# RECAP OF BOHR AND SCHRÖDINGER MODELS

— Energy levels are discrete in both and are given by the same formula

$$E_n = - \frac{m_e e^4}{32 \pi^2 \hbar^2 \epsilon_o^2} \frac{1}{n^2}$$

$$= - R_H / n^2$$

— Radii of different orbits are discrete in the Bohr model and given as

$$r_n = \frac{4 \pi \epsilon_o \hbar^2}{m_e e^2} n^2$$

$$= a_o n^2$$

— In the Schrödinger model there is no definite radius; only the most probable radius, or the mean radius. The most probable radius matches the Bohr prediction in the case of the ground state.

— Furthermore, the radial wavefunction is a function not only of the principle quantum number $n$, but also of the angular momentum quantum numbers, $\ell$ and $m_\ell$. Thus the spatial distribution of the electron in the Schrödinger model is complex, and varies with $n, \ell, m_\ell$.

— However, the energy levels depend only on $n$, and are degenerate in $\ell$ and $m_\ell$   ( $\ell = 0, 1, \cdots n-1$ ;  $-\ell \leq m_\ell \leq \ell$ )

## FINE STRUCTURE OF THE ENERGY LEVELS

— Certain lines in the spectrum of Hydrogen when observed with a very high resolution appear as doublets.

— e.g. the Ly−$\alpha$ and H−$\alpha$ lines, corresponding to $n=2 \to 1$ and $n = 3 \to 2$ transitions are not singlets but closely spaced doublets

— there is no explanation for this in the Schrödinger's model. The schrödinger equation takes into account all electrostatic interactions. and no correction is expected on this.

— However since we are dealing with moving charges ( orbiting electrons) we should take into account the magnetic interaction also.

— Since the difference in the energy levels corresponding to the doublet splitting is small  $\Delta E / E \simeq 10^{-4}$, we can treat the magnetic interaction perturbatively.

▶ We first calculate the magnetic field experienced by the electron due to the nucleus.

In the rest frame of the electron the nucleus appears to revolve around the origin, thereby creating a magnetic field, given by the Biot-Savart law

$$\vec{B} = \frac{\mu_0}{4\pi} i \int \frac{d\vec{l} \times \hat{n}}{r^3}$$

We assume here that the orbit is definite and circular (i.e. in the Bohr description, not as in the Schrödinger description)

For a nucleus of charge $Ze$, and a revolution frequency $\omega$ and radius of the orbit $\vec{r}$, the magnetic field will be given by

$$I = Ze \frac{\omega}{2\pi} \quad ; \quad d\vec{l} \times \vec{r} = d\vec{r} \times \vec{r}$$
$$= \frac{d\vec{r}}{dt} \times \vec{r} \, dt$$

$$\therefore \quad \vec{B} = \frac{\mu_0}{4\pi} \frac{Ze\omega}{2\pi} \int \frac{d\vec{r}}{dt} \times \frac{\vec{r}}{r^3} \, dt$$

where the integral is over the entire orbit in time $0 < t < \frac{2\pi}{\omega}$

$$\therefore \quad \vec{B} = \frac{\mu_0}{4\pi} Ze \frac{\vec{v} \times \vec{r}}{r^3}$$

▶

$$= \frac{\mu_0}{4\pi} \frac{Ze}{m} \frac{\vec{L}}{r^3} \qquad \text{in the ref frame of the electron.}$$

When this quantity is transformed from the electron frame of ref back to the nuclear frame of reference we get an additional factor of ½ due to the fact that the ref frames are non-inertial

▶

$$\therefore \quad \vec{B}_{nucl} = \frac{\mu_0}{8\pi} \frac{Ze}{m} \frac{\vec{L}}{r^3} \qquad \text{in the "normal" or CoM or or nuclear ref. frame.}$$

we ignore the minor diff between CoM and nuclear frames

▶ The presence of a magnetic field at the site of the electron alone does not change the energy of the electron (magnetic field does no work on a charge)

▶ For the interaction to be non-zero, there must be a current loop or a magnetic dipole at the site of the electron.
~~This~~ Such a magnetic dipole was proposed for the electron following the experiments of Stern and Gerlach by Uhlenbeck and Gondsmit.

▶ The magnetic dipole moment of any current loop, is given by

$$\vec{\mu} = i\, \vec{A}$$

which the case of a circular path traced by a charged particle ~~p~~ can be written as (for uniform circular motion)

$$\vec{\mu} = q\, \frac{\omega}{2\pi} \cdot \pi r^2 \, \hat{\omega}$$

$$= \frac{q}{2m}\, \vec{L}$$

> SPECIAL CASE
> if $|L| = 1\hbar$ and $q = e$
> $m = m_e$
> $$|\mu| = \frac{e\hbar}{2m_e}$$
> is called the Bohr Magneton

▶ Uhlenbeck and Gondsmit proposed that the electron has a "spin" angular momentum (intrinsic to the electron, unrelated to its path in ~~any~~ any external reference) and a resultant spin magnetic dipole moment

$$\vec{\mu_c} = \frac{-e}{2m_e}\, \vec{s}$$

It is later found that this is incorrect in magnitude and should be written as

$$\vec{\mu_s} = -g_s\, \frac{e}{2m_e}\, \vec{s}$$

where $g = 2$ for relativistic consistency. as given by Dirac's theory

▶ Thus
$$\vec{\mu_s} = \frac{e}{m_e}\, \vec{s}$$

The interaction energy of the spin magnetic moment and the magnetic field due to the nucleus can now be calculationed:

▶ $$H_{int} = -\vec{\mu}_s \cdot \vec{B}_{nucl}$$

$$= + \frac{e}{m_e}\,\vec{s} \cdot \frac{\mu_0}{4\pi}\,\frac{Ze}{2m_e}\,\frac{\vec{L}}{r^3}$$

$$= + \frac{\mu_0}{4\pi}\,\frac{Ze^2}{2m_e^2\,r^3}\,\vec{L}\cdot\vec{s} \qquad\qquad (Z=1 \text{ for hydrogen})$$

This is called the spin-orbit interaction due to the apperance of $\vec{L}\cdot\vec{s}$
We recall that both $\vec{L}$ and $\vec{S}$ are quantised and we must take this into account in calculating $\vec{L}\cdot\vec{S}$. Let $\vec{J} = \vec{L} + \vec{S}$ be the net angular momentum of the electron (orbital + spin)

then $$\vec{J} = \vec{L} + \vec{S} \quad\Rightarrow\quad \vec{J}\cdot\vec{J} = \vec{L}\cdot\vec{L} + \vec{S}\cdot\vec{S} + 2\vec{L}\cdot\vec{S}$$

Hence $$J(J+1)\,\hbar^2 = \left[ L(L+1)\hbar^2 + s(s+1)\hbar^2 + 2\vec{L}\cdot\vec{s}\right]$$

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

Thus $\vec{L}\cdot\vec{S}$ is quantised.
The net interaction is

$$H_{int} = \frac{\mu_0}{4\pi}\,\frac{Ze^2}{2m_e^2 r^3}\,\frac{\hbar^2}{2}\left[ J(J+1) - L(L+1) - s(s+1)\right]$$

in which $S = \frac{1}{2}$ and $L$ is the orbital angular momentum as given by the Bohr-Schrödinger model.
For brevity the above expression is written as

$$H_{int} = \frac{A}{r^3}\left[ j(j+1) - \ell(\ell+1) - s(s+1)\right]$$

clearly, this takes multiple, discrete values.

Note now, that we have assumed that the electron is primarily in the electrostatic field of the nucleus, described the Schrödinger equation and in turn by the wavefunction

$$\Psi(\vec{r}) = R_{n\ell}(r)\, Y_{\ell m}(\theta, \phi)$$

▶ $\Psi$ is an energy eigenfunction, as also an angular momentum eigenfunction with eigenvalues $E_n$, $\ell(\ell+1)\hbar^2$, $m_\ell \hbar$ respectively.

But $\lambda$ ~~the~~ $\Psi$ is NOT an eigenfunction of $H_{int}$ describing the magnetic spin-orbit interaction.

the magnitude of $H_{int}$ is hence calculated as

$$\langle H_{int} \rangle = A\left[ J(J+1) - L(L+1) - S(S+1) \right] \left\langle \frac{1}{r^3} \right\rangle$$

where

$$\left\langle \frac{1}{r^3} \right\rangle = \left\langle \Psi_{n\ell m} \left| \frac{1}{r^3} \right| \psi_{n\ell m} \right\rangle$$

It can be shown that

▶ $$A\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{(Z\alpha)^4}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell+1)} \qquad \text{where} \quad \alpha = \frac{e^2}{(4\pi\epsilon_0)c\hbar}$$

If we instead took $1/r^3$ to simply have the value $(a_0 n^2)^{-3}$, then $A\left\langle \frac{1}{r^3} \right\rangle \sim \frac{(Z\alpha)^4}{n^3} mc^2$

Thus the spin-orbit interaction changes the energy levels by

▶ $$\langle H_{int} \rangle_{n\ell} = \frac{(Z\alpha)^4 \, mc^2}{n^3 \ell \left(\ell + \frac{1}{2}\right)(\ell+1)} \left[ J(J+1) - \ell(\ell+1) - s(s+1) \right]$$

where ~~~~~~~~~~~~~~ $j = \ell-s$ or $\ell+s$    for $\ell \geq 1$

$= s$    for $\ell = 0$

— This results in two energy levels. $j = \frac{1}{2}, \frac{3}{2}$

— Explains the doublets observed in the spectra.

Magnitude of the correction: ($H_\alpha$ line)

$$Z = 1 \quad, \quad \alpha = \frac{1}{137} \quad, \quad n = 2 \quad, \quad j = \frac{1}{2} \text{ or } \frac{3}{2}$$

$$\langle H_{int} \rangle \quad \sim \quad 10^{-4} \text{ eV}$$

Primary $H_\alpha$ line at 656.28 nm , splitting $\sim$ 0.014 nm !

The fine structure correction to the energy levels of H leads to the splitting of states with the same $\ell$ value into two states determined by their $j$ values : $j = \ell + \frac{1}{2}$, $\ell - \frac{1}{2}$. For $\ell = 0$ $j = \frac{1}{2}$ is the only possibility. Thus the fine structure energy levels are uniquely determined by their $n, \ell, j$ values.

This correction is due to the magnetic, or spin-orbit coupling. The correction due to spin orbit coupling is of order

$$\left\| \frac{(Z\alpha)^4}{n^3 \ell (\ell + \frac{1}{2})(\ell + 1)} \right.$$

there is another correction of the same order, namely the relativistic correction to the Kinetic energy of the electron.

▶ The relativistic Kinetic energy is given by

$$\left\| \begin{aligned} KE &= mc^2 - m_0 c^2 \\ &= [p^2 c^2 + m_0^2 c^4]^{1/2} - m_0 c^2 \\ &= \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \cdots \end{aligned} \right.$$

The correction to the electron energy level is

$$\Delta H_{rel} = - \langle \Psi_{n\ell m} | p^4 | \Psi_{n\ell m} \rangle \cdot \frac{1}{8m^3 c^2}$$

To calculate $\langle p^4 \rangle$ we note that

$$\left| p^4 = (p^2)^2 = [2m(E - V)]^2 \right.$$

$$\therefore \quad \langle p^4 \rangle = 4m^2 [E^2 - 2m E \langle V \rangle + \langle V^2 \rangle]$$

$$= 4m^2 \left[ E + 2E \frac{Ze^2}{4\pi\epsilon_0} \langle \frac{1}{r} \rangle + \left( \frac{Ze^2}{4\pi\epsilon_0} \right)^2 \langle \frac{1}{r^2} \rangle \right]$$
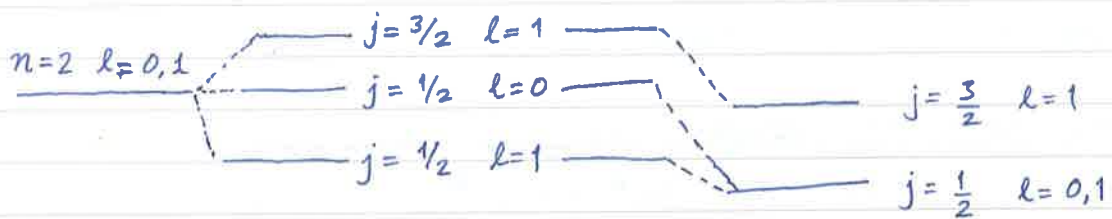
▶

$$\begin{aligned} \Delta H_{rel} &= \frac{-1}{8m_0^3 c^2} \langle p^4 \rangle \\ &= - (Z\alpha)^4 m_0 c^2 \frac{1}{2n^3} \left[ \frac{1}{\ell + \frac{1}{2}} - \frac{3}{4n} \right] \end{aligned}$$

The net correction to order $(Z\alpha)^4$ is

$$\Delta H = \Delta H_{SO} + \Delta H_{rel}$$

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

Thus the net correction to order $(Z\alpha)^4$ which includes the spin-orbit and first order relativistic mass correction is dependent only on $n$ and $j$. It does not depend on $l$.

$$n=2 \quad l=0,1$$

$j=3/2 \quad l=1$

$j=1/2 \quad l=0$

$j=1/2 \quad l=1$

$j=\frac{3}{2} \quad l=1$

$j=\frac{1}{2} \quad l=0,1$

Bohr/Schrö Energy

With S.O. correction

with relativistic correction

▶ The L-S coupling is the interaction of the electron spin with the magnetic field of the nucleus seen by the electron on account of its own orbital motion

▶ However, similar to the electron spin, the proton too has a spin and we must take into account the interaction between the proton spin magnetic moment and the orbital moment.

- The proton spin mag moment $\vec{\mu}_p = \gamma_p \dfrac{e}{2 M_p c} \vec{S}_p$ analogous to the electron but with a $\gamma_p$ pre-factor, the gyromagnetic ratio $\gamma_p = \cancel{5.58} \; 2.79$

- The magnetic field with which this spin moment interacts is the same as the one that is responsible for the fine structure i.e. electron-spin-orbit coupling without the Thomas factor
$$\vec{B}_{orb} = \left(\frac{\mu_0}{4\pi}\right) \frac{Ze}{m_e} \frac{\vec{l}}{r^3}$$

- Hence the interaction $H_{PSO} = -\vec{\mu}_p \cdot \vec{B}_{orb}$

$$= -\frac{\mu_0}{4\pi} \gamma_p \frac{Ze^2}{M_p m_e} \frac{1}{r^3 c} \vec{l} \cdot \vec{S}_p \quad \text{(MKS)}$$

(with $Z=1$ for p Hydrogen)

$$= \gamma_p \frac{Ze^2}{M_p m_e r^3 c^2} \vec{l} \cdot \vec{S}_p \quad \text{(CGS)}$$

▶ We have included so far only one part of the effect; we have not included the effect of the interaction of the nuclear (proton) spin with the electron spin. To calculate this we first need the magnetic field due to the proton spin moment at the site of the electron:

$$\vec{B}_{PSM} = \frac{\mu_0}{4\pi} \left\{ \frac{1}{r^3} \left[ 3 \frac{(\vec{\mu}_p \cdot \vec{r})\,\vec{r}}{r^2} - \vec{\mu}_p \right] + \frac{8\pi}{3} \vec{\mu}_p \, \delta(\vec{r}) \right\}$$

and the interaction energy is $H_{SS} = -\vec{\mu}_e \cdot \vec{B}_{PSM}$

$$H_{SS} = \frac{\mu_0}{4\pi} \frac{\gamma_p e^2}{m_e m_p c} \left\{ \frac{1}{r^3} \left[ 3(\vec{S}_p \cdot \hat{r})(\vec{S}_e \cdot \hat{r}) - \vec{S}_p \cdot \vec{S}_e \right] + \frac{8\pi}{3} (S_p \cdot S_e) \delta^3(\vec{r}) \right\}$$

The general expression for the shift in energy due to the nuclear (proton) spin magnetic ~~dipo~~ moment would require the calculation of $H_{PSO}$ and $H_{SS}$ expectation values

of these the $H_{PSO}$ term can be calculated analogous to the $H_{SO}$ fine structure calculation done earlier (which introduced the $j$ quantum number). In a similar manner, yet another angular momentum quantum number is now needed:

$$\vec{F} = \vec{J} + \vec{S}_p = \vec{L} + \vec{S}_p + \vec{S}_e$$

which has the familiar properties

$$\hat{F}^2 \Psi = f(f+1) \Psi \quad , \quad F_z \Psi = m_f \Psi$$

where $f = j \pm \frac{1}{2}$ (two values)

Thus the $H_{PSO}$ and $H_{SS}$ interactions together lead to further splitting of levels. The hyperfine splitting is the most important for the ~~s (ℓ=0) states, as~~ ~~it lift~~ ground state of the H atom. due to its astronomical relevance. For the ground state (or any $\ell=0$ state) the $H_{PSO}$ term vanishes since $\vec{\ell}=0$. In the second contribution $H_{SS}$ only the $\delta$-function term is non-zero, the first term averages out to zero.

$$\therefore \Delta E_{HFS} = \langle H_{SS} \rangle = \frac{\mu_0}{4\pi} \frac{\gamma_p e^2}{m_e m_p c} \cdot \frac{8\pi}{3} \langle 1s | S_p \cdot S_e | 1s \rangle$$

since for the ground state $L=0$, $F^2 = S_e^2 + S_p^2 + 2 S_p \cdot S_e$

$$\vec{S}_p \cdot \vec{S}_e = \frac{\hbar^2}{2} \left[ f(f+1) - s_p(s_p+1) - s_e(s_e+1) \right]$$

$$= \frac{\hbar^2}{2} \left[ f(f+1) - \frac{3}{2} \right]$$

Thus $\Delta E_{HFS} = \frac{m_e}{M_p} \alpha^4 mc^2 \frac{4\gamma_p}{3n^3} \left[ f(f+1) - \frac{3}{2} \right]$

for the ground state.

▶ For the ground state this works out to

$$\Delta E_{HFS} = 5.9 \times 10^{-6} \, eV \qquad 1s, \ \ell=0, \ f=1 \rightarrow f=0$$

This difference corresponds to $\nu = 1420 \, MHz$ or $\lambda = 21 \, cm$. This transition is one of the most important lines in the astrophysical context.

▶ For $\ell \neq 0$ the HFS splitting works out to

$$\Delta E_{HFS} = \frac{m_e}{m_p} \ \alpha^4 \ mc^2 \frac{r_p}{2n^3} \frac{\pm 1}{(f+\frac{1}{2})(\ell+\frac{1}{2})}$$

## LAMB SHIFT AND THE DARWIN TERM

Yet another set of corrections apply to each of the FS & HFS corrections are found.

The ·Darwin term corresponds to the zitterbewegung for $\ell=0$ states and gives $\quad \langle H_d \rangle = (Z\alpha)^4 \ mc^2 \frac{1}{2n3}$

while the lamb shift is due to QED effects

$$\langle H_{lamb} \rangle = \alpha^5 mc^2 \frac{1}{4n^3} \left[ K(n,\ell) \pm \frac{1}{\pi(j+\frac{1}{2})(\ell+\frac{1}{2})} \right]$$

## COMPLETE FINE STRUCTURE AND DIRAC THEORY

$$E_{nj} = m_0 c^2 \left\{ 1 - \frac{1}{2} \frac{(Z\alpha)^2}{n^2} \left[ 1 + \frac{(Z\alpha)^2}{n} \left( \frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right) \right] + \cdots \right\}$$