Chapter 7 The Hydrogen Atom in Wave Mechanics

From the end of Chap 5, the 3D time independent Schrodinger eq gives

$$H\Psi = E\Psi \rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right)+U(x,y,z)\Psi(x,y,z)=E\,\Psi(x,y,z)$$

If the potential energy is spherically symmetric, you should use spherical coordinates instead of cartesian (Chap 7 slide 1)

Because the PE is only a function of r $U(x,y,z)=U(r)$ the energy eigenstates can have the form

$$\Psi(r,\theta,\phi)=R_{n_\ell}(r)\,\Theta_{\ell,m_\ell}(\theta)\,\Phi_{m_\ell}(\phi)$$

To understand what this is trying to tell us, go back to classical mechanics (Chap 7 slide 2)

What causes a time dependent angular momentum

$$\frac{d\vec{L}}{dt}=\frac{d}{dt}(\vec{r}\times\vec{p})=\frac{d\vec{r}}{dt}\times\vec{p}+\vec{r}\times\frac{d\vec{p}}{dt}=0+\vec{r}\times\vec{F}=\vec{\tau}$$ torque

(Chap 7 slides 3, 4)

What is the quantum mechanical version of $\vec{L}$?

$$L_{x,op}=y\,P_{z,op}-z\,P_{y,op}=y\frac{\hbar}{i}\frac{\partial}{\partial z}-z\frac{\hbar}{i}\frac{\partial}{\partial y}$$
$$L_{y,op}=z\frac{\hbar}{i}\frac{\partial}{\partial x}-x\frac{\hbar}{i}\frac{\partial}{\partial z}$$
$$L_{z,op}=x\frac{\hbar}{i}\frac{\partial}{\partial y}-y\frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$(L_{x,op}\,r)=y\frac{\hbar}{i}\frac{\partial r}{\partial z}-z\frac{\hbar}{i}\frac{\partial r}{\partial y}=y\frac{\hbar}{i}\frac{z}{r}-z\frac{\hbar}{i}\frac{y}{r}=0$$

similar for $L_{y,op}$ and $L_{z,op}$

$$(L_{x,op}R(r))=y\frac{\hbar}{i}\frac{\partial R(r)}{\partial z}-z\frac{\hbar}{i}\frac{\partial R(r)}{\partial y}=y\frac{\hbar}{i}\frac{dR(r)}{dr}\frac{\partial r}{\partial z}-z\frac{\hbar}{i}\frac{dR(r)}{dr}\frac{\partial r}{\partial y}=0$$

There are some peculiar properties of the angular momentum. In classical mechanics, L_x, L_y, L_z are separately well defined. In QM, the eigenstates of one component of $\vec{L}_{op}$ is <u>not</u> an eigenstate of either of the other two.

$$L_{x,op}(y+iz)^a = y\frac{\hbar}{i}\frac{\partial}{\partial z}(y+iz)^a - z\frac{\hbar}{i}\frac{\partial}{\partial y}(y+iz)^a$$

$$= y\frac{\hbar}{i}\,i\,a(y+iz)^{a-1} - z\frac{\hbar}{i}\,a(y+iz)^{a-1}$$

$$= \hbar a(y+iz)^{a-1}(y+iz) = \hbar a(y+iz)^a$$

This means $(y+iz)^a$ is an eigenstate of $L_{x,op}$ with eigenvalue $\hbar a$. To be continuous a = integer ≥ 0
Show $(y-iz)^a$ is an eigenstate with eigenvalue $-\hbar a$ with a = integer ≥ 0

The eigenstates and eigenvalues are $L_{y,op}(z \pm ix)^b = \pm \hbar b (z \pm ix)$
$L_{z,op}(x \pm iy)^{m_\ell} = \pm \hbar m_\ell (x \pm iy)^{m_\ell}$

For conventions (Chap 7 slides 5-8)

The θ, ϕ part of $\psi(r,\theta,\phi) = R_{n\ell}(r)\,\Theta_{\ell,m_\ell}(\theta)\,\Phi_{m_\ell}(\phi)$
The equation that determines $R_{n\ell}(r)$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R_{n\ell}}{dr^2} + \frac{2}{r}\frac{dR_{n\ell}(r)}{dr}\right) + \left(U(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right)R_{n\ell}(r) = E_{n\ell}R_{n\ell}(r)$$

For hydrogen $U(r) = -\frac{ke^2}{r}$ $\Rightarrow$ $E_{n\ell} = -\frac{ke^2}{2a_0}\frac{1}{n^2} = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$ etc
(Chap 7 slide 9, 10)

The volume element $dx\,dy\,dz = r^2\sin\theta\,dr\,d\theta\,d\phi$

The radial probability density

$$P(r)\,dr = \int_{\text{all angles}} r^2 |R_{n\ell}(r)|^2 |\Theta_{\ell m_\ell}(\theta)|^2 |\Phi_{m_\ell}(\phi)|^2 \sin\theta\,d\theta\,d\phi\,dr$$

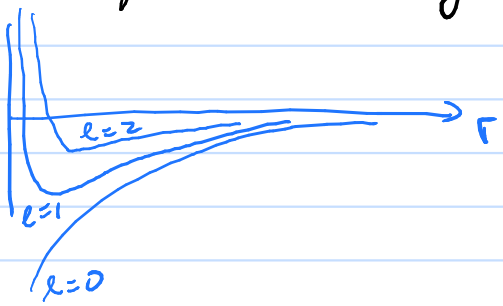
$$= r^2 |R_{n\ell}(r)|^2 dr$$

For hydrogen atom, the number of radial nodes = $n-\ell-1$

Important notation $\ell=0 \rightarrow$ "s", $\ell=1 \rightarrow$ "p", $\ell=2 \rightarrow$ "d"
$\ell=3 \rightarrow$ "f", $\ell=4 \rightarrow$ "g", (the rest are alphabetical)

1s	$n=1, \ell=0, m=0$	rad nodes	0
2s	$n=2, \ell=0, m=0$	" "	1
2p	$n=2, \ell=1, m=-1,0,1$	" "	0
3s	$n=3, \ell=0, m=0$	" "	2
3p	$n=3, \ell=1, m=-1,0,1$	" "	1
3d	$n=3, \ell=2, m=-2,-1,0,1,2$	" "	0

Important aspect: higher ℓ means probability density is pushed further out by centrifugal force



$$U_{eff}(r) = U(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}$$

Another important feature: one photon absorbed or emitted can change n by amount depending on energy of photon

$$hf = -\frac{13.6\,eV}{n_i^2} - \left(-\frac{13.6\,eV}{n_f^2}\right)$$

Emit $n_i > n_f$
Absorb $n_i < n_f$

By far strongest transitions $\Delta\ell = 1$ or -1, $\Delta m = -1, 0, 1$
$\ell=0 \rightarrow \ell=0$ forbidden

The electron and the proton have intrinsic angular momentum that is called Spin

$$L_{op}^2 Y_{\ell m_\ell}(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_{\ell m_\ell}(\theta,\phi) \qquad L_{z,op} Y_{\ell m_\ell}(\theta,\phi) = \hbar m_\ell Y_{\ell m_\ell}(\theta,\phi)$$

$$S_{op}^2 \chi_{s,m_s} = \hbar^2 s(s+1) \chi_{s,m_s} \qquad S_{z,op} \chi_{s,m_s} = \hbar m_s \chi_{s,m_s}$$

$m_s = -s, -s+1, \ldots, s-1, s$

Electrons, protons, neutrinos, quarks have $s = 1/2$

Some composite particles are tightly bound enough to be considered an object with a spin

$^4He_2$ atom $s = 0$

Deuterium nucleus $s = 1$

^{13}C nucleus $s = 1/2$

The ground state of the hydrogen atom is actually 4 states = 3 states ($S_{tot} = 1$) and 1 state ($S_{tot} = 0$). These energies are separated by 1420.40... MHz $\rightarrow \lambda_{light} = 21$ cm

Can be used to map H atoms in the universe.

The quantization of the angular momentum and spin can be easily observed using magnetic fields. The classical magnetic dipole moment for an electron

$$\vec{\mu} = iA = \frac{q}{2m}\vec{L} \qquad \vec{\mu} = -\frac{e}{2m}\vec{L}$$

The quantum scale of $\mu = \mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24}\ \frac{J}{T}$

Bohr magneton $= 0.672\ \frac{K}{T}\ k_B$ ← Boltzmann

The intrinsic magnetic moment of electron is

$\vec{\mu}_e = -g\frac{e}{2m}\vec{S}_e$ $\quad g \cong 2$ can be calculated!!

The corrections to $g = 2$ tested by current experiments.

There is a potential energy associated with a magnetic dipole in a magnetic field

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

This can lead to forces on the object if $\vec{B}$ depends on position

$\vec{F} = -\vec{\nabla} PE$ from classical

More interesting is the size and sign of the force depends on the quantum state.
The Stern-Gerlach experiment showed the quantization of angular momentum. It also shows how to go from quantization in x from that in z. (Chap 7 slide 11)

If the atom has low enough center of mass energy and the magnetic field has a minimum in $|\vec{B}|$, the atom can be trapped by the magnetic field. (Chap 7 slides 12-15)

The proton magnetic dipole moment is much smaller than the electrons. The electrons in most condensed matter are forced by ~1eV scale energies to anti align with each other - mostly canceling out.

$$H = -\vec{\mu}\cdot\vec{B} = -|\mu|\frac{\vec{S}\cdot\vec{B}}{|S|}$$

Define z-direction to be $\hat{B} \rightarrow \vec{B} = B\hat{z}$

$$H\chi_{s,m_s} = -|\mu|\frac{1}{|S|}B S_z \chi_{s,m_s} = -\frac{|\mu|}{\hbar s} B \hbar m_s \chi_{s,m_s}$$

The energy separation is proportional to B with a well known slope. The corrections to the slope depend on material near proton. NMR/MRI pages

Recently, great interest in the highly excited states of atoms. The $\ell=0, 1$, maybe 2, maybe 3 have somewhat different energy due to core electron Li^+, Na^+, Rb^+, Cs^+ (Chap 7 Slide 16)

New kind of molecule (Chap 7 Slide 17)