

Fine Structure of Hydrogen

• relativistic corrections + spin-orbit

$$\Delta E_{FS} \sim \alpha^4 mc^2$$

Relativistic: $K = \sqrt{p^2 c^2 + m^2 c^4} - mc^2$
 $\approx \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2} + \dots$

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\hat{H}_0} - \underbrace{\frac{e^2}{4\pi\epsilon_0}}_{\hat{V}_C} \frac{1}{r} - \underbrace{\frac{\hat{p}^4}{8m^3 c^2}}_{\hat{V}}$$

$$\left[\frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \right] |n\ell m m_s\rangle = E_n^0 |n\ell m m_s\rangle$$

↳ this is an eigenstate of the unperturbed Hamiltonian

$$\Rightarrow \hat{p}^2 |n\ell m m_s\rangle = 2m(E_n^0 - \hat{V}_C) |n\ell m m_s\rangle$$

$$\begin{aligned} \Delta E_{rel} &= \langle n\ell m m_s | -\frac{\hat{p}^4}{8m^3 c^2} | n\ell m m_s \rangle \\ &= \frac{1}{8m^3 c^2} \langle n\ell m m_s | (2m)^2 (E_n^0 - \hat{V}_C)^2 | n\ell m m_s \rangle \\ &= \frac{1}{2mc^2} \langle n\ell m m_s | [E_n^{02} - 2E_n^0 \hat{V}_C + \hat{V}_C^2] | n\ell m m_s \rangle \\ &= \frac{1}{2mc^2} \langle n\ell m m_s | \left[E_n^{02} - 2E_n^0 \frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{r^2} \right] | n\ell m m_s \rangle \end{aligned}$$

Aside: $\langle n\ell m m_s | \frac{1}{r^2} | n\ell m m_s \rangle$

$$\int d^3r' |r'\rangle \langle r'| \int d^3r |r\rangle \langle r|$$

$$= \int d^3r \int d^3r' \underbrace{\langle n\ell m m_s | r' \rangle}_{\Psi_{n\ell m m_s}(r')} \underbrace{\langle r' | \frac{1}{r^2} | r \rangle}_{\frac{1}{r^2} \langle r' | r \rangle} \underbrace{\langle r | n\ell m m_s \rangle}_{\Psi_{n\ell m m_s}(r)}$$

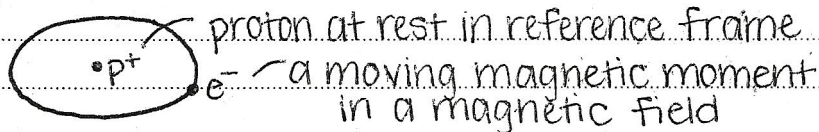
$$= \int d^3r |\Psi_{n\ell m m_s}(r)|^2 \frac{1}{r^2} \sim \frac{1}{a^3 n^3}, \frac{1}{r}, \frac{1}{r^2} \quad a = \text{Bohr radius}$$

"You're stuck on a desert island and you absolutely must calculate this matrix element or else the world is going to be blown up by aliens. You have the sand, a tiny stick, and 15 seconds before you're responsible for the death of everyone you love."

$$\Delta E_{rel} = \frac{-\alpha^4 mc^2}{2n^4} \left[\frac{n}{l+1/2} - \frac{3}{4} \right]$$

↳ change in energy = sandwich of the perturbation

Spin-Orbit



in the e^- frame: r - charge of the electron

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0 e}{2r T} \text{ - period} = \frac{\mu_0 e L}{4\pi m r^3} = \frac{e L}{4\pi m r^3 c^2 \epsilon_0}$$

$c^2 = 1/\mu_0 \epsilon_0$

$$L = mvr = mr \frac{2\pi r}{T}$$

L - angular momentum in the frame of the proton

$$\hat{H} = -\hat{\mu} \cdot B \text{ - magnetic field}$$

$\hat{\mu}$ - magnetic moment

$\hat{H}$ - Hamiltonian related to spin-orbit only

$$= - \left(\frac{-eg}{2m} \hat{S} \right) \left(\frac{eL}{4\pi m r^3 c^2 \epsilon_0} \right)$$

L - Can't just be viewed as a spinning ball of charge
 must use "fudge factor", g

g - gyromagnetic factor

→ heavy particles - small dipole moment

→ light particles - large dipole moment

$$g_{e^-} = 2 + \frac{\alpha}{\pi} + \dots$$

$$= \frac{1}{2} g \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2 c^2 r^3} \hat{S} \cdot \hat{L}$$

$$\frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$$

"Thomas Precession" - factor to correct for switching reference frames from the moving electron to the stationary proton

→ What's the expectation value in the unperturbed state?

- Creates shifts in energy values

$$(\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}$$

$$\langle nlm m_s | \hat{L}^2 | nlm m_s \rangle$$

$$\hbar^2 l(l+1) | nlm m_s \rangle$$

$\hat{S}$ - total spin, not z -component

$$\langle nlm m_s | \hat{S}^2 | nlm m_s \rangle$$

$$\hbar^2 \frac{1}{2}(\frac{1}{2}+1) | nlm m_s \rangle$$

10/19/12

Fine Structure of Hydrogen, con't

• relativistic corrections + spin orbit

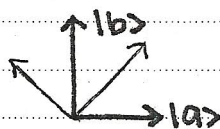
$$\hat{H}_{rel} = \frac{-\hat{p}^4}{8m^3c^2}$$

$$\hat{H}_{s.o.} = \frac{q}{2} \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2c^2r^3} \hat{S} \cdot \hat{L}$$

$$\Delta E_{rel} = \frac{-\alpha^4 mc^2}{2n^4} \left(\frac{n}{l + \frac{1}{2}} - \frac{3}{4} \right)$$

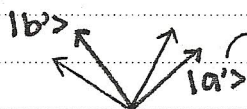
↳ energy now depends both on n & l

$|n, l=1, m=-1, 0, 1, m_s=\pm\frac{1}{2}\rangle$
 $|n, l=0, m=0, m_s=\pm\frac{1}{2}\rangle$ } same energy $\Rightarrow$ degenerate



$$\hat{H}_0(\alpha|a\rangle + \beta|b\rangle) = E_0(\alpha|a\rangle + \beta|b\rangle)$$

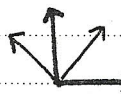
↳ unperturbed Hamiltonian



also eigenstates of this unperturbed Hamiltonian

↳ applying the perturbation "lifts" this degeneracy

→ forces us to choose the correct original basis that is close to the perturbation (which is assumed "small")



$|n, l, m, m_s\rangle$

$|n, l=1, j=3/2, m_j=1/2\rangle =$



$|n, l, j, m_j\rangle$

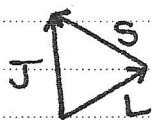
$\begin{cases} \# |n, l=1, m=1, m_s=-1/2\rangle + \\ \# |n, l=1, m=0, m_s=1/2\rangle \end{cases}$

↳ Clebsch-Gordon coefficients

$|n, l=1, j=1/2, m_j=1/2\rangle =$

$\begin{cases} \# |n, l=1, m=1, m_s=-1/2\rangle + \\ \# |n, l=1, m=0, m_s=1/2\rangle \end{cases}$

↳ new CG coefficients create a new set of states with the same l and therefore the same energy (degenerate)



$$\hat{J}^2 = (\hat{L} + \hat{S})^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{S} \cdot \hat{L}$$

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

$$\Delta E_{s.o.} = \langle n, l, j, m_j | \frac{e^2}{8\pi\epsilon_0} \frac{1}{m^2c^2} \frac{1}{r^3} \frac{1}{2} (\hat{J}^2 - \hat{L}^2 - \hat{S}^2) | n, l, j, m_j \rangle$$

$$\hbar^2 [j(j+1) - l(l+1) - \frac{1}{2}(1+\frac{1}{2})]$$

$$= \frac{e^2}{8\pi\epsilon_0} \frac{\hbar^2}{m^2c^2} [j(j+1) - l(l+1) - \frac{3}{4}] \langle n, l, j, m_j | \frac{1}{r^3} | n, l, j, m_j \rangle$$

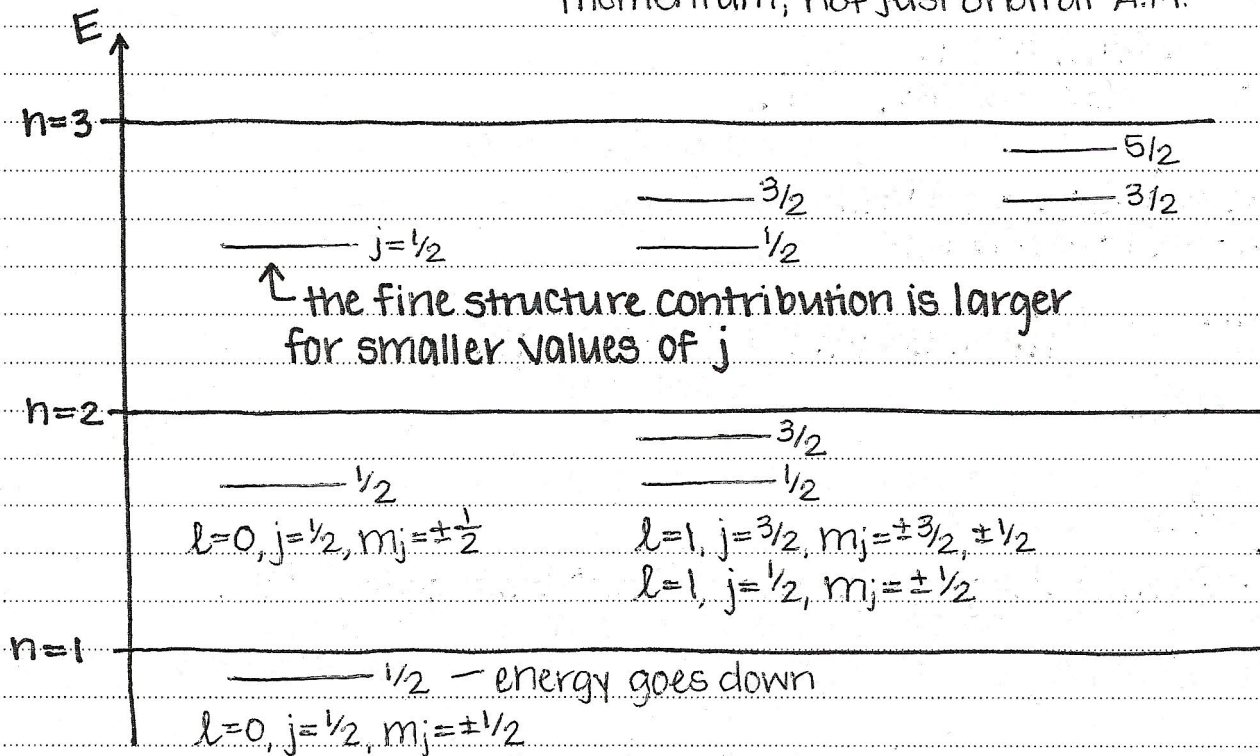
$$\frac{1}{l(l+\frac{1}{2})(l+1)n^3} \frac{1}{a^3} \leftarrow \text{Bohr radius}$$

$j = l \pm \frac{1}{2}$, but in either case with minimum $j = \frac{1}{2}$ and $n = 1$, the contribution of this for most states will be negative

$$\Delta E_{f.s.} = \frac{\alpha^4 mc^2}{4n^4} \left[\frac{3}{2} - \frac{2n}{j + \frac{1}{2}} \right]$$

$\Delta E_{rel} + \Delta E_{s.o.}$

L dependent only on total angular momentum, not just orbital A.M.



Zeeman Effect

$\hat{H}_z = -(\hat{\mu}_L + \hat{\mu}_S) \cdot \mathbf{B}$

magnetic moment due to spin
 magnetic dipole (not an operator)
 → behaves classically
 magnetic moment due to orbital motion (angular momentum)
 part of the Hamiltonian that describes the interaction with $\mathbf{B}$

$$= -\left(-\frac{e}{2m}\hat{\mathbf{L}} - \frac{e}{2m}g\hat{\mathbf{S}}\right) \cdot \mathbf{B}$$

$g_e = 2.0002...$ (gyromagnetic factor)

Weak Field Zeeman Effect

Zeeman Energy $\ll$ Fine-Structure

$$\sim (e\hbar/m)\mathbf{B}$$

$$\sim \alpha^4 mc^2$$

$$\Rightarrow \mathbf{B} \ll \frac{\alpha^4 m^2 c^2}{e\hbar}$$

Weak field limit

want to use states with good $|n \ell j m_j\rangle$ for perturbation

total z-component

total (orbital + spin)

unperturbed states calculated without $\mathbf{B}$ -field

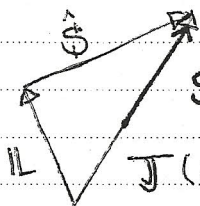
$$\Delta E_z = \langle n \ell j m_j | \frac{e}{2m}(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \mathbf{B} | n \ell j m_j \rangle$$

$\mathbf{B} \hat{=}$ $\mathbf{B}$ -field in the z-direction

$$\frac{e}{2m}(\hat{L}_z + 2\hat{S}_z)B$$

$$\hat{J}_z + \hat{S}_z$$

Aside: Classical Model for Average Values



$$S_{\text{avg}} = \frac{\mathbf{S} \cdot \mathbf{J}}{J^2} = \frac{L^2 + J^2 - S^2}{2} \frac{J}{J^2}$$

$\mathbf{J}$ (conserved)

$$\Delta E_z = B \frac{e\hbar}{2m} \langle n \ell j m_j | m_j + m_j \frac{(\ell(\ell+1) - j(j+1) - \frac{1}{2}(\frac{1}{2}+1))}{2j(j+1)} | n \ell j m_j \rangle$$

$$\Delta E_z = \underbrace{\frac{e\hbar}{2m}}_{\text{Landé factor}} \left[1 + \frac{l(l+1) - j(j+1) - 3/4}{2j(j+1)} \right] m_j B$$

Bohr magneton $\approx 579 \times 10^{-5} \text{ eV/T}$

↳ even if you apply a large $\vec{B}$ -field (0.1T), you only change the energy by a very small amount

Zeeman Effect, con't

Recap: part of the Hamiltonian that interacts with B

$$\hat{H}_z = -(\hat{\mu}_L + \hat{\mu}_S) \cdot B \approx \frac{e}{2m} (\hat{L} + 2\hat{S}) \cdot B$$

Weak-field: (zeeman energy $\ll$ fine-structure energy)

$$\Delta E_z = \langle n l j m_j | \frac{e}{2m} (\hat{L} + 2\hat{S}) \cdot B | n l j m_j \rangle$$

states chosen to work well with fine structure

$$= \frac{e\hbar}{2m} \left[\frac{1 + j(j+1) - l(l+1) + 3/4}{2j(j+1)} \right] m_j B$$

Landé factor

Bohr magneton $\sim 5 \times 10^{-5} \text{ eV/T}$

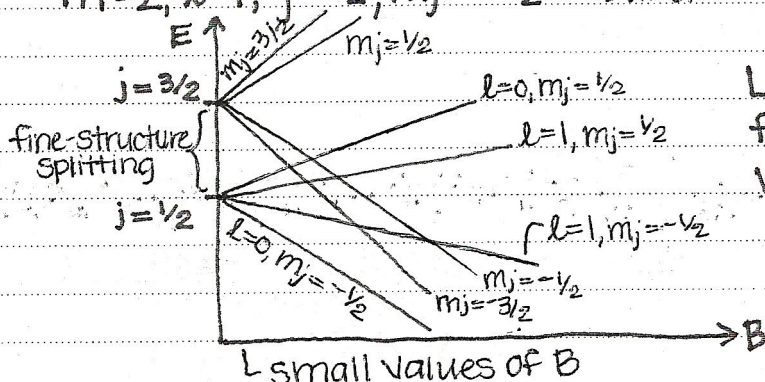
"There is a lesson to be learned here: just do what your advisor says!
You are not Peter Zeeman! And getting fired will not win you
the Nobel Prize!"

Example: $n=2$ levels in Hydrogen

$|n=2, l=0, j=1/2, m_j=\pm 1/2\rangle$ Landé = ± 1

$|n=2, l=1, j=3/2, m_j=\pm 3/2, \pm 1/2\rangle$ Landé = $\pm 2, \pm 2/3$

$|n=2, l=1, j=1/2, m_j=\pm 1/2\rangle$ Landé = $\pm 1/3$



Landé factor determines how fast the energy goes up or down when subjected to a B-field.

→ if it weren't for spin, none of this could be explained

Strong-Field Zeeman (Paschen-Back)

Zeeman energy $\gg$ fine-structure energy

$$\Delta E_z = \langle n l m_l m_s | \frac{e}{2m} (\hat{L} + 2\hat{S}) \cdot B | n l m_l m_s \rangle$$

$$= \frac{e\hbar}{2m} (m_l + 2m_s) B$$

P.B. coeff.

no longer have to use a basis suited for fine-structure

→

Example: $n=2$ levels of Hydrogen

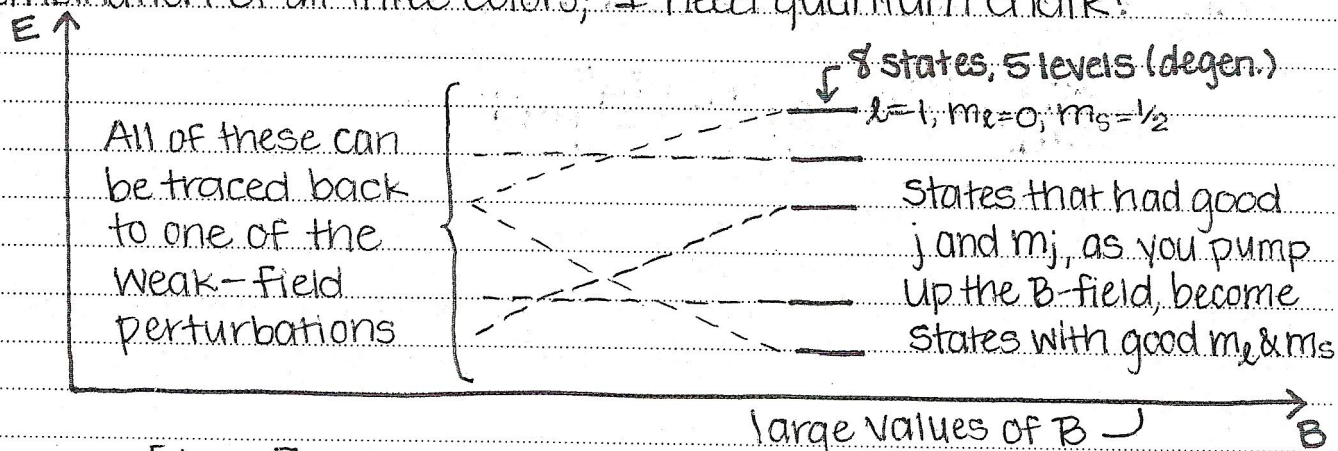
$|n=2, l=0, m_l=0, m_s=\pm\frac{1}{2}\rangle$ P.B. = ± 1

$|n=2, l=1, m_l=-1, m_s=\pm\frac{1}{2}\rangle$ P.B. = $0, -2$

$|n=2, l=1, m_l=0, m_s=\pm\frac{1}{2}\rangle$ P.B. = ± 1

$|n=2, l=1, m_l=1, m_s=\pm\frac{1}{2}\rangle$ P.B. = $2, 0$

"Should I draw this blue, pink, or green? It's a linear combination of all three colors; I need quantum chalk!"



Which $[j, m_j]$ states get traced back to is determined by what happens in the intermediate field case.

Hyperfine Structure

→ result of the interaction between the electron's and the proton's magnetic moments

↪ magnetic moment of the electron $\approx -\frac{e}{m} \hat{S}$ ($g_{1/2} \approx 1$)

$$\hat{H}_{\text{hf}} = -\hat{\mu}_e \cdot \mathbf{B} = -\hat{\mu}_e \cdot \left[\frac{\mu_0}{4\pi} \frac{1}{r^3} \left(\frac{3}{r^2} (\hat{\mu}_p \cdot \mathbf{r}) \mathbf{r} - \mu_p \right) + \frac{2\mu_0}{3} \mu_p \delta(\mathbf{r}) \right]$$

↪ magnetic moment of the proton
 $\approx \frac{e}{2m} g_p \hat{S}$ ($g_p \approx 5.58$)

Hyperfine Structure

→ Effective only for the ground state (otherwise negligible)

$$\hat{H}_{h.f.} = \frac{e^2}{2mM} g_p \hat{S}_e \cdot \hat{S}_p \left[\underbrace{\frac{\mu_0}{4\pi} \left(\frac{3}{r^2} \hat{r}^i \hat{r}^j - \delta^{ij} \right)}_{\text{first part}} + \underbrace{\frac{2\mu_0}{3} \delta^{ij} \delta(r)}_{\text{second part}} \right]$$

↑ electron mass
↑ proton mass

For the ground state:

$$\Delta E_{h.f.} = \langle n=1, l=0, m_l=0, m_s=\pm 1/2, m_p=\pm 1/2 | \hat{H}_{h.f.} | 1, 0, 0, \pm 1/2, \pm 1/2 \rangle$$

↳ unperturbed ground state

↳ z-component of the proton spin

$$\int d^3r |r\rangle \langle r| = \int dr d\Omega |r\theta\phi\rangle \langle r\theta\phi|$$

↳ spherical coords

First part:

$$\sim \int_0^\infty dr r^2 \int_0^\pi d\cos(\theta) \int_0^{2\pi} d\phi \underbrace{\Psi_{\text{ground}}^*(r, \theta, \phi)}_{\Psi_{\text{ground}}^*(r)} \left[\frac{3}{r^2} r^i r^j - \delta^{ij} \right] \underbrace{\Psi_{\text{ground}}(r, \theta, \phi)}_{\Psi_{\text{ground}}(r)}$$

↑ neglect constants for time being

$$\begin{aligned} r^1 &= r \sin(\theta) \cos(\phi) \\ r^2 &= r \sin(\theta) \sin(\phi) \\ r^3 &= r \cos(\theta) \end{aligned}$$

$$= \int_0^\infty dr r^2 |\Psi_{\text{gr}}(r)|^2 \int d\Omega \left[\frac{3}{r^2} r^i r^j - \delta^{ij} \right]$$

↳ $\int d\Omega$ integral over all angles (unit sphere)

Mathematical Aside:

$$\begin{aligned} \int_{\text{sphere}} d\Omega r^i r^j &= A \delta^{ij} \\ \downarrow \text{sum over } i=j \\ 4\pi \int_{\text{sphere}} d\Omega &= 3A \end{aligned} \quad \uparrow = \frac{1}{3} \delta^{ij}$$

$$= \int_0^\infty dr r^2 |\Psi_{\text{gr}}(r)|^2 \underbrace{\int d\Omega \left[\frac{3}{r^2} r^i r^j - \delta^{ij} \right]}_0$$

$$= 0$$

Second part: (full contribution to the hyperfine perturbation)

$$\Delta E_{h.f.} = \frac{e^2}{2mM} \frac{\mu_0}{4\pi} \langle n=1, l=0, m_l=0, m_s=\pm 1/2, m_p=\pm 1/2 | \hat{S}_e \cdot \hat{S}_p \delta(r) | 1, 0, 0, \pm 1/2, \pm 1/2 \rangle$$

$$\begin{aligned} \hat{S}_e \cdot \hat{S}_p &= \hat{S}_e^2 + \hat{S}_p^2 + 2\hat{S}_e \hat{S}_p = (\hat{S}_e + \hat{S}_p)^2 = \hat{S}_T^2 \\ &= \frac{1}{2} (\hat{S}^2 - \hat{S}_e^2 - \hat{S}_p^2) \end{aligned} \quad \text{↳ total spin}$$

need new basis because m_s and m_p are not well-defined for $(\hat{S}^2 - \hat{S}_e^2 - \hat{S}_p^2)$

→ choose S_T - total spin (0 or 1)

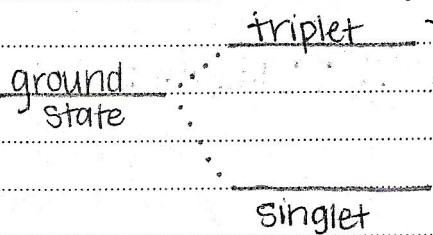
and m_T - z-component of total spin $(-S_T, \dots, 0, \dots, S_T)$

$$\Delta E_{h.f.} = \frac{e^2}{2mM} \frac{\mu_0}{4\pi} \langle n=1, l=0, m_l=0, S_T, m_T | \frac{1}{2} (\hat{S}_e^2 - \hat{S}_e^2 - \hat{S}_p^2) | 1, 0, 0, S_T, m_T \rangle$$

$\downarrow$ $S(r)$ only valid for $r=0$

$$= \frac{e^2}{2mM} \frac{\mu_0}{4\pi} |\psi_{\text{ground}}(0)|^2 \frac{1}{2} [S_T(S_T+1) - \frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1)]$$

$$= \frac{e^2}{2mM} \frac{\mu_0}{8\pi} |\psi_{\text{gr}}(0)|^2 \begin{cases} \frac{1}{2}, S_T=1 \text{ (triplet)} \\ -\frac{3}{2}, S_T=0 \text{ (singlet)} \end{cases}^{-3/2}$$



because of hyperfine structure,
we can now transition between
these two levels

$\lambda = 21 \text{ cm}$ } 21 cm radiation
 $\nu = 1420 \text{ MHz}$ } for mapping HII!

Variational Method

Aside: Eigenvalues & Expectation Values

$$\hat{H}|n\rangle = E_n|n\rangle$$

$$\langle n|\hat{H}|n\rangle = E_n \underbrace{\langle n|n\rangle}_1 = E_n$$

Ground state has smallest E_n

⇒ smallest expectation values

Variational principle: among all states ($\langle\psi|\psi\rangle = 1$), the ground state has the smallest $E = \langle\psi|\hat{H}|\psi\rangle$

$$\begin{aligned} \text{Proof: } \langle\psi|\hat{H}|\psi\rangle &= \sum_{n,m} \langle m|\psi_m^* \hat{H} \psi_n|n\rangle \\ &= \sum_{n,m} \psi_m^* \psi_n E_n \underbrace{\langle n|m\rangle}_{\delta_{nm}} \\ &= \sum_n E_n |\psi_n|^2 \geq E_{\text{ground}} \end{aligned}$$

↳ if all components are zero except the ground state, this will produce the lowest energy.

Anything else non-zero will contribute to E_n

Variational method:

1. Guess a bunch of $|\psi\rangle_s$ - not an iterative method, no problems of convergence

2. Find the $E = \langle\psi|\hat{H}|\psi\rangle$

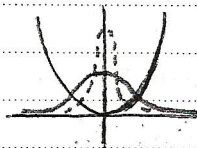
3. The best approximation to the true ground state is the $|\psi\rangle$ with the smallest value of E

* A variational calculation gives a rigorous upper-bound on the ground state energy E_{ground}

* However, your calculation is as good as your guesses

Example: Harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2} \hat{x}^2$$



$|\psi\rangle = \int dx \psi(x) |x\rangle$ "You talk to your muses and they whisper in your ear what would be a good guess"

$$\psi_b(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx}$$

↳ Variational parameter

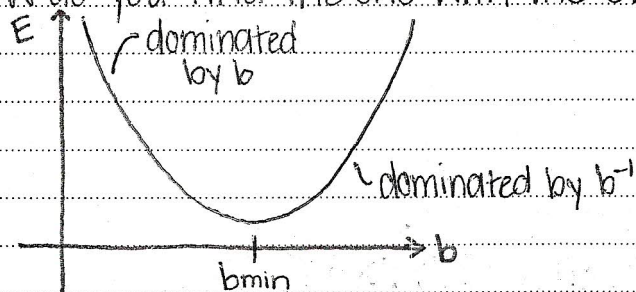
(open → a whole family of answers)

$$E(b) = \underbrace{\langle\psi|}_{\text{I}} \underbrace{\hat{H}}_{\text{I}} \underbrace{|\psi\rangle}_{\text{I}}$$

$$E(b) = \int_{-\infty}^{\infty} dx \psi_b^*(x) \left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m\omega^2}{2} x^2 \right] \psi_b(x)$$

$$= \frac{\hbar^2}{2m} b + \frac{m\omega^2}{8b}$$

How do you find the one with the smallest energy?



↑ use a derivative to find min value

$$0 = \frac{dE(b)}{db} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} \Big|_{b=b_{\min}}$$

$$b_{\min} = m\omega / 2\hbar$$

$$\psi_{b_{\min}}(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega}{2\hbar} x^2}$$

$$E_{\text{ground}} = \frac{\hbar^2}{2m} \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \frac{2\hbar}{m\omega} = \frac{\hbar\omega}{2} \leftarrow \text{exact known ground state solution}$$

"It's always better to speak German. And if you can't, at least speak English with a British accent. Or you can just speak like me and sound like Count Dracula. Mwa ha ha, I have been practicing for tonight."

Example: Helium atom

$$\hat{H} = \underbrace{\frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2)}_{\text{kinetic energy}} - \underbrace{\frac{e^2}{4\pi\epsilon_0} \left(\frac{2}{r_1} + \frac{2}{r_2} \right)}_{\text{Coulomb repulsion}} - \underbrace{\frac{1}{|r_1 - r_2|}}_{\text{interaction term (nucleus-e\#1, nucleus-e\#2)}}$$

- spin-singlet

$$\psi(r_1, r_2) = \frac{Z^3}{\pi a^3} e^{-\frac{Z}{a}(r_1 + r_2)}$$

↑
Bohr radius

↑
variational parameter

→ use atomic number, Z , as variational parameter (cannot be > 2)

Rewrite Hamiltonian such that $\Psi(r_1, r_2)$ is an eigenstate

$$\hat{H} = \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z-2}{r_1} + \frac{Z-2}{r_2} + \frac{1}{|r_1 - r_2|} \right)$$

H' - non-interacting particles of charge Z

$$E(Z) = \langle \Psi | H' + \frac{e^2}{4\pi\epsilon_0} (Z-2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_1 - r_2|} | \Psi \rangle$$

$$= 2E_0(Z) + \frac{e^2}{4\pi\epsilon_0} (Z-2) 2 \langle \frac{1}{r} \rangle_0 + \frac{e^2}{4\pi\epsilon_0} \langle \Psi | \frac{1}{|r_1 - r_2|} | \Psi \rangle$$

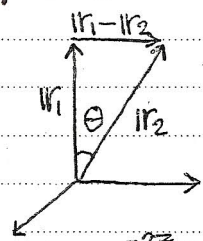
ground state of the Hydrogen atom with charge Z

expectation value of one particle in the ground state (moving around a nucleus with charge Z)

$$\langle \Psi | \frac{1}{|r_1 - r_2|} | \Psi \rangle = \int d^3r_1 d^3r_2 \left(\frac{Z^3}{\pi a^3} \right)^2 \frac{1}{|r_1 - r_2|} e^{-\frac{2Z}{a}(r_1 + r_2)}$$

$$= \int d^3r_1 \left(\frac{Z^3}{\pi a^3} \right)^2 e^{-\frac{2Z}{a}r_1} \int d^3r_2 \frac{1}{|r_1 - r_2|} e^{-\frac{2Z}{a}r_2}$$

$$\int_0^\infty dr_2 \int_{-1}^1 d\cos(\theta) \int_0^{2\pi} d\phi \frac{e^{-\frac{2Z}{a}r_2}}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos(\theta)}}$$



$$= \int d^3r_1 \left(\frac{Z^3}{\pi a^3} \right)^2 e^{-\frac{2Z}{a}r_1} \int_0^\infty dr_2 r_2^2 2\pi e^{-\frac{2Z}{a}r_2} \frac{(|r_1 + r_2| - |r_1 - r_2|)}{r_1 r_2}$$

$$2\pi e^{-\frac{2Z}{a}r_2} \cdot \frac{2}{r_2} \text{ (larger of } r_1 \text{ and } r_2)$$

$$4\pi \int_0^{r_1} dr_2 r_2^2 e^{-\frac{2Z}{a}r_2} + \int_{r_1}^\infty dr_2 r_2^2 e^{-\frac{2Z}{a}r_2}$$

$$\frac{\pi a^3}{Z^3} \frac{1}{r_1} \left[a \left(e^{\frac{2Z}{a}r_1} - 1 \right) - Zr_1 \right]$$

$$= \int d^3r_1 \left(\frac{Z^3}{\pi a^3} \right)^2 e^{-\frac{2Z}{a}r_1} \left\{ \frac{\pi a^3}{Z^3} \frac{1}{r_1} \left[a \left(e^{\frac{2Z}{a}r_1} - 1 \right) - Zr_1 \right] \right\}$$

$$= \frac{5}{8} \frac{Z}{a}$$

$$\rightarrow E = \underbrace{-2Z^2 \alpha^2 \frac{mc^2}{2}}_{E_0(Z)} + \underbrace{2Z \frac{\alpha \hbar c}{a} (Z-2)}_{\alpha^2 mc^2} + \underbrace{Z \frac{5}{8} \frac{\alpha \hbar c}{a}}_{\alpha^2 mc^2}$$

$$= -\alpha^2 \frac{1}{2} mc^2 [-2Z^2 + 2Z(Z-2) + 5/8 Z]$$

$$0 = \frac{dE}{dz} \Big|_{z=z_{\min}}$$

$$\Rightarrow z_{\min} = \frac{27}{16} \approx 1.69 \quad \text{shielding} \rightarrow \text{effective charge} < 2$$

(perfect shielding $z=1$)

$$E_{\min} = \frac{\alpha^2 mc^2}{2} \left[2z^2 - \frac{27}{4} \right] \Big|_{z=\frac{27}{16}} \approx -77.5 \text{ eV}$$

Upper bound

actual answer $\approx -79 \text{ eV}$ (from experiment)

11/2/12

Variational Methods, con't

Example: Hydrogen Atom

$$l=0: \hat{H} = \frac{-\hbar^2}{2m} \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \right) - \frac{e^2}{4\pi\epsilon_0 r}$$

1. Ansatz

$$\psi(r) \sim \frac{1}{\lambda^{3/2}} e^{-r/\lambda} \quad \text{Variational parameter: how far you have to go in } r \text{ to make your wavefunction die off appreciably}$$

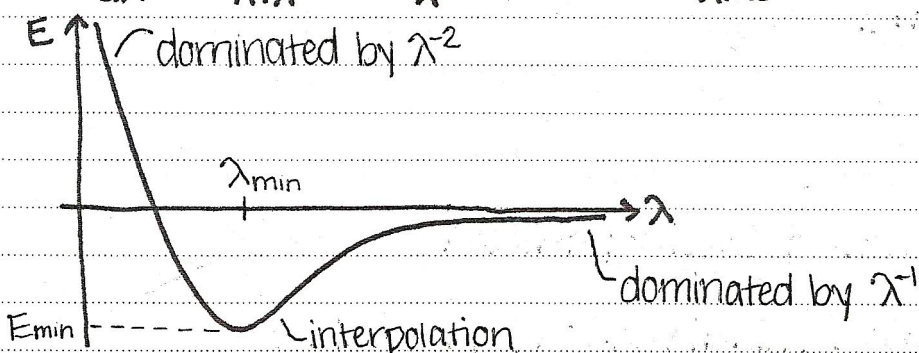
2. $E = \langle \psi | \hat{H} | \psi \rangle$

$$E = \left\langle \frac{\hat{p}^2}{2m} \right\rangle + \langle \hat{V} \rangle$$

$$= \# \frac{\hbar^2}{m} \frac{1}{\lambda^2} - \# \frac{e^2}{4\pi\epsilon_0 \lambda} \quad \text{chosen by dimensional analysis}$$

3. $E_{\min} = ?$

$$0 = \frac{dE}{d\lambda} = -\frac{\# \hbar^2}{m \lambda^3} + \frac{\# \alpha \hbar c}{\lambda^2} \Rightarrow \lambda_{\min} \sim \frac{\hbar}{\alpha m c}$$



$$E(\lambda = \lambda_{\min}) \sim \# \frac{\hbar^2}{m} \frac{\alpha^2 m^2 c^2}{\hbar^2} - \# \alpha \hbar c \frac{\alpha m c}{\hbar}$$

$\sim \alpha^2 m c^2$ (as expected from perturbation theory)

→ The best way of thinking is not in terms of the Schrödinger equation, but in terms of minimizing the energy

Another Ansatz: $\psi(r) \sim \frac{1}{\lambda^{3/2}} e^{-r^2/\lambda^2}$ Gaussian

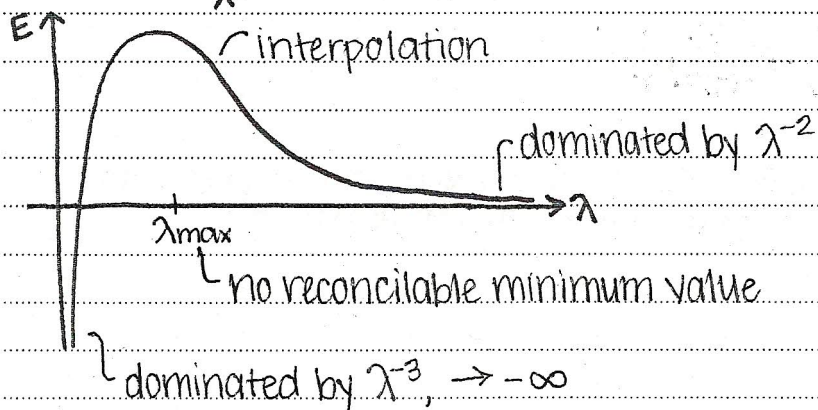
$$E = \# \frac{\hbar^2}{m} \frac{1}{\lambda^2} - \# \frac{\alpha \hbar c}{\lambda} \Rightarrow \lambda_{\min} \sim \frac{\hbar}{\alpha m c}, \quad E(\lambda_{\min}) \sim \alpha^2 m c^2$$

our numerical factors have changed, but even with a stupid ansatz, you get an answer that is still in the right neighborhood!

including the numerical factors: $E(\lambda_{\min}) = \frac{-4}{3\pi} \alpha^2 m c^2$

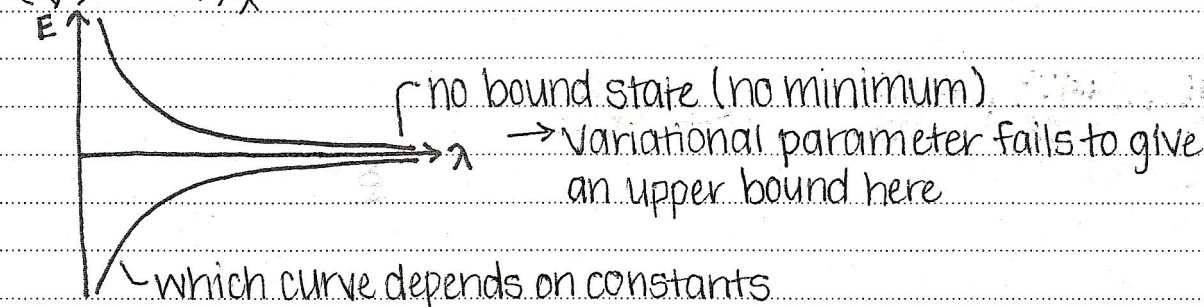
0.42 - correct answer = 0.5

If your potential was now $-\beta/r^3$ (dipole approximation)
 $\Rightarrow \langle \hat{V} \rangle \sim -\frac{\beta}{\lambda^3}$ $\hookrightarrow$ collapses at short distances



$$V = -\beta/r^2$$

$$\langle \hat{V} \rangle \sim -\frac{\beta}{\lambda^2}$$

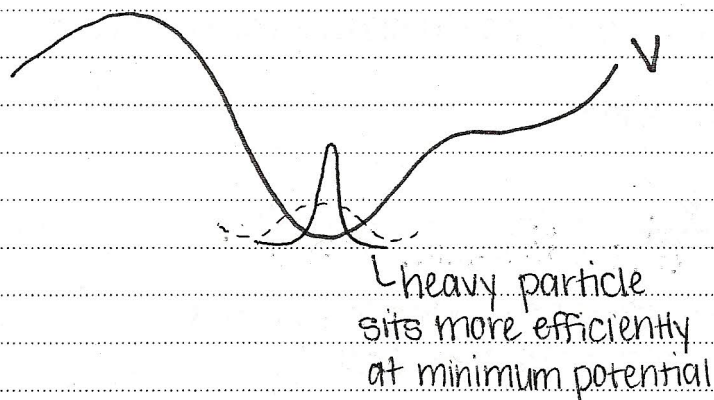


What happens if you have a heavier particle?

(like a muon $\rightarrow$ original Hamiltonian)

- Collapse prevention term (kinetic energy / uncertainty principle) is less effective

i.e. the particle will sit (and fluctuate) closer to the minimum energy value (potential)



"If you put an elephant at the bottom of a potential, you don't talk about that elephant having quantum fluctuations because its wavefunction is very steep"

11/5/12

WKB Approximation

"It's called WKB because it was invented by a guy named Jeff"

Valid for: semiclassical situations, excited states, etc.

Basic Idea: $V(x) = \text{constant}$, $\Psi(x) = A e^{\pm \frac{i}{\hbar} \int^x \sqrt{2m(E-V)} dx}$

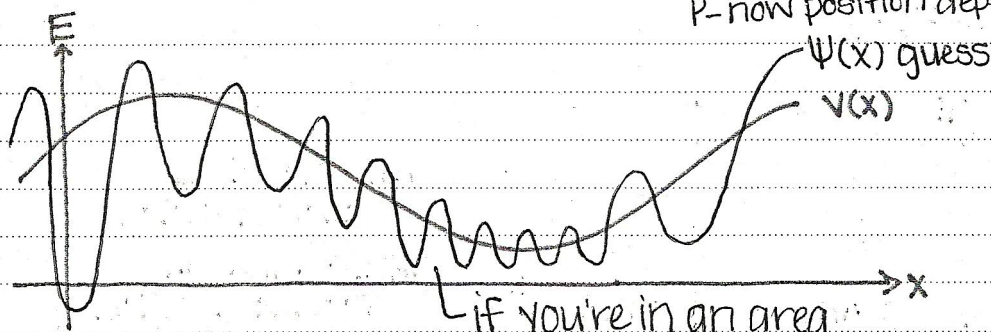


Plane wave to the right or left

Variation in space, slow compared to variation in Ψ

$V(x)$ varies slowly, $\Psi(x) \approx A(x) e^{\pm \frac{i}{\hbar} \int^x \sqrt{2m[E-V(x)]} dx}$

P - now position dependent



If you're in an area where $x \gg E$, the particle has more momentum and oscillates faster

changes slowly

General Form: $\Psi(x) = A(x) e^{\frac{i\phi(x)}{\hbar}}$, look at $\hbar \rightarrow 0$ limit (regions of small $\hbar \rightarrow$ fast phase change)

* By small $\hbar$, we mean small compared to what's on top $\rightarrow \hbar \ll \psi$

"It's Alice in Wonderland, you can choose to see yourself as unusually small or the bugs as unusually big!"

$$\frac{d}{dx} \Psi = \left(A' + \frac{i}{\hbar} \Psi' A \right) e^{i\phi/\hbar}$$

$$\frac{d^2}{dx^2} \Psi = \left(A'' + \frac{iA}{\hbar} \Psi'' + \frac{2i}{\hbar} \Psi' A' - \frac{\Psi'^2}{\hbar^2} A \right) e^{i\phi/\hbar}$$

Schrödinger Equation: $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi = (E - V) \Psi$

$$\left[A'' + \frac{i}{\hbar} A \Psi'' + \frac{2i}{\hbar} A' \Psi' - \frac{\Psi'^2}{\hbar^2} A \right] e^{i\phi/\hbar} = \frac{-2m}{\hbar^2} (E - V) A e^{i\phi/\hbar}$$

$\sim \hbar^0$ $\sim \hbar^{-1}$ $\sim \hbar^{-2}$ $\sim \hbar^{-2}$
 $\uparrow$ really $\uparrow$ small correction dominates for small $\hbar$

Neglecting small correction terms:

$$\Rightarrow \Psi'^2 = 2m[E - V(x)]$$

$\hookrightarrow$ satisfies the Schrödinger equation to $1/\hbar^2$ order

$$\Psi' = \pm \sqrt{2m[E - V(x)]}$$

$A\psi'' + 2A'\psi' = 0$ Schrödinger eq. satisfied to $1/\hbar$ order

$$(A^2\psi')' \Rightarrow A = \frac{\text{const}}{(\psi')^{1/2}} = \frac{\text{constant}}{(2m[E-V(x)])^{1/4}}$$

In the WKB Approximation:

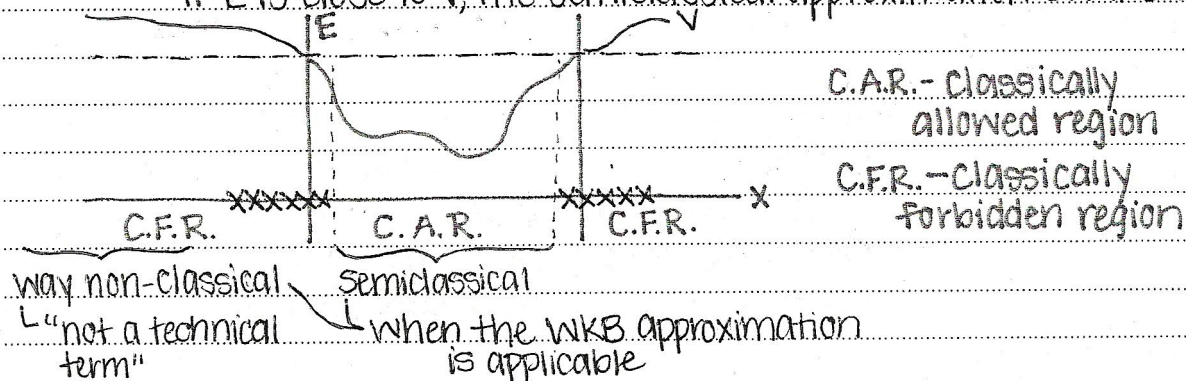
$$\psi(x) = \frac{\text{constant}}{(2m[E-V(x)])^{1/4}} e^{\pm i/\hbar \int^x dx' \sqrt{2m[E-V(x')]} P(x')}$$

Validity region: $\frac{\psi'A'}{\hbar} \ll \frac{A\psi'^2}{\hbar^2} \Rightarrow \underbrace{\sqrt{2m(E-V)}}_{P(x)} \frac{d}{dx} \frac{1}{[2m(E-V)]^{1/4}} \ll \frac{1}{\hbar} \frac{2m(E-V)}{[2m(E-V)]^{1/4}}$

$\hookrightarrow$ neglecting constants $\frac{P(x)}{P(x)^{3/2}} \frac{d}{dx} V \ll \frac{1}{\hbar} P^2(x)$

$$\Rightarrow \frac{1}{P(x)} \frac{dV}{dx} \ll \frac{1}{\hbar} P^2(x)$$

if E is close to V , the semiclassical approximation breaks down



Intuitive interpretation:

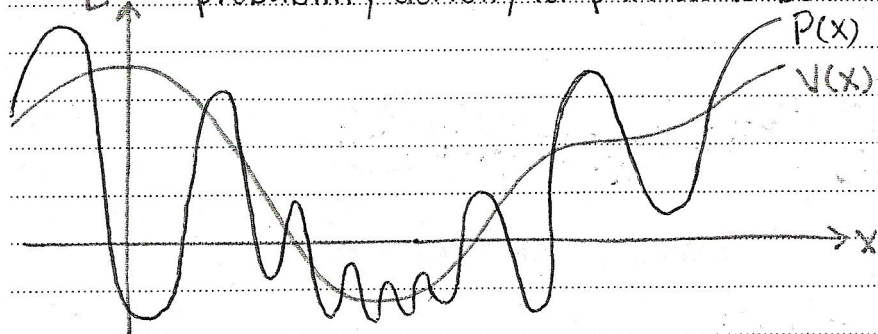
$$\psi(x) \approx \frac{\text{const}}{\sqrt{P(x)}} e^{\pm i/\hbar \int^x dx' P(x')}$$

$$P(x) = m \cdot v(x)$$

$\hookrightarrow$ velocity

$$|\psi(x)|^2 \approx \frac{\text{const}}{m \cdot v(x)}$$

$\hookrightarrow$ probability density for particle to be at x



$\rightarrow$ the phase changes to be like the local momentum

$\rightarrow$ oscillations change quickly while potential varies slowly

11/7/12

WKB Approximation, con't

$\psi(x) = \frac{C}{\sqrt{p(x)}} e^{\pm \frac{i}{\hbar} \int^x dx' p(x')}$

 ~ (velocity)^{-1/2}

[determined by normalization] $\sqrt{2m[E - V(x')]} \quad \leftarrow \text{no lower bound needed because it's in the exponent}$

Less likely to find the particle when it's moving quickly

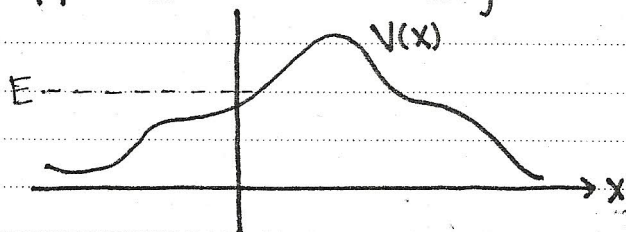
$\int^x p$ sets your wavelength

Valid For: $\psi' \gg \frac{A'}{A} \Rightarrow \frac{1}{p(x)} \ll \frac{1}{p} \frac{dp}{dx}$ — the length over which the wavelength changes

$\sqrt{p(x)} \frac{d}{dx} [p(x)]^{-1/2} \sim \frac{1}{p(x)} \frac{dp}{dx}$

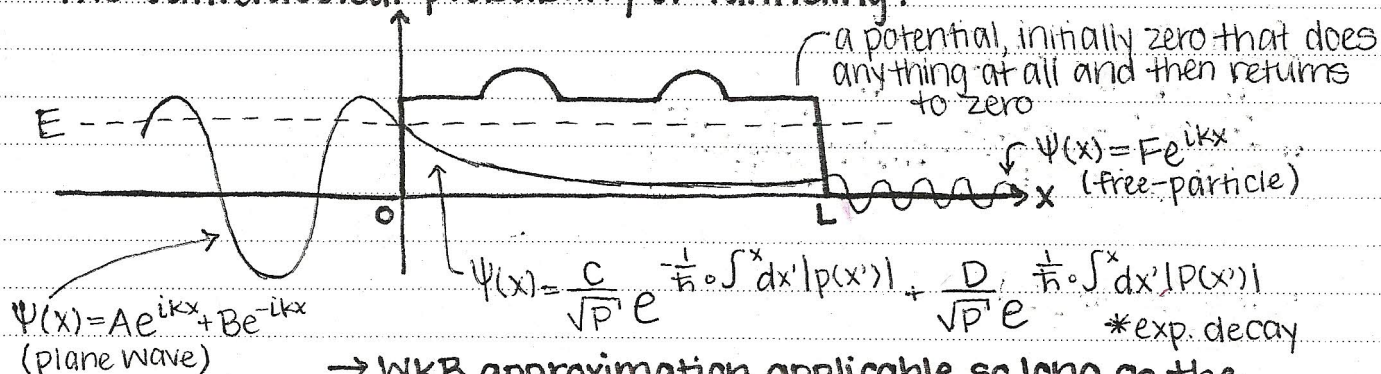
→ the wavelength must change slowly in order for the WKB approximation to be valid

Application: Tunneling



Classically, the particle will hit the potential barrier and slide back down.

Suppose you have a generic potential. How do you determine the semiclassical probability of tunneling?



→ WKB approximation applicable so long as the potential varies slowly with respect to x

* for large L , $D=0$

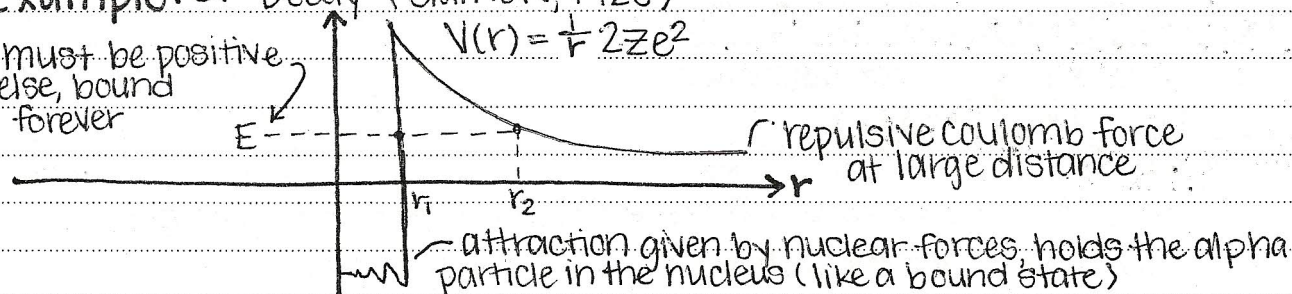
Tunneling Probability: $\frac{|F|^2}{|A|^2}$ — the ratio of the magnitudes of the wavefunctions determines how much tunneling happens

$$\sim e^{-\frac{2}{\hbar} \int^L dx \sqrt{2m[V(x) - E]}} \quad (\text{for large } L)$$

→

Example: α -Decay (Gamow, 1928)

must be positive
else, bound
forever



r_1 - point where the coulomb force shuts off & nuclear force takes over

r_2 - distance beyond which the alpha particle can move classically

$$E = \frac{2Ze^2}{r_2}$$

↓ "Gamma for Gamow!"

tunneling probability $\sim e^{-2\gamma}$

$$\gamma = \frac{1}{\hbar} \int_{r_1}^{r_2} dr \sqrt{2m \left(\frac{2Ze^2}{r} - \frac{2Ze^2}{r_2} \right)}$$

mass of the α -particle

$2mE \left(\frac{r_2}{r} - 1 \right)$

$$= \frac{\sqrt{2mE}}{\hbar} \int_{r_1}^{r_2} dr \sqrt{\frac{r_2}{r} - 1}$$

$$= \frac{\sqrt{2mE}}{\hbar} \left[r_2 \left(\frac{\pi}{2} - \arcsin \left(\sqrt{\frac{r_1}{r_2}} \right) - \sqrt{r_1(r_2 - r_1)} \right) \right]$$

assume $r_2 \gg r_1$ (which is about the size of the nucleus)

$$\Rightarrow \frac{\sqrt{2mE}}{\hbar} \left[\frac{\pi r_2}{2} - 2\sqrt{r_1 r_2} \right]$$

$$= \frac{\sqrt{2mE}}{\hbar} \left[\frac{\pi}{2} \frac{2Ze^2}{E} - 2\sqrt{r_1} \sqrt{\frac{2Ze^2}{E}} \right]$$

r_2 is not useful, E is measurable in the lab

$$= \# \frac{1}{\sqrt{E}} - \# \sqrt{Zr_1}$$

$\approx 2\sqrt{\text{MeV}}$

$\approx 1.5 \sqrt{\text{Fermi length}}$

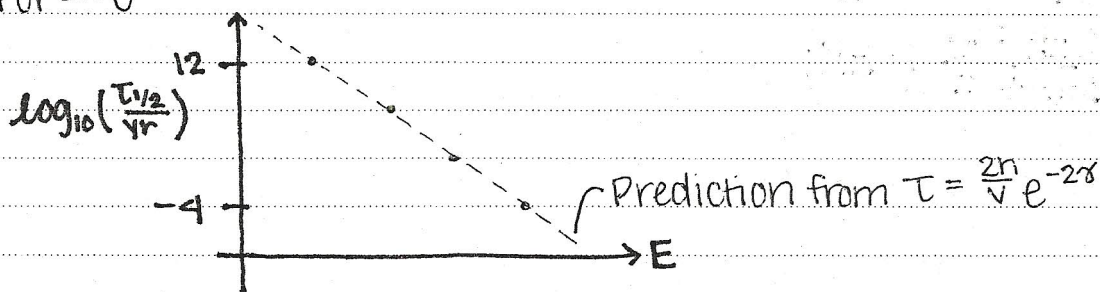
tunneling probability
at each attempt

$$T_{1/2} = \frac{2r_1}{v} e^{-2\gamma}$$

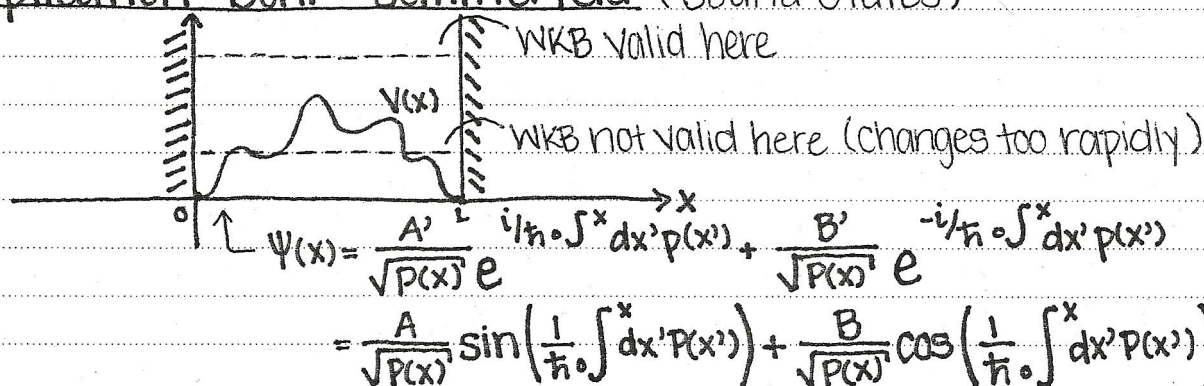
velocity of the α -particle inside the nucleus

$1/2$ lifetime of the α -decay

For ^{238}U



Application: Bohr-Sommerfeld (Bound States)



Boundary conditions: $\Psi(0) = 0 \Rightarrow B = 0$

$\Psi(L) = 0 \Rightarrow \sin\left(\frac{1}{\hbar} \int^L dx' p(x')\right) = 0$

$\Rightarrow \frac{1}{\hbar} \int^L dx' p(x') = n\pi$ for $n=1, 2, 3, \dots$

Bohr-Sommerfeld quantization condition:

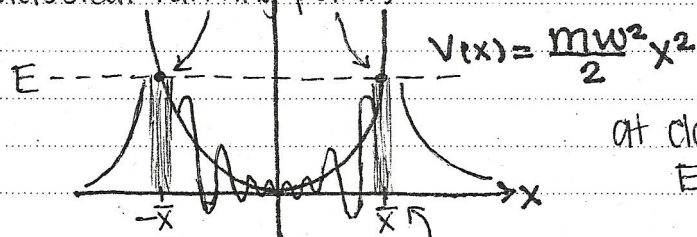
→ An approximation, discovered BEFORE quantum mechanics

$$\oint dx \sqrt{2m[E - V(x)]} = n\pi\hbar \text{ for } n=1, 2, 3$$

↑ actually $(n + 1/2)$ for potentials with 2 turning points & proper mathematical care taken

Example: Harmonic Oscillator

Classical turning points



at classical turning points
 $E = \frac{1}{2} m\omega^2 \bar{x}^2$

WKB breaks down when KE is comparable to $V(x)$

→ We must assume that the area in which the WKB approximation breaks down is sufficiently narrow and that we may thereby apply the Bohr-Sommerfeld formula

$$\text{BS.} = \int_{-\bar{x}}^{\bar{x}} dx \sqrt{2m(E - \frac{m\omega^2}{2}x^2)}$$

$$= \underbrace{\sqrt{2mE}}_{\frac{E}{\omega} \pi} \sqrt{\frac{2E}{m\omega^2}} \frac{\pi}{2} = n\pi\hbar$$

$$\Rightarrow E = n\hbar\omega \text{ for } n=1,2,3$$

exact result: $E = \hbar\omega(n + \frac{1}{2})$ for $n=0,1,2,\dots$

→ only off by $\frac{1}{2}\hbar\omega$ which is very good since for $n \gg 1$, $E \approx n\hbar\omega$
and Bohr-Sommerfeld is mostly valid for highly excited states

11/9/12

Even More WKB Approximation

Recap: $\downarrow$ normalization constant

$$\Psi(x) = \frac{C}{\sqrt{P(x)}} e^{\pm i/\hbar \int^x dx' P(x')} \sqrt{2m[E-V(x)]}$$

Valid For: $\frac{\hbar}{P(x)} \ll \frac{\hbar}{\frac{1}{P} \frac{dP}{dx}}$

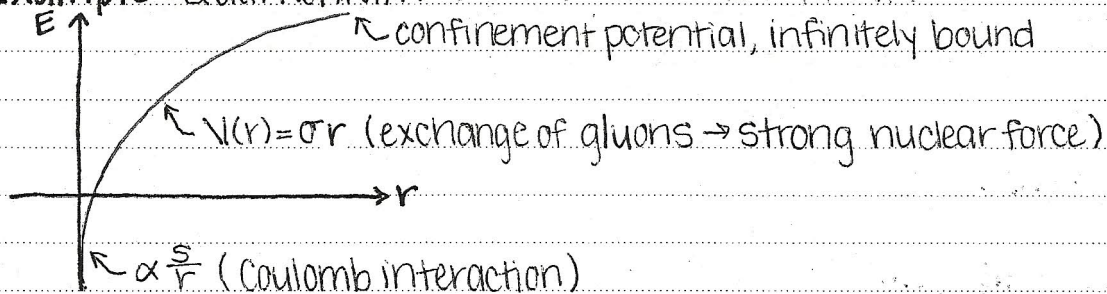
DeBroglie wavelength @ position x

$\Rightarrow$ Transmission Probability $\sim e^{-\frac{2}{\hbar} \int dx \sqrt{2m[V(x)-E]}}$ $\leftarrow$ quantum tunneling

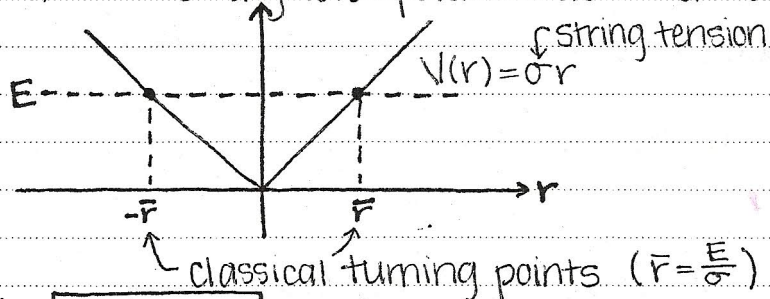
$\Rightarrow$ Quantization Condition $\int_{x_1}^{x_2} dx \sqrt{2m[E-V(x)]} = n\pi\hbar$ for $n=1,2,3,\dots$

$\leftarrow$ Bohr-Sommerfeld (for a potential well)

Example: Quarkonium



$\Rightarrow$ Approximate strong force potential as a 1-dimensional linear force



$$-\bar{r} \int^{\bar{r}} dr \sqrt{2m(E - \sigma r)} = n\pi\hbar$$

$\rightarrow$ change variables

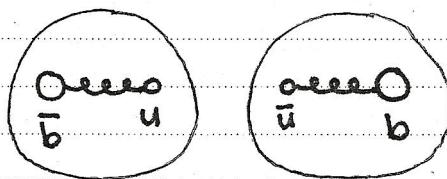
$$r = y \frac{E}{\sigma}$$

$$dr = \frac{E}{\sigma} dy$$

$$\Rightarrow \frac{E}{\sigma} \int_{-1}^1 dy \sqrt{2mE - 2m\sigma r}$$

$$\sqrt{2mE} \frac{E}{\sigma} \int_{-1}^1 dy \sqrt{1-y}$$

$\frac{4\sqrt{2}}{3}$



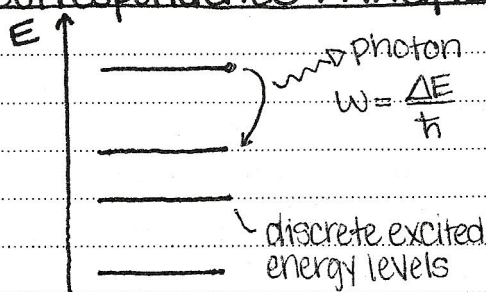
$\uparrow$ by pulling apart b and $\bar{b}$, you create an up and $\bar{u}$ quark that are bound infinitely to b and $\bar{b}$

$\rightarrow$

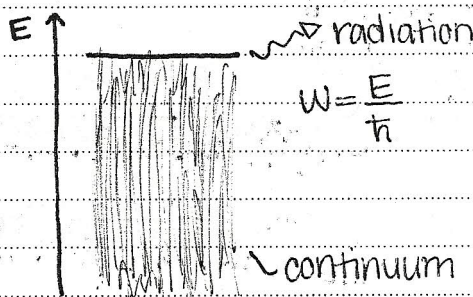
$$\Rightarrow \frac{\sqrt{2m}}{\sigma} E^{3/2} = \frac{3n\pi\hbar}{4\sqrt{2}}$$

$$E = \left(n \frac{3\pi\hbar\sigma}{8\sqrt{m}} \right)^{2/3} \quad \uparrow \text{the asymptotic behavior will be } 2/3$$

Correspondence Principle



- Quantum -



- Classical -

Use Bohr-Sommerfeld Quantization Condition to show that quantum energy level changes have the same frequency as the classical model

→ only valid for highly excited states, not valid for the transition from the first excited state to ground.

$$x_1 \int_{x_1}^{x_2} dx P(x) = n\pi\hbar$$

$\downarrow \frac{d}{dn}$

$$x_1 \int_{x_1}^{x_2} dx \frac{1}{2P(x)} 2m \frac{dE}{dn} = \pi\hbar$$

$\underbrace{\quad}_{\sim \nu(x)^{-1} \text{ (classical velocity at position } x)^{-1}}$

$$\frac{1}{2}T$$

$\sim$ period to go from $x_1 \rightarrow x_2$ and back

$$\Rightarrow \frac{dE}{dn} = \frac{2\pi\hbar}{T} = \hbar\omega$$

$\approx \Delta E$

↑ When you transition from one excited state to another, the frequency of the photon emitted is exactly the same as the classical radiation frequency!

11/12/12

Time-Dependent Perturbation Theory

Goal: Find the time evolution (approximately)

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{unperturbed Hamiltonian}} + \underbrace{\hat{V}(t)}_{\substack{\text{perturbation} \\ \text{(may be time dependent)}}}$$

(time independent, soln. known)

Time evolution of the unperturbed system: ($\hat{H} = \hat{H}_0$)

$$\hat{H}_0 |n\rangle = E_n^0 |n\rangle$$

known

Postulate II of QM:

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H}_0 |\Psi(t)\rangle$$

$$\sum_k \Psi_k(t) |k\rangle = \sum_m \Psi_m(t) |m\rangle$$

time independent

$$\sum_k i\hbar \frac{d}{dt} \Psi_k(t) |k\rangle = \sum_m E_m^0 \Psi_m(t) |m\rangle$$

$\Downarrow \langle n |$

$$i\hbar \frac{d}{dt} \Psi_n(t) = E_n^0 \Psi_n(t)$$

OR

$$i\hbar \frac{d}{dt} \begin{pmatrix} \Psi_1(t) \\ \Psi_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1^0 & 0 & 0 \\ 0 & E_2^0 & 0 \\ 0 & 0 & \ddots \end{pmatrix} \begin{pmatrix} \Psi_1(t) \\ \Psi_2(t) \\ \vdots \end{pmatrix}$$

$\Downarrow$

$$\Psi_n(t) = e^{-iE_n^0 t/\hbar} \Psi_n(t=0)$$

Time evolution of the perturbed system:

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = \hat{H}_0 |\Psi(t)\rangle + \underbrace{\hat{V} |\Psi(t)\rangle}_{\sum_m \Psi_m(t) \hat{V} |m\rangle}$$

$\Downarrow \langle n |$

$$i\hbar \frac{d}{dt} \Psi_n(t) = E_n^0 \Psi_n(t) + \sum_m \Psi_m(t) \langle n | \hat{V} | m \rangle$$

$V_{nm}(t) \rightarrow$ does not vanish for $n \neq m$
like previous terms

$$i\hbar \frac{d}{dt} \begin{pmatrix} \Psi_1(t) \\ \Psi_2(t) \\ \vdots \end{pmatrix} = \begin{pmatrix} E_1^0 + V_{11} & V_{12} & V_{13} \\ V_{21} & E_2^0 + V_{22} & V_{23} \\ V_{31} & V_{32} & \ddots \end{pmatrix} \begin{pmatrix} \Psi_1(t) \\ \Psi_2(t) \\ \vdots \end{pmatrix}$$

$\rightarrow$ System of differential equations

Approximation assumptions:

1. assume E_n^0 is large compared to $V_{nm}(t)$

(assumed block diagonalization is not an option)

2. assume the system starts at

$$|\Psi(0)\rangle = |i\rangle^0$$

↑ initial (if no perturbation, wavefunction will stay here)

0th order approximation: neglect V

$$\Psi_n(t) = 0 \quad \text{for } n \neq i$$

$$\Psi_i(t) = e^{-iE_i^0 t/\hbar} \quad \text{for } n = i$$

1st order approximation: linear in V

$$i\hbar \frac{d}{dt} \Psi_n(t) = E_n^0 \Psi_n(t) + \sum_m V_{nm}(t) \Psi_m(t)$$

↳ exact solution (build small corrections from here)

⇒ Plug in 0th order Ψ_i for each Ψ_m

$$\simeq E_n^0 \Psi_n(t) + V_{ni}(t) e^{-iE_i^0 t/\hbar}$$

↑ corrections here $\propto V$

$$\Rightarrow \Psi_n(t) = \frac{-i}{\hbar} e^{-iE_i^0 t/\hbar} \int_0^t dt' V_{ni}(t') e^{\frac{-i(E_i^0 - E_n^0)}{\hbar} t'} \quad \text{for } n \neq i$$

$$\Rightarrow \Psi_i(t) = e^{-iE_i^0 t/\hbar} \left(1 - \frac{i}{\hbar} \int_0^t dt' V_{ii}(t') \right) \quad \text{for } n = i$$

11/14/12

Time-Dependent Perturbation, con't

Recap:

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle = (\hat{H}_0 + \hat{V}(t)) |\Psi(t)\rangle$$

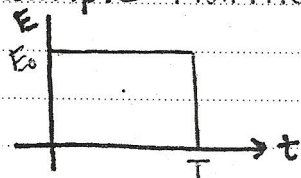
$\hat{H}_0$ ↑ unperturbed $\hat{V}(t)$ ↓ Potential perturbation

Initial Condition $|\Psi(0)\rangle = |i\rangle$

$$|\Psi(t)\rangle = \sum_n \psi_n(t) |n\rangle$$

$$\text{Solve: } \psi_n(t) \approx \frac{-i}{\hbar} e^{-iE_i t/\hbar} \int_0^t dt' V_{ni}(t') e^{-i(E_i - E_n)t'/\hbar} + \dots$$

Example: Harmonic Oscillator with an External E-Field



→ assume the system starts in the ground state

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2} \hat{x}^2 + \underbrace{eE_0 \hat{x} \theta(t) \theta(T-t)}_{\text{electric potential energy}}$$

→ Just plug into general solution

$$\psi_{n \neq 0}(t) = \frac{-i}{\hbar} e^{-i\omega(n+1/2)t} \int_0^T dt' \underbrace{\langle n | eE_0 \hat{x} | 0 \rangle}_{V_{n0}} e^{-i\hbar\omega(1/2 - (n+1/2))t'/\hbar}$$

$$= \frac{-i}{\hbar} eE_0 e^{-i\omega(n+1/2)t} \langle n | \hat{x} | 0 \rangle \underbrace{\int_0^T dt' e^{i\omega n t'}}_{\frac{e^{i\omega n T} - 1}{i\omega n}}$$

$$\text{but } \langle n | \hat{x} | 0 \rangle = \langle n | \sqrt{\frac{\hbar}{2m\omega}} (\hat{a} + \hat{a}^\dagger) | 0 \rangle = \sqrt{\frac{\hbar}{2m\omega}} \delta_{n1} \text{ so}$$

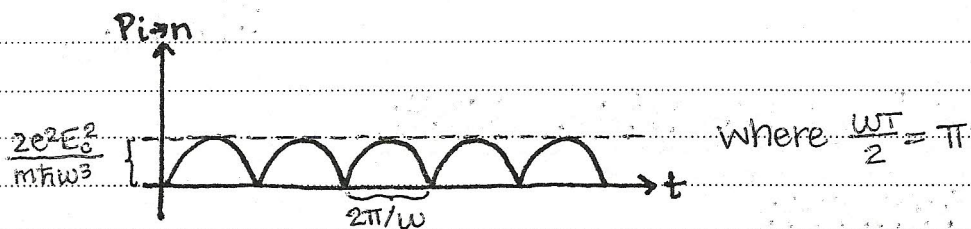
$$\psi_i = \frac{-i}{\hbar} \frac{eE_0}{i\omega} e^{-i\omega t/2} \sqrt{\frac{\hbar}{2m\omega}} (e^{i\omega t} - 1)$$

$$\psi_{n \neq 1} = 0$$

Probability of transition from $|0\rangle \rightarrow |1\rangle$

$$P_{0 \rightarrow 1}(t) = |\psi_i|^2 = \left(\frac{eE_0}{\hbar\omega} \right)^2 \frac{\hbar}{2m\omega} |e^{-i\omega t/2}|^2 \left| e^{i\omega T/2} 2i \left(\frac{e^{i\omega T/2} - e^{-i\omega T/2}}{2i} \right) \right|^2$$

$$= \frac{2e^2 E_0^2}{m\hbar\omega} \frac{\sin^2(\omega T/2)}{\omega^2} \text{ for } t > T$$



Consider $t < T$

$$P(t) \sim \sin^2(\omega t) \xrightarrow{t \ll \frac{1}{\omega}} t^2$$

$$\Rightarrow \frac{dP}{dt} = \alpha t$$

So the rate of transition $\frac{dP}{dt} \sim T$ and is not constant. This is in clear disagreement with the law of radioactive decay.

$$P_{\text{not decay}} \sim e^{-T/\tau}$$

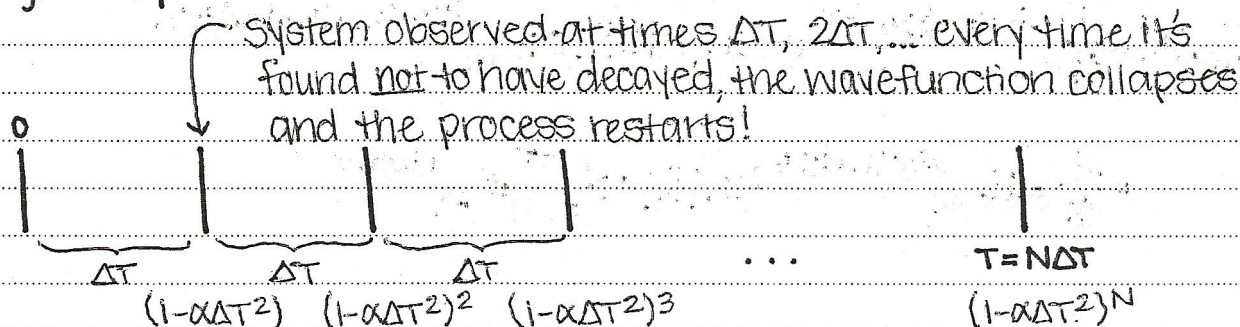
$$P_{\text{decay}} = 1 - P_{\text{not decay}}$$

$$\approx 1 - 1 + \frac{T}{\tau} + \dots$$

↑ linear!

We will explain this discrepancy later. For now, let us note that because $P \sim T^2$ for small enough T .

Thought Experiment



Probability of initial state = 1

$$P_{\text{not decay}}(T) = (1 - \alpha \Delta T^2)^N \approx \underbrace{\left(1 - \alpha \left(\frac{T}{N}\right)^2\right)^N}_{\left(\frac{T}{N}\right)^2} \approx 1 - \frac{\alpha N \Delta T^2}{N^2} \xrightarrow{N \rightarrow \infty} 1$$

"Quantum Zero Effect" $\rightarrow$ a watched pot never boils

Example: Sinusoidal Perturbation

$$\hat{H} = \hat{H}_0 + \hat{V} \cos(\omega t)$$

↳ time independent

Solution:

$$\Psi_{n \neq i}(t) = \frac{-i}{\hbar} e^{-iE_i t/\hbar} \int_0^t dt' V_{ni} \cos(\omega t') e^{-i \underbrace{\frac{(E_i - E_n)}{\hbar}}_{\equiv \omega_0} t'}$$

$$\Psi_{n \neq i}(t) = \frac{-i}{\hbar} e^{-iE_i t/\hbar} V_{ni} \int_0^t dt' \frac{e^{i\omega t' - i\omega_0 t'} + e^{-i\omega t' + i\omega_0 t'}}{2}$$

$$= \frac{-i}{2\hbar} e^{-iE_i t/\hbar} V_{ni} \left[\frac{e^{i(\omega - \omega_0)t} - 1}{i(\omega - \omega_0)} + \frac{e^{-i(\omega + \omega_0)t} - 1}{-i(\omega + \omega_0)} \right]$$

dominates
if $\omega \approx \omega_0$

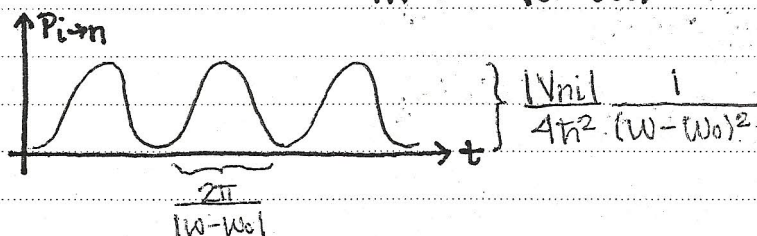
ω_0 = unperturbed frequency
 ω = perturbed frequency

$$\approx \frac{-i}{2\hbar} V_{ni} e^{-iE_i t/\hbar} \frac{e^{i(\omega - \omega_0)t} - 1}{\omega - \omega_0}$$

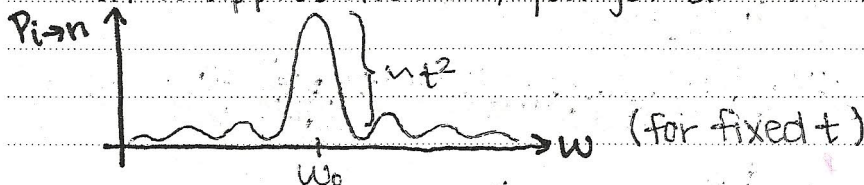
$$= -\frac{V_{ni}}{2\hbar} \frac{i}{\omega - \omega_0} e^{-iE_i t/\hbar + \frac{(\omega - \omega_0)t}{2}} \frac{e^{i(\omega - \omega_0)t/2} - e^{-i(\omega + \omega_0)t/2}}{i}$$

Probability of transition from $i \rightarrow n$

$$P_{i \rightarrow n}(t) = |\Psi_n(t)|^2 = \frac{|V_{ni}|^2}{4\hbar^2} \frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2}$$



When ω approaches ω_0 , you get Quantum Resonance.



Did this using 2 assumptions

① $\hat{V}$ is small

② $\omega \approx \omega_0$

Rotating Wave Approximation

→ dropping the term $e^{i(\omega + \omega_0)t}$ is the same as taking the perturbation to be

$$V_{fi}(t) = V_{fi} \frac{1}{2} e^{-i\omega t}$$

$$V_{if}(t) = V_{if} \frac{1}{2} e^{i\omega t}$$

all others = 0

$$|\Psi(t)\rangle = \sum_n \Psi_n(t) |n\rangle$$

With this perturbation, we can solve the problem easily

→

$$\text{TDSE: } i\hbar \frac{d}{dt} \Psi_n(t) = E_n^0 \Psi_n(t) + \sum_m V_{n \neq m} \Psi_m(t)$$

if we restrict ourselves to $|i\rangle^0$ and $|f\rangle^0$

$$i\hbar \frac{d}{dt} \Psi_i(t) = E_i^0 \Psi_i(t) + V_{fi} \Psi_f(t) e^{i\omega t}$$

$$i\hbar \frac{d}{dt} \Psi_f(t) = E_f^0 \Psi_f(t) + V_{if} \Psi_i(t) e^{-i\omega t}$$

$$\Psi_i(0) = 1$$

$$\Psi_f(0) = 0$$

→ solving this set of equations

$$\Rightarrow \text{define: } C_i(t) = e^{iE_i^0 t/\hbar} \Psi_i(t)$$

$$C_f(t) = e^{iE_f^0 t/\hbar} \Psi_f(t)$$

$$\Rightarrow i\hbar \frac{d}{dt} \Psi_i = \left[i\hbar \frac{d}{dt} C_i + E_i^0 C_i \right] e^{-iE_i^0 t/\hbar} = E_i^0 e^{-iE_i^0 t/\hbar} C_i + \frac{V_{if}}{2} e^{i\omega t/2 - iE_i^0 t/\hbar} C_f$$

$$i\hbar \frac{d}{dt} \Psi_f = \left[i\hbar \frac{d}{dt} C_f + E_f^0 C_f \right] e^{-iE_f^0 t/\hbar} = E_f^0 e^{-iE_f^0 t/\hbar} C_f + \frac{V_{fi}}{2} e^{-i\omega t/2 - iE_i^0 t/\hbar} C_i$$

$$\frac{dC_i}{dt} = \frac{-i}{2\hbar} V_{if} e^{i(\omega - \frac{E_f^0 - E_i^0}{\hbar})t} C_f = \frac{-i}{2\hbar} V_{if} e^{i(\omega - \omega_0)t} C_f$$

$$\frac{dC_f}{dt} = \frac{-i}{2\hbar} V_{fi} e^{-i(\omega - \frac{E_f^0 - E_i^0}{\hbar})t} C_i = \frac{-i}{2\hbar} V_{fi} e^{-i(\omega + \omega_0)t} C_i$$

want to uncouple these two equations, so take the time derivative of the second equation

$$\begin{aligned} i\hbar \frac{d^2}{dt^2} C_f(t) &= \frac{V_{fi}}{2} \left[\frac{d}{dt} C_i - i(\omega - \omega_0) C_i \right] e^{-i(\omega - \omega_0)t} \\ &= \frac{V_{fi}}{2} \left[\frac{V_{if}}{2} e^{i(\omega - \omega_0)t} C_f - i(\omega - \omega_0) \hbar e^{i(\omega - \omega_0)t} \frac{dC_f}{dt} \right] e^{-i(\omega - \omega_0)t} \end{aligned}$$

$$i\hbar \frac{d^2}{dt^2} C_f = \frac{|V_{if}|^2}{4} C_f + \hbar(\omega - \omega_0) \frac{dC_f}{dt}$$

try solutions of the form:

$$\text{ansatz: } C_f(t) \sim C e^{i\lambda t}$$

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Even More Time-Dependent Perturbation

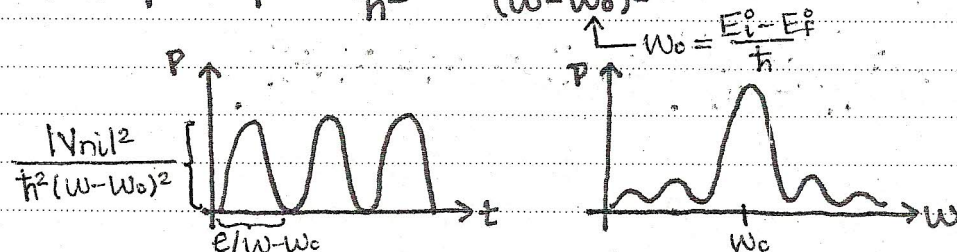
Recall example:

$$\rightarrow \hat{H} = \hat{H}_0 + \hat{V} \cos(\omega t)$$

$$|\psi(0)\rangle = |i\rangle$$

$$|\psi(t)\rangle = \sum_n \psi_n(t) |n\rangle$$

$$P_{i \rightarrow n} = |\psi_n(t)|^2 \approx \frac{|V_{ni}|^2}{\hbar^2} \frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2}$$



→ "Exact" calculation ($\omega \approx \omega_0$, but V not necessarily small)

$$i\hbar \frac{d}{dt} \psi_n(t) = E_n^0 \psi_n(t) + \sum_m V_{nm} \psi_m(t)$$

↔

$$C_i(t) = e^{iE_i^0 t / \hbar} \psi_i(t)$$

$$C_f(t) = e^{iE_f^0 t / \hbar} \psi_f(t)$$

↔

$$i\hbar \frac{d}{dt} C_i = \frac{-i}{2\hbar} V_{if} e^{i(\omega - \omega_0)t} C_f$$

$$i\hbar \frac{d}{dt} C_f = \frac{-i}{2\hbar} V_{fi} e^{-i(\omega - \omega_0)t} C_i$$

→ decouple C_i & C_f →

$$\frac{d^2}{dt^2} C_f = -i(\omega - \omega_0) \frac{dC_f}{dt} - \frac{|V_{if}|^2}{4\hbar^2} C_f$$

Ansatz: $C_f \sim e^{-i\lambda t}$

$$-\lambda^2 = (\omega - \omega_0)\lambda - \frac{|V_{if}|^2}{4\hbar^2}$$

$$\lambda_{\pm} = \frac{-(\omega - \omega_0)}{2} \pm \frac{1}{2} \sqrt{(\omega - \omega_0)^2 + \frac{|V_{if}|^2}{\hbar}}$$

ω_R

$$\Rightarrow C_f(t) = e^{i(\omega - \omega_0)t/2} [A \cos(\omega_R t) + B \sin(\omega_R t)]$$

initial condition: $C_f(0) = 0 \Rightarrow A = 0$

$$\frac{d}{dt} C_i = \frac{-i}{2\hbar} V_{if} e^{i(\omega - \omega_0)t - i(\omega - \omega_0)t/2} B \sin(\omega_R t)$$

$$\Rightarrow C_i(t) = \frac{i2\hbar}{V_{fi}} e^{i(\omega - \omega_0)t/2} B \left[-i \frac{(\omega - \omega_0)}{2} \sin(\omega_R t) + \omega_R \cos(\omega_R t) \right]$$

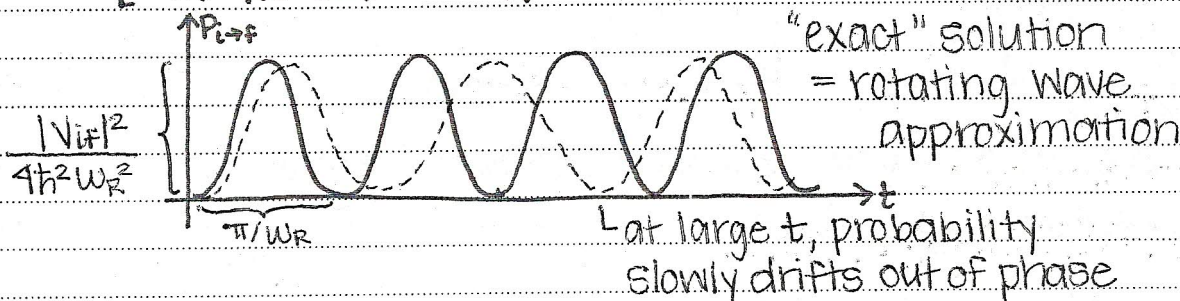
Second initial condition: $C_i(0)=1 \Rightarrow B = V_{if}/2\hbar\omega_R$
 finally, in the rotating wave approximation

$$\Psi_f(t) = e^{-iE_f^0 t/\hbar} C_f(t) = \frac{-i}{2\hbar\omega_R} V_{if} e^{-iE_f^0 t/\hbar - i(\omega - \omega_0)t/2} \sin(\omega_R t)$$

$$P_{i \rightarrow f} = |\Psi_f(t)|^2 = \frac{|V_{if}|^2}{4\hbar} \frac{\sin^2(\omega_R t)}{\omega_R^2}$$

$$\omega_R = \frac{1}{2} \sqrt{(\omega - \omega_0)^2 + \frac{|V_{if}|^2}{\hbar}} \approx \frac{1}{2} |\omega - \omega_0| + \theta \left(\left| \frac{V_{if}}{\omega - \omega_0} \right|^2 \right)$$

$$P_{i \rightarrow f} \approx \left[\frac{|V_{if}|^2}{4\hbar^2 (\omega - \omega_0)^2} + \theta \left(\left(\frac{V_{if}}{\omega - \omega_0} \right)^2 \right) \sin^2(|\omega - \omega_0| + \theta(v^2)) \right]$$



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Atoms & Light

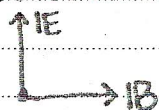
Approximations (electric dipole approximations)

- atom is quantum mechanical, light is classical

↳ Schrödinger's eq.

↳ Maxwell's eqs.

- atom is non-relativistic $\Rightarrow$ keep only $\mathbf{IE}$



$$e(\mathbf{IE} + \mathbf{v} \times \mathbf{IB})$$

↳ because the atom is non-relativistic, the magnetic force is negligible

- wavelength of light $\gg$ size of atom (except x-rays)

$\Rightarrow$ take $\mathbf{IE}$ to be uniform in space

* Energy difference between atomic levels is comparable to the atomic levels themselves

$$\frac{\hbar c}{\lambda} \sim \hbar \omega \sim \Delta E \sim \frac{p^2}{2m} \sim \left(\frac{\hbar}{\Delta x} \right)^2 \frac{1}{2m} \sim \frac{p}{m} \frac{\hbar}{\Delta x}$$

↳ wavelength of light

↳ size of atom

$$\frac{p}{mc} \ll 1$$

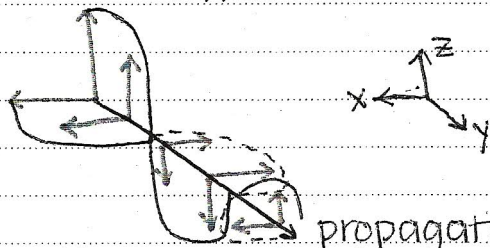
this is non-relativistic atoms exchanging light amongst themselves

Under these assumptions:

↳ polarization along the z-axis

$$\hat{V} = -eE_0 \hat{z} \cos(\omega t)$$

↳ E field that oscillates with frequency ω



propagation

$$P_{a \rightarrow b}(t) \approx \left| \frac{-i}{\hbar} e^{-iE_a t/\hbar} \int_0^t dt' eE_0 \cos(\omega t') \langle b | \hat{z} | a \rangle e^{-\frac{i(E_a - E_b)t}{\hbar}} \right|^2$$

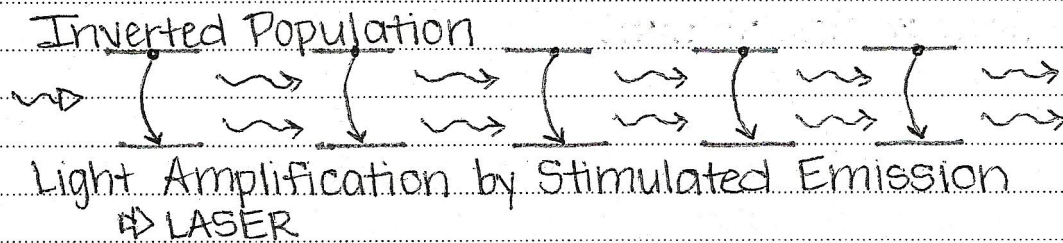
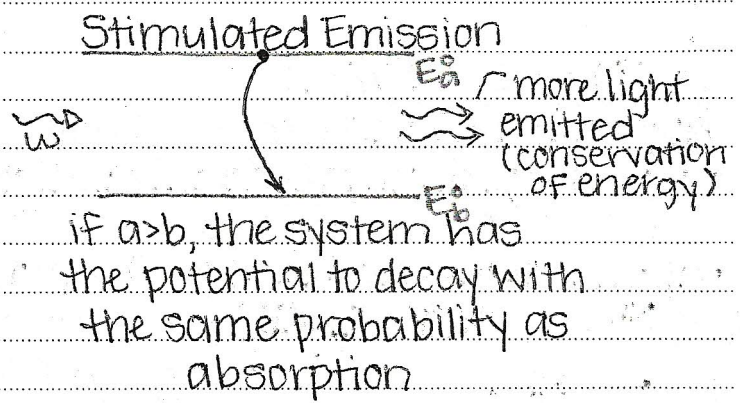
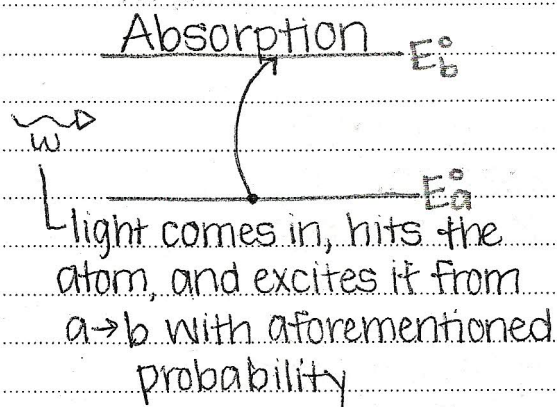
↳ probability of changing from state a to state b

"off-diagonal" electric dipole

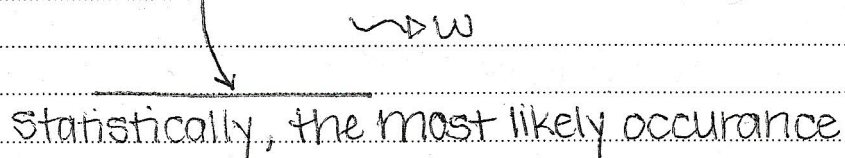
$$\approx \frac{E_0^2}{\hbar^2} \underbrace{|\langle a | e \hat{z} | b \rangle|^2}_{\substack{\text{electric dipole} \\ \text{operator} \\ \text{if } a=b}} \left| \frac{e^{-i(\omega - \omega_0)t} - 1}{-2i(\omega - \omega_0)} \right|^2$$

$$\frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2}$$

This is true regardless if $E_a > E_b$ or $E_a < E_b$



Spontaneous Emission



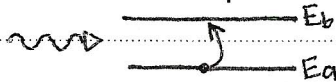
Atoms & Light, con't

$$P_{a \rightarrow b} = \frac{|E_0^2|}{\hbar^2} \underbrace{|\langle b | e \hat{z} | a \rangle|^2}_{\text{"off-diagonal" dipole moment}} \frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2}$$

frequency of light $\uparrow \frac{E_b - E_a}{\hbar}$

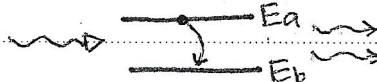
This describes:

Absorption



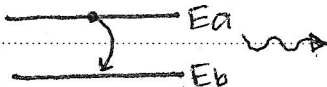
&

Stimulated Emission



But does not describe:

Spontaneous Emission



Incoherent Light (When phases change randomly)

→ lots of different transition probabilities for lots of different ω 's

$$\Psi_n = \frac{-V_{ni}}{\hbar} \sum_{\omega} \frac{\sin((\omega - \omega_0)t)}{\omega - \omega_0} e^{-iE_n t/\hbar + i(\omega - \omega_0)t/2} A(\omega)$$

Fourier transform amplitudes

"this is true because it is written in your notebook and therefore it must be true"

$$P_{i \rightarrow n} = |\Psi_n|^2 = \sum_{\omega} \frac{|V_{ni}|^2}{\hbar^2} \frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2} |A(\omega)|^2$$

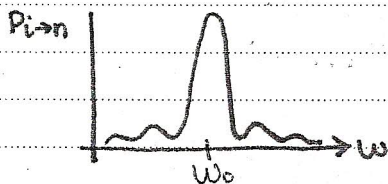
averages out ≈ 0 for practical purposes

$$+ \sum_{\omega \neq \omega'} \frac{|V_{ni}|^2}{\hbar^2} \frac{\sin((\omega - \omega_0)t)}{\omega - \omega_0} \frac{\sin((\omega' - \omega_0)t)}{\omega' - \omega_0} e^{i(\omega - \omega')t/2} A(\omega) A^*(\omega')$$

interference terms

$$t \gg \frac{1}{\omega - \omega_0} \quad \frac{|V_{ni}|^2}{\hbar^2} \int_0^\infty d\omega \rho(\omega) \frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2}$$

how much light is in a particular frequency



the larger t is, the more sharply peaked this probability curve is
→ the closer ω is to ω_0

$$P_{i \rightarrow n} \approx \frac{|V_{ni}|^2}{\hbar^2} \rho(\omega_0) \int_{(\omega - \omega_0)t = x}^\infty d\omega \frac{\sin^2((\omega - \omega_0)t)}{(\omega - \omega_0)^2} = \frac{\pi}{2} \frac{|V_{ni}|^2}{\hbar^2} \rho(\omega_0) t$$

rate

transition probability back to being $\propto t$, not t^2 like it was for very small t

→

for incoherent light: (previously single frequency)

$$P_{a \rightarrow b} = \frac{E_0^2}{\hbar^2} \frac{\pi}{2} |\langle b | e \hat{z} | a \rangle|^2 t$$

~ linear on t !

→ more intuitive to write in terms of energy density (power)

$$u = \frac{\epsilon_0}{2} E_0^2 + \frac{1}{2\mu_0} B_0^2$$

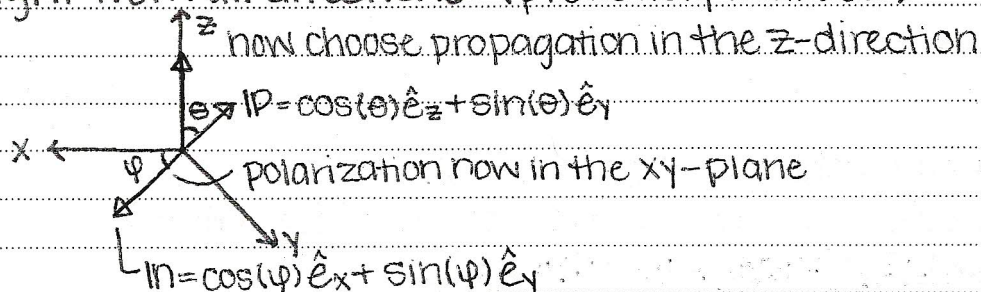
$$\langle u \rangle = \frac{1}{2} \epsilon_0 \langle E_0^2 \rangle$$

~ average over time

when you write in terms of u , $\rho(\omega)$, the amount of energy in each frequency, is automatically taken care of.

$$P_{a \rightarrow b} = \frac{u \pi}{\hbar^2 \epsilon_0} |\langle b | e \hat{z} | a \rangle|^2 t$$

light from all directions: (previously localized)



~ polarization of the atom

$$IP = \langle b | e \hat{r} | a \rangle$$

→ property of the state of the atom before & after the light

$$|\langle b | e \hat{z} | a \rangle|^2 \text{ -- generalizes to -- } \int_0^\pi d\theta \int_0^{2\pi} d\phi |\langle b | \hat{p} \cdot \hat{n} | a \rangle|^2$$

"atom polarization" → ↑ light polarization

$$= |\langle b | \hat{p} | a \rangle|^2 \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin^2(\theta) \sin^2(\phi)$$

1/3

$$P_{a \rightarrow b} = \frac{u \pi}{3 \epsilon_0 \hbar^2} |\langle b | \hat{p} | a \rangle|^2 t$$

Paulo's Mumbo-Jumbo on Quantum ElectroDynamics

$$\frac{1}{c^2} \frac{d^2}{dt^2} \begin{Bmatrix} IE \\ IB \\ IA \\ \psi \end{Bmatrix} - \nabla^2 \begin{Bmatrix} IE \\ IB \\ IA \\ \psi \end{Bmatrix} = 0 \Rightarrow \frac{d^2}{dt^2} \psi_k + \underbrace{c^2 k^2}_{\omega^2} \psi_k = 0$$

Vector potential A
electric potential ψ

↑ Fourier transform of any component of IE, IB, IA, ψ , etc

→ one harmonic oscillator for each value of $\vec{k}$ (momentum vector)

~ wavefunction specified by what state each of the modes is in

$$|\Psi\rangle = |0, 2, 32, 0, \dots\rangle \text{ (can also be linear combinations)}$$

~ all completely independent oscillators

→

$| \text{ground} \rangle = | 0, 0, 0, \dots \rangle = | \text{vacuum} \rangle$ (no photons)

$\hat{H} | \text{ground} \rangle = \left(\underbrace{\frac{1}{2} \hbar \omega_0 + \frac{1}{2} \hbar \omega_1 + \dots}_{\text{infinite}} \right) | 0, 0, 0, \dots \rangle$
↓ dependent on k, so it changes from oscillator to oscillator

→ the energy of the ground state, the state that must have the lowest energy, is infinite!

$| \text{an excited} \rangle = | 0, 1, 0, 0, \dots \rangle$

$\hat{H} | \text{an excited} \rangle = (\text{infinite} + \hbar \omega_1) | \text{an excited} \rangle$

additional energy of one excited oscillator

Classically,

$$\langle 0 | \hat{x} | 0 \rangle = 0$$

↳ average value of the position of the harmonic oscillator

$$\langle 0 | \hat{x}^2 | 0 \rangle \neq 0$$

↳ a measure of how broad the spread of the ground state is (zero-point energy)

Similarly,

$$\langle \text{ground} | \hat{E} | \text{ground} \rangle = 0 \text{ (no photons in the vacuum state)}$$

$$\langle \text{ground} | \hat{E}^2 | \text{ground} \rangle \neq 0$$

↳ fluctuation of the electric field in the ground state is non-zero. These zero-point jiggles

knock the atoms into transition

⇒ SPONTANEOUS EMISSION

"the point of this exercise was not to explain anything, but to confuse you!"

Einstein's A&B (explanation of spontaneous emission)

→ only allowed to use Planck's formula for Black Body Radiation

$$\begin{array}{c} \text{———— } E_b \\ \text{———— } E_a \end{array} \quad \frac{dN_b}{dt} = \underbrace{B_{ab} N_a \rho(\omega_0)}_{\substack{\text{absorption} \\ \uparrow P_{a \rightarrow b}}} - \underbrace{B_{ba} N_b \rho(\omega_0)}_{\substack{\text{stimulated emission} \\ \uparrow P_{b \rightarrow a}}} - \underbrace{A N_b}_{\text{spontaneous emission}}$$

N_b - # atoms in state b

N_a - # atoms in state a

↳ will happen more often for more photons in state a, or photons w/ the right frequency

↳ decay rate of the atom in splendid isolation

If $A=0$, spontaneous emission does not exist



in equilibrium: $\frac{dN_b}{dt} = 0$, $\frac{N_a}{N_b} = \frac{e^{-E_a/k_B T}}{e^{-E_b/k_B T}} = e^{\hbar\omega_0/k_B T}$ ↑ ω_0 is the difference in E_a & E_b
Boltzmann factor

$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1}$ ← Planck's formula, only known quantum of the time
 ↳ density of photons at a particular frequency
 (density of energy in each mode)

$$A N_b = \left(e^{\hbar\omega_0/k_B T} N_b B_{ab} - N_b B_{ba} \right) \frac{\hbar}{\pi^2 c^3} \frac{\omega_0^3}{e^{\hbar\omega_0/k_B T} - 1}$$

these A & B coefficients are the probability of an atom to decay or not, independent of temperature. But this equation must hold for all temperatures

$$\Rightarrow B_{ba} = B_{ab} = B$$

causes temperature dependence to disappear!

$$A = \frac{\hbar}{\pi^2 c^3} \omega_0^3 B$$

If B is non-zero, A is also non-zero and therefore spontaneous emission must exist!

Spontaneous Emission

Einstein's A & B: (spontaneous emission rates)

$$A = \frac{\hbar}{\pi^2 c^3} \omega_0^3 B$$

$B = B_{ab} = B_{ba}$

$A = \rho(\omega_0) B$ (known transition rate for stimulated emission)

$$= \frac{\hbar}{\pi^2 c^3} \omega_0^3 \frac{\pi}{3 \epsilon_0 \hbar^2} |P|^2$$

$$= \frac{\omega_0^3}{3 \pi \epsilon_0 c^3 \hbar} |P|^2$$

Rate of spontaneous emission:

$$A = \frac{\omega_0^3}{3 \pi \epsilon_0 \hbar c^3} |\langle f | P | i \rangle|^2 \quad \omega_0 = \frac{E_f - E_i}{\hbar}$$

Example: Spontaneous Emission of a Harmonic Oscillator

$A \propto \sum_{n'=0}^3 \langle f | P | i \rangle = \langle f | q \hat{x} | i \rangle$
 $P = q \langle n | \hat{x} | n' \rangle = \sqrt{\hbar/2m\omega} (\sqrt{n'} \delta_{n,n'-1} + \sqrt{n'+1} \delta_{n,n'+1})$
 $\uparrow$ emission when $n' < n$

$$A = \frac{\omega_0^3}{3 \pi \epsilon_0 \hbar c^3} |\langle f | P | i \rangle|^2$$

$$= q^2 \left(\sqrt{\frac{\hbar n'}{2m\omega}} \right)^2 \frac{\omega_0^3}{3 \pi \epsilon_0 \hbar c^3} = \frac{q^2 n \omega^2}{6 \pi \epsilon_0 m c^3}$$

lifetime of emission: $\frac{1}{A} = \frac{6 \pi \epsilon_0 m c^3}{q^2 n \omega^2}$

Power: $\frac{\hbar \omega}{\text{lifetime}} = A \hbar \omega = \frac{q^2 \hbar \omega^3 n}{6 \pi \epsilon_0 m c^3}$

$$= \frac{q^2 \omega^2}{6 \pi \epsilon_0 m c^3} (\hbar \omega n) = \frac{q^2 \omega^2}{6 \pi \epsilon_0 m c^3} (E_n - \frac{1}{2} \hbar \omega)$$

$E_n - \frac{1}{2} \hbar \omega$

→ Classically: Power emitted by an atom

$$P = \frac{q^2 a^2}{6 \pi \epsilon_0 c^3} \quad (\text{Larmor's Formula})$$

where a = acceleration

• for a harmonic oscillator:

$$x(t) = x_0 \cos(\omega t)$$

$$\rightarrow a = \frac{d^2 x}{dt^2} = -x_0 \omega^2 \cos(\omega t)$$

$$\int_0^{2\pi} a^2 dt = \frac{x_0^2 \omega^2}{2}$$

$$\rightarrow E = \frac{m \omega^2}{2} x_0^2$$

$$\text{power} = \frac{q^2 x_0^2 \omega^4}{6\pi\epsilon_0 c^3} \frac{1}{2} = \frac{q^2 \omega^4}{6\pi\epsilon_0 c^3} \frac{E}{m\omega^2}$$

$$= \frac{q^2 \omega^2 E}{6\pi\epsilon_0 mc^3}$$

↳ same as power derived quantum mechanically
for highly excited states ($E \gg \hbar\omega$)

quantum $m \rightarrow \infty$ → classical

Selection Rules

↳ electric dipole approximation ~ matrix elements

$$\langle f | \hat{r} | i \rangle = \int d^3r \underbrace{\langle f | r \rangle}_{\Psi_f^*(r)} \underbrace{\hat{r} \langle r | i \rangle}_{\Psi_i(r)} = 0$$

↳ both even or both odd functions

Generalizations:

$$\cdot [\hat{L}_z, \hat{z}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{z}] = 0 - 0 = 0$$

↳ forget m_s — spin given by dipole appx.

$$0 = \langle n'l'm' | [\hat{L}_z, \hat{z}] | nlm \rangle = \underbrace{\langle n'l'm' | \hat{L}_z \hat{z} }_{\langle n'l'm' | \hbar m' } - \underbrace{\hat{z} \hat{L}_z | nlm \rangle}_{\hbar m | nlm \rangle}$$

$$= \hbar(m' - m) \langle n'l'm' | \hat{z} | nlm \rangle$$

$$\Rightarrow \langle n'l'm' | \hat{z} | nlm \rangle = 0 \text{ unless } m' = m$$

Selection Rules

Valid for:

- 1st order perturbation
- electric dipole approximation $\Leftrightarrow P \sim \langle f | \hat{r} | i \rangle$
 - Wavelength of light is much larger than the size of the atom $\downarrow$ position operator
 - emitting and receiving photons that have zero orbital angular momentum $\uparrow$ Polarization of the atom

The Rules:

$$\bullet [\hat{L}_z, \hat{z}] = 0$$

$$\Leftrightarrow \langle n'l'm' | \hat{z} | nlm \rangle = 0 \text{ unless } m' = m$$

$$\bullet [\hat{L}_z, \hat{x}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{x}] = -\hat{y}[\hat{p}_x, \hat{x}] = i\hbar\hat{y}$$

$$[\hat{x}\hat{p}_x, \hat{x}] = 0 \quad -i\hbar$$

$$i\hbar \langle n'l'm' | \hat{y} | nlm \rangle = \langle n'l'm' | [\hat{L}_z, \hat{x}] | nlm \rangle = \hbar(m'-m) \langle n'l'm' | \hat{x} | nlm \rangle$$

↳ how to calculate matrix elements y if you know x

$$\bullet [\hat{L}_z, \hat{y}] = [\hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \hat{y}] = \hat{x}[\hat{p}_x, \hat{y}] = -i\hbar\hat{x}$$

$$-i\hbar \langle n'l'm' | \hat{x} | nlm \rangle = \langle n'l'm' | [\hat{L}_z, \hat{y}] | nlm \rangle = \hbar(m'-m) \langle n'l'm' | \hat{y} | nlm \rangle$$

↳ how to calculate matrix elements x if you know y

→ Allows us to write by combining:

$$i \langle n'l'm' | \hat{y} | nlm \rangle = i(m'-m)^2 \langle n'l'm' | \hat{y} | nlm \rangle$$

$\Leftrightarrow$ only holds if

$$(m'-m)^2 = 1 \text{ or } \langle n'l'm' | \hat{y} | nlm \rangle = 0$$

which is equivalent to saying

$$\Delta m = 1 \text{ or } \langle n'l'm' | \hat{x} | nlm \rangle = 0$$

In summary

$$\Leftrightarrow \Delta m = 0, \pm 1$$

if $\Delta m = 0$, the z -component can be assumed non-zero

if $\Delta m = \pm 1$, the x - and y -components can be assumed non-zero

$$\begin{aligned} \bullet [L^2, [L^2, z]] &= [L^2, ([L_x^2, z] + [L_y^2, z] + [L_z^2, z])] \\ &= [L^2, (L_x[L_x, z] + [L_x, z]L_x + L_y[L_y, z] + [L_y, z]L_y + L_z[L_z, z] + [L_z, z]L_z)] \\ &\quad y[p_x, z] = -i\hbar y \quad -x[p_x, z] = i\hbar x \quad 0 \\ &= [L^2, (L_x(-i\hbar y) + (-i\hbar y)L_x + L_y(i\hbar x) + (i\hbar x)L_y)] \\ &= [L^2, i\hbar(-L_x y - y L_x + L_y x + x L_y)] \\ &\quad i\hbar z + y L_x \quad -i\hbar z + x L_y \\ &= [L^2, i\hbar(2x L_y - i\hbar z - 2y L_x - i\hbar z)] \end{aligned}$$

$$\begin{aligned}
&= [L^2, 2i\hbar(xL_y - yL_x - iz)] \\
&= 2i\hbar([L^2, xL_y] - [L^2, yL_x] - i\hbar[L^2, z]) \\
&= 2i\hbar(\underbrace{[L^2, x]}_0 L_y + x \underbrace{[L^2, L_y]}_0 - \underbrace{[L^2, y]}_0 L_x - y \underbrace{[L^2, L_x]}_0 - i\hbar(L^2 z - z L^2)) \\
&= 2i\hbar[(yL_z - zL_y - i\hbar x)L_y - 2i\hbar(zL_x - xL_z - i\hbar y)L_x - i\hbar(L^2 z - z L^2)] \\
&= -2\hbar^2(2yL_z L_y - 2zL_y^2 - 2zL_x^2 - 2i\hbar x L_y + 2xL_z L_x + 2i\hbar y L_x - L^2 z + z L^2) \\
&\quad - 2z(L_x^2 + L_y^2 + L_z^2) + 2zL_z^2 \\
&= -2\hbar^2(2yL_z L_y - 2i\hbar x L_y + 2xL_z L_x + 2i\hbar y L_x + 2zL_z^2 - 2zL^2 - L^2 z + z L^2) \\
&= -2\hbar^2(zL^2 + L^2 z) - 4\hbar^2(\underbrace{(yL_z - i\hbar x)L_y}_{L_z y} + \underbrace{(xL_z + i\hbar y)L_x}_{L_z x} + zL_z L_z) \\
&= 2\hbar^2(zL^2 + L^2 z) - 4\hbar^2(\underbrace{L_z y L_y + L_z x L_x + L_z z L_z}_{L_z(\mathbf{r} \cdot \mathbf{L}) = 0}) \\
&= 2\hbar^2(zL^2 + L^2 z)
\end{aligned}$$

Or, since this also holds for x and y , we can more succinctly write,

$$\begin{aligned}
\cdot [\hat{L}^2, [\hat{L}^2, \hat{r}]] &= 2\hbar^2(\hat{r}\hat{L}^2 + \hat{L}^2\hat{r}) \\
2\hbar^2 \langle n'l'm' | \hat{r} \hat{L}^2 + \hat{L}^2 \hat{r} | nlm \rangle &= \langle n'l'm' | [\hat{L}^2, [\hat{L}^2, \hat{r}]] | nlm \rangle \\
2\hbar^4(l(l+1) + l'(l'+1)) \langle n'l'm' | \hat{r} | nlm \rangle &= \hbar^2(l'(l'+1) - l(l+1)) \\
2\hbar^4(l(l+1) + l'(l'+1)) \langle n'l'm' | \hat{r} | nlm \rangle &= \hbar^2(l'(l'+1) - l(l+1)) \langle n'l'm' | [\hat{L}^2, \hat{r}] | nlm \rangle \\
(l'+l+1)^2 + (l'-l)^2 - 1 &= \hbar^2(l'(l'+1) - l(l+1)) \langle n'l'm' | \hat{r} | nlm \rangle \\
((l'+l+1)^2 + (l'-l)^2 - 1) \langle n'l'm' | \hat{r} | nlm \rangle &= (l'(l'+1) - l(l+1))(l'(l'+1) - l(l+1)) \langle n'l'm' | \hat{r} | nlm \rangle \\
&\quad ((l'+l+1)(l'-l))^2
\end{aligned}$$

$$\Rightarrow \frac{[(l'+l+1)^2 + (l'-l)^2] - (l'(l'+1) - l(l+1))^2}{-[(l'+l+1)^2 - 1][(l'-l)^2 - 1]} = 0 \text{ or } \langle n'l'm' | \hat{r} | nlm \rangle = 0$$

L all 3 components zero here!

either one of these could be zero

This holds if:

$\Delta l = \pm 1$ (doesn't matter if $l > l'$ or $l' > l$)
or $l = l' = 0 \rightarrow$ but if $l = l'$, this guarantees
or $\langle n'l'm' | \hat{r} | nlm \rangle = 0$

$\uparrow$ undesirable result, we don't want to force
all three elements to be zero!

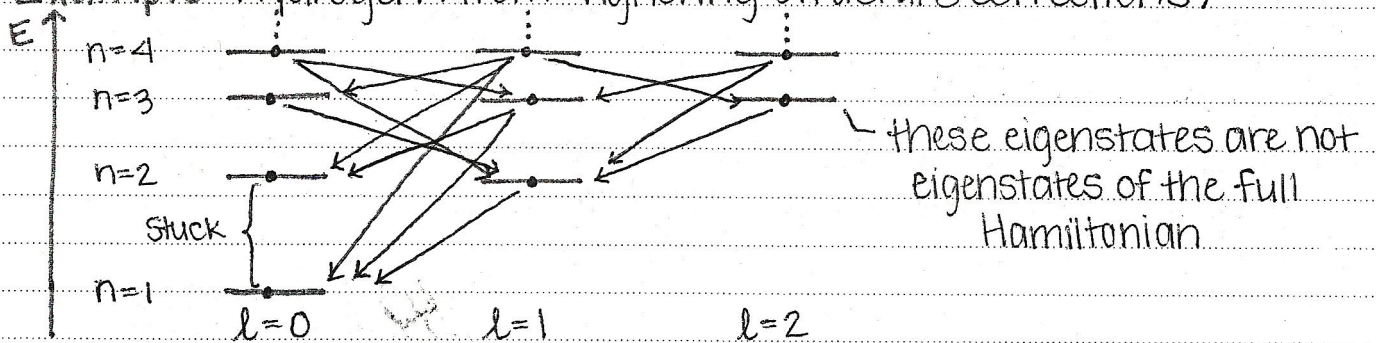
Complete Summary

$$\Rightarrow \Delta l = \pm 1, \Delta m = 0, \pm 1 \leftarrow$$

Wigner-Eckart Theorem

$\rightarrow$

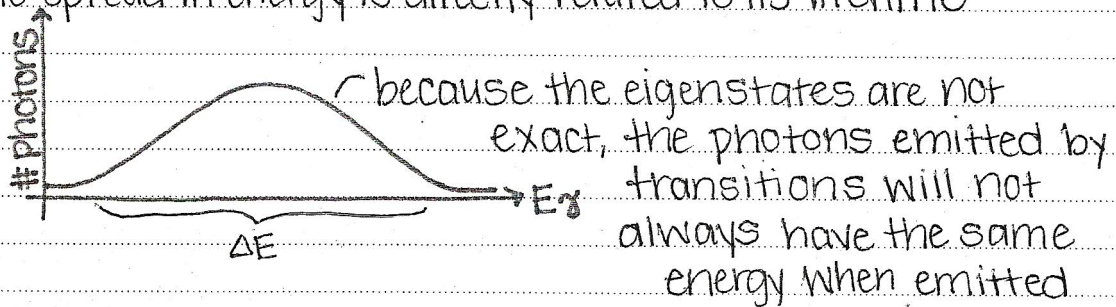
Example: Hydrogen Atom (ignoring structure corrections)



When the state decays, it must also change l by ± 1
 → you can put Hydrogen in an excited state for $l=0$ that can never decay by the electric dipole approximation (though it can decay in second order perturbation theory by emitting two photons at once)

$\Delta E \propto \frac{1}{\tau}$ (energy spread due to lack of Full Hamiltonian)

↳ the spread in energy is directly related to its lifetime

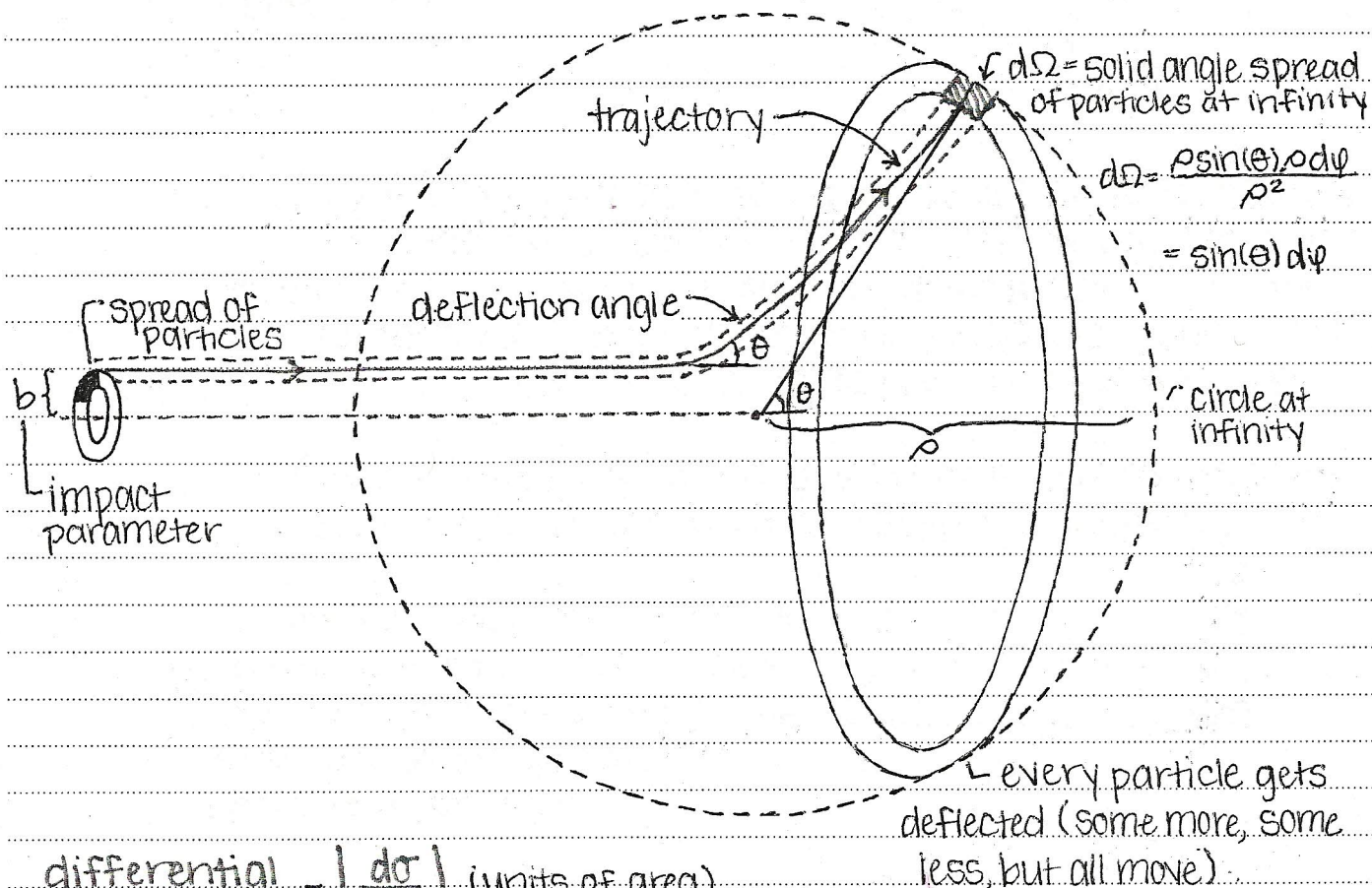


Scattering

"Do you know what scattering is? You throw things at each other and figure them out! Want to know how a clock works? Throw it at your friend, gears come out! And you're like, "Oh! That's how it works!"

Classical Scattering:

"Remember, in classical physics, particles have both position and momentum at the same time! How weird!"



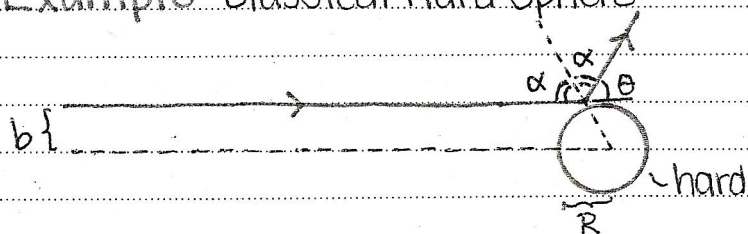
differential cross-section = $\left| \frac{d\sigma}{d\Omega} \right|$ (units of area)

↑ cross-section always positive

total cross-section = $\int d\Omega \left| \frac{d\sigma}{d\Omega} \right| = \sigma$

Only way this does not blow up to infinity is if your potential has a finite range ("and this is why scattering in classical mech. is really just stupid")

Example: Classical Hard Sphere



"examples are good for the soul"

$2\alpha + \theta = \pi$

$$b = R \sin(\alpha) = R \sin\left(\frac{\pi}{2} - \frac{\theta}{2}\right) = R \cos\left(\frac{\theta}{2}\right)$$

$$\frac{d\sigma}{d\Omega} = \left| \frac{b db d\theta}{\sin(\theta) d\theta} \right| = \frac{b}{\sin(\theta)} \frac{db}{d\theta} = \frac{R \cos(\theta/2) R \sin(\theta/2)}{2 \sin(\theta)} = \frac{R^2}{4}$$

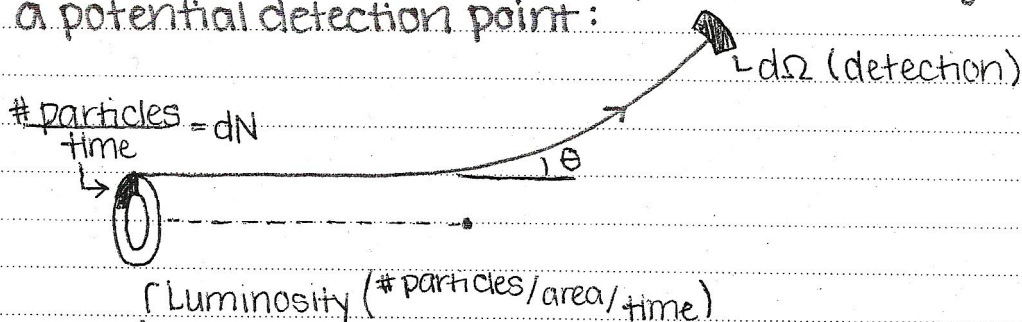
needed this to go away because it gets deformed from scattering

$$\sigma = \int_{4\pi} d\Omega \frac{R^2}{4} = \pi R^2$$

exactly as expected

"This is true for any hard shape: a hard square, a hard pony... in the spirit of quantum physics, use a cat and shoot it with water..."

Now assume an infinite flux of particles moving towards a potential detection point:



$$dN = \int b db d\theta$$

$\sigma = \text{area}$

how many particles of this infinite flux that pass through this given cross-section (this gets rid of our impact parameter, which is hard to find in classical mechanics and impossible in Quantum Mechanics)

$$\text{differential cross-section} = \frac{1}{\int d\Omega} \frac{dN}{d\Omega} = \frac{d\sigma}{d\Omega}$$

Quantum scattering:

→ must make a "wave packet" to compromise between position and momentum

Goal - find a solution to the time-independent Schrödinger equation that takes this form:

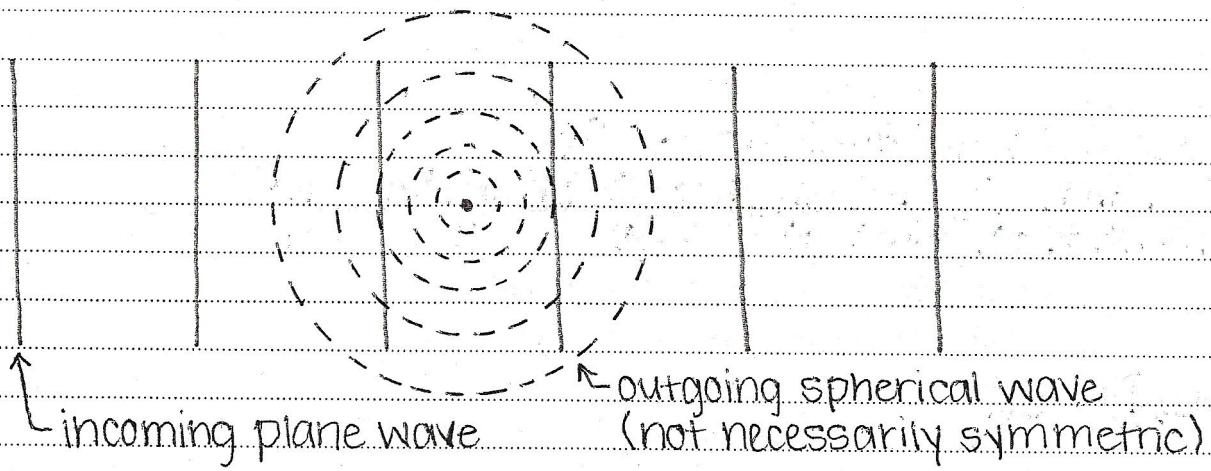
arbitrary normalization $\int$ plane wave moving in the z-direction towards

$$\Psi(r, \theta) \longrightarrow A \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right]$$

the scattering center

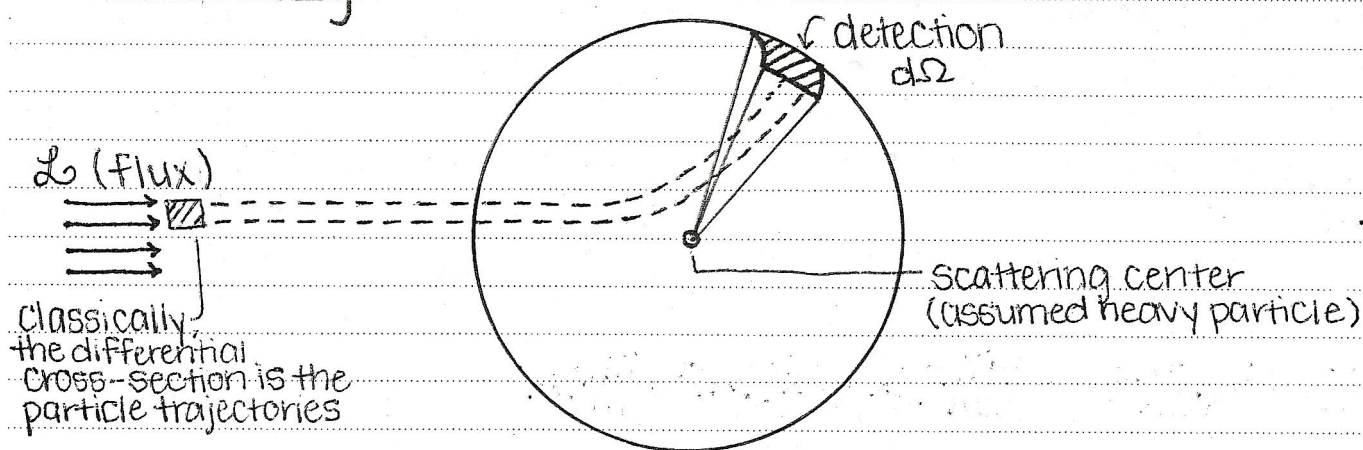
no ϕ dependence (for simplicity)

outgoing spherical wave



11/30/12

Scattering



$$\frac{1}{L} \frac{dN}{d\Omega} = \frac{d\sigma}{d\Omega} = \text{differential cross-section (units of area)}$$

particles/time

↑ Luminosity (# particles/time/area)

* In quantum scattering, the differential cross-section cannot describe a specific area because the particles don't have trajectories, they come from all over with a certain probability
→ probability density

$$\text{total cross-section} = \int d\Omega \frac{d\sigma}{d\Omega}$$

For quantum scattering, find a solution to the TISE that takes the following form:

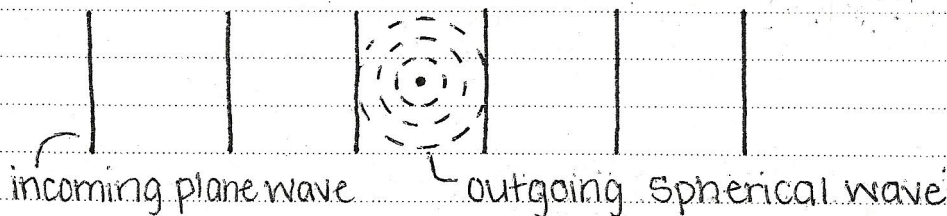
normalization → incoming plane wave

$$\Psi(r, \theta) \xrightarrow{r \rightarrow \infty} A \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right]$$

outgoing spherical wave

$f(\theta)$ - scattering amplitude (complex number)

this equation only valid for large distances
(need TDSE near scattering center)



→

Aside: Probability Density

$$\mathbf{j} = \frac{-i\hbar}{2m} (\Psi^* \nabla \Psi - \nabla \Psi^* \Psi)$$



hole in space

$$\frac{d}{dt} |\Psi|^2 + \nabla \cdot \mathbf{j} = 0$$

#particles going through hole
 $= \int da \cdot \mathbf{j} \cdot \hat{n}$

* every point in space has a different probability flow

$$\mathcal{L}_{\text{flux}} = \text{incoming} = \frac{-i\hbar}{2m} (\underbrace{\Psi^* \nabla \Psi}_{-\nabla \Psi^* \Psi}) = \frac{\hbar k}{m} |\Psi|^2$$

$$\frac{d\sigma}{dN} = \frac{1}{\mathcal{L}} \frac{dN}{d\Omega} = \frac{m}{\hbar k |\Psi|^2} \left(|f|^2 \frac{-i\hbar}{2m} (\mathbf{i}k + \mathbf{i}k) \frac{|\Psi|^2}{r^2} \right) r^2 d\Omega \frac{1}{d\Omega}$$

$$= |f(\theta)|^2$$

$$\rightarrow Af \frac{d}{dr} \frac{e^{ikr}}{r} = Af \left[\frac{ik}{r} - \frac{1}{r^2} \right] e^{ikr}$$

negligible for large r

Born Approximation: small potential ($f(\theta)$ and e^{ikr}/r are very small)

→ finding $f(\theta)$ using perturbation theory

$$\Psi(r) = \Psi_{\text{in}} + \Psi_{\text{refl}}$$

$$\text{satisfies: } \frac{\hbar^2}{2m} \nabla^2 (\underbrace{\Psi_{\text{in}}}_{\text{incoming}} + \underbrace{\Psi_{\text{refl}}}_{\text{outgoing}}) + \underbrace{V(\Psi_{\text{in}} + \Psi_{\text{refl}})}_{\approx V\Psi_{\text{in}}} = E(\Psi_{\text{in}} + \Psi_{\text{refl}})$$

$$\left[\underbrace{\nabla_r^2 + \frac{2mE}{\hbar^2}}_{\text{linear operator}} \right] \underbrace{\Psi_{\text{refl}}(r)}_{\text{want to know}} = - \left(\frac{2m}{\hbar^2} \right) \underbrace{V(r) \Psi_{\text{in}}(r)}_{\text{known}}$$

$$Ax = b$$

$$\underbrace{A^{-1}A}_{\mathbb{I}} x = A^{-1}b$$

↑ Works for any b

Inverse of operator ⇒ Green's function

$$AA^{-1} = \mathbb{I}$$

$$\left[\underbrace{\nabla_r^2 + \frac{2mE}{\hbar^2}}_{k^2} \right] G(r, r') = \delta(r - r')$$

note that it's independent of potential! "any b"

$$x = A^{-1}b$$

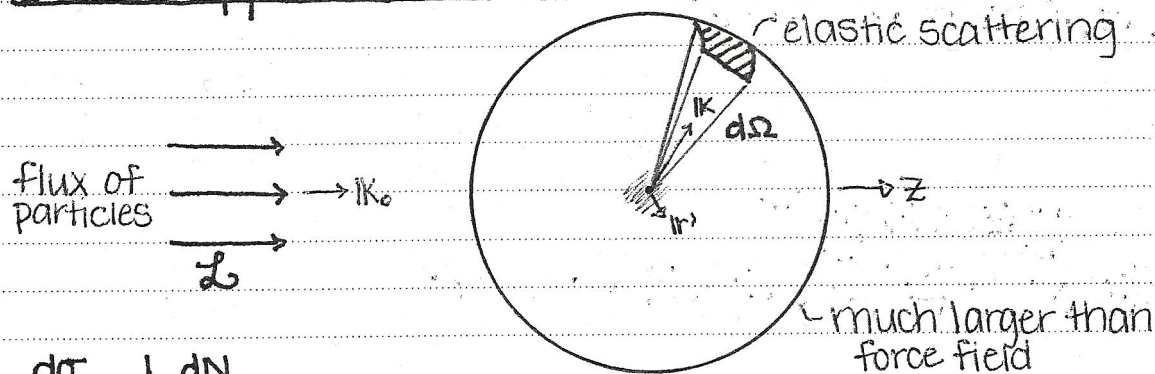
$$\Rightarrow \Psi_{\text{refl}}(r) = - \left(\frac{2m}{\hbar^2} \right) \int d^3r' G(r, r') V(r') \Psi_{\text{in}}(r')$$

$$\uparrow k = \sqrt{2mE}/\hbar$$

$$G(r, r') = \frac{-1}{4\pi} \frac{e^{ik|r-r'|}}{|r-r'|}$$

↑ Coulomb Law

Born Approximation



$$\frac{d\sigma}{d\Omega} = \frac{1}{L} \frac{dN}{d\Omega}$$

↳ differential cross-section: What size hole on the left where the particles originate has the same size as the detection hole on the infinite circle

In QM: Solutions of the TISE that take the form

$$\Psi(r, \theta) \underset{r \rightarrow \infty}{\sim} A \left[\underbrace{e^{ikz}}_{\Psi_{in}} + f(\theta) \underbrace{\frac{e^{ikr}}{r}}_{\Psi_{scat}} \right]$$

$$\frac{d\sigma}{d\Omega} = |f(\theta, \psi)|^2$$

scattering amplitude, typically complex

Born Approximation: $V_{small} \rightarrow \Psi_{scat} \ll \Psi_{in}$

↳ just a plane wave, solution to the free Schrödinger eq.

$$\frac{-\hbar^2}{2m} \nabla_r^2 (\Psi_{in}(r) + \Psi_{scat}(r)) + V(r) (\Psi_{in}(r) + \Psi_{scat}(r)) = E (\Psi_{in}(r) + \Psi_{scat}(r))$$

$V(r) \Psi_{in}(r)$

$$\left[\nabla_r^2 + \frac{2mE}{\hbar^2} \right] \Psi_{scat}(r) = - \left(\frac{2m}{\hbar^2} \right) V(r) \Psi_{in}(r)$$

→ Multiply by the Green's function; the inverse

$$\Psi_{scat}(r) = - \left(\frac{2m}{\hbar^2} \right) \int d^3r' G(r, r') V(r') \Psi_{in}(r')$$

$$[\nabla_r^2 + k^2] G(r, r') = \delta(r - r')$$

↳ applicable for any potential

What is $G(r, r')$?

$$G(r, r') = \frac{-1}{4\pi} \frac{e^{ik|r-r'|}}{|r-r'|} \quad (\text{units of } 1/\text{length})$$

↳ r' is a parameter, not a variable. can choose to center coordinates around r' ($r' = 0$)

In spherical coordinates centered around r' :

$$\nabla_r^2 \left(\frac{e^{ikr}}{r} \right) \left(\frac{-1}{4\pi} \right) = \frac{-1}{4\pi} \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} \frac{e^{ikr}}{r}$$

$$\underbrace{\left[\frac{ik}{r} - \frac{1}{r^2} \right] e^{ikr}}_{[ikr-1]e^{ikr}}$$

$$\underbrace{[ikr-1]e^{ikr}}_{[ik-k^2r-ik]e^{ikr}}$$

$$= -\frac{1}{4\pi} (-k^2) \frac{1}{r} e^{ikr}$$

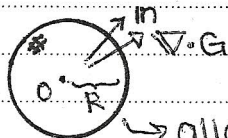
$$\left[\nabla_r^2 + k^2 \right] \left(\frac{-1}{4\pi} \frac{e^{ikr}}{r} \right) = \frac{-1}{4\pi} \frac{e^{ikr}}{r} (-k^2 + k^2) = 0, \quad r \neq 0$$

↳ but 0 is not a δ -function

What about $r=0$?

→ integrate around 0 to get a δ -function

$$\nabla_r G(r, r') = \frac{-1}{4\pi} \left(\frac{ik}{r} - \frac{1}{r^2} \right) e^{ikr} \hat{e}_r$$



↳ allows us to use Gauss' theory

$$\int dV \nabla_r^2 G = \int dS \nabla_r G(r, r') \cdot \hat{n} = \underbrace{4\pi R^2}_{\text{area of sphere}} \left(\frac{-1}{4\pi} \right) \left(\frac{ik}{R} - \frac{1}{R^2} \right) e^{ikR} \xrightarrow{R \rightarrow 0} 1$$

sphere centered at r' , radius R same sphere

$$\Rightarrow \nabla_r^2 G(r, r') = \delta(r - r')$$

the Laplacian everywhere is zero except right where the charge is

$$\Psi_{\text{scat}}(r) = \frac{2m}{4\pi\hbar^2} \int d^3r' \frac{e^{ik|r-r'|}}{|r-r'|} V(r') e^{ikz'}$$

↳ the z-component of r'
 $\hat{k} \hat{e}_z \cdot r' = k_0 \cdot r'$

$$K|r-r'| = k\sqrt{r^2 + r'^2 - 2r \cdot r'}$$

$$= kr \sqrt{1 - 2\frac{r \cdot r'}{r^2} + r'^2/r^2}$$

$$\approx kr \left[1 - \frac{r \cdot r'}{r^2} + \dots \right] = kr - k \hat{k} \cdot r'$$

$$\approx \frac{-m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int d^3r' V(r') e^{-i(k-k_0) \cdot r'}$$

$$\Rightarrow \underbrace{f(\theta, \varphi)}_{\text{direction of } k} = \frac{-m}{2\pi\hbar^2} \int d^3r' V(r') e^{-i(\underbrace{k-k_0}_{\text{momentum transfer}}) \cdot r'}$$

Born Approximation, con't

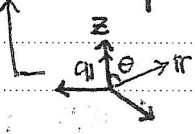
Scattering amplitude:

$$f(\theta, \varphi) = \frac{-m}{2\pi\hbar^2} \int d^3r' V(r') e^{-i(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r}'}$$

$\mathbf{k}$ - direction of $\mathbf{k}$ - $\mathbf{k}_0$ fixed
 $\mathbf{k}_0$ - momentum transfer
 $\mathbf{k}$ in the direction of the incident wave
 $\mathbf{k}_0$ in the direction of the reflected wave

Simplification:

If $V(r) = V(r)$ (spherically symmetric)

$$\begin{aligned}
 f &= \frac{-m}{2\pi\hbar^2} \int_0^\infty dr' \int_0^{2\pi} d\varphi \int_{-1}^1 d\cos(\theta) e^{-iqr' \cos(\theta)} r'^2 V(r') \\
 &= \frac{-m}{\hbar^2} \int_0^\infty dr' r'^2 V(r') \frac{e^{iqr' \cos(\theta)} - e^{-iqr' \cos(\theta)}}{-iqr'} \Big|_{-1}^1 \\
 &= \frac{-2m}{q\hbar^2} \int_0^\infty dr' r' V(r') \sin(qr')
 \end{aligned}$$


Example: Soft Sphere (sphere has a potential to interact with incoming particles, but particles can also potentially pass through)

$$V(r) = \begin{cases} V_0, & r < R \\ 0, & r > R \end{cases}$$

R - radius of the sphere
 Spherically symmetric

$$f(\theta) = \frac{-2m}{q\hbar^2} \int_0^R dr r V_0 \sin(qr)$$

$$= \frac{-2m}{q^3\hbar^2} V_0 [\sin(qR) - qR \cos(qR)] \quad (\text{exact solution})$$

$$\approx \frac{-2mV_0}{q\hbar^2} \int_0^R dr r \sin(qr)$$

expand for qR very small

$$= \frac{-2mV_0}{q\hbar^2} \left[\frac{qR^2}{2} + \frac{q^3 R^5}{3! \cdot 5} + \dots \right]$$

$$\approx \frac{-2mV_0}{\hbar^2} R^2 + \dots$$

for small q (small E), the leading term (scattering amplitude at zero momentum) is independent of q !

It's a constant!

→ Even if $V(r)$ is not constant, if it is some complicated thing, this allows us to say that our scattering amplitude is just $f \sim \int_0^\infty dr r^2 V(r)$ no matter what is applied (assumed V does not vary too quickly)

Partial Wave Analysis

Solving the 3-dimensional Schrödinger equation with a Ψ that isn't necessarily spherically symmetric

ANY function can be expanded like this

$$\Psi(r, \theta) = A \sum_{l=0}^{\infty} \frac{U_l(r)}{r} P_l(\cos(\theta)) \quad , \quad U_l(0) = 0 \quad \text{necessary or the } \Psi \text{ blows up}$$

assume no Ψ -dependence

Legendre Polynomials

different coefficients for each value of r

$$\left[\frac{-\hbar^2}{2m} \nabla^2 + V \right] \Psi = E \Psi \Rightarrow \left[\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] U_l(r) = E U_l(r)$$

* this does not apply for the Coulomb force

centrifugal barrier

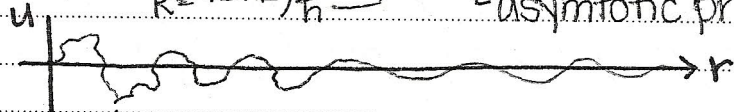
assume potential goes to 0 really quickly for large r (fast = faster than $1/r^2$)

at large enough r : free particle behavior (plane wave)

$$U_l(r) \rightarrow \sin(kr + \bar{\delta}_l)$$

$$k = \sqrt{2mE}/\hbar$$

asymptotic phase, l -dependent



any arbitrary function will, at large r , become a sine wave

$$\Psi(r, \theta) = A \sum_{l=0}^{\infty} a_l \frac{U_l(r)}{r} P_l(\cos(\theta))$$

$$\xrightarrow{r \rightarrow \infty} A \sum_{l=0}^{\infty} a_l \frac{\sin(kr + \bar{\delta}_l)}{r} P_l(\cos(\theta))$$

Want to choose a_l such that this wavefunction look like a scattering problem at large r (plane wave in $\rightarrow$ spherical wave out)

Goal: Choose a_l such that $\Psi(r, \theta)$ looks like

$$\Psi = A \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right]$$

→

Boundary Condition:

$$\Psi(r, \theta) \xrightarrow{r \rightarrow \infty} A \left[e^{ikz} + f(\theta) \frac{e^{ikr}}{r} \right]$$

$z = r \cos(\theta)$

orthogonal set of polynomials

$$\sum_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos(\theta)) \quad f(\theta) = \sum_{l=0}^{\infty} f_l P_l(\cos(\theta))$$

Spherical Bessel functions

$$f_l = \frac{2l+1}{2} \int d\cos(\theta) f(\theta) P_l(\cos(\theta))$$

$$= A \sum_{l=0}^{\infty} \left[(2l+1) i^l j_l(kr) + f_l \frac{e^{ikr}}{r} \right] P_l(\cos(\theta))$$

dependent on how this behaves at large r

$$\xrightarrow{r \rightarrow \infty} A \sum_{l=0}^{\infty} P_l(\cos(\theta)) \left[\frac{(2l+1) i^l}{kr} \sin(kr - \frac{l\pi}{2}) + f_l \frac{e^{ikr}}{r} \right]$$

general solution for the Schrödinger equation

$$a_l \frac{e^{ikr} e^{i\delta_l} - e^{-ikr} e^{-i\delta_l}}{2ir} = \frac{(2l+1)}{kr} e^{il\pi/2} \frac{(e^{ikr - i\pi/2} - e^{-ikr + i\pi/2})}{2i} + f_l \frac{e^{ikr}}{r}$$

$i^l = e^{il\pi/2}$

$$-a_l e^{-i\delta_l} = -\frac{(2l+1)}{k} e^{il\pi} \quad (e^{il\pi})^l = (-1)^l$$

$$\Rightarrow a_l = \frac{(2l+1)}{k} e^{i(\delta_l - l\pi)}$$

$$a_l e^{i\delta_l} = \frac{(2l+1)}{k} + f_l$$

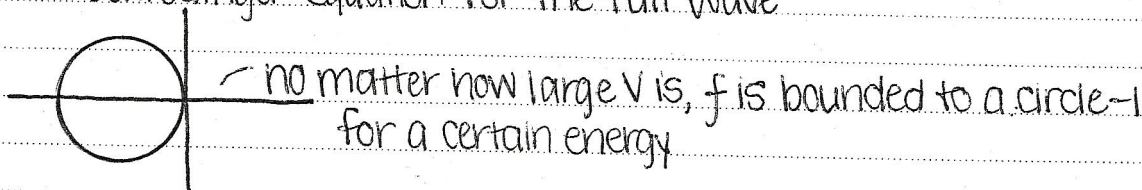
$$\Rightarrow f_l = \frac{(2l+1)}{k} e^{2i(\delta_l - l\pi/2)} - \frac{(2l+1)}{k}$$

$\delta_l = \text{Phase shift}$

bounded!

$$\Rightarrow f_l = \frac{2l+1}{k} (e^{i2\delta_l} - 1)$$

partial wave $\Rightarrow$ allows you to solve multiple one-dimensional Schrödinger equations instead of trying to solve the three-dimensional Schrödinger equation for the full wave



$\rightarrow$ Different from Born appx. where V must be small to be applicable

total scattering cross-section

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \int d\Omega |f(\theta)|^2$$

$$= \int d\Omega \sum_{l', l=0}^{\infty} f_l P_l(\cos(\theta)) f_{l'}^* P_{l'}(\cos(\theta))$$

$$= \sum_{l', l} f_l f_{l'}^* \underbrace{\int d\Omega P_l(\cos(\theta)) P_{l'}(\cos(\theta))}_{(4\pi/(2l+1)) \delta_{ll'} \text{ - because of orthogonality}}$$

$$= \sum_{l=0}^{\infty} \frac{4\pi}{2l+1} |f_l|^2 = \sum_{l=0}^{\infty} \frac{4\pi}{(2l+1)} \frac{(2l+1)^2}{k^2} \underbrace{(1+1+2\cos(2\delta_l))}_{\sin^2(\delta_l)}$$

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

Unitarity Bound:

if unbounded, violates unitarity

$$\sigma_l = \frac{4\pi}{k^2} (2l+1) \sin^2(\delta_l) \leq \frac{4\pi}{k^2} (2l+1)$$

partial wave cross-section is bounded

* Unitarity $\rightarrow$ every particle that goes in comes out (constant magnitude)

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Partial Wave Analysis

Recap: One-Dimensional Schrödinger Equation

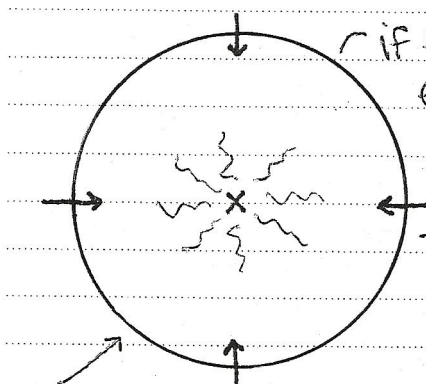
$$\textcircled{1} \left[\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 l(l+1)}{2mr^2} \right] U_l(r) = E U_l(r)$$

Boundary condition: $U_l(r=0) = 0$

$$\textcircled{2} U_l(r) \xrightarrow{r \rightarrow \infty} A \sin(kr - \frac{l\pi}{2} + \delta_l(k)) \quad \text{phase shift}$$

$$\textcircled{3} \frac{d\sigma}{d\Omega} = |f(\theta)|^2 = \left| \sum_{l=0}^{\infty} \underbrace{\frac{(2l+1)}{k}}_{f_l} (e^{i2\delta_l} - 1) P_l(\cos(\theta)) \right|^2$$

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



if there is no potential, wavefunction will evolve in time like it shrinks and then expands (free particle)

if there is a potential, complicated things may happen, but at infinity the wavefunction will look like the free particle because of unitarity, but it will have picked up some phase shift, $\delta_l(k)$

* note that this is still the TISE!

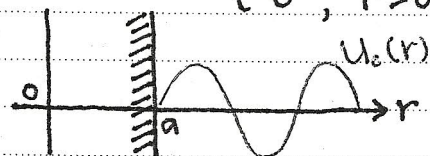
incoming/outgoing
spherical wave

But our initial condition is a plane wave...

→ a plane wave is just a linear combination of spherical waves, so instead of a single 'l', we now have all 'l's' (different partial waves will have different phases)

Example: Hard Sphere (S-wave $\Rightarrow l=0$)

$$\frac{-\hbar^2}{2m} U_0'' + \begin{cases} \infty, & r < a \\ 0, & r > a \end{cases}, \quad U_0(r) = E_0 U(r)$$

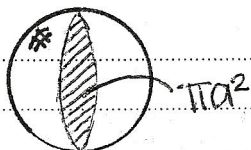


$$\Rightarrow U_0(r) = A \sin(kr + \delta_0)$$

Boundary condition: $U_0(r=a) = 0$

$$\Rightarrow ka + \delta_0 = 0$$

$$\delta_0 = -ka$$



$$\sigma_{\text{s-wave}} = \frac{4\pi}{k^2} \sin^2(ka) \xrightarrow{ka \ll 1} 4\pi a^2$$

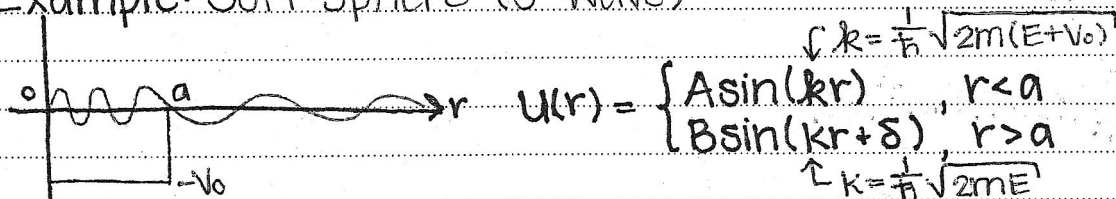
$\hookrightarrow$ 4x the geometric cross-section of the sphere
 $\hookrightarrow$ small energy approximation

If we were to go to higher ℓ -values, we would need SBF's

Things to know about spherical bessel functions:

1. asymptotic behavior
2. where the zeroes are

Example: Soft Sphere (S-wave)



Boundary condition: $u(a+) = u(a-)$

$$\rightarrow A \sin(ka) = B \sin(ka + \delta)$$

Boundary condition: $u'(a+) = u'(a-)$

$$\rightarrow A k \cos(ka) = B k \cos(ka + \delta)$$

$\hookrightarrow$ although there are many unknowns, we only need to find this (normalization arbitrary)

$$\Rightarrow \tan(\delta) = \frac{\frac{k}{ka} \tan(ka) - \tan(ka)}{1 + \frac{k}{ka} \tan(ka) \tan(ka)}$$

$$\xrightarrow{ka \ll 1} \delta \approx \tan(\delta) \approx ka \left[\frac{\tan(ka)}{ka} - 1 \right]$$

There's an energy $\xrightarrow{\tan \rightarrow \infty} ka = \pi/2 \Rightarrow \delta = \pi/2$

bound states appear

$\hookrightarrow$ largest cross section possible!
 $\sin^2(\pi/2) = 1$

$\rightarrow$ You reach the unitarity bound!