I. Time-dependent Perturbation Theory

II. Fermi's Golden Rule

Read Chapter 23 Sections 1, 2, 3

I. Time-dependent perturbation theory

Consider again the effect of $H = H_0 + H_1$

H_0: has known eigenfunctions $|\varphi_n\rangle$ and eigenvalues E_n

H_1: arbitrary

this is what we just did for H_1 small:

If $H_1 \neq f(t)$ we can study H with the time-independent Schrodinger equation, then just multiply by $e^{\frac{-iEt}{\hbar}}$ later.

(short-cut to solving the time-dependent Sch. Eq.; this E must include perturbative corrections $E^{(1)}$, $E^{(2)}$, etc.)

this is what we will do now:

But if $H_1 = H_1(t)$, this causes H to be H(t), so we must solve the time-dependent Schrodinger equation from the beginning.

Assume:

(i) the eigenfunctions $|\varphi_n\rangle$ and eigenvalues E_n of H_0 are known:

$H_0|\varphi_n\rangle = E_n^{(0)}|\varphi_n\rangle$ and

$|\varphi_n\rangle = e^{\frac{-iE_n^{(0)}t}{\hbar}}|\hat{\varphi}_n\rangle \qquad \left(\langle\hat{\varphi}_m|\hat{\varphi}_n\rangle = \delta_{mn}\right)$

(ii) the eigenfunctions $|\varphi_n\rangle$ of H are not yet known, but they solve $H|\Psi_n\rangle = i\hbar\frac{\partial}{\partial t}|\Psi_n\rangle$

(iii) The $|\varphi_n\rangle$ can form a basis in which $|\Psi_n\rangle$ can be expanded:

$|\Psi_n(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle \qquad c_n(t) = \langle\varphi_n|\Psi_n\rangle$

Goal: find $c_n(t)$

To solve $c_n(t)$, plug $|\Psi_n(t)\rangle$ directly into the time-dependent Schrodinger equation

$$\mathrm{H}\sum_n c_n(t)\left|\varphi_n\right\rangle = i\hbar\frac{\partial}{\partial t}\left[\sum_n c_n(t)\left|\varphi_n\right\rangle\right]$$

$$\left(H_0+H_1\right)\sum_n c_n(t)\left|\varphi_n\right\rangle = i\hbar\sum_n\left\{c_n(t)\frac{\partial}{\partial t}\left|\varphi_n\right\rangle+\frac{\partial}{\partial t}\left(c_n(t)\right)\left|\varphi_n\right\rangle\right\}$$

$$= i\hbar\sum_n\left\{c_n(t)\left(\frac{-iE_n^{(0)}}{\hbar}\right)\left|\varphi_n\right\rangle+\left(\frac{\partial}{\partial t}c_n(t)\right)\left|\varphi_n\right\rangle\right\}$$

Rewrite:

$$\sum_n c_n(t)\left(H_0-E_n^{(0)}\right)\left|\varphi_n\right\rangle+\sum_n\left(c_n(t)H_1-i\hbar\frac{\partial}{\partial t}c_n(t)\right)\left|\varphi_n\right\rangle=0$$

$= 0$ because $\mathrm{H}_0\left|\varphi_n\right\rangle = E_n^{(0)}\left|\varphi_n\right\rangle$

multiply by $\left\langle\varphi_k\right|$

$$\sum_n\left[c_n(t)\left\langle\varphi_k\right|H_1\left|\varphi_n\right\rangle-i\hbar\frac{\partial}{\partial t}c_n(t)\left\langle\varphi_k\middle|\varphi_n\right\rangle\right]=0$$

Plug in:

$$\left|\varphi_n\right\rangle = e^{\frac{-iE_n^{(0)}t}{\hbar}}\left|\hat{\varphi}_n\right\rangle$$

$$\left|\varphi_k\right\rangle = e^{\frac{-iE_k^{(0)}t}{\hbar}}\left|\hat{\varphi}_k\right\rangle$$

$$\left\langle\varphi_k\right| = e^{\frac{+iE_k^{(0)}t}{\hbar}}\left\langle\hat{\varphi}_k\right|$$

$$\sum_n c_n(t)\left\langle\hat{\varphi}_k\right|H_1\left|\hat{\varphi}_n\right\rangle e^{\frac{-i\left(E_k^{(0)}-E_n^{(0)}\right)t}{\hbar}}-i\hbar\sum_n\frac{\partial}{\partial t}c_n(t)\left\langle\hat{\varphi}_k\middle|\hat{\varphi}_n\right\rangle e^{\frac{-i\left(E_k^{(0)}-E_n^{(0)}\right)t}{\hbar}}=0$$

call this "$\mathrm{H}_{1_{kn}}$"

call $\frac{\left(E_k^{(0)}-E_n^{(0)}\right)}{\hbar}$ "ω_{kn}"

I. Time-dependent Perturbation Theory (continued)

II. Fermi's Golden Rule

III. The Variational Method

Read Chapter 23 Section 1, except Traut from com to lab

$$\sum_n c_n H_{1_{kn}} e^{i\omega_{kn}t} - i\hbar \tfrac{\partial}{\partial t} c_k = 0$$

This is an exact equation that relates each coefficients (the c_k 'th) to all the other coefficients (the $\sum_n c_n$)

It is impossible to solve analytically for arbitrary H_1

If H_1 is "small", assume:

(1) The $c_n(t)$ are almost constants, not really functions of t

(2) @ t=0, the state of the system is known, so

one coefficient (call is $c_j(t=0)) = 1$

all the rest =0

(3) Then since the c_n are constants, c_j remains ≈ 1

even at later t, and the other $c_{n\neq j}$ remain ≈ 0

So in this approximation the equation becomes

$$H_{1_{kj}} e^{i\omega_{kj}t} - i\hbar \tfrac{\partial}{\partial t} c_k \approx 0$$

Solve it:

$$c_k = \delta_{kj} \frac{-i}{\hbar} \int_0^t dt' e^{\frac{i\left(E_k^{(0)} - E_j^{(0)}\right)t}{\hbar}} \left\langle \hat{\varphi}_k \middle| H_1 \middle| \hat{\varphi}_j \right\rangle$$

So if the system began with $c_j = 1$, $c_{n\neq j} = 0$ @ t=0, the probability that the system is in state

k @ t=t′ is $\left|c_k(t')\right|^2$

Example solution of c_k

$$\text{if } H_1(t) = \left\{ \begin{array}{cc} 0 & t<0 \\ \text{consant} & \text{if } t \geq 0 \end{array} \right\}$$

then

$$c_k = \delta_{kj} - \frac{i}{\hbar}\mathcal{H}_{1_{kj}} \int_0^t dt' e^{i\omega_{kj}t'}$$

$$= \delta_{kj} - \frac{i}{\hbar}\mathcal{H}_{1_{kj}} \left(\frac{1}{i\omega_{kj}}\right) e^{i\omega_{kj}t'}\Big|_0^t$$

$$= \delta_{kj} - \frac{i}{\hbar}\frac{\mathcal{H}_{1_{kj}}}{i\omega_{kj}}\left(e^{i\omega_{kj}t} - 1\right)$$

$$\boxed{c_k = \delta_{kj} + \frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\left(1 - e^{i\omega_{kj}t}\right)}$$

Note k indexes the coefficient being examined ($c_k = \langle \varphi_k | \Psi \rangle$) while j indexed the one coefficient (c_j) which has non-zero @ t=0

II. Fermi's Golden Rule

Recall c_k when $k \neq j$ [where initially c_j was the only non-zero amplitude] for $H_1(t) = \begin{array}{ll} \mathcal{H} & (t>0) \\ 0 & (t<0) \end{array}$

$$c_{k\neq j} = \frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\left(1 - e^{-i\omega_{kj}t}\right)$$

Probability (observing state k @ time t) = $\left|c_k\right|^2$

$$=\left|\frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\right|^2\left(1-e^{-i\omega_{kj}t}\right)\left(1-e^{+i\omega_{kj}t}\right)$$

$$=\left|\frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\right|^2\left(1-e^{+i\omega_{kj}t}-e^{-i\omega_{kj}t}+1\right)$$

$$=\left|\frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\right|^2\left\{2-2\left(\frac{e^{+i\omega_{kj}t}+e^{-i\omega_{kj}t}}{2}\right)\right\}$$

$$=\left|\frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\right|^2 2\left\{1-\left(\cos\omega\mathrm{t}\right)\right\}$$

$$=\left|\frac{\mathcal{H}_{1_{kj}}}{\hbar\omega_{kj}}\right|^2 4\left\{\tfrac{1}{2}-\tfrac{1}{2}\left(\cos\omega\mathrm{t}\right)\right\}$$

↓

use $\cos 2x=\cos^2 x-\sin^2 x=(1-\sin^2 x)-\sin^2 x=1-2\sin^2 x$

so $\tfrac{1}{2}\cos 2x=\tfrac{1}{2}-\sin^2 x$

so $\tfrac{1}{2}-\tfrac{1}{2}\cos 2x=\sin^2 x$

Probability of transition from $\left\langle\varphi_j\right|\rightarrow\left\langle\varphi_k\right|=\left|\frac{2\mathcal{H}_{1_{kj}}}{E_k^{(0)}-E_j^{(0)}}\right|^2\sin^2\left(\frac{\omega_{kj}t}{2}\right)$

Now we want to know

Probability (system that begins in state $\left\langle\varphi_j\right|$ makes a transistion to *any* other states, given infinite time)

Probability (system that begins in state $\langle \varphi_j |$ makes a transistion to *any* other states, given infinite time)

$$=\sum_k \text{Probability } (\mathrm{j} \rightarrow \mathrm{k})$$

$$=\sum_k \left| \frac{2\mathcal{H}_{1_{kj}}}{E_k^{(0)} - E_j^{(0)}} \right|^2 \sin^2\left(\frac{\omega_{kj} t}{2}\right)$$

If states $\langle \varphi_k |$ are continuously distributed (i.e. scattering states) rather than discretely distributed (i.e. bound states), then $\sum \rightarrow \int dn$

$$= \int dn_k \left| \frac{2\mathcal{H}_{1_{kj}}}{E_k^{(0)} - E_j^{(0)}} \right|^2 \sin^2\left(\frac{\omega_{kj} t}{2}\right)$$

If there is a degeneracy @ $\mathrm{E}=\mathrm{E}_k^0$, so there is a density of states there,

$\rho\left(\mathrm{E}_k^0\right) = \dfrac{dn}{d\mathrm{E}_k^0}$, then $\mathrm{dn} = \rho \cdot \mathrm{dE}$

$$= \int d\mathrm{E}_k^0 \rho\left(\mathrm{E}_k^0\right) \left| \frac{2\mathcal{H}_{1_{kj}}}{E_k^{(0)} - E_j^{(0)}} \right|^2 \sin^2\left(\frac{\left(E_k^{(0)} - E_j^{(0)}\right)t}{2\hbar}\right)$$

$$\text{Let } x \equiv \left(\frac{\left(E_k^{(0)} - E_j^{(0)}\right)t}{2\hbar}\right)$$

$$\left|E_k^{(0)} - E_j^{(0)}\right|^2 = \frac{4\hbar^2 x^2}{t^2} \qquad \text{and} \qquad \mathrm{dx} = \mathrm{d}E_k^{(0)} \cdot \frac{t}{2\hbar}$$

$$\text{Prob}_{tot} = \int \frac{2\hbar}{t} dx \rho(x) 4 \left|\mathcal{H}_1\right|^2 \frac{t^2}{4\hbar^2 x^2} \sin^2 x$$

consider the case where $\rho(x) = \bar{\rho}$, average density over all final states, a constant and $\left|\mathcal{H}_1\right|^2 = \bar{H}_1^2$, average value of $\langle \varphi_k | H | \varphi_j \rangle$ over all $\langle \varphi_k |$, also a constant

Then

$$\text{Prob}_{tot} = \frac{2t}{\hbar} \bar{H}_1^2 \bar{\rho} \int_{-\infty}^{+\infty} dx \frac{\sin^2 x}{x^2}$$

π

Probability(system transitions out of $\langle \varphi_j |$ due to H_1) = $\frac{2\pi t}{\hbar} \bar{H}_1^2 \bar{\rho}$

So $\boxed{\text{transition } rate = \frac{d\text{Prob}}{dt} = \frac{2\pi}{\hbar} \bar{H}_1^2 \bar{\rho}}$ this is Fermi's Golden Rule

we worked this out for $H_1 = \begin{matrix} const & \text{if } t > 0 \\ 0 & \text{if } t < 0 \end{matrix}$

but it is true for any H_1

I. The Variational Method

II. Intro to Scattering Theory

III. Probability current of scattered particles

I. The Variational Method

This is what you use if you want to find the ground state energyof a system but have a Hamiltonian $\mathrm{H}\left(\neq f(t)\right)$ which cannot be written as $\mathrm{H}_0 + \lambda H_1$

i.e., this is what to use if H either

(1) does not have any term that looks like a familiar solved H_0, or

(2) has an H_1 but it is not "small" with respect to H_0

Procedure:

(i) Given H

(ii) pick any normalized Ψ=Ψ(a,b,c,...) where (a,b,c,...) are some variables

(iii) calculate $\langle\Psi|H|\Psi\rangle$

(iv) minimize $\langle\Psi|H|\Psi\rangle$ with respect to its variables, for example

require $\frac{\partial}{\partial b}\langle\Psi|H|\Psi\rangle = 0,$ solve for b, plug b back into $\langle\Psi|H|\Psi\rangle$

(v) the minimized $\langle\Psi|H|\Psi\rangle$ you get is guaranteed to be $\geq$ the real E_g. so it is an upper limit on E_g.

Prove this:

Let Ψ= trial wavefunction

Let $|\varphi_n\rangle =$ the set of true but unknown eigenfunctions of H

$\left(H|\varphi_n\rangle = E_n|\varphi_n\rangle\right)$

Because the $|\varphi_n\rangle$ are the eigenfunctions of something, they can be a basis in which to expand Ψ:

$$|\Psi\rangle = \sum_n |\varphi_n\rangle \underbrace{\langle\varphi_n|\Psi\rangle}_{c_n} = \sum_n c_n|\varphi_n\rangle$$

Find $\langle H\rangle = \langle\Psi|H|\Psi\rangle$

$$= \left\langle \sum_m c_m|\varphi_m\rangle \middle| H\sum_n c_n|\varphi_n\rangle\right\rangle$$

$$= \sum_m\sum_n c_m^* c_n \langle\varphi_m|H\varphi_n\rangle$$

$$\mathrm{E}_n|\varphi_n\rangle$$

$$= \sum_m\sum_n c_m^* c_n \mathrm{E}_n \underbrace{\langle\varphi_m|\varphi_n\rangle}_{\delta_{mn}}$$

$$\langle H\rangle = \sum_n |c_n|^2 E_n$$

But $E_n \geq \mathrm{E}_{ground}$ since n could be any level

So $\langle H\rangle \geq \sum_n |c_n|^2 E_g$

$$\langle H\rangle \geq E_g \sum_n |c_n|^2$$

what is $\sum_n |c_n|^2$?

$|\Psi\rangle$ is normalized:

$$1=\langle\Psi|\Psi\rangle=\left\langle\sum_m c_m\varphi_m\middle|\sum_n c_n\varphi_n\right\rangle$$

$$=\sum_{m,n}c_m^*c_n\langle\varphi_m|\varphi_n\rangle$$

$$\delta_{mn}$$

$$1=\sum_n|c_n|^2$$

So $\langle H\rangle\geq E_g$ regardless of what Ψ was chosen

To make $\langle H\rangle$ approach E_g, minimize it

Example use of the Variational Method:

Suppose $H=\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}m\omega^2x^2$ (this is the Simple Harmonic Oscillator (SHO), suppose you did not know how to solve this exactly)

Guess $\Psi=Ae^{-bx^2}$ (b is a variable we can use later in the minimization)

Normalize Ψ:

$$1=|A|^2\int_{-\infty}^{+\infty}e^{-2bx^2}\,dx=|A|^2\sqrt{\tfrac{\pi}{2b}}$$

So $A=\left[\frac{2b}{\pi}\right]^{\frac{1}{4}}$

Calculate $\left\langle H\right\rangle = \left\langle \Psi \middle| H \middle| \Psi \right\rangle$

$$\left[\frac{2b}{\pi}\right]^{\frac{1}{2}} \int_{-\infty}^{+\infty} dx e^{-bx^2} \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right] e^{-bx^2}$$

$$\left\langle H\right\rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

Minimize:

$$0 = \frac{\partial}{\partial b}\left\langle H\right\rangle = \frac{\hbar^2}{2m} - \frac{8m\omega^2}{64b^2} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2}$$

So $8b^2 = \dfrac{2m^2\omega^2}{\hbar^2}$

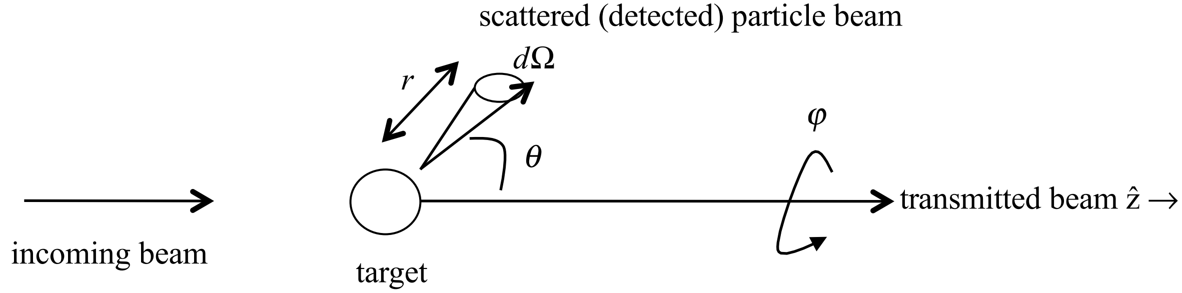
$$b = \frac{m\omega}{2\hbar}$$

Plug this back into $\left\langle H\right\rangle$:

$$\left\langle H\right\rangle_{\min imized} = \frac{\hbar^2 m\omega}{2m2\hbar} + \frac{m\omega^2 2\hbar}{8m\omega} = \frac{\hbar\omega}{4} + \frac{\omega\hbar}{4} = \frac{\hbar\omega}{2}$$ which is the exact E_{ground} for this H

I. Intro to Scattering Theory

This picture illustrates the parameters and jargon of scattering

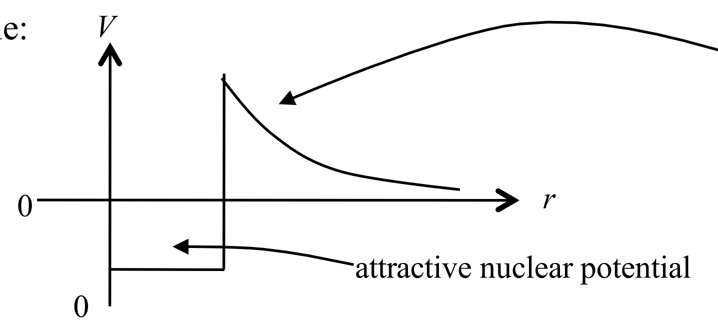


Why do we care about scattering?

Convention: attractive potentials are drawn as negative

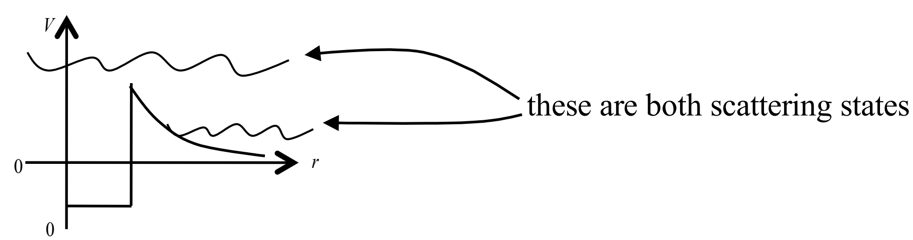
repulsive potentials are drawn as positive

Example:



apparent "centrifugal barrier" potential this is the $\frac{\hbar^2 \ell(\ell+1)}{2mr^2}$ term in the Radial Equation

Any time a particle state is an eigenfunction of the H(including the potential) but the state has E > 0, it is a scattering state



Facts about Scattering States:

(i) So scattering states are no less relevant than bound states $\rightarrow$ both kinds give information about the shape of the potential
(ii) Recall that the eigenfunctions of a hamiltonian form a basis--so we do not have a basis if we take the bound (E<0) states alone.
(iii) whereas bound states are quantized, scattering states are continuously distributed in energy

Goal: describe $\Psi_{\text{scattered particle}}$
Assumptions:
1) Before scattering, particle is free, travelling in $\hat{z}$

plane wave

Call it $\varphi_k(\vec{r}) = e^{ikz}$

its momentum is $p=\hbar k$

Goswami uses "φ" for incoming, "Ψ" for outgoing
ignore normalization for now

2) Assume $V \neq V(t)$
3) If the $V=V\left(\left|r\right|\right)$ only, then the outgoing particles are spherically symmetrically distributed, so far from the center of V, the outgoing scattered waves reunite a plane wave again; they will have no dependence on "r" other than $\Psi_{scattered} \sim \dfrac{e^{ikr}}{r}$
This is a "spherical wave", like a plane wave but weighted by r to maintain probability conservation as the diameter of the wavefront increases with r.

I. Probability Current in Scattering

II. Different Cross-sections

III. The Born Approximation

4) The scattering may actually send more particles into a particular direction in θ and φ.

So allow $\Psi_{scatter} = f(\theta,\varphi)\cdot\frac{e^{ikr}}{r}$

$f(\theta,\varphi)$ is the scattering amplitude

5) The total wave detected after the scattering is

$$\Psi_{tot} = \begin{pmatrix} \text{the part of the incident wave that} \\ \text{transmitted without being modified} \end{pmatrix} + \begin{pmatrix} \text{the scattered} \\ \text{wave} \end{pmatrix}$$

$$\Psi_{TOT}^{outgoing} = e^{ikz} + f(\theta,\varphi)\cdot\frac{e^{ikr}}{r}$$

II. Probability Currents in Scattering

Recall that the Ψ is related to the particle's probability of location but the only way to get a sense of the motion of the particles themselves is to calculate the probability current.

Recall $\vec{J}_{prob} = \frac{\hbar}{2mi}\left(\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*\right)$

So $\vec{J}_{prob}^{incident} = \frac{\hbar}{2mi}\left(\varphi^*\vec{\nabla}\varphi - \varphi\vec{\nabla}\varphi^*\right)$

$$\begin{aligned} \varphi &= e^{ikz} \\ \nabla\varphi &= ike^{ikz}\hat{z} \\ \varphi^* &= e^{-ikz} \\ \nabla\varphi^* &= -ike^{-ikz}\hat{z} \end{aligned}$$

$$= \frac{\hbar}{2mi}\left(e^{-ikz}ike^{ikz} - e^{ikz}(-ik)e^{-ikz}\right)\hat{z}$$

$$= \frac{\hbar}{2mi}\left(2ik\right)\hat{z} = \frac{\hbar k}{m}\hat{z} = \frac{\vec{p}}{m}$$ as expected

$$\vec{J}^{scattering}_{prob} = \frac{\hbar}{2mi}\left(\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*\right)$$

$$\Psi = e^{ikz} + f(\theta,\varphi)\cdot\frac{e^{ikr}}{r}$$

so $\nabla\Psi$ will have r, θ, and φ terms. Examine each separately.

In spherical coordinates $\nabla\Psi = \hat{r}\frac{\partial\Psi}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial\Psi}{\partial\theta} + \hat{\varphi}\frac{1}{r\sin\theta}\frac{\partial\Psi}{\partial\varphi}$

To get θ dependence of J, let $\nabla\Psi \to \frac{1}{r}\frac{\partial}{\partial\theta}$ only

$$\Psi^{scat} = f(\theta,\varphi)\cdot\frac{e^{ikr}}{r}$$

$$\Psi^{scat*} = f^*(\theta,\varphi)\cdot\frac{e^{-ikr}}{r}$$

$$So\ J_\theta \equiv \hat{\theta}\cdot\vec{J}^{scattering}_{prob} = \frac{\hbar}{2mi}\left[\frac{f^*e^{-ikr}}{r}\frac{1}{r}\frac{\partial f}{\partial\theta}\frac{e^{+ikr}}{r} - \frac{fe^{+ikr}}{r}\frac{1}{r}\frac{\partial f^*}{\partial\theta}\frac{e^{-ikr}}{r}\right]$$

$$= \frac{\hbar}{2mi}\frac{1}{r^3}\left[f^*\frac{\partial f}{\partial\theta} - f\frac{\partial f^*}{\partial\theta}\right] \sim \frac{1}{r^3}$$

So the total σ_θ at any particular radius "r" is

$\hat{\theta}\cdot\vec{J}r^2 d\Omega \sim \frac{1}{r^3}r^2 d\Omega \sim \frac{d\Omega}{r}$ so as $r\to\infty$, $J_\theta \to 0$

Similarly, $J_\varphi \sim \frac{1}{r^3}$, so as $r\to\infty$, $J_\varphi \to 0$

To get the r-dependence of J, let $\nabla\Psi \to \frac{\partial}{\partial r}$ only

$$\frac{\partial}{\partial r}\left(\frac{fe^{ikr}}{r}\right) = f\left[\frac{rike^{ikr} - e^{ikr}}{r^2}\right] = \frac{fe^{ikr}}{r^2}(ikr-1)$$

So $J_r \equiv \hat{r}\cdot\vec{J}^{scat}_{prob} = \frac{\hbar}{2mi}\left[\left(\frac{f^* e^{-ikr}}{r}\right)\left(\frac{fe^{+ikr}}{r^2}\right)(+ikr-1) - \left(\frac{fe^{+ikr}}{r}\right)\left(\frac{f^* e^{-ikr}}{r^2}\right)(-ikr-1)\right]$

$= \frac{\hbar}{2mi}\frac{|f|^2}{r^3}\left[+ikr-1+ikr+1\right]$

$= \frac{\hbar}{2mi}\frac{|f|^2}{r^3}\left[2ikr\right]$

$= \frac{\hbar k}{m}\frac{|f|^2}{r^2}$

So the total # particles at any particular radius r is

$$\vec{J}^{scat}\cdot\overrightarrow{dArea} = \hat{r}\cdot\vec{J}r^2 d\Omega = \frac{\hbar k|f|^2}{m}\frac{r^2}{r^2}d\Omega = \underbrace{\frac{\hbar k|f|^2}{m}}_{\text{independent of r}} d\Omega = p|f|^2\, d\Omega$$

So as $r \to \infty$, the outward current is all in the $\hat{r}$ direction

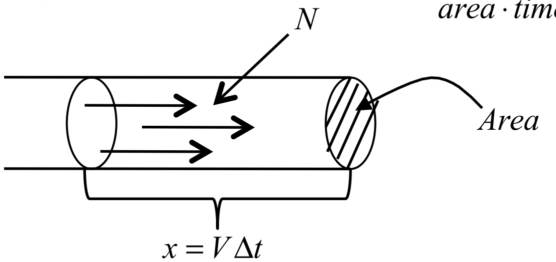
III Different cross section

Amount of scattering per θ and per φ is indicated by the "different cross section" of the process

(Amount of scattering per θ and per φ = amount of scattered particles that are directed by the target into a specific θ and φ; "different cross section" = symbol $\frac{d\sigma}{d\Omega}$)

To define $\frac{d\sigma}{d\Omega}$, assume

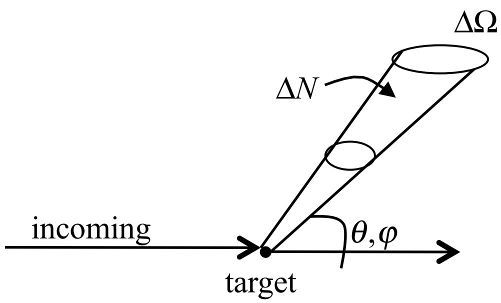
(i) incident beam is a current of $\frac{\text{N particles}}{area \cdot time}$



$\text{N=J}^{inc}_{prob} \cdot \hat{z}$

(ii) target scatters ΔN particles into solid angle ΔΩ per unit time

centered on angle (θ,φ)



$\Delta\text{N=J}^{scat} \cdot \overrightarrow{dArea}$

Notice N and ΔN have different units

$\frac{d\sigma}{d\Omega}$ is defined by

$$\frac{d\sigma}{d\Omega} = \lim_{\Delta\Omega \to 0} \frac{1}{N} \frac{\Delta N}{\Delta\Omega}$$

this has units of $\frac{area}{steradian}$

Plug in $\text{N=J}^{inc} \cdot \hat{z} = \frac{\hbar k}{m}$

and $\Delta\text{N=J}^{scat} \cdot \overrightarrow{dArea} = \frac{\hbar k}{m}\left|f\right|^2 d\Omega$

Then $\dfrac{d\sigma}{d\Omega} = \dfrac{1}{\frac{\hbar k}{m}} \dfrac{\frac{\hbar k}{m}\left|f\right|^2 d\Omega}{d\Omega} = \left|f\left(\theta,\varphi\right)\right|^2$

A typical area that enters in a scattering process is 10^{-24} cm^2 $\equiv$ "1 barn"

$\sqrt{\dfrac{d\sigma}{d\Omega}}$

III. The Born Approximation

For a potntial of arbitrary strength and range, we must calculate $f\left(\theta,\varphi\right)$ using a procedure called *Paritcle Wave Analysis* (we will do this next time)

But if we know that the potential is weak and has a short range, we can approximate the results by using time-dependent perturbation theory:

Simplfying assumptions:

(i) Effect of the short range:

Assume that the potential turns on when the particle is within its range, and then turns off. So V ≅ V(t) and we can use the time-dependent pertubation theory

(ii) Effect of the weakness:

Assume that before and after scattering (i.e. when the potential is "turned off") the particle has E >> V. This means that the strength of scattering is small, so the final state is still a plane wave (not a sperical wave), with only its momentum altered

So assume $\Psi_i = \dfrac{1}{\sqrt{V}} e^{i\vec{k}_i \vec{r}}$ and

$$\Psi_f = \frac{1}{\sqrt{V}} e^{i\vec{k}_f \vec{r}}$$

(iii) Recall time dependent perturbation theory leads (for some situations) to Fermi's Golden Rule:

Transition rate between 2 states $\equiv$ $W = \dfrac{\text{dProb}}{dt} = \dfrac{2\pi}{\hbar}\overline{H^2_{1_{i\to f}}}\,\bar{\rho}$

$\bar{\rho}$ = average density of final states

$\overline{H^2_{1_{i\to f}}} = \langle final | H_1 | initial \rangle$

usually the two states are different bound levels of a potential

Here, treat Ψ_i and Ψ_f as the 2 levels

(iv) Relate W to $\dfrac{d\sigma}{d\Omega}$ to set information about $f(\theta,\varphi)$, the nature of the potential itself

$\leftarrow |f(\theta,\varphi)|^2$

Recall $\dfrac{\text{\# of incident particles}}{\text{unit area}\cdot\text{unit time}} = N^{inc} = \vec{J}^{inc}\cdot\hat{z} = |J_{inc}|$

$$\frac{\text{\# of incident particles scattered into } (\theta,\varphi)}{\text{unit area}\cdot\text{unit time}} = N^{inc}\cdot\frac{d\sigma}{d\Omega} = J_{inc}\cdot\frac{d\sigma}{d\Omega}$$

Definition of W: transition rate from $\Psi_i \to \Psi_f$ (where Ψ_f could go into and θ,φ)

I. Born Approximation (continued)

II. Partial Wave Analysis

So the transition rate per unit solid angle$=\dfrac{W}{4\pi}$

This is equivalent to $\dfrac{\text{\# incident particles scattered into } (\theta,\varphi)}{\text{unit area} \cdot \text{ unit time}}$

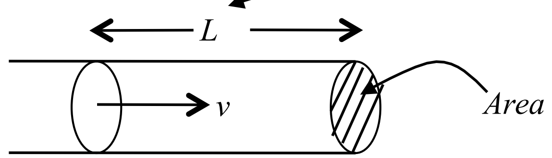
So $J_{inc} \cdot \dfrac{d\sigma}{d\Omega} = \dfrac{W}{4\pi}$

$$\frac{d\sigma}{d\Omega} = \frac{1}{J_{inc}} \cdot \frac{W}{4\pi}$$

Plug in:

incident beam:

length a particle travelling with velocity v traverses in a unit time



$$J_{inc} = \frac{number}{area \cdot time} \cdot \frac{L}{L} = \frac{number \cdot length}{volume \cdot time}$$

velocity of incoming particle

$v=\dfrac{p}{m} = \dfrac{\hbar k}{m}$

Ψ_{inc} is normalized so that

$\dfrac{number}{volume} = \dfrac{1}{V}$

So $J_{inc} = \dfrac{\hbar k}{mV}$

Now we need $W=\dfrac{2\pi}{\hbar}\overline{\left|H_{1_{i\to f}}\right|^2}\bar{\rho}$

To calculate density of states ρ

Need total # of states in the 6-dimensional phase space volume:

$\Delta x, \Delta y, \Delta z, \Delta p_x, \Delta p_y, \Delta p_z$

To do coordinate space part, consider plane waves in a box ("infinite 3D well") of size:

LxLxL=V

$$\Psi = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$

Boundary conditions demand:

$$k_x = \frac{2\pi n_x}{L} \qquad (n_x = ..., -2, -1, 0, 1, 2, ...)$$

$$k_y = \frac{2\pi n_y}{L}$$

$$k_z = \frac{2\pi n_z}{L}$$

# of states $d^3 n$ in box is

$$d^3 n = dn_x dn_y dn_z = \left(\frac{Ldk_x}{2\pi}\right)\left(\frac{Ldk_y}{2\pi}\right)\left(\frac{Ldk_z}{2\pi}\right)$$

$$= \frac{L^3}{(2\pi)^3} dk_x dk_y dk_z$$

↓

use $p=\hbar k$

so $dp=\hbar dk$, then $dk=\frac{dp}{\hbar}$

also $L^3 = V$

$$= \frac{V}{(2\pi)^3} \frac{dp_x}{\hbar} \frac{dp_y}{\hbar} \frac{dp_z}{\hbar}$$

$$= \frac{V}{(2\pi\hbar)^3} V_{phase\ \mathrm{space}}$$

convert to spherical coordinates

$$V_{phase\ \mathrm{space}} = p^2 dp \sin\theta_p d\theta_p d\varphi_p$$

$$= p^2 dp d\Omega_p$$

integrate over $d\Omega_p \rightarrow 4\pi$

$$= p^2 dp 4\pi$$

↓

Then $d^3 n = \frac{V}{(2\pi\hbar)^3} 4\pi p^2 dp$

So $\rho = \frac{d^3 n}{dE} = \frac{V}{(2\pi\hbar)^3} 4\pi p^2 \frac{dp}{dE}$

density of states: $\rho(\mathrm{E})=\frac{d^3n}{dE}=\frac{V\cdot 4\pi}{(2\pi\hbar)^3}p_f^2\frac{dp_f}{dE} \rightarrow \frac{mVk}{2\pi^2\hbar^2}$

using non-relativistic $\mathrm{E}_f=\frac{p_f^2}{2m}$, then $\mathrm{p}_f=\hbar k_f$

$$\overline{H_{1_{i\to f}}}=\overline{\langle final|H_1|initial\rangle}=\overline{\langle final|V|initial\rangle}$$

$$=\int_0^{Volume} d^3rH_1(\vec{r})e^{i(\vec{k}_i-\vec{k}_f)\cdot\vec{r}}$$

Define $\vec{\mathrm{q}}\equiv\vec{k}_i-\vec{k}_f$ called the "momentum transfer"

Then

$$\mathrm{H}_{1_f}=\frac{1}{V}\int_0^V d^3rH_1(\vec{r})e^{i\vec{q}\cdot\vec{r}}$$

$$=\frac{2\pi}{V}\int_{r=0}^{\infty}r^2\,drH_1(\vec{r})\int_{\theta=0}^{\pi}e^{iqr\cos\theta}\sin\theta\,d\theta$$ where $\int_0^{2\pi}d\varphi=2\pi$

$$=\underbrace{\frac{4\pi}{qV}\int_{r=0}^{\infty}H_1(\vec{r})\sin qr\cdot r^2dr}_{\text{"H}_1\text{(q)"}}$$ the standard form for the Born Approximation

So $W=\frac{2\pi}{\hbar}\overline{\left|H_1\right|^2}\bar{\rho}$

$$=\frac{2\pi}{\hbar}\left(\frac{4\pi}{qV}\right)^2\overline{\left|H_1(q)\right|^2}\,\frac{mV\ k_f}{2\pi^2\hbar^2}$$

Then

$$\frac{d\sigma}{d\Omega}=\frac{1}{J_{inc}}\frac{W}{4\pi}$$

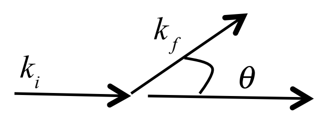
$$=\frac{mV}{\hbar k_i}\frac{1}{4\pi}\frac{16\pi m}{\hbar^3 q^2 V}\overline{\left|H_1(q)\right|^2}k_f$$

$$\left|f(\theta,\varphi)\right|^2=\frac{d\sigma}{d\Omega}=\frac{4m^2}{\hbar^4 q^2}\overline{\left|H_1(q)\right|^2}\,\frac{k_f}{k_i}$$

If the scatter is elastic, $k_f=k_i$, so $\frac{k_f}{k_i}=1$

However $q^2=\left|\vec{k}_f-\vec{k}_i\right|^2\neq 0$

$$q=\left|\vec{k}_f-\vec{k}_i\right|=\sqrt{\left(\vec{k}_f-\vec{k}\right)\cdot\left(\vec{k}_f-\vec{k}\right)}=\sqrt{k_f^2+k_i^2-2k_ik_f\cos\theta}$$



if elastic $k_f=k_i\equiv k$

$$=\sqrt{2k^2\frac{(1-\cos\theta)}{\sqrt{2}}}\cdot\sqrt{2}$$

$$=2k\sqrt{\frac{(1-\cos\theta)}{2}}=2k\sqrt{\sin^2\left(\frac{\theta}{2}\right)}=2k\sin\left(\frac{\theta}{2}\right)$$

$$f(\theta,\varphi)=\sqrt{\left|f(\theta,\varphi)\right|^2}=\sqrt{\frac{d\sigma}{d\Omega}}=-\frac{2m}{\hbar^2 q}\left|H_1(q)\right|\xrightarrow{\text{if elastic}}\boxed{\frac{-m\left|H_1(q)\right|}{\hbar^2 k\sin\left(\frac{\theta}{2}\right)}}$$

this $f(\theta,\varphi)$ is valid in the Born Approximation

II. Partial Wave Analysis

Goal: For a potential V, find the scattering state, then extract $f(\theta,\varphi)$

Must solve Schrodinger Equation:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi_{scatter} = E\Psi_{scatter}$$

Consider 3D V, so $\Psi=\Psi\left(r,\theta,\varphi\right)$. Try to solve Schrodinger Equation by separation of variables, so guess

$$\Psi_{scatter} = \boldsymbol{z}(r)\cdot g(\theta,\varphi)$$

Plug in, recall

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial\varphi^2}}_{\frac{-L^2}{\hbar^2 r^2}}$$

So we get $\left[\frac{-\hbar^2}{2mr^2}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hbar^2 L^2}{2m\hbar^2 r^2} + (V-E)\right]\boldsymbol{z}(r)\cdot g(\theta,\varphi) = 0$

$$\frac{-\hbar^2}{2mr^2}g(\theta,\varphi)\frac{\partial}{\partial r}\left(\frac{r^2\partial\boldsymbol{z}(r)}{\partial r}\right) + \frac{\boldsymbol{z}(r)L^2}{2mr^2}g(\theta,\varphi) + (V-E)\boldsymbol{z}(r)\cdot g(\theta,\varphi) = 0$$

Multiply by $\frac{-2mr^2}{\hbar^2\boldsymbol{z}(r)\cdot g(\theta,\varphi)}$:

$$\frac{1}{\mathfrak{z}(r)}\frac{\partial}{\partial r}\left(\frac{r^2\partial\mathfrak{z}(r)}{\partial r}\right)-\frac{L^2g(\theta,\varphi)}{\hbar^2g(\theta,\varphi)}-\frac{2mr^2}{\hbar^2}(V-E)=0$$

$$\frac{1}{\mathfrak{z}(r)}\frac{\partial}{\partial r}\left(\frac{r^2\partial\mathfrak{z}(r)}{\partial r}\right)-\frac{2mr^2}{\hbar^2}(V-E)=\frac{L^2g(\theta,\varphi)}{\hbar^2g(\theta,\varphi)}$$

f(r) only   f(θ,φ) only

So both sides = same constant, call it $\ell(\ell+1)$

Then RHS becomes:

$$\frac{L^2g(\theta,\varphi)}{\hbar^2g(\theta,\varphi)}=\ell(\ell+1)$$

$$L^2g(\theta,\varphi)=\hbar^2\ell(\ell+1)g(\theta,\varphi)$$

This is solved if $g(\theta,\varphi)=Y_{\ell m}(\theta,\varphi)$, the usual spherical harmonics

LHS becomes:

$$\frac{1}{\mathfrak{z}(r)}\frac{\partial}{\partial r}\left(\frac{r^2\partial\mathfrak{z}(r)}{\partial r}\right)-\frac{2mr^2}{\hbar^2}(V-E)=\ell(\ell+1)$$

When we studied the hydrogen atom, then V=$V_{Coulomb}=\frac{-Ze^2}{r}$, and $\mathfrak{z}(r)$ was only solved by

$R_{n\ell}$ (Laguere Polynomials)

Now for general V, $\mathfrak{z}(r)$ is not limited to be $R_{n\ell}(r)$

I. Partial Wave Analysis (continued)

II. How to find the phase shifts

Especially since "n" indexes bound state level, $\mathcal{R}(r) \neq \mathcal{R}_n(r)$ for scattering.

Since there is and "ℓ" in the equation just call $\mathcal{R}(r) = \mathcal{R}_\ell(r)$ for now.

So

$$\Psi_{scat} = \Psi_{\substack{scat\\ \ell m}}(r,\theta,\varphi) = \mathcal{R}_\ell(r)\cdot Y_{\ell m}(\theta,\varphi)$$

The most general Ψ_{scat} will include all possible ℓ, m values, so

$$\Psi_{scat} = \sum_\ell \sum_m \mathcal{R}_\ell(r)\cdot Y_{\ell m}(\theta,\varphi)$$

Study the radial equation for the $\mathcal{R}$'s:

$$\frac{1}{\mathcal{R}(r)}\frac{\partial}{\partial r}\left(\frac{r^2\partial\mathcal{R}(r)}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(V-E) = \ell(\ell+1)$$

$$\downarrow$$

Define $k^2(r) \equiv \frac{2m}{\hbar^2}\big(E - V(r)\big)$

$$\frac{1}{\mathcal{R}(r)}\left(r^2\frac{d^2}{dr^2} + 2r\frac{d}{dr}\right)\mathcal{R}(r) - r^2k^2 = \ell(\ell+1)$$

$$\downarrow$$

Multiply by $\frac{\mathcal{R}(r)}{r^2}$

$$\left(\frac{d^2}{dr^2} + 2r\frac{d}{dr}\right)\mathcal{R}(r) - k^2\mathcal{R}(r) - \frac{\ell(\ell+1)}{r^2}\mathcal{R}(r) = 0$$

Given V(r) get k, solve for $\mathcal{R}(r)$,

How to do this in practice:

(1) consider region where $r \to \infty$

I. Partial Wave Analysis (continued)

Read Chapter 19

If $V \sim \frac{1}{r^n}$ $(n \geq 2)$, then

$$k^2 - \frac{\ell(\ell+1)}{r^2} \sim \frac{2mE}{\hbar^2} - \frac{2m}{\hbar^2 r^n} - \frac{\ell(\ell+1)}{r^2} \xrightarrow[r\to\infty]{} \underbrace{\frac{2mE}{\hbar^2}}$$

← call this $(k')^2$, not a function of r

$\left(\text{So note this approximation does NOT work for } V_{Coulomb} \sim \frac{1}{r^1}\right)$

So as $r \to \infty$, the radial equation

$$\left[\frac{d^2}{dr^2} + 2r\frac{d}{dr} - k'^2 - \frac{\ell(\ell+1)}{r^2}\right] \mathcal{R}(r) = 0$$

Define $\rho \equiv k'r$ *this only works if k'=com

then $\frac{d}{dr} = k'\frac{d}{d\rho}$ etc.

$$\downarrow$$

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + 1 - \frac{\ell(\ell+1)}{\rho^2}\right] \mathcal{R}(\rho) = 0$$

This is the Bessel Equation so the solutions are:

$$\mathcal{R}(\rho) = Aj_\ell(\rho) + Bn_\ell(\rho)$$

n_ℓ are irregular at r=0, so set B=0

$$\text{Then } \mathcal{R}(\rho) \sim j_\ell(\rho) \xrightarrow[r\to\infty]{} \frac{1}{\rho}\sin\left(\rho - \ell\frac{\pi}{2}\right)$$

Plug in $\rho \equiv k'r$ and

$$\sin x = \frac{e^{ix} - e^{-ix}}{2i} = \frac{-1}{2i}\left(e^{-ix} - e^{ix}\right)$$

$$\mathcal{R}(r) \xrightarrow[r\to\infty]{} \sim \frac{1}{2ik'r}\left(\underbrace{e^{-i\left(k'r-\ell\frac{\pi}{2}\right)}}_{\text{incoming spherical wave}} - \underbrace{e^{i\left(k'r-\ell\frac{\pi}{2}\right)}}_{\text{outgoing spherical wave}} \right)$$

outgoing spherical wave
so it was reasonable to predict that

$$\Psi_{TOT} = e^{ikz} + \frac{f(\theta,\varphi)e^{ikr}}{r}$$

we will find that $f(\theta,\varphi)$ is given by the "ℓ" 's

incoming spherical wave

So we have $\Psi(\mathrm{r},\theta,\varphi)$ for $\mathrm{r} \to \infty$ ($\mathrm{V} \to 0$)

(ii) Use $\Psi\left(\mathrm{r} \to \infty\right)$ as a model for $\Psi\left(\mathrm{r} < \infty\right)$

It turns out that the only effect of adding a V is to make

$$\mathcal{R}(r < \infty,\ \text{with V} \neq 0) \sim \frac{1}{2ikr}\left(\underbrace{e^{-i\left(kr-\ell\frac{\pi}{2}\right)}}_{\text{incoming wave unchanged}} - \underbrace{S_\ell(k)}e^{i\left(kr-\ell\frac{\pi}{2}\right)} \right)$$

incoming wave
unchanged

$S_\ell(k)$ must satisfy $\left|S_\ell\right|^2 = 1$

This guarantees that probability is conserved when we take $\Psi^*\Psi = \mathcal{R}^*\mathcal{R}Y^*Y$

(i.e., the potential does not allow any particles to be created or destroyed, it just changes their direction of travel)

$$\left|S_\ell(k)\right|^2 = 1$$

$S_\ell(k) = e^{i\left(something_\ell(k)\right)}$ By convention "something" is called $2\delta_\ell(k)$

$$z(r<\infty)\sim\frac{-1}{2ikr}\left(1\cdot e^{-i\left(kr-\ell\frac{\pi}{2}\right)}-e^{i2\delta_\ell(k)}e^{i\left(kr-\ell\frac{\pi}{2}\right)}\right)$$

$$=\frac{-1}{2ikr}\left(e^{i\delta_\ell}e^{-i\delta_\ell}e^{-i\left(kr-\ell\frac{\pi}{2}\right)}-e^{i2\delta_\ell(k)}e^{i\left(kr-\ell\frac{\pi}{2}\right)}\right)$$

$$=\frac{-e^{i\delta_\ell}}{kr}\left(\frac{e^{-i\left(kr-\ell\frac{\pi}{2}+\delta_\ell\right)}-e^{i\left(kr-\ell\frac{\pi}{2}+\delta_\ell\right)}}{2i}\right)$$

$$=\frac{e^{i\delta_\ell}}{kr}\sin\left(kr-\ell\frac{\pi}{2}+\delta_\ell\right)$$

This looks like $z(r\to\infty)$ except: (1) multiplied by $e^{i\delta_\ell}$ (which disappears when we calculate $\Psi^*\Psi$) and (2) the wave is phase-shifted

Interim conclusions:

(1) The principal effect upon a wave of scattering from a potential is to be phase-shifted

(2) Recall $\Psi_{scat}^{general}=\sum_{\ell,m}z_\ell(r)Y_{\ell,m}(\theta,\varphi)$

each scattered wave is a superposition of waves representing different angular momentum ℓ states.

Each ℓ state gets a different phase shift δ_ℓ

(3) all of this is appropriate only for V ~ $\frac{1}{r^n}$, n ≥ 2, so not for the Coulomb potential

The way to handle the Coulomb potential is to write it as

$$V \sim \frac{e^{-ar}}{r} \quad \left(\text{which falls off faster than } \frac{1}{r}\right),$$

do the whole calculation, then at the end let a $\rightarrow$ 0.

(iv) Goal is find the $\delta_\ell 's$

I. How to find the phase shifts δ_ℓ

First Question:

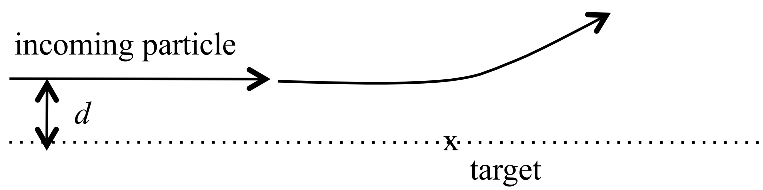
It looks like Ψ^{scat} requires an infinite # of δ_ℓ's

$\left(\Psi^{scat} = \sum_{\ell=0}^{\infty} z_\ell Y_{\ell,m} \right)$. Do we really need them all?

sin(......+δ_ℓ)

Answer: No.

Suppose that the incident particle is not aiming directly at the target. Define the impact parameter "d" as the perpendicular distance by which it is offset



So relative to the target, the incident particle has angular momentum $|L| = |r \text{ x p}| = d \cdot p$

Suppose the range of the potential is r_0. Then scattering is negligible if $d > r_0$

But $d = \frac{L}{p}$

But $L = \sqrt{\ell(\ell+1)}\hbar \approx \ell\hbar$

$d \cong \frac{\ell\hbar}{p}$

But $p = \hbar k$

I. Finding the $\delta_\ell 's$ for a scattering problem: Example

II. The relationship between δ_ℓ and f(θ,φ)

III. Totoal cross section

IV. The Optical Theorem

Read Chapter 19

↓

So scattering is negligible for

$d > r_0$

↓

$\frac{\ell}{k} > r_0$

↓

$\ell > r_0 k$

So $d \simeq \frac{\ell\hbar}{\hbar k} = \frac{\ell}{k}$

So if we estimate the potential's range r_0 and know the incident particle's $k=\frac{p}{\hbar}$, we need only sum $\sum_{\ell=0}^{\sim r_0 k}$

Often this includes only $\ell = 0$

Second Question: How to find the δ_ℓ's that do contribute?

Procedure:

(i) Specify the potential and the energy (~k) of the incident particle

(ii) Determine $\ell_{\max} \geq r_0 k$

(iii) Solve the Radial Equation for time independent Schrodinger Equation inside the potential: get $\mathscr{r}_{inside}$

(iv) Solve the Radial Equation for time independent Schrodinger Equation outside the potential:

(i.e. where the potential is free) get $\mathscr{r}_{outside} = \mathscr{r}(\delta_\ell)$

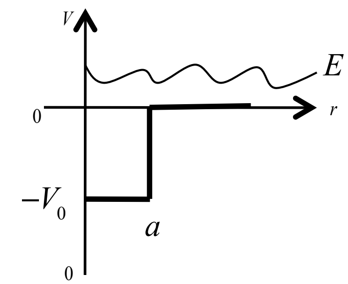
I. Example to find phase shifts δ_ℓ

II. The relationship between δ_ℓ and f(θ,φ)

Read Chapter 19, Section 1 only

(v) Match $\mathcal{R}_{inside}$ and $\mathcal{R}_{outside}$ and thier derivatives at boundary and solve for δ_ℓ

Example: s-wave scattering from a square well potential at low energy



(i) Given $V(r)=\begin{cases} -V & \text{for } r < a \\ 0 & \text{for } r \geq a \end{cases}$

incident particle has low energy that

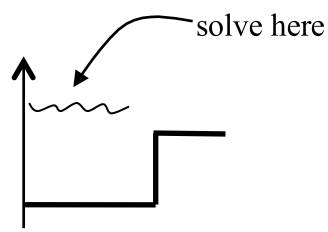
$\frac{2m(E)}{\hbar^2} = k \ll \frac{1}{a}$, so $ka \ll 1$

(ii) Recall we only consider angular momentum ℓ states with $\ell <$ (range)$\cdot$(k), so

$1 \ll a \cdot k$ means consider only ℓ=0

(iii) Solve Radial Equation inside well but not below top of well

i.e. for $r < a$ but for $E > 0$



$$\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{2m}{\hbar^2}\left(E - V(r) - \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right)\right]\mathcal{R}_{inside} = 0$$

let $u_{inside} \equiv r\mathcal{R}_{inside}$ and ℓ=0

$\downarrow$

$$\frac{d^2}{dr^2}u_{inside} + \frac{2m}{\hbar^2}\left(E - V(r)\right)u_{inside} = 0$$

Define $k_{in} \equiv \sqrt{\frac{2m}{\hbar^2}\left(E - V\right)} = \sqrt{\frac{2m\left(E + V_0\right)}{\hbar^2}}$

$\downarrow$

$$\frac{d^2u_{in}}{dr^2}+k_{in}^2u_{in}=0$$

$$u_{in}=A\sin k_{in}r+B\cos k_{in}r$$

When r=0, $u_{in}=r\mathcal{R}_{in}=B$

$=0\cdot\mathcal{R}_{in}=B$

this means $\mathcal{R}_{in}\to\infty$ unless B=0

So set B=0

$$u_{in}=A\sin k_{in}r \qquad r<a$$

(iv) Solve Radial Equation outside well but for E > 0:

$$\frac{d^2u_{out}}{dr^2}+\frac{2m}{\hbar^2}\left[E-\underbrace{V(r)}_{=0\text{ outside}}\right]u_{outside}=0$$

Let $k_{out}=\sqrt{\frac{2mE}{\hbar^2}}$

$$\frac{d^2u_{out}}{dr^2}+k_{out}u_{out}=0$$

$$u_{out}=C\sin k_{out}r+D\cos k_{out}r$$

$$=F\sin\left(k_{out}r+\delta_{\ell=0}\right)$$

(v) Match solutions at r = a:

$u_{in}(a) = u_{out}(a)$

$$A \sin k_{in} a = F \sin\left(k_{out} a + \delta_0\right)$$ "Equation 1"

(vi) Match derivatives:

$$k_{in} A \cos k_{in} a = k_{out} F \cos\left(k_{out} a + \delta_0\right)$$ "Equation 2"

(vii) To solve for δ_0, divide $\frac{Eq1}{Eq2}$:

$$\frac{1}{k_{in}} \tan\left(k_{in} a\right) = \frac{1}{k_{out}} \tan\left(k_{out} a + \delta_0\right)$$ "Equation 3"

Remember this

use $\tan\left(x + y\right) = \frac{\tan x + \tan y}{1 - \tan x \tan y}$

↓

$$\frac{1}{k_{in}} \tan\left(k_{in} a\right) = \frac{1}{k_{out}} \left[\frac{\tan\left(k_{out} a\right) \tan \delta_0}{1 - \tan\left(k_{out} a\right) \tan \delta_0} \right]$$

$$\tan \delta_0 = \frac{\left(\frac{k_{out}}{k_{in}}\right) \tan\left(k_{in} a\right) - \tan\left(k_{out} a\right)}{1 + \left(\frac{k_{out}}{k_{in}}\right) \tan\left(k_{out} a\right) \tan\left(k_{in} a\right)}$$

Define some K such that

$$\tan\left(\mathrm{Ka}\right) \equiv \left(\frac{k_{out}}{k_{in}}\right) \tan\left(k_{in} a\right)$$

↓

$$\tan\delta_0 = \frac{\tan(Ka) - \tan(k_{out}a)}{1+\tan(Ka)\tan(k_{out}a)}$$

use trig identity

$$\tan(x\text{-}y) = \frac{\tan x - \tan y}{1+\tan x \tan y}$$

$$\tan\delta_0 = \tan(Ka - k_{out}a)$$

equate the arguments

So

$$\delta_0 = Ka - k_{out}a$$

$$\boxed{\delta_0 = \tan^{-1}\left(\frac{k_{out}}{k_{in}}\tan(k_{in}a)\right) - k_{out}a}$$

for a square well

II. The relationship between δ_ℓ and $f(\theta,\varphi)$

Recall from physics reasoning we expect after scattering

$$\Psi^{tot} = e^{ikz} + \frac{f(\theta,\varphi)e^{ikr}}{r}$$ The δ_ℓ's are related to the $f(\theta,\varphi)$

So

$$\frac{f(\theta,\varphi)e^{ikr}}{r} = \Psi^{tot}_{scat} - e^{ikz}$$

$$\Psi^{tot}_{scat} = \sum_{\ell,m} \mathcal{R}_\ell(r) Y_{\ell,m}$$

But $Y_{\ell,m} = \left[\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}\right]^{1/2} (-1)^m e^{im\varphi} P^m_\ell$ $\left(P^m_\ell \text{ are Legendre Polynomials}\right)$

If the incident wave is a plane wave travelling in $\hat{z}$, it can have no angular momentum vector pointed in $\hat{z}$ (i.e. it is not rotating toward $\hat{\phi}$) No angular momentum in $\hat{z}$ $\Rightarrow$ quantum number m=0 for the initial state. Since angular momentum is conserved, the final states must also have m=0.

So set $Y_{\ell,m} = Y_{\ell,0} = \left[\frac{2\ell+1}{4\pi}\right]^{1/2} P_\ell$

and set $\mathrm{r}_\ell(r) = \dfrac{e^{i\delta_\ell}}{kr}\sin\left(kr - \dfrac{\ell\pi}{2} + \delta_\ell\right)$

Multiply $\mathscr{R}\cdot \mathrm{Y}_{\ell m}$ by an unspecified coeficient C_ℓ to smooth the transition from $\mathscr{R}(r \to \infty)$ to $\mathscr{R}(r < \infty)$

$$\text{the } \Psi_{scat} = \sum_\ell \mathrm{C}_\ell P_\ell(\theta)\frac{\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)}{kr}$$

We want to write $\mathrm{e}^{ikz} = f(P_\ell, etc.)$ too.

$\mathrm{e}^{ikz} = \mathrm{e}^{ikr\cos\theta}$

expand this in the basis set of hydrogenic eigenfunctions

$$\mathrm{e}^{ikr\cos\theta} = \sum_\ell a_\ell j_\ell Y_{\ell,m} \to \sum_\ell a_\ell j_\ell P_\ell$$

since m=0, we can replace $Y_{\ell,m} \to P_\ell$

multiply both sides by P_ℓ , integrate over θ

$$\underbrace{\int_0^\pi \mathrm{e}^{ikr\cos\theta} P_{\ell'}(\theta)\sin\theta\, d\theta}_{2\mathrm{i}^{\ell'} j_{\ell'}(kr)} = \sum_{\ell=0}^{\infty} a_\ell j_\ell(kr) \underbrace{\int P_\ell P_\ell' \sin\theta\, d\theta}_{\left(\frac{2}{2\ell+1}\delta_{\ell\ell'}\right)}$$

So we have

$$2\mathrm{i}^{\ell'} j_{\ell'} = \sum_{\ell=0}^{\infty} a_\ell j_\ell \left(\frac{2}{2\ell+1}\right)\delta_{\ell\ell'}$$

$$2\mathrm{i}^{\ell'} j_{\ell'} = a_{\ell'} j_{\ell'} \left(\frac{2}{2\ell'+1}\right)$$

So $a_\ell = i^\ell\left(2\ell+1\right)$

We are studying everything at relatively large distance from the scatter, so use asymptotic form of j, so relplace

$$j_\ell \rightarrow \frac{\sin\left(kr - \frac{\ell\pi}{2}\right)}{kr}$$

So $\mathrm{e}^{ikz} = \sum_\ell a_\ell j_\ell P_\ell = \sum_\ell i^\ell\left(2\ell+1\right) j_\ell P_\ell$

Then $\frac{f(\theta,\varphi)e^{ikr}}{r} = \sum_\ell C_\ell P_\ell \frac{\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)}{kr} - \sum_\ell i^\ell\left(2\ell+1\right) P_\ell \frac{\sin\left(kr - \frac{\ell\pi}{2} + \delta_\ell\right)}{kr}$

This is solved if $C_\ell = i^\ell\left(2\ell+1\right)e^{i\delta_\ell}$ and

$$f(\theta,\varphi) = \frac{1}{k}\sum_\ell \left(2\ell+1\right)e^{i\delta_\ell}\sin\delta_\ell P_\ell$$

The $\frac{d\sigma}{d\Omega} = \left|f(\theta,\varphi)\right|^2 = \frac{1}{k^2}\left|\sum_\ell \left(2\ell+1\right)e^{i\delta_\ell}\sin\delta_\ell P_\ell\right|^2$

II. Total cross section

The total cross section "σ" is the integral of $\frac{d\sigma}{d\Omega}$ over all solid angles, so it gives an indicator of the total strength of scattering: σ indicates how much flux is removed from the incident beam

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int d\Omega \frac{1}{k^2} \left| \sum_{\ell} (2\ell+1) e^{i\delta_\ell} \sin\delta_\ell P_\ell(\theta) \right|^2$$

$$\left[\sum_{\ell} (2\ell+1) e^{i\delta_\ell} \sin\delta_\ell P_\ell(\theta) \right]^* \left[\sum_{\ell'} (2\ell'+1) e^{i\delta_{\ell'}} \sin\delta_{\ell'} P_{\ell'}(\theta) \right]$$

$$\left(e^{i\delta_\ell}\right)^* = e^{-i\delta_\ell}$$

$$\sigma = \sum_{\ell} \sum_{\ell'} \left(\frac{2\ell+1}{k} \right) \left(\frac{2\ell'+1}{k} \right) e^{i(\delta_\ell - \delta_{\ell'})} \sin\delta_\ell \sin\delta_{\ell'} \underbrace{\int d\Omega P_\ell(\theta) P_{\ell'}(\theta)}_{\frac{4\pi}{2\ell+1}\delta_{\ell,\ell'}}$$

$$\boxed{\sigma = \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2 \delta_\ell}$$

I. The Optical Theorem

II. Resonances

III. Intro to the real Hydrogen Atom

IV. Relativistic KE

V. Spin-Orbit Coupling

III. The Optical Theorem

Recall

$$\frac{d\sigma}{d\Omega} = f(\theta,\varphi) = \underbrace{\frac{1}{k}\sum_{\ell=0}^{\infty}\left(2\ell+1\right)e^{i\delta_\ell}\sin\delta_\ell P_\ell(\theta)}$$

Since there is no φ dependence on this side, this can just be called f(θ)

Consider the case where θ=0

Then f(θ=0)=f(0)= $\sum_\ell \frac{\left(2\ell+1\right)}{k} \underbrace{e^{i\delta_\ell}}_{\cos\delta_\ell + i\sin\delta_\ell} \sin\delta_\ell \underbrace{P_\ell(\theta=0)}_{1}$

$$f(0)=\sum_\ell \frac{\left(2\ell+1\right)}{k}\cos\delta_\ell \sin\delta_\ell + i\underbrace{\sum_\ell \frac{\left(2\ell+1\right)}{k}\sin^2\delta_\ell}_{\frac{k}{4\pi}\cdot\sigma}$$

So $\mathrm{Im}\left(f(0)\right)=\frac{k}{4\pi}\cdot\sigma$, or

$$\boxed{\sigma = \frac{4\pi}{k}\mathrm{Im}\left(f(0)\right)}$$ The Optical Theorem

What this means:

Recall θ=0 is the direction of the incident beam.
σ represents how much of the incident flux is removed by the scattering
The "removal" is due to destructive interference between the incident and scattered waves
in the θ=0 direction.
(The $\frac{4\pi}{k}$ and the "Im" are not obvious to interperet without more work.)

IV. Resonances

Recall $\tan\delta_0 = \dfrac{\tan(Ka) - \tan(k_{out}a)}{1 + \tan(Ka)\tan(k_{out}a)}$

Since K, $k_{out} \sim \sqrt{E}, \sqrt{E - V_0}$, it is possible to choose values of E that make RHS $\rightarrow \infty$

so $\tan\delta_0 \rightarrow \infty$,

so $\delta_0 \rightarrow \dfrac{n\pi}{2}$

when this happens, $\sin\delta_0 \rightarrow \sin\left(\dfrac{n\pi}{2}\right) \rightarrow 1$

Recall $\sigma = \dfrac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1)\sin^2\delta_\ell$

suppose we are in the regime where only ℓ=0 contributes to the scattering

Then $\sigma \Rightarrow \dfrac{4\pi}{k^2}\sin^2\delta_0$

so when $\sin\delta_0 \rightarrow 1$, this σ is maximized

The matching of E to V_0 and a that achieves this is a resonant of the scattering condition.

I. The Real Hydrogen Atom-Intro

Message: Up to now we studied the energy levels of an e^- in H by assuming that the Hamiltonian is just:

$$H=\left(KE+\underset{\substack{\text{due to}\\\text{nucleus}}}{V_{coulomb}}\right)=\left(\frac{p^2}{2m}-\frac{Ze^2}{r}\right)$$

we get $E_n^{(0)}=\dfrac{-me^4}{2\hbar^2 n^2}$

This was only an approximation, for these reasons:

(1) We used KE=$\dfrac{p^2}{2m}$. This is non-relativistic. Need $KE_{relativistic}$

(2) From the point of view of the e^-, the nucleus appears to be moving. So the nucleus is a moving charge: it creates a $\vec{B}$ as well as the $\dfrac{-Ze^2}{r}$ that the e reacts to.

Plan:

(1) Calculate $H_{\substack{rel\\KE}}=H_{\substack{non-rel\\KE}}-H_{\substack{rel\\\text{"correction"}}}$

(2) Calculate $H_{\substack{\text{due to}\\\text{nucleus B}}}$ ← "$H_{spin-orbit}$"

(3) Write $H_{TOT} = \underbrace{H_{\substack{non-rel \\ KE}} + V_{Coulomb}}_{\text{call this } H_0} - \underbrace{H_{\substack{rel \\ \text{"correction"}}} + H_{spin-orbit}}_{\text{call this } H_1}$

$= H_0 + H_1$

(4) Use Pertubation Theory to get $E_n = E_n^{(0)} + E_n^{(1)}$

II. $H_{\substack{relativistic \\ KE}}$

Recall from Special Relativity, the total energy of a free (not in a potential) object is:

$$E=\left(p^2c^2 + m^2c^4\right)^{\frac{1}{2}} = KE + \underbrace{\text{rest mass energy}}_{mc^2}$$

So $KE=\left(p^2c^2 + m^2c^4\right)^{\frac{1}{2}} - mc^2$

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

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

Expand in Binomial Series

$$(1+x)^k = 1 + kx + \frac{k(k-1)}{2!}x^2 + \dots$$

here $x=\frac{p^2}{m^2c^2}$ and $k=\frac{1}{2}$

$$\text{KE}=\text{mc}^2\left(1+\frac{p^2}{2m^2c^2}+\frac{1}{2}\left(\frac{-1}{2}\right)\frac{1}{2}\frac{p^4}{m^4c^4}+....\right)-\text{mc}^2$$

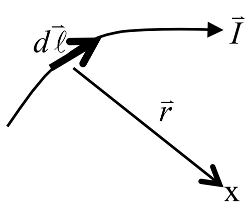
$$=\frac{p^2}{2m}-\frac{1}{8}\frac{p^4}{m^3c^2}+...$$

So $\text{KE}\approx \text{KE}_{non-rel}-\frac{p^4}{8m^3c^2}$

call this $H_{\substack{relativistic\\ correction}}$

III. Spin-Orbit Coupling

Recall the Biot-Savart Law from E&M:



$\vec{B}(\text{at x})=\frac{\mu_0}{4\pi}I\frac{d\vec{\ell}\times\vec{r}}{r^3}$

Suppose the I is due to just one charge q moving during time dt

Then $\text{I}d\vec{\ell}=\frac{q}{dt}d\vec{\ell}=q\frac{d\ell}{dt}=q\vec{v}$

$\vec{B}(\text{at x})=\frac{\mu_0}{4\pi}q\frac{\vec{v}\times\vec{r}}{r^3}$

Suppose "x" is the location of the e^- in the rest frame at the e^-, the apparently moving q that produces the $\vec{B}$ is the proton, so q=+e

If the e's velocity with respect to the proton is defined as "v" the the p's velocity with respect to the e must be "-v"

So to find the $\vec{B}$ at the location of the e, let

$q \to +e$

$v \to -v$

Then $\vec{B}=\frac{\mu_0 e}{4\pi}\frac{\left(-\vec{v}\right)\times\vec{r}}{r^3}$

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

Convert to Gaussian units

$$\vec{B}_{reverse}=\frac{e}{c}\frac{\vec{r}\times\vec{v}}{r^3}$$

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

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

$$\boxed{\vec{B}_{\substack{\text{at e due}\\ \text{to p}}}=\frac{e}{mc}\frac{\vec{L}}{r^3}}$$

Recall that e^- has an intrinsic magnetic moment $\vec{m}=\frac{-e}{mc}\vec{s}$

and an object with an $\vec{m}$ develops additional potential energy when it is placed in a $\vec{B}$:

I. Intro to coupled 2-particle wavefunctions

II. Finding $E_n^{(1)}$ for $H_{\substack{relativistic\\correction}} + H_{spin-orbit}$

III. The fine structure of the H spectrum

$$H = -\vec{m}\cdot\vec{B}$$
$$= -\left[\frac{e\vec{s}}{mc}\right]\cdot\left[\frac{e\vec{L}}{mcr^3}\right]$$
$$= \frac{e^2}{m^2c^2r^3}\vec{s}\cdot\vec{L}$$

Notice we have not been entirely consistent because we used relativistic formulas $\left(E=\sqrt{p^2c^2+m^2c^4}\right)$ for the H_{rel} correction but non-relativistic $\vec{r}$ and $\vec{p}$ for $H_{\text{due to B}}$

If we put relativity into the $H_{\text{due to B}}$ we get another $\frac{1}{2}$

So $H=\frac{1}{2}\left\{\frac{e^2}{m^2c^2r^3}\vec{s}\cdot\vec{L}\right\}$

$$\text{"}H_{spin-orbit}\text{"} = \frac{e^2}{2m^2c^2r^3}\vec{s}\cdot\vec{L}$$

this is the proton's $\vec{L}$ relative to the electron

this is the electron spin

IV. Intro to coupled 2-particle wavefunctions

We know that for $H=\frac{p^2}{2m}-\frac{Zez}{r}$,

$$E_n^{(0)} = -\frac{me^4}{2\hbar^2n^2} \quad \text{for } e^- \text{ in H.}$$

We want to find $E_n^{(1)}$, the first-order correction due to the perturbation $H_1 \equiv H_{\substack{relativistic\\correction}} + H_{spin-orbit}$

$$= -\frac{p^4}{8m^3c^2} + \frac{e^2\vec{s}\cdot\vec{L}}{2m^2c^2r^3}$$

So we need $\langle\Psi|H_1|\Psi\rangle = E_n^{(1)}$

Question: what to use for "$|\Psi\rangle$" ?

$H_{\substack{relativistic\\correction}}$ concerns only the e's behavior so it seems possible to use $|\Psi\rangle = |\Psi_{n\ell m}\rangle$, usual hydrogen wavefunction

However, $H_{spin-orbit}$ involves $\vec{s}$ (due to e^{-E}) and $\vec{L}$ (due to p) so the $|\Psi\rangle$ must represent the

combined system of 2 objects with (coupled) angular momentum

we will show how to find the representation of such a coupled system. For now, assume it exists.

What must the $|\Psi_{combined\ \text{e-p}}\rangle$ be like:

Recall total angular momentum $\vec{J}$ from Chapter 11

Suppose we ignore the proton's spin. Then for the e-p system:

$\boxed{\vec{J} = \vec{L}_{proton} + \vec{s}_{electron}}$ (in the rest frame of the e^-)

I. Calculate $E_n^{(1)}$ for $H_{\substack{rel \\ corr}} + H_{\substack{spin \\ orbit}}$

II. The fine structure of hydrogen

III. Anomolous Zeeman Effect

One way to describe the $|\Psi\rangle$ of the coupled e-p system is to represent:

The unperturbed energy level of the e $\rightarrow$ n

The total angular momentum of e and p $\rightarrow$ j

The "m" quantum # that goes with j $\rightarrow$ m_j

The part of the total angualr momentum due to the proton $\rightarrow \ell$

The part of the total angular momentum due to the e $\rightarrow$ s

Call this combined wavefunction $|n\ell jm_j\rangle$ (supress the s, assumed to be $\frac{1}{2}|e\rangle$)

So the operators that $\underbrace{\text{have eigenvalues}}_{\text{are diagonal}}$ in this basis are

$$J^2|n\ell jm_j\rangle = j(j+1)\hbar^2|n\ell jm_j\rangle$$

$$L^2|n\ell jm_j\rangle = \ell(\ell+1)\hbar^2|n\ell jm_j\rangle$$

$$\boxed{H_{\text{unperturbed e}}}|n\ell jm_j\rangle = \frac{-me^4}{2\hbar^2 n^2}|n\ell jm_j\rangle = E_n|n\ell jm_j\rangle$$

$$H_{\text{unperturbed e}} = \frac{p^2}{2m} - \frac{Ze^2}{r}$$

$$J_z|n\ell jm_j\rangle = m_j\hbar|n\ell jm_j\rangle$$

$$S^2|n\ell jm_j\rangle = s(s+1)\hbar^2|n\ell jm_j\rangle$$

V. Finding $E_n^{(1)}$ for $H_{\substack{relativistic\\correction}} + H_{spin-orbit}$

We want $E_n^{(1)} = \langle\Psi|H_1|\Psi\rangle$

$$= \langle\Psi|\left[\frac{-p^4}{8m^3c^2} + \frac{e^2\vec{s}\cdot\vec{L}}{2m^2c^2r^3}\right]|\Psi\rangle$$

$$= \left\langle \Psi_{n\ell m} \right| \left[\frac{-p^4}{8m^3c^2} \right] \left| \Psi_{n\ell m} \right\rangle + = \left\langle n\ell j m_j \right| \left[\frac{e^2 \vec{s} \cdot \vec{L}}{2m^2c^2r^3} \right] \left| n\ell j m_j \right\rangle$$

do this first

Recall $\text{H}_{\underset{e}{unperturbed}} \equiv H_0 = \frac{p^2}{2m} - \frac{e^2}{r}$

So $\frac{p^2}{2m} = H_0 + \frac{e^2}{r}$

So $\frac{p^4}{4m^2} = \left(H_0 + \frac{e^2}{r} \right)^2$

So $\frac{-p^4}{8m^3c^2} = \frac{-1}{2mc^2} \left(H_0 + \frac{e^2}{r} \right)^2$

So $\left\langle \Psi_{n\ell m} \right| \left[\frac{-p^4}{8m^3c^2} \right] \left| \Psi_{n\ell m} \right\rangle =$

$$= \frac{-1}{2mc^2} \left\langle \Psi_{n\ell m} \right| \left(H_0 + \frac{e^2}{r} \right) \left(H_0 + \frac{e^2}{r} \right) \left| \Psi_{n\ell m} \right\rangle$$

$$= \frac{-1}{2mc^2} \left\langle \Psi_{n\ell m} \right| \left(H_0 + \frac{e^2}{r} \right) \left[E_n^0 \left| \Psi_{n\ell m} \right\rangle + \frac{e^2}{r} \left| \Psi_{n\ell m} \right\rangle \right]$$

$$= \frac{-1}{2mc^2} \left\langle \Psi_{n\ell m} \right| \left[E_n^0 \underbrace{\left(H_0 + \frac{e^2}{r} \right) \left| \Psi_{n\ell m} \right\rangle}_{E_n^0 \left| \Psi_{n\ell m} \right\rangle + \frac{e^2}{r} \left| \Psi_{n\ell m} \right\rangle} + e^2 \underbrace{\left(H_0 + \frac{e^2}{r} \right)}\underbrace{\frac{1}{r}} \left| \Psi_{n\ell m} \right\rangle \right]$$

commute (the two braced factors $\left(H_0 + \frac{e^2}{r} \right)$ and $\frac{1}{r}$)

$$= \frac{-1}{2mc^2}\left\langle \Psi_{n\ell m}\right|\left[\left(E_n^0\right)^2\left|\Psi_{n\ell m}\right\rangle + E_n^0 e^2 \frac{1}{r}\left|\Psi_{n\ell m}\right\rangle + e^2\frac{1}{r}\underbrace{H_0\left|\Psi_{n\ell m}\right\rangle}_{E_n^0\left|n\ell j m_j\right\rangle} + e^4\frac{1}{r^2}\left|\Psi_{n\ell m}\right\rangle\right]$$

$$= \frac{-1}{2mc^2}\left[\underbrace{\left\langle \Psi_{n\ell m}\right|\left(E_n^0\right)^2\left|\Psi_{n\ell m}\right\rangle}_{\left(E_n^0\right)^2} + E_n^0 e^2\underbrace{\left\langle \Psi_{n\ell m}\right|\frac{1}{r}\left|\Psi_{n\ell m}\right\rangle}_{\frac{1}{a_0 n^2}} + E_n^0 e^2\underbrace{\left\langle \Psi_{n\ell m}\right|\frac{1}{r}\left|\Psi_{n\ell m}\right\rangle}_{\frac{1}{a_0 n^2}} + e^4\underbrace{\left\langle \Psi_{n\ell m}\right|\frac{1}{r^2}\left|\Psi_{n\ell m}\right\rangle}_{\frac{1}{a_0^2 n^3\left(\ell+\frac{1}{2}\right)}}\right]$$

where a_0 = the Bohr radius $\equiv \frac{\hbar^2}{me^2}$

Plug in $R_{n\ell}Y_{\ell m}$, etc., do expectation values or look them up in Goswami Eq 13.25

$$\text{So } \left\langle H_{\substack{rel\\corr}}\right\rangle = \frac{-1}{2mc^2}\left[\left(\frac{me^4}{2\hbar^2 n^2}\right)^2 + 2e^2\left(\frac{-me^4}{2\hbar^2 n^2}\right)\left(\frac{1}{a_0 n^2}\right) + \frac{e^4}{a_0^2 n^3\left(\ell+\frac{1}{2}\right)}\right]$$

Define $\alpha \equiv \frac{e^2}{\hbar c}$ "the fine structure constant"

$$E^{(1)}_{\substack{n\\rel.corr.}} = \left\langle H_{\substack{rel\\corr}}\right\rangle = \frac{-mc^2\alpha^4}{2}\left[\frac{1}{n^3\left(\ell+\frac{1}{2}\right)} - \frac{3}{4n^4}\right]$$

We don't know effect of $\vec{s}\cdot\vec{L}$ on $\left|n\ell j m_j\right\rangle$ we only know effect of J^2, L^2, s^2, J_z. So we have to rewrite $\vec{s}\cdot\vec{L}$ in terms of some of those:

I. Finding the $E^{(1)}_{n_{spin-orbit}}$ (continued)

II. The fine structure of Hydrogen

Recall $\vec{J}=\vec{L}+\vec{S}$, so

$$J^2 = \vec{J}\cdot\vec{J} = \left(\vec{L}+\vec{S}\right)^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S},$$

So $\vec{L}\cdot\vec{S} = \dfrac{J^2 - L^2 - S^2}{2}$

So we want

$$\left\langle H_{spin-orbit}\right\rangle = \left\langle n\ell jm\right| \frac{e^2}{4m^2c^2r^3}\left(J^2 - L^2 - S^2\right)\left| n\ell jm\right\rangle$$

$$= \frac{e^2}{4m^2c^2}\left\{\hbar^2\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\left\langle n\ell jm\right|\frac{1}{r^3}\left|n\ell jm\right\rangle\right\}$$

we will see later in Chapter 17 that the $\left|n\ell jm\right\rangle$ are linear combinations $\sum_i a_i R_{n\ell} Y_{\ell m_\ell}\left|s,m_s\right\rangle_i$

e^- p e spin

*Clebsch-Gordan coefficients

So $\left\langle n\ell jm\right|\frac{1}{r^3}\left|n\ell jm\right\rangle =$

$$\left\langle R_{n\ell}\right|\frac{1}{r^3}\left|R_{n\ell}\right\rangle\cdot\left\{\left\langle\Psi_{\ell m}\middle|\Psi_{\ell m}\right\rangle\left\langle s,m_s\middle|s,m_s\right\rangle\ldots\right\}$$

Again do expectation value of look up Goswami Eq 13.26

1 by normalization

$$\frac{1}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \quad \text{for } \ell \neq 0$$

So $\left\langle H_{spin-orbit}\right\rangle = \frac{e^2\hbar^2}{4m^2c^2}\frac{\left[j(j+1)-\ell(\ell+1)-s(s+1)\right]}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)}$

Recall the relationship between $\vec{J}$, $\vec{L}$, and $\vec{S}$:

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

It turns out that the eigenvalues are related by

$$j = \begin{cases} \ell + s \\ or \\ \ell - s \end{cases} \qquad \text{(we will see this in Chapter 17)}$$

Plug in s=$\frac{1}{2}$ and j=$\ell \pm$ s and $\alpha \equiv \frac{e^2}{\hbar c}$

$$E^{(1)}_{n_{spin-orbit}} = \left\langle H_{spin-orbit}\right\rangle = \frac{mc^2\alpha^4}{4}\cdot\frac{1}{n^2\ell(\ell+\frac{1}{2})(\ell+1)}\cdot\begin{Bmatrix} \ell \\ -\ell-1 \end{Bmatrix} \qquad \begin{matrix}\text{when } j=\ell+s \\ \text{when } j=\ell-s\end{matrix}$$

V. The fine structure of the hydrogen spectrum

Recall the unperturbed energy levels:

$$E^{(0)}_n = \frac{-me^4}{2\hbar^2 n^2}\cdot\frac{c^2}{c^2} = \frac{-mc^2\alpha^2}{2n^2}$$

Compare $\quad E^{(1)}_{n_{rel.corr.}} = -mc^2\left[\text{number of order 1, depending on } \ell\right]\alpha^4$

and $\quad E^{(1)}_{n_{spin-orbit}} = +mc^2\left[\text{number of order 1, depending on } \ell\right]\alpha^4$

$$E^{(1)}_{n_{TOT}} = E^{(1)}_{n_{rel.corr.}} + E^{(1)}_{n_{spin-orbit}} = \frac{-mc^2\alpha^2}{2n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right]$$

$j=\ell+s$ or $\ell-s$, $s=\frac{1}{2}$

(we have derived this for $\ell \neq 0$)

If you plug in

e =$1.6\text{x}10^{-19}$ C

$\hbar$ = $1.05\text{x}10^{-34}$ J$\cdot$s

c = $3\text{x}10^{8}$ m/s

you get $\alpha = \dfrac{1}{137}$

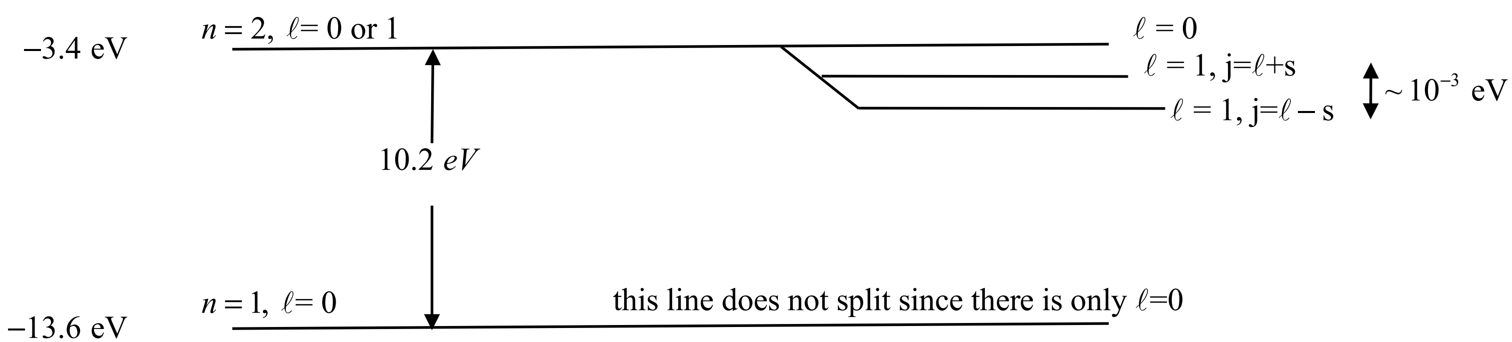
"The most important dimensionless # in physics", since it relates the fundamental constants of

E&M $\rightarrow$ e, QM $\rightarrow$ $\hbar$, relativity $\rightarrow$ c

So the correction $E_n^{(1)}$ are α^2 times smaller than the unperturbed levels

$$\left(\tfrac{1}{137}\right)^2 = 5x10^{-5}$$

So the result looks like



The relative smallness of the splitting compared with the separation between unperturbed levels is why the splitting is called a "fine structure"

I. Compare 3 sources of line splitting

i) spinless classical charge q moving in $\vec{B}_{external}$

$$H = \frac{1}{2\mu}\left[p + \frac{eA}{c}\right]^2 - e\varphi$$

(p ↑) classical momentum of electron

get cross term $\vec{A} \cdot \vec{p}$

↓

Because $\vec{L} = \vec{r} \times \vec{p}$ and

$\vec{B} = \nabla \times A$

$\boxed{\frac{1}{2}\vec{B} \cdot \vec{L}}$ } leads to "Normal Zeeman Effect" in which energy levels depend on $\vec{B} \cdot \vec{L}$

(ii) real e^- moving in field of nucleus

↓ has spin s

↓ has magnetic moment

$M = \frac{-e\vec{S}}{mc}$

↓ a charge moving in e's reference frame so it is a current loop as seen by e

↓ produces a $\vec{B}$

↓ Biot Savart Law: B=f(L)

energy=-m $\cdot$ B $\Rightarrow \boxed{\vec{S} \cdot \vec{L}}$ "spin-orbit coupling contribution"

iii) real e moving in $\vec{\mathrm{B}}_{external}$

L and S

leads to magnetic moment

$$\mathrm{M}_L = \frac{-eL}{2mc}$$

leads to magnetic moment

$$\mathrm{M}_s = \frac{-e}{2mc} S \cdot g$$

where g=2, also non-classical

note non-classical minus signs

Then E= $-M_{TOT} \cdot B = \boxed{\frac{e}{2mc}\left(\vec{\mathrm{L}} + 2\vec{\mathrm{S}}\right) \cdot \vec{B}}$ "anamolous Zeeman Effect"

Re This effect, 2 questions:

i) How do the non-classical terms (e.g. g=2) arise?

ii) How to calculate energy levels?

II. How does electron g=2 arise

Introduce conceptually the Dirac Equation = relativistic version of the Schrodinger Equation

Assume Special Relativity: $\mathrm{E}^2 = m^2c^2 + p^2c^4$

Choose units in which c=1. Take square root.

$E = \pm\sqrt{m^2 + p^2}$

We are used to replacing E by operator $i\frac{\partial}{\partial t}$

p by ∇

Hard to make a direct replacement for the $\sqrt{}$

Dirac guessed that the "relativistic Schrodinger Equation" would look like:

(E) (p) (m)

$$i\frac{\partial}{\partial t}\Psi = -i\vec{\alpha}\cdot\vec{\nabla}\Psi + \beta m\Psi$$

To recover $E^2 = m^2 + p^2$, it turns out that the 3 α components are constructed from the Pauli matrices

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ -\sigma_i & 0 \end{pmatrix} \quad \text{and} \quad 3 = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix} \qquad \text{(both 4x4)}$$

So the Dirac Equation operators are 4x4 matrices.

Dirac Equation: $\left(i\gamma^\mu \frac{\partial}{\partial x^\mu} - m\right)\Psi = 0$, $\gamma^0 = \beta\cdot 1$, $\gamma^i = \beta\alpha^i$, sum over repeated inices

Expect the solutions Ψ to be 4-component column vectors. In the proper basis the look like:

$$\begin{pmatrix} 1 \\ 0 \\ \dfrac{\vec{\sigma} \cdot \vec{p}}{E+m} \\ 0 \end{pmatrix}$$

particle, spin up

$$\begin{pmatrix} 0 \\ 1 \\ 0 \\ \dfrac{\vec{\sigma} \cdot \vec{p}}{E+m} \end{pmatrix}$$

particle, spin down

$$\begin{pmatrix} 0 \\ \dfrac{\vec{\sigma} \cdot \vec{p}}{E-m} \\ 0 \\ 1 \end{pmatrix}$$

antiparticle, spin down

$$\begin{pmatrix} \dfrac{\vec{\sigma} \cdot \vec{p}}{E-m} \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

particle, spin up

Check that Dirac Equation converts to Schrodinger Equation in non-relativistic limit

Recall how to insert an electromagnetic field into a Hamiltonian:

Recall $\mathrm{H}_{\substack{free \\ particle}} = \frac{p^2}{2m}$ but

$$\mathrm{H}_{\substack{particle \\ \text{in EM} \\ \text{field}}} = \frac{\left(p - \frac{qA}{c}\right)^2}{2m} + q\phi$$

So in Dirac Equation let $\mathrm{i}\frac{\partial}{\partial x^\mu} \to \mathrm{i}\frac{\partial}{\partial x^\mu} - eA_\mu$

Dirac Equation becomes

$$\mathrm{i}\gamma^\mu \left(\mathrm{i}\frac{\partial}{\partial x^\mu} - ieA_\mu \right)\Psi - m\Psi = 0$$

Call $\Psi = \begin{pmatrix} \chi_1 \\ \chi_2 \\ \varphi_1 \\ \varphi_2 \end{pmatrix} e^{-ip\cdot x}$

use $\frac{\partial}{\partial t} \to E$, etc, γ's represent couplings through off-diagonal

$$\left(E - m - eA_0\right)\chi = -\vec{\sigma}\cdot\left(i\nabla + eA\right)\varphi$$

$$\left(E - m - eA_0\right)\varphi = -\vec{\sigma}\cdot\left(i\nabla + eA\right)\chi$$

Non-relativistic limit: $\mathrm{E} \approx \mathrm{m}$ $(\mathrm{p} \to 0)$

and $|eA_0| \ll m$

Solve simultaneously to get

$$\left(E - m - eA_0\right)\chi \approx \left(\frac{1}{2m}\right)\left[\vec{\sigma}\cdot\left(i\nabla + eA\right)\right]^2 \chi$$

A useful identity (check by direct substitution):

$$\left(\vec{\sigma}\cdot\vec{V}\right)^2 = \left|V\right|^2 + i\vec{\sigma}\cdot\left(\vec{V}\times\vec{V}\right)$$

Then

$$\text{(E-m)}\chi \approx \left[eA_0 + \frac{1}{2m}\left|i\nabla + eA\right|^2 + \frac{i\vec{\sigma}}{2m}\cdot\left(i\nabla + eA\right)\times\left(i\nabla + eA\right)\right]\chi$$

Apply vector identities to get

$$\text{(E-m)}\chi \approx \left\{eA_0 + \frac{1}{2m}\left(i\nabla + eA\right)^2 + \frac{i}{2m}\vec{\sigma}\cdot\left(i\nabla + eA\right)\right\}\chi$$

KE (E-m), φ (eA_0), -p ($i\nabla$)

$$\frac{i\cdot ie}{2m}\vec{\sigma}\cdot\left(\nabla\times A\right)$$

B ($\nabla\times A$)

So the associated Hamiltonian is

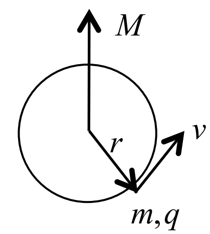
$$\text{H} \approx \frac{1}{2m}\left(p - eA\right)^2 - \frac{e}{2m}\vec{\sigma}\cdot\vec{B} + e\varphi$$

Recall $\text{S}=\frac{\sigma}{2}$, so

$$\text{H} \approx \frac{1}{2m}\left(p - eA\right)^2 - \frac{e}{m}\vec{S}\cdot\vec{B} + e\varphi$$

$$H \approx \frac{1}{2m}\left(p - eA\right)^2 - \boxed{\frac{e}{m}\vec{S}\cdot\vec{B}} + e\varphi$$

focus on this



Recall classical magnetic moment of a circulating current is

$M = (\text{current}) \cdot (\text{area enclosed}) = I \cdot \pi r^2$

But $I = \dfrac{q}{time} = q \cdot \dfrac{v}{2\pi r}$

So $M_{classical} = \dfrac{qv}{2\pi r} \cdot \pi r^2 = \dfrac{qvr}{2}$

But classical angular momentum $L = mvr \rightarrow vr = \dfrac{L}{m}$

So $M_{classical} = \dfrac{q}{2m} L$

Now replace $L_{classical} \rightarrow S$

Then $\dfrac{e}{m}\vec{S}\cdot\vec{B} \leftrightarrow 2 \cdot \vec{M}_{classical} \cdot \vec{B}$

This is the electron gyromagnetic ratio (leads to g-factor)

I. Anomolous Zeeman Levels

II. Hyperfine Structure

2) Now find anomolous Zeeman energy levels

ignore for now

$$H = H_{unperturbed} + H_{spin-orbit} + H_{rel} + H_{\substack{anom\\Zeeman}}$$

$$= \frac{p^2}{2m_e} - \frac{Ze^2}{r} + \frac{1}{2m^2c^2}\frac{Ze^2}{r^3}\vec{L}\cdot\vec{S} + \frac{e}{2m_e c}(L+2S)\cdot B$$

$\vec{L}\cdot\vec{S}$ coupling forces us to use the $|jm\rangle$ basis

focus on this

$$E = \left\langle H_{\substack{anom\\Z}} \right\rangle$$

Let $\vec{B} = B\hat{z}$, so e.g. $S\cdot B = S_z|B|$

$$= \left\langle jm \right| \frac{e}{2m_e c}(L+2S)\cdot B \left| jm \right\rangle$$

rewrite $(L+2S) = (L+S) + S = J + S$

$$= \frac{eB}{2m_e c}\left\langle jm \right| J_z + S_z \left| jm \right\rangle$$

$$= \frac{eB}{2m_e c}\left[\left\langle jm \right| J_z \left| jm \right\rangle + \left\langle jm \right| S_z \left| jm \right\rangle\right]$$

$\left\langle jm \right| J_z \left| jm \right\rangle$: $\hbar m \left\langle jm | jm \right\rangle$, where $\left\langle jm | jm \right\rangle = 1$

$\left\langle jm \right| S_z \left| jm \right\rangle$: need uncoupled basis

Goswami Table 12.1 gives some general C-G coefficients:

$j \backslash m_s$	$+\frac{1}{2}$	$-\frac{1}{2}$
$\ell+\frac{1}{2}$	$\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}$	$\sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}$
$\ell-\frac{1}{2}$	$\sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}$	$-\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}$

note these are m_j NOT m_s

Consider $\left\langle jm_j \middle| S_z \middle| jm_j \right\rangle$

when j=$\ell+\frac{1}{2}$, this is

$$\left\{\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\left\langle +\tfrac{1}{2}\right| + \sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}\left\langle -\tfrac{1}{2}\right|\right\}\left|S_z\right|\underbrace{\left\{\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\left|+\tfrac{1}{2}\right\rangle + \sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}\left|-\tfrac{1}{2}\right\rangle\right\}}$$

$$\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\underbrace{S_z\left|m_s=+\tfrac{1}{2}\right\rangle}_{\underbrace{\hbar \mathrm{m}_s\left|+\frac{1}{2}\right\rangle}_{\hbar\left(+\frac{1}{2}\right)\left|+\frac{1}{2}\right\rangle}} + \sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}\underbrace{S_z\left|m_s=-\tfrac{1}{2}\right\rangle}_{\underbrace{\hbar \mathrm{m}_s\left|-\frac{1}{2}\right\rangle}_{\hbar\left(-\frac{1}{2}\right)\left|-\frac{1}{2}\right\rangle}}$$

$$= \sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\hbar\left(+\tfrac{1}{2}\right)\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\left\langle+\tfrac{1}{2}\middle|+\tfrac{1}{2}\right\rangle+\sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}\hbar\left(-\tfrac{1}{2}\right)\sqrt{\frac{\ell+\frac{1}{2}-m}{2\ell+1}}\left\langle-\tfrac{1}{2}\middle|-\tfrac{1}{2}\right\rangle$$

$$+\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\underbrace{\left\langle+\tfrac{1}{2}\middle|-\tfrac{1}{2}\right\rangle}_{0}+\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\sqrt{\frac{\ell+\frac{1}{2}+m}{2\ell+1}}\underbrace{\left\langle-\tfrac{1}{2}\middle|+\tfrac{1}{2}\right\rangle}_{0}$$

$$=\frac{\hbar}{2}\left[\frac{\ell+\frac{1}{2}+m}{2\ell+1}-\frac{\ell+\frac{1}{2}-m}{2\ell+1}\right]$$

$$=\frac{\hbar}{2}\left[\frac{2m}{2\ell+1}\right]$$

$$=\frac{\hbar m_j}{2\ell+1} \qquad \text{for } j=\ell+\tfrac{1}{2}$$

Similarly we get

$$=\frac{-\hbar m_j}{2\ell+1} \qquad \text{for } j=\ell-\tfrac{1}{2}$$

Combine these with the $\langle J_z \rangle$ terms to get

$$E_{\substack{anom\\Zeeman}} = \frac{eB}{2m_e c}\left[\hbar m_j \pm \frac{\hbar m_j}{2\ell+1}\right] = \frac{eB\hbar m_j}{2m_e c}\left[1 \pm \frac{1}{2\ell+1}\right] \qquad \text{for } j=\ell \pm \tfrac{1}{2}$$

I. Hyperfine Structure

spin of nucleus generates a $\vec{B}$ field, e^- responds to this B in addition to the one related to the apparent linear motion of nucleus in e's rest frame.

Let nuclear magnetic moment $\vec{M}_I = \dfrac{Zeg_N}{2M_N c}$ ← mass (M_N)

Also let $\vec{M}_{es}$ = magnetic moment of electron's spin

$H_{hyperfine}$ has 3 "$-M \cdot B$" terms:

$$= \frac{-\mu_0}{4\pi}\left\{ \underbrace{\frac{q}{m_e R^3}}_{\substack{\vec{B}\text{ generated by e}\\ \text{as current loop in}\\ \text{p frame}}} \vec{L}\cdot\vec{M}_I + \underbrace{\frac{1}{R^3}\left[3\left(M_{es}\cdot n\right)\left(M_I\cdot n\right) - M_{es}\cdot M_I\right]}_{M_I\cdot\left[\text{B generated by e spin}\right]} + \underbrace{\frac{8}{3}M_{es}\cdot M_I\delta(R)}_{\text{"Fermi contact term"}}\right\}$$

Contact term corrects for the fact that p is not point like so its internal $\vec{B}$ differs from the external one.

$$\left\langle H_{hyperfine}\right\rangle \simeq \frac{1}{2000}\left\langle H_{spin-orbit}\right\rangle$$

I. More on systems with identical particles

A) Exchange energy for interacting particles

Consider 2 indistinguishable particles 1 and 2 which can take positions α and β

Their allowed 2-particle wavefunctions are

$$\Psi^S = \tfrac{1}{\sqrt{2}}\left[\Psi_{\alpha(1)}\Psi_{\beta(2)} + \Psi_{\beta(1)}\Psi_{\alpha(2)}\right]$$

$$\Psi^A = \tfrac{1}{\sqrt{2}}\left[\Psi_{\alpha(1)}\Psi_{\beta(2)} - \Psi_{\beta(1)}\Psi_{\alpha(2)}\right]$$

Let them interact

$$\text{H}=\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+\underbrace{W\left(\left|\vec{r}_1-\vec{r}_2\right|\right)}$$

typically coulomb potential but could be anything

Treat it as a perturbation.

Then 1st order correction to system's energy is:

(considering all allowed combinations):

$$\langle\Psi|W|\Psi\rangle =$$

$$\frac{1}{2}\int\left(\Psi^*_{\alpha(1)}\Psi^*_{\beta(2)} \pm \Psi^*_{\beta(1)}\Psi^*_{\alpha(2)}\right)W\left(\Psi_{\alpha(1)}\Psi_{\beta(2)} \pm \Psi_{\beta(1)}\Psi_{\alpha(2)}\right)d^3 1 d^3 2$$

$$\left.\begin{aligned} &= \frac{1}{2}\int\left|\Psi_{\alpha(1)}\right|^2 W\left|\Psi_{\beta(2)}\right|^2 d^3 1 d^3 2 \\ &+\frac{1}{2}\int\left|\Psi_{\beta(1)}\right|^2 W\left|\Psi_{\alpha(2)}\right|^2 d^3 1 d^3 2 \end{aligned}\right\} \quad \text{note if } r_2 \leftrightarrow r_1, \text{ F=L}$$

$$\left.\begin{aligned} &\pm\frac{1}{2}\int\Psi^*_{\alpha(1)}\Psi_{\beta(1)}W\Psi^*_{\beta(2)}\Psi_{\alpha(2)}d^3 1 d^3 2 \\ &\pm\frac{1}{2}\int\Psi^*_{\beta(1)}\Psi_{\alpha(1)}W\Psi^*_{\alpha(2)}\Psi_{\beta(2)}d^3 1 d^3 2 \end{aligned}\right\} \quad \text{if } r_2 \leftrightarrow r_1, \text{ O=I}$$

$$= \underbrace{\overset{\text{"2F"}}{\int\left|\Psi_{\alpha(1)}\right|^2 W\left|\Psi_{\beta(2)}\right|^2 d^3 1 d^3 2}}_{\text{"Direct Integral D"}} \pm \underbrace{\overset{\text{"2O"}}{\int\Psi^*_{\alpha(1)}\Psi_{\beta(1)}W\Psi^*_{\beta(2)}\Psi_{\alpha(2)}d^3 1 d^3 2}}_{\text{"Exchange" Integral E}}$$

"Direct Integral D"

can be interpreted classically as the coulomb interaction between 2 charge densities ("electron clouds") distributed according to the wavefunctions of the particles.
Gives a positive # since identical particles (e.g. $2e^-$'s)

"Exchange" Integral E

No classical interpretation. A purely QM interference integral. Magnitude also positive. To see this:

For concreteness, let W= $\frac{e^2}{\vec{r}_1 - \vec{r}_2} = \frac{e^2}{r_{12}}$

Define $\rho(1) = \Psi^*_{\alpha(1)} \Psi_{\beta(1)}$

So $\rho(2) = \Psi^*_{\alpha(2)} \Psi_{\beta(2)}$

$\rho^*(2) = \Psi_{\alpha(2)} \Psi^*_{\beta(2)}$

Then $E = e\int \Psi^*_{\alpha(1)} \Psi_{\beta(1)} d^3 1 \int \frac{e\Psi^*_{\beta(2)} \Psi_{\alpha(2)}}{r_{12}} d^3 2$

$$= e\int \rho(1) \underbrace{\int \frac{\rho^*(2)}{r_{12}} d^3 2 d^3 1}$$

call this V(1), the electrostatic potential observed at 1 due to charge distribution at 2

Slater App 19

By Green's Theorem, for any function V,

$$V(1) = \frac{-1}{4\pi} \int_{\substack{all \\ space}} \frac{\nabla^2 V(2)}{r_{12}} d^3 2$$

Require equal integrands,

So $\rho^*(2) = \frac{-1}{4\pi} \nabla^2 V(2)$

Consequently $\rho(1) = \frac{-1}{4\pi} \nabla^2 V^*(1)$

Plug these into E:

E= $\frac{-1}{4\pi}\int V(1)\nabla^2 V^*(1)d^3 1$

vector identity: $\nabla\cdot\left(V\nabla V^*\right)=V\nabla^2 V^*+\nabla V\cdot\nabla V^*$

Integrate over all space. But divergence Theorem:

$\int_V \nabla\cdot\upsilon\, dVol=\int_S \upsilon\, dA$

Assume v(r $\to\infty)\to\infty$, so $\int V\nabla V^*\, dA\to 0$

Then $\frac{-1}{4\pi}\int V(1)\nabla^2 V^*(1)d^3 1\Rightarrow\frac{+1}{4\pi}\int\nabla V^*(1)\nabla V(1)d^3 1$

$=\frac{1}{4\pi}\int\left|\nabla V(1)\right|^2 d^3 1$

≥ 0

So $\left\langle W\right\rangle = D+E$

Since both D and E are definitely non-negative, antisymmetric states have lower energy than their symmetric partners.

The joint probability for finding both particle's now

$$\left|\Psi(1,2)\right|^2 d^3 1 d^3 2 = \left[\left|\Psi_{\alpha(1)}\right|^2 \left|\Psi_{\beta(2)}\right|^2 + \left|\Psi_{\alpha(2)}\right|^2 \left|\Psi_{\beta(1)}\right|^2 \pm \Psi^*_{\alpha(1)} \Psi_{\beta(1)} \Psi^*_{\beta(2)} \Psi_{\alpha(2)} \pm \Psi^*_{\alpha(2)} \Psi_{\beta(2)} \Psi^*_{\beta(1)} \Psi_{\alpha(1)}\right] d^3 1 d^3 2$$

Io not a simple product--so particles' motion is correlated.

B) Statistical repulsion of non-interacting particles

Consider 2 identical non-interacting particles in space. It is difficult to visualize their wavefunction in 3-D as it has 3x2=6 dimensions, so limit each to 1-D. To keep the particles bounded (as they would be in an atom) but to avoid explicit boundary conditions, place both on the same ring of circumference L.

Typical wavefunction (must fit on ring, single valued) is

$$\Psi_m(1) = \frac{1}{L} e^{ik_m x_1} \qquad \mathrm{k}_m = \frac{2\pi m}{L} \qquad m=0, \pm 1, \pm 2, \ldots$$

↑ particle #1

Symmetrical 2-particle wavefunction (allowing particles to have different momenta, $p_1 = \hbar k_m$ and $p_2 = \hbar k_n$) :

$$\Psi^S = \frac{1}{L\sqrt{2}}\left[e^{ik_m x_1} e^{ik_n x_2} + e^{ik_m x_2} e^{ik_n x_1} \right]$$

$$= \frac{1}{L\sqrt{2}}\left[e^{i\left(k_m x_1 + k_n x_2\right)} + e^{i\left(k_m x_2 + k_n x_1\right)} \right]$$

$$= \frac{1}{L\sqrt{2}} e^{i\frac{1}{2}\left(x_1 + x_2\right)\left(k_m + k_n\right)}\left[e^{i\frac{1}{2}\left(k_m - k_n\right)\left(x_1 - x_2\right)} + e^{-i\frac{1}{2}\left(k_m - k_n\right)\left(x_1 - x_2\right)} \right]$$

Let $x \equiv \frac{1}{2}\left(x_1 + x_2\right)$ centroid position

$k \equiv k_m + k_n$ $\hbar k$=total momentum

Note: $e^{iy} + e^{-iy} = 2\cos y$

$$\Psi^S(1,2) = \frac{1}{L\sqrt{2}} e^{ikx} \cdot 2\cos\left[\tfrac{1}{2}\left(k_m - k_n\right)\left(x_1 - x_2\right) \right]$$

Probability of finding one particle in dx_1 and other in dx_2 is

$$\left|\Psi^S(1,2)\right|^2 dx_1 dx_2 = \frac{2}{L^2}\cos^2\left[\tfrac{1}{2}\left(k_m - k_n\right)\left(x_1 - x_2\right) \right] dx_1 dx_2$$

Note implications:

1) when $\left[\frac{1}{2}(k_m - k_n)(x_1 - x_2)\right] = \frac{\pi}{2}$, Prob=0 for particles to be in dx_1 and dx_2

2) if either $k_m = k_n$ or $x_1 = x_2$, Prob=max

$\therefore$ tendancy of particles to coalesce when in symmetric state

Conversely for antisymmetric 2 particle states:

$$|\Psi_a|^2 = \frac{2}{L^2}\sin^2\left[\frac{1}{2}(k_m - k_n)(x_1 - x_2)\right] \qquad \text{"statistical repulsion"}$$

Note these particles are non-interacting (W=0)

C) Compare statistical repulsion to Pauli Principle

Let Ψ(r)= spatial wavefunction for a single particle

Let χ_{m_s} = spinwavefunction for a single particle

Let $U_\alpha \equiv \Psi\chi$

Then general antisymmetric wavefunction for 2 particles is

particle #

$$U_{\alpha\beta}(1,2) = \frac{1}{\sqrt{2}}\left[U_{\alpha(1)}U_{\beta(2)} - U_{\alpha(2)}U_{\beta(1)}\right]$$

position, spin, etc.

Rewrite determinant: $\frac{1}{\sqrt{2}}\begin{vmatrix} U_{\alpha(1)} & U_{\beta(1)} \\ U_{\alpha(2)} & U_{\beta(2)} \end{vmatrix}$

Generalize for n particles in an antisymmetric state

$$U(1,...,n)=\frac{1}{\sqrt{n!}}\begin{vmatrix} U_{\alpha_1(1)} & U_{\alpha_2(1)} & \cdots & U_{\alpha_n(1)} \\ U_{\alpha_1(2)} & U_{\alpha_2(2)} & \cdots & U_{\alpha_n(2)} \\ \vdots & \vdots & \ddots & \vdots \\ U_{\alpha_1(n)} & U_{\alpha_2(n)} & \cdots & U_{\alpha_n(n)} \end{vmatrix}$$

"Slater Determinant"

These are exact only for truly (non-physical) non-interacting particles, but for physical particles they form an adequate zeroth-order wavefunction for perturbative calculations.

Pauli: " No 2 e's in an atom can have exactly the same state": no two columns can be equal.
If they are, det=0

e.g. $\alpha_1 \overset{?}{\equiv} \alpha_2$

Statistical repulsion: If 2 electrons with same quantum numbers are at same point in space, combined Ψ vanishes: No two rows can be equal

I. Helium atom: Nucleus +2 e's

Plan: First predict ground state energy:

i) Let $H=\underbrace{\frac{p_1^2}{2\mu}+\frac{p_2^2}{2\mu}-\frac{2e^2}{r_1}-\frac{2e^2}{r_2}}_{H_0}+\underbrace{\frac{e^2}{\left|\vec{r}_1-\vec{r}_2\right|}}_{H_{pert}}$

H_0: electrons each interact only with the Z=2 nucleus

H_{pert}: e's repel each other

ii) Correction #1: for charge screening of nucleus by each e^- from the point of view of other e^- So $Z_{effective} \neq 2$

Use Variational Method

iii) Correction #2: correlation effects, radial and angular, due to coulomb repulsion.

iv) Next predict excited states' energies

v) Correct for nucleus motion:

Carry out plan:

Let $\alpha = \frac{Zme^2}{\hbar^2 4\pi\varepsilon_0}$

Recall that the normalized ground state wavefunction for a single e in H is:

$$\Psi(\mathrm{r}) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r} \qquad \text{(Goswami Equation 13.23)}$$

(1) Get baseline wavefunction:

Guess unperturbed unsymmetrized 2-e wavefunction is:

$$\Psi^{(0)}(\mathrm{r}_1, r_2) = \left(\frac{\alpha^3}{\pi}\right)^{\frac{1}{2}} e^{-\alpha r_1} e^{-\alpha r_2}$$

(2) Get baseline energy:

Recall for hydrogen atom $\mathrm{E}_n = \frac{-mZ^2e^4}{2\hbar^2 n}$

when n=1, Z=1, $\mathrm{E}_0^{hyd} = -13.6$ eV = "1 Rydberg"

Here everything is the same except:

(i) $\mathrm{Z}^2 = 1^2 \Rightarrow \mathrm{Z}^2 = 2^2$ (helium atom)

(ii) # electrons $1 \rightarrow 2$, so unperturbed equation is

$$\left[H_{e\#1} + H_{e\#2}\right]\Psi = E\Psi$$

$\mathrm{E}_{\#1} + E_{\#2}$ but each with $Z^2 = 2^2$

So $\mathrm{E}_{(0)} = -2\left|\frac{m(2)^2 e^4}{2\hbar^2 1}\right| = 8(-13.6\text{ eV})$=-108.8 eV

Add perturbation

(iii) $\text{E}^{(1)} = \left\langle \Psi^0 \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2| 4\pi\varepsilon_0} \right| \Psi^0 \right\rangle$

$$= \iint \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \frac{|\Psi^0(r_1, r_2)|^2}{4\pi\varepsilon_0} dVol_1\, dVol_2$$

6 fold integral

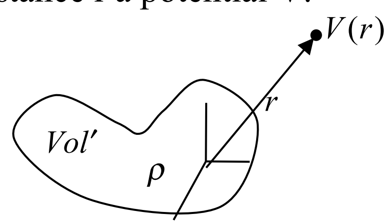
$$= \iint \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \frac{\alpha^3}{\pi} \frac{\alpha^3}{\pi} \frac{e^{-2\alpha r_1} e^{-2\alpha r_2}}{4\pi\varepsilon_0} dVol_1\, dVol_2$$

Rewrite

$$\text{E}^{(1)} = \frac{\alpha^3 e}{4\pi\varepsilon_0} \int dVol_1 e^{-2\alpha r_1} \underbrace{\left[\frac{\alpha^3}{\pi} e \int \frac{e^{-2\alpha r_2}}{|\vec{r}_1 - \vec{r}_2|} dVol_2 \right]}_{\text{Call this } V(r_1)}$$

Recall from E&M that a charge density "ρ" generates at distance r a potential V:

$$\text{V} = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho\, dVol'}{r}$$

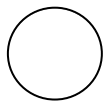


So here $V(r_1)$ is the potential generated by a spherically symmetric charge distribution of density

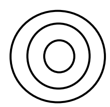
$$\rho = \frac{\alpha^3 e}{\pi} e^{-2\alpha r_2}$$

$$E^{(1)} = \frac{\alpha^3 e}{4\pi\varepsilon_0}\int dVol_1 e^{-2\alpha r_1}\left[\frac{\alpha^3}{\pi} e\int\frac{e^{-2\alpha r_2}}{\left|\vec{r}_1-\vec{r}_2\right|}dVol_2\right]$$

Here is ρ:

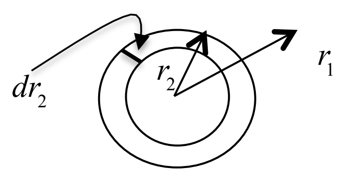


Subdivide it into shells:



A particular shell has radius r_2, thickness dr_2.

Want to evaluate V9r) at $r=r_1$



Again from E&M,

if $r_1 > r_2$, V is same as if ρ were concentrated at origin

Then $\left|\vec{r}_1-\vec{r}_2\right| \to r_1$

$dVol_1$ shell$=4\pi r_2^2 dr_2$

$$\text{So } V=\frac{1}{4\pi\varepsilon_0}\left[\int_0^{r_1}\frac{\alpha^3 e}{\pi}\frac{e^{-2\alpha r_2} r_2^2 dr_2 4\pi}{r_1}+\int_{r_1}^{\infty}\frac{\alpha^3 e}{\pi}\frac{e^{-2\alpha r_2} r_2^2 dr_2 4\pi}{r_2}\right]$$

$$=\frac{\alpha^3 e}{\pi\varepsilon_0}\left[\frac{1}{r_1}\int_0^{r_1} e^{-2\alpha r_2} r_2^2\, dr_2+\int_{r_1}^{\infty} e^{-2\alpha r_2} r_2\, dr_2\right]$$

$$V = \frac{e}{4\pi\varepsilon_0 r_1}\left[1-(1+\alpha r_1)e^{-2\alpha r_1}\right]$$

Plug this V into $E^{(1)}$:

$$E^{(1)} = \frac{\alpha^3 e}{4\left(4\pi\varepsilon_0\right)}\int_0^\infty r_1^2 dr_1 \sin\theta d\theta d\varphi e^{-2\alpha r_1}\left[\frac{e}{4\pi\varepsilon_0 r_1}\left[1-(1+\alpha r_1)e^{-2\alpha r_1}\right]\right]$$

$$= \frac{5}{8}\frac{e^2\alpha}{4\pi\varepsilon_0} = +34 \text{ eV}$$

So $E=E^{(0)} + E^{(1)} = -108.8 \text{ eV} + 34.0 \text{ eV}=-74.8 \text{ eV}$

(compare measured value is -78.975 eV)

(iv) Now add screening

Each e^- does not have a "clear view" of the Z=2 nucleus--generally the presence of the other e^- screens part of the nuclear charge.

Use Variational Method to find $Z_{effective}$ as perturbation theory is at limit of applicability (forst-order correction $E^{(1)} = 34$ is same order of magnitude as

Recall the vVariational Method

This is what you use if you want to fint the ground state energy (E_g) but have a Hamiltonian H($\neq$ f(t)) which cannot be written as $H_0 + \lambda H_1$

i.e., this is what to use if H either

(1) does not have any term that looks like a familiar solved H_0, or

(2) has an H_1 but it is not "small" with respect to H_0

Procedure:

(i) Given H

(ii) Pick any normalized Ψ=Ψ(a,b,c,...) ← some variable

(iii) Calculate $\langle \Psi | H | \Psi \rangle$

(iv) Minimize $\langle \Psi | H | \Psi \rangle$ with respect to its variables, for example require $\frac{\partial}{\partial b}\langle \Psi | H | \Psi \rangle = 0$, solve for b, plug b back into $\langle \Psi | H | \Psi \rangle$

(v) the minimized $\langle \Psi | H | \Psi \rangle$ you get is guaranteed to be $\geq$ to the real E_g, so it is an upper limit on E_g

Carry out procedure on Helium ground state:

(i) identify H

For each electron i let $H_i = \frac{-\hbar^2\nabla_i^2}{2m} - \frac{Ze^2}{r_i}$

Then $H_{TOT} = H_1 + H_2 + \frac{e^2}{|r_1 - r_2|}$

We will calculate $\langle\Psi|H|\Psi\rangle$ as 3 separate terms:

$$\langle\Psi|H_1|\Psi\rangle + \langle\Psi|H_2|\Psi\rangle + \langle\Psi|\frac{e^2}{|r_1 - r_2|}|\Psi\rangle$$

(ii) Choose Ψ. Recall it can be anything

Let $\Psi = \Phi(\vec{r}_1)\Phi(\vec{r}_2)$, where each Φ_i's the solution of

$$\left[\frac{-\hbar^2}{2m}\nabla_i^2 - \frac{Z_{eff}e^2}{r_i}\right]\Phi_i = E\Phi_i$$

Since this looks just like the hydrogen hamiltonian with $Z \rightarrow Z_{eff}$, expect E=E(hydrogen with Z_{eff}):

$$E = \frac{-mZ_{eff}^2 e^4}{2\hbar^2} = \frac{-mc^2 Z_{eff}^2 \alpha^2}{2} \qquad \left(\text{where } \alpha = \frac{e^2}{\hbar c}\right)$$

Calculate $\langle\Psi|H_1|\Psi\rangle$:

$$\iint d^3r_1 d^3r_2 \Phi^*(\vec{r}_1)\Phi^*(\vec{r}_2)\left[\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{r_1}\right]\Phi(\vec{r}_1)\Phi(\vec{r}_2)$$

$$\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}e^2}{r_1} + \frac{Z_{eff}e^2}{r_1} - \frac{Ze^2}{r_1}$$

$$\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}e^2}{r_1} + \frac{\left(Z_{eff} - Z\right)e^2}{r_1}$$

$$= \underbrace{\int d^3r_2 \Phi^*(\vec{r}_2)\Phi(\vec{r}_2)}_{1}\left[\underbrace{\int d^3r_1 \Phi^*(\vec{r}_1)\left[\frac{-\hbar^2}{2m}\nabla_1^2 - \frac{Z_{eff}e^2}{r_1}\right]\Phi(\vec{r}_1)}_{E} + \int d^3r_1 \Phi^*(\vec{r}_1)\left[\frac{\left(Z_{eff} - Z\right)e^2}{r_1}\right]\Phi(\vec{r}_1)\right]$$

$$= E + \left(Z_{eff} - Z\right)e^2 \underbrace{\int d^3r_1 \frac{\left|\Phi(\vec{r}_1)\right|^2}{r_1}}_{=\frac{Z_{eff}me^2}{\hbar^2}}$$

expectation value $\left\langle \frac{1}{r} \right\rangle$ for hydrogenic Ψ's, see Goswami Eq 13.25

$$\left\langle H_1 \right\rangle = E + \left(Z_{eff} - Z\right)\frac{Z_{eff}me^4}{\hbar^2}$$

Same answer for $\left\langle \mathrm{H}_2 \right\rangle$

Also from the perturbation calculation, $\left\langle \Psi \middle| \frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|} \middle| \Psi \right\rangle = \frac{5}{8}\frac{e^2\alpha}{4\pi\varepsilon_0} = \frac{5}{8}\frac{Zme^4}{\hbar^2\left(4\pi\varepsilon_0\right)}$

Just let $\mathrm{Z} \rightarrow \mathrm{Z}_{eff}$

Then $\left\langle H \right\rangle = \left\langle H_1 \right\rangle + \left\langle \mathrm{H}_2 \right\rangle + \left\langle \frac{e^2}{\left|\vec{r}_1 - \vec{r}_2\right|} \right\rangle =$