Intro to Quantum Mechanics II

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This is an advanced undergraduate course, offered in spring 2013 at Columbia University. Required Course textbook: Griffiths, *Introduction to Quantum Mechanics.* Office Hours Tu 12:00-2:00.

Contents

1 Identical Particles

1.1 Continue from Last Semester

Lecture 1 (1/22/13)

Last semester, we finished Griffiths chapters 1-4. We ended with spin-angular momentum coupling.

Spin

$[S_x, S_y] = i\hbar S_z$, $[S_y, S_z] = i\hbar S_x$, $[S_z, S_x] = i\hbar S_y$

$\vec{S}^2 = S_x^2 + S_y^2 + S_z^2 = \hbar^2 s(s+1)$, where $s = 0, 1/2, 1, 3/2...$ s is fixed for particular particle, e.g $s = 0$ Higgs Bosons, $s = 1/2$ electrons, $s = 1$ photons. s integer are Bosons, s half integer are Fermions

Choose z direction $S_z = \hbar m_s$, where $m_s = s, s-1, ..., -s$.

Example. Electrons

$s = 1/2$, and $m_s = \pm 1/2$.

wave function $\psi(\vec{r}, s) = \psi(\vec{r}, m_s) = f_+\chi_+ + f_-\chi_- = \begin{pmatrix} f_+ \\ f_- \end{pmatrix}$ (note we write $\psi(\vec{r}, s)$, but we actually mean $\psi(\vec{r}, m_s)$)

Recall Normalization for no spin wave function,

$$1 = \int d^3r \, |\psi(\vec{r})|^2$$

For spin 1/2

$$1 = \int d^3r (|f_+|^2 + |f_-|^2)$$

If $\psi = F(r)(a\chi_+ + b\chi_-)$,

$$1 = \int d^3r \, |F(r)|^2 \, (|a|^2 + |b|^2)$$

Angular Momentum

$$\vec{L} = \vec{r} \times \vec{P}$$

$[L_x, L_y] = i\hbar L_z$ etc

$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2 = \hbar^2 l(l+1)$,where $l = 0, 1, 2, 3...$
$L_z = \hbar m_l$, where $m_l = l, l-1, ..., -l$.

Spin-Angular Momentum Coupling

$$\vec{J} = \vec{L} + \vec{S}$$

$[J_x, J_y] = i\hbar J_z$ etc
$\vec{J}^2 = J_x^2 + J_y^2 + J_z^2 = \hbar^2 j(j+1)$,where

$$j = l + s, l + s - 1, ..., |l - s| \tag{1.1}$$

$J_z = \hbar m_j$, where $m_j = j, j-1, ..., -j$.

$$m_j = m_s + m_l$$

Example. Electron in Hydrogen
1s,2s,3s... $l = 0$, $s = 1/2 \implies j = 1/2$
2p,3p,4p,...$l = 1$, $s = 1/2 \implies j = 3/2,\ 1/2$
3d,4d,5d,...$l = 2$, $s = 1/2 \implies j = 5/2,\ 3/2$

Proof. (sketchy proof of (1.1)) Consider $l = 1$, $s = 1/2$ there are 6 states

$$\left|m_l = 1\, m_s = \frac{1}{2}\right\rangle \implies m_j = \frac{3}{2}$$

$$\left|m_l = 1\, m_s = -\frac{1}{2}\right\rangle \implies m_j = \frac{1}{2}$$

$$\left|m_l = 0\, m_s = \frac{1}{2}\right\rangle \implies m_j = \frac{1}{2}$$

$$\left|m_l = 0\, m_s = -\frac{1}{2}\right\rangle \implies m_j = -\frac{1}{2}$$

$$\left|m_l = -1\, m_s = \frac{1}{2}\right\rangle \implies m_j = -\frac{1}{2}$$

$$\left|m_l = -1\, m_s = -\frac{1}{2}\right\rangle \implies m_j = -\frac{3}{2}$$

so the top and last states must have $j = 3/2$, but the middle four can be $j = 1/2$ or $j = 3/2$. That is

$$\left| j = \frac{3}{2}\, m_j = \frac{3}{2} \right\rangle = \left| m_l = 1\, m_s = \frac{1}{2} \right\rangle$$

but

$$\left| j = \frac{3}{2}\, m_j = \frac{1}{2} \right\rangle = a \left| m_l = 1\, m_s = -\frac{1}{2} \right\rangle + b \left| m_l = 0\, m_s = \frac{1}{2} \right\rangle$$

where a, b are Clebsch-Gordan coefficients. □

The complete proof will be done in grad school.

We here need to know adding two momentum j_1, j_2

$$j_{total} = j_1 + j_2, ..., |j_1 - j_2|$$

Important example to remember are two electrons spin couple.

There are four states

$$|s = 1\, m_s = 1\rangle = |\uparrow\uparrow\rangle \tag{1.2}$$

$$|s = 1\, m_s = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \tag{1.3}$$

$$|s = 1\, m_s = -1\rangle = |\downarrow\downarrow\rangle \tag{1.4}$$

$$|s = 0\, m_s = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \tag{1.5}$$

notice the first three are symmetric wrt interchange electrons 1, 2; the last state is antisymmetric.

1.2 Many Particles States

$$\Psi = \Psi(\vec{r}_1, s_1, \vec{r}_2, s_2, ..., \vec{r}_N, s_N, t)$$

Normalization

$$\sum_{s_1, s_2, ..., s_N} \int d^3 r_1 \int d^3 r_2 ... \, |\Psi|^2 = 1$$

$$H = \left(\frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + ... \right) + V(\vec{r}_1, ...)$$

$$P_1^2 = -\hbar \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right)$$

Example. Two particle (no spin)

$$\psi = \psi(\vec{r}_1, \vec{r}_2)$$

sometimes if separable,

$$\psi = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)$$

this may sometimes be just an approximation.

Suppose

$$V(\vec{r}_1 - \vec{r}_2)$$

then in classical mechanics we define

$$\vec{R}_{cm} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$$

$$M_{total} = m_1 + m_2$$

$$\vec{r} = \vec{r}_1 - \vec{r}_2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

In QM

$$\begin{aligned} H &= \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + V(\vec{r}_1 - \vec{r}_2) \\ &= \frac{P_{cm}^2}{2M_{tot}} + \frac{P^2}{2\mu} + V(\vec{r}) \end{aligned} \tag{1.6}$$

where $\hat{P} = \frac{\hbar}{i}\frac{\partial}{\partial r}$ is the relative momentum.

$$[(P_{cm})_j, (R_{cm})_k] = \frac{\hbar}{i}\delta_{jk}$$

$$[P_j, r_k] = \frac{\hbar}{i}\delta_{jk}$$

$$[P_{cm}, \vec{r}] = 0$$

$$[P, \vec{R}_{cm}] = 0$$

where $(P_{cm})_x = \frac{\hbar}{i}\frac{\partial}{\partial x_{cm}}$

Exercise. show

$$-\frac{\hbar^2}{2m_1}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\vec{\nabla}_2^2 = -\frac{\hbar^2}{2M_{tot}}\vec{\nabla}_{cm}^2 - \frac{\hbar^2}{2\mu}\vec{\nabla}_r^2$$

Last semester, we showed for Hydrogen the bound states energy

$$E_n = -\frac{me^4}{2\hbar^2 n^2} \tag{1.7}$$

Bohr radius

$$a = \frac{\hbar^2}{me^2} \tag{1.8}$$

(In our class, unit $4\pi\epsilon_0 = 1$)

Now we know to be correct, we should put μ to replace m

$$\mu = \frac{m_e m_p}{m_e + m_p} = \frac{m_e}{m_e/m_p + 1} \approx m_e$$

But for Positronium (e^+, e^-) this replacement makes big difference

$$\mu = \frac{m_e}{2}$$

1.3 Two Identical Particles

Suppose we want to know the probability of finding electrons 1, 2 at time t at spatial points p_1, p_2 with states ϕ_1, ϕ_2. Because indistinguishable natural of electrons (and also due to uncertainty principle, impossible to know the path of electron evolution), we don't know at time t at spatial points p_1, p_2 with states ϕ_1, ϕ_2 are the electron 1, 2, or 2, 1.

Question. *If spins are different, how can they be identical particles?*

No problem. If at t, we find one electron spins up and the other one spin down, but we still don't know which one changed spin.

Question. *If two identical electrons are that one on earth, one on the moon, can we still not be able to distinguish them?*

That is very interesting. That relates to the interpretation of QM.

Let us define *exchange operator*

$$P\psi(r_1, s_1, r_2, s_2) = \psi(r_2, s_2, r_1, s_1)$$

P is Hermitian. And clearly

$$P^2 = I$$

so the eigenvalues of P must be ± 1.

If $\psi(r_1, s_1, r_2, s_2)$ happens to be an eigenfunction of P with $p = 1$, then

$$\psi(r_1, s_1, r_2, s_2) = \psi(r_2, s_2, r_1, s_1)$$

If $\psi(r_1, s_1, r_2, s_2)$ happens to be an eigenfunction of P with $p = -1$, then

$$\psi(r_1, s_1, r_2, s_2) = -\psi(r_2, s_2, r_1, s_1)$$

Although a priori ψ does not have to be eigenfunction of P, the next theorem will tell us, it has to be.

Theorem. *(Law of physics) All two identical particle states are eigenstates of P.*

Theorem. *(spin-statistics theorem) If spin of the two identical particles is integer, eigenvalue is 1; if spin is half integer, eigenvalue is -1.*

This is more deeper theorem. In fact, in general relativity, one can show that if system obeys Lorentz invariance, then spin-statistics theorem is true.

Now let us look back two electrons spin-spin couple Helium example (1.2) - (1.5).

Suppose

$$\psi(r_1, r_2, s_1, s_2) = f(r_1, s_1)g(r_2, s_2)$$

then suppose we are in one of the ground states

$$\psi = Ne^{-r_1/a}e^{-r_2/a} \left|\uparrow\uparrow\right\rangle$$

this is not allowed, because ψ has to be antisymmetric.

So

$$\psi = NF(r_1 r_2)\,|\uparrow\uparrow\rangle$$

F must be antisymmetric, similarly in (1.3), (1.4), however in (1.5)

$$\psi = NK(r_1 r_2)\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

K must be symmetric. In other words of *Pauli exclusion principle* for two electrons,

If total spin = 1, spin function = sym, so spatial function = anti; If total spin = 0, spin function = anti-sym, spatial function = symmetric.

Lecture 2 (1/24/13)

It is hard to give a general statement of this. For spin orbit coupling. If one wants to consider the total spin of three electrons, then it is only possible to construct completely symmetric state, but not possible to construct completely anti symmetry state.

Now let's consider non-interacting particles in 1D box, from last time we know let $\psi_n(x)$, $n = 1, 2, 3$ to be the eigenstates of 1D ∞ potential well. If the two particles are distinguishable

$$\psi(x_1, x_2) = \psi_n(x_1)\psi_{n'}(x_2)$$

If the two are Bosons

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}(\psi_n(x_1)\psi_{n'}(x_2) + \psi_{n'}(x_1)\psi_n(x_2))$$

If two are Fermions

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}(\psi_n(x_1)\psi_{n'}(x_2) - \psi_{n'}(x_1)\psi_n(x_2))$$

What about in 3 dimensions, what about spins?

Let's first consider two electrons: one here, the other on the Moon.

Assume

$$\begin{aligned}\Psi(1,2) &= \psi(\vec{r}_1,\vec{r}_2)\chi(s_1,s_2) \\ &= \frac{1}{\sqrt{2}}[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)]\chi(s_1,s_2) \qquad (1.9)\end{aligned}$$

Because the two electrons are way apart, we have either ψ_a is only non-zero here and ψ_b is only non-zero on Moon or the other way around. Hence (1.9) has only one term (i.e. can both $\psi_a(\vec{r}_1)$, $\psi_a(\vec{r}_2)$ be nonzero, neither can $\psi_b(\vec{r}_1)$, $\psi_b(\vec{r}_2)$), but we don't a priori know which term is zero because the two electrons are indistinguishable, i.e. we don't know exact what goes into the argument of ψ_a, should $\psi_a(\vec{r}_1)$ or $\psi_a(\vec{r}_2)$, but we do know if one is on earth, the other must be on moon, so one of the products of $\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$ and $\psi_b(\vec{r}_1)\psi_a(\vec{r}_2)$ must be zero

Now let's do a measurement F which depends on positions

$$\begin{aligned}\langle F(\vec{r}_1,\vec{r}_2)\rangle &= \frac{1}{2}\int d^3r_1 \int d^3r_2 F(\vec{r}_1,\vec{r}_2)\left|\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right|^2 \\ &= \frac{1}{2}\int d^3r_1 \int d^3r_2 F(\vec{r}_1,\vec{r}_2)[\left|\psi_a(\vec{r}_1)\right|^2\left|\psi_b(\vec{r}_2)\right|^2 \\ &\qquad + \left|\psi_b(\vec{r}_1)\right|^2\left|\psi_a(\vec{r}_2)\right|^2 \\ &\qquad \pm\psi_a^*(\vec{r}_1)\psi_a(\vec{r}_2)\psi_b^*(\vec{r}_2)\psi_b(\vec{r}_1) \\ &\qquad \pm\psi_a(\vec{r}_1)\psi_a^*(\vec{r}_2)\psi_b(\vec{r}_2)\psi_b^*(\vec{r}_1)]\end{aligned}$$

The last two terms are zero, for the reason given above. Hence

$$\langle F(\vec{r}_1,\vec{r}_2)\rangle = \frac{1}{2}\int d^3r_1 \int d^3r_2 F(\vec{r}_1,\vec{r}_2)[\left|\psi_a(\vec{r}_1)\right|^2\left|\psi_b(\vec{r}_2)\right|^2 + \left|\psi_b(\vec{r}_1)\right|^2\left|\psi_a(\vec{r}_2)\right|^2]$$

In other words, the "±" sign in (1.9) make no difference, more we can treat them just as distinguishable particles.

Now we take two electrons close by, i.e. wave functions ψ_a, ψ_b have overlap, and let ψ_a, ψ_b be two orthogonal eigenstates.

Let's calculate

$$\left\langle(\vec{r}_1-\vec{r}_2)^2\right\rangle = \left\langle r_1^2 + r_2^2 - 2\vec{r}_1\cdot\vec{r}_2\right\rangle$$

Use the calculation we did before

$$\begin{aligned}
\langle r_1^2 \rangle &= \frac{1}{2}\int d^3r_1 \int d^3r_2 \left|\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \pm \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right|^2 \\
&= \frac{1}{2}\int d^3r_1 \int d^3r_2 r_1^2 \left|\psi_a(\vec{r}_1)\right|^2 \left|\psi_b(\vec{r}_2)\right|^2 \\
&\quad + \frac{1}{2}\int d^3r_1 \int d^3r_2 r_1^2 \left|\psi_b(\vec{r}_1)\right|^2 \left|\psi_a(\vec{r}_2)\right|^2 \\
&\quad \pm \frac{1}{2}\int d^3r_1 \int d^3r_2 r_1^2 \psi_a^*(\vec{r}_1)\psi_a(\vec{r}_2)\psi_b^*(\vec{r}_2)\psi_b(\vec{r}_1) \\
&\quad \pm \frac{1}{2}\int d^3r_1 \int d^3r_2 r_1^2 \psi_a(\vec{r}_1)\psi_a^*(\vec{r}_2)\psi_b(\vec{r}_2)\psi_b^*(\vec{r}_1) \\
&= \frac{1}{2}\int d^3r_1 r_1^2 \left|\psi_a(\vec{r}_1)\right|^2 + \frac{1}{2}\int d^3r_1 r_1^2 \left|\psi_b(\vec{r}_1)\right|^2 \pm 0 \pm 0 \\
&= \frac{1}{2}(\langle r_1^2 \rangle_a + \langle r_1^2 \rangle_b)
\end{aligned}$$

the two 0s are due to orthogonality for example $\int d^3r_2 \psi_a^*(\vec{r}_1)\psi_a(\vec{r}_2) = 0$. Similarly one can get

$$\langle r_2^2 \rangle = \frac{1}{2}(\langle r_2^2 \rangle_a + \langle r_2^2 \rangle_b)$$

Of course particles 1,2 are indistinguishable, so no way we can tell that given wave function ψ_a the possibility of find particle at r is really to find particle 1 or 2, so mathematically

$$\langle r^2 \rangle_a = \frac{1}{2}(\langle r_1^2 \rangle_a + \langle r_2^2 \rangle_a)$$

$$\langle r^2 \rangle_b = \frac{1}{2}(\langle r_1^2 \rangle_b + \langle r_2^2 \rangle_b)$$

the 1/2 factor is because only one of the two particles can occupy at r.

Hence

$$\langle r_1^2 + r_2^2 \rangle = \langle r_1^2 \rangle + \langle r_2^2 \rangle = \langle r^2 \rangle_a + \langle r^2 \rangle_b$$

Now we calculate

$$\begin{aligned}\langle \vec{r}_1 \cdot \vec{r}_2 \rangle &= \frac{1}{2}\int d^3r_1 \int d^3r_2 \vec{r}_1 \cdot \vec{r}_2 \left|\psi_a(\vec{r}_1)\right|^2 \left|\psi_b(\vec{r}_2)\right|^2 \\ &\quad + \frac{1}{2}\int d^3r_1 \int d^3r_2 \vec{r}_1 \cdot \vec{r}_2 \left|\psi_b(\vec{r}_1)\right|^2 \left|\psi_a(\vec{r}_2)\right|^2 \\ &\quad \pm \frac{1}{2}\int d^3r_1 \int d^3r_2 \vec{r}_1 \cdot \vec{r}_2 \psi_a^*(\vec{r}_1)\psi_a(\vec{r}_2)\psi_b^*(\vec{r}_2)\psi_b(\vec{r}_1) \\ &\quad \pm \frac{1}{2}\int d^3r_1 \int d^3r_2 \vec{r}_1 \cdot \vec{r}_2 \psi_a(\vec{r}_1)\psi_a^*(\vec{r}_2)\psi_b(\vec{r}_2)\psi_b^*(\vec{r}_1) \\ &= \frac{1}{2}(\langle \vec{r}_1 \rangle_a \langle \vec{r}_2 \rangle_b + \langle \vec{r}_2 \rangle_a \langle \vec{r}_1 \rangle_b) \\ &\quad \pm \frac{1}{2}(\langle \vec{r}_1 \rangle_{ab} \langle \vec{r}_2 \rangle_{ab}^* + \langle \vec{r}_1 \rangle_{ab}^* \langle \vec{r}_2 \rangle_{ab})\end{aligned}$$

where

$$\langle \vec{r}_1 \rangle_{ab} \equiv \int d^3r_1 \vec{r}_1 \psi_a^*(\vec{r}_1)\psi_b(\vec{r}_1)$$

(we break $\vec{r}_1 \cdot \vec{r}_2$ into two independent integrals and pretend the angle correlation doesn't matter. An more refined calculation uses $\langle \vec{r}_1 \cdot \vec{r}_2 \rangle = \langle x_1 x_2 \rangle + \langle y_1 y_2 \rangle + \langle z_1 z_2 \rangle$, $\psi(\vec{r}) = \psi(x)\psi(y)\psi(z)$ will give $\mp$ terms too, which is all we need for the follow up discussion.)

Use similar argument before

$$\langle \vec{r} \rangle_a = \frac{1}{2}(\langle \vec{r}_1 \rangle_a + \langle \vec{r}_2 \rangle_a)$$

$$\langle \vec{r} \rangle_b = \frac{1}{2}(\langle \vec{r}_1 \rangle_b + \langle \vec{r}_2 \rangle_b)$$

That follows

$$\langle \vec{r}_1 \rangle_a = \langle \vec{r} \rangle_a + \Delta \quad \langle \vec{r}_2 \rangle_a = \langle \vec{r} \rangle_a - \Delta$$

$$\langle \vec{r}_1 \rangle_b = \langle \vec{r} \rangle_b + \delta \quad \langle \vec{r}_2 \rangle_b = \langle \vec{r} \rangle_b - \delta$$

We arrive

$$\frac{1}{2}(\langle \vec{r}_1 \rangle_a \langle \vec{r}_2 \rangle_b + \langle \vec{r}_2 \rangle_a \langle \vec{r}_1 \rangle_b) = \langle \vec{r} \rangle_a \langle \vec{r} \rangle_b - \Delta \cdot \delta \approx \langle \vec{r} \rangle_a \langle \vec{r} \rangle_b$$

Similarly one can show

$$\frac{1}{2}(\langle\vec{r}_1\rangle_{ab}\langle\vec{r}_2\rangle^*_{ab}+\langle\vec{r}_1\rangle^*_{ab}\langle\vec{r}_2\rangle_{ab})\approx|\langle\vec{r}\rangle_{ab}|^2$$

Therefore we arrive

$$\left\langle(\vec{r}_1-\vec{r}_2)^2\right\rangle=\langle\vec{r}\rangle_a+\langle\vec{r}\rangle_b-2\langle\vec{r}\rangle_a\langle\vec{r}\rangle_b\mp2|\langle\vec{r}\rangle_{ab}|^2$$

Note

The upper sign $-\leftrightarrow+$ in spatial part or sym in spatial $\leftrightarrow$ electron closer $\leftrightarrow$ asym in spin $\leftrightarrow$ $s=0$ called "para",

The lower sign $+\leftrightarrow-$ in spatial part or asym in spatial $\leftrightarrow$ electron further apart $\leftrightarrow$ sym in spin $\leftrightarrow$ $s=1$ called "ortho"

The names "para", "ortho" are from two different Helium atoms states.

e.g. In making Hydrogen molecule, two electrons should get closer together, forming *covalent bond*. That is the $s=0$ state. There is a general misstatement in lower level chemistry class, people are told that covalent bond when two electrons one spin up and the other spin. That is of course correct for the singlet state, but that is not sufficient, since one spin up and the other down could be $s=1$ state (cf. (1.3)).

1.4 Hydrogen and Helium atoms

Last lecture we mentioned Hydrogen energy and Bohr radius (cf. (1.7), (1.8)) Note if $E>0$ then it is unbounded state, i.e. electron leaves proton.

When $n=1$, then $l=0$, there is $1s$ configuration (s for sharp).

When $n=2$, then $l=0,1$, there are $2s$, $2p$ configurations (p for principal).

When $n=3$, then $l=0,1,2$, there are $3s$, $3p$, $3d$ configurations (d for diffuse).

When $n=4$, then $l=0,1,2,3$, there are $4s$, $4p$, $4d$, $4f$ configurations (f for fine).

(Those names came from 19 century spectroscopy)

Recall

$$j=(l+s),...,|l-s|$$

$1s$ has two states $j = 1/2$, $m_j = \pm 1/2$, so is $2s$. The ground stare energy is -13.6eV.

$2p$ has 6 states $j = 3/2$, $m_j = \pm 1/2, \pm 3/2$, $j = 1/2$, $m_j = \pm 1/2$.

$3d$ has 10 states.

Why energy of $2s$ is equal to $2p$?

recall

$$H = \frac{p^2}{2m} - \frac{e^2}{r}$$

This is very special to potential $1/r$. The analogy situation happens in classical mechanics. Why the orbit is a closed curve (one ellipse)? Because it only happens if the potential is proportional to $1/r$ or r^2.

Later we will add more term to the Hamiltonian, to include $\vec{L}$, $\vec{S}$ interaction, then we will see the energy splits.

Helium Ion

He^+ is just like Hydrogen

$$E_n = -\frac{mZ^2e^4}{2\hbar^2}\frac{1}{n^2} = 4 \times \text{Hydrogen}$$

$$a = \frac{\hbar^2}{Ze^2m} = \frac{1}{2} \times \text{Hydrogen}$$

That makes sense, a is smaller, because positive charge of the nuclear is twice bigger.

Similarly for Li^{++}, which has one electron and $Z = 3$.

Helium Atom

Recall for atom with Z electrons

$$H = \sum_{j=1}^{Z}\left(\frac{p_j^2}{2m} - \frac{Ze^2}{r_j}\right) + \frac{1}{2}\sum_{j\neq k}^{Z}\frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

To start, we ignore electron-electron term, so

$$H = \frac{p_1^2}{2m} - \frac{Ze^2}{r_1} + \frac{p_1^2}{2m} - \frac{Ze^2}{r_1}$$

$Z = 2$.

Before worry about symmetry, let

$$\psi(1,2) = \psi_{nlm}(\vec{r}_1)\psi_{n'l'm'}(\vec{r}_2) \times \text{spin}$$

use idea of $H\psi = E\psi \implies (H_1 + H_2)\psi = (E_n + E_{n'})\psi$, we should have

$$E = -\frac{Z^2e^4m}{2\hbar^2}(\frac{1}{n^2} + \frac{1}{n'^2})$$

so the ground state we get

$$E = 8(-13.6) = -109\text{eV}$$

(Actually removing one electron requires 24.5eV, and removing the second electron requires 4(13.6)eV, so the actual ground state of He is the sum of the two values -79eV. We will get to that value later in the course.)

Lecture 3 (1/29/13)

Let's now analyze Helium atom carefully.

The total wave function for the two electrons is antisymmetric

$$\frac{1}{\sqrt{2}}[\psi_{nlm_lm_s}(1)\psi_{n'l'm'_lm'_s}(2) - \psi_{n'l'm'_lm'_s}(1)\psi_{nlm_lm_s}(2)]$$

We first claim that the $(n = 2, n' = 2)$ state is unstable, i.e. both electrons have $n = 2$.

Energy for the ground state as we showed last time

$$E_{(1,1)} = (-13.6)(2^2)\left(\frac{1}{1} + \frac{1}{1}\right) = -2\epsilon$$

set $\epsilon = (13.6)(2^2)$, the ground state has to be para ($S = 0$). The two electrons have same $n = 1$, same $l = 0$, same $m_l = 0$, so they have to have different m_s. So

the total spin $S = 0$. This state is sometimes denoted as (1s)(1s) or $(1s)^2$ or

$$^1S_0$$

Here we use

$$^{2S+1}X_J$$

symbol, where S means total spin, $2S + 1$ gives the number of states of different m_S, X means the total angular momentum

$$l = 0 \quad X = S$$

$$l = 1 \quad X = P$$

$$l = 2 \quad X = D$$

$$l = 3 \quad X = F$$

$$l = 4 \quad X = G$$

$$l = 5 \quad X = H$$

$$l = 6 \quad X = I$$

and $J = S + L$ is the total spin + total angular momentum, $j = s + l, ..., |s - l|$.

The next energy state is (1,2)

$$E_{(1,2)} = -\epsilon \left(\frac{1}{1} + \frac{1}{2^2} \right) = -1.25\epsilon$$

In this state, there are many degenerated states, the two electrons can be (1s)(2s) or (1s)(2p). (1s)(2s) has total angular momentum $l = 0$, and (1s)(2p) has $l = (l_1 + l_2), ..., |l_1 - l_2| = 1$.

Later we will show that that $l = 1$ has higher energy than $l = 0$

This takes care of the angular momentum part. Because now n are different, the two electrons can well have same spins: both up, both down or one up one down, so $m_s = 1, 0, -1$.

Recall para state has the two electrons closer than in ortho, after we consider

the 2 electrons interaction part

$$\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

we will see that energy of para is higher than ortho.

In summary

For the energy (1,2) states, we have big split between (1s)(2s) and (1s)(2p) due to $l = 0$ or 1. Then for (1s)(2s) there is another split but smaller split due to $S = 0$ or 1: para state energy $>$ ortho. This results two different energy (1s)(2s) states

$$^1S_0 \qquad ^3S_1$$

Similarly for (1s)(2p) there is split due to $S = 0$ or 1, this results 1 para and 3 ortho energy states (3 is because $j = s + l, ..., |s - l| = 2, 1, 0$)

$$^1P_1 \qquad ^3P_0 \quad ^3P_1 \quad ^3P_2$$

Later we will show that the 3 ortho states will split too, but even smaller split.

The next energy state is (1,3)

$$E_{(1,2)} = -\epsilon \left(\frac{1}{1} + \frac{1}{3^2} \right) = -1.11\epsilon$$

we have big split between (1s)(3s), (1s)(3p), and (1s)(3d) due to $l = 0$, 1 or 2. Then for each of the three there is another split due to $S = 0$ or 1: para v.s ortho. This results two different (1s)(3s) states

$$^1S_0 \qquad ^3S_1$$

1 para state and 3 ortho (1s)(3p) states

$$^1P_1 \qquad ^3P_0 \quad ^3P_1 \quad ^3P_2$$

1 para state and 3 ortho (1s)(3d) states (3 is because $j = s + l, ..., |s - l| = 1 + 2, 2, 2 - 1 = 3, 2, 1$)

$$^1D_2 \qquad ^3D_1 \quad ^3D_2 \quad ^3D_3$$

Then we can go on for $(1, 4)$ energy state and all the way to $(1, \infty)$, i.e. one electron becomes ionized. As n gets bigger, the energy splits get smaller.

We also see that

$$E_{(1,\infty)} = -\epsilon$$

The energy for (2,2)

$$E_{(2,2)} = -\epsilon \left(\frac{1}{2^2} + \frac{1}{2^2} \right) = -\epsilon/2$$

This proves the claim that $(2, 2)$ state is unstable. In this state, one electron will give the other a little bit energy, then the other becomes free, and total energy decreases.

1.5 Periodic Table

We finished characterizing one electron atoms and two electrons atoms. Now we study many electrons.

H			He
LiBe			——2p——Ne
–3s–			——3p——Ar
–4s–		————-3d————-	——4p——Kr
–5s–		————-4d————-	——5p——Xe
–6s–	4f	————-5d————-	——6p——Rn
–7s–	5f	————-6d————-	——-(?)——-

Form the table, it's easy to see that the energy level is going from

1s — 2s 2p — 3s 3p — 4s 3d 4p — 5s 4d 5p — 6s 4f 5d 6p — 7s 5f 6d (?)

then become unstable. The first column elements are most active, and the last column are inert gas (noble gas). The 4f, 5d elements have very high angular momentum, so they give many interesting magnetic properties.

One can use the energy shells ($n = 1, 2, ..$) and sub shells $s, p, d..$ to fill the electrons, as below

H (1s)
He $(1s)^2$
Li $(1s)^2(2s)$
Be $(1s)^2(2s)^2$
B $(1s)^2(2s)^2(2p)$
C $(1s)^2(2s)^2(2p)^2$
N $(1s)^2(2s)^2(2p)^3$
O $(1s)^2(2s)^2(2p)^4$
F $(1s)^2(2s)^2(2p)^5$
Ne $(1s)^2(2s)^2(2p)^6$

To fill the shells and subshell, just remember the configuration of inert gas. They give those magic numbers: 2 (i.e. 2e fill $n = 1$), 2+8=10 (i.e. 8e fill $n = 2$), 10+8=18, 18+18=36,....

Because the outer most subshell gives most interesting physical, chemical properties, we want to know the total spin, total angular momentum of the outer most subshell of the ground state configuration. We use the symbol again

$$^{2S+1}X_J$$

We already did for H, He.

Let's do Li.

Outer sub shell (2s), so

$$S = 1/2 \quad L = 0 \quad J = 1/2$$

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

Be $(2s)^2$ $L = 0$, then one must spin up and the other spins down $S = 0$, $J = 0$

$$^1S_0$$

To do more, Mr. Hund gave some rules.

Theorem. *(Hund's Rules) for lowest energy groundstate*

1) Largest S

2) Largest L consistent with rule 1) and gives antisymmetry

3) If the subshell is $\leq$ half filled, $J = |L - S|$. If the subshells is $>$ half filled, $J = L + S$.

The first two rules have the following physical intuitions. We know from Helium, spin split is the first thing we look at within a subshell. When S is the largest, we have most symmetric in spin, so antisymmetric in space, so electrons are far apart. Once the spin is picked, we then look for largest L, this means electrons are bit far away from the nuclei, so they are more far a part from each other. This also reduces energy. The third rule is more observational.

Now let's do B $(1s)^2(2s)^2(2p)$.

$$S = 1/2 \quad L = 1$$

then

$$J = 1/2 \text{ or } 3/2$$

By rule 3),

$$^2P_{1/2}$$

C $(1s)^2(2s)^2(2p)^2$

$$S = 0, 1 \quad L = 0, 1, 2$$

Rule 1) says $S = 1$.

Rule 2) says $L = 2$ is not allowed, because then both spin and spatial parts would be symmetric (recall the highest weight state is always symmetric), hence $L = 1$.

Rule 3) says $J = 0$

$$^3P_0$$

N $(1s)^2(2s)^2(2p)^3$

Rule 1) says $S = 3/2$. This is symmetric state in spin, then they have to have different $m_l = 1, 0, -1$, otherwise if two electrons have same m_l, then exchange

these two electrons will result a same wave function, which is not allowed, so $L = 0$

$$^4S_{3/2}$$

One can use Hund's rule go very far, but then things get complicated, which we will explain later.

Lastly, what about size of atoms? As numbers of (sub)shells get bigger and bigger, the size is actually roughly the same. This makes sense, because for chemical reaction to happen, we need atoms to get together. If some atoms are much bigger than the others, they would have hard time to move and fit into together. Experiment data shows

density of Li: .53g/cm^3 and the atom mass is 6.9

density of U: 19.1g/cm^3 and the atom mass is 238

The ratio between the densities is 36, and ratio between the two masses is 34.5, so the sizes are about the same, as atom grows 34.5 times heavier.

1.6 Nucleus

Lecture 4 (1/31/13)

We know nucleus are packed tightly by protons and neutrons. The force between them gets a quite "technical" name: strong force. It is very strong, so the electric repulsion among protons can be ignored. Recall the energy for chemical reaction is measured in eV, energy for nuclear reaction is in MeV. The strong force is also a very short range force. In fact for protons, neutrons within the same nuclei may not exert on each other, if they are not neighbors. Recall the size of atom $\sim 10^{-8}$cm, size of nuclei $\sim 10^{-13}$cm.

Let's consider one proton or neutron, the potential is given by

$$V = V_0 + Ar^2 + Br^3 + ...$$

the reason there is no r^{-n}, or r terms is because they will give singularities when we calculate force $F = -\nabla V$, since $r = \sqrt{x^2 + y^2 + z^2}$, we will also drop V_0 and drop r^3 or higher terms, for V_0 is not important and for force is short range.

Now we are in 3D SHO, so

$$\psi \leftrightarrow (n_x, n_y, n_z)$$

$$E = (n_x + n_y + n_z + \frac{3}{2})\hbar w$$

set $N \equiv n_x + n_y + n_z$.

$N = 0$, so $(n_x = 0, n_y = 0, n_z = 0)$ so $l = 0$, we can fill this energy state using 2 protons and 2 neutrons, $2p + 2n \implies {}^4\text{He}$. Recall protons and neutrons are spin 1/2 particles. Pauli says not identical spin 1/2 particle in same states, but 1 proton and 1 neutron are not identical particle. So the magic number is 2.

Next energy level $N = 1$,

$$(1,0,0)\ (0,1,0)\ (0,0,1)$$

here $l = 1$, we can fill this energy state using 6 protons and 6 neutrons, $8p{+}8n \implies {}^{16}\text{O}$. the magic number is $2 + 6 = 8$.

$N = 2$

$$(2,0,0)\ (0,2,0)\ (0,0,2)(1,1,0)\ (0,1,1)\ (1,0,1)$$

here $l = 0, 2$, the magic number is $8 + 12 = 20$. $20p + 20n \implies {}^{40}\text{Ca}$

$N = 3$, there are 3 of type of $(3,0,0)$, 3 of type of $(2,1,0)$, and 1 of (1,1,1). Here $l = 1, 3$, the magic number is $20 + 20 = 40$. $40p + 40n \not\Rightarrow$ (?) the simple argument doesn't work.

Note: to understand total l in each of the cases above, one needs to know spherical harmonics.

In summary

The ratio between

$$\frac{\#\text{ neutrons}}{\#\text{ protons}}$$

is about 1 for small atomic number, and increases as atomic number gets big.

e.g. Uranium ^{238}U has 92p and 146n.

As we showed in our simple argument the energy levels are the same for neutrons and protons. So if there are more protons in the nucleus, we know they

will become neutrons to reduce energy via Beta decay, and vise verse

$$p \to n + e^+ + \nu$$

$$n \to p + e^- + \bar{\nu}$$

Beta decay can only happen within a nuclei.

But as atomic number gets big, energy levels are not the same for protons and neutrons. Electric forces will take into account. So protons have higher energy levels.

After heavier atom gets split (nuclear diffusion), it decays much faster. ^{238}U has half life of billion years, and after split, it has half life of 20 years, so nuclear wastes are dangerous.

1.7 Solids (no nuclei)

We use gas of elections in an empty box (L_x, L_y, L_z) as a model for solids. That is because for solids atoms are packed in lattices, and if we ignore the presence of nucleus (we will take them into account next lecture) and as always ignore electrons interaction, the outer shell electrons are free to move within the box, so we have 3D ∞ well problem.

States

$$\psi = N \sin k_x x \sin k_y y \sin k_z z$$

$$k_x = \frac{n_x \pi}{L_x} \quad k_y = \frac{n_y \pi}{L_y} \quad k_z = \frac{n_z \pi}{L_z}$$

where n_x, n_y, n_z are positive integers.

$$E = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m}k^2$$

set $\vec{k} = (k_x, k_y, k_z)$ in the $k-$space.

So we can count the number of states in the $k-$space, since each state is specified by (k_x, k_y, k_z), i.e. $\vec{k}$. So each state is a discrete dot in the 1st octant of k_x, k_y, k_z axes, and the increments (or separations) in k_x, k_y, k_z directions are π/L_x, π/L_y, π/L_z. If we associate the up out most corner of the volume element with

the volume element itself, then there exists a nice relation between the volume in $k-$ space and number of states with energies equal or below some maximal energy, say E_F (Fermi energy)

Because we always fill energy state from low to high, let's denote filled states with highest energy E_F,

$$E_F = \frac{\hbar^2}{2m} k_F^2 \tag{1.10}$$

where $\hbar\vec{k}$ called Fermi momentum. Therefore

$$\begin{aligned} \#\text{ states with } E \leq E_F (k^2 \leq k_F^2) &= 2 \times \frac{\text{volume in } k \text{ space with } k^2 \leq k_F^2}{\text{volume element}} \\ &= 2 \frac{\frac{1}{8}\left(\frac{4\pi}{3} k_F^3\right)}{\frac{\pi^3}{V}} \\ &= \frac{V}{3\pi^2} k_F^3 \\ &\equiv N_q \end{aligned} \tag{1.11}$$

where $2\times$ is due to 2 electron spin states, $1/8$ is in 1st octant, π^3/V is the volume element, $V = L_x L_y L_z$. We set that value to be N_q number of free electrons. Then we can solve for

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{V} N_q\right)^{2/3} = \frac{\hbar^2}{2m} \left(3\pi^2 \rho\right)^{2/3} \tag{1.12}$$

where $\rho = \#$ free electrons pre volume.

Note: (1) We get (1.12) independent of size of solid. This justifies that picking the material to be cubic at the beginning of the calculation should not matter.

(2) In (1.11), we don't need to worry about the shell of the sphere we use and the grid edge of the $k-$ space. That is because the number (volume) in (1.11) is very big (10^{23}), the shell doesn't matter.

(3) In reality, for given E_F, electrons are not going to completely packed below E_F. Due to thermos fluctuation, some electrons in state close to E_F may jump above E_F.

We can now calculate the total energy of the N_q free electrons, using (1.10)

$$\begin{aligned} E &= 2\frac{1}{8}\int_0^{k_F} dk(4\pi k^2)\left(\frac{\pi^3}{V}\right)^{-1}\frac{\hbar^2 k^2}{2m} \\ &= \frac{\hbar^2 V}{10\pi^2 m}k_F^5 \\ &= \frac{\hbar^2}{10\pi^2 m}(3\pi^2 N_q)^{5/3}V^{-2/3} \end{aligned} \tag{1.13}$$

notice in the integration above we used spherical coordinate, that is where $4\pi k^2$ came from. And $\left(\frac{\pi^3}{V}\right)^{-1}$ factor is just due to transfer from sum to integration, e.g. if we want to find

$$\sum_{n,m=1}^{100}(m+n)^2$$

we write

$$\int_1^{100}(x+y)^2\frac{dxdy}{A}$$

A is the size in $x-y$ space. Recall in Fourier, one needs to divide $1/(2\pi)^{d/2}$.

Now let's suppose we apply pressure on solid, use (1.13),

$$P = -\frac{\partial E}{\partial V} = \frac{(3\pi^2)^{2/3}}{5m}\hbar^2\rho^{5/3}$$

this definition $P = -\frac{\partial E}{\partial V}$ of courses consistent with gas, which we used as the model. It is also consistent quantum mechanically, think of for the ∞ square well, if we make the well smaller, recall

$$E_n \sim \frac{1}{L^2}$$

so all levels of energy get higher.

For copper $P \sim 10^{12}\mathrm{N/m}^2$ very big, so solids are rigid.

Note: normally people refer this using Bulk modulus, defined as

$$B = -V\frac{dP}{dV}$$

for copper $B = 1.3 \times 10^{11}\text{N/m}^2$.

This concept of Fermi pressure also used in astrophysics. We know after sum burns out, it will be a white dwarf, and heavier star will become a neutron star. White dwarf is 2000 times smaller than neutron stars.

1.8 Solids (with nucleus)

Lecture 5 (2/5/13)

Now let's put nucleus in and suppose the nucleus are fixed dots in the material with equal spacing a. Free electrons are moving around the material. From electrons point of view the potentials are the same from one unit cell to another unit. In 1D, this says

$$V(x+a) = V(x)$$

Of course physically $V(x)$ doesn't go on forever, in other word, x is only suitable in some interval. But to analyze the behavior of electron inside of the material, what potential is on the boundary of the material is irrelevant, because it is too far away. This enable us to postulate the boundary condition as imagining that the two ends of the material is glued together, i.e. $V(x)$ is defined on a circle with circumference Na, we can label the positions of nucleus at $0, a, 2a, ..., (N-1)a$.

We define shift operator D, s.t.

$$D\psi = \tilde{\psi}$$

where $\tilde{\psi}(x) = \psi(x+a)$. Because Hamiltonian involves derivative and value of potential at x, i.e. Hamiltonian is local, it doesn't care the effect of shift, hence

$$[D, H] = 0$$

that is there exists simultaneous eigenstates of D and H.

For D

$$D^N = I$$

if λ is an eigenvalue of D, $\lambda^N = 1 \implies \lambda = e^{2\pi i n/N}$, $n = 0, 1, 2, ..., N-1$, set

$$K = \frac{2\pi n}{Na}$$

then $\lambda = e^{iKa}$, or

$$\psi(x+a) = e^{iKa}\psi(x) \tag{1.14}$$

Hence the wave function was a phase shift from one unit to the next unit, although $|\psi(x+a)| = |\psi(x)|$. This is very reasonable, since $|\psi(x+a)| = |\psi(x)|$ is the only physically requirement, by adding N different phases, we get some freedom in choosing different wave functions.

(1.14) implies we the wave function has the form

$$\psi(x) = e^{iKa}u_K(x)$$

where $u_K(x) = u_K(x+a)$ a periodic function with period a.

To do anything further, we need to specify $V(x)$. Here we choose a simplest possible

$$V(x) = -\beta \sum_{j=0}^{N-1} \delta(x - ja)$$

notice that the potential says, electrons are completely free in each a away from the nucleus , and gets attack into the nucleus when it is at the nucleus position, but this simple V model gives a lot features that agree with the experiments.

Boundary condition 1: ψ is continuous at $x = 0$.

$$\psi(0^+) = \psi(0^-)$$

It follows

$$\psi(0^+) = e^{-iKa}\psi(a^-) \tag{1.15}$$

Boundary condition 2: gives condition on $\psi'(0)$.

$$\begin{aligned} \psi'' &= \frac{2m}{\hbar^2}(V - E)\psi \\ &= -\frac{2m}{\hbar^2}\beta\delta(x)\psi + ... \end{aligned}$$

$$\int_{0^-}^{0^+} \psi'' = \int_{0^-}^{0^+} -\frac{2m}{\hbar^2}\beta\delta(x)\psi + ...$$

It gives

$$\psi'(0^+) - \psi'(0^-) = -\frac{2m}{\hbar^2}\beta\psi(0)$$

or in the interval $(0, a)$

$$\psi'(0^+) = e^{-iKa}\psi'(a^-) - \frac{2m}{\hbar^2}\beta\psi(0) \tag{1.16}$$

In the interval $(0, a)$, away from δ function, we have free particles ($-\frac{\hbar^2}{2m} = E\psi$), so

$$\psi = A\sin qx + B\cos qx$$

with

$$E = \frac{\hbar^2 q^2}{2m}$$

Let's solve ψ

By (1.15),

$$B = e^{-iKa}[A\sin qa + B\cos qa] \tag{1.17}$$

By (1.16)

$$qA = e^{-iKa}[qA\cos aq - qB\sin qa] - \frac{2m}{\hbar^2}\beta B \tag{1.18}$$

(1.17) $\Longrightarrow$

$$A\sin qa = [e^{iKa} - \cos qa]B$$

(1.18) $\Longrightarrow$

$$(1 - e^{-iKa}\cos qa)A\sin qa = (-e^{-iKa}\sin^2 qa - \frac{2m}{q\hbar^2}\beta\sin qa)B$$

combine the two

$$(1 - e^{-iKa}\cos qa)(e^{iKa} - \cos qa) = -e^{-iKa}\sin^2 qa - \frac{2m}{q\hbar^2}\beta\sin qa$$

simplify

$$e^{iKa} - 2\cos qa + e^{-iKa}\cos^2 qa = -e^{-iKa}\sin^2 qa - \frac{2m}{q\hbar^2}\beta\sin qa$$

so

$$2\cos Ka - 2\cos qa = -\frac{2m}{q\hbar^2}\beta \sin qa$$

That is

$$\cos Ka = \cos qa - \frac{am\beta}{\hbar^2}\frac{\sin qa}{qa} \tag{1.19}$$

Set $RHS = f(q)$, for (1.19) to have solution

$$|f(q)| \leq 1$$

Observing the plot of $f(q)$, one can see there are disjoint intervals, so this shows bands and gaps on the energy levels. Let's show q is in fact quantized, i.e. energy is discrete. Recall

$$K = \frac{2\pi n}{Na}$$

So there are N possible K's and there are $N/2$ possible $\cos Ka$'s, so in each allowed q intervals, there are $N/2$ discrete q's so there are $N/2$ energy bands, so there are actually N different wave functions. That is because for each q, there are two different K's. Recall the wave functions is patched piece by piece. In interval $(0, a)$ is

$$\psi(x) = A\sin qa + B\cos qa$$

then in the next interval $\psi(x)$ is given by

$$\psi(x + a) = e^{iKa}\psi(x)$$

The two different K's give different $e^{iKa} = \cos K + i\sin Ka$, one is the conjugate of the other.

In 3D, things are more complicated, but the general result still hold, N states become $2N$, by counting spins.

Notice applying electric fields will cause electron to more. If the band is partial filled, it is a conductor; fully filled, insulator, which require a significant energy to force electron to go to next band that is separated by a gap. In fact, if the energy is large enough one can break an insulator to a conductor.

2 Time-Independent Perturbation Theory

2.1 Non-Degenerated

Lecture 6 (2/7/13)

Suppose we are given

$$H = H^0 + \lambda H'$$

where H^0 is the Hamiltonian of a solved problem, and H' (here we denote prime not "1", because it is not the first correct to the Hamiltonian) is some additional term, λ is small constant. So the idea is to use the solved problem

$$H^0 \left|\psi_n^0\right\rangle = E_n^{(0)} \left|\psi_n^0\right\rangle$$

$$\left\langle\psi_n^0\middle|\psi_m^0\right\rangle = \delta_{mn}$$

to find $|\psi_n\rangle$ the true state vector

$$H \left|\psi_n\right\rangle = E_n \left|\psi_n\right\rangle \tag{2.1}$$

How small should λ be for the method to work? The energy of H should be similar to H^0 with some shifts that can be calculated. And we usually calculate energy correction to the 2nd order, so if we see that 1st is much smaller than 0th order, and 2nd order is much smaller than the 1st order, then we're pretty confident the method should work.

That is we hope we can write things in power series.

$$\left|\psi_n\right\rangle = \left|\psi_n^0\right\rangle + \lambda \left|\psi_n^1\right\rangle + \lambda^2 \left|\psi_n^2\right\rangle + ... \tag{2.2}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ... \tag{2.3}$$

If we have $\left|\lambda E_n^{(1)}\right| \gg \left|\lambda^2 E_n^{(2)}\right|$, we believe they may converge.

To find out a rule of calculating $E_n^{(1)}$, $E_n^{(2)}$,..., we substitute (2.2), (2.3) into (2.1), suppose we can do that

$(H^0+\lambda H')(\left|\psi_n^0\right\rangle+\lambda \left|\psi_n^1\right\rangle+\lambda^2 \left|\psi_n^2\right\rangle+...) =$

$$(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + ...)(\left|\psi_n^0\right\rangle + \lambda \left|\psi_n^1\right\rangle + \lambda^2 \left|\psi_n^2\right\rangle + ...)$$

Because λ is small, we can do each order of λ separately.

$O(\lambda^0):\ H^0 \left|\psi_n^0\right\rangle = E_n^{(0)} \left|\psi_n^0\right\rangle$

$O(\lambda^1):\ \lambda \left(H^0 \left|\psi_n^1\right\rangle + H' \left|\psi_n^0\right\rangle\right) = \lambda \left(E_n^{(0)} \left|\psi_n^1\right\rangle + E_n^{(1)} \left|\psi_n^0\right\rangle\right)$

$O(\lambda^2):\ \lambda^2 \left(H^0 \left|\psi_n^2\right\rangle + H' \left|\psi_n^1\right\rangle\right) = \lambda^2 \left(E_n^{(0)} \left|\psi_n^2\right\rangle + E_n^{(1)} \left|\psi_n^1\right\rangle + E_n^{(2)} \left|\psi_n^0\right\rangle\right)$

Apply $\langle\psi_n^0|$ to $O(\lambda^1)$, get

$$E_n^{(0)} \left\langle\psi_n^0\middle|\psi_n^1\right\rangle + \left\langle\psi_n^0\middle|H'\middle|\psi_n^0\right\rangle = E_n^{(0)} \left\langle\psi_n^0\middle|\psi_n^1\right\rangle + E_n^{(1)}$$

so

$$E_n^{(1)} = \left\langle\psi_n^0\middle|H'\middle|\psi_n^0\right\rangle$$

1st Energy Correction

$$\lambda E_n^{(1)} = \left\langle\psi_n^0\middle|\lambda H'\middle|\psi_n^0\right\rangle$$

Find $|\psi_n^1\rangle$, use $O(\lambda^1)$, get

$$\left(H^0 - E_n^{(0)}\right) \left|\psi_n^1\right\rangle = -\left(H' - E_n^{(1)}\right) \left|\psi_n^0\right\rangle$$

we know everything on RHS, write

$$\left|\psi_n^1\right\rangle = \sum_{m \neq n} c_m^{(n)} \left|\psi_m^0\right\rangle + \alpha \left|\psi_n^0\right\rangle \tag{2.4}$$

because $|\psi_n^0\rangle$'s form a complete basis. Plugging this in

$$\sum_{m \neq n} c_m^{(n)} \left(H^0 - E_n^{(0)}\right) \left|\psi_m^0\right\rangle + \alpha \left(H^0 - E_n^{(0)}\right) \left|\psi_n^0\right\rangle = -\left(H' - E_n^{(1)}\right) \left|\psi_n^0\right\rangle$$

so apply $\langle\psi_l^0|$, get

$$\sum_{m \neq n} c_m^{(n)} \left\langle\psi_l^0\right| H^0 - E_n^{(0)} \left|\psi_m^0\right\rangle = -\left\langle\psi_l^0\right| H' - E_n^{(1)} \left|\psi_n^0\right\rangle$$

If $l = n$,

$$0 = -\left\langle \psi_n^0 \middle| H' \middle| \psi_n^0 \right\rangle + E_n^{(1)}$$

If $l \neq n$,

$$\sum_{m \neq n} c_m^{(n)} \left(\left\langle \psi_l^0 \right| E_l^{(0)} \left| \psi_m^0 \right\rangle - \left\langle \psi_l^0 \right| E_n^{(0)} \left| \psi_m^0 \right\rangle \right) = -\left\langle \psi_l^0 \right| H' \left| \psi_n^0 \right\rangle$$

so

$$c_l^{(n)} \left(E_l^{(0)} - E_n^{(0)} \right) = -\left\langle \psi_l^0 \right| H' \left| \psi_n^0 \right\rangle$$

so

$$c_l^{(n)} = \frac{-\left\langle \psi_l^0 \right| H' \left| \psi_n^0 \right\rangle}{E_l^{(0)} - E_n^{(0)}}$$

1st correction in wave function

$$\lambda \left| \psi_n^1 \right\rangle = \lambda \sum_{l \neq n} \frac{\left\langle \psi_l^0 \right| H' \left| \psi_n^0 \right\rangle}{E_n^{(0)} - E_l^{(0)}} \left| \psi_l^0 \right\rangle + \lambda \alpha \left| \psi_n^0 \right\rangle \tag{2.5}$$

so the true state

$$\left| \psi_n \right\rangle = \left| \psi_n^0 \right\rangle + \sum_{l \neq n} \frac{\left\langle \psi_l^0 \right| \lambda H' \left| \psi_n^0 \right\rangle}{E_n^{(0)} - E_l^{(0)}} \left| \psi_l^0 \right\rangle + \lambda \alpha \left| \psi_n^0 \right\rangle + O(\lambda^2) \tag{2.6}$$

Use normalization to determine α

$$\langle \psi_n | \psi_n \rangle = (1 + \lambda\alpha)(1 + \lambda\bar{\alpha}) \left\langle \psi_n^0 \middle| \psi_n^0 \right\rangle + O(\lambda^2)$$

so we want

$$\alpha + \bar{\alpha} = 0$$

or α is pure imaginary, $\alpha = ib$, then $1 + \lambda\alpha \approx e^{ib\lambda}$, only add phase, what is why we don't have to include this term, or just set $\alpha = 0$.

Note we are doing non-degenerated perturbation. So all $E_l^{(0)}$'s in (2.6) are distinct, and the choice of $\{|\psi_m^0\rangle\}$ in (2.4) is unique, because for self-adjoint operator, eigenvectors corresponding to distinct eigenvalues are orthogonal. When we study degenerated perturbation, we will encounter issues that the denominator in (2.6) could be 0 and the choice of $\{|\psi_m^0\rangle\}$ in (2.4) become ambiguous.

In practice, we first obtain

$$E_n^{(1)} \to \left|\psi_n^1\right\rangle \to E_n^{(2)} \to \left|\psi_n^2\right\rangle$$

usually stop at $E_n^{(2)}$, expression for $E_n^{(2)}$ is already hard enough, which we will do next lecture.

Example. Helium

Recall Hamiltonian $H = H^0 + \lambda H'$

$$H^0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}$$

$$\lambda H' = \frac{e^2}{|r_1 - r_2|}$$

Energy for ground state of H^0 is -109eV, and use that state one can get the 1st correction

$$E_{gs}^{(1)} = \left\langle \psi_{gs}^0 \middle| \frac{e^2}{|r_1 - r_2|} \middle| \psi_{gs}^0 \right\rangle = 34.0\text{eV}$$

$$E = -109 + 34 = -75\text{eV}$$

Next time will do the 2nd order correction to get really close to the experiment value -79eV. But there is another way to get the 2nd order correction. That is "variation method".

Example. Suppose

$$H = \frac{p^2}{2m} + \frac{1}{2}mw^2x^2 + \frac{1}{2}mw^2\beta x^2$$

we know the exact solution to this if we treat $(\text{freq})^2 = w^2(1+\beta)$

$$E_n = \hbar w\sqrt{1+\beta}(n + \frac{1}{2})$$

Now use perturbation, suppose β is small, so

$$H^0 = \frac{p^2}{2m} + \frac{1}{2}mw^2x^2$$

$$\beta H' = \frac{1}{2} m w^2 \beta x^2$$

then

$$E_n^{(0)} = \hbar w (n + \frac{1}{2})$$

$$\beta E_n^{(1)} = \frac{1}{2} m w^2 \beta \left\langle n \middle| x^2 \middle| n \right\rangle$$

Recall

$$x = \sqrt{\frac{\hbar}{2mw}} (a_+ + a_-)$$

where

$$a_+ |n\rangle = \sqrt{n+1}\, |n+1\rangle$$

$$a_- |n\rangle = \sqrt{n}\, |n-1\rangle$$

so

$$\begin{aligned} \beta E_n^{(1)} &= \frac{1}{2} m w^2 \beta \frac{\hbar}{2mw} \langle n | a_+ a_- + a_- a_+ | n \rangle \\ &= \frac{\hbar w \beta}{4} \left((\sqrt{n})^2 + (\sqrt{n+1})^2 \right) \\ &= \hbar w (n + \frac{1}{2}) \frac{\beta}{2} \end{aligned}$$

compare the exact solution

$$E_n = \hbar w (n + \frac{1}{2})(1 + \frac{\beta}{2} + O(\beta^2))$$

Lecture 7 (2/12/13)

Find $E_n^{(2)}$.

Apply $\langle \psi_n^0 |$ to $O(\lambda^2)$

$$O(\lambda^2): \ \lambda^2 \left(H^0 |\psi_n^2\rangle + H' |\psi_n^1\rangle \right) = \lambda^2 \left(E_n^{(0)} |\psi_n^2\rangle + E_n^{(1)} |\psi_n^1\rangle + E_n^{(2)} |\psi_n^0\rangle \right)$$

$$E_n^{(0)} \left\langle \psi_n^0 \middle| \psi_n^2 \right\rangle + \left\langle \psi_n^0 \middle| H' \middle| \psi_n^1 \right\rangle = E_n^{(0)} \left\langle \psi_n^0 \middle| \psi_n^2 \right\rangle + E_n^{(1)} \left\langle \psi_n^0 \middle| \psi_n^1 \right\rangle + E_n^{(2)}$$

so

$$E_n^{(2)} = \left\langle \psi_n^0 \middle| H' \middle| \psi_n^1 \right\rangle$$

here $\langle\psi_n^0|\psi_n^1\rangle = 0$ because we have set $\alpha = 0$ in (2.5). Therefore

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\langle\psi_m^0|\, H' \,|\psi_n^0\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}} \tag{2.7}$$

2nd Energy Correction

$$\lambda^2 E_n^{(2)} = \sum_{m\neq n} \frac{\left|\langle\psi_m^0|\, \lambda H' \,|\psi_n^0\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}$$

notice if $|\psi_n\rangle$ is the ground state, then the 2nd correction $E_n^{(2)} \leq 0$ always.

Example. Helium ground state 2nd correction

$$E^{(2)} = \sum_{j\neq \text{gs}} \frac{\left|\left\langle j\left|\frac{e^2}{|r_2 - r_j|}\right|(1s)^2\right\rangle\right|^2}{E_{gs}^{(0)} - E_j^{(0)}}$$

Example.

$$H = \frac{p^2}{2m} + \frac{1}{2}mw^2x^2 + \lambda x^b \tag{2.8}$$

where b is odd. This is a case we really need 2nd order, because the 1st order gives zero

$$E^{(1)} = \langle n|x^b|n\rangle = \int dx\, |\psi_n(x)|^2\, x^b = 0$$

for x^b is an odd function. However 2nd order is easy

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left|\langle m|x^b|n\rangle\right|^2}{\hbar w(n+\frac{1}{2}) - \hbar w(m+\frac{1}{2})}$$

use $x = \sqrt{\frac{\hbar}{2mw}}(a_+ + a_-)$. One can easily see that there are only finite many non-zero terms, for m and n should be close within a few ladders.

Suppose $b = 1$

$$\langle m|x|n\rangle = \sqrt{\frac{\hbar}{2mw}} \begin{cases} \sqrt{n+1} & m = n+1 \\ \sqrt{n} & m = n-1 \\ 0 & \text{otherwise} \end{cases}$$

so

$$\lambda^2 E_n^{(2)} = \frac{\lambda^2 \hbar}{2mw}\left(\frac{n+1}{\hbar w(-1)} + \frac{n}{\hbar w(1)}\right) = \frac{-\lambda^2}{2mw^2}$$

We can compare this with the exact solution, so we rewrite (2.8)

$$H = \frac{p^2}{2m} + \frac{1}{2}mw^2(x + \frac{\lambda}{mw^2})^2 - \frac{1}{2}mw^2\frac{\lambda^2}{m^2w^4}$$

showing that the energy of the first part is still $\hbar w(n+1/2)$ + 2nd order correction, because the shift in x should not change energy.

2.2 Degenerated Perturbation

One would have trouble to apply (2.7) when $E_n^{(0)} - E_m^{(0)} = 0$ and $\langle\psi_m^0|H'|\psi_n^0\rangle \neq 0$.

Suppose we have degeneracy 2.

$$H^0\left|\psi_j^0\right\rangle = E^{(0)}\left|\psi_j^0\right\rangle \; j = 1,2 \quad \left\langle\psi_1^0\middle|\psi_2^0\right\rangle = 0 \tag{2.9}$$

We define

$$\left|\psi^0\right\rangle = c_1\left|\psi_1^0\right\rangle + c_2\left|\psi_2^0\right\rangle$$

such that

$$H'\left|\psi^0\right\rangle = E'\left|\psi^0\right\rangle$$

solve for c_1, c_2

$$c_1 H'\left|\psi_1^0\right\rangle + c_2 H'\left|\psi_2^0\right\rangle = E'(c_1\left|\psi_1^0\right\rangle + c_2\left|\psi_2^0\right\rangle)$$

apply $\langle\psi_1^0|$,

$$c_1\left\langle\psi_1^0\middle|H'\middle|\psi_1^0\right\rangle + c_2\left\langle\psi_1^0\middle|H'\middle|\psi_2^0\right\rangle = c_1 E'$$

apply $\langle\psi_2^0|$,

$$c_1\left\langle\psi_2^0\middle|H'\middle|\psi_1^0\right\rangle + c_2\left\langle\psi_2^0\middle|H'\middle|\psi_2^0\right\rangle = c_2 E'$$

This can be written in matrix form

$$\begin{pmatrix} w_{11} & w_{12} \\ w_{21} & w_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E'\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

(clearly $w_{12}^* = w_{21}$) then this becomes to solve eigenvalue problem, we set the determinant of

$$\begin{pmatrix} w_{11} - E' & w_{12} \\ w_{21} & w_{22-E'} \end{pmatrix}$$

to be 0, yield

$$E'_{\pm} = \frac{w_{11} + w_{22} \pm \sqrt{(w_{11} - w_{22})^2 - 4|w_{12}|^2}}{2} \tag{2.10}$$

then use E'_+, one can find the eigenvector (c_{1+}, c_{2+}), that will in turn give $\left|\psi_+^0\right\rangle$, similarly E'_- will give $\left|\psi_-^0\right\rangle$.

$\left|\psi_+^0\right\rangle$, $\left|\psi_-^0\right\rangle$ satisfy (2.9), so

$$E'_+ = \left\langle\psi_+^0\right|H'\left|\psi_+^0\right\rangle = E_+^{(1)}$$

$$E'_- = \left\langle\psi_-^0\right|H'\left|\psi_-^0\right\rangle = E_-^{(1)}$$

i.e. $E'_\pm$ are $E_\pm^{(1)}$. And now we don't need to do second order perturbation, because $\left\langle\psi_-^0\right|H'\left|\psi_+^0\right\rangle = 0$.

If in case one from the beginning has chosen $\left|\psi_\pm^0\right\rangle$ in place of $\left|\psi_j^0\right\rangle$ $j = 1, 2$, one will see $w_{12} = 0$, so 2nd correction is 0. One can also see that from (2.10)

$$E'_\pm = \max / \min\{w_{11}, w_{22}\} = E_\pm^{(1)}$$

In general $E_\pm^{(1)}$ are different, so $\left|\psi_\pm^0\right\rangle$ is unique and independent of initial choice of $\left|\psi_j^0\right\rangle$ $j = 1, 2$. If $E_\pm^{(1)}$ are the same, that means H and H' share the same eigenspace spanned by $\left|\psi_\pm^0\right\rangle$, this means we don't need to use perturbation on that space at all, because $\left|\psi_\pm^0\right\rangle$ are the exact solutions to $H + H'$.

2.3 Hydrogen Atom-Fine Structure

Relativistic Effect

Two familiar formulas

$$E = \frac{mc^2}{\sqrt{1 - v^2/c^2}} \quad \vec{p} = \frac{m\vec{v}}{\sqrt{1 - v^2/c^2}}$$

so

$$E^2 = p^2c^2 + m^2c^4$$

or

$$\begin{aligned} E &= mc^2\sqrt{1+\frac{p^2}{m^2c^2}} = mc^2[1+\frac{p^2}{2m^2c^2} - \frac{1}{8}(\frac{p^2}{m^2c^2})^2 + ...] \\ &\approx mc^2 + \frac{p^2}{2m} - \frac{1}{8}\frac{p^4}{m^3c^2} \end{aligned}$$

so now

$$H = mc^2 + \frac{p^2}{2m} - \frac{e^2}{r} - \frac{1}{8}\frac{p^4}{m^3c^2}$$

the first term is rest energy, second term is kinetic energy, and the last term is relativistic correction,

Rest energy

$$mc^2 \approx 500\text{keV}$$

Electron energy

$$\frac{p^2}{2m} \approx \frac{e^2}{r} \approx \frac{e^2}{a} \approx 13\text{eV} \approx \alpha^2 mc^2$$

where $a = \frac{\hbar^2}{me^2}$ Bohr radius, $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$ dimensionless constant, called "fine structure constant".

Relativistic correction

$$\frac{p^4}{m^3c^2} \approx \frac{e^4}{mc^2a^2} = \frac{e^2}{a}\alpha^2 = \alpha^4 mc^2 = 0.0014\text{eV}$$

Next lecture, we will show

Spin-Orbit Coupling Correction. It is also on the order of $\alpha^4 mc^2$. Then we will do Lamb shift is of $\alpha^5 mc^2$. Why do people even care what the next corrections are if they are so much different in magnitude? Because experiments can measure them with extremely precision. And they agree the theory very well.

Let's calculate 1st energy correction

$$H_{rel} = -\frac{p^4}{8m^3c^2} \quad H^0 = \frac{p^2}{2m} - \frac{e^2}{r}$$

so

$$\begin{aligned}
\langle\psi_n^0|H_{rel}|\psi^0\rangle &= -\frac{1}{2mc^2}\left\langle\psi_n^0\middle|\left(\frac{p^2}{2m}\right)^2\middle|\psi^0\right\rangle \\
&= -\frac{1}{2mc^2}\left\langle\psi_n^0\middle|\left(H^0+\frac{e^2}{r}\right)\left(H^0+\frac{e^2}{r}\right)\middle|\psi^0\right\rangle \\
&= -\frac{1}{2mc^2}\left\langle\psi_n^0\middle|\left(E^{(0)}+\frac{e^2}{r}\right)\left(E^{(0)}+\frac{e^2}{r}\right)\middle|\psi^0\right\rangle \\
&= -\frac{1}{2mc^2}\{(E^{(0)})^2 + 2E^{(0)}e^2\left\langle\psi_n^0\middle|\frac{1}{r}\middle|\psi_n^0\right\rangle + e^4\left\langle\psi_n^0\middle|\frac{1}{r^2}\middle|\psi_n^0\right\rangle\}
\end{aligned}$$

next time we will show

$$\left\langle\psi_n^0\middle|\frac{1}{r}\middle|\psi_n^0\right\rangle = \frac{1}{n^2a} \tag{2.11}$$

$$\left\langle\psi_n^0\middle|\frac{1}{r^2}\middle|\psi_n^0\right\rangle = \frac{1}{(l+\frac{1}{2})n^3a^2} \tag{2.12}$$

It follows that

$$E_n^{(1)} = -\frac{1}{2mc^2}(E_n^{(0)})^2\left(\frac{4n}{l+\frac{1}{2}} - 3\right) \sim \alpha^2 E_n^{(0)}$$

This result is rather surprising. It says 2p energy is lower than 2s by the relativistic consideration.

Lecture 8 (2/14/13)

We now show (2.11), (2.12), and use the following theorem discovered independently by Feynman and Hellmann.

Theorem. *(Feynman-Hellmann theorem)*

$$\left\langle\psi_n\middle|\frac{\partial H}{\partial\lambda}\middle|\psi_n\right\rangle = \frac{\partial E_n}{\partial\lambda}$$

Use $H = \frac{p^2}{2m} - \frac{e^2}{r}$

$$\frac{\partial H}{\partial(e^2)} = -\frac{1}{r}$$

so

$$\left\langle nlm\left|-\frac{1}{r}\right|nlm\right\rangle = \frac{\partial}{\partial e^2}\left(-\frac{me^4}{2\hbar^2 n^2}\right) = -\frac{me^2}{\hbar^2 n^2} = -\frac{1}{an^2}$$

For (2.12), use

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - \frac{e^2}{r}$$

Recall from last semester, without viral theorem, we have to do

$$\int dr r^2 \int d\theta \int d\psi \sin\theta (\psi^* \frac{l(l+1)}{r^2}\psi)$$

where $\psi = R(r)Y_{lm}(\theta, \psi)$,

$$R \sim e^{-\rho}\left(\sum c_k \rho^k\right)\rho^l$$

the sum terminates at some k_{max} and $n = k_{max} + l + 1$, therefore

$$\begin{aligned}\frac{\hbar^2}{2m}(2l+1)\left\langle\frac{1}{r^2}\right\rangle &= \frac{\partial E}{\partial l} = \frac{\partial}{\partial l}\left(-\frac{me^4}{2\hbar^2(k_{max}+l+1)^2}\right) \\ &= \frac{me^4}{\hbar^2 n^3}\end{aligned}$$

so we have (2.12).

For relativistic correction, we don't need to do 2nd order perturbation under the same n. Since

$$[\vec{L}^2, p^2] = 0 \implies [\vec{L}^2, p^4] = 0$$

H_{rel} commutes with $\vec{L}^2$. Hence

$$\left\langle nlm_l\left|H_{rel}L^2\right|nl'm_l'\right\rangle = \hbar^2 l'(l'+1)\left\langle nlm_l|H_{rel}|nl'm_l'\right\rangle$$

$$\left\langle nlm_l\left|L^2 H_{rel}\right|nl'm_l'\right\rangle = \hbar^2 l(l+1)\left\langle nlm_l|H_{rel}|nl'm_l'\right\rangle$$

It follows

$$\langle nlm_l|H_{rel}|nl'm_l'\rangle = 0$$

if $l \neq l'$. Similar result holds for $m_l \neq m_l^{'}$.

Spin-Orbit Coupling

Consider electron at rest, and proton is moving around the electron. so proton produces a current I. That causes magnetic field B, and the magnetic exerts force on electron, because electron has magnetic moment $\vec{\mu}$. So putting things together,

$$I = \frac{e}{T} = \frac{ev}{2\pi r} = \frac{emvr}{2\pi mr^2} = \frac{e|L|}{2\pi mr^2}$$

By Biot-Savart

$$\vec{B} = \frac{2\pi}{c}\frac{I}{r} = \frac{e|L|\hat{L}}{cmr^3}$$

$$\vec{\mu} = \frac{g(-e)}{2mc}\vec{S}$$

where $g = 2(1 + \frac{\alpha}{\pi} + ...) \approx 2$

$$H_{spin-orbit} \sim -\vec{\mu} \cdot \vec{B} = \frac{ge^2}{2m^2c^2}\frac{1}{r^3}\vec{L} \cdot \vec{S}$$

Because electron is not in a rest frame, we need Thomas precession to add to the H

$$\Delta E_{thoms} = -\frac{1}{2m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\vec{L} \cdot \vec{S}$$

where $V = -e^2/r$, so finally the correct

$$H_{spin-orbit} = \frac{(g-1)e^2}{2m^2c^2}\frac{1}{r^3}\vec{L} \cdot \vec{S}$$

(There are number of books have mistakenly taken $g/2$ in place of $g - 1$.) The magnitude of this correction is

$$\approx \frac{e^2}{m^2c^2a^3}\hbar^2 = \alpha^2\left(\frac{e^2}{a}\right) \sim \alpha^4 mc^2$$

same order as relativistic correction.

To do perturbation, we want to pick a good basis

$$|nlm_l m_s\rangle \text{ or } |nljm_j\rangle?$$

Since $[\vec{L}\cdot\vec{S}, L_z] \neq 0$, $[\vec{L}\cdot\vec{S}, S_z] \neq 0$, but $[\vec{L}\cdot\vec{S}, L^2] = 0$, $[\vec{L}\cdot\vec{S}, \vec{J}] = 0$, as we learned before

$$\left\langle nljm_j \middle| H_{spin-orbit} \middle| nl'j'm_j' \right\rangle = 0$$

if $l \neq l'$, $j \neq j'$, or $m_j \neq m_j'$. So $|nljm_j\rangle$ is better.

$\vec{J}^2 = (\vec{L}+\vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L}\cdot\vec{S} \implies \vec{L}\cdot\vec{S} = \frac{1}{2}(\vec{J}^2 - \vec{L}^2 - \vec{S}^2)$

$$\left\langle \vec{L}\cdot\vec{S} \right\rangle = \frac{\hbar^2}{2}[j(j+1) - l(l+1) - \frac{3}{4}]$$

and

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l+\frac{1}{2})(l+1)n^3a^3}$$

we get

$$E^{(1)}_{spin-orbit} = \frac{e^2}{2m^2c^2}\frac{\hbar^2}{2}\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+\frac{1}{2})(l+1)n^3a^3}$$

Combine relativistic and spin-orbit

$$E_{fine\,structure} = (E_n^{(0)})^2\frac{1}{2mc^2}\left[\frac{-4n}{l+1/2} + 3 + \frac{2n[j(j+1) - l(l+1) - 3/4]}{l(l+1/2)(l+1)}\right]$$

Since $j = l \pm 1/2$ or $l = j \pm 1/2$, plug them into above, they give the same result

$$E^{(1)}_{fs} = (E_n^{(0)})^2\frac{1}{2mc^2}\left[3 - \frac{4n}{j+1/2}\right] \tag{2.13}$$

so $E^{(0)} + E^{(1)}$ is

$$E_{nj} = -\frac{e^2}{2an^2}\{1 + \frac{\alpha^2}{n^2}(\frac{n}{j+1/2} - \frac{3}{4})\}$$

In the derivation of spin-orbit, we did not consider the case $l = 0$ separately. Since $l = 0$, $\vec{L}\cdot\vec{S} = 0$, in this review there is no spin-orbit interaction, but nevertheless the formula above works for all l, i.e. all j. That is because when we did relativistic correction, we cheated, we used

$$\int d^3r\psi^*\nabla^4\psi = \int d^3r(\nabla^2\psi^*)(\nabla^2\psi)$$

but when $l = 0$, the boundary term at $r = 0$ gives singularity, hence the integration

by parts didn't work out properly.

The proper way to do fine structure is through Dirac.

1927-1928 Dirac wanted to do Schrodinger equation relativistically, instead of

$$\frac{i\hbar\partial}{\partial t}\psi = E\psi = (\frac{p^2}{2m} + V)\psi$$

he used

$$\frac{i\hbar\partial}{\partial t}\psi = (\sqrt{p^2c^2 + m^2c^4} + V)\psi$$

but to make $\vec{p}^2$ identify to $-\frac{\hbar^2}{2m}\nabla^2$, he had to consider it as a matrix and ψ is a 4-vector. Then he found Dirac equation, and then he found his equation has to have

(1) for spin 1/2 particle to have opposite charge and same mass. (he predicted antiparticles)

(2) $g = 2$ (In QED quantize magnetic field, then $g = 2 + \frac{\alpha}{\pi} + A\alpha^2 + B\alpha^4 + C\alpha^5 + ...$ which each coefficient has been calculated through integration of over 20 variables and they all agree experiment extremely well.)

(3) Hydrogen atom spectrum, in particular fine structure. His calculation is done without considering orbit, hence no Thomas patch.

2.4 Lamb shift

Lecture 9 (2/19/13)

This is at the order of $\alpha^5 mc^2$. After quantizing EM field, one can create or destroy photons, so one needs to put in additional term $H_{interaction\,with\,EM\,field}$. This turns out to be hilarious calculation, one would have to do 2nd perturbation

$$\sum \frac{|\langle n|H_{inter\,EM}|m\rangle|^2}{E_n - E_m}$$

The shift of energy depends on whether it is a free electron, bound electron of Hydrogen 1s, or 2p, ...

Overall before Lamb shift, energy of $2P_{1/2} = 2S_{1/2}$, after Lamb $2P_{1/2} < 2S_{1/2}$, so energy is now labeled by

$$E_{nlj}$$

But still electrons that spins up or down give the same energy, i.e. Hamiltonian

still commutes m_s. We will see that will not be the case after we consider Zeeman effect.

2.5 Zeeman Effect

Consider putting in an external $\vec{B}$ field, which is in the z direction. The electron has magnetic moments due to spin and orbit around the nuclei, hence

$$\vec{\mu}_l = -\frac{e}{2mc}\vec{L}$$

and

$$\vec{\mu}_s = -\frac{ge}{2mc}\vec{S}$$

So

$$H_{Zeeman} = -(\vec{\mu}_l + \vec{\mu}_s)\cdot\vec{B} = \frac{e}{2mc}(\vec{L} + 2\vec{S})\cdot\vec{B} = \frac{e}{2mc}(L_z + 2S_z)B_z$$

We study three cases.

(1) weak field: Strength of $B_{ext} \ll B_{internal}$, hence fine structure is dominated. H_Z as perturbed Hamiltonian on the eigenstates of $H^0 = H_{Bohr} + H_{fs}$.

(2) strong field: $B_{ext} \gg B_{internal}$, H_Z as perturbation on H^0, then H_{fs} as perturbation on $H_{Bohr} + H_Z$.

(3) intermediate field: next lecture.

Weak Field

Recall $|nljm_j\rangle$ are good basis for fine structure, and it is also good for Zeeman, because

$$[\vec{L}^2, H_Z] \propto [\vec{L}^2, \vec{L}] + 2[\vec{L}^2, \vec{S}] = 0 + 0 = 0$$

$$[J_z, L_z] = [J_z, S_z] = 0$$

$$[\vec{J}^2, H_Z] \propto [\vec{J}^2, \vec{L}] + 2[\vec{J}^2, \vec{S}] = 0 + 0 = 0$$

that term $[\vec{J}^2, \vec{S}] = 0$ is only meant in the sense of time averaging. Claim

$$\left\langle \vec{S} \right\rangle = \left\langle \frac{\vec{S}\cdot\vec{J}}{\vec{j}^2}\vec{J} \right\rangle \tag{2.14}$$

This is saying that the component along $\vec{J}$ is equal to $\left\langle \vec{S} \right\rangle$. The proof is much machinery, so just believe in this one.

Therefore

$$\left\langle nljm_j \middle| H_Z \middle| nl'j'm'_j \right\rangle = 0$$

if $l \neq l'$, $j \neq j'$, or $m_j \neq m'_j$.

So 1st order energy

$$\frac{eB}{2mc} \langle nljm_j | L_z + 2S_z | nljm_j \rangle \;=\; \frac{eB}{2mc} \langle nljm_j | J_z + S_z | nljm_j \rangle \qquad (2.15)$$

Using (2.14), and notice

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

Therefore (2.15) gives

$$\frac{eB}{2mc} \hbar m_j [1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}] = \mu_B g_L B m_j \qquad (2.16)$$

we set the quantity in square bracket to be g_L, called Lande factor, and call $\frac{e\hbar}{2mc} \equiv \mu_B \approx 5.8 \times 10^{-5}$eV/Tesla, Bohr magneton. If g was 1, as thought by people before QM, then g_L would be just 1, so the early people thought Zeeman effect was just $\mu_B B m_j$.

We can list the energy shifts for the 8 Hydrogen states of $n = 2$.

Set $\beta = \mu_B B_{ext}$, $E_2 = (-13.6)/4$ Bohr energy for $n = 2$, set $\gamma = (13.6)\frac{\alpha^2}{64}$ then (2.13), (2.16) become

$$E_{fs} = -\gamma(\frac{8n}{2j+1} - 3) \qquad (2.17)$$

$$E_Z = \beta g_L m_j$$

1st correction energy of 8 Hydrogen states of $n = 2$. In $|n\, l\, j\, m_j\rangle$

$$\left.\begin{array}{rcl} |2,0,1/2,1/2\rangle & = & E_2 - 5\gamma + \beta \\ |2,0,1/2,-1/2\rangle & = & E_2 - 5\gamma - \beta \\ |2,1,3/2,3/2\rangle & = & E_2 - \gamma + 2\beta \\ |2,1,3/2,-3/2\rangle & = & E_2 - \gamma - 2\beta \\ & & \\ |2,1,3/2,1/2\rangle & = & E_2 - \gamma + 2\beta/3 \\ |2,1,1/2,1/2\rangle & = & E_2 - 5\gamma + \beta/3 \\ |2,1,3/2,-1/2\rangle & = & E_2 - \gamma - 2\beta/3 \\ |2,1,1/2,-1/2\rangle & = & E_2 - 5\gamma - \beta/3 \end{array}\right\} \tag{2.18}$$

Strong Field

The basis $|nlm_l m_s\rangle$ are good states for H_Z, i.e. the 2nd perturbation will be 0, so we should choose them for the strong field case, then

$$\langle nlm_l m_s|H_Z|nlm_l m_s\rangle = \beta(m_l + 2m_s)$$

then one can show 1st order fine structure perturbation on this basis

$$\langle nlm_l m_s|H_{fs}|nlm_l m_s\rangle = \gamma\frac{64}{n^3}(\frac{3}{4n} - \frac{l(l+1) - m_l m_s}{l(l+1/2)(l+1)})$$

We can list the energy shifts for the 8 Hydrogen states of $n = 2$. In $|nlm_l m_s\rangle$

$$\left.\begin{array}{rcl} |2,0,0,1/2\rangle & = & E_2 + \beta - 5\gamma \\ |2,0,0,-1/2\rangle & = & E_2 - \beta - 5\gamma \\ |2,1,1,1/2\rangle & = & E_2 + 2\beta - \gamma \\ |2,1,-1,-1/2\rangle & = & E_2 - 2\beta - \gamma \\ & & \\ |2,1,0,1/2\rangle & = & E_2 + \beta - 7\gamma/3 \\ |2,1,1,-1/2\rangle & = & E_2 + 0 - 11\gamma/3 \\ |2,1,-1,1/2\rangle & = & E_2 + 0 - 11\gamma/3 \\ |2,1,0,-1/2\rangle & = & E_2 - \beta - 7\gamma/3 \end{array}\right\} \tag{2.19}$$

Lecture 10
(2/21/13)

Summary from last time,

We saw that

$$H_Z \sim L_z + 2S_z$$

is diagonal in $m_l m_s$ basis, and

$$H_{fs} \sim \vec{L} \cdot \vec{S} \sim J^2 - L^2 - S^2$$

is diagonal in jm_j basis.

Intermediate Field

Now we have to use degenerated perturbation. Choose jm_j basis. (we could choose $m_l m_s$ basis, too.)

Clebsch-Gordan coefficients give

$$\psi_1 = \left| l=0, j=\frac{1}{2}, m_j=\frac{1}{2} \right\rangle = \left| l=0, m_l=0, m_s=\frac{1}{2} \right\rangle$$

$$\psi_2 = \left| l=0, j=\frac{1}{2}, m_j=-\frac{1}{2} \right\rangle = \left| l=0, m_l=0, m_s=-\frac{1}{2} \right\rangle$$

$$\psi_3 = \left| l=1, j=\frac{3}{2}, m_j=\frac{3}{2} \right\rangle = \left| l=1, m_l=1, m_s=\frac{1}{2} \right\rangle$$

$$\psi_4 = \left| l=1, j=\frac{3}{2}, m_j=-\frac{3}{2} \right\rangle = \left| l=1, m_l=-1, m_s=-\frac{1}{2} \right\rangle$$

$$\psi_5 = \left| l=1, j=\frac{3}{2}, m_j=\frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} \left| l=1, m_l=0, m_s=\frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| l=1, m_l=1, m_s=-\frac{1}{2} \right\rangle$$

$$\psi_6 = \left| l=1, j=\frac{1}{2}, m_j=\frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} \left| l=1, m_l=0, m_s=\frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| l=1, m_l=1, m_s=-\frac{1}{2} \right\rangle$$

$$\psi_7 = \left| l=1, j=\frac{3}{2}, m_j=-\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} \left| l=1, m_l=-1, m_s=\frac{1}{2} \right\rangle + \sqrt{\frac{2}{3}} \left| l=1, m_l=0, m_s=-\frac{1}{2} \right\rangle$$

$$\psi_8 = \left| l=1, j=\frac{1}{2}, m_j=-\frac{1}{2} \right\rangle = -\sqrt{\frac{2}{3}} \left| l=1, m_l=-1, m_s=\frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} \left| l=1, m_l=0, m_s=-\frac{1}{2} \right\rangle$$

Then use (2.17) and

$$E_Z = \beta(m_l + 2m_s)$$

we can calculate the 1st order energy correction $\langle nljm_j|H_{fs} + H_Z|nljm_j\rangle$ for $n = 2$, which are just the diagonal elements of the following matrix that is obtained in the basis of ψ_{1-8}

$$\begin{pmatrix}
-5\gamma+\beta & & & & & & & \\
& -5\gamma-\beta & & & & & & \\
& & -\gamma+2\beta & & & & & \\
& & & -\gamma-2\beta & & & & \\
& & & & -\gamma+\frac{2}{3}\beta & -\frac{\sqrt{2}}{3}\beta & & \\
& & & & -\frac{\sqrt{2}}{3}\beta & -5\gamma+\frac{1}{3}\beta & & \\
& & & & & & -\gamma-\frac{2}{3}\beta & -\frac{\sqrt{2}}{3}\beta \\
& & & & & & -\frac{\sqrt{2}}{3}\beta & -5\gamma-\frac{1}{3}\beta
\end{pmatrix}$$

So one can see these 8 diagonal elements agree exactly to (2.18). We did not have issue in the weak field limit before. Because $|nljm_j\rangle$ basis are eigenstates of $H + H_{fs}$, then we did perturbation of H_Z on $|nljm_j\rangle$, and for example the second perturbation energy correction of ψ_6 will be

$$E^{(2)}_{\psi_6} = \sum_{j\neq 6} \frac{|\langle\psi_j|H_Z|\psi_6\rangle|^2}{E_{\psi_6} - E_{\psi_j}} = \frac{|\langle\psi_5|H_Z|\psi_6\rangle|^2}{E_{\psi_6} - E_{\psi_5}} = \frac{(-\frac{\sqrt{2}}{3}\beta)^2}{(-5\gamma+\frac{1}{3}\beta) - (-\gamma+\frac{2}{3}\beta)} \ll 0$$

for weak field since $\gamma \gg \beta$.

But for intermediate field we do perturbation of $H_Z + H_{fs}$ on $|nljm_j\rangle$ of eigenstates of H_{Bohr}, and for example the second perturbation energy correction of ψ_6 will be

$$E^{(2)}_{\psi_6} = \sum_{j\neq 6} \frac{|\langle\psi_j|H_{fs} + H_Z|\psi_6\rangle|^2}{E_{\psi_6} - E_{\psi_j}} = \sum_{j\neq 6} \frac{|\langle\psi_j|H_Z|\psi_6\rangle|^2}{E_{n=2} - E_{n=2}} = \frac{(-\frac{\sqrt{2}}{3}\beta)^2}{0} \gg 1$$

so $|nljm_j\rangle$ are not good basis now. We need to find a good basis that diagonalizes the matrix.

After diagonalizing the matrix, we obtain four new diagonal elements

$$\begin{aligned}
\epsilon_5 &= E_2 - 3\gamma + \frac{\beta}{2} + \sqrt{4\gamma^2 + \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \\
\epsilon_6 &= E_2 - 3\gamma + \frac{\beta}{2} - \sqrt{4\gamma^2 + \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \\
\epsilon_7 &= E_2 - 3\gamma - \frac{\beta}{2} + \sqrt{4\gamma^2 - \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}} \\
\epsilon_8 &= E_2 - 3\gamma - \frac{\beta}{2} - \sqrt{4\gamma^2 - \frac{2}{3}\gamma\beta + \frac{\beta^2}{4}}
\end{aligned}$$

One can easily see that for weak field $\gamma \gg \beta$

$$\epsilon_5 = E_2 - 3\gamma + \frac{\beta}{2} + 2\gamma(1 + \frac{\beta}{12\gamma}) = E_2 - \gamma + \frac{2}{3}\beta$$

agrees the fifth diagonal element of the original matrix, or the fifth equation in (2.18).

If $\gamma \ll \beta$,

$$\epsilon_5 = E_2 - 3\gamma + \frac{\beta}{2} + \frac{\beta}{2}(1 + \frac{4}{3}\frac{\gamma}{\beta}) = E_2 + \beta - \frac{7}{3}\gamma$$

which agrees the fifth equation in (2.19).

When Hydrogen is placed in an external electric field, one will get Stark effect, where spin is irrelevant and one will have to diagonalize 9 by 9 matrix.

2.6 Hyperfine Structure

Lecture 11 (2/26/13)

Recall fine structure is interaction of $\vec{S}$, $\vec{L}$ + relativistic correction.

Hyperfine is interaction of electron and proton magnetic moments

$$\vec{\mu}_e = \frac{g_e(-e)}{2m_e c}\vec{S}_e \qquad \vec{\mu}_p = \frac{g_p e}{2m_p c}\vec{S}_p$$

where $g_p \approx 5.59$, because proton is made of 3 quarks. Each quark has $g \approx 2$, mass of quark $\approx m_p/3 \approx 300MeV$, charge of quark $2e/3$ for up and $-e/3$ for down.

Hyperfine energy is at the order,

$$(\text{fine structure}) \times \frac{m_e}{m_p}$$

for Hydrogen in ground state

$$E' = \frac{8}{3} \underbrace{\frac{e^2}{2a}}_{13.6eV} a^2 \frac{m_e}{m_p} \propto \frac{1}{h^2} \left\langle \vec{S}_e \cdot \vec{S}_p \right\rangle$$

Compute $\vec{S}_e \cdot \vec{S}_p$ similar as before, let total spin $\vec{F} = \vec{S}_e + \vec{S}_p$, then $F = 0, 1$ and $F^2 = \hbar^2 F(F+1)$, then

$$\vec{S}_e \cdot \vec{S}_p = \frac{F^2 - S^2 - F^2}{2} = \begin{cases} -\frac{3}{4}\hbar^2 & F = 0 \\ \frac{1}{4}\hbar^2 & F = 1 \end{cases}$$

The energy split between

$$E(F=1) - E(F=0)$$

gives the famous 21 cm wave radiation. Notice unlike in Zeeman, here there is no preferred z direction. So the radiation left out in the universe is detected in all directions.

3 Variational Principle

3.1 Reyleigh-Ritz

It provides a quick method to estimate ground state E_{gs}.

Theorem. *(Reyleigh-Ritz) Choose any normalized wave function $\psi(\vec{r})$ then*

$$\langle \psi | H | \psi \rangle = \int d^3 r \psi * H\psi \geq E_{gs}$$

Proof. $\psi(\vec{r}) = \sum c_n \phi_n(\vec{r})$, where ϕ_n is energy eigenstates,

$$\langle\psi|H|\psi\rangle = \sum_{n,m} c_n^* c_m \langle\phi_n|H|\phi_m\rangle = \sum |c_n|^2 E_n \geq \left(\sum |c_n|^2\right) E_{gs} = E_{gs}$$

□

So our line of attack is to try some ψ, then adjust ψ to make $\langle\psi|H|\psi\rangle$ as smaller as possible. If no further smaller, we think we reach E_{gs}.

Example. Particle in a 1D box $[0, L]$, try

$$\psi(x) = \begin{cases} Ax & 0 < x < \frac{L}{2} \\ A(L-x) & \frac{L}{2} < x < L \end{cases}$$

Normalization says

$$\int dx|\psi|^2 = \int_0^{L/2} dx A^2 x^2 + \int_{L/2}^{L} dx A^2 (L-x)^2 = A^2 \frac{L^3}{12} = 1 \implies A = \sqrt{\frac{12}{L^3}}$$

Now do $H\psi$, $H = \frac{P^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

$$\frac{d\psi}{dx} = \begin{cases} A & 0 < x < \frac{L}{2} \\ -A & \frac{L}{2} < x < L \\ 0 & |x| > L \end{cases}$$

$$\frac{d^2\psi}{dx^2} = A\delta(x) - 2A\delta(x - \frac{L}{2}) + A\delta(x - L)$$

then

$$\langle\psi|H|\psi\rangle = -\frac{\hbar^2}{2m}\int dx \psi \frac{d^2\psi}{dx^2} = -\frac{\hbar^2}{2m}[A\psi(0) - 2A\psi(\frac{L}{2}) + A\psi(L)] = -\frac{A^2 L\hbar^2}{2m} = 12\frac{h^2}{2mL^2}$$

Indeed

$$\langle\psi|H|\psi\rangle > E_{gs} = \pi^2 \frac{h^2}{2mL^2}$$

note: One can get the same result without δ functions, use

$$\left\langle \psi \middle| \frac{P^2}{2m} \middle| \psi \right\rangle = \frac{1}{2m} \langle P\psi | P\psi \rangle$$

3.2 Ground state Helium Energy

We now use variational method to compute ground state Helium

Example. Helium

Experiment gives $E_{gs} = -78.975eV$, perturbation 0th, 1st orders give

$$E^0 = -109eV \qquad E^0 + E^1 = -75eV$$

We start from Hydrogen ground state, with a charge from $Z = 1 \to Z' \in (1, 2)$, later we will find the optimal Z'

$$\psi(\vec{r}_1, \vec{r}_2) = \sqrt{\frac{(Z')^3}{\pi a^3}} e^{-Z' r_1/a} \sqrt{\frac{(Z')^3}{\pi a^3}} e^{-Z' r_2/a}$$

we can view this change as a change on a from $a \to a/Z'$, so that many of the calculations for Hydrogen will be taken over for free, e.g.

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a} \to \frac{Z'}{a} \qquad \left\langle \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right\rangle = \frac{5}{8a} \to \frac{5Z'}{8a}$$

Now

$$\begin{aligned} H &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \\ &= \left(\frac{p_1^2}{2m} - \frac{Z'e^2}{r_1} \right) + \left(\frac{p_2^2}{2m} - \frac{Z'e^2}{r_2} \right) + \frac{(Z'-2)e^2}{r_1} + \frac{(Z'-2)e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \end{aligned}$$

With another change of view on $e^2 \to Z'e^2$, we get

$$E_1 = -\frac{e^2}{2a} \to Z'^2 E_1$$

of part of H, $\left(\frac{p_1^2}{2m} - \frac{Z'e^2}{r_1}\right)$, the Z' ionized atom. Therefore

$$\begin{aligned}\langle H\rangle &= 2Z'^2E_1 + 2\frac{(Z'-2)Z'e^2}{a} + \frac{5Z'e^2}{8a} \\ &= E_1\left(2Z'^2 - 4(Z'-2)Z' + \frac{5}{4}Z'\right) \\ &\overset{\min}{=} E_1(\frac{1}{2}(\frac{3}{2})^6) = -77.5eV\end{aligned}$$

min when $Z' = 27/16$.

People have tried different $\psi(\vec{r}_1, \vec{r}_2)$ with 2000 terms and got E_{gs} Helium to 18 decimal places closer to $-79eV$.

Remark. 1) One sack back of variational method is that there is no way to know how close we are to E_{gs}. More worse, even we are close to E_{gs}, but the trial wave function may no where close to the true ground state wave function.

2) One can find the second lowest energy level, 1st excited state, by variational principle. Suppose one know the ψ_{gs}, then try

$$\psi \perp \psi_{gs}$$

then minimize $\langle\psi|H|\psi\rangle$.

3.3 Ionized Hydrogen Molecules

Lecture 12 (2/28/13)

We now do another 3 bodies problem

Example. Molecules H_2^+

$$H = \frac{P_1^2}{2m_p} + \frac{P_2^2}{2m_p} + \frac{P^2}{2m_e} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R}$$

$r_{1,2}$ distance from electron to two protons, R distance between two protons. We are not much interested in exact form of $\psi(\vec{r}_e, \vec{r}_{p_1}, \vec{r}_{p_2})$ but interested in showing that variational method predicts such bonding exists .

One can think this as a perturbation problem

$$H^0 = \frac{P^2}{2m_e} - \frac{e^2}{r_1} - \frac{e^2}{r_2} \qquad H' = \frac{P_1^2}{2m_p} + \frac{P_2^2}{2m_p} + \frac{e^2}{R}$$

Because by momentum conservation, the momentum of election in H_2^+ should equal to proton momentum, but protons are much heavier, proton moves much slower. In other words any slow changes distant of two proton, instantaneously change electron ground state. This allows us to separate the electron problem H^0 from the proton problem H'. Hence we first solve electron problem, find V_{elec} ground state energy of electron when protons are not moving and R apart. Then we put

$$V_{proton}(R) = V_{elec}(R) + \frac{e^2}{R} \tag{3.1}$$

and solve the 2 bodies problem, cf (1.6)

$$H = \frac{p^2}{2\mu} + \frac{P^2}{2M} + V(R)$$

The two protons not to fly off, i.e. forming a bond iff V has a minimum. We know what V looks like at when $R \to 0$, $V \to \infty$, because strong force is very strong. As $R \to \infty$, the system has lowest energy when the electron binds with one proton and let the other proton go, so $V(\infty) \to E_1 = -\frac{e^2}{2a} = -13.6eV$. (In 1D if V is negative somewhere, then there exists certainly some bound state. This is not true in 2D or 3D.)

Question: what is in between, does it have a minimum? To answer it, we need to find $V_{elec}(R)$. To find $V_{elec}(R)$, we use variational method. Notice variational method can only prove bonding exist, but it can not prove bonding doesn't exist.

Try test function

$$\psi = A(\psi_0(\vec{r}_1) + \psi_0(\vec{r}_2)) \tag{3.2}$$

where $\psi_0 = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$. The reason we have the same A for both is that the problem is symmetric. The reason we use + not − is that as we'll see in the calculation + correctly shows energy is lowest when the election is in the middle of two protons.

We may guess that if minimum of V_{elec} exists, it should be at the order of

$R \sim a$, and $V_{elec}(\min) \sim \frac{e^2}{a}$. This clarifies that why in (3.1), for the two body problem we only consider the additional electric energy $\frac{e^2}{R}$. That is because all other energies are not in that order. E.g vibration energy, say two protons are vibrating around $V(\min)$ like simple harmonic oscillator, then

$$w = \sqrt{\frac{k}{m_p}} = \sqrt{\frac{V''}{m_p}} \sim \sqrt{\frac{e^2}{m_p a^3}} = \frac{1}{a}\sqrt{\frac{e^2}{m_p}\frac{m_e e^2}{\hbar^2}} = \frac{1}{\hbar}\sqrt{\frac{m_e}{m_p}}\frac{e^2}{a} \implies \hbar w = \sqrt{\frac{m_e}{m_p}}\frac{e^2}{a}$$

Rotational energy (here w not the same w above)

$$K = \frac{1}{2}Iw^2 = \frac{L^2}{2I}$$

L angular momentum $L \sim \hbar$, $I \sim m_p R^2 \sim m_p a^2$, so

$$K \sim \frac{\hbar^2}{m_p a^2} = \frac{m_e}{m_p}\frac{e^2}{a}$$

Now back to (3.2), find A

$$1 = |A|^2 \int d^3r |\psi_0(r_1)|^2 + |\psi_0(r_2)|^2 + 2\underbrace{\psi_0^*(r_1)\psi_0(r_2)}_{I} = 2|A|^2(1+I)$$

I is called overlap integral. Next

$$\begin{aligned} H\psi &= \left(\frac{P^2}{2m_e} - \frac{e^2}{r_1} - \frac{e^2}{r_2}\right)\psi_0(r_1) + \left(\frac{P^2}{2m_e} - \frac{e^2}{r_2} - \frac{e^2}{r_1}\right)\psi_0(r_2) \\ &= \left(E_1 - \frac{e^2}{r_2}\right)\psi_0(r_1) + \left(E_2 - \frac{e^2}{r_1}\right)\psi_0(r_2) \end{aligned}$$

$$\begin{aligned}
\langle\psi|H\psi\rangle &= |A|^2[E_1\int d^3r|\psi_0(r_1)+\psi_0(r_2)|^2+\underbrace{\int d^3r\psi_0^*(r_1)(-\frac{e^2}{r_2})\psi_0(r_1)}_{D}+(1\leftrightarrow 2)\\
&\quad+\underbrace{\int d^3r\psi_0^*(r_1)(-\frac{e^2}{r_1})\psi_0(r_2)}_{X}+(1\leftrightarrow 2)]\\
&= E_1-2\frac{|A|^2e^2}{a}D-2\frac{|A|^2e^2}{a}X\\
&= E_1\left(1+\frac{2}{1+I}(D+X)\right)
\end{aligned}$$

D is called direct integral, X is called exchange integral. To integral I, D, X over all spaces, we use spherical coordinate, put one proton at the origin, and the other at $(0,0,R)$, then put

$$\begin{cases} r_1 = r \\ r_2 = \sqrt{R^2+r^2-2Rr\cos\theta} \end{cases}$$

For the $(1\leftrightarrow 2)$ integral, do the same and put $r_2 = r$, and $r_1 = \sqrt{R^2+r^2-2Rr\cos\theta}$, so clearly the values should be the same.

Lecture 13 (3/5/13)

After some calculation,

$$I = e^{-R/a}[1+\frac{R}{a}+\frac{1}{3}(\frac{R}{a})^2]$$

$$D = \frac{a}{R}-(1+\frac{a}{R})e^{-2R/a}$$

$$X = (1+\frac{R}{a})e^{-R/a}$$

They show as $R\to\infty$, $\langle H\rangle \to E_1$.

Now we can graph $\langle\psi|H|\psi\rangle\,(R)$, Griffiths figure 7.7, showing there is one minimum $< E_1$, so by variational principal, the actual ground state does have some minimums. Question: Is the minimum stable? We don't know. There may be more than one minimum, i.e. exist some local but not global minimums. In that case, fluctuation such as vibration may push the bonding out of local minimum.

4 WKB Approximation

4.1 WKB

W for Wentzel; K for Kramers; B for Brillouin. Within months after Schrodinger published paper, they separately figure out WKB or in french it is called BKW, or in British call WKBJ.

Recall for 1D step potential

$$V(x) = \begin{cases} 0 & x < 0 \\ V & x > 0 \end{cases}$$

If $E < V$, in the classically allowed region ($x < 0$),

$$\psi \sim e^{\pm ikx}, \sin kx, \cos kx \tag{4.1}$$

$k = \sqrt{2m(E-0)}/\hbar$. In the classically forbidden region ($x > 0$),

$$\psi \sim e^{\pm kx} \tag{4.2}$$

where $k = \sqrt{2m(V-E)}$.

We saw the same things happen for the 1D box potential and SHO potential. Exponential die out in forbidden region, and oscillations in classically allowed region, as energy state goes high, more jigging appear, because in classically allowed region $E \uparrow$, $k \uparrow$, so $\lambda \downarrow$.

We want to apply the solution of constant potential (either $V > E$ or $V < E$) to a general situation. Suppose we have a potential $V(x)$ s.t. $V'(x)$ is very small, precisely

$$\lambda V' \ll V \tag{4.3}$$

λ is the same λ below,

$$p(x) = \sqrt{2m(E - V(x))}, \quad k(x) = \frac{p(x)}{\hbar}, \quad \lambda(x) = \frac{2\pi}{k(x)} \tag{4.4}$$

(4.3) says

$$\frac{\Delta V}{\Delta x} \ll \frac{V}{\lambda} \tag{4.5}$$

if we take $\Delta x \sim \lambda$, we should not see any noticeable change in V. Or state differently, in the region where V changes, we want to have many and many oscillation occur there. This explains the left hand side of (4.5).

The right hand side of (4.5) can be made more precise by replacing

$$\frac{\Delta V}{\Delta x} \ll \frac{E - V}{\lambda} \tag{4.6}$$

that is because in determined the wave function, it is the quantity $E - V$ that really matters, cf (4.4).

Now choose A, ϕ real,

$$\psi(x) = A(x)e^{i\phi(x)} \tag{4.7}$$

looking for a SHO wave like solution of Schrodinger equation:

$$\psi'' = -\frac{1}{\hbar^2} 2m(E - V)\psi$$

Since

$$\psi'(x) = (A' + i\phi' A)\, e^{i\phi} \quad \psi''(x) = (A'' + 2iA'\phi' + iA\phi'' - A\phi'^2)e^{i\phi}$$

real part gives

$$A'' - A\phi'^2 = \frac{-2m}{\hbar^2}(E - V)A \implies -\frac{A''}{A} + \phi'^2 = \frac{p^2(x)}{\hbar^2} \tag{4.8}$$

Imaginary part

$$2A'\phi' + A\phi'' = 0 \implies \frac{d}{dx}(A^2\phi') = 0 \implies A = \frac{c}{\sqrt{\phi'}} \tag{4.9}$$

(4.6) suggests

$$V' \ll p^3 \implies p' \ll p^2$$

Combine equations (4.8), (4.9), we get roughly

$$\frac{\phi''^2}{\phi'^2} + \frac{\phi'''}{\phi'} + \phi'^2 = \frac{p^2(x)}{\hbar^2}$$

So we may confidently say $\phi' \sim p$ and all other terms are negligible, so

$$\phi' = \pm\frac{1}{\hbar}p \implies \phi(x) = \pm\frac{1}{\hbar}\int^x dsp(s) + \text{const}$$

So

$$\psi(x) = \frac{c}{\sqrt{\phi'}} e^{\pm\frac{i}{\hbar}\int^x dsp(s)} \tag{4.10}$$

is the SHO wave like solution to the Schrodinger equation with the assumption (4.6).

The $\pm$, right/left moving, in (4.10) are determined by the energy level and boundary conditions. Consider a

$$V(x) = \begin{cases} (x+1)^2 & x < 0 \\ (x-1)^2 & x > 0 \end{cases}$$

For given $E > 1$, it is clearly that there are two 2 turning point. Near the turning points (4.6) is not satisfied, even worse p in the denominator blow up. It is obvious in the classically allowed region we need to flip the $\pm$ after the wave hits the tuning points. For $E < 1$, there are four turning points, and three forbidden region. We will study more closely next time. If $E = 1$, the point $x = 0$ is ambiguous. It is not so clearly it is a turning point or not? Shall we flip $\pm$? Fortunately it is not physically common situation to be exact $E = 1$.

The c in (4.10) is also important. It partially comes from the unspecified lower bound of the integral $\int^x dsp(s)$. Question: where is the lower bound? Moreover if we immerse our choices of c, can we get a complete set of solution out of WKB method?

These questions will be addressed in the follow up lectures.

Example. We now use WKB to solve ∞ equal well $[0, a]$.

$$\psi(a)$$

Put

$$\begin{aligned}\psi &= \frac{1}{\sqrt{p}}[c_+ e^{i\phi(x)} + c_- e^{i\phi(x)}] \\ &= \frac{1}{\sqrt{p}}[c_1 \sin\phi(x) + c_2 \cos\phi(x)]\end{aligned}$$

Choose the lower bound of integral to 0, i.e.

$$\phi(x) = \frac{1}{\hbar}\int_0^x dsp(s)$$

then

$$\psi(0) = 0 \implies c_2 = 0$$

$$\psi(a) = 0 \implies \sin\phi(a) = 0 \implies \phi(a) = n\pi$$

Hence

$$\int_0^a dx\sqrt{2mE} = n\pi\hbar \tag{4.11}$$

we obtain some quantization

$$\implies E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

gives the correct result. If pick other point as lower bound, possibly both sin, cos will be there. But the end result is the same.

Lecture 14 (3/12/13)

Example. Consider potential $V = \frac{1}{2}w^2x^2$, energy is given E. So turning points $\pm a$, $a = \sqrt{2E/mw^2}$

$$p = \sqrt{2m(E - \frac{1}{2}mw^2x^2)} = \sqrt{2mE(1 - x^2/a^2)}$$

$$\phi(x) = \int_{-a}^x dsp(s)$$

Use (4.11)

$$\int_{-a}^{a} dx\sqrt{2mE}\sqrt{1-\frac{x^2}{a^2}} = n\pi\hbar \tag{4.12}$$

So

$$\sqrt{2mE}\frac{a\pi}{2} = n\pi\hbar \implies E = n\hbar w$$

This is very close to the correct result $E_n = \hbar w(n+\frac{1}{2})$ when n is big. This exemplifies that when n is big, E is big so (4.6) is more satisfied.

We derived (4.11) from ∞ square, and it is also applicable here. We guess (4.11) is a very general statement, so there may be deep theory behind. So now we say (4.11) gives correct answer for ∞ straight high well and gives relatively correct answer for parabolic potential.

4.2 Tunneling

Suggested by the idea of (4.1), (4.2) that moving from classically allowed to forbidden region corresponds to move from imaginary to real, one can get WKB in forbidden region,

$$\psi(x) = \frac{1}{\sqrt{|p(x)|}}[Ae^{\beta(x)} + Be^{-\beta(x)}]$$

where still $p = \sqrt{2m(E-V)}$, $\beta = \frac{1}{\hbar}\int^x ds\sqrt{2m(V(s)-E)}$. And the formula works as long as

$$\lambda V' \ll |E-V| \tag{4.13}$$

Consider

$$V(x) = \begin{cases} 0 & x \in I = (-\infty, 0) \\ V > 0 & x \in II = (0, a) \\ 0 & x \in III = (a, \infty) \end{cases}$$

Assume the incident wave is coming from $-\infty$ to the right. So in I we should have both incident and reflection waves

$$\psi_I = Ae^{ikx} + Be^{-ikx}$$

$$\psi_{II} = Ce^{Kx} + De^{-Kx}$$

$$\psi_{III} = Fe^{ikx}$$

$k = \frac{1}{\hbar}\sqrt{2mE}$, $K = \frac{1}{\hbar}\sqrt{2m(V-E)}$. Ignore Ce^{Kx} because must be decay.

We use WKB for ψ_{II}. From our experience with (4.11), WKB works extremely well as ∞ straight edge potentials, so let's assume we have very high and not too wide barrier in II

$$\psi_{II} = De^{-\frac{1}{\hbar}\int_0^x ds\sqrt{2m(V(x)-E)}}$$

Match at $x = a$,

$$|\psi_{III}(a)|^2 = |\psi_{II}(a)|^2 \implies |F| = |D|e^{-\frac{1}{\hbar}\int_0^x ds\sqrt{2m(V(x)-E)}} \ll |D|$$

so not much transmitted. Match at $x = 0$

$$|A| \sim |B| \sim |D|$$

Then the transmitted factor

$$\left|\frac{F}{A}\right|^2 \sim e^{-\frac{2}{\hbar}\int_0^x ds\sqrt{2m(V(x)-E)}} \tag{4.14}$$

4.3 Nuclear Physics

Heavy isotopes are all unstable. It will decay via α or β

α decay

$$(Z, A) \to \alpha + (Z-2, A-4)$$

Z number protons, A number of elements: protons+neutrons. α particle He nucleus $2p + 2n$

β decay neutron becomes protons

$$(Z, A) \to e^-, \nu + (Z+1, A)$$

The decay processes is done in multiple steps, e.g.

$$A \to A-4 \to A-8 \to ... \to A-4k$$

until reach stable state.

$A = 4n$, e.g.

$$^{232}\text{Th} \to ... \to ^{208}\text{Pb}$$

consists of 7 α decays (the process gets slower and slower. The first α decay has a life time 3×10^{-7} seconds and the last one has a life time 1.4×10^{10} years) and 5 β decays (lift time 3 minutes to 5.75 years). The process gives up α energy $= 4.05$MeV. α decay of ^{212}Po gives up energy 8.95MeV.

(1 year $\approx \pi \times 10^7$ seconds.)

$A = 4n + 2$, e.g. $^{238}\text{U} \to ... \to$ Pb in 10 billion years

$A = 4n + 3$, e.g. $^{235}\text{U} \to ... \to$

$A = 4n + 1$, has no more decays. They happened when the solar system was young. Look up "supernova".

4.4 Gamow Model

Gamow proposed potential of α particles in radioactive atoms, $Z \approx 90$. If $Z < 50$ the physics of nuclear is different.

see Griffiths figure 8.5, r_1 is nuclear radius. For $r < r_1$ we don't know exact the sharp and it doesn't matter, but we know nuclear forces are short range, and the potential there is negative, because of binding. Question: if α somehow passes r_1, can it passes through r_2, then it becomes free?

We have a tunneling problem, so (4.14) says the probability of tunneling $e^{-2\gamma}$. Clearly as $E \uparrow$, $\gamma \downarrow$, so more tunneling. Actual $E \sim 4 - 8MeV$. Furthermore if we assume within r_1, α is moving at speed v, then it takes

$$\frac{2r_1}{v} \text{ sec}$$

to for one α particle to begin tunneling again if it didn't succeed last time. The probability of escape is $e^{-2\gamma}$. So in 1sec the number of escaped α is at the order (because there may be multiple α bouncing in $r < r_1$)

$$\sim \frac{1}{\frac{2r_1}{v}} e^{-2\gamma}$$

so the half time of radiation or call the rate of tunneling is

$$\sim \frac{2r_1}{v} e^{2\gamma}$$

we ignore any factors and take rate to be

$$T_{1/2} \sim e^{2\gamma} \tag{4.15}$$

Lecture 15 (3/14/13)

We compute γ. Let Z be number of protons of atom after α has passed r_1,

$$\begin{aligned}
\gamma &= \frac{1}{\hbar}\int_{r_1}^{r_2} dr\sqrt{2m(V-E)} \\
&= \frac{1}{\hbar}\int_{r_1}^{r_2} dr\sqrt{2m(\frac{2Ze^2}{r}-\frac{2Ze^2}{r_2})} \\
&= \frac{1}{\hbar}\int_{r_1}^{r_2} dr\sqrt{2mE}\sqrt{\frac{r_2}{r}-1} \\
&= \frac{\sqrt{2mE}}{\hbar}[r_2(\frac{\pi}{2}-\sin^{-1}\sqrt{\frac{r_1}{r_2}})-\sqrt{r_1(r_2-r_1)}]
\end{aligned}$$

Assume $r_1 \ll r_2$,

$$\gamma = \frac{\sqrt{2mE}}{\hbar}(\frac{\pi r_2}{2}-2\sqrt{r_1 r_2}) = K_1\frac{Z}{\sqrt{E}} - K_2\sqrt{Zr_1} \tag{4.16}$$

$K_1 = \frac{e^2\pi\sqrt{2m}}{\hbar} = 1.98\sqrt{MeV}$, $K_2 = \frac{4\sqrt{m}e}{\hbar} = 1.49\frac{1}{\sqrt{fm}}$ fm =Fermi $= 10^{-13}cm$

From (4.15), (4.16), we plot

$$\ln T_{1/2} \text{ v.s. } \frac{1}{\sqrt{E}}$$

they indeed agree experimental data, giving straight lines.

4.5 WKB Patches

Recall WKB assumes (4.13) or

$$\frac{\hbar V'}{p} \ll |E - V|$$

WKB works very well at ∞ square turning points, $V = \infty$, $V' = \infty$, maybe because $\infty \ll \infty$. For other turning points $p \to 0$, we have trouble, so is in the Gamow model $r = r_2$ turning point.

Let us consider a bad turning point $x_0 = 0$, V, V' finite and $V'(x_0) > 0$. In some distance away from p, these regions: I, left of p and II, right of p, are good for WKB. So WKB says

$$\psi_I \sim \frac{1}{\sqrt{p}}[Be^{\frac{i}{\hbar}\phi(x)} + Ce^{-\frac{i}{\hbar}\phi(x)}] \quad \phi(x) = \int^x dsp(s) \tag{4.17}$$

$$\psi_{II} \sim \frac{1}{\sqrt{|p|}}[Fe^{\frac{1}{\hbar}\beta(x)} + De^{-\frac{1}{\hbar}\beta(x)}] \quad \beta(x) = \int^x ds|p(s)| \tag{4.18}$$

We consider an intermediate region that covers the region between I and II and also overlaps with I and II. Linearize $V(x)$ near x_0,

$$V(x) = V(0) + V'(0)x = E + V'(0)x$$

This assumes $V(x)$ is approximately a linear function, or at least it keeps growth all the way on the right of x_0 in the patch region so the growth gets a bit in region II too. Similar thing for the left side of x_0.

Solve Schrodinger in the patch region

$$\frac{d^2\psi_p}{dx^2} = \frac{2m}{\hbar^2}V'(0)x\psi_p \tag{4.19}$$

Define $\alpha^3 \equiv \frac{2m}{\hbar^2}V'(0)$, $z = \alpha x$,

$$\frac{d^2\psi}{dz^2} = z\psi \tag{4.20}$$

The solutions are Airy functions Ai, Bi

$$Ai(z) = \frac{1}{\pi}\int_0^\infty ds \cos(\frac{s^3}{3} + sz) \tag{4.21}$$

$$Bi(z) = \frac{1}{\pi}\int_0^\infty ds \left(e^{-\frac{s^3}{3}+sz} + \sin(\frac{s^3}{3} + sz)\right) \tag{4.22}$$

e.g. check (4.21)

$$\begin{aligned}
\frac{d^2Ai}{dz^2} &= \frac{1}{\pi}\int_0^\infty ds(-s)^2 \cos(\frac{s^3}{3} + sz) \\
&= \frac{1}{\pi}\int_0^\infty ds \left[\frac{\partial}{\partial s}\left(-\sin(\frac{s^3}{3} + sz)\right) + z\cos(\frac{s^3}{3} + sz)\right] \\
&= z\psi
\end{aligned}$$

because $\int_0^\infty ds \frac{\partial}{\partial s}\left(-\sin(\frac{s^3}{3} + sz)\right) = 0$

From knowledge of complex variable, $z \gg 0$

$$Ai(z) \sim \frac{e^{-\frac{2}{3}z^{3/2}}}{2\sqrt{\pi}z^{1/4}} \qquad Bi(z) \sim \frac{e^{\frac{2}{3}z^{3/2}}}{\sqrt{\pi}z^{1/4}}$$

for $z \ll 0$

$$Ai(z) \sim \frac{\sin\left(\frac{2}{3}(-z)^{2/3} + \frac{\pi}{4}\right)}{\sqrt{\pi}(-z)^{1/4}} \qquad Bi(z) \sim \frac{\cos\left(\frac{2}{3}(-z)^{2/3} + \frac{\pi}{4}\right)}{\sqrt{\pi}(-z)^{1/4}}$$

Now we solve (4.19),

$$\psi_p(z) = aAi(z) + bBi(z) \tag{4.23}$$

On the right of x_0, in the overlap region we have

$$\psi_{II} = \frac{1}{\sqrt{|p|}} De^{-\frac{1}{\hbar}\beta(x)}$$

ignore $e^{\frac{1}{\hbar}\beta(x)}$ because $V(0) > 0$.

$$\begin{aligned}
\beta(x) &= \int_0^x ds|p(s)| \\
&= \int_0^x ds\sqrt{2m(V-E)} \\
&= \int_0^x ds\sqrt{2mV'(0)s} \\
&= \sqrt{2mV'(0)}\frac{2}{3}x^{3/2} \\
&= \frac{2}{3}\hbar z^{3/2}
\end{aligned}$$

so

$$\psi_{II} = \frac{D}{\sqrt{\hbar\alpha}z^{1/4}}e^{-\frac{2}{3}z^{3/2}}$$

which matches to $z \gg 0$ asymptote of Ai, so we find a, b in (4.23)

$$a = \sqrt{\frac{4\pi}{\hbar\alpha}}D \quad b = 0$$

$b = 0$ because we know the wave dies out in II.

Do the other side of x_0, start from

$$\psi_p = \sqrt{\frac{4\pi}{\hbar\alpha}}DAi(z)$$

For $z \ll 0$

$$\begin{aligned}
\psi_p &= \frac{2D}{\sqrt{\hbar\alpha}}\frac{\sin\left(\frac{2}{3}(-z)^{2/3}+\frac{\pi}{4}\right)}{(-z)^{1/4}} \\
&= \frac{2D}{\sqrt{\hbar\alpha}}\frac{1}{(-z)^{1/4}}\frac{1}{2i}\left(e^{\frac{i\pi}{4}}e^{i\frac{2}{3}(-z)^{2/3}} - e^{-\frac{i\pi}{4}}e^{-i\frac{2}{3}(-z)^{2/3}}\right)
\end{aligned}$$

which is expected to match (4.17), so

$$\begin{cases} B = -iDe^{\frac{i\pi}{4}} \\ C = iDe^{-\frac{i\pi}{4}} \end{cases}$$

Both left and right moving waves are presented as expected, that is the reason why we start from ψ_{II} because we know ψ_{II} has only one wave.

Hence

$$\begin{cases} \psi_I(x) = \frac{2D}{\sqrt{p}} \sin\left(\frac{1}{\hbar}\int_x^0 dsp(s) + \frac{\pi}{4}\right) & (1) \\ \psi_{II}(x) = \frac{D}{\sqrt{|p|}} e^{-\frac{1}{\hbar}\int_0^x ds|p(s)|} & (2) \end{cases} \tag{4.24}$$

now $\psi_{I,II}$ are the solutions in regions I, II and they are matched with ψ_p in the overlap regions, and ψ_p is the solution in the patch region.

Notice the boundary of the integration in (4.24) includes 0. That is not an issue because $p \to 0$ near 0, the integral still converges, if we only do

$$\int_\epsilon^x ds|p(s)| \text{ or } \int_x^{-\epsilon} dsp(s)$$

so that ϵ is strictly inside of region I or II, then we just have a different constant D, which is after all determined by the normalization.

Recall a few lecture ago, we did (4.12), it is not quite correct to put

$$\int pdx = n\pi\hbar$$

for parabolic potentials, although it is correct for ∞ square wells. As a quick check of (4.24), we want to get the right this time.

First suppose we have a system that has 2 turning points $x_1 < x_2$. x_1 is a ∞ straight edge, $V'(x_2) > 0$. So we just follow the same derivation above, starting with $\psi_{x>x_2}$, then find the connecting ψ inside of $x_1 < x < x_2$ which is

$$\psi_{x_1<x<x_2}(x) \sim \frac{1}{\sqrt{p}} \sin\left(\frac{1}{\hbar}\int_x^{x_2} dsp(s) + \frac{\pi}{4}\right)$$

(compare this to (4.24)-(1), here x_2 is not necessary $x_0 = 0$. Looking at the final formula (4.24)-(1), we notice the origin of reference doesn't matter, so we are free to replace 0 by x_2) now we have another turning point x_1, so we need to connect to $\psi_{x<0}$ as well, but $\psi_{x<0} \equiv 0$, so

$$\psi_{x_1<x<x_2}(x_1) \sim \frac{1}{\sqrt{p}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x_2} dxp(x) + \frac{\pi}{4}\right) = 0$$

so

$$\int_{x_1}^{x_2} pdx = (n - \frac{1}{4})\pi\hbar$$

Now if the system has 2 turning points $x_1 < x_2$. $V'(x_1) < 0$, $V'(x_2) > 0$. Start from $\psi_{x>x_2}$, as before we get

$$\psi_{x_1<x<x_2} \sim \frac{1}{\sqrt{p}} \sin\left(\frac{1}{\hbar}\int_x^{x_2} dsp(s) + \frac{\pi}{4}\right) \tag{4.25}$$

We can also start from $\psi_{x<x_1}$, this will change the derivative by $x \to -x$, $V'(0) \to -V'(0)$, $\alpha \to -\alpha$ but z is the same. After some steps, one gets

$$\psi_{x_1<x<x_2} \sim \frac{1}{\sqrt{p}} \sin\left(\frac{1}{\hbar}\int_{x_1}^{x} dsp(s) + \frac{\pi}{4}\right) \tag{4.26}$$

norm of (4.25) and (4.26) have to the same for all $x_1 < x < x_2$, that is

$$\sin\left(\frac{1}{\hbar}\int_{x_1}^{x} + \frac{\pi}{4}\right) = -\sin\left(\frac{1}{\hbar}\int_{x}^{x_1} - \frac{\pi}{4}\right) = \pm\sin\left(\frac{1}{\hbar}\int_{x}^{x_2} + \frac{\pi}{4}\right)$$

therefore

$$(\frac{1}{\hbar}\int_x^{x_2} + \frac{\pi}{4}) - (\frac{1}{\hbar}\int_x^{x_1} - \frac{\pi}{4}) = \frac{1}{\hbar}\int_{x_1}^{x_2} + \frac{\pi}{2} = n\pi$$

so

$$\int_{x_1}^{x_2} dxp(x) = (n - \frac{1}{2})\pi\hbar \qquad n = 1, 2, ... \tag{4.27}$$

This gives the correct formula of energy quantization.

Lecture 16 (3/26/13)

Example. Let's do Griffiths problem 8.15

(a) Solve ψ for potential looks like Griffiths figure 8.13.

$$\psi_{x>x_2} = \frac{D}{\sqrt{|p|}} e^{-\frac{1}{\hbar}\int_{x_2}^{x} ds|p(s)|}$$

$$\psi_{x_1<x<x_2} = \frac{2D}{\sqrt{p}} \sin(\frac{1}{\hbar}\int_x^{x_2} dsp(s) + \frac{\pi}{4})$$

For region $-x_1 < x < x_1$ we have to do some work, first write

$$\psi_{x_1<x<x_2} = -\frac{2D}{\sqrt{p}}\sin(\frac{1}{\hbar}\int_{x_1}^{x} dsp(s) - \theta - \frac{\pi}{4})$$

where $\theta = \frac{1}{\hbar}\int_{x_1}^{x_2} pdx$, shift $x_1 = 0$, so we change the problem to connect two waves

$$\psi_{x>0} = -\frac{2D}{\sqrt{p}}\sin(\frac{1}{\hbar}\int_{x_1}^{x} dsp(s) - \theta - \frac{\pi}{4})$$

$$\psi_{x<0} = \frac{1}{\sqrt{|p|}}[Fe^{\frac{1}{\hbar}\int_x^0 |p|ds} + Ge^{-\frac{1}{\hbar}\int_x^0 |p|ds}]$$

For $V'(0) < 0$, set $\alpha^3 = 2m(-V'(0))/\hbar^2$, $z = \alpha x$, pitch function

$$\psi_p = aAi(\alpha x) + bBi(\alpha x)$$

For $x < 0$, z is still $\gg 0$, so asymptotically we need

$$\begin{cases} a = 2G\sqrt{\frac{\pi}{\hbar\alpha}} \\ b = F\sqrt{\frac{\pi}{\hbar\alpha}} \end{cases}$$

For $x > 0$, asymptotically

$$\begin{aligned} \frac{a}{\sqrt{\pi}(\alpha x)^{1/4}}\sin(\frac{2}{3}(\alpha x)^{3/2} + \frac{\pi}{4}) + \frac{b}{\sqrt{\pi}(\alpha x)^{1/4}}\cos(\frac{2}{3}(\alpha x)^{3/2} + \frac{\pi}{4}) \\ = -\frac{2D}{\sqrt{p}}\sin(\frac{2}{3}(\alpha x)^{3/2} - \theta - \frac{\pi}{4}) \end{aligned}$$

So we can solve for a, b, hence solve for G, F, so we get

$$\psi_{-x_1<x<x_1} = \frac{D}{\sqrt{|p|}}[2\cos\theta e^{\frac{1}{\hbar}\int_x^{x_1}|p|ds} + \sin\theta e^{-\frac{1}{\hbar}\int_x^{x_1}|p|ds}]$$

(b) Because V is symmetric, from experience with SHO, we think the ground state is ψ even, so $\psi'(0) = 0$, i.e. $x = 0$ is anti node. The next state is odd $\psi(0) = 0$ so $x = 0$ is a node.

Odd: $\tan\theta = -2e^{\phi}$ Even: $\tan\theta = 2e^{\phi}$, $\phi = \frac{1}{\hbar}\int_{-x_1}^{x_1} ds|p(s)|$

(c) suppose high wide barriers $\phi \gg 1$, $e^{\phi} \approx \infty$, $\theta \approx (n+\frac{1}{2})\pi$, or more precisely for $n = 1$, put

$$\theta = \frac{\pi}{2} - \epsilon$$

then

$$\tan\theta = \frac{\sin(\frac{\pi}{2} - \epsilon)}{\cos(\frac{\pi}{2} - \epsilon)} = \frac{1}{\epsilon} = \pm 2e^{\phi} \implies \theta = \frac{\pi}{2} \mp \frac{e^{-\phi}}{2}$$

(d) suppose high wide barriers, and SHO potential, compute

$$\theta = \frac{1}{\hbar}\int_{x_1}^{x_2} \sqrt{2m(E - \frac{1}{2}mw^2(x-a)^2)}dx = ... = \frac{\pi E}{\hbar w}$$

so

$$E_{odd/even} = \frac{\hbar w}{2} \mp \frac{\hbar w}{2\pi}e^{-\phi}$$

hence the energy split $\Delta E = \frac{\hbar w}{\pi}e^{-\phi}$

(e) Let $|\psi_1\rangle$ be the ground state, $|\psi_2\rangle$ be the 1st excited state, put

$$|\Psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle$$

Let $c_1 = c_2 = \frac{1}{\sqrt{2}}$, particle almost entirely on one of two valleys. "Almost" is because e.g. at $x = 0$, not completely cancel out. (whiles $c_1 = -c_2 = \frac{1}{\sqrt{2}}$, particle almost entirely on the other valley)

Then the time dependent wave function

$$\begin{aligned} |\Psi(t)\rangle &= c_1 |\psi_1\rangle e^{-iE_1 t/\hbar} + c_2 |\psi_2\rangle e^{-iE_2 t/\hbar} \\ &= e^{-i\frac{\hbar w}{2}t/\hbar}\left[c_1 |\psi_1\rangle e^{i\Delta E t/2\hbar} + c_2 |\psi_2\rangle e^{-i\Delta E t/2\hbar}\right] \end{aligned}$$

with the initial condition s.t. at $t = 0$, the wave is concentrated on one of two valleys. After time t s.t.

$$\Delta E t/2\hbar = \pi/2$$

$c_2 \to -c_2$, so particle almost entirely on the other valley. Then another $\Delta E t/2\hbar = \pi/2$ come back. So oscillates with period

$$\frac{2\hbar\pi}{\Delta E} \tag{4.28}$$

Here V is symmetric, so wave oscillates back and forth, but for Gamow, V is not symmetric, so once α is gone, it is gone.

The problem has a physical model: Ammonia molecules NH_3. The three H atoms stay on a plane, N oscillates vertically in and out of the plane, with period (4.28), where ΔE is measurable through microwave.

5 Time-Dependent Perturbation Theory

5.1 Time-Dependent Perturbation

Only few time-independent Hamiltonian are exactly solvable, but if the time varying part is small, we can do perturbation

$$H = H^0 + H'(t)$$

and

$$H'(0) = 0 \qquad H^0 |\psi_i\rangle = E_i |\psi_i\rangle$$

where $|\psi_i\rangle$ from an orthonormal basis. Suppose for any state $|\psi\rangle$, if

$$|\psi(0)\rangle = \sum_j c_j(0) |\psi_j\rangle$$

we think

$$|\psi(t)\rangle = \sum_j c_j(t) |\psi_j\rangle e^{-iE_j t/\hbar} \tag{5.1}$$

solves Schrodinger

$$(H^0 + H') |\psi\rangle = i\hbar \frac{d}{dt} |\psi\rangle \tag{5.2}$$

Substitute (5.1) in (5.2),

$$LHS = \sum_j c_j E_j |\psi_j\rangle e^{-iE_j t/\hbar} + c_j H' |\psi_j\rangle e^{-iE_j t/\hbar}$$

$$RHS = \sum_j c_j E_j |\psi_j\rangle e^{-iE_j t/\hbar} + \dot{c}_j i\hbar |\psi_j\rangle e^{-iE_j t/\hbar}$$

hence

$$\sum \dot{c}_j i\hbar \left|\psi_j\right\rangle e^{-iE_j t/\hbar} = \sum c_j H' \left|\psi_j\right\rangle e^{-iE_j t/\hbar}$$

Apply $\langle\psi_i|$ to above

$$i\hbar \dot{c}_i e^{-iE_i t/\hbar} = \sum c_j \left\langle\psi_i|H'|\psi_j\right\rangle e^{-iE_j t/\hbar}$$

Put $H'_{ij} = \langle\psi_i|H'|\psi_j\rangle$ then

$$\dot{c}_i = -\frac{i}{\hbar}\sum_j H'_{ij} e^{-i(E_j - E_i)t/\hbar} c_j$$

or in matrix form (possible $\infty \times \infty$ sizes, but we will only study finite sizes, mostly 2 states system)

$$C' = -\frac{i}{\hbar} MC \tag{5.3}$$

where

$$C' = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix} \quad M_{ij} = H'_{ij} e^{-i(E_j - E_i)t/\hbar}$$

If M is independent of time,

$$C(t) = e^{-\frac{i}{\hbar}Mt} C(0)$$

If M is matrix function of time,

$$C(t) = e^{-\frac{i}{\hbar}\int_0^t dt' M(t')} C(0)$$

What is $e^{-\frac{i}{\hbar}\int_0^t dt' M(t')}$?

Lecture 17 (3/28/13)

We use time ordered operator, and expend. Because $H'(t)$ is small, we hope higher order terms can be neglected.

$$\begin{aligned} C(t) &= \mathcal{T} \exp[-\frac{i}{\hbar}\int_0^t dt' M(t')] C(0) \\ &= [I + (-\frac{i}{\hbar})\int_0^t dt' M(t') + \frac{1}{2}(-\frac{i}{\hbar})^2 \int_0^t dt' \int_0^t dt'' M(t')M(t'') + ...] C(0) \end{aligned} \tag{5.4}$$

Being consistent, we put "later on left" for product of integrations. We simplify the 2nd order term

$$\begin{aligned}\int_0^t dt' \int_0^t dt'' M(t')M(t'') &= \int_0^t dt' \int_0^{t'} dt'' M(t')M(t'') + \int_0^t dt' \int_{t'}^t dt'' M(t')M(t'') \\ &= \int_0^t dt' \int_0^{t'} dt'' M(t')M(t'') + \int_0^t dt'' \int_0^{t''} dt' M(t'')M(t') \\ &= 2\int_0^t dt' \int_0^{t'} dt'' M(t')M(t'') \qquad (5.5)\end{aligned}$$

The second equality follows from change order of integration, and "later on left"

$$\begin{cases} M(t')M(t'') & \text{if } t' > t'' \\ M(t'')M(t') & \text{if } t'' > t' \end{cases}$$

a more rigorous derivation uses step function $\theta(t'' - t')$ to show (5.5).

By induction the 3rd order term becomes

$$\int_0^t dt' \int_0^t dt'' \int_0^t dt''' M(t')M(t'')M(t''') = 6\int_0^t dt' \int_0^{t'} dt'' \int_0^{t''} dt''' M(t')M(t'')M(t''')$$

so the $n!$ factors are canceled.

Check (5.4) is indeed correct expression

$$\begin{aligned}\dot{C} &= -\frac{i}{\hbar}M(t) + (-\frac{i}{\hbar})^2 \int_0^t dt'' M(t)M(t'') + ... \\ &= -\frac{i}{\hbar}M(t)[I - \frac{i}{\hbar}\int_0^t dt'' M(t'') + ...] \\ &= -\frac{i}{\hbar}M(t)C\end{aligned}$$

So we are done with general time dependent perturbation. Now come to see some specific cases.

5.2 Two-State System

Two-state system $(1, 2)$ with different energies $E_2 > E_1$.

Assume $H'_{11} = H'_{22} = 0$, i.e. perturbation vanishes at either state. Let

$$w_0 = \frac{E_2 - E_1}{\hbar} > 0$$

Recall $H'_{12} = \langle\psi_1|H'|\psi_2\rangle \quad H'_{21} = H'^*_{12} \quad M_{ij} = H'_{ij}e^{-i(E_j-E_i)t/\hbar}$. $M_{11} = M_{22} = 0$ $M_{12} = H'_{12}e^{-iw_0t}$.

If H' is independent of time, it is very simple. By (5.3)

$$\begin{aligned}\dot{c}_1(t) &= -\frac{i}{\hbar}H'_{12}e^{-iw_0t}c_2 \\ \dot{c}_2(t) &= -\frac{i}{\hbar}H'_{21}e^{iw_0t}c_1\end{aligned}$$

Then

$$\begin{aligned}\ddot{c}_2 &= -\frac{i}{\hbar}H'_{21}e^{iw_0t}\dot{c}_1 + \frac{w_0}{\hbar}H'_{21}e^{iw_0t}c_1 \\ &= -\frac{1}{\hbar^2}|H'_{12}|^2c_2 + iw_0\dot{c}_2\end{aligned}$$

Try $c_2(t) = e^{i\lambda t}c_2(0)$, then

$$\lambda = \frac{w_0 \pm \beta}{2}, \qquad \beta = \sqrt{w_0^2 + \frac{4}{\hbar^2}|H'_{12}|^2}$$

so

$$c_2(t) = Ae^{\frac{i}{2}(w_0+\beta)t} + Be^{-\frac{i}{2}(w_0-\beta)t}$$

Suppose $c_1(0) = 1$, $c_2(0) = 0$. $B = -A$, from there, we get

$$\begin{cases} c_1 = e^{-iw_0t/2}\left(\frac{iw_0}{2}\sin\frac{\beta t}{2} + \cos\frac{\beta t}{2}\right) \\ c_2 = e^{iw_0t/2}\frac{H'_{21}}{i\hbar}\frac{2}{\beta}\sin\frac{\beta t}{2} \end{cases} \tag{5.6}$$

$|c_1|^2$ and $|c_2|^2$ oscillating show the system transition from state 1 to states 1 & 2, and $|c_1|$ is never 0. Sometimes $|c_2|$ is 0, so the system will be completely back to state 1.

Although (5.6) may not look like $|c_1|^2 + |c_2|^2 = 1$, it should be, because

$$\begin{aligned}\frac{d}{dt}[|c_1|^2 + |c_2|^2] &= \frac{d}{dt}C^*C = \dot{C}^*C + C^*\dot{C} \\ &= \frac{i}{\hbar}C^*MC + C^*(-\frac{i}{\hbar}MC) = 0\end{aligned}$$

Now suppose H' is time dependent.

By (5.4)

$$c_1 = c_1(0) - \frac{i}{\hbar}\int_0^t dt' H'_{12} e^{-iw_0t'} c_2(0) - \frac{1}{\hbar}\int_0^t dt' \int_0^{t'} dt'' H'_{12}(t')H'_{21}(t'')e^{-iw_0t'}e^{iw_0t''}c_1(0) + ...$$

The second term used

$$M(t')M(t'') = \begin{pmatrix} 0 & a \\ a^* & 0 \end{pmatrix}\begin{pmatrix} 0 & b \\ b^* & 0 \end{pmatrix} = \begin{pmatrix} ab^* & 0 \\ 0 & a^*b \end{pmatrix}$$

For c_2, do $1 \leftrightarrow 2$, $w_0 \leftrightarrow -w_0$.

Suppose $c_1(0) = 1$, $c_2(0) = 0$. Then

$$c_1(t) = 1 - \frac{1}{\hbar}\int_0^t dt' \int_0^{t'} dt'' H'_{12}(t')H'_{21}(t'')e^{-iw_0t'}e^{iw_0t''}$$

$$c_2(t) = -\frac{i}{\hbar}\int_0^t dt' H'_{21}e^{iw_0t'} + O(t^3)$$

Suppose $H'(t) = V(\vec{r})\cos wt$, for example the perturbation is caused by shinning lights. Then

$$\begin{aligned}c_2 &= -\frac{i}{2\hbar}V_{21}\int_0^t dt' \left(e^{i(w_0+w)t'} + e^{i(w_0-w)t'}\right) + ... \\ &= -\frac{V_{21}}{2\hbar}\left(\frac{e^{i(w_0+w)t} - 1}{w_0 + w} + \frac{e^{i(w_0-w)t'} - 1}{w_0 - w}\right) + ...\end{aligned}$$

Lecture 18 (4/2/13)

We are interested in resonance when $|w_0 - w| \ll w_0 + w$, so all other terms are negligible,

$$c_2 = -\frac{V_{21}}{2\hbar}\frac{2ie^{i(w_0-w)t/2}\sin\frac{(w_0-w)t}{2}}{w_0 - w}$$

So the probability of transition into state 2 is

$$P_{1\to 2} = |c_2|^2 = \frac{|V_{21}|^2}{\hbar^2}\frac{\sin^2\frac{w_0-w}{2}t}{(w_0-w)^2} \tag{5.7}$$

For fixed w, frequency of external light, the graph of $P_{1\to 2}$ v.s. t shows the system comes back to state 1 periodically.

For fixed t, varying w, the graph of $P_{1\to 2}$ v.s. w shows that it peaks near w_0 with highest value

$$\frac{|V_{21}|^2 t^2}{4\hbar^2}$$

Of course as time goes on, when $\frac{|V_{21}|^2 t^2}{4\hbar^2}$ becomes > 1, our simple perturbation analysis needs to be modified.

5.3 Photon Absorption & Stimulated Emission

To understand better about the interaction between the two-state system and the external field, we need to study EM. Suppose we have a EM radiation propagating in y direction, and $\vec{\epsilon}$ electric field in z direction,

$$\vec{\epsilon} = \hat{z}\epsilon_0 \cos(wt - \vec{k}\cdot\vec{r})$$

The light itself was produced by some atoms, so

$$|\vec{k}| = \frac{w}{c} = \frac{1}{c}\frac{\Delta E}{\hbar} \sim \frac{1}{c\hbar}\frac{e^2}{a} = \alpha\frac{1}{a}$$

when the light passes the atoms

$$\vec{k}\cdot\vec{r} \sim \alpha\frac{1}{a}a = \alpha$$

is constant, so ignore $\vec{k}\cdot\vec{r}$.

$$H' = -z\vec{\epsilon} = -qz\epsilon_0 \cos wt \tag{5.8}$$

We know e.g. for Hydrogen eigenstate

$$\langle\psi_1|z|\psi_1\rangle = \langle\psi_2|z|\psi_2\rangle = 0$$

and

$$q\,\langle\psi_2|z|\psi_1\rangle = \vec{p}_z$$

called electric dipole moment.

Hence (5.7) gives

$$P_{1\to 2}(t) = \left(\frac{|p_z|\epsilon_0}{\hbar}\right)^2 \frac{\sin^2(w_0 - w)t/2}{(w_0 - w)^2} \tag{5.9}$$

The analysis we have done so far gives photon absorption of radiation

$$[\text{atom state 1}] + \gamma \to [\text{atom state 2}] \tag{5.10}$$

γ photon.

If we do the same analysis with a reversed initial conditions

$$c_1(0) = 0\ c_2(0) = 1$$

and exchange $1 \leftrightarrow 2$, $w_0 \leftrightarrow -w_0$ $V_{12} \leftrightarrow V_{21}$ everywhere, we will get $P_{2\to 1}$ similar to (5.9). This gives stimulated emission

$$[\text{atom state 2}] + \gamma \to [\text{atom state 1}] + 2\gamma \tag{5.11}$$

2γ is from energy conservation. Why not photon with twice energy? We need advanced QM to answer that. In fact photons of both sides are in the same energy $\hbar w$.

We should not confused by the looks of (5.10), (5.11), which look like chemical reaction. They are not. γ here is treated as wave and the transition is going back and forth. At this stage, we have not yet treated interaction as exchange of particles.

5.4 Spontaneous Emission

What about spontaneous emission?

$$[\text{atom state } 2] \rightarrow [\text{atom state } 1] + \gamma$$

This looks odd. Without putting any H', atom degrades from an eigenstate 2 to 1. Is eigenstate 2 really eigenstate? It turns out state 2 is not so stable, because the actual Hamiltonian

$$(\text{protons+electrons}) + (\text{EM field})$$

EM field is quantized.

$$\text{EM field} = \sum (\text{simple harmonic oscillators})$$

One SHO for each $\vec{k}$ and each polarization. If one oscillator has $n = 1$ and all others $n = 0$, then it is state with one photon.

Two ways to do spontaneous emission:

1) Quantize EM field. Absorption, number of photons go down

$$a\,|N\rangle = \sqrt{N}\,|N-1\rangle$$

emission number of photons go up

$$a^+\,|N\rangle = \sqrt{N+1}\,|N+1\rangle$$

Griffiths explanation is not quite correct.

2) We use Einstein trick. He invented before Heisenberg, Schrodinger sorted out QM.

Einstein trick is to combine photon absorption and stimulated emission, so we need to look at γ with all ranges of w in the all space.

Energy in radiation

$$\rho(w)dw$$

in range w to $w + dw$

Energy density of EM in our unit

$$\rho(w) = u = \frac{1}{8\pi}\epsilon_0^2$$

we write $u = K\epsilon_0^2$. so

$$P_{1\to 2}(t) = \int \frac{|p_z|^2\rho(w)}{K\hbar^2}\frac{\sin^2(w_0-w)t/2}{(w_0-w)^2}dw$$

We cannot do the integral unless know what $\rho(w)$ is, but we know $\frac{\sin^2(w_0-w)t/2}{(w_0-w)^2}$ is very peck at w_0, so if we assume $\rho(w)$ doesn't vary much around w_0, then

$$\begin{aligned} P_{1\to 2}(t) &= \frac{|p_z|^2\rho(w_0)}{K\hbar^2}\int_{-\infty}^{\infty}\frac{\sin^2(w_0-w)t/2}{(w_0-w)^2}dw \\ &= \frac{|p_z|^2\rho(w_0)}{K\hbar^2}\frac{t\pi}{2} \end{aligned}$$

so if at t we have 100 atoms and $P_{1\to 2}(t) = 80\%$, it means 80 of them are likely at state 2. If $P_{1\to 2}(t+\Delta t) = 85\%$, then we can say the rate of absorption at t is 5%. In other words the rate of absorption is

$$R_{1\to 2}(t) = \frac{|p_z|^2\rho(w_0)}{K\hbar^2}\frac{\pi}{2}$$

which is also the rate of stimulating emission.

We average all spaces

$$|p_z|^2 = |\langle\psi_1|z|\psi_2\rangle|^2 = \frac{1}{3}|\langle\psi_1|r|\psi_2\rangle|^2 = \frac{1}{3}|\vec{p}|^2$$

so

$$R_{1\to 2}(t) = \frac{4\pi^2|\vec{p}|^2\rho(w_0)}{3\hbar^2}$$

This approximation still uses photons of same energy, which is fairly accurate. Think of lasers (same frequency) produced by chain of reaction.

Now combine absorption and stimulated emission.

$$N_{1,2} = \text{ number of atoms in state 1, 2}$$

Then

$$\frac{dN_2}{dt} = -N_2 A - N_2 R_{2\to 1} + N_1 R_{1\to 2}$$

where A is rate of spontaneous emission.

In thermal equilibrium

$$\frac{dN_2}{dt} = 0$$

Boltzmann statistics says

$$\frac{N_1}{N_2} = \frac{e^{-E_1/kT}}{e^{-E_2/kT}} = e^{(E_2-E_1)/kT}$$

Plank says

$$\rho(w) = \frac{\hbar}{\pi^2 c^3} \frac{w^3}{e^{\hbar w/kT} - 1}$$

therefore

$$\begin{aligned} A &= (\frac{N_1}{N_2} - 1)\frac{4\pi^2|\vec{p}|^2\rho(w_0)}{3\hbar^2} \\ &= \left(e^{w_0\hbar/kT} - 1\right)\frac{4\pi^2|\vec{p}|^2}{3\hbar^2}\frac{\hbar}{\pi^2 c^3}\frac{w_0^3}{e^{\hbar w_0/kT} - 1} \\ &= \frac{4w_0^3}{3\hbar c^3}|\vec{p}|^2 = \frac{4w_0^3 e^2}{3\hbar c^3}|\left\langle\psi_1|r|\psi_2\right\rangle|^2 \end{aligned} \tag{5.12}$$

Lecture 19 (4/4/13)

The first part of $w_0^3 = (w_0)(w_0)^2$, (w_0), gives natural time scale and the other part, $(w_0)^2$, sets the energy scale, so more energy more transitions. We can estimate A,

$$w_0 = \frac{\Delta E}{\hbar} \sim \frac{e^2}{a}\frac{1}{\hbar} \qquad \left\langle\psi_1|r|\psi_2\right\rangle \sim a$$

$$A \sim \frac{e^2}{\hbar c^3}(\frac{e^2}{a}\frac{1}{\hbar})^3 a^2 = (\frac{e^2}{\hbar c})^4\frac{c}{a} = \frac{1}{137^4}\frac{3\times 10^{10} cm/sec}{5\times 10^{-8} cm} \sim 10^9 sec^{-1}$$

Experiment: Hydrogen $2p \to 1s$ rate $6.27 \times 10^8 sec^{-1}$.

5.5 Selection Rule

More precious calculation we need to specify the initial and final state

$$|n'l'm'm'_s\rangle \to |nlmm_s\rangle$$

and compute $\langle\psi_1|\vec{r}|\psi_2\rangle$. The exact value of

$$|\langle\psi_1|\vec{r}|\psi_2\rangle|^2 = |\langle\psi_1|x|\psi_2\rangle|^2 + |\langle\psi_1|y|\psi_2\rangle|^2 + |\langle\psi_1|z|\psi_2\rangle|^2$$

is painful, but finding out when it is 0 is doable.

(1)

$$\langle n'l'm'|\vec{r}|nlm\rangle = 0 \text{ unless } m_s = m'_s$$

(2) Since $[L_z, z] = 0$, $[L_z, x] = i\hbar y$, $[L_z, y] = -i\hbar x$, so

$$\begin{aligned} 0 &= \langle n'l'm'|[L_z, z]|nlm\rangle \\ &= \hbar m' \langle n'l'm'|z|nlm\rangle - \langle n'l'm'|z|nlm\rangle \hbar m \\ &= \hbar(m' - m) \langle n'l'm'|z|nlm\rangle \end{aligned}$$

Hence

$$\langle n'l'm'|z|nlm\rangle = 0 \text{ unless } m = m'$$

(3)

$$\begin{aligned} \langle n'l'm'|y|nlm\rangle\, i\hbar &= \langle n'l'm'|[L_z, x]|nlm\rangle \\ &= \hbar(m' - m) \langle n'l'm'|x|nlm\rangle \\ -\langle n'l'm'|x|nlm\rangle\, i\hbar &= \langle n'l'm'|[L_z, y]|nlm\rangle \\ &= \hbar(m' - m) \langle n'l'm'|y|nlm\rangle \end{aligned}$$

From above

$$\begin{aligned} \langle n'l'm'|x|nlm\rangle &= (m' - m)^2 \langle n'l'm'|x|nlm\rangle \\ \langle n'l'm'|y|nlm\rangle &= (m' - m)^2 \langle n'l'm'|y|nlm\rangle \end{aligned}$$

Hence

$$\langle n'l'm'|x|nlm\rangle = 0 \text{ unless } m' - m = \pm 1$$

$$\langle n'l'm'|y|nlm\rangle = 0 \text{ unless } m' - m = \pm 1$$

Example. Consider

$$|n'1m\rangle \to |n00\rangle$$

so $m = -1, 0, 1$. All three transitions are allowed by selection rule.

$$\begin{aligned}\langle n'1m|x,y,z|n00\rangle &= \int_0^\infty drr^2 \int d\phi d\theta \sin\theta R^*_{n'1}(r)R_{n0}(r)Y^*_{1m}(\theta,\phi)Y_{00}(\theta,\phi)x,y, \text{ or } z \\ &= \int_0^\infty drr^3 R^*_{n'1}(r)R_{n0}(r) \underbrace{\int d\phi d\theta \sin\theta Y^*_{1m}(\theta,\phi)Y_{00}(\theta,\phi)\frac{x,y, \text{ or } z}{r}}_{\equiv I(m;x,y, \text{ or } z)}\end{aligned}$$

Recall

$$\begin{aligned}Y_{00} &= \sqrt{\frac{1}{4\pi}} \\ Y_{10} &= \sqrt{\frac{3}{4\pi}}\cos\theta = \sqrt{\frac{3}{4\pi}}\frac{z}{r} \\ Y_{11} &= -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi} = -\sqrt{\frac{3}{8\pi}}\frac{x+iy}{r} \\ Y_{1-1} &= \sqrt{\frac{3}{8\pi}}\cos\theta e^{i\phi} = \sqrt{\frac{3}{8\pi}}\frac{x-iy}{r}\end{aligned}$$

So

$$I(m=0,z) = \int d\phi d\theta \sin\theta \sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{4\pi}}(\frac{z}{r})^2$$

$$I(m=0,x) = \int d\phi d\theta \sin\theta \sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{4\pi}}(\frac{z}{r})(\frac{x}{r}) = 0$$

because for any point (x,y,z) we find $(-x,y,z)$ as a pair, showing the function is odd. Similarly

$$I(m=0,y) = 0$$

$$I(m=1,z) = -\int d\phi d\theta \sin\theta \sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}}\frac{x-iy}{r}\frac{z}{r} = 0$$

$$\begin{aligned}I(m=1,x) &= -\int d\phi d\theta \sin\theta \sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}}\frac{x-iy}{r}\frac{x}{r} \\ &= -\int d\phi d\theta \sin\theta \sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}}(\frac{x}{r})^2\end{aligned}$$

Hence we find rate $|n'10\rangle \to |n00\rangle$

$$\sim \left|\sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{4\pi}}\int d\phi d\theta \sin\theta(\frac{z}{r})^2\right|^2 = \left|\sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{4\pi}}\int d\phi d\theta \sin\theta\cos^2\theta\right|^2$$
$$= \frac{3}{(4\pi)^2}(\frac{4\pi}{3})^2 = \frac{1}{3}$$

rate $|n'11\rangle \to |n00\rangle$

$$\sim \left|\sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}}\int d\phi d\theta \sin\theta(\frac{x}{r})^2\right|^2 + \left|\sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}}\int d\phi d\theta \sin\theta(\frac{y}{r})^2\right|^2 = 2\frac{3}{2(4\pi)^2}(\frac{4\pi}{3})^2 = \frac{1}{3}$$

which is also the same value of rate $|n'1-1\rangle \to |n00\rangle$.

So the rate is independent of m. This means rate is the same whatever z is pointing to.

Now continue selection rule.

(4) Since $[L^2,[L^2,\vec{r}]] = 2\hbar^2(\vec{r}L^2 + L^2\vec{r})$

$$\langle n'l'm'|\big[L^2,[L^2,\vec{r}]\big]|nlm\rangle = \langle n'l'm'|L^2[L^2,\vec{r}]|nlm\rangle - \langle n'l'm'|[L^2,\vec{r}]L^2|nlm\rangle$$

$$\begin{aligned}
LHS &= 2\hbar^2\langle n'l'm'|(\vec{r}L^2 + L^2\vec{r})|nlm\rangle \\
&= 2\hbar^4[l(l+1)+l'(l'+1)]\langle n'l'm'|\vec{r}|nlm\rangle \\
RHS &= \hbar^2[l'(l'+1)-l(l+1)]\langle n'l'm'|[L^2,\vec{r}]|nlm\rangle \\
&= \hbar^2[l'(l'+1)-l(l+1)][\langle n'l'm'|L^2\vec{r}|nlm\rangle - \langle n'l'm'|\vec{r}L^2]|nlm\rangle] \\
&= \hbar^4[l'(l'+1)-l(l+1)]^2\langle n'l'm'|\vec{r}|nlm\rangle
\end{aligned}$$

so either $\langle n'l'm'|\vec{r}|nlm\rangle = 0$ or

$$2l(l+1)+2l'(l'+1) = [l'(l'+1)-l(l+1)]^2$$

$$\begin{aligned} LHS &= (l'+l)^2 + (l'-l)^2 + 2(l'-l) \\ &= (l'+l+1)^2 - 1 + (l'-l)^2 \\ RHS &= [l'^2 - l^2 + l' - l]^2 \\ &= [(l'+l+1)(l'-l)]^2 \end{aligned}$$

Do

$$0 = RHS - LHS = [(l'+l+1)^2 - 1][(l'-l)^2 - 1]$$

But if $(l'+l+1)^2 = 0 \implies l = l' = 0$ don't work because this case

$$\int d\psi d\theta \sin\theta (\sqrt{\frac{1}{4\pi}})^2 \frac{"x, y, z"}{r} = 0$$

no transition. So we want

$$(l'-l)^2 = 1$$

Interpretation is conservation of angular momentum. Photon spin $L_1 = 1$, atom spin $L_2 = l$

$$l' = L_1 + L_2 = l+1, \not{\ }, \ l-1$$

not l is explained in advanced QM.

So we obtain section rule: no transition unless $m' = m$ or $m = m \pm 1$, and $l' = l \pm 1$. Notice no transition means almost no transition because we arrived (5.12) after ignoring many small terms.

5.6 Forbidden Transition

cf Griffiths problem 9.21

If we include the small $\vec{k} \cdot \vec{r}$ term in (5.8), and Taylor expend

$$\begin{aligned} H' &= \vec{\epsilon_0} \cos(wt - \vec{k} \cdot \vec{r}) \cdot (e\vec{r}) \\ &= \vec{\epsilon_0} [\cos wt + (\vec{k} \cdot \vec{r}) \sin wt + (\vec{k} \cdot \vec{r})^2 \cos wt + ..] \cdot (e\vec{r}) \\ &= e\vec{\epsilon_0} \cdot \vec{r} \cos wt + e(\vec{k} \cdot \vec{r})(\vec{\epsilon_0} \cdot \vec{r}) \sin wt + ... \end{aligned}$$

The first term is electric dipole radiation, the second term is electric quadrupole

and magnetic dipole radiation, the rate is lower than the first term by

$$(\vec{k} \cdot \vec{r}) \sim (\frac{a}{\lambda})$$

Consider $2S$ in Hydrogen.

$$2S \to 1S$$

so $\Delta m = 0$, $\Delta l = 0$ Forbidden transition is still not possible. After some calculation, electric quadrupole radiation 0, magnetic dipole 0, in fact all multipole radiations give 0.

But from fine structure $2s$ is not the lowest state

$$E(2S_{1/2}) - E(2P_{1/2}) = 4.35 \times 10^{-6} eV$$

so it should decay. It happens in two steps, second order perturbation 2 level decay

$$2S_{1/2} \to 2P_{1/2} \to 1S$$

The first step takes 20 years, and the second step takes 1/7 second.

5.7 MASER

Lecture 20 (4/9/13)

Microwave Amplification by Stimulated Emission of Radiation

Ammonia molecules NH_3. The three H atoms stay on a plane, N oscillates vertically in and out of the plane. Let $|I\rangle$, $|O\rangle$ be the two states where N is mostly in or out of the plane. Let 1,2 be states

$$|1\rangle = \frac{|I\rangle + |O\rangle}{\sqrt{2}} \qquad |2\rangle = \frac{|I\rangle - |O\rangle}{\sqrt{2}}$$

then 1 is symmetric ground state, and 2 is antisymmetric 1st excited state.

$$\Delta E = E_2 - E_1 = 10^{-4} eV$$

$(1eV \sim k_B T \sim 11600K)$ So we have it in room temperature.

Apply electric field $\vec{\epsilon}$, do perturbation

$$H' = \vec{\mu} \cdot \vec{\epsilon}$$

Assume $|I\rangle$, $|O\rangle$ are eigenstate of H' with values $\pm\mu\epsilon$.

If no electric field

$$\langle I|H_0|I\rangle = \frac{\langle 1+2|H_0|1+2\rangle}{2} = \frac{E_1+E_2}{2} = E_{av} = \langle O|H_0|O\rangle$$

$$\langle I|H_0|O\rangle = \frac{\langle 1+2|H_0|1-2\rangle}{2} = \frac{E_1-E_2}{2} = \langle O|H_0|I\rangle$$

so H written in the basis of $|I\rangle$, $|O\rangle$ is

$$H = H_0 + H' = \begin{pmatrix} E_{av}+\mu\epsilon & -\frac{\Delta E}{2} \\ -\frac{\Delta E}{2} & E_{av}-\mu\epsilon \end{pmatrix} = E_{av}I + \begin{pmatrix} \mu\epsilon & -\frac{\Delta E}{2} \\ -\frac{\Delta E}{2} & -\mu\epsilon \end{pmatrix}$$

So eigenvalue of H

$$E = E_{av} \pm \sqrt{(\mu\epsilon)^2 + \frac{1}{4}(\Delta E)^2}$$

as applied $\epsilon \uparrow$,

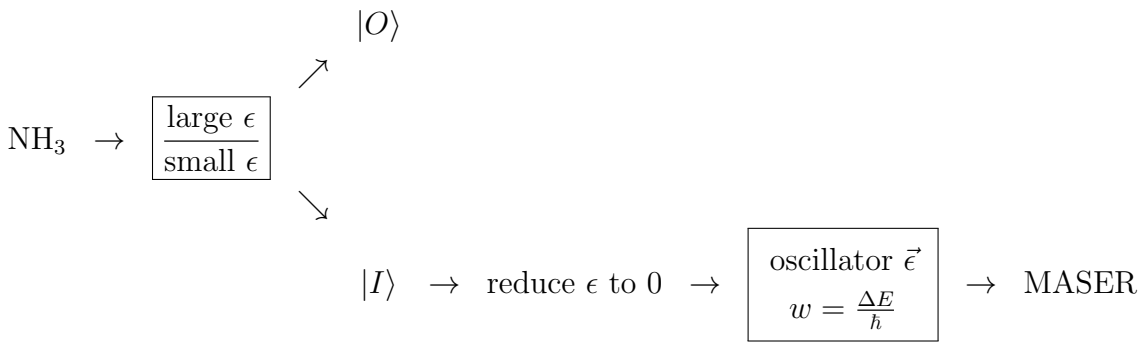
$$E \to E_{av} \pm \mu\epsilon$$

and

$$H \to \begin{pmatrix} E_{av}+\mu\epsilon & 0 \\ 0 & E_{av}-\mu\epsilon \end{pmatrix}$$

so $|I\rangle$, $|O\rangle$ become eigenstates with eigenvalues $E_{av} \pm \mu\epsilon$. The transitions from $|2,1\rangle$ states to $|I,O\rangle$ states are continuous and smooth, so we expect since at the beginning $\epsilon = 0$, $|2\rangle$ has higher energy then $|1\rangle$, as $\epsilon \uparrow$ we believe pure$|2\rangle$ will all become $|I\rangle$ with even higher energy, and pure $|1\rangle$ will all become $|O\rangle$ with even lower energy. One can also reverse the process if we start with some pure $|I\rangle$ and $\epsilon \downarrow$, we will end up with some pure $|2\rangle$ states.

Below is the flow chart for produce MASER.



Stating some room temperature NH_3 gas. There are about equal amount of $|1,2\rangle$ states. Fill the gas into a region where two constant electric fields, one big on one side and the other on the other half region. Because energy of $|O\rangle$ is $E_{av} - \mu\epsilon$, $|O\rangle$ prefers to stay in bigger electric field region, for that will reduce its energy. Whiles $|I\rangle$ prefers smaller electric field region. After obtaining pure $|I\rangle$, smoothly reduce $\epsilon \to 0$, so we have pure $|2\rangle$ states, 1st excited states. Put a oscillating electric field. Once the first atom starts spontaneous emission, produce first γ, it will be used to do stimulated emission, hence a chain of reaction starts, and light of same frequency is produced.

6 Adiabatic Approximation

We don't always have

$$H(t) = H_0 + H'(t)$$

$H'(t)$ small, so we now study another method to handle time dependent Hamiltonian.

6.1 Adiabatic Theory

Suppose $H(t)$ is slowly varying. Say $H(R(t))$, R some parameter. E.g.

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

where k is time varying. It is possible to have more than one varying parameters.

We hope if we do things slowly, then at each intermediate stage the complete set of eigenstates of initial Hamilton evolve and becomes the complete set of eigenstates of later Hamilton. Mathematically it is called eigenvalue no crossing. cf Lax Linear Algebra. The idea is if we start with $H(0)$ that has no degeneracy, and H changes slowly, later on $H(t)$ has no degeneracy and the nth eigenvector of $H(0)$ becomes the nth eigenvector of $H(t)$. That is because, I learned from Prof. Tabak, e.g. consider $H(t) = A + tB$ where A, B are constant real symmetric matrices. The dimension of the space of real $n \times n$ symmetric matrices is $n(n+1)/2$, while the dimension of its subspace with repeated eigenvalues is $n(n+1)/2-2$. In general, a one-dimensional curve $H(t)$ will not intersect a codimension 2 manifold.

Like in Ammonia example above

$$\{|2,1\rangle\} \to \{|I,O\rangle\}$$

For more convincing proof of adiabatic theory see Griffiths 1st edition, not 2nd edition proof.

Now suppose at some t, we have a complete set of orthonormal eigenstates

$$H(t)\,|\psi_m(t)\rangle = E_m\,|\psi_m(t)\rangle \quad \langle\psi_m(t)|\psi_n(t)\rangle = \delta_{mn}$$

Since they are complete, we can write any state

$$|\Psi(t)\rangle = \sum_n c_n(t)\,|\psi_n(t)\rangle\, e^{i\theta_n(t)}$$

where

$$\theta_n(t) = -\frac{1}{\hbar}\int_0^t E_n(t')dt'$$

called "dynamics phase". We don't combine $e^{i\theta_n(t)}$ into $c_n(t)$ because it has a reason.

Plug into Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\,|\Psi\rangle = H(t)\,|\Psi\rangle$$

$$LHS = i\hbar \sum_n \left(\dot{c}_n |\psi_n\rangle + c_n \left|\dot{\psi}_n\right\rangle + -\frac{i}{\hbar} E_n c_n |\psi_n\rangle \right) e^{i\theta_n(t)}$$

$$RHS = \sum_n c_n E_n |\psi_n\rangle$$

So

$$\sum_n \left(\dot{c}_n |\psi_n\rangle + c_n \left|\dot{\psi}_n\right\rangle \right) e^{i\theta_n(t)} = 0$$

Apply $\langle\psi_m|$

$$\dot{c}_m = -\sum_n c_n \left\langle \psi_m \middle| \dot{\psi}_n \right\rangle e^{i(\theta_n - \theta_m)}$$

To compute $\left\langle \psi_m \middle| \dot{\psi}_n \right\rangle$, we do

$$\frac{d}{dt} \left(H(t) |\psi_n(t)\rangle = E_n |\psi_n\rangle \right)$$

$$\dot{H} |\psi_n\rangle + H \left|\dot{\psi}_n\right\rangle = \dot{E}_n |\psi_n\rangle + E_n \left|\dot{\psi}_n\right\rangle$$

apply $\langle\psi_m|$

$$\left\langle \psi_m \middle| \dot{H} \middle| \psi_n \right\rangle + E_m \left\langle \psi_m \middle| \dot{\psi}_n \right\rangle = \dot{E}_n \delta_{mn} + E_n \left\langle \psi_m \middle| \dot{\psi}_n \right\rangle \tag{6.1}$$

So if $n \neq m$,

$$\left\langle \psi_m \middle| \dot{\psi}_n \right\rangle = \frac{\left\langle \psi_m \middle| \dot{H} \middle| \psi_n \right\rangle}{E_n - E_m}$$

(more work need to done for degeneracy, but we won't do it, so $H(t)$ has distinct eigenvalues $\forall\ t$).

If $n = m$, (6.1) says

$$\left\langle \psi_m \middle| \dot{H} \middle| \psi_m \right\rangle = \dot{E}_m$$

so we find

$$\dot{c}_m = -c_m \left\langle \psi_m \middle| \dot{\psi}_m \right\rangle - \sum_{n \neq m} c_n \frac{\left\langle \psi_m \middle| \dot{H} \middle| \psi_n \right\rangle}{E_n - E_m} e^{i(\theta_n - \theta_m)}$$

Now use adiabatic approximation, $\dot{H}$ is small, so forget about the sum

$$\dot{c}_m = -c_m \left\langle \psi_m \middle| \frac{d}{dt} \psi_m \right\rangle$$

hence

$$c_m(t) = c_m(0) e^{i\gamma_m(t)}$$

where

$$\gamma_m(t) = i \int_0^t dt' \left\langle \psi_m(t') \middle| \frac{d}{dt'} \middle| \psi_m(t') \right\rangle$$

called "geometric phase". Notice $\gamma_m(t)$ is real, because

$$\frac{d}{dt} \left(\langle \psi_m | \psi_m \rangle = 1 \right)$$

$$\left\langle \psi_m \middle| \frac{d}{dt} \psi_m \right\rangle + \left\langle \frac{d}{dt} \psi_m \middle| \psi_m \right\rangle = 0 \implies \left\langle \psi_m \middle| \frac{d}{dt} \psi_m \right\rangle \text{ is pure imaginary}$$

Therefore

$$|\Psi(t)\rangle = \sum_n e^{i\theta_n(t)} e^{i\gamma_n(t)} c_n(0) \, |\psi_n(t)\rangle$$

so it looks like $\forall t \ |\psi_n(t)\rangle$ still act a complete set of eigenstates.

Lecture 21 (4/11/13)

More interestingly if we start $|\Psi(0)\rangle = |\psi_n(0)\rangle$ as an eigenstate, i.e. $c_n(0) = 1$ all others are 0, then

$$|\Psi(t)\rangle = e^{i\theta_n(t)} e^{i\gamma_n(t)} \, |\psi_n(t)\rangle \tag{6.2}$$

we will pick up some phases. We will see γ is path dependent if H depends on more than one parameters, so it is called geometric phase; $\theta_n(t)$, $|\psi_n(t)\rangle$ depend only on $H(t)$.

6.2 Barry Phase

We study $\gamma(t)$ in (6.2) carefully. Suppose there are more than one time varying parameters in H, so are in $|\psi_n(t)\rangle = |\psi_n(R_{1,2,..,N}(t))\rangle$. We compute

$$\begin{aligned}\gamma_n(t) &= i\int_0^t dt' \left\langle \psi_n(t') \middle| \frac{d}{dt'}\psi_n(t') \right\rangle \\ &= i\sum_j \int_0^t dt' \frac{dR_j}{dt'} \left\langle \psi_n(R(t')) \middle| \frac{\partial}{\partial t'}\psi_n(R(t')) \right\rangle\end{aligned}$$

because $\frac{d\psi_n}{dt} = \sum_j \frac{\partial \psi_n}{\partial R_j}\frac{dR_j}{dt}$.

So one may attempt to write

$$\gamma_n(t) \stackrel{?}{=} i\int_{\vec{R}(0)}^{\vec{R}(t)} d\vec{R} \left\langle \psi_n(R(t')) \middle| \frac{\partial}{\partial t'}\psi_n(R(t')) \right\rangle$$

What does this mean?

Even more interesting if H under some slow changes and at the end, t, it comes back to $H(t) = H(0)$, so $|\psi_n(t)\rangle = |\psi_n(0)\rangle$, but

$$|\Psi(t)\rangle = e^{i\gamma_n(t)}\,|\psi_n(0)\rangle = e^{i\gamma_n(t)}\,|\Psi(0)\rangle$$

We will show an example of this type $\vec{R}(0) = \vec{R}(t)$ but $\gamma(t)$, Barry phase, $\neq 0$. So path integral does depend on path.

Another variance of this kind of experiment: take a beam of particles (all in same eigenstate $|\psi_n(0)\rangle$) split it into two so that one beam passes through an adiabatically changing potential, while the other does not. After time t combine the two beams, we will see interference

$$\Psi \sim |\psi_n(0)\rangle\,(1 + e^{i\gamma_n(t)})$$

$$|\Psi|^2 \sim \cos^2\frac{\gamma}{2}$$

We now look at one of few exactly solvable problems. It gives a good example of how to make an adiabatically changing potential.

Example. Consider Elections in rotating B field

$$\vec{B}(t) = B_0 \left(\sin\alpha \cos wt, \sin\alpha \sin wt, \cos\alpha\right)$$

$$H = -\vec{\mu} \cdot \vec{B} = \frac{eg}{2mc}\vec{S} \cdot \vec{B} = \frac{e}{mc}\vec{S} \cdot \vec{B}$$

electron spin 1/2, choose stander basis

$$S = \frac{\hbar}{2}\vec{\sigma}\ \sigma_x = \begin{pmatrix} & 1 \\ 1 & \end{pmatrix}\ \sigma_y = \begin{pmatrix} & -i \\ i & \end{pmatrix}\ \sigma_z = \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \tag{6.3}$$

Ignoring all other degrees of freedom.

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \leftrightarrow S_z = \frac{\hbar}{2} \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix} \leftrightarrow S_z = -\frac{\hbar}{2}$$

$$H = \frac{e\hbar}{2mc}\vec{\sigma} \cdot \vec{B} = w_1 \frac{\hbar}{2} \begin{pmatrix} \cos\alpha & e^{-iwt}\sin\alpha \\ e^{iwt}\sin\alpha & -\cos\alpha \end{pmatrix}$$

setting

$$w_1 = \frac{eB_0}{mc} \approx \frac{E}{\hbar/2}$$

Eigenvalues of $\begin{pmatrix} \cos\alpha & e^{-iwt}\sin\alpha \\ e^{iwt}\sin\alpha & -\cos\alpha \end{pmatrix}$ are ± 1, e.g. find eigenvector χ_+ with eigenvalue 1

$$\begin{pmatrix} \cos\alpha & e^{-iwt}\sin\alpha \\ e^{iwt}\sin\alpha & -\cos\alpha \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}$$

so

$$a\cos\alpha + be^{-iwt}\sin\alpha = a$$

then

$$\frac{b}{a} = \frac{1-\cos\alpha}{\sin\alpha}e^{iwt} = \frac{2\sin^2\frac{\alpha}{2}}{2\sin\frac{\alpha}{2}\cos\frac{\alpha}{2}}e^{iwt} = \frac{\sin\frac{\alpha}{2}}{\cos\frac{\alpha}{2}}e^{iwt}$$

Similarly find eigenvector χ_- with -1. We want them to be orthonormal

$$\chi_+(t) = \begin{pmatrix} \cos\frac{\alpha}{2} \\ e^{iwt}\sin\frac{a}{2} \end{pmatrix} \qquad \chi_-(t) = \begin{pmatrix} e^{-iwt}\sin\frac{\alpha}{2} \\ -\cos\frac{a}{2} \end{pmatrix}$$

we want to see how an arbitrary state evolves. Solve Schrodinger

$$i\hbar\dot{\chi} = H\chi \tag{6.4}$$

with

$$\chi(t) = f(t)e^{-iwt/2}\chi_+(t) + g(t)e^{iwt/2}\chi_-(t)$$

RHS of (6.4)

$$H\chi = \frac{\hbar w_1}{2}[fe^{-iwt/2}\chi_+ - ge^{iwt/2}\chi_-]$$

LHS of (6.4)

$$i\hbar\dot{\chi} = i\hbar[(\dot{f} - \frac{iw}{2}f)e^{-iwt/2}\chi_+ + fe^{-iwt/2}\dot{\chi}_+ + (\dot{g} + \frac{iw}{2}g)e^{iwt/2}\chi_- + ge^{iwt/2}\dot{\chi}_-]$$

Because

$$\chi_+^\dagger H\chi = i\hbar\chi_+^\dagger\dot{\chi} \qquad \chi_-^\dagger H\chi = i\hbar\chi_-^\dagger\dot{\chi}$$

above become

$$\begin{cases} \dot{f} = (\cdots)f + (\cdots)g \\ \dot{g} = (\cdots)f + (\cdots)g \end{cases}$$

then eliminate g, then take t derivative of the first equation, we obtain

$$\ddot{f} = (\cdots)\dot{f} + (\cdots)f$$

showing f is oscillating with frequency λ. Put in initial condition $t = 0$, $f = 1$, $g = 0$ (i.e. starting at χ_+)

$$\begin{cases} f = & \cos\frac{\lambda t}{2} - i\frac{w_1 - \cos\alpha}{\lambda}\sin\frac{\lambda t}{2} \\ g = & i\frac{w}{\lambda}\sin\alpha\sin\frac{\lambda t}{2} \end{cases}$$

with

$$\lambda = \sqrt{w^2 + w_1^2 - 2ww_1\cos\alpha}$$

Later time probability transition to χ_-

$$|\langle\chi(t)|\chi_-(t)\rangle|^2 = |g|^2 = (\frac{w}{\lambda}\sin\alpha\sin\frac{\lambda t}{2})^2$$

If $\vec{B}$ field rapidly varying or more precisely $w \gg w_1$,

$$\lambda \approx w$$

so the probability of transition

$$\sim \left(\sin\alpha\sin\frac{\lambda t}{2}\right)^2$$

If $\vec{B}$ field slowly varying or more precisely $w \ll w_1$,

$$\lambda \approx w_1$$

so the probability of transition

$$\sim \left(\frac{w}{\lambda}\right)^2 \ll 1$$

Hence small varying H makes eigenvector stay eigenvector.
In the adiabatic limit

$$\chi(t) = e^{-iw_1t/2}e^{i(w\cos\alpha)t/2}e^{-iwt/2}\chi_+(t)$$

we compute dynamical phase

$$\theta(t) = -\frac{1}{\hbar}\int_0^t E_+dt' = -\frac{1}{\hbar}\int_0^t \frac{w_1\hbar}{2}t' = -\frac{w_1t}{2}$$

so what is left is the geometric phase

$$\gamma(t) = (\cos\alpha - 1)\frac{wt}{2}$$

In particular, at $t = 0$ we start out with

$$\chi(0) = \chi_+(0) = \begin{pmatrix} \cos\frac{\alpha}{2} \\ \sin\frac{\alpha}{2} \end{pmatrix}$$

after time $T = \frac{2\pi}{w}$, H becomes $H(0)$, but

$$\chi(t) = e^{i\gamma(T)}\chi_+(0)$$

$\gamma(T)$ is Barry phase.

6.3 Aharonov-Bohm Effect

We now study more about geometric phase. It is beyond the discussion of adiabatic motion.

Consider an electron confined to a ring C of radius b, inside the ring there is a concentric $\vec{B}$ field produced by a ∞ long solenoid of radius a, $a < b$. So there is no $\vec{B}$ on the electron path.

Recall

$$\vec{B} = \nabla \times \vec{A} \quad \vec{E} = -\frac{\partial \vec{A}}{\partial t} - \nabla\phi$$

and gauge invariant

$$\vec{A} \to \vec{A} + \nabla F(\vec{x}, t) \quad \phi \to \phi - \frac{\partial F(\vec{x}, t)}{\partial t}$$

give the same $\vec{E}$, $\vec{B}$. And we are told $\vec{E}$, $\vec{B}$ are measurable, and $\vec{A}$, ϕ are not directly measurable.

The Lagrangian for charge particle

$$L = \frac{1}{2}m\vec{v}^2 + q\vec{v} \cdot \vec{A} + ...$$

this is indeed correct, because it produces Lorentz force

$$p_j \equiv \frac{\partial L}{\partial v_j} = (m\vec{v} + q\vec{A})_j$$

and we find Hamiltonian

$$\begin{aligned} H &= \sum p_j v_j - L \\ &= \frac{1}{2m}(\vec{p} - q\vec{A})^2 + ... \end{aligned}$$

plus some terms we don't care. Schrodinger equation

$$H\psi = \frac{1}{2m}[\frac{\hbar}{i}\nabla - q\vec{A}]^2\psi = E\psi \tag{6.5}$$

want to calculate ψ for the particle on the ring C situated in $x-y$ plane. What is $\vec{A}$?

$$\oint_C d\vec{l}\cdot\vec{A} = \iint_{\text{area enclosed by } C} dS(\nabla\times\vec{A})_\perp = \iint dSB_z = \Phi$$

Φ magnetic flux.

Use coulomb gauge, we pick $\vec{A}$ along $\hat{\phi}$, spherical angle,

$$\oint_C d\vec{l}\cdot\vec{A} = 2\pi bA = \phi \implies \vec{A} = \hat{\phi}\frac{\Phi}{2\pi b} \tag{6.6}$$

This is indeed one plausible $\vec{A}$, because

$$\vec{A}(\rho) = \begin{cases} \hat{\phi}\frac{\pi\rho^2 B}{2\pi\rho} & \rho < a \\ \hat{\phi}\frac{\pi b^2 B}{2\pi\rho} & \rho > a \end{cases}$$

in spherical coordinate and on $x-y$ plane $\theta = \pi/2$, $\hat{\theta} = \hat{z}$

$$\vec{B}(\rho) = \nabla\times\vec{A} = -\frac{1}{\rho}\frac{\partial}{\partial\rho}(\rho A_\phi)\hat{\theta} = \begin{cases} B\hat{z} & \rho < a \\ 0 & \rho > a \end{cases}$$

Try $\psi = ce^{i\lambda\varphi}$ for (6.5)

$$\frac{1}{2m}\left(\frac{\hbar}{i}(\frac{1}{b}\frac{d}{d\phi}) - \frac{q\Phi}{2\pi b}\right)^2\psi = E\psi$$

so

$$\frac{1}{2m}\left(\frac{\hbar\lambda}{b}-\frac{q\Phi}{2\pi b}\right)^2 e^{i\lambda\varphi}=Ee^{i\lambda\varphi}$$

check it is correct by doing $\left(\frac{\hbar}{i}\nabla-q\vec{A}\right)$ once treating ∇ as grad then another time treating ∇ as divergence.

Because wave function is single valued and continuous, $\psi(0)=\psi(2\pi)$, λ must be integers, so

$$E_n=\frac{1}{2m}\left(\frac{\hbar n}{b}-\frac{q\Phi}{2\pi b}\right)^2 \quad n=0,\pm1,... \tag{6.7}$$

is quantized. Hence somehow $\vec{B}$ has some effects on the electron where no $\vec{B}$ field to be found.

Lecture 22 (4/16/13)

We want to see this leads to geometric phase.

A beam of particles of state ψ is split in two, and passes one side of a long solenoid then they are recombined. No $\vec{B}$ on the paths. If ψ' satisfies

$$i\hbar\frac{\partial\psi}{\partial t}=\left((\frac{\hbar}{i}\nabla)^2+V\right)\psi$$

then the each split beam is in state $\psi'_{1,2}$, and

$$\psi'_{1,2}=e^{ig_{1,2}(\vec{\gamma})}\psi \tag{6.8}$$

where

$$g_{1,2}(\vec{\gamma})=\frac{q}{\hbar}\int_{\vec{\gamma}_{1,2}} d\vec{r}'\cdot\vec{A}(\vec{r}')$$

depends on the path it travels, so it is too a geometric phase. The key point to understand is that the wave function ψ or ψ' is localized, it spreads in the vicinity of the charges. As the charges move, ψ' moves with it, so the coordinate of ψ' is a moving coordinate, as in the Barry's proof of how this $g(\vec{\gamma})$ agrees the old definition, where he puts ψ in a moving box, see Griffiths. However the factor $g(\vec{\gamma})$ is a global function. Because Schrodinger equation and ∇ operator are local, so we can still treat $g(\vec{\gamma})$ as local when we take derivatives, cf (6.10), where we use fundamental theorem of calculus. At the same time we need to make sure $g(\vec{\gamma})$ is well-defined (i.e. single valued) globally. This is taken care of by picking a

specific branch cut that does not interfere with the usage of fundamental theorem of calculus. That is to pick a branch cut where the particle will not pass. E.g. if beam 1 passes the right side of $\vec{B}$ field, pick branch cut for g_1 to be on the left side of the $\vec{B}$ field.

Let us show (6.8) is indeed correct, i.e. it satisfies

$$i\hbar\frac{\partial\psi'}{\partial t} = \left((\frac{\hbar}{i}\nabla - q\vec{A})^2 + V\right)\psi' \tag{6.9}$$

Take

$$\begin{aligned}\frac{\hbar}{i}\nabla\psi' &= \frac{\hbar}{i}(\nabla\psi + i\psi\nabla g)e^{ig} \\ &= \frac{\hbar}{i}(\nabla\psi + i\frac{q}{\hbar}\vec{A}\psi)e^{ig}\end{aligned} \tag{6.10}$$

and

$$(\frac{\hbar}{i}\nabla - q\vec{A})\psi' = (\frac{\hbar}{i}\nabla\psi)e^{ig}$$

$$\begin{aligned}(\frac{\hbar}{i}\nabla - q\vec{A})^2\psi' &= (\frac{\hbar}{i}\nabla - q\vec{A})(\frac{\hbar}{i}\nabla\psi)e^{ig} \\ &= -\hbar^2 e^{ig}\nabla^2\psi \\ &= -\hbar^2 e^{ig}\frac{V\psi - i\hbar\frac{\partial\psi}{\partial t}}{\hbar^2}\end{aligned}$$

Hence we get (6.9).

In other words, when the two beams recombine

$$\begin{aligned}\psi_1' + \psi_2' &= e^{ig_2}(1 + e^{i(g_1 - g_2)})\psi \\ &= \sim \cos\frac{g_1 - g_2}{2}\psi\end{aligned}$$

we are going to see interference

$$g_1 - g_2 = \frac{q}{\hbar}\oint \vec{A}\cdot d\vec{r} = \frac{q}{\hbar}\Phi$$

Φ magnetic flux of the area enclosed by the two paths. If $\vec{B}$ is not there, then

clearly no interference.

Notice the whole discussion is gauge independent. Adding ∇F to $\vec{A}$ will not change the integral

$$\oint \vec{A} \cdot d\vec{r} = \oint (\vec{A} + \nabla F) \cdot d\vec{r}$$

More is true. cf Griffiths problem 4.61. If we add ∇F to $\vec{A}$, there will be another phase factor $e^{iqF/\hbar}$ to all ψ, but this is not a geometric phase and not cause any changes to our discussion.

6.4 Dirac String

Experimental fact: no magnetic monopole. Have not found many. Only found once (early 1980s on valentine day).

Suppose it does exist. so we have similar coulomb's law

$$\vec{B} = Q_m \frac{\hat{r}}{r^2}$$

What is $\vec{A}$ for magnetic monopole, try

$$\vec{A} = (-y, x, 0) \frac{Q_m}{r(r+z)} = \hat{\phi} \frac{Q_m \sin\theta}{r+z} \tag{6.11}$$

$$\begin{aligned}
(\nabla \times \vec{A})_x &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \\
&= -Q_m \frac{\partial}{\partial z} \frac{x}{r(r+z)} \\
&= -Q_m x \left(-\frac{1}{r(r+z)^2} + \frac{\partial r}{\partial z} \frac{\partial}{\partial r} \frac{1}{r(r+z)} \right) \\
&= Q_m x \left(\frac{1}{r(r+z)^2} + \frac{z}{r} \left(\frac{1}{r^2(r+z)} + \frac{1}{r(r+z)^2} \right) \right) \\
&= Q_m \frac{x}{r^3}
\end{aligned}$$

so (6.11) is indeed correct, but it is singular along negative z axis. By the way one

can check

$$\vec{A} = (-y, x, 0)\frac{Q_m}{r(r-z)}$$

works too and it has branch cut along positive z axis.

Let us take $\vec{A}$ in (6.11), we put the monopole at the origin, then we take a small loop along the $-z$ axis. The loop is distance r from the origin and it has azimuthal angle θ very close to π.

QM says

$$e^{i\frac{q}{\hbar}\oint \vec{A}\cdot d\vec{l}} \tag{6.12}$$

is detectable by interference. Let us compute this for the small loop

$$\oint \vec{A}\cdot d\vec{l} = 2\pi r\sin\theta\frac{Q_m\sin\theta}{r+z} = 2\pi Q_m\frac{r\sin^2\theta}{r(1+\cos\theta)} = 2\pi Q_m(1-\cos\theta)$$

Now shrink loop to almost a point $\theta \to \pi$, so

$$\oint \vec{A}\cdot d\vec{l} = 4\pi Q_m$$

Therefore $e^{i\frac{q}{\hbar}\oint \vec{A}\cdot d\vec{l}}$ is not detectable if

$$\frac{q}{\hbar}4\pi Q_m = 2\pi n$$

$n = 0, \pm 1, ...$ hence

$$Q_m q = \frac{n}{2}\hbar$$

Let $q = -e$ one electron,

$$Q_m = \frac{1}{2e\hbar}n$$

this shows if magnetic monopole exists and (6.12) is not detectable, then magnetic charge is quantized. Then do the another way

$$q = \frac{n}{2Q_m}\hbar$$

we see that electric charge has to be quantized.

Is (6.12) detectable? How to product $\vec{A}$ in (6.11) if we don't have monopole

yet? We use a half ∞ thin long solenoid. On the finite end, its $\vec{A}$ is very close to (6.11). So we have $\vec{A}$, and we check that (6.12) is not detectable.

So now all eyes are on finding monopoles, because it will help us to get grand unification.

6.5 Grand Unification

Are there magnetic monopoles? How to find them?

Gigantic superconductor annulus have been made to detect monopoles. Scientists are hoping to catch some flying in the universe and falling to the earth. Once magnetic monopole passes the annulus, it will create a supercurrent, because superconductor has no resistance and that magnetic monopole passes the annulus will produce changing $\vec{B}$ field.

The screen will show that before magnetic monopole enters there is a constant background current, then after it enters, a jump in current level. There was only once in early 1980s, seeing current jump. Never happened again.

If it does exist, calculation has shown that the flux of magnetic monopole to the ratio of size of the earth is

1 per football field per year

Grand unification tries to combine all known theories into one theory: big bang.

Theory of electromagnetism, and theory of weak interaction have similar order of coupling constants g, g'. However theory of quantum chromodynamics coupling g_{QCD}. At low energy

$$g_{QCD} \gg g, g'$$

So the theory of quantum chromodynamics doesn't come along well with the other two theories. We know $g_{QCD} \downarrow$ as energy goes higher. At energy $10^{15\sim16}$GeV,

$$g_{QCD} \approx g, g'$$

We assume all three g, g' and g_{QCD} meet at high energy, and assume we

already know all of particles, the theory (1978-1979) predicts there exists magnetic monopoles with mass $\sim 10^{16\sim17}GeV$, and they can be produced right after big bang. The theory also calculate number of monopoles being produced and how many still survived today. They are off $\sim 10^2$ by observations.

Cosmological inflation is another implication of the grand unification. It goes back to begging the answer of existence of magnetic monopoles. Cosmological inflation theory explains the origin of CMB (cosmic microwave background) radiation is the quantum fluctuation from the early universe. The theory also explains why two photons that are several light years apart have same temperatures.

7 Scattering

Lecture 23 (4/18/13)

The situation we are going to examine is that in an empty universe, we have some potential concentrated at some region (i.e. short range forces, how short is it? not coulomb type. we will deliberate more). The exact strength, type, size, ... of the potential are unknown. We are going to hit it with some waves or particles and result scattering. From the scattering we want to get some information of the potential.

7.1 Classical Scattering

Classic means wave or particle has definite trajectory.

Let potential set in the origin, particles are coming from parallel to the $-z$ axis. We assume the potential is symmetric around z axis, i.e. independent of ϕ. This is not a general situation. E.g. proton has spin, but we don't consider them.

Let b be the impart parameter, i.e. distance b from the $-z$ axis. The cross section of the incident particles with b look like an annulus of radius b with width db. Pick a small area on the annulus, denote it $d\sigma$, then

$$d\sigma = (db)(bd\phi)$$

The scattering particles coming out like a sphere. Pick a small area on the

sphere, denote it dA, then

$$dA = r^2 \sin\theta d\theta d\phi$$

Since r is irrelevant, what coming out at angle (θ, ϕ) will stay in that direction. So we are interested in the scattering particles of given solid angles,

$$d\Omega = \sin\theta d\theta d\phi$$

More important quantity is the ration: Differential cross section

$$D(\theta) \equiv \frac{d\sigma}{d\Omega} = \frac{b}{\sin\theta}\left|\frac{d\theta}{db}\right|$$

so ϕ drops out. Notice because there is a corresponding relation between b and θ, so there is only one variable in D. The absolute sign is to accommodate the fact that usually $d\theta/db < 0$ because the closer to the core, the more defect it gets. This fact doesn't depend whether incident charges have some sign as the potential or opposite sign, as e.g. showing in Rutherford scattering.

Example. Hard sphere of radius a at the origin, let α be the incident angle, then

$$\theta = \pi - 2\alpha \text{ and } \sin\alpha = \frac{b}{a}$$

so

$$D(\theta) = \frac{a\cos\frac{\theta}{2}}{\sin\theta}\left|-\frac{a}{2}\sin\frac{\theta}{2}\right| = \frac{a^2}{4} \tag{7.1}$$

Total cross section

$$\sigma = \int d\Omega D(\theta) = \pi a^2$$

meaning these particles (if assume incident particles are uniformly distributed) πa^2 will hit the sphere, and it is also the total amount of scattered particles.

cf Griffiths problem 11.1. One can do the same for Rutherford scattering with $\frac{1}{r}$ potential. Incident q_1, and q_2 fixed at the origin. In Griffiths unit

$$D(\theta) = \left[\frac{q_1 q_2}{(4\pi\epsilon_0)(4E\sin^2\frac{\theta}{2})}\right]^2 \tag{7.2}$$

We find

$$\sigma_{tot} = \int d\Omega D(\theta) \propto \int d\theta \frac{\sin\theta}{\sin^4 \frac{\theta}{2}} \to \infty$$

meaning never able to get far away to ignore coulomb potential. So from now on we assume scatter potential fell off faster than $1/r$.

(7.2) is moderately painful calculation in classical mechanics. This becomes ridiculously painful to calculate it in quantum mechanics.

7.2 Quantum Scattering

We need to have a frame work for both particles and waves. Define luminosity

$$L = \frac{\text{\# incident particles or wave packets}}{(\text{area})(\text{time})}$$

which is set up by the experiment. The old differential cross section

$$D(\theta) = \frac{d\sigma}{d\Omega} = \frac{1}{L}\frac{dN}{d\Omega} \tag{7.3}$$

where $dN/d\Omega$ is # of scatter particles per unit time in solid angle $d\Omega$.

Recall last semester when we did scattering matrix (Griffiths 1st edition section 2.7 or problem 2.52), we used stationary states as incoming wave

$$\psi = Ae^{ikz}$$

One can check this is indeed a right moving wave, because $\Psi(z,t) = Ae^{i(kz-Et/\hbar)}$, $k = \sqrt{2mE}/\hbar$.

We claim the outgoing scattering wave is of the form

$$\psi = A\frac{e^{ikr}}{r}f(\theta) \tag{7.4}$$

hence it's spherical wave with scattering amplitude $f(\theta)$. So far from the potential, the detected wave is

$$\psi \approx A[e^{ikz} + \frac{e^{ikr}}{r}f(\theta)] \tag{7.5}$$

One big difference quantum and classical scattering is that in classical scattering,

the detected particles has only the scattering part. What is coming in is what is coming out. But here we have two parts, in addition to what is coming in is what is coming out, is that the scattering wave will interfere with the incoming wave.

Let's first check (7.4) makes sense. In particular why $f(\theta)$ has no r dependence and (7.4) $1/r$.

Recall probability current

$$\frac{d|\psi|^2}{dt} = -\nabla\vec{j}$$

$$\vec{j} = \frac{\hbar}{2im}(\psi^*\nabla\psi - \psi\nabla\psi)$$

For plane incoming wave Ae^{ikz}

$$\vec{j}_{incoming} = \frac{\hbar|A|^2}{2im}\left(e^{-ikz}ike^{ikz}\hat{z} - e^{ikz}(-ike^{-ikz})\hat{z}\right) = \frac{\hbar k|A|^2}{m}\hat{z}$$

For (7.4), use $\vec{\nabla} = \frac{1}{\partial r}\hat{r} + \frac{1}{r}\frac{1}{\partial\theta}\hat{\theta}$

$$\nabla\psi = A\left(f(\theta)(\frac{ik}{r} - \frac{1}{r^2})e^{ikr}\hat{r} + f'(\theta)\frac{1}{r^2}e^{ikr}\hat{\theta}\right)$$

$$\psi^*\nabla\psi = |A|^2\left(|f|^2(\frac{ik}{r^2} - \frac{1}{r^3})\hat{r} + f^*f'\frac{1}{r^3}\hat{\theta}\right)$$

ignore $1/r^3$ because it is much smaller than $1/r^2$, then

$$\begin{aligned}\vec{j}_{outgoing} &= \frac{\hbar}{m}\Im\left(\psi^*\nabla\psi\right) \\ &= \frac{\hbar k|A|^2|f|^2}{mr^2}\hat{r}\end{aligned}$$

But

$$\vec{j}_{incoming}dV = \vec{j}_{outgoing}dV \implies d\sigma = \frac{|f|^2}{r^2}r^2d\Omega$$

That is

$$D(\theta) = |f(\theta)|^2$$

showing indeed $f(\theta)$ has no r dependence and (7.4) $1/r$.

Two ways of calculating $f(\theta)$: partial wave analysis and Born approximation.

7.3 Partial Wave Analysis

From last semester we learned that for spherical symmetric potential, wave function should be

$$\psi = R_n(r)Y_{lm}(\theta,\phi) = \frac{u(r)}{r}Y_{lm}$$

and Y_{lm} are spherical harmonics. u satisfies

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left(\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} + V(r)\right)u = Eu \tag{7.6}$$

Solving (7.6) is not easy. We do it in 3 regions.

(1) Far region. Ignore both $V(r)$ and $1/r^2$, so

$$\frac{d^2u}{dr^2} = -k^2u$$

$$u = Ce^{ikr} + De^{-ikr}$$

choose $D = 0$ because of outgoing.

(2) Intermediate region

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u = -k^2u$$

$$u = Arj_l(kr) + Brn_l(kr) \tag{7.7}$$

where j_l, n_l are spherical Bessel functions.

$$j_0(x) = \frac{\sin x}{x} \quad j_1(x) = \frac{\sin x}{x^3} - \frac{\cos x}{x}$$

$$n_0(x) = -\frac{\cos x}{x} \quad n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$$

although they are singular at $x = 0$, it is ok because we are in intermediate region.

At large x, the solution (7.7) should match e^{ikz}/r. We need to pick A, B so

that we can use Hankel's function 1st, not 2nd kind,

$$h_l^{(1)} = j_l + in_l \to \frac{1}{x}(-i)^{l+1}e^{ix} \tag{7.8}$$

$$h_l^{(2)} = j_l - in_l \to \frac{1}{x}(i)^{l+1}e^{-ix} \tag{7.9}$$

for $x \gg 1$.

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(3) Because V is unknown, solution in the region of V is unknown.

So the best we can do is to get the solution in region intermediate + far is

$$\psi = \sum_{lm} c_{lm} h_l^{(1)} Y_{lm}(\theta, \phi)$$

or combining with the incoming wave,

$$\psi = A\left(e^{ikz} + \sum_{lm} c_{lm} h_l^{(1)} Y_{lm}(\theta, \phi)\right) \tag{7.10}$$

Since the solution is too spherical symmetric $m = 0$,

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta)$$

where P is Legendre polynomials, e.g.

$$P_0(x) = 1 \quad P_1(x) = x \quad P_2(x) = \frac{3x-1}{2}$$

$$\int_{-1}^{1} dx P_l(x) P_{l'}(x) = \delta_{ll'} \frac{2}{2l+1} \quad \int_0^{\pi} d\theta \sin\theta P_l(\cos\theta) P_{l'}(\cos\theta) = \delta_{ll'} \frac{2}{2l+1}$$

and

$$P_l(1) = 1 \quad \forall l$$

We replace c_{lm} in (7.10) by some other factors

$$\psi = A\left(e^{ikz} + k\sum_l i^{l+1}(2l+1) a_l h_l^{(1)}(kr) P_l(\cos\theta)\right) \tag{7.11}$$

so that in deference to (7.8) for far region $r \gg 1$ (7.11) becomes

$$\psi \approx A[e^{ikz} + \underbrace{\sum_l (2l+1)a_l P_l(\cos\theta)}_{f(\theta)} \frac{1}{r} e^{ikr}] \tag{7.12}$$

a_l, $l = 0, 1, 2, ..$ called partial wave amplitudes which has no θ dependence.

Use that region, we can easily get σ_{tot}

$$D(\theta) = |f(\theta)|^2 = \sum_l \sum_{l'} (2l+1)a_l P_l(\cos\theta)(2l'+1)a_{l'}^* P_{l'}(\cos\theta)$$

$$\begin{aligned} \sigma_{tot} &= \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \sum_{l,l'} (2l+1)a_l P_l(\cos\theta)(2l'+1)a_{l'}^* P_{l'}(\cos\theta) \\ &= 4\pi \sum_l (2l+1)|a_l|^2 \end{aligned} \tag{7.13}$$

Now reorganize (7.11), by writing

$$e^{ikz} = \sum_{lm} A_{lm} j_l(kr) + B_{lm} n_l(kr) Y_{lm}(\theta, \phi)$$

Cartesian coordinate into spherical coordinate. We know e^{ikz} is independent of ϕ and it doesn't blow up at the origin. Recall for $x \ll 1$

$$j_l \sim \frac{2^l l!}{(2l+1)!} x^l \qquad n_l \sim \frac{(2l)!}{2^l l!} \frac{1}{x^{l+1}} \tag{7.14}$$

The exact formula (we won't prove it) is Rayleigh's formula

$$e^{ikz} = \sum_l i^l (2l+1) j_l(kr) P_l(\cos\theta)$$

So (7.11) has a better looking

$$\psi = A \sum_l i^l (2l+1)[j_l(kr) + ika_l h_l^{(1)}(kr)] P_l(\cos\theta) \tag{7.15}$$

solution in both intermediate and far regions. Unfortunately we cannot get A because it is obtained from overall normalization, but we know the solution in region of V.

Example. Quantum hard sphere scattering

$$V = \begin{cases} \infty & r \leq a \\ 0 & r > a \end{cases}$$

$$\psi(r = a, \theta) = 0 \, \forall \theta$$

so

$$j_l(ka) + ika_l h_l^{(1)}(ka) = 0$$

then

$$a_l = \frac{ij_l(ka)}{kh_l^{(1)}(ka)}$$

Suppose incoming wave has low energy, i.e. small k. Assume ka is small, $n_l \gg j_l$ by (7.14)

$$a_l = \frac{ij_l(ka)}{k[j_l(ka) + in_l(ka)]} \approx \frac{j_l(ka)}{kn_l(ka)} \approx \left(\frac{2^l l!}{(2l)!}\right)^2 \frac{1}{k(2l+1)}(ka)^{2l+1}$$

then by (7.13)

$$\sigma_{tot} = \frac{4\pi}{k^2} \sum_l \frac{1}{2l+1} \left(\frac{2^l l!}{(2l)!}\right)^4 (ka)^{4l+2}$$

low $l = 0$ dominate. This is true in almost all cases not just hard sphere scattering.

$$\sigma_{tot} = \frac{4\pi}{k^2}(ka)^2 = 4\pi a^2$$

as if radius of the sphere is twice as big as classical scattering.

7.4 Boundary: Phase Shift

Continue from the hard sphere scatter. We now do a hard wall scattering. Suppose incoming wave Ae^{ikz} perpendicularly hits a big (but finite) hard wall, so clearly

the scattering wave (reflected wave) should be

$$Be^{-ikz}$$

By conservation of probability

$$|A| = |B|$$

so

$$B = -Ae^{2i\delta}$$

and

$$\psi = A(e^{ikz} - e^{i(2\delta - kz)}) \tag{7.16}$$

Let us find out δ.

Use (7.15). Since $j_l = \frac{1}{2}(h_l^{(1)} + h_l^{(2)})$

$$\psi = A\sum_l i^l(2l+1)[(\frac{1}{2} + ika_l)h_l^{(1)}(kr) + \frac{1}{2}h_l^{(2)}(kr)]P_l(\cos\theta)$$

For $r \gg 1$, by (7.8), (7.9)

$$\psi = \sum_l A_l \frac{2l+1}{kr}[(1 + 2ika_l)e^{ikr} - (-1)^l e^{-ikr}]P_l(\cos\theta) \tag{7.17}$$

compare it to (7.12). They are actually the same things. Here we just write e^{ikz} into spherical harmonics. Roughly

$$e^{ikz} \sim \sum_{l=0}^{\infty} A_l[e^{ikr} - (-1)^l e^{-ikr}]P_l(\cos\theta)$$

Now we define δ_l through

$$e^{2i\delta_l} \equiv 1 + 2ika_l \tag{7.18}$$

then (7.17) looks a lot like (7.16), by identifying e^{-ikr} as incoming wave and $e^{i(kr+2\delta)}$ outgoing reflected wave.

Hence

$$a_l = \frac{e^{2i\delta_l} - 1}{2ik} = \frac{1}{k} e^{i\delta_l} \sin \delta_l$$

Just like a_l, δ_l is a constant independent of k, θ, and depend only on l and a_l, so we identify it as phase shift. a_l for the hard wall scatter can be calculated similar as for the hard sphere scattering problem.

In other words, after we decompose incoming plane wave into combination of spherical waves of different l, the reflected spherical waves have phase shifted by δ_l. Reflection causes phase shift but it doesn't change l, so in (7.17) the incoming wave of angular momentum l should have the same probability of the outgoing, i.e.

$$\left|(1 + 2ika_l)e^{ikr}\right|^2 = \left|-(-1)^l e^{-ikr}\right|^2 \tag{7.19}$$

showing $1 + 2ika_l$ is purely imaginary, so our definition (7.18) makes sense.

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Therefore by (7.12), (7.13)

$$f(\theta) = \frac{1}{k} \sum_l (2l + 1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta)$$

$$\sigma_{tot} = \frac{4\pi}{k^2} \sum_l (2l + 1) \sin^2 \delta_l$$

From here if we put $\theta = 0$, forward scattering amplitude,

$$f(0) = \frac{1}{k} \sum_l (2l + 1) e^{i\delta_l} \sin \delta_l$$

We get

Theorem. *(Optical Theorem)*

$$\sigma_{tot} = \frac{4\pi}{k} Im f(0)$$

This comes from conservation of probability, not depending on whether V is spherical symmetric or not.

There are some variances of hard wall scattering, see Griffiths problem 11.5

Example. E.g. let $V_0 > E > 0$,

$$V(x) = \begin{cases} 0 & x < -a \\ V_0 & -a < x < 0 \\ \infty & x > 0 \end{cases}$$

repulsive potential. after the wave hits $-a$, it has an exponential tail goes into $-a$. Work out the calculation, one will find the wave length increases by $2\delta_l/k$, because of the shift of $e^{i(kr+2\delta_l)}$

If take

$$V(x) = \begin{cases} 0 & x < -a \\ -V_0 & -a < x < 0 \\ \infty & x > 0 \end{cases}$$

a finite well, it will attack the tail into the well, so the the wave length decreases by $2\delta_l/k$, i.e. δ_l is negative. If we make the well deeper, it shifts more, and it approaches the limit that wave length decreases by a.

What we have impose in (7.19) is elastic scattering.

There are also inelastic scattering cases,

$$|1 + 2ika_l| < 1$$

so we are losing particles. But if inelastic scattering occurs, there must be some elastic scatterings.

Define

$$1 + 2ika_l = S_l$$

then

$$f(\theta) = \frac{1}{2ik} \sum (2l+1)(S_l - 1)P_l(\cos\theta)$$

$$\sigma_{elastic} = \frac{\pi}{k^2} \sum (2l+1)|1 - S_l|^2$$

$$\sigma_{inelastic} = \frac{\pi}{k^2} \sum (2l+1)(1 - |S_l|^2)$$

$$\sigma_{tot} = \sigma_{elastic} + \sigma_{inelastic} = \frac{2\pi}{k^2}\sum(2l+1)(1-\Re S_l)$$

So optical theorem is still true

$$\sigma_{tot} = \frac{4\pi}{k}\mathrm{Im}f_{elastic}(0)$$

7.5 Born Approximation

Solve

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

with $k = \sqrt{2mE}/\hbar$, or write in convenient form

$$(\nabla^2 + k^2)\psi(\vec{r}) = Q(\vec{r}) \tag{7.20}$$

where $Q(\vec{r}) = \frac{2m}{\hbar^2}V(\vec{r})\psi(\vec{r})$. Suppose there is some function $G(\vec{r})$ solves

$$(\nabla^2 + k^2)\psi(\vec{r}) = \delta^3(\vec{r})$$

Then the solution to (7.20) is

$$\psi(\vec{r}) = \int d\vec{r}_0 G(\vec{r} - \vec{r}_0)Q(\vec{r}_0) \tag{7.21}$$

Indeed

$$\begin{aligned}(\nabla^2 + k^2)\psi(\vec{r}) &= \int d\vec{r}_0(\nabla^2 + k^2)G(\vec{r} - \vec{r}_0)Q(\vec{r}_0) \\ &= \int d\vec{r}_0\delta(\vec{r} - \vec{r}_0)Q(\vec{r}_0) = Q(\vec{r})\end{aligned}$$

Or write (8.3) in terms of ψ itself

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int d\vec{r}_0 G(\vec{r} - \vec{r}_0)\frac{2m}{\hbar^2}V(\vec{r}_0)\psi(\vec{r}_0) \tag{7.22}$$

with $\psi_0(\vec{r})$ satisfies

$$(\nabla^2 + k^2)\psi_0(\vec{r}) = 0$$

For scattering problem we take $\psi_0 = Ae^{ikz}$.

(7.22) is useless as far as computation is concerned. Let $g(\vec{r}) = \frac{2m}{\hbar^2}G(\vec{r})$, apply (7.22) twice we get

$$\begin{aligned}\psi(\vec{r}) &= \psi_0(\vec{r}) + \int d\vec{r}_0 g(\vec{r}-\vec{r}_0)V(\vec{r}_0)[\psi_0(\vec{r}) + \int d\vec{r}_1 g(\vec{r}_0-\vec{r}_1)V(\vec{r}_1)\psi(\vec{r}_1)] \\ &= \psi_0(\vec{r}) + \int d\vec{r}_0 g(\vec{r}-\vec{r}_0)V(\vec{r}_0)\psi_0(\vec{r}) + \int d\vec{r}_0 d\vec{r}_1 g(\vec{r}-\vec{r}_0)V(\vec{r}_0)g(\vec{r}_0-\vec{r}_1)V(\vec{r}_1)\psi(\vec{r}_1)\end{aligned}$$

apply (7.22) again into above

$$\begin{aligned}\psi(\vec{r}) &= \psi_0(\vec{r}) + \int d\vec{r}_0 g(\vec{r}-\vec{r}_0)V(\vec{r}_0)\psi_0(\vec{r}) + \int d\vec{r}_0 d\vec{r}_1 g(\vec{r}-\vec{r}_0)V(\vec{r}_0)g(\vec{r}_0-\vec{r}_1)V(\vec{r}_1)\psi_0(\vec{r}_1) \\ &\quad + \int d\vec{r}_0 d\vec{r}_1 d\vec{r}_2 g(\vec{r}-\vec{r}_0)V(\vec{r}_0)g(\vec{r}_0-\vec{r}_1)V(\vec{r}_1)g(\vec{r}_1-\vec{r}_2)V(\vec{r}_2)\psi(\vec{r}_2)\end{aligned} \quad (7.23)(7.24)$$

We can ignore the 3rd order term. We get 0th order, unscattered wave. 0th + 1st orders is 1st Born approximation, wave scatters once in V. 0th + 1st + 2nd orders is 2nd order Born, wave scattered twice in V.

So to compute Born we need to know function g or G, the Greens function for $(\nabla^2 + k^2)$

Fourier G

$$G(\vec{r}) = \frac{1}{(2\pi)^{3/2}}\int d^3\vec{s}\, e^{i\vec{s}\cdot\vec{r}}\tilde{G}(\vec{s})$$

$$(\nabla^2+k^2)G(\vec{r}) = \frac{1}{(2\pi)^{3/2}}\int d^3\vec{s}(-s^2+k^2)e^{i\vec{s}\cdot\vec{r}}\tilde{G}(\vec{s}) = \delta = \frac{1}{(2\pi)^3}\int d^3\vec{s}\, e^{i\vec{s}\cdot\vec{r}}$$

so

$$(-s^2+k^2)\tilde{G}(\vec{s}) = \frac{1}{(2\pi)^{3/2}}$$

Then

$$G(\vec{r}) = \frac{1}{(2\pi)^3}\int d^3\vec{s}\, e^{i\vec{s}\cdot\vec{r}}\frac{1}{k^2-s^2}$$

choose $\vec{s}_z$ along $\vec{r}$

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$$
\begin{aligned}
G(\vec{r}) &= \frac{1}{(2\pi)^3}\int_0^\infty ds s^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi \frac{e^{irs\cos\theta}}{k^2-s^2} \\
&= \frac{2\pi}{(2\pi)^3}\int_0^\infty ds s^2 \int_{-1}^1 d(\cos\theta) \frac{e^{irs\cos\theta}}{k^2-s^2} \\
&= \frac{1}{(2\pi)^2}\int_0^\infty ds s^2 \frac{1}{k^2-s^2}\frac{e^{irs}-e^{-irs}}{irs} \\
&= \frac{1}{(2\pi)^2}\frac{1}{r}\int_0^\infty ds \frac{s}{k^2-s^2}\sin rs \\
&\vdots \\
&= -\frac{e^{ikr}}{4\pi r}
\end{aligned}
$$

after complex contour integral, one gets one answer. It depends on poles and choice of counters.

Since we didn't solve the integral, let's check the answer.

$$
\begin{aligned}
\nabla^2 G &= -\nabla^2 \frac{e^{ikr}}{4\pi r} \\
&= -\frac{1}{4\pi r}\nabla^2 e^{ikr} - 2\nabla e^{ikr}\cdot\nabla\frac{1}{4\pi r} - e^{ikr}\nabla^2\frac{1}{4\pi r} \qquad (7.24)
\end{aligned}
$$

Since $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + ...$, 1st term on the right

$$
-\frac{1}{4\pi r}\nabla^2 e^{ikr} = -\frac{1}{4\pi r}(-k^2 + \frac{2ik}{r})e^{ikr}
$$

Second term

$$
-2\nabla e^{ikr}\cdot\nabla\frac{1}{4\pi r} = -2(ike^{ikr}\hat{r})\cdot(-\frac{1}{4\pi r^2}\hat{r}) = \frac{2ik}{4\pi r^2}e^{ikr}
$$

So the last term had better give δ. Indeed

$$
\nabla^2\frac{1}{r} = \nabla\cdot(\nabla\frac{1}{r}) = \nabla\cdot(-\frac{\hat{r}}{r^2}) \qquad (7.25)
$$

by Gauss

$$
\iiint d^3\vec{r}\nabla\cdot(-\frac{\hat{r}}{r^2}) = \iint d\vec{s}\cdot(-\frac{\hat{r}}{r^2}) = 4\pi\int dr r^2(-\frac{1}{r^2}) = -4\pi
$$

[It is incorrect to do (7.25) as

$$\nabla^2 \frac{1}{r} = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \right) \frac{1}{r} = \frac{2}{r^3} - \frac{2}{r^3} = 0$$

ignoring the singularity at $r = 0$.]

so

$$\nabla \cdot (-\frac{\hat{r}}{r^2}) = -4\pi\delta^3(\vec{r})$$

Hence the last term in (7.24),

$$-e^{ikr}\nabla^2 \frac{1}{4\pi r} = e^{ikr}\delta^3(\vec{r})$$

so

$$(\nabla^2 + k^2)G = e^{ikr}\delta^3(\vec{r}) = \delta^3(\vec{r})$$

We can see that in the checking above, if we put $k \to -k$, it will work too, so

$$G(\vec{r}) = -\frac{e^{-ikr}}{4\pi r}$$

is another Green solution, but as we will see this means incoming prorogation.

1st Born Approximation

From (7.23),

$$\psi(\vec{r}) = Ae^{ikz} + A\frac{2m}{\hbar^2}\int d^3\vec{r}_0(-\frac{e^{ik|\vec{r}-\vec{r}_0|}}{4\pi|\vec{r}-\vec{r}_0|})V(\vec{r}_0)e^{ik(\hat{z}\cdot\vec{r}_0)}$$

The integral is zero unless $\vec{r}_0$ is inside V, because V is short range. So suppose we're interested in $r \gg r_0$

$$\begin{aligned} |\vec{r}-\vec{r}_0| &= (r^2 + r_0^2 - 2\vec{r}\cdot\vec{r}_0)^{1/2} \\ &= r(1 - \frac{2\vec{r}\cdot\vec{r}_0}{r^2} + \frac{\vec{r}_0}{r^2})^{1/2} \\ &= r(1 - \frac{\vec{r}\cdot\vec{r}_0}{r^2} + ...) \\ &\approx r - \hat{r}\cdot\vec{r}_0 \end{aligned}$$

So

$$\psi(\vec{r}) = Ae^{ikz} - A\frac{m}{2\pi\hbar^2}\int d^3\vec{r}_0 \frac{e^{ikr}e^{-ik\hat{r}\cdot\vec{r}_0}}{r - \hat{r}\cdot\vec{r}_0}V(\vec{r}_0)e^{ik(\hat{z}\cdot\vec{r}_0)}$$

neglect $\hat{r}\cdot\vec{r}_0$ in the denominator

$$\psi(\vec{r}) = Ae^{ikz} - A\frac{m}{2\pi\hbar^2}\frac{e^{ikr}}{r}\int d^3\vec{r}_0 e^{-ik\hat{r}\cdot\vec{r}_0}V(\vec{r}_0)e^{ik(\hat{z}\cdot\vec{r}_0)}$$

Now it is clear that if we had used $G = -\frac{e^{-ikr}}{4\pi r}$, the factor in front of the integral would be e^{-ikr}/r, no good.

Let $\vec{k}' = k\hat{z}$, incoming wave vector, and $\vec{k} = k\hat{r}$, outgoing wave vector, and let $\vec{k} - \vec{k}' = \vec{q}$, then

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int d^3\vec{r}_0 e^{-i\vec{k}\cdot\vec{r}_0}V(\vec{r}_0)e^{i\vec{k}'\cdot\vec{r}_0}$$

drop $_0$ because no $\vec{r}$ presented, no confusion between $\vec{r}$ and $\vec{r}_0$,

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int d^3\vec{r} e^{-i\vec{q}\cdot\vec{r}}V(\vec{r}) \tag{7.26}$$

Assume V is spherical symmetric. This is more than just independent of ϕ as we assumed in partial wave analysis. But (7.26) doesn't assume independent of ϕ, but it does assume V is short range (so we can do $r \gg r_0$) and weak, so higher order terms in (7.23) can be neglected.

$$\begin{aligned} f(\theta) &= -\frac{m}{2\pi\hbar^2}\int_0^\infty dr r^2 \int_{-1}^1 d(\cos\theta)\int_0^{2\pi} d\phi e^{-iqr\cos\theta}V(r) \\ &= -\frac{2m}{\hbar^2 q}\int_0^\infty dr r\sin(qr)V(r) \end{aligned}$$

Since $\vec{k} - \vec{k}' = \vec{q}$ and $|\vec{k}| = |\vec{k}|$, we can write $|\vec{q}|$ as

$$\begin{aligned} q^2 &= k^2 + k'^2 - 2\vec{k}\cdot\vec{k}' \\ &= 2k^2(1 - \cos\theta) \\ &= (2k\sin\frac{\theta}{2})^2 \end{aligned}$$

so

$$q = 2k \sin \frac{\theta}{2}$$

where θ is the scattering angle.

Example. Soft Sphere

$$V = \begin{cases} V_0 & r < a \\ 0 & r > a \end{cases}$$

is spherical symmetric, so

$$\begin{aligned} f(\theta) &= -\frac{2m}{\hbar^2 q} V_0 \int_0^a dr r \sin(qr) \\ &= -\frac{2m}{\hbar^2 q} V_0 \frac{1}{q^2} \left(\sin(qa) - qa\cos(qa)\right) \end{aligned}$$

Suppose low E, i.e. low k, so $qa \ll 1$, then use

$$\sin x - x\cos x = \left(x - \frac{x^3}{6} + ...\right) - x\left(1 - \frac{x^2}{2} + ...\right)$$

$$(\sin(qa) - qa\cos(qa)) = (qa)^3(-\frac{1}{6} + \frac{1}{2})$$

so

$$f(\theta) = -\frac{2m}{\hbar^2 q} V_0 \frac{1}{q^2} \frac{(qa)^3}{3} = -\frac{2mV_0}{\hbar^2} \frac{a^3}{3}$$

If let $V_0 \to \infty$, it doesn't look like $f(\theta)$ for hard sphere. That is because 1st Born approximation assumes weak potential. Or slightly more precisely we want

$$\int GV$$

to be small, so the 2nd order $(\int GV)^2$ is even smaller. In this problem 1st Born requires

$$\int GV \sim (V_0 \frac{1}{a} a^3) = (V_0 a^2)$$

small.

7.6 YuKawa Particle

cf Griffiths example 11.5,

$$V = \beta \frac{e^{-\mu r}}{r} \tag{7.27}$$

put $\mu = 0$, we get coulomb potential. From YuKawa potential, we get

$$f(\theta) = -\frac{2m}{\hbar}\beta \frac{1}{\mu^2 + q^2}$$

q is defined earlier. Or

$$\frac{d\sigma}{d\Omega} = |f|^2 = \left(\frac{2m\beta}{\hbar}\right)^2 \frac{1}{(\mu^2 + 4k^2 \sin^2 \frac{\theta}{2})^2} \tag{7.28}$$

take $\mu \to 0$, we have Rutherford scattering. Recall earlier we said that σ_{tot} diverges for coulomb potential, however YuKawa potential works fine.

(7.28) has been measured and fitted data.

In 1935, YuKawa revolutionarily proposed that scattering given by (7.28) was from potential (7.27), whose scattering interaction was related to an unknown particle with mass μ. That is because photon with mass 0 is the agent of coulomb interaction and coulomb potential is

$$V \sim \frac{1}{r}$$

YuKawa's idea was very radical. At the time people didn't generally invent new particles to fit theories. At the time people only knew

$$e^-,\ p,\ n$$

and Dirac just predicted e^+.

1936-7 Found muon (μ) mass 105MeV. Not quite right. YuKawa's μ should have mass $(130 - 140)$MeV and it should interact with nucleus, and has spin 0. But newly found μ doesn't interact with nucleus, and has spin 1/2.

Then WWII happened, people were busy killing each other.

1947 YuKawa became professor at our physics department. The same year Π

pion was found. It fits YuKawa's description, so it is the YuKawa's particle.

8 QM Interpretations

8.1 Hidden Variables

After years of study QM, one may think he understands QM, but really?

1935 Einstein and two others (P and R) coauthored "Can quantum mechanical description of physical reality be considered complete?"

EPR said no, i.e. there were hidden variables. The article was very clear to read.

Later Bohr wrote a paper of same title. He said Yes. In his paper however hardcore was mislogic and appeased to psychological reasoning.

1960s people realized there were real measurements could be done to testify "hidden" variables.

EPR's arguments used momentum and positions, but they can be simplified by using spins.

Consider 2 spin 1/2 particles A, B, in the state that has total spin $S = 0$ and $S_z = 0$.

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow\rangle_A |\downarrow\rangle_B - |\downarrow\rangle_A |\uparrow\rangle_B \right) \tag{8.1}$$

which is an entangled state, meaning no matter how far apart 2 pins are correlated.

This can be produced in a lab, take Π^0, spin 0, it will decay into e^- and e^+

$$\Pi^0 \to e^- + e^+$$

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Suppose many duplicate copies of such particles A_n, B_n (same n means a pair) of state (8.1) have been produced, and Alice and Bob processes A_n, and B_n separately. Alice and Bob are a few light years apart so there should be no instant causal relations between the two.

If Alice measure A_1 spin z direction and gets $\uparrow$, then later if Bob measure B_1 spin z direction should get $\downarrow$. If Alice measure A_1 spin z direction and gets $\downarrow$, then later if Bob measure B_1 spin z direction should get $\uparrow$. No problem.

Now Bob wants to measure x direction. Recall from last semester we learned (8.1) could be written in $S_x\pm$

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|S_x+\rangle_A\,|S_x-\rangle_B - |S_x-\rangle_A\,|S_x+\rangle_B\right)$$

So if now Alice measure A_2 spin z direction and gets $\uparrow$, then later if Bob measure B_2 spin x direction should get 50% S_x+ and 50% S_x-. If Alice measure A_2 spin z direction and gets $\downarrow$, then later if Bob measure B_2 spin x direction he should get 50% S_x+ and 50% S_x-. Still no problem.

Now suddenly Alice too starts measuring x direction. Alice measure A_3 spin x direction and gets S_x+, then later if Bob measure B_3 spin x direction should get 100% S_x-, not 50% S_x+ and 50% S_x- any more.

So according to EPR, Alice has influenced Bob's measurements instantly. Or in other words Bob now knows Alice has changed from measuring z direction to x direction, so valuable information has traveled with speed faster than light.

It seems to violate causality, but actually it doesn't. Bob measure B_3 spin x direction gets S_x-. What about B_4, B_5, ...? If from that on Alice keeps measuring spin in x direction, the results of Bob's measurement will still turn out to be half + half −, so in that sense, Bob has no way knowing Alice has switched to measure x direction or not.

Although EPR's argument has a little flawed, it didn't undermined the fact that EPR did not like quantum mechanics. Classically if we know position and velocity of every air molecule in the room, we should be able to calculate the motions and interactions of all molecules. Hence because we don't have complete knowledge of all the variables, we have to use some probabilistic way to describe things, as we learn in thermodynamics and quantum mechanics. In other words, EPR believe physical objects have their definite states before measurements are taken place, and the reason we cannot calculate them because there are variables we don't know. These hidden variables may or may never be accessible to us, but they are there.

Now we discuss Bell's inequality and Greenberger–Horne–Zeilinger state. Bell shows there is no hidden variable. GHZ shows non commuting state is not definite.

8.2 Bell's Inequality

Let λ be long list of variables, let $\rho(\lambda)$ be probability density of λ in Π^0 decay, so

$$\int \cdots \int d\lambda \rho(\lambda) = 1 \text{ and } \rho(\lambda) > 0$$

Let $A(\hat{a}, \lambda)$ be result for particle A measured spin in $\hat{a}$ direction, $\hat{a} = \hat{x}$, $\hat{y}$, or $\hat{z}$. So $A(\hat{a}, \lambda) = \pm 1$. (forget about factor $\hbar/2$). Similar define $B(\hat{a}, \lambda)$. So λ includes $\hat{a}$. In fact we can think λ includes everything, every piece of information of the whole universe, so the variable λ in A knows everything about B, vis visa. Therefore λ is the same in the arguments of both A and B.

More is true

$$B(\hat{a}, \lambda) = -A(\hat{a}, \lambda) \tag{8.2}$$

for any λ that specify that measurements on A, B are in direction $\hat{a}$.

Or

$$B(-\hat{a}, \lambda) = A(\hat{a}, \lambda)$$

for any λ that specify that measurement on A is in $\hat{a}$ and on B is in $-\hat{a}$.

Take product of results (AB). For any λ, if $\hat{a} = \hat{b}$, $(AB) = -1$; if $\hat{a} = -\hat{b}$, $(AB) = 1$.

Consider general average of product

$$P(\hat{a}, \hat{b}) = \int d\lambda \rho(\lambda) A(\hat{a}, \lambda) B(\hat{b}, \lambda)$$

so all information in λ except A is measured in $\hat{a}$ and B is measured in $\hat{b}$ will be integrated over, so none of them will show up.

Now use (8.2)

$$\begin{aligned} P(\hat{a}, \hat{b}) &= -\int d\lambda \rho(\lambda) A(\hat{a}, \lambda) A(\hat{b}, \lambda) \\ P(\hat{a}, \hat{c}) &= -\int d\lambda \rho(\lambda) A(\hat{a}, \lambda) A(\hat{c}, \lambda) \end{aligned}$$

$$P(\hat{a}, \hat{b}) - P(\hat{a}, \hat{c}) = -\int d\lambda \rho(\lambda) \Big[A(\hat{a}, \lambda) A(\hat{b}, \lambda) - A(\hat{a}, \lambda) A(\hat{b}, \lambda) A(\hat{b}, \lambda) A(\hat{c}, \lambda) \Big]$$

So

$$\begin{aligned}\left|P(\hat{a},\hat{b})-P(\hat{a},\hat{c})\right| &= \left|\int d\lambda\rho(\lambda)A(\hat{a},\lambda)A(\hat{b},\lambda)\left[1-A(\hat{b},\lambda)A(\hat{c},\lambda)\right]\right| \\ &\leq \int d\lambda\rho(\lambda)\left[1-A(\hat{b},\lambda)A(\hat{c},\lambda)\right]=1+P(\hat{a},\hat{c})\end{aligned}$$

because $A(\hat{a},\lambda)A(\hat{b},\lambda)$ is the only thing that may be $-$.

We obtain Bell's inequality for any $\hat{a}$,$\hat{b}$ and $\hat{c}$

$$\left|P(\hat{a},\hat{b})-P(\hat{a},\hat{c})\right|\leq 1+P(\hat{a},\hat{c})$$

If we take

$$\hat{a}=\hat{z}\qquad \hat{b}=\cos\theta\hat{z}+\sin\theta\hat{x}$$

what does QM tell us about $P(\hat{a},\hat{b})$? QM says $P(\hat{a},\hat{b})$ is the expectation value on state ψ (8.1), i.e.

$$\begin{aligned}P(\hat{a},\hat{b}) &= \left\langle\psi\right|(\vec{S}^{(A)}\cdot\vec{a})\otimes(\vec{S}^{(B)}\cdot\vec{b})\left|\psi\right\rangle \\ &= \left\langle\psi\right|\sigma_z^{(A)}\otimes(\cos\theta\sigma_z^{(B)}+\sin\theta\sigma_x^{(B)})\left|\psi\right\rangle\end{aligned}$$

forget factor $\hbar/2$. Use (6.3)

$$\sigma_z^{(A)}\otimes\sigma_z^{(B)}\left|\psi\right\rangle=\frac{1}{\sqrt{2}}\left[-\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}-(-1)\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}\right]=-\left|\psi\right\rangle$$

$$\sigma_z^{(A)}\otimes\sigma_x^{(B)}\left|\psi\right\rangle=\frac{1}{\sqrt{2}}\left[\begin{pmatrix}1\\0\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix}-(-1)\begin{pmatrix}0\\1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}\right]=\frac{1}{\sqrt{2}}\left(\left|\uparrow\uparrow\right\rangle+\left|\downarrow\downarrow\right\rangle\right)$$

which has total spin 1 and it is orthogonal to $\left|\psi\right\rangle$. Therefore QM says

$$P(\hat{a},\hat{b})=-\cos\theta$$

Pick $\hat{a}=\hat{z}$, $\hat{b}=\hat{x}$, $\hat{c}=\frac{1}{\sqrt{2}}(\hat{z}+\hat{x})$,

$$\left|P(\hat{a},\hat{b})-P(\hat{a},\hat{c})\right|=\left|0+\frac{1}{\sqrt{2}}\right|\approx .707 \tag{8.3}$$

$$1 - P(\hat{b}, \hat{c}) = 1 - \frac{1}{\sqrt{2}} \approx .303 \tag{8.4}$$

violating Bell's inequality. So either QM is correct, or hidden variables exist.

Experiment has done with photon and look for polarization, confirming that (8.3), (8.4) are correct, so no hidden variables.

8.3 Greenberger–Horne–Zeilinger

Suppose we have three particles state

$$|\psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow\uparrow\uparrow\rangle - |\downarrow\downarrow\downarrow\rangle)$$

Measure $S_x^{(1)} S_y^{(2)} S_z^{(3)}$

$$\sigma_x^{(1)}\sigma_y^{(2)}\sigma_y^{(3)} |\psi\rangle = \frac{1}{\sqrt{2}} [(i)(i)|\downarrow\downarrow\downarrow\rangle - (-i)(-i)|\uparrow\uparrow\uparrow\rangle] = |\psi\rangle$$

Similarly show

$$\sigma_y^{(1)}\sigma_x^{(2)}\sigma_y^{(3)} |\psi\rangle = |\psi\rangle \qquad \sigma_y^{(1)}\sigma_y^{(2)}\sigma_x^{(3)} |\psi\rangle = |\psi\rangle$$

EPR said particles had definite spins. So what can $|\psi\rangle$ have for x and y directions

One possibility: all three particles have definite spin S_x+, then we can simple fill the $\hat{y}$ row by all + as one possibility.

particles	1	2	3
$\hat{x}$	+	+	+
$\hat{y}$	+	+	+

Try one of three particles has definite spin S_x-, say $S_x^{(1)}-$, then we want to find some possible spins for $\hat{y}$ row. $yxy = 1 \implies y_1 = y_3$, $yyx = 1 \implies y_1 = y_2$, but $xyy = 1 \implies y_2 = -y_3$, not possible

particles	1	2	3
$\hat{x}$	-	+	+
$\hat{y}$			

Try two of three particles have definite spin S_x-, then we want to find some possible spins for $\hat{y}$ row. $yyx = 1 \implies y_1 = y_2$, $xyy = 1 \implies y_2 = -y_3$, $yxy = 1 \implies y_1 = -y_3$, so we find another possibly

particles	1	2	3
$\hat{x}$	-	-	+
$\hat{y}$	+	+	-

Try three particles have definite spin S_x-, don't work.

particles	1	2	3
$\hat{x}$	-	-	-
$\hat{y}$			

Therefore if particles of state $|\psi\rangle$ have both $\hat{x}$ and $\hat{y}$ definite spins then

$$S_x^{(1)} S_x^{(2)} S_x^{(3)} = 1$$

But QM says

$$\left\langle \psi \middle| S_x^{(1)} S_x^{(2)} S_x^{(3)} \middle| \psi \right\rangle = -1$$

8.4 Many Worlds interpretation

So particles have no definite state until we make measurement. Why is measurement so special? Why is it treated differently compare to the rest of theory?

Bohr said yes measurement was different, it collapsed the wave function.

$$|\text{experimentalist}\rangle \frac{|\uparrow\rangle + |\downarrow\rangle}{\sqrt{2}} \xrightarrow{\text{Bohr}} |\text{experimentalist}\rangle |\uparrow\rangle$$

But many worlds people say if the experimentalist obtains $|\uparrow\rangle$, there is another parallel copy of universe where the result is $|\downarrow\rangle$

$$|\text{experimentalist}\rangle \frac{|\uparrow\rangle + |\downarrow\rangle}{\sqrt{2}} \xrightarrow{\text{MW}} \frac{|\text{experimentalist } \uparrow\rangle + |\text{experimentalist } \downarrow\rangle}{\sqrt{2}}$$

Same thing for the cat. It lives here may be dead in some other universe or vice versa.