Transitions in atoms:

assume non-degenerate states

$$\Psi_1(\vec{r},t) = u_1(\vec{r})\, e^{-iE_1 t/\hbar}$$

$$\Psi_2(\vec{r},t) = u_2(\vec{r})\, e^{-iE_2 t/\hbar}$$

each is ideally stationary

presuppose some superposition state of these two

$$\Psi(\vec{r},t) = a_1(t)\,\Psi_1 + a_2(t)\,\Psi_2$$

w/ $|a_1|^2 + |a_2|^2 = 1$

electron charge distrib is

$$\rho(\vec{r},t) = e\,|\Psi(\vec{r},t)|^2$$

for $a_1 = 0$ $\rho(\vec{r},t)$ isn't moving

for mix. state ρ moves around.

accel. charge radiates

∴ calc. dipole moment:

$$\vec{\mu} \equiv \int e\,\vec{r}\,\Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,dV$$

cross terms → $(E_2 - E_1)/\hbar \equiv \omega_{21}$ (or ω_0)

$$\vec{\mu} = \int e\,\vec{r}\,|a_1|^2 |u_1|^2\, dV + \int e\,\vec{r}\,|a_2|^2 |u_2|^2\, dV$$
$$+ \int e\,\vec{r}\left(a_1 a_2^* u_1 u_2^* e^{i\omega_0 t} + a_1^* a_2 u_1^* u_2 e^{-i\omega_0 t}\right) dV$$

parity of integrand is odd.

oscill. dipole moment is

$$\vec{\mu}_{osc} = \mathrm{Re}\left[2 a_1 a_2^* \vec{\mu}_{21} e^{i\omega_0 t} \right]$$

$$\vec{\mu}_{21} \equiv \int u_2^* (e\vec{r})\, u_1 \, dV \quad = \text{dipole matrix element}$$

classical radiation power

$$P_{rad} = \frac{1}{4\pi\epsilon_0} \frac{2}{3} \frac{(\ddot{\mu})^2}{c^3} \qquad \mu = q\ddot{x} \text{ classically.}$$

here we have sinusoidal oscillations

$$P_{rad} = \frac{\mu'^2 \omega_0^4}{12\pi\epsilon_0 c^3} \qquad \text{where } \mu' \equiv 2|a_1 a_2^* \vec{\mu}_{21}|$$

separate out $|a_1|^2 |a_2|^2$ from P_{rad}:

$$P_{rad} = P'_{rad} |a_1|^2 |a_2|^2$$

now had eqn for energy:

$$\frac{dE}{dt} = -P_{rad} \qquad \begin{aligned} E &= |a_1|^2 E_1 + |a_2|^2 E_2 \\ &= |a_1|^2 E_1 + |a_2|^2 (h\nu_0 + E_1) \\ &= E_1 + |a_2|^2 h\nu_0 \end{aligned}$$

$\downarrow$

$$\frac{d}{dt}|a_2|^2 = -\frac{1}{\tau_{sp}} |a_1|^2 |a_2|^2$$

$$\text{w/ } \tau_{sp} = \frac{3h\epsilon_0 c^3}{16\pi^3 \nu_0^3 n |\mu|^2} \qquad |\mu| = |\vec{\mu}_{12}|$$

this eqn has a tanh( ) solution, which is incorrect. it does not account for <u>source</u> of mixture of states, which is perturbation from vacuum (zero-point) fluctuations of E+M field.

Correct solution: $|a_2(t)|^2 = |a_2(0)|^2 e^{-t/\tau_{sp}}$

- spontaneous decay rate depends on $|\mu|^2$

In Dirac notation, atomic parameter that is important is:

$$\langle 2|-e\vec{r}|1\rangle = -e\int \Psi_2^*(\vec{r})\,\vec{r}\,\Psi_1(\vec{r})\,d^3r$$

- some transitions are forbidden b/c of parity:

  Ψ_1 even, Ψ_2 odd (or vice versa) $\vec{\mu}_{21} \to 0$

  ex: no $2S \to 1S$ transitions

- also there is an angular momentum selection rule:

  $\Delta l = \pm 1$

Easy way to remember:

- photon is boson, spin ± 1 (R or L circ polariz.)
- conserve ang. mom. through Δl rule
- can go from $2S \to 1S$ with 2 photons

Exceptions:

- magnetic dipole, electric quadrupole etc
  $\Rightarrow$ longer lifetime.
- states may not be "pure"
  external (molecule, crystal) and internal perturbations (spin-orbit, hyperfine, ...) lead to energy eigenfns which are a mixture of states

Absorption + stimulated emission.

here we start with an external perturbation

- treat e-m wave classically.

Atom: $H\Psi_n = E_n \Psi_n$

incident field $E(0,t) = \vec{E}_0 \sin(\omega t)$ any ω

atom at $\vec{r} = 0$

assume: interaction energy is from electric dipole only

$$H' = \vec{\mu}\cdot\vec{E} = -e\,\vec{r}\cdot\vec{E}_0 \sin\omega t$$

also: - transition rate is slow ($\tau \gg 1/\omega_0$), weak applied field

- ω is near ω_0

Time-dependent pert. thy gives transition rate:

$$W_{12} = \frac{\pi^2}{3h^2}|\mu_{21}|^2 E_0^2\, \delta(\nu-\nu_0) \qquad \text{"Fermi's golden rule"}$$

dirac delta function is there b/c we must integrate over ν to get actual rate:

- energy density of field - $\rho = \dfrac{n^2 \epsilon_0 E_0^2}{2}$ or $I = \dfrac{c}{n}\rho = \frac{1}{2} c n \epsilon_0 E_0$

  typically $\rho = \rho(\omega)$

- lineshape of transition:

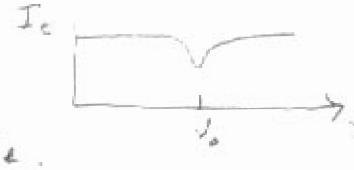
  $g(\nu-\nu_0)$ is normalized s.t. $\int g(\nu-\nu_0)\,d\nu = 1$

  e.g. Lorentzian (natural)

$$g(\nu-\nu_0) = \frac{2}{\pi\nu_0}\,\frac{1}{1+\left(\frac{2(\nu-\nu_0)}{\Delta\nu_0}\right)^2}$$

  $\Delta\nu_0$ = FWHM of line

Notes



- scan with tunable laser. $g(\nu-\nu_0)$ gives absorption profile.

- absorption rate $W_{12} \propto I$ (weak field limit)

- calculation is identical for stimulated emission, except initial conditions are reversed

$\rightarrow \quad \mu_{21} = \mu_{12}^*$

and $\quad W_{12} = W_{21}$ for single atom, btw well-defined states.

- final rate is sum over all combinations of degenerate states $\rightarrow$ g weighting factors.

- homogeneous broadening: all atoms have same lineshape
  - natural broadening (cold gas)
  - collisional broadening.
  - lattice/strain broadening
- inhomogeneous broadening: distribution of different lineshapes
  - Doppler broadening: all same $g(\nu-\nu_0)$ in rest frame; distribution of velocities $\rightarrow$ Gaussian shape

Absorption by homog. broadened transition:

change in power / volume : $dP \quad \rightarrow \quad \frac{dP}{dt} = -W_h N_t h\nu$ (number density of atoms)

$W_h \propto I \qquad$ intensity $= F \cdot h\nu \qquad F$ = photon flux

$\therefore$ qty $\frac{W_h}{F}$ is independent of field $\rightarrow$ cross-section $\equiv \sigma_h(\nu)$

$$\frac{dP}{dt} = \frac{dI}{dz} = h\nu\frac{dF}{dz} = -\sigma_h F N_t h\nu$$

$$\rightarrow F(z) = F(0)\, e^{-N_t \sigma_h z} \qquad \text{"Beer's Law"}$$

absorption coeff : $\alpha = N_t \sigma_h$

for gain: $g = N_t \sigma_h$ (opposite sign)

Inhomogeneous case:

integrate over distribution of lineshapes to get observed lineshape. (treat later)

- pure Doppler $\sigma_h^{sa} \rightarrow \delta(\nu - \nu_0) \rightarrow$ Gaussian
- mix $\rightarrow$ "Voigt" profile.

Einstein A, B

$$W_{21} \equiv B_{21}\rho_{\nu_0} \qquad \rho_{\nu_0} = \rho(\nu_0)$$

$$W_{12} \equiv B_{12}\rho_{\nu_0}$$

A_{21} = spont rate = A

in equilib: $A N_2^e + B_{21}\rho_{\nu_0} N_2^e = B_{12}\rho_{\nu_0} N_1^e$

also in equilib $\dfrac{N_2^e}{N_1^e} = e^{-h\nu_0/kT}$

$$\rightarrow \rho_{\nu_0} = \frac{A}{B_{12}e^{+h\nu_0/kT} - B_{21}}$$

for Blackbody: $\rho_\nu = \dfrac{8\pi\nu^2}{c_n^3}\dfrac{h\nu}{e^{h\nu/kT}-1}$ $\qquad c_n = c/n$

$\therefore B_{12} = B_{21}$ and $\dfrac{A}{B} = \dfrac{8\pi h\nu_0^3 n^3}{c^3} = \rho_{\nu_0}$ of vacuum field.