Chapter 12

Absorption and Emission of Radiation: Time Dependent Perturbation Theory Treatment

Want Hamiltonian for Charged Particle in E & M Field
Need the potential *U*.

Force on Charged Particle:

$$\vec{F} = e\left[\vec{E} + \frac{1}{c}\left(\vec{V}\times\vec{B}\right)\right]$$

Force (generalized form in Lagrangian mechanics)
***j*th component:**

$$F_j = -\frac{\partial U}{\partial q_j} + \frac{d}{dt}\left(\frac{\partial U}{\partial \dot{q}_j}\right)$$

U is the potential
q_j are coordinates

Example:

$$F_x = -\frac{\partial U}{\partial x} + \frac{d}{dt}\left(\frac{\partial U}{\partial V_x}\right)$$

since:

$$V_x = \frac{dx}{dt} = \dot{x}$$

Use the two equations for *F* to find *U*,
the potential of a charged particle in an E & M field

Once we have *U*, we can write:

$$\underline{H} = \underline{H}^0 + \underline{H}'$$

Where $\underline{H}'$ is the time dependent perturbation

Use time dependent perturbation theory.

Using the Standard Definitions from Maxwell's Eqs.

$$\vec{B} = \vec{\nabla} \times \vec{A} \qquad\qquad \vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A} - \vec{\nabla}\phi$$

$\vec{A} \equiv$ vector potential

$\phi \equiv$ scalar potential

Force on Charged Particle:

$$\vec{F} = e\left[\vec{E} + \frac{1}{c}\left(\vec{V} \times \vec{B}\right)\right]$$

Then:

$$\vec{F} = e\left[-\vec{\nabla}\phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t} + \frac{1}{c}\left(\vec{V} \times \vec{\nabla} \times \vec{A}\right)\right]$$

Components of F, F_x, etc…

$$(\nabla\phi)_x = \frac{d\phi}{dx}$$

$$\left(\vec{V} \times \vec{\nabla} \times \vec{A}\right)_x = V_y\left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right) - V_z\left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}\right)$$

$$\left(\vec{V}\times\vec{\nabla}\times\vec{A}\right)_x = V_y\left(\frac{\partial A_y}{\partial x}-\frac{\partial A_x}{\partial y}\right)-V_z\left(\frac{\partial A_x}{\partial z}-\frac{\partial A_z}{\partial x}\right)$$

Adding and Subtracting $V_x\dfrac{\partial A_x}{\partial x}$

$$\left(\vec{V}\times\vec{\nabla}\times\vec{A}\right)_x = V_y\frac{\partial A_y}{\partial x}+V_z\frac{\partial A_z}{\partial x}+V_x\frac{\partial A_x}{\partial x}-V_x\frac{\partial A_x}{\partial x}-V_y\frac{\partial A_x}{\partial y}-V_z\frac{\partial A_x}{\partial z}$$

Total time derivative of A_x is

$$\frac{dA_x}{dt}=\frac{\partial A_x}{\partial t}+\left(V_x\frac{\partial A_x}{\partial x}+V_y\frac{\partial A_x}{\partial y}+V_z\frac{\partial A_x}{\partial z}\right)$$

Due to explicit variation of A_x with time.

Due to motion of particle - Changing position at which A_x is evaluated.

Then:

$$\frac{\partial A_x}{\partial t} - \frac{dA_x}{dt} = -V_y \frac{\partial A_x}{\partial y} - V_z \frac{\partial A_x}{\partial z} - V_x \frac{\partial A_x}{\partial x}$$

Using this

$$\left(\vec{V} \times \vec{\nabla} \times \vec{A}\right)_x = \frac{\partial}{\partial x}\left(\vec{V} \cdot \vec{A}\right) - \frac{dA_x}{dt} + \frac{\partial A_x}{\partial t}$$

Since:

$$\frac{\partial}{\partial x}\left(\vec{V} \bullet \vec{A}\right) = \vec{V}\frac{\partial \vec{A}}{\partial x} + \underbrace{\cancel{\frac{\vec{A}\,\partial \vec{V}}{\partial x}}}_{0} = V_x \frac{\partial A_x}{\partial x} + V_y \frac{\partial A_y}{\partial x} + V_z \frac{\partial A_z}{\partial x}$$

Substituting these pieces into equation for F_x

$$F_x = e\left[-\frac{\partial\phi}{\partial x} - \frac{1}{c}\frac{\partial A_x}{\partial t} + \frac{1}{c}(\vec{V}\times\vec{\nabla}\times\vec{A})_x\right]$$

cancels

$$\left(\vec{V}\times\vec{\nabla}\times\vec{A}\right)_x = \frac{\partial}{\partial x}\left(\vec{V}\cdot\vec{A}\right) - \frac{dA_x}{dt} + \frac{\partial A_x}{\partial t}$$

Then $$F_x = e\left[-\frac{\partial}{\partial x}\left(\phi - \frac{1}{c}\vec{A}\cdot\vec{V}\right) - \frac{1}{c}\frac{dA_x}{dt}\right]$$

$$A_x = \frac{\partial}{\partial V_x}\left(\vec{A}\cdot\vec{V}\right)$$

substitute

because $$\frac{\partial}{\partial V_x}\left(\vec{A}\cdot\vec{V}\right) = \frac{\partial}{\partial V_x}\left(A_xV_x + A_yV_y + A_zV_z\right)$$

$$= A_x\frac{\partial V_x}{\partial V_x} + V_x\frac{\partial A_x}{\partial V_x} + A_y\frac{\partial V_y}{\partial V_x} + \cdots$$

$$1 \quad + \quad 0 \quad + \quad 0 \quad + \quad 0$$

***A* not function of *V* &**
V_y V_z independent of V_x

Therefore

$$F_x = e\left[-\frac{\partial}{\partial x}\left(\phi - \frac{1}{c}\vec{A}\cdot\vec{V}\right) - \frac{1}{c}\frac{d}{dt}\left(\frac{\partial}{\partial V_x}\left(\vec{A}\cdot\vec{V}\right)\right)\right]$$

$$F_x = \left[-\frac{\partial}{\partial x}\left(e\phi - \frac{e}{c}\vec{A}\cdot\vec{V}\right) + \frac{d}{dt}\left(\frac{\partial}{\partial V_x}\left(e\phi - \frac{e}{c}\vec{A}\cdot\vec{V}\right)\right)\right]$$

Since ϕ is independent of V, can add in.

Goes away when taking $\dfrac{\partial}{\partial V_x}$

The general definition of F_x is:

$$F_x = -\frac{\partial}{\partial x}U + \frac{d}{dt}\left(\frac{\partial}{\partial V_x}U\right)$$

$U \rightarrow$ **potential**

Therefore:

$$U = e\phi - \frac{e}{c}\vec{A}\cdot\vec{V}$$

Legrangian:

$$L = T - U$$

$T \equiv$ Kinetic Energy

For charged particle in E&M Field:

$$L = T - e\phi + \frac{e}{c}\vec{A}\cdot\vec{V}$$

$$T = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$$

The *ith* component of the momentum is give by

$$P_i = \frac{\partial L}{\partial \dot{q}_i}$$

where:

$$\dot{q}_i = \frac{dq_i}{dt} = V_i$$

$$\dot{q}_x = \dot{x} = V_x$$

Therefore, $$P_x = m\dot{x} + \frac{e}{c}A_x$$

The classical Hamiltonian:

$$H = P_x \dot{x} + P_y \dot{y} + P_z \dot{z} - L$$

$$\left(P_x = m\dot{x} + \frac{e}{c} A_x, \text{ etc.}\right)$$

$$L = T - e\phi + \frac{e}{c} \vec{A} \cdot \vec{V}$$

$$T = \frac{1}{2} m \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2 \right)$$

Therefore

$$H = \left(m\dot{x}^2 + \frac{e}{c} A_x \dot{x} \right) + \left(m\dot{y}^2 + \frac{e}{c} \dot{y} A_y \right) + \left(m\dot{z}^2 + \frac{e}{c} \dot{z} A_z \right)$$

$$-\frac{1}{2} m \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2 \right) - \frac{e}{c} \left(\dot{x} A_x + \dot{y} A_y + \dot{z} A_z \right) + e\phi$$

This yields:

$$H = \frac{1}{2} m \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2 \right) + e\phi$$

Want H in terms of momentum P_x, P_y, P_z
since we know how to go from classical momentum to QM operators.

Multiply by m/m

$$H = \frac{1}{2m}\left((m\dot{x})^2 + (m\dot{y})^2 + (m\dot{z})^2 \right) + e\phi$$

Using:

$$P_i = m\dot{q}_i + \frac{e}{c}A_i \quad \text{then} \quad m\dot{q}_i = P_i - \frac{e}{c}A_i$$

Classical Hamiltonian for a charged particle in any combination of electric and magnetic fields is:

$$H = \frac{1}{2m}\left[\left(p_x - \frac{e}{c}A_x \right)^2 + \left(p_y - \frac{e}{c}A_y \right)^2 + \left(p_z - \frac{e}{c}A_z \right)^2 \right] + e\phi$$

QM Hamiltonian

Make substitution: $p_x \Rightarrow -i\hbar \dfrac{\partial}{\partial x}$

Then the term:

$$\left(p_x - \frac{e}{c}A_x\right)^2 \Rightarrow -\hbar^2 \frac{\partial^2}{\partial x^2} + \frac{e^2}{c^2}|A_x|^2 + i\frac{\hbar e}{c}\frac{\partial}{\partial x}A_x + i\frac{\hbar e}{c}A_x\frac{\partial}{\partial x}$$

Same. Pick up factor of two

The operator operates on a function, ψ.
Using the product rule:

$$i\frac{\hbar e}{c}\frac{\partial}{\partial x}A_x\psi(x) = i\frac{\hbar e}{c}\frac{\partial A_x}{\partial x}\psi(x) + i\frac{\hbar e}{c}A_x\frac{\partial \psi(x)}{\partial x}$$

$$\left(p_x - \frac{e}{c}A_x\right)^2 \Rightarrow -\hbar^2 \frac{\partial^2}{\partial x^2} + \frac{e^2}{c^2}|A_x|^2 + i\frac{\hbar e}{c}\frac{\partial A_x}{\partial x} + 2i\frac{\hbar e}{c}A_x\frac{\partial}{\partial x}$$

The total QM Hamiltonian in three dimensions is:

$$\underline{H} = \frac{1}{2m}\left(-\hbar^2\nabla^2 + \frac{e^2}{c^2}|A|^2 + \frac{i\hbar e}{c}\vec{\nabla}\cdot\vec{A} + 2\frac{i\hbar e}{c}\vec{A}\cdot\vec{\nabla}\right) + e\phi$$

This is general for a charged particle in any combination of electric and magnetic fields

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For light ➔ E & M Field

$\phi = 0$ **(no scalar potential)**

And since

$$\vec{\nabla}\cdot\vec{A} + \frac{1}{c^2}\frac{\partial\phi}{\partial t} = 0$$

(Lorentz Gauge Condition)

Then:

$$\vec{\nabla}\cdot\vec{A} = 0$$

Weak field approximation: $|A|^2$ **is negligible**

Therefore, for a weak light source

$$\underline{H} = \frac{1}{2m}\left(-\hbar^2\nabla^2 + \frac{2i\hbar e}{c}\vec{A}\cdot\vec{\nabla}\right)$$

kinetic energy of particle

For many particles interacting through a potential *V*,
add potential term to Hamiltonian.
Combine potential energy term with kinetic energy term to get normal many particle Hamiltonian for an atom or molecule.

$$\underline{H}^0 = -\sum_j \frac{\hbar^2}{2m_j}\nabla_j^2 + V$$

Time independent

The remaining piece is time dependent portion due to light.

$$\underline{H}' = \sum_j \frac{e}{m_j c} i\hbar \underline{\vec{A}}_j \cdot \underline{\vec{\nabla}}_j$$

The total Hamiltonian is

$$\underline{H} = \underline{H}^0 + \underline{H}'$$

Use $\underline{H}^0 + \underline{H}'$ in time dependent perturbation calculation.

E & M Field → Plane wave propagating in z direction (x-polarized light)

unit vectors
$$\vec{i} \Rightarrow x$$
$$\vec{j} \Rightarrow y$$
$$\vec{k} \Rightarrow z$$

$$\vec{A} = \vec{i} A_x \quad \text{with} \quad A_x = A_x^0 \cos\left[2\pi\nu\left(t - \frac{z}{c}\right)\right]$$

vector potential

To see this is E & M plane wave, use Maxwell's equations

$$\vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{A} = \vec{i}\,\frac{2\pi\nu}{c} A_x^0 \sin 2\pi\nu\left(t - \frac{z}{c}\right)$$

$$\vec{B} = \vec{\nabla} \times \vec{A} = \vec{j}\,\frac{2\pi\nu}{c} A_x^0 \sin 2\pi\nu\left(t - \frac{z}{c}\right)$$

$$\vec{\nabla} \times \vec{A} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \dfrac{\partial}{\partial x} & \dfrac{\partial}{\partial y} & \dfrac{\partial}{\partial z} \\ A_x & 0 & 0 \end{vmatrix}$$

Equal amplitude $\vec{B}$ and $\vec{E}$ fields,
perpendicular to each other,
propagating along z.

To use time dependent perturbation theory we need:

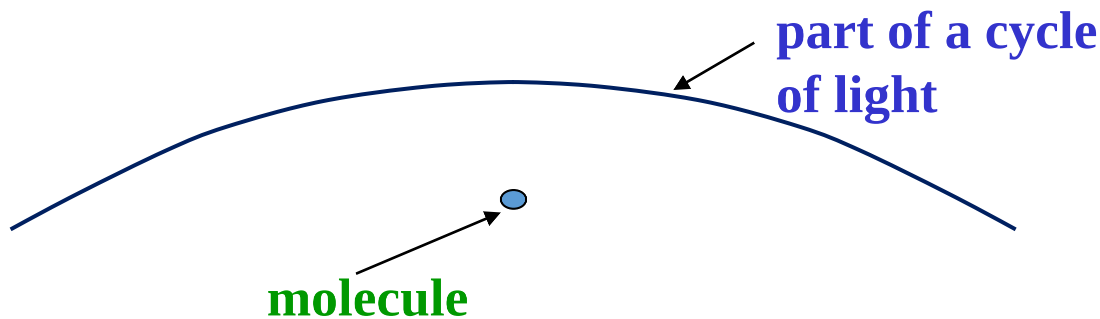
$$\left\langle \Psi_m^0 \middle| \underline{H}' \middle| \Psi_n^0 \right\rangle = \left\langle \Psi_m^0 \middle| -\sum_j \frac{e}{m_j c} \underline{A}_{xj} \underline{P}_{xj} \middle| \Psi_n^0 \right\rangle$$

Dipole Approximation:

Most cases of interest, wavelength of light much larger than size of atom or molecule

$\lambda > 2\,x\,10^3\,\text{Å} = 200$ **nm**

atom, molecule $\simeq 1 - 10\,\text{Å}$



Take A_x constant spatially $\rightarrow$ **two particles in different parts of molecule will experience the same A_x at given instant of time.**

Dipole Approximation:

Pull A_x out of bracket since it is constant spatially

$$\left\langle \Psi_m^0 \middle| \underline{H}' \middle| \Psi_n^0 \right\rangle = -\frac{e}{c} A_x \sum_j \frac{1}{m_j} \left\langle \Psi_m^0 \middle| \underline{P}_{xj} \middle| \Psi_n^0 \right\rangle$$

$$= i \frac{e\hbar}{c} A_x \sum_j \frac{1}{m_j} \left\langle \Psi_m^0 \middle| \frac{\partial}{\partial x_j} \middle| \Psi_n^0 \right\rangle$$

$\frac{\partial}{\partial x_j}$ **doesn't operate on time dependent part of ket, pull time dependent phase factors out of bracket.**

$$\left\langle \Psi_m^0(q,t) \middle| \underline{H}' \middle| \Psi_n^0(q,t) \right\rangle = i \frac{e\hbar}{c} A_x e^{i(E_m - E_n)t/\hbar} \sum_j \frac{1}{m_j} \left\langle \psi_m^0(q) \middle| \frac{\partial}{\partial x_j} \middle| \psi_n^0(q) \right\rangle$$

Need to evaluate $\left\langle \psi_m^0 \middle| \frac{\partial}{\partial x_j} \middle| \psi_n^0 \right\rangle$

Can express in terms of x_j rather then $\frac{\partial}{\partial x_j}$

First for one particle ψ's can write following equations:

(1) $$\frac{d^2\psi_m^{0*}}{dx^2}+\frac{2m}{\hbar^2}\left[E_m - V(x)\right]\psi_m^{0*}=0$$

complex conjugate of Schrödinger equation

(2) $$\frac{d^2\psi_n^{0}}{dx^2}+\frac{2m}{\hbar^2}\left[E_n - V(x)\right]\psi_n^{0}=0$$

Left multiply (1) by $x\psi_n^0$

Left multiply (2) by $x\psi_m^{0*}$

(1) $$x\psi_n^0\frac{d^2\psi_m^{0*}}{dx^2}+\frac{2m}{\hbar^2}x\psi_n^0\psi_m^{0*}E_m-\cancel{\frac{2m}{\hbar^2}V(x)x\psi_n^0\psi_m^{0*}}=0$$

(2) $$x\psi_m^{0*}\frac{d^2\psi_n^{0}}{dx^2}+\frac{2m}{\hbar^2}x\psi_m^{0*}\psi_n^0E_n-\cancel{\frac{2m}{\hbar^2}V(x)x\psi_m^{0*}\psi_n^0}=0$$

Subtract

$$x\psi_n^0\frac{d^2\psi_m^{0*}}{dx^2}-x\psi_m^{0*}\frac{d^2\psi_n^{0}}{dx^2}+\frac{2m}{\hbar^2}\psi_m^{0*}x\psi_n^0(E_m-E_n)=0$$

$$x\psi_n^0 \frac{d^2\psi_m^{0*}}{d\,x^2} - x\psi_m^{0*} \frac{d^2\psi_n^0}{d\,x^2} + \frac{2m}{\hbar^2}\psi_m^{0*} x\psi_n^0 (E_m - E_n) = 0$$

Transpose

$$\frac{2m}{\hbar^2}(E_n - E_m)\psi_m^{0*} x\psi_n^0 = x\psi_n^0 \frac{d^2\psi_m^{0*}}{d\,x^2} - x\psi_m^{0*} \frac{d^2\psi_n^0}{d\,x^2}$$

Integrate

$$\frac{2m}{\hbar^2}\left(E_n - E_m\right)\int_{-\infty}^{\infty} \psi_m^{0*} x\psi_n^0 dx = \int_{-\infty}^{\infty}\left(x\psi_n^0 \frac{d^2\psi_m^{0*}}{dx^2} - x\psi_m^{0*} \frac{d^2\psi_n^0}{dx^2}\right)dx$$

This is what we want. $\left\langle \psi_m^0 \middle| x \middle| \psi_n^0 \right\rangle$

Need to show that it is equal to $\left\langle \psi_m^0 \middle| \frac{\partial}{\partial x_j} \middle| \psi_n^0 \right\rangle$

$$\frac{2m}{\hbar^2}(E_n - E_m)\int_{-\infty}^{\infty}\psi_m^{0*} x\psi_n^0 dx = \int_{-\infty}^{\infty}\left(x\psi_n^0\frac{d^2\psi_m^{0*}}{dx^2} - x\psi_m^{0*}\frac{d^2\psi_n^0}{dx^2}\right)dx$$

Integrate right hand side by parts:

$$\left\{\begin{array}{ll} u = x\psi_n^0 & \\ dv = \dfrac{d^2\psi_m^{0*}}{dx^2}dx & \displaystyle\int_{-\infty}^{\infty} u\,dv = uv\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} v\,du \end{array}\right\}$$

and collecting terms

Because wavefunctions vanish at infinity, this is 0, so we have:

$$= \int_{-\infty}^{\infty}\left[-\frac{d}{dx}\left(x\psi_n^0\right)\frac{d\psi_m^{0*}}{dx} + \frac{d}{dx}\left(x\psi_m^{0*}\right)\frac{d\psi_n^0}{dx}\right]dx$$

using product rule

$$= -\psi_n^0\frac{d\psi_m^{0*}}{dx} - x\frac{d\psi_n^0}{dx}\frac{d\psi_m^{0*}}{dx} + \psi_m^{0*}\frac{d\psi_n^0}{dx} + x\frac{d\psi_m^{0*}}{dx}\frac{d\psi_n^0}{dx}$$

2nd and 4th terms cancel

$$= \int_{-\infty}^{\infty}\left(-\psi_n^0\frac{d\psi_m^{0*}}{dx} + \psi_m^{0*}\frac{d\psi_n^0}{dx}\right)dx \qquad = 2\int_{-\infty}^{\infty}\psi_m^{0*}\frac{d\psi_n^0}{dx}dx$$

Integrating this by parts → equals second term

Therefore, finally, we have:

$$\left\langle \psi_m^0 \middle| \frac{d}{dx} \middle| \psi_n^0 \right\rangle = -\frac{m}{\hbar^2}\left(E_m - E_n\right)\left\langle \psi_m^0 \middle| \underline{x} \middle| \psi_n^0 \right\rangle$$

This can be generalized to more then one particle by summing over x_j.

Substituting into

$$\left\langle \Psi_m^0(q,t) \middle| \underline{H}' \middle| \Psi_n^0(q,t) \right\rangle = i\frac{e\hbar}{c} A_x e^{i(E_m - E_n)t/\hbar} \sum_j \frac{1}{m_j} \left\langle \psi_m^0(q) \middle| \frac{\partial}{\partial x_j} \middle| \psi_n^0(q) \right\rangle$$

gives

$$\left\langle \Psi_m^0(q,t) \middle| \underline{H}' \middle| \Psi_n^0(q,t) \right\rangle = -i\frac{1}{c\hbar} A_x (E_m - E_n) x_{mn} e^{i(E_m - E_n)t/\hbar}$$

with:

$$x_{mn} = \left\langle \psi_m^0 \middle| e\sum_j \underline{x}_j \middle| \psi_n^0 \right\rangle$$

Operator – (charge × length) - dipole

***x*-component of "transition dipole."**

Absorption & Emission Transition Probabilities

$$\frac{dC_m}{dt} = -\frac{i}{\hbar}\sum_n C_n \left\langle \Psi_m^0(q,t) \middle| \underline{H}' \middle| \Psi_n^0(q,t) \right\rangle$$

Equations of motion of coefficients

Time Dependent Perturbation Theory:

Take system to be in state $\left|\Psi_n^0(q,t)\right\rangle$ at $t = 0$

$C_n = 1$ $\qquad C_{m \neq n} = 0$

Short time → $C_{m \neq n} \approx 0$

Using result for E&M plane wave:

$$\frac{dC_m}{dt} = -\frac{1}{c\hbar^2} A_x \left(E_m - E_n\right) x_{mn} e^{i\left(E_m - E_n\right)t/\hbar}$$

No longer coupled equations.

$$x_{mn} = \left\langle \psi_m^0 \middle| e\sum_j \underline{x}_j \middle| \psi_n^0 \right\rangle$$

Transition dipole bracket.

For light of frequency ν:

$$A_x = A_x^0 \cos(2\pi\nu t)$$

vector potential

$$= \frac{1}{2} A_x^0 \left(e^{i2\pi\nu t} + e^{-i2\pi\nu t} \right)$$

Therefore:

note sign difference

$$\frac{dC_m}{dt} = -\frac{1}{2c\hbar^2} A_x^0 x_{mn} \left(E_m - E_n \right) \left(e^{i\left(E_m - E_n + h\nu\right)t/\hbar} + e^{i\left(E_m - E_n - h\nu\right)t/\hbar} \right)$$

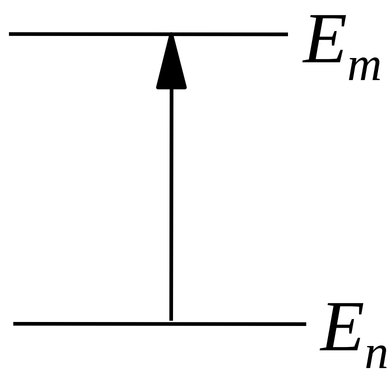
Multiplying through by dt, integrating and choosing constant of integration such that $C_m = 0$ at $t = 0$

note sign differences

$$C_m = \frac{i}{2c\hbar} A_x^0 x_{mn} \left(E_m - E_n\right) \left[\frac{e^{i\left(E_m - E_n + h\nu\right)t/\hbar} - 1}{\left(E_m - E_n + h\nu\right)} + \frac{e^{i\left(E_m - E_n - h\nu\right)t/\hbar} - 1}{\left(E_m - E_n - h\nu\right)} \right]$$

Rotating Wave Approximation

Consider Absorption $E_m > E_n$



This term large, keep.

Drop first term.

$(E_m - E_n - h\nu) \rightarrow 0$ **as** $h\nu \rightarrow (E_m - E_n) \Rightarrow$ **denominator goes to 0**

For Absorption – Second Term Large → Drop First Term

Then,
Probability of finding system in $\left|\Psi_m^0\right\rangle$ as a function of frequency, ν → $C_m^* C_m$

Using the trig identities:

$$\left(e^{ix}-1\right)\left(e^{-ix}-1\right)=2(1-\cos x)=4\sin^2 x/2$$

Get:

$$C_m^* C_m=\frac{1}{c^2\hbar^2}\left|A_x^0\right|^2\left|x_{mn}\right|^2\left(E_m-E_n\right)^2\frac{\sin^2\left[\dfrac{(E_m-E_n-h\nu)t}{2\hbar}\right]}{\left[(E_m-E_n-h\nu)\right]^2}$$

$E_m-E_n=E$ **energy difference between two eigenkets of $\underline{H}^0$**

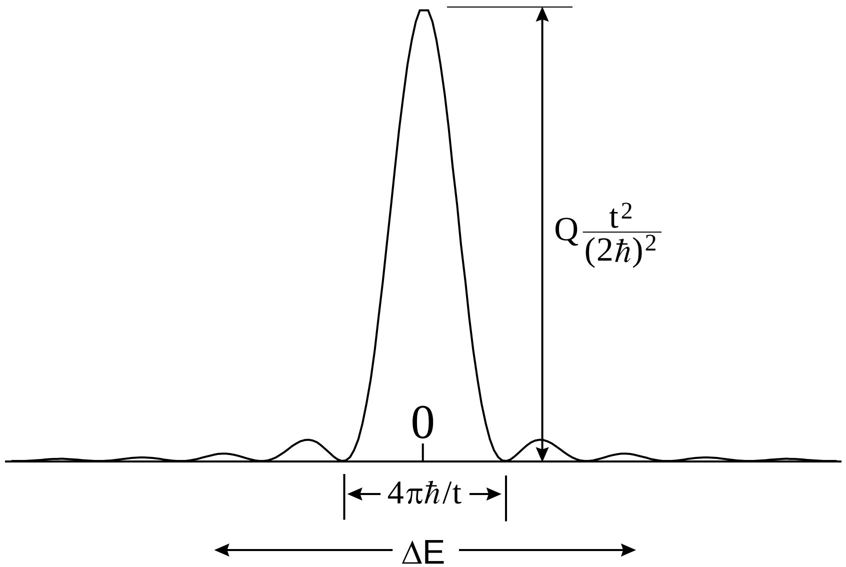
$\Delta E=E-h\nu$ **amount radiation field is off resonance.**

$E_m - E_n = E$ energy difference between two eigenkets of $\underline{H}^0$

$\Delta E = E - h\nu$ amount radiation field is off resonance.

Plot of $C_m^* C_m$ vs ΔE:

Maximum at ΔE=0



$$\left|C_m\right|^2_{\max} = Q\frac{t^2}{(2\hbar)^2}$$

$$Q = \frac{1}{c^2\hbar^2}\left|A_x^0\right|^2\left|x_{mn}\right|^2\left(E_m - E_n\right)^2$$

Maximum probability $\propto t^2$ – square of time light is applied.

Probability only significant for width ~$4\pi\hbar/t$ 1 ps → 67 cm^{-1}

Determined by uncertainty principle. For square pulse: $\Delta\nu\Delta t = 0.886$

1 ps → 30 cm^{-1} from uncertainty relation

The shape is a square of zeroth order spherical Bessel function.

t increases → Height of central lobe increases, width decreases.
Most probability in central lobe

10 ns pulse → Width ~0.03cm^{-1}, virtually all probability

$t \to \infty$ → $C_m^* C_m$ → Dirac delta function $\delta(\Delta E = 0)$; $h\nu = (E_m - E_n)$

Total Probability → Area under curve

$$\int_{-\infty}^{\infty} C_m^* C_m d\Delta\nu = \frac{1}{h}\int_{-\infty}^{\infty} C_m^* C_m d\Delta E = \frac{Q}{h}\int_{-\infty}^{\infty} \frac{\sin^2(\Delta E t/2\hbar)}{(\Delta E)^2} d\Delta E$$

$$= \frac{Q}{h}\frac{t}{2\hbar}\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx$$

$$Q = \frac{1}{c^2\hbar^2}\left|A_x^0\right|^2 \left|x_{mn}\right|^2 \left(E_m - E_n\right)^2$$

$$= \frac{Qt}{4\hbar^2}$$

Probability linearly proportional to time light is applied.

Since virtually all probability at $\Delta E = 0$,

evaluate $\left|A_x^0\right|^2$ **(in Q) at frequency** $(E_m - E_n)/\hbar = \nu_{mn}$

Therefore:

Related to intensity of light as shown below.

$$C_m^* C_m = \frac{\pi^2 \nu_{mn}^2}{c^2 \hbar^2} \left|A_x^0(\nu_{mn})\right|^2 \left|x_{mn}\right|^2 t$$

transition dipole bracket

Probability increases linearly in *t*.

Can't let $C_m^* C_m$ **get too big if time dependent perturbation theory used.**

Limited by excited state lifetime.

Must use other methods for high power, "non-linear" experiments (Chapter 14).

Have result in terms of vector potential, A_x^0.

Want in terms of intensity, I.

Poynting vector:

$$\vec{S} = \frac{c}{4\pi}\vec{E} \times \vec{B}$$

For plane wave:

$$\vec{S} = \vec{k}\,\frac{c}{4\pi}\frac{4\pi^2\nu^2}{c^2}\left|A_x^0\right|^2 \sin^2 2\pi\nu(t - z/c)$$

Intensity → time average magnitude of Poynting vector

Average sin^2 term over t from 0 to 2π → 1/2

Therefore:

$$I_x = \frac{\pi\nu^2}{2c}\left|A_x^0\right|^2$$

and

$$C_m^* C_m = \frac{2\pi}{c\hbar^2} I_x \left|x_{mn}\right|^2 t$$

Linear in intensity.
Linear in time.

This is the big result.

$$C_m^* C_m = \frac{2\pi}{c\hbar^2} I_x \left| x_{mn} \right|^2 t$$

Linear in intensity.
Linear in time.

$$x_{mn} = \langle m | \underline{x} | n \rangle$$

Transition dipole bracket for x polarized light.

Can have light with polarizations *x*, *y*, or *z*, i. e., I_x, I_y, I_z

Then:

$$C_m^* C_m = \frac{2\pi}{c\hbar^2} \left[I_x \left| x_{mn} \right|^2 + I_y \left| y_{mn} \right|^2 + I_z \left| z_{mn} \right|^2 \right] t$$

x_{mn}, y_{mn}, and z_{mn} are the transition dipole brackets for light polarized along *x*, *y*, and *z*, respectively

Another definition of "strength" of radiation fields

radiation density:

average

$$\rho(\nu_{mn}) = \frac{1}{4\pi}\overline{E^2(\nu_{mn})}$$

$$\overline{E^2(\nu_{mn})} = \frac{2\pi^2\nu_{mn}^2}{c^2}\left|A^0(\nu_{mn})\right|^2$$

Then

$$\left|A^0(\nu_{mn})\right|^2 = \frac{2c^2}{\pi\nu_{mn}^2}\rho(\nu_{mn})$$

Isotropic radiation

$$\left|A_x^0(\nu_{mn})\right|^2 = \left|A_y^0(\nu_{mn})\right|^2 = \left|A_z^0(\nu_{mn})\right|^2 = \frac{1}{3}\left|A^0(\nu_{mn})\right|^2$$

For isotropic radiation

$$C_m^* C_m = \frac{2\pi}{3\hbar^2}\left\{\left|x_{mn}\right|^2 + \left|y_{mn}\right|^2 + \left|z_{mn}\right|^2\right\}\rho(\nu_{mn})t$$

Einstein "*B* Coefficients" for absorption and stimulated emission

Probability of transition taking place in unit time (absorption) for isotropic radiation

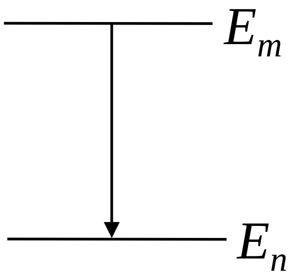
$$B_{n\to m}\rho(\nu_{mn}) = \frac{2\pi}{3\hbar^2}\left|\mu_{mn}\right|^2 \rho(\nu_{mn})$$

where

$$\left|\mu_{mn}\right|^2 = \left|x_{mn}\right|^2 + \left|y_{mn}\right|^2 + \left|z_{mn}\right|^2$$

transition dipole bracket

For emission (induced, stimulated) everything is the same except keep first exponential term in expression for probability amplitude.



stimulated emission
need radiation field

Previously, initial state called *n*.
Now initial state *m*, final state *n*.
$E_m > E_n$.

$$C_n = \frac{i}{2c\hbar} A_x^0 x_{mn} \left(E_n - E_m\right) \left[\frac{e^{i\left(E_n - E_m + h\nu\right)t/\hbar} - 1}{\left(E_n - E_m + h\nu\right)} + \frac{e^{i\left(E_m - E_m - h\nu\right)t/\hbar} - 1}{\left(E_n - E_m - h\nu\right)} \right]$$

Rotating wave approximation. Keep this term.

$$B_{m\to n}\rho(\nu_{mn}) = B_{n\to m}\rho(\nu_{mn})$$

Einstein *B* coefficient for absorption equals *B* coefficient for stimulated emission.

Restrictions on treatment

1. Left out spontaneous emission
2. Treatment only for weak fields
3. Only for dipole transition
4. Treatment applies only for $C_m^* C_m \ll 1$
5. If transition dipole brackets all zero

$$\left| \mu_{mn} \right| = 0$$

Higher order terms lost when we took vector potential constant spatially over molecule:

Lose → Magnetic dipole transition
Electric Quadrupole
Magnetic Quadrupole
Electric Octapole
etc…

Only important if dipole term vanishes.

Einstein "*A* coefficient" – Spontaneous Emission

$B_{m\to n}$, $B_{n\to m}$ **Einstein *B* Coefficients**

induced emission **absorption**

Want: $A_{m\to n}$ **spontaneous emission coefficient**

N_m **= number of systems (molecules) in state of energy** E_m **(upper state)**

N_n **= number of systems (molecules) in state of energy** E_n **(lower state)**

At temp *T*, Boltzmann law gives:

$$\frac{N_m}{N_n} = \frac{e^{-E_m/k_B T}}{e^{-E_n/k_B T}} = e^{-h\nu_{mn}/k_B T}$$

At equilibrium:

rate of downward transitions = rate of upward transitions

$$N_m\left\{A_{m\to n}+B_{m\to n}\,\rho(\nu_{mn})\right\}=N_n B_{n\to m}\rho(\nu_{mn})$$

spontaneous emission **stimulated emission** **absorption**

Using

$$\frac{N_m}{N_n}=\frac{e^{-E_m/k_B T}}{e^{-E_n/k_B T}}=e^{-h\nu_{mn}/k_B T}$$

$$e^{-h\nu_{mn}/k_B T}=\frac{B_{n\to m}\rho(\nu_{mn})}{A_{m\to n}+B_{m\to n}\,\rho(\nu_{mn})}$$

Solving for $\rho(\nu_{mn})$

$$\rho(\nu_{mn})=\frac{A_{m\to n}e^{-h\nu_{mn}/k_B T}}{-B_{m\to n}e^{-h\nu_{mn}/k_B T}+B_{n\to m}}$$

$$B_{n\to m} = B_{m\to n}$$

Then:

$$\rho(\nu_{mn}) = \frac{\dfrac{A_{m\to n}}{B_{m\to n}}}{e^{h\nu_{mn}/k_B T} - 1}$$

Take "sample" to be black body, reasonable approximation.
Planck's derivation (first QM problem)

$$\rho(\nu_{mn}) = \frac{8\pi h\nu_{mn}^3}{c^3} \frac{1}{e^{h\nu_{mn}/k_B T} - 1}$$

Gives

$$A_{m\to n} = \frac{8\pi h\nu_{mn}^3}{c^3} B_{m\to n}$$

$$A_{m\to n} = \frac{32\pi^3 \nu_{mn}^3}{3c^3\hbar} \left|\mu_{mn}\right|^2$$

Spontaneous emission – no light necessary,
$I = 0$, ν^3 dependence.

Spontaneous Emission:

ν^3 **dependence**

No spontaneous emission - NMR

$\nu \cong 10^8$ **Hz**

Optical spontaneous emission

$\nu \cong 10^{15}$ **Hz**

Typical optical spontaneous emission time, 10 ns (10^{-8} s).

$$\left(\frac{\nu_{NMR}}{\nu_{optical}}\right)^3 = \left(\frac{10^8}{10^{15}}\right)^3 = 10^{-21}$$

NMR spontaneous emission time – 10^{13} s (>10^5 years).
Actually longer, magnetic dipole transition much weaker than optical electric dipole transition.

Quantum Treatment of Spontaneous Emission (Briefly)

Radiation Field → Photons

State of field $|n\rangle$ **same as Harmonic Oscillator kets**

Number operator

$$a^{+}a|n\rangle = n|n\rangle$$

number of photons in field

Absorption:

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

annihilation operator

Removes photon – probability proportional to bracket squared

$\propto n \propto$ **intensity**

need photons for absorption

Emission

one more photon in field

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

creation operator

Probability $\propto$ n + 1

when n very large n >> 1, n $\propto$ Intensity

However, for

$n = 0$ $\qquad a^+ |0\rangle = \sqrt{1}\,|1\rangle$

Still can have emission from excited state in absence of radiation field.

QM *E*-field operator:

$$\underline{E}_{\vec{k}} = i(\hbar\omega_{\vec{k}}/2\varepsilon_o V)^{1/2}\varepsilon_{\vec{k}}\left\{\underline{a}_{\vec{k}}\exp(-i\omega_{\vec{k}}t + i\vec{k}\cdot\vec{r}) - \underline{a}^+_{\vec{k}}\exp(i\omega_{\vec{k}}t + i\vec{k}\cdot\vec{r})\right\}$$

Even when no photons, *E*-field not zero. Vacuum state. All frequencies have *E*-fields. "Fluctuations of vacuum state."

Fourier component at $\Delta E = \hbar\omega$ induces spontaneous emission.