10. The Hydrogen Atom

10.1 The Ideal Hydrogen Atom

(Gesiarowickz, 8)

The electron moves in the electrostatic field due to the proton (a central potential).

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}.$$

Let $\mu_e =$ the mass of the electron. The TISE is

$$\left[-\frac{\hbar^2}{2\mu_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi(\underline{r}) = E\psi(\underline{r}).$$

$$\psi(\underline{r}) = R_{k,\ell}(r)Y_{\ell,m_\ell}(\theta,\phi),$$

where

$$\left[-\frac{\hbar^2}{2\mu_e}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right) - \frac{e^2}{4\pi\varepsilon_0 r}\right]R_{k,\ell}(r) = E_{k,\ell}R_{k,\ell}(r).$$

We consider bound states of the electron.

$$E_{k,\ell} < 0,$$

$$R_{k,\ell}(r) = \sum_i a_i r^i.$$

For the solution not to diverge for $r >> 1$, the series has to be finite $(a_i = 0, i \geq p)$, where p is the maximum value we want to consider. This gives a constraint on the number of different solutions for a given ℓ.

$$k + \ell = 1,2,3,...$$

$$k = 1,2,3,...$$

We know

$$\ell = 0,1,2,3,...$$

$$n \equiv k + \ell = 1,2,3,...$$

$$\ell = 0,1,2,...,n-1$$

So we know that the energy can be represented as,

$$E_{k,\ell} = E_n = -\frac{E_I}{n^2}$$

where

$$E_I = \frac{\mu_e e^4}{2\hbar^2(4\pi\varepsilon_0)^2} \approx 13.6eV.$$

Degeneracy of E_n can be represented as, for a given n,

$$\ell = 0,1,..,n-1$$

$$m_\ell = -\ell, -\ell+1, ..., \ell$$

which is $2\ell + 1$ values.

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

We haven't taken the spin into account yet - $\left[\hat{H}_c, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z\right]$ are compatible observables, and we have previously only considered $\left\{\hat{H}_c, \hat{L}^2, \hat{L}_z\right\}$. $s = \frac{1}{2}$ for the electron, so $m_s = \frac{1}{2}, -\frac{1}{2}$. Eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$ are

$$|s, m_s\rangle = \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle, \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle.$$

So we will gain a factor of 2 in the previous equation, i.e. $2n^2$ eigenfunctions.

Remember that we define the total angular momentum as

$$\underline{J} = \underline{L} + \underline{S},$$

$$\left\{\hat{H}_C, \hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2\right\}.$$

We expect to still have degeneracy of $2n^2$ eigenfunctions.

Let $\hat{H}_c = \hat{H}_0$ for the ideal hydrogen atom.

Compatible observables	Eigenfunctions
$\hat{H}_0, \hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z$	$\lvert n, \ell, m_\ell m_s\rangle$ $\left(s = \frac{1}{2}\right)$, usually not written.
$\hat{H}_0, \hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$	$\lvert n, j, m, \ell\rangle$ $\left(s = \frac{1}{2}\right)$

$$\langle n, \ell, m_\ell, m_s | n', \ell', m_\ell', m_s'\rangle = \delta_{nn'}\delta_{\ell\ell'}\delta_{m_\ell m_\ell'}\delta_{m_s m_s'}$$

n	ℓ	m_ℓ	m_s	Number of states
1	0	0	$-\frac{1}{2}, \frac{1}{2}$	2
2	0	0	$-\frac{1}{2}, \frac{1}{2}$	8
	1	$-1, 0, 1$	$-\frac{1}{2}, \frac{1}{2}$	
3				18

n	j	m	ℓ	Number of states
1	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	0	2
2	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	0	8
	$\frac{1}{2}$	$-\frac{1}{2}, \frac{1}{2}$	1	
	$\frac{3}{2}$	$-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$		
3				18

NB:

$j = \ell + s, \ell + s - 1, \ldots, |\ell - s|$

$-j \le m \le j$
$-\ell \le m_\ell \le \ell$

10.2 Fine Structure Corrections

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$a_0 = \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{\mu_e}$$

The uncertainty in the momentum is

$$p_0 \approx \frac{\hbar}{a_0} = \alpha\mu_e c$$

where $\alpha =$ structure constant.

$$a \approx \frac{v}{c} = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}$$

If the electron has momentum p, then the total energy

$$E = c\sqrt{\mu_e^{\,2}c^2 + p^2} = c^2\mu_e\sqrt{\frac{p^2}{c^2\mu_e^{\,2}} + 1}$$

(Remember $E^2 = p^2c^2 + m^2c^4$)
Expanding this gives

$$E = \mu_e c^2 + \frac{p^2}{2\mu_e} - \frac{p^4}{8\mu_e^{\,3}c^2} + \ldots$$

This gives the first relativistic correction. Taking the ratio of the second and third terms gives

$$\frac{\dfrac{p^4}{8\mu_e^{\,2}c^2}}{\dfrac{p^2}{2\mu_e}} = \frac{p^2}{4\mu_e c^2} = \frac{1}{4}\left(\frac{v}{c}\right)^2 \approx \alpha^2,$$

so it is only a small correction. How does this change the expectation value for the energy? $\hat{H}_R$ represents this change.

$$\hat{H}_R = -\frac{1}{2\mu_e c^2}\left(\frac{\hat{P}^2}{2\mu_e}\right)^2 = -\frac{1}{2\mu_e c^2}\left(\hat{H}_0 + \frac{e^2}{4\pi\varepsilon_0 r}\right)^2$$

$$\left\langle \hat{H}_R \right\rangle = E_R = \left\langle n, j, m, \ell \right| \hat{H}_R \left| n, j, m, \ell \right\rangle$$

$$= \frac{1}{2\mu_e c^2}\left[\underbrace{\left\langle H_0^{\,2}\right\rangle}_{E_n^{\,2}} + 2\underbrace{\left\langle H_0 \right\rangle}_{E_n}\left\langle \frac{e^2}{4\pi\varepsilon_0 r}\right\rangle + \left\langle \left(\frac{e^2}{4\pi\varepsilon_0 r}\right)^2 \right\rangle\right]$$

To figure out the last two brackets, we need to figure out $\left\langle r^{-1}\right\rangle$ and $\left\langle r^{-2}\right\rangle$.

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0 n^2}$$

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

So we can now write

$$\langle H_R \rangle = -\frac{|E_n|}{n}\alpha^2\left(\frac{2}{2\ell+1} - \frac{3}{4n}\right)$$

So the correction provides an energy that depends on ℓ and n. If we take $n = 2$, then we get values of $\ell = 0,1$. Instead of having just one energy level at E_n, we now have two at $\hat{H}_0 + \hat{H}_R$, one for each of the two possible ℓ states.

10.3 Spin-Orbit Corrections

$\underline{E}$: electrostatic field due to the proton.

In the frame of the electron moving with velocity $\underline{v}$, we see a magnetic field given by

$$\underline{B} = \frac{1}{c^2}\underline{v} \times \underline{E}.$$

$\phi(r)$: electrostatic potential due to the proton.

$$\underline{E} = -\nabla\phi = -\frac{\underline{r}}{r}\frac{d\phi}{dr},$$

$$\underline{B} = \frac{1}{c^2 r}\frac{d\phi}{dr}\underline{v} \times \underline{r}.$$

Using the momentum of the electron, we can write

$$\underline{B} = \frac{1}{rc^2\mu_e}\frac{d\phi}{dr}\underline{p} \times \underline{r},$$

where we can write $\underline{p} \times \underline{r} = \underline{\ell}$. In QM, we write

$$\underline{B} = \frac{1}{rc^2\mu_e}\frac{d\phi}{dr}\hat{\underline{L}}.$$

The magnetic momentum associated to the spin is

$$\hat{\underline{M}}_s = -\frac{e}{\mu_e}\hat{\underline{S}}.$$

The interaction of $\hat{\underline{M}}_s$ with $\underline{B}$ gives a contribution

$$\hat{H}_{SO} = -\underline{B} \cdot \hat{\underline{M}}_s$$

In the case of a hydrogen atom, we have

$$\phi(r) = \frac{e}{4\pi\varepsilon_0 r}$$

so we get

$$\hat{H}_{SO} = \frac{1}{2}\frac{e^2}{\mu_e{}^2 c^2 4\pi\varepsilon_0 r^3}\hat{\underline{L}} \cdot \hat{\underline{S}}$$

The half comes from relativistic effects. In can be found using the relativistic Schrödinger equation.

$$\left[\hat{\underline{L}} \cdot \hat{\underline{S}}, \hat{L}_z\right] \neq 0$$

$$\left[\hat{\underline{L}} \cdot \hat{\underline{S}}, \hat{S}_z\right] \neq 0$$

So the eigenfunctions $|n, \ell, m_\ell, m_s\rangle$ are not eigenfunctions of $\hat{H}_{SO}$. We can write

$$\underline{L} \cdot \underline{S} = \frac{\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)}{2}$$

so we can use the other set of eigenfunctions, $|n, j, m, \ell\rangle$ as eigenfunctions of $\hat{H}_{S0}$.
We can write the expectation value of H_{S0} as

$$E_{S0} = \langle H_{S0} \rangle = \langle n, j, m, \ell | \hat{H}_{S0} | n, j, m, \ell \rangle$$

$$E_{S0} = \frac{\hbar^2}{4} \frac{e^2}{\mu_e^{\,2} c^2 4\pi\varepsilon_0} \left[j(j+1) - \ell(\ell+1) - s(s+1) \right] \left\langle \frac{1}{r^3} \right\rangle$$

We can find that

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

where $\ell \neq 0$. We can rearrange E_{S0} such that

$$E_{S0} = \frac{|E_n|}{n} \alpha^2 \left(\frac{2}{2\ell+1} - \frac{2}{2j+1} \right)$$

We can make an estimate of the orbital magnitude to get a feel for how significant this is. $\underline{L} \sim \hbar$, $\underline{S} \sim \hbar$, $r \sim a_0$.

$$E_{S0} \sim \frac{e^2}{4\pi\varepsilon_0 \mu_e^{\,2}} \frac{\hbar^2}{a_0^{\,3}}$$

Comparing this with the standard energy gives

$$\frac{E_{S0}}{\dfrac{e^2}{a_0 4\pi\varepsilon_0}} \approx \frac{\hbar^2}{\mu_e^{\,2} e^2 a_0^{\,2}} = \alpha^2 .$$

We normally put these two perturbations into one correction, the fine structure correction E_F.

$$E_F = E_R + E_{S0} = \frac{|E_n|}{n} \alpha^2 \left(\frac{3}{4n} - \frac{2}{2j+1} \right)$$

This depends on n and j, not ℓ any more. It can be proven that it is also valid for $\ell = 0$.

10.4 The Anomalous Zeeman Effect

Magnetic moment associated to $\hat{L}$ is

$$\underline{\hat{M}_L} = -\frac{e}{2\mu_e} \underline{\hat{L}},$$

which is proportional to the angular momentum. The magnetic moment is associated to the spin.

$$\underline{\hat{M}_s} = -\frac{e}{\mu_e} \underline{\hat{S}}$$

In the presence of an external magnetic field $\underline{B}$,

$$\hat{H}_m = -\underline{B} \cdot \underline{\hat{M}_L} - \underline{B} \cdot \underline{\hat{M}_s} = -\underline{B}\left(\underline{\hat{M}_L} + \underline{\hat{M}_s} \right)$$

For $\underline{B}$ in the "Z" direction:

$$\hat{H}_m = \frac{eB}{2\mu_e} \left(\hat{L}_z + 2\hat{S}_z \right)$$

(the 2 is from spin degeneracy?)

Taking the energy to be the expectation value of $\hat{H}_m$:

$$E_m = \langle H_m \rangle = \frac{eB}{2\mu_e}\left(\langle L_z \rangle + 2\langle S_z \rangle\right).$$

This is around $10^{-4}\frac{eV}{T}B$. Remember that for fine splitting, $\langle H_F \rangle \approx 10^{-4}eV$. So if we have around 1T of magnetic field, then this contribution will be comparable to that from fine splitting. If it is a lot smaller than 1 Telsa, then it is just a small correction. On the other extreme, if the magnetic field is larger than 1 Tesla then we can neglect the fine splitting contribution. We will now look at these two extremes.

10.4.1 Strong Magnetic Field

For $B >> 1T$, $\hat{H}_m >> \hat{H}_F$.

We can neglect $\hat{H}_F$ and consider the Hamiltonian to be $\hat{H}_0 + \hat{H}_m$.

From before, we have

$$\hat{H}_m = \frac{eB}{2\mu_e}\left(\hat{L}_z + 2\hat{S}_z\right).$$

$|n,\ell,m_\ell,m_s\rangle$ are eigenfunctions of $\hat{H}_m$, and then of $\hat{H}_0 + \hat{H}_m$. The energy from the magnetic field will be

$$\langle H_m \rangle = \langle n,\ell,m_\ell,m_s | \hat{H}_m | n,\ell,m_\ell,m_s \rangle = \frac{eB}{2\mu_e}\left(\langle L_z \rangle + 2\langle S_z \rangle\right) = \frac{eB}{2\mu_e}\left(m_\ell\hbar + 2m_s\hbar\right)$$

so the total energy will be

$$\langle H_0 + H_m \rangle = E_n + \frac{eB\hbar}{2\mu_e}\left(m_\ell + 2m_s\right)$$

10.4.2 Weak Magnetic Field

For $B << 1T$, $\hat{H}_m << \hat{H}_F$.

$\hat{H}_m$ gives a small correction to the energy levels of $\hat{H}_0 + \hat{H}_f$.

Eigenfunctions	$\hat{H}_0$	$\hat{H}_F$	$\hat{H}_m$
$\|n,\ell,m_\ell,m_s\rangle$	Yes	No	Yes
$\|n,j,m,\ell\rangle$	Yes	Yes	No

Remember that:

$\left[\hat{J}^2, L_z\right] \neq 0$

$\left[\hat{J}^2, S_z\right] \neq 0$

For the first line, the compatible observables are:

$\left\{\hat{H}_0 + \hat{H}_F, \hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2\right\}$

So for example, $\left[\hat{H}_0 + \hat{H}_F, \hat{J}_z\right] = 0$, and also $\left[\hat{H}_0 + \hat{H}_F, \hat{J}_Y\right] = \left[\hat{H}_0 + \hat{H}_F, \hat{J}_x\right] = 0$.

So $\left[\hat{H}_0 + \hat{H}_F, \underline{\hat{J}}\right] = 0$. So $\underline{J}$ is a constant of motion.

$\left[\hat{H}_0 + \hat{H}_F, \hat{L}^2\right] = 0$

$\left[\hat{H}_0 + \hat{H}_F, \hat{S}^2\right] = 0$

So $\|S\|$ is the constant of motion.
Also, $\|L\|$ is the constant of motion.

We then have $\underline{J} = \underline{L} + \underline{S}$.
As $\underline{J}$ is fixed, then all $\underline{L}$ and $\underline{S}$ can do is precess around $\underline{J}$.
Let $\underline{L_{\|}}$ and $\underline{S_{\|}}$ be the components of $\underline{L}$ and $\underline{S}$ in the direction of $\underline{J}$.

$$\langle \underline{L} \rangle = \underline{L_{\|}}$$

$$\langle \underline{S} \rangle = \underline{S_{\|}}$$

$$\underline{L_{\|}} = \frac{(\underline{L} \cdot \underline{J})\underline{J}}{\|\underline{J}\|^2}$$

$$\underline{S_{\|}} = \frac{(\underline{S} \cdot \underline{J})\underline{J}}{\|\underline{J}\|^2}$$

We will now use these results in QM using operators.

$$\langle H_m \rangle = \frac{eB}{2\mu_e}\left(\langle L_z \rangle + 2\langle S_z \rangle\right)$$

$$\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}} \to \hat{J}_z = \hat{L}_z + \hat{S}_z$$

$$\langle H_m \rangle = \frac{eB}{2\mu_e}\left(\langle J_z \rangle + \langle S_z \rangle\right)$$

$$\langle S_z \rangle = \frac{\langle \underline{S} \cdot \underline{J} \rangle}{\langle \hat{J}^2 \rangle}\langle J_z \rangle$$

For the state $|n, j, m, \ell\rangle$;

$$\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}} \to \underline{L} = \underline{J} - \underline{S}$$

$$\hat{L}^2 = \hat{J}^2 + \hat{S}^2 - 2\underline{\hat{J}} \cdot \underline{\hat{S}}$$

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

$$\langle \underline{\hat{J}} \cdot \underline{\hat{S}} \rangle = \frac{1}{2}\left[\langle \hat{J}^2 \rangle + \langle \hat{S}^2 \rangle - \langle \hat{L}^2 \rangle\right]$$

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

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

$$\langle H_m \rangle = \frac{eB}{2\mu_e}\left[\langle J_z \rangle + \langle S_z \rangle\right] = \frac{eB}{2\mu_e} g m\hbar$$

g is called the Lambé factor.

$$g = 1 + \frac{\left[j(j+1) + \tfrac{3}{4} - \ell(\ell+1)\right]}{2j(j+1)}$$

Example: Energy levels and degeneracy for $n = 2$

1) $\hat{H}_0$ eigenfunctions, $|n,\ell,m_\ell,m_s\rangle$ or $|n,j,m,\ell\rangle$

Energy $E_n = -\frac{E_i}{n^2}$, so only one possible energy.

E_n	Degeneracy $2n^2$
E_2	8

2) $\hat{H}_0 + \hat{H}_F$, eigenfunctions $|n,j,m,\ell\rangle$

Energy: $E_n + E_F(n,j) = E_2 + E_F(j)$

$n=2$, $\ell = 0,...,n-1$, so $\ell = 0,1$.

$j = \ell + s,...,|\ell - s|$.

$\ell = 0$, $j = \frac{1}{2}$

$\ell = 1$, $j = \frac{3}{2},...,\frac{1}{2}$ in steps of 1 → only $\frac{3}{2}$ and $\frac{1}{2}$

$-j \le m \le j$

J	m	ℓ
$\frac{1}{2}$	$-\frac{1}{2},\frac{1}{2}$	0, 1
$\frac{3}{2}$	$-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}$	1

$E_2 + E_F(j)$	Degeneracy $2n^2$
$E_2 + E_F\left(\frac{1}{2}\right)$	4
$E_2 + E_F\left(\frac{3}{2}\right)$	4

3) Weak Zeeman Effect

$\hat{H}_0 + \hat{H}_F + \hat{H}_m$, $|n,j,m,\ell\rangle$

$E = E_n + E_F(n,j) + E_m(j,\ell,m)$

$E_m = \mu_B Bgm$, where $g = \frac{1 + j(j+1) + \frac{3}{4} - \ell(\ell+1)}{2j(j+1)}$

j	m	ℓ	g	mg
$\frac{1}{2}$	$-\frac{1}{2},\frac{1}{2}$	0,1	$2,\frac{2}{3}$	$-1,1,-\frac{1}{3},\frac{1}{3}$
$\frac{3}{2}$	$-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2}$	1	$\frac{4}{3}$	$-2,-\frac{2}{3},\frac{2}{3},2$

The energy level E_2 splits into 8 energy levels, with degeneracy 1.

4) Zeeman Effect – Strong Magnetic Field

$\hat{H}_0 + \hat{H}_m$, eigenfunction $|n,\ell,m_\ell,m_s\rangle$.

Energy $E = E_2 + E_m(m_\ell,m_s)$

$E_m = \mu_B B(m_\ell + 2m_s)$

ℓ	m_ℓ	m_s	$m_\ell + 2m_s$
0	0	$-\frac{1}{2}, \frac{1}{2}$	$-1, 1$
1	$-1, 0, 1$	$-\frac{1}{2}, \frac{1}{2}$	$-2, 0, -1, 1, 0, 2$

E_m / μ_B	Degeneracy
-2	1
-1	2
0	2
1	2
2	1

The energy level E_2 is split into 5.