23- Time dependent perturbation theory, Born approximation.

(1) $\left\{ \quad H = H_0 + \mathcal{H} \right.$ H_0 time independent
$\mathcal{H}$ may be time dependent

Unperturbed Scr. eq.

(2) $$i\hbar \dot{\psi}_0 = H_0 \psi_0$$

has solution

(3) $$\psi_0 = \sum \underbrace{a_n^{(0)}}_{\text{constants.}} u_0^{(n)} e^{-\frac{i}{\hbar} E_0^{(n)} t}$$

(4) $$H_0 u_0^{(n)} = E_0^{(n)} u_0^{(n)}$$

Solve Schr eq

(5) $$i\hbar \dot{\psi} = (H_0 + \mathcal{H})\psi$$

by

(6) $$\psi = \sum a_n(t)\, u_0^{(n)} e^{-\frac{i}{\hbar} E_0^{(n)} t}$$

then multiply by $\widetilde{u_0^{(s)}}$ to left + use orthonormality and (4).

(7) $$\dot{a}_s = -\frac{i}{\hbar} \sum_n a_n \langle s | \mathcal{H} | n \rangle e^{\frac{i}{\hbar}(E_0^{(s)} - E_0^{(n)})t}$$

(8) $$\langle s | \mathcal{H} | n \rangle = \widetilde{u_0^{(s)}}\, \mathcal{H} u_0^{(n)} = \int u_0^{*(s)} \mathcal{H} u_0^{(n)} dx = \mathcal{H}_{sn}$$

(7) is exact. Use it approximately by substituting in right hand side $a_n(0)$ for $a_n(t)$. Then

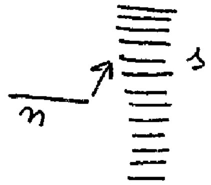
(9) $$a_s(t) \simeq a_s(0) - \frac{i}{\hbar} \sum_n a_n(0) \int_0^t \mathcal{H}_{sn}(t)\, e^{\frac{i}{\hbar}(E_0^{(s)} - E_0^{(n)})t} dt$$

Important special case. at $t=0$ system in state n. Then $a_n(0)=1$, all other a's are zero.

$$(10)\quad (s \neq n) \qquad a_s(t) = -\frac{i}{\hbar}\int_0^t \mathcal{H}_{sn}(t)\, e^{\frac{i}{\hbar}(E_0^{(s)}-E_0^{(n)})t}\, dt$$

Matrix element $\mathcal{H}_{sn}(t)$ causes transitions $n \to s$.

Transitions from n to a continuum of states



Assume $\mathcal{H}_{sn}$ indep. of time, then

$$(11)\quad \begin{cases} a_s(t) = -\mathcal{H}_{sn}\dfrac{e^{\frac{i}{\hbar}(E_0^s-E_0^n)t}-1}{E_0^s-E_0^n} \\[2ex] |a_s(t)|^2 = 4|\mathcal{H}_{sn}|^2 \dfrac{\sin^2\frac{t}{2\hbar}(E_0^{(s)}-E_0^{(n)})}{(E_0^{(s)}-E_0^{(n)})^2} \end{cases}$$

Prob of transition to one state s

$$(12)\quad \begin{cases} P(t) = \sum_s |a_s(t)|^2 = 4\overline{|\mathcal{H}_{sn}|^2}\sum \dfrac{\sin^2\frac{t}{2\hbar}(E^s-E^n)}{(E^s-E^n)^2} = \\[2ex] = 4\,\overline{|\mathcal{H}_{sn}|^2}\,\rho(E_n)\underbrace{\displaystyle\int\frac{\sin^2\frac{t}{2\hbar}(E^s-E^n)\, d(E^s-E^n)}{(E^s-E^n)^2}}_{\frac{\pi t}{2\hbar}} \\[2ex] = t\,\dfrac{2\pi}{\hbar}|\mathcal{H}_{sn}|^2\rho(E_n) \end{cases}$$

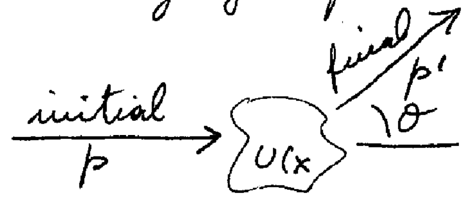
$$\int\frac{\sin^2\alpha x}{x^2}dx = \pi\alpha$$

$$(13)\quad \begin{cases} \rho(E_n) = \text{no of states } s\text{, close to } E_n \text{ per unit energy interval.} \\[2ex] \boxed{\text{Rate of transition} = \dfrac{2\pi}{\hbar}\overline{|\mathcal{H}_{sn}|^2}\,\rho(E_n)} \end{cases}$$

Discuss: distribution of final states as function of t & relation with uncertainty principle

Example : Born approximation.

(14) Scattering by a potential $U(\vec{x})$



$|p'| = |p|$

$U(x) = \mathcal{H}$ treated as perturbation

(15) initial state $\frac{1}{\sqrt{\Omega}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{x}}$ (Ω = vol. of box)

final state $\frac{1}{\sqrt{\Omega}} e^{\frac{i}{\hbar}\vec{p}'\cdot\vec{x}}$

$$\langle p' | \mathcal{H} | p \rangle = \frac{1}{\Omega} \underbrace{\int U(x)\, e^{\frac{i}{\hbar}(\vec{p}-\vec{p}')\cdot\vec{x}}\, d^3x}_{\text{Fourier transform of } U}$$

$$= \frac{1}{\Omega} U_{p-p'}$$

(16) No of final states in solid angle $d\omega$ per unit energy interval

$$\rho_{d\omega} = \frac{\Omega\, d\omega}{(2\pi\hbar)^3} \frac{p^2\, dp}{v\, dp} = \frac{\Omega p^2}{8\pi^3\hbar^3 v} d\omega$$

v = velocity $\quad v\,dp = dE$ (correct also relativistically)

Rate of transitions into $d\omega$

$$d\omega \frac{v}{\Omega}\frac{d\sigma}{d\omega} = \frac{2\pi}{\hbar}\left|\frac{1}{\Omega} U_{p-p'}\right|^2 \frac{\Omega p^2}{8\pi^3\hbar^3 v} d\omega$$

(17)
$$\boxed{\frac{d\sigma}{d\omega} = \frac{1}{4\pi^2\hbar^4}\frac{p^2}{v^2}\left|U_{p-p'}\right|^2}$$

(18) For non relativistic mechanics $m = \frac{p}{v}$

$$\frac{d\sigma}{d\omega} = \frac{m^2}{4\pi^2\hbar^4}\left|U_{p-p'}\right|^2$$

Limits of validity (discuss)

(19) $\frac{1}{\hbar} L\left(\sqrt{p^2 \pm 2mU} - p\right) \ll 1$

<u>Scattering by Coulomb center</u>

(20)
$$U = \frac{zZe^2}{r}$$
$$U_{p-p'} = zZe^2 \int \frac{e^{\frac{i}{\hbar}(\vec{p}-\vec{p}')\cdot\vec{x}}}{r}\, d^3x = \frac{4\pi z Z e^2}{\frac{1}{\hbar^2}\left|\vec{p}-\vec{p}'\right|^2} = \frac{4\pi\hbar^2 z Z e^2}{4p^2\sin^2\frac{\theta}{2}}$$

use $\nabla^2\varphi = -4\pi \frac{e^{i\alpha x}}{r} \Rightarrow \varphi$

(21) $$\frac{d\sigma}{d\omega} = \frac{z^2Z^2}{4}\left(\frac{me^2}{p^2}\right)^2 \frac{1}{\sin^4\frac{\theta}{2}}$$ (Identical to classical Rutherford formula)

Suggested discussion topics.

<u>Scattering by potential well</u> – <u>Nuclear forces</u>

<u>Limit of long wave length</u> – isotropic scattering

" " <u>short</u> " " – forward "

<u>Role of the mass (neutrino)</u>

<u>Exponential decay of original state in case (11)</u>

24 - Emission and absorption of radiation.

(1) $$\mathcal{H} = eBz\cos\omega t$$

B = amplitude,

at $t=0$ atom in state n. From (23-(10))

(2) $$a_m(t) = -\frac{i}{\hbar} eBz_{mn}\int_0^t \cos\omega t\, e^{i\omega_{mn}t}\,dt$$

$$\omega_{mn} = \frac{E^{(m)}-E^{(n)}}{\hbar} > 0 \qquad \cos\omega t = \frac{e^{i\omega t}+e^{-i\omega t}}{2}$$

$\hbar\omega_{mn}$ m n

this term only important when $\omega \simeq \omega_{mn}$ then

$$a_m(t) \simeq -\frac{ieB}{2\hbar} z_{mn}\int_0^t e^{i(\omega_{mn}-\omega)t}\,dt =$$

$$= +\frac{eB}{2\hbar} z_{mn}\frac{e^{-i(\omega-\omega_{mn})t}-1}{\omega-\omega_{mn}}$$

Comments on resonance

(3) $$|a_m(t)|^2 = \frac{e^2B^2}{\hbar^2}|z_{mn}|^2\frac{\sin^2\frac{t}{2}(\omega-\omega_{mn})}{(\omega-\omega_{mn})^2}$$

Light intensity $= \dfrac{cB^2}{8\pi}$

Absorption from continuum overlapping ω_{mn}

(4) $$\frac{cB^2}{8\pi} = \frac{dI}{d\omega}d\omega \qquad \text{Substitute in (3), then } \int d\omega$$

use $\displaystyle\int \frac{\sin^2\alpha x}{x^2}dx = \pi\alpha$

$$|a_m|^2 = t\times\frac{4\pi^2e^2}{c\hbar^2}|z_{mn}|^2\frac{dI}{d\omega}$$

ω = ang. frequency <u>not</u> solid angle!

(5) $$\boxed{\text{Rate of absorption} = \frac{4\pi^2e^2}{c\hbar^2}|z_{mn}|^2\frac{dI}{d\omega}}$$

factor 1/3 from averaging over direction of polarization

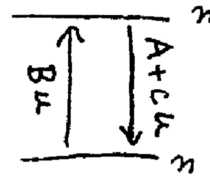
For isotropic radiation of volume energy density $u(\omega)\,d\omega$

(6) $$\text{Rate of absorption} = \frac{4\pi^2e^2}{3\hbar^2}|\vec{x}_{mn}|^2 u(\omega_{mn})$$

Relationship between emission & absorption could be derived from quantum electrodynamics — However simpler to use Einsteins A & B method

This B is a coefficient. Has nothing to do with B of page 1

Rate of $n \to m$ $\quad B\,u(\omega)\,N(n) =$



From (6)

$$(7) \qquad B = \frac{4\pi^2 e^2}{3\hbar^2}\left|\vec{x}_{mn}\right|^2$$

Rate of $m \to n$) $\quad [A + C\,u(\omega)]\,N(m)$

this is number of atoms in state (n) or (m)

forced transitions

Spontaneous transitions

For thermal equilibrium

$$(8) \qquad \frac{N(m)}{N(n)} = e^{-\frac{E^{(m)}-E^{(n)}}{kT}} = e^{-\frac{\hbar\omega_{mn}}{kT}}$$

Boltzmann distribution

At equilibrium: Rate $n \to m$ = Rate $m \to n$

$$(9) \qquad \frac{A}{B\,u(\omega)} + \frac{C}{B} = \frac{N_n}{N_m} = e^{\frac{\hbar\omega}{kT}}$$

Planck's law

$$(10) \qquad u = \frac{\hbar\omega^3/\pi^2c^3}{e^{\frac{\hbar\omega}{kT}} - 1}$$

$$\frac{\pi^2c^3}{\hbar\omega^3}\frac{A}{B}\left(e^{\frac{\hbar\omega}{kT}} - 1\right) + \frac{C}{B} = e^{\frac{\hbar\omega}{kT}}$$

(15)

Must hold at all T's Therefore:

$$\frac{\pi^2c^3}{\hbar\omega^3}\frac{A}{B} = 1 \qquad \frac{C}{B} = 1$$

Einstein's relations

(16

$$(11) \qquad \boxed{A = \frac{\hbar\omega^3}{\pi^2c^3}B \;;\quad C = B}$$

Then from (7)

$$(12) \qquad \boxed{\frac{1}{\tau} = A = \frac{4}{3}\frac{e^2\omega^3}{\hbar c^3}\left|\vec{x}_{mn}\right|^2}$$

for spontaneous transitions

(17

(12) generalized to many particles by change

(13) $\quad e\vec{x} \to \sum e_i \vec{x}_i$ (sum to all particles)

(14) $\quad \frac{1}{\tau} = \frac{4}{3}\frac{\omega^3}{\hbar c^3}\left|\sum e_i \langle m|\vec{x}_i|n\rangle\right|^2$

Intensity of radiation proportional to square of matrix element of coordinates (for one electron) or of electric moment (13) for several charged particles.

<u>Discuss</u> – Limitations to validity of (12)

dimensions of atom $\ll \lambdabar$ of radiation

Quadrupole radiation

<u>Case of central forces – Selection rules</u> (See Lect 7)

Spherical harmonics identities

$$(15)\begin{cases}\sqrt{\frac{8\pi}{3}}\,Y_{11}\,Y_{l,m-1} = \sqrt{\frac{(l+m)(l+1+m)}{(2l+1)(2l+3)}}\,Y_{l+1,m} - \sqrt{\frac{(l-m)(l+1-m)}{(2l+1)(2l-1)}}\,Y_{l-1,m}\\[2ex] \sqrt{\frac{4\pi}{3}}\,Y_{10}\,Y_{l,m} = \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}}\,Y_{l+1,m} + \sqrt{\frac{l^2-m^2}{(2l+1)(2l-1)}}\,Y_{l-1,m}\\[2ex] \sqrt{\frac{8\pi}{3}}\,Y_{1,-1}\,Y_{l,m+1} = \sqrt{\frac{(l-m)(l+1-m)}{(2l+1)(2l+3)}}\,Y_{l+1,m} - \sqrt{\frac{(l+m)(l+1+m)}{(2l+1)(2l-1)}}\,Y_{l-1,m}\end{cases}$$

$$(16)\left\{\quad \sqrt{\frac{8\pi}{3}}\,Y_{11} = -\sin\vartheta\, e^{i\varphi};\quad \sqrt{\frac{4\pi}{3}}\,Y_{10} = \cos\vartheta;\quad \sqrt{\frac{8\pi}{3}}\,Y_{1,-1} = \sin\vartheta\, e^{-i\varphi}\right.$$

Follows: The matrix elements of the coordinates vanish unless

(17) $\qquad l' = l \pm 1$ and $m' = m \pm 1$ or m $\qquad$ Selection rules

Matrix elements

$$
(18)\quad
\begin{cases}
\langle n', l+1, m+1 \,|\, x+iy \,|\, n, l, m\rangle = -\mathcal{J}\sqrt{\dfrac{(l+m+2)(l+1+m)}{(2l+1)(2l+3)}} \\[2ex]
\langle n', l+1, m+1 \,|\, x-iy \,|\, n, l, m\rangle = 0 \\[2ex]
\langle n', l+1, m \,|\, z \,|\, n, l, m\rangle = \mathcal{J}\sqrt{\dfrac{(l+1)^2-m^2}{(2l+1)(2l+3)}} \\[2ex]
\langle n', l+1, m-1 \,|\, x+iy \,|\, n, l, m\rangle = 0 \\[2ex]
\langle n', l+1, m-1 \,|\, x-iy \,|\, n, l, m\rangle = \mathcal{J}\sqrt{\dfrac{(l+1-m)(l+2-m)}{(2l+1)(2l+3)}}
\end{cases}
$$

$$
(19)\qquad \mathcal{J} = \int_0^\infty R_{nl}(r)\, R_{n', l+1}(r)\, r^3\, dr
$$

Derive

$$
(20)\quad
\begin{cases}
\left|\langle n', l+1, m+1 \,|\, \vec{x} \,|\, n, l, m\rangle\right|^2 + \left|\langle n', l+1, m \,|\, \vec{x} \,|\, n\, l\, m\rangle\right|^2 + \\[1ex]
+ \left|\langle n', l+1, m-1 \,|\, \vec{x} \,|\, n, l, m\rangle\right|^2 = \dfrac{l+1}{2l+1}\,\mathcal{J}^2 \quad (\text{indep. of } m)
\end{cases}
$$

$$
(21)\quad
\begin{cases}
\text{Therefore: rate of transition} \\
\qquad (n, l, m) \rightarrow (n', l+1 \text{ any } m') \\
\qquad = \dfrac{4}{3}\,\dfrac{e^2\omega^3}{\hbar c^3}\,\dfrac{l+1}{2l+1}\,\mathcal{J}^2
\end{cases}
$$

Comments on independence of $\underline{m}$

Similarly

$$
(22)\quad
\begin{cases}
\text{Rate}\left(n, l, m \rightarrow n', l-1, \text{any } m\right) = \\[1ex]
\qquad = \dfrac{4}{3}\,\dfrac{e^2\omega^3}{\hbar c^3}\,\dfrac{l}{2l-1}\left\{\displaystyle\int_0^\infty R_{nl}(r)\, R_{n', l-1}(r)\, r^3\, dr\right\}^2
\end{cases}
$$

Example – Life time of 2p state of hydrogen

$$R_{1s}(r) = \frac{2}{a^{3/2}}\, e^{-r/a}\,; \quad R_{2p}(r) = \frac{1}{\sqrt{24a^3}}\,\frac{r}{a}\, e^{-r/2a}$$

$$J = \int R_{1s}\, R_{2p}\, r^3\, dr = \frac{192\sqrt{2}}{243}\, a$$

$$\text{Rate}\,(2p \to 1s) = \frac{294912}{177147}\,\frac{e^2\omega^3 a^2}{\hbar c^3} \qquad \omega = \frac{3}{4}\,\frac{me^4}{2\hbar^3}$$

$$= \frac{1152}{6561}\left(\frac{e^2}{\hbar c}\right)^3\left(\frac{me^4}{2\hbar^3}\right) \qquad a = \frac{\hbar^2}{me^2}$$

$$= 1.41 \times 10^9\ \text{sec}^{-1}$$

$$= \frac{\text{Ryd}}{\hbar} = 2.067 \times 10^{16}\ \text{sec}^{-1}$$

$$\frac{e^2}{\hbar c} = \frac{1}{137}$$

Topics for discussion

Permitted + forbidden lines

Metastable states

Generalization of selection rules

Irradiation by a linear oscillator

Sum rule + effective number of electrons

Polarization of emitted light