^i = \epsilon^{ijk}\frac{\partial}{\partial x^j}A^k = \epsilon^{ijk}\frac{\partial}{\partial x^j}\left[\frac{1}{2}\epsilon^{klm}B^l x^m\right]$$
$$= \frac{1}{2}\epsilon^{kij}\epsilon^{klm}B^l\frac{\partial x^m}{\partial x^j}, \quad \text{where } \frac{\partial B^l}{\partial x^j} = 0.$$
$$= \frac{1}{2}\left(\delta^{il}\delta^{jm} - \delta^{im}\delta^{jl}\right)B^l\delta^{jm}$$
$$= \frac{1}{2}\left(3\delta^{il} - \delta^{il}\right)B^l = B^i$$

$$\therefore \quad \vec{\nabla}\times\left(\frac{1}{2}\vec{B}\times\vec{r}\right) = \vec{B}$$

if $\vec{B}$ is constant.

~~If~~ $\vec{B} = B\hat{z}$, then

$$\vec{A} = \frac{B}{2}\left[\hat{z} \times (x\hat{x} + y\hat{y} + z\hat{z})\right]$$

$$= \frac{B}{2}\left[+x\hat{y} - y\hat{x}\right].$$

We have ~~computed~~ constructed the Hamiltonian for a Hydrogen-like atom in the free space as $(\vec{E} = \vec{B} = \vec{0})$

$$H_0 = \frac{\vec{p}^2}{2m} - \frac{k_1 Z e^2}{r}.$$

Under the electromagnetic field, the expression is modified as

$$H \to H - q\phi$$

$$\vec{p} \to \vec{p} - \frac{q}{\alpha}\vec{A}$$

Here, the charge of the electron is $q = -e$

Therefore,

$$H = \frac{(\vec{p} + \frac{e}{\alpha}\vec{A})^2}{2m} - \frac{k_1 Z e^2}{r}.$$

Note that the electrostatic potential energy is already included in H_0. So, the correction appears only in the kinetic energy.

$$(\vec{p}+\frac{e}{\alpha}\vec{A})^2 = (\vec{p}+\frac{e}{\alpha}\vec{A})\cdot(\vec{p}+\frac{e}{\alpha}\vec{A})$$
$$= \vec{p}^{\,2} + \frac{e}{\alpha}(\vec{A}\cdot\vec{p}+\vec{p}\cdot\vec{A}) + \left(\frac{e}{\alpha}\right)^2\vec{A}^{\,2}$$

Therefore

$$H = H_0 + \frac{e}{2m\alpha}(\vec{A}\cdot\vec{p}+\vec{p}\cdot\vec{A}) + \frac{e^2}{2m\alpha^2}\vec{A}^{\,2}$$

Note that $\vec{p} = -i\hbar\vec{\nabla}$

In the position space, arbitrary ket $|nlm\rangle$.

$$\cancel{\langle\vec{x}|\vec{p}\cdot\vec{A}|a\rangle}$$
$$\cancel{= -i\hbar\vec{\nabla}\cdot\langle\vec{x}|\vec{A}|a\rangle + i\hbar}$$

$$\vec{p}\cdot\vec{A}|nlm\rangle$$
$$= \int d^3x\, |\vec{x}\rangle\langle\vec{x}|\, \vec{p}\cdot\vec{A}|nlm\rangle$$
$$= \int d^3x\, |\vec{x}\rangle (-i\hbar\vec{\nabla})\cdot\langle\vec{x}|\vec{A}|nlm\rangle$$
$$= \int d^3x\, |\vec{x}\rangle\, (-i\hbar\vec{\nabla})\cdot\left(\vec{A}(\vec{x})\langle\vec{x}|nlm\rangle\right)$$
$$= \int d^3x\, |\vec{x}\rangle\Big[(-i\hbar\vec{\nabla}\cdot\vec{A})\langle\vec{x}|nlm\rangle \cancel{+\vec{A}(\vec{x})\cdot i\hbar\vec{\nabla}}$$
$$+ (-i\hbar\vec{A}\cdot\vec{\nabla})\langle\vec{x}|nlm\rangle\Big].$$

We have a freedom to choose the gauge without changing the physical fields such as $\vec{E}$ and $\vec{B}$. Let us choose the Coulomb gauge $\vec{\nabla}\cdot\vec{A}=0$. Then,

$$\vec{p}\cdot\vec{A} = \vec{A}\cdot\vec{p} \quad \text{(Coulomb gauge)}$$

Then $H = H_0 + \frac{e}{m\alpha}\vec{A}\cdot\vec{p} + \left(\frac{e^2}{2m\alpha^2}\right)\vec{A}^2$ (Coulomb gauge)

Substituting $\vec{A} = \frac{B}{2}(-y\hat{x} + x\hat{y})$ into $\vec{A}\cdot\vec{p}$

$$\vec{A}\cdot\vec{p} = \frac{B}{2}(-y\hat{x} + x\hat{y})\cdot\vec{p} = \frac{B}{2}(-yp_x + xp_y)$$

$$= \frac{B}{2}\underbrace{(xp_y - yp_x)}$$

This is L_z, the z component of the orbital angular momentum

$$= \frac{B}{2}L_z = \frac{1}{2}(\vec{B}\cdot\vec{L}) \quad \text{(Coulomb gauge)}$$

$$\vec{A}^2 = \frac{B^2}{4}(x^2+y^2)$$

Therefore,

$$H = H_0 + \frac{e\vec{B}\cdot\vec{L}}{2m\alpha} + \frac{e^2B^2}{8m\alpha^2}(x^2+y^2). \quad \text{(Coulomb gauge)}$$

Note that $e > 0$ and $\alpha = \begin{cases} 1 : \text{MKSA} \\ c : \text{HL \& G}. \end{cases}$

We recall that

$$V = -\vec{\mu}\cdot\vec{B}$$

$$= -(\vec{\mu}_L + \vec{\mu}_S)\cdot\vec{B} \quad \text{and} \quad \vec{\mu}_L + \vec{\mu}_S = -\mu_B\left(\frac{\vec{L} + g\vec{S}}{\hbar}\right)$$

$$= \frac{e\hbar}{2m\alpha}\left(\frac{\vec{L}+g\vec{S}}{\hbar}\right)\cdot\vec{B} \qquad \mu_B = \frac{e\hbar}{2m\alpha} > 0.$$

We find that $+\frac{e\vec{B}\cdot\vec{L}}{2m\alpha}$ matches the magnetic dipole moment term due to the orbital angular momentum.

We need to add the spin contribution.

After correcting the spin contribution to the magnetic dipole moment, we find that

$$H = H_0 + \frac{e\vec{B}\cdot(\vec{L}+g\vec{S})}{2m\alpha} + \frac{e^2B^2}{8m\alpha^2}(x^2+y^2),$$

in the Coulomb Gauge.

If the magnetic field is weak, then the quadratic term proportional to B^2 is negligible.

$$\Rightarrow H \underset{\text{(Coulom Gauge)}}{\approx} H_0 + \frac{e\vec{B}\cdot(\vec{L}+g\vec{S})}{2m\alpha},$$

$$= H_0 + \frac{e\vec{B}\cdot[\vec{J}+(g-1)\vec{S}]}{2m\alpha},$$

where $\vec{J} = \vec{L}+\vec{S}$. Note that $g \approx 2$, $g-1 \approx 1$.

The eigenket $|S, l, J, J_z\rangle$ is

$$\left|J=l\pm\tfrac{1}{2}, J_z=m\right\rangle = \begin{bmatrix} \pm\sqrt{\dfrac{l\pm m+\frac{1}{2}}{2l+1}}\, Y_{l\,m-\frac{1}{2}}(\theta,\phi) \\ \sqrt{\dfrac{l\mp m+\frac{1}{2}}{2l+1}}\, Y_{l\,m+\frac{1}{2}}(\theta,\phi) \end{bmatrix}$$

$\begin{pmatrix}1\\0\end{pmatrix}$ is the spin-up ($m_s=+\frac{1}{2}$) state

$\begin{pmatrix}0\\1\end{pmatrix}$ is the spin-down ($m_s=-\frac{1}{2}$) state, respectively

Because $J_z | J = l \pm \frac{1}{2}, J_z = m \rangle = m\hbar \, | l \pm \frac{1}{2}, m \rangle$

S

$$S_z | J = l \pm \tfrac{1}{2}, J_z = m \rangle = \frac{\hbar}{2} \begin{bmatrix} \pm\sqrt{\frac{l \pm m + \frac{1}{2}}{2l+1}} \, Y_{l\, m-\frac{1}{2}}(\theta, \phi) \\ -\sqrt{\frac{l \mp m + \frac{1}{2}}{2l+1}} \, Y_{l\, m+\frac{1}{2}}(\theta, \phi) \end{bmatrix}$$

$$\langle J_z \rangle_{l \pm \frac{1}{2}, m} = \langle l \pm \tfrac{1}{2}, m | J_z | l \pm \tfrac{1}{2}, m \rangle$$

$$= m\hbar$$

$$\langle S_z \rangle_{l \pm \frac{1}{2}, m} = \frac{\hbar}{2} \left[\frac{l \pm m + \frac{1}{2}}{2l+1} - \frac{l \mp m + \frac{1}{2}}{2l+1} \right],$$

where the angular integrals are all identities.

$$= \frac{\hbar}{2(2l+1)} \left[\pm 2m \right] = \pm \frac{m\hbar}{2l+1}$$

$$\therefore \langle J_z + (g-1) S_z \rangle_{l \pm \frac{1}{2}, m} = m\hbar \left[1 \pm \frac{(g-1)}{2l+1} \right]$$

$$\simeq m\hbar \left[1 \pm \frac{1}{2l+1} \right]$$

Therefore, the first-order energy shift is

μ_B $\quad J_z$

$$\Delta_{l \pm \frac{1}{2} m} = \frac{e\hbar B}{2m\alpha} \, m \left[1 \pm \frac{1}{2l+1} \right]$$

$$= \mu_B B \, m \left[1 \pm \frac{1}{2l+1} \right], \quad \mu_B = \frac{e\hbar}{2m\alpha} > 0$$

This is called the Zeeman effect.