A collection of atoms has atoms in superpositions of their eigenstates. They make transitions between eigenstates under the action of an external perturbation.

Without loss of generality, we may model this system by a two-level system between which transitions occur under an external influence.

The perturbation is a time dependent perturbation $\hat{H}'$ to the original hamiltonian $\hat{H}_0$ and the equation of motion of this system is

originally: $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}_0 \Psi$

with solutions $\Psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$

to which we apply the shorthand: $\omega_n = E_n/\hbar$, so that

$$\Psi_n(\vec{r}, t) = \psi_n(\vec{r})\, e^{-i\omega_n t}$$

and the general state of the system (unperturbed) would be

$$\Psi \equiv \Psi_{(grand)} = \sum_n \psi_n(\vec{r})\, e^{-i\omega_n t}$$

For a two level atom this reduces to $\Psi = c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}$ with $|c_1|^2 + |c_2|^2 = 1$, to conserve probability.

To find the changes due to the perturbation we need to solve

$$i\hbar \frac{\partial \Psi}{\partial t} = (\hat{H}_0 + \hat{H}')\Psi$$

substituting $\Psi = c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}$ in the above, we get

$$i\hbar\left[-i\omega_1 c_1 \psi e^{-i\omega_1 t} + \dot{c}_1\psi_1 e^{-i\omega_1 t} - i\omega_2 c_2 e^{-i\omega_2 t} + \dot{c}_2\psi_2 e^{-i\omega_2 t}\right]$$
$$= \hat{H}_0\left[c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}\right] + \hat{H}'\left[c_1\psi_1 e^{-i\omega_1 t} + c_2\psi_2 e^{-i\omega_2 t}\right]$$

$$\left[i\hbar\left[\dot{c}_1 e^{-i\omega_1 t}\psi_1 + \dot{c}_2 e^{-i\omega_2 t}\psi_2\right] = \hat{H}'\left[c_1 e^{-i\omega_1 t}\psi_1 + c_2 e^{-i\omega_2 t}\psi_2\right]\right]$$

we premultiply the eqn by ψ_1^* or ψ_2^* and perform a spatial integration

$$i\hbar\left[\dot{c}_1 e^{-i\omega_1 t}\langle\psi_1|\psi_1\rangle + \dot{c}_2 e^{i\omega_2 t}\langle\psi_1|\psi_2\rangle\right] = c_1 e^{-i\omega_1 t}\langle\psi_1|\hat{H}'|\psi_1\rangle + c_2 e^{-i\omega_2 t}\langle\psi_1|\hat{H}'|\psi_2\rangle$$

$\langle\psi_1|\psi_1\rangle = 1$, $\langle\psi_1|\psi_2\rangle = 0$, $\langle\psi_1|\hat{H}'|\psi_1\rangle = H'_{11}$, $\langle\psi_1|\hat{H}'|\psi_2\rangle = H'_{21}$

Swabeshi

$$i\hbar\,\dot{c}_1\,e^{-i\omega_1 t} = c_1 e^{-i\omega_1 t} H'_{11} + c_2 e^{-i\omega_2 t} H'_{21}$$

$$\therefore\ \dot{c}_1 = \frac{-i}{\hbar}\left[c_1 H'_{11} + c_2 H'_{21}\exp\left[-i(\omega_2-\omega_1)t\right]\right]$$

- $\dot{c}_1$: rate of change of population of ψ_1
- H'_{11}, H'_{21}: matrix elements of the perturbation
- $\exp[-i(\omega_2-\omega_1)t]$: resonance condition for mixing ψ_1 and ψ_2

Had we pre-multiplied by ψ_2^* we would have got the condition for c_2

$$\dot{c}_2 = \frac{-i}{\hbar}\left[c_1 H'_{21}\exp\left[+i(\omega_2-\omega_1)t\right] + c_2 H'_{22}\right]$$

we use the shorthand: $\omega_{21} = \omega_2 - \omega_1$ henceforth

EXTERNAL RADIATION AS A PERTURBATION

In this case the perturbing field is an oscillating electric and magnetic fields that are out of phase

$$\mathcal{E} = \mathcal{E}_0 \exp\left[i(Kx-\omega t)\right]$$
$$\mathcal{B} = \mathcal{B}_0 \exp\left[i(Kx-\omega t+\pi/2)\right]$$

Since the typical wavelengths λ associated with visible or UV radiation (which is energetic enough to excite most atoms) is much larger than the atomic size, [$\lambda \cong 100\,nm$, $r_{atom} \sim 0.1\,nm$], we may take the electric field to be constant in space for this treatment of radiation interaction.

constant in space $\Rightarrow$ $e^{ikx} = 1 + ikx + (ikx)^2/2! + \cdots \cong 1$

Thus we can take $\mathcal{E} = \mathcal{E}_0 \cos(\omega t)$ and $\mathcal{B} = \mathcal{B}_0 \sin(\omega t)$.
The magnetic interaction with radiation is $-\vec{\mu}\cdot\vec{\mathcal{B}}$
The electric interaction with radiation is $-\vec{p}\cdot\vec{\mathcal{E}}$
The former is much weaker than the latter and is hence ignored.

Thus $\hat{H}' = -\vec{p}\cdot\vec{\mathcal{E}}$

$= +ez\,\mathcal{E}_0\cos(\omega t)$

since $\vec{p} = -e\vec{r}$ and $\hat{\mathcal{E}}_0$ may be taken to be along $\hat{z}$

CALLED DIPOLE APPROXIMATION

We then obtain

$$H'_{11} = \langle \psi_1 | z | \psi_1 \rangle \mathcal{E}_0 \cos(\omega t) \quad \Big\} \equiv 0$$
$$H'_{22} = \langle \psi_2 | z | \psi_2 \rangle \mathcal{E}_0 \cos(\omega t)$$

These two matrix elements are identically zero due to the odd parity of z but

$$H'_{21} = H'_{12} = \langle \psi_1 | z | \psi_2 \rangle \mathcal{E}_0 \cos(\omega t)$$ can be non-zero, if

ψ_1 and ψ_2 are of opposite parities.

If we define $\Omega_{21} = \frac{e\mathcal{E}_0}{\hbar} \langle \psi_1 | z | \psi_2 \rangle$, then the equations for $\dot{c}_1$ and $\dot{c}_2$ take the form

$$\dot{c}_1 = -i\Omega_{21} \cos(\omega t)\, e^{-i\omega_{21}t}\, c_2$$

$$\dot{c}_2 = -i\Omega_{21} \cos(\omega t)\, e^{+i\omega_{21}t}\, c_1$$

- Ω is called "Rabi Frequency"
- Ω_{21} is interpreted as the "hopping" rate between states 1 and 2
- Ω_{21} is not to be confused with the freq of radiation, which is ω_{21}

The quantity $e\langle \psi_2 | z | \psi_1 \rangle$ is the expectation value of the quantum mechanical dipole moment, called the dipole matrix element

WEAK RADIATION

Let us assume that the external radiation is weak, i.e. $N_{photons} \ll N_{atoms}$. If the atoms are originally in their ground state (usually the case, since temperatures are low compared to excitation energies), then we can make a further approximation:

$$c_2(t) \ll c_1(t) \quad \forall t \; ; \quad c_1(t) \simeq 1$$

but $c_2(t) \neq 0$ and $|c_1(t)|^2 + |c_2(t)|^2 = 1$ at all times.

The earlier equations simplify to

$$\dot{c}_2 = -i\Omega_{21} \cos(\omega t')\, e^{+i\omega_{21}t'}$$ [where t' is the running variable for time]

$$= \frac{-i}{2}\Omega_{21} \left\{ \exp\left[i(\omega+\omega_{21})t'\right] + \exp\left[-i(\omega-\omega_{21})t'\right] \right\}$$

~~edited~~ #

To obtain $c_2(t)$ from this equation we need to integrate from $t'=0$ to $t'=t$. Noting that $c_2(0)=0$, we get

$$c_2(t) = -\frac{i}{2}\Omega_{21}\left[\frac{e^{i(\omega+\omega_{21})t'}}{\omega+\omega_{21}} - \frac{e^{-i(\omega-\omega_{21})t'}}{\omega-\omega_{21}}\right]_0^t$$

$$= \frac{i}{2}\Omega_{21}\left[\frac{1-e^{i(\omega+\omega_{21})t}}{\omega+\omega_{21}} - \frac{1-e^{-i(\omega-\omega_{21})t}}{\omega-\omega_{21}}\right]$$

If ω and ω_{21} differ widely, then $|c_2(t)|^2$ changes very slowly and the system mostly stays in $|1\rangle$ with weak oscillations to $|2\rangle$.

However, if $\omega \simeq \omega_{21}$ then the second term makes a large contribution to $c_2(t)$ and we may write

$$c_2(t) = -\frac{i}{2}\Omega_{21}\left[\frac{1-e^{-i(\omega-\omega_{21})t}}{(\omega-\omega_{21})}\right]$$

$$= -\frac{i}{2}\Omega_{21}\, e^{-i(\omega-\omega_{21})t/2}\left[\frac{e^{+i(\omega-\omega_{21})t/2} - e^{-i(\omega-\omega_{21})t/2}}{\omega-\omega_{21}}\right]$$

$$\therefore \left[|c_2(t)|^2 = \left(\frac{\Omega_{21}}{2}\right)^2 \left[\frac{\sin[(\omega-\omega_{21})t/2]}{(\omega-\omega_{21})/2}\right]^2\right]$$

This is the probability of transition to state $|2\rangle$ from state $|1\rangle$. Recall, that $\Omega_{21} = eE_0\langle z_{21}\rangle/\hbar$, so under this approximation only states with different parities are coupled.

RATES OF SPONTANEOUS AND INDUCED EMISSION FOR AN ENSEMBLE OF ATOMS : EINSTEIN A & B COEFFICIENTS (1917)

We have calculated the transition rate for a single atom subject to an external radiation field by applying a semi-classical treatment. We found that the emission and absorption rates are equal.
When we have an ensemble of atoms, it is observed that there are fewer atoms in higher states than in lower states in accordance with the Boltzmann distribution.
This means that if there is a radiation field of energy density $u(\nu)\,d\nu$ which the ensemble of atoms is exposed to, then the ~~probability~~ rate of absorption of radiation will be given by

$$\frac{dP_{ij}}{dt} = B_{ij}(\nu)\, u(\nu) .$$

where $|i\rangle$ and $|j\rangle$ are two atomic states.

$B_{ij}(\nu)$ is a coefficient of absorption, which we expect will be related to the $|c_2(t)|^2$ that we calculated earlier for a single atom.

As seen earlier the $|i\rangle \rightarrow |j\rangle$ excitation and $|j\rangle \rightarrow |i\rangle$ transition rates are equal in the perturbative quantum mechanical treatment, which means that the ~~probability~~ rate of emission must also be given by a similar expression

$$\frac{dP_{ji}}{dt} = B_{ji}(\nu)\, u(\nu)\, d\nu$$

~~Both~~ If the excitation and de-excitation rates in the presence of radiation are identical, then the populations in the two states at equilibrium cannot be in conformity with the Boltzmann distribution [the upper $|j\rangle$ level must be less populated].

Hence, there must be another emission channel, which does not depend on the external radiation (which is consistent with experimental observation of emission of radiation, e.g. fluorescence, phosphorescence)
We call this the spontaneous emission ~~rate~~ probability

$$\frac{dP'_{ji}}{dt} = A_{ji} \qquad [\text{does not depend on } u(\nu)]$$

At equilibrium the populations in the two levels must be given by

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} \exp\left(-h\nu_{ji}/KT\right)$$

g: statistical weight
j: upper level i: lower level

and the rates of population / de-population are related by

$$N_j \left[\frac{dP_{ji}}{dt} + \frac{dP'_{ji}}{dt}\right] = N_i \frac{dP_{ij}}{dt}$$

Substitute for P_{ij} P_{ji} and P'_{ji} in terms of A, B, u
Combining the two equations at equilibrium we get

$$u(\nu) = \frac{A_{ji}/B_{ji}}{(g_j/g_i)(B_{ij}/B_{ji})\left[\exp\left(-h\nu_{ji}/kT\right) - 1\right]}$$

For this ensemble in equilibrium with radiation, we can compare this expression with the energy density of black body radiation:

$$u(\nu) = 8\pi h \frac{\nu^3}{c^3} \frac{1}{\exp\left(-h\nu/KT\right) - 1}$$

$$\Rightarrow \quad g_j B_{ij} = g_i B_{ji} \qquad A_{ji} = \left(8\pi h \nu_{ji}^3/c^3\right) B_{ji}$$

Thus the spontaneous emission rate is proportional to the induced emission rate.

This is a purely classical treatment. In classical electrodynamics the simplest radiating system is a Hertzian dipole which is oscillating.

The power radiated by a dipole of moment p_0 is given by

$$P = \frac{2}{3} \frac{\omega^4}{4\pi\epsilon_0 c^3} \langle p^2 \rangle$$

$$= \frac{1}{3} \frac{\omega^4}{4\pi\epsilon_0 c^3} p_0^2$$

Swabashi

The q.m. analogy of this oscillating dipole in the atomic context is simply the dipole moment of the atomic electron, for which the dipole moment is $-\langle e\vec{r}\rangle$ or $-e\langle i|\vec{r}|j\rangle$

The average value of this dipole moment is $\frac{e^2|\langle \vec{r}_{ij}\rangle|^2 + |\langle \vec{r}_{ji}\rangle|^2}{2}$ the square.

↑ assuming equal stat weights.

since $\langle \vec{r}_{ij}\rangle = \langle \vec{r}_{ji}\rangle$ it follows, that

$$\langle p^2\rangle_{class} = 2e^2|\langle r_{ij}\rangle|^2_{qm.}$$

∴ By analogy $\langle P_{qm}\rangle = \frac{4}{3}\frac{\omega_{ij}^4 e^2}{4\pi\epsilon_0 c^3}|\langle r_{ij}\rangle|^2$

The emitted power must be the same as that giving rise to the spontaneous emission. (which is the classical radiation effect)

If there are N atoms in the excited state

$$\langle P\rangle = A N h\nu$$
$$= A_{ji} N_j h\nu_{ji}$$

comparing this with $\langle P_{qm}\rangle$ above we get

$$A_{ji} = \frac{2}{3}\frac{\omega_{ji}^3 e^2}{\epsilon_0 hc^3}|\langle r_{ij}\rangle|^2$$

~~Snail~~ If we compare the induced absorption rate with the quantum mechanically obtained transition rate for a 2 level system using time-dependent perturbation theory, we find the analogy

$$\frac{dP_{ij}}{dt} = B_{ij}(\nu)\,u(\nu) \iff \left(\frac{\Omega_{21}}{2}\right)^2 \langle \cos^2(\omega t)\rangle_{\text{cycle average}}$$

$$B_{ij}\,\frac{1}{2}\epsilon_0 E_0^2 = \left(\frac{e\mathcal{E}_0}{2\hbar}\right)^2 |\langle z_{21}\rangle|^2\,\frac{1}{2}$$

∵ $u(\nu) = N_\nu h\nu$
$= \frac{1}{2}\epsilon_0 E^2$
↑ energy density of the electric field.

$$\therefore B_{ij} = \frac{\pi}{2}\frac{e^2}{\epsilon_0 \hbar^2}\,\frac{1}{3}\,|r_{ij}|^2$$

$C_2(t)$ is related to B_{ij} since both represent the same transition (classically it is called induced absorption, & in the perturbative treatment it is simply the transfer rate)

$$|C_2(t)|^2 = \left(\frac{\Omega}{2}\right)^2 \left[\frac{\sin\left[(\omega-\omega_{12})t/2\right]}{(\omega-\omega_{12})/2}\right]^2 .$$

This is a function of incident freq. ω, but because of the nature of the function in [ ], the value of $|C_2(t)|^2$ is significant only for a narrow band of ω, say $\omega_{21} \pm \Delta\omega$. Hence the value of $C_2(t)$ integrated over all frequencies may be treated as a near δ-function.

$$|C_2(t)|^2 = \frac{u(\omega)}{2\epsilon_0}\frac{e^2}{\hbar^2}|z_{21}|^2 \cdot 2\pi t\, \delta(\omega_0)$$

$$\frac{|C_2(t)|^2}{t} = \frac{\pi e^2}{3\epsilon_0\hbar^2}|r_{21}|^2 u(\omega_0)$$

NOTE

$$\Omega^2 = \frac{\epsilon_0^2 |\langle 2|\, e\vec{z}\,|1\rangle|^2}{\hbar^2} = \frac{2u(\omega)}{\epsilon_0}\cdot\frac{e^2}{\hbar^2}|z_{21}|^2$$

In calculating the transition rate to the excited state $|2\rangle$ (from the ground state $|1\rangle$) in the presence of radiation, we assumed that $c_2(t) \simeq 0$ and $c_1(t) \simeq 1$ That is we obtained the absorption rate. Eqs on 1 Feb p③

Let us now consider the reverse case, namely when the upper state is fully populated and the lower state is empty. That is

for $t < 0$, $c_2(t) = 1$ and $c_1(t) = 0$

and we wish to find what $c_1(t)$ is for $t \gg 0$; This will allow us to obtain some features of the emission. Unlike the case of absorption we will not be able to take $c_2(t) \simeq 1$ for $t > 0$, however, for the following reason

We have seen (Einstein's conjecture) that there exists a spontaneous emission channel (corresponding to the A coefficient) which depopulates the upper level. The rate of depopulation can be written as

$$\dot{N}_2 = -A_2 N_2$$

$$\text{or} \quad N_2(t) = N_2(0)\, e^{-A_2 t}$$

If there are multiple lower levels to which spontaneous decays are allowed, then we take

$$A_2 = A_{2\to 1} + A_{2\to 1'} + A_{2\to 1''} + \cdots$$

Corresponding to this A_2, we can define the level lifetime, or the mean lifetime of $|2\rangle$ as $\langle t_2 \rangle = \tau = 1/A_2$.

This decay of the upper level population is in conflict with our earlier assumption, that $c_2(t) = 1$ for $t < 0$ and $c_2(t) \simeq 1$ [i.e. $1-\epsilon$] for $t > 0$. The correct description of $c_2(t)$ for the case of emission is

$$c_2(t) = \exp(-t/2\tau) \quad \text{for } t > 0$$
$$= 1 \quad \text{fo } t < 0$$

This makes $|c_2(t)|^2$ consistent with the depopulation due to the spontaneous decay channel

Within this approximation

The upper state is then given by

$$\psi_2(\vec{r}, t) = c_2(t)\, \psi_2(r)\, e^{-iE_2 t/\hbar}$$

$$= e^{-t/2\tau - iE_2 t/\hbar}\, \psi_2(r)$$

This form of $\psi_2(\vec{r},t)$ satisfies the Schrödinger eqn with a modified definition of the energy eigenvalue:

$$i\hbar \frac{\partial}{\partial t}\psi_2(\vec{r},t) = \left[E_2 - \frac{i\hbar}{2\tau}\right]\psi_2(\vec{r},t)$$

↑ This is different from E_2, and is said to be virtual energy, corresponding to an uncertainty in E, on account of a finite lifetime.

To obtain $c_1 c_2(t)$ we need to solve

$$\dot{c}_1(t) = \frac{-i\Omega}{2} e^{i\omega t}$$

$$\dot{c}_1(t) = -i\Omega \cos(\omega t) \exp[-i\omega_{21} t]\, c_2(t)$$

$$\frac{dc_1}{dt} = \frac{-i\Omega}{2}\left(e^{i\omega t} + e^{-i\omega t}\right) e^{-i\omega_{21} t}\, e^{-t/2\tau}$$

as before we replace the running variable t in the above eqn by t' and integrate from 0 to t to obtain $c_1(t)$

$$c_1(t) = \frac{-i\Omega}{2}\int_0^t \left(e^{i\omega t'} + e^{-i\omega t'}\right) e^{-i\omega_{21} t'}\, e^{-t/2\tau}$$

$$= \frac{-i\Omega}{2}\,\frac{\exp[i(\omega-\omega_{21})t - t/2\tau] - 1}{i(\omega-\omega_{21}) - 1/2\tau}$$

where we have, once again used the fact that the integral has a significant value only when $\omega \simeq \omega_{21}$ and is zero elsewhere.

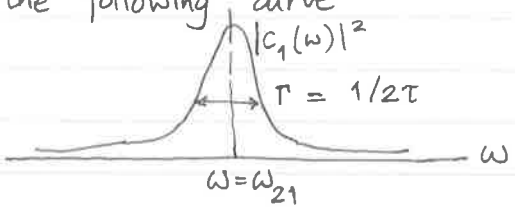
as $t \to \infty$, the term $\exp[i(\omega-\omega_{21})t - t/2\tau] \to 0$, so

$$|c_1(t)|^2_{\substack{t\to\infty \\ (t\gg\tau)}} = \frac{\Omega^2}{4}\left|\frac{1}{i(\omega-\omega_{21}) - 1/2\tau}\right|^2$$

$$|c_{21}|^2 = \frac{\Omega^2}{4}\left[\frac{1}{(\omega-\omega_{21})^2 + 1/4\tau^2}\right]$$

Thus the probability of populating the lower state appears as a function of ω (the frequency of emitted radiation, which is not exactly ω_{21}, but close to it) and the finite lifetime of the upper state.

How do we interpret this quantity? If we plot C_1 as a function of ω we get the following curve



$|C_1|^2$ reaches half of max at $\omega = \omega_{21} \pm \frac{1}{2\tau}$

We interpret this as: when C_2 has decayed completely (or when C_1 and C_2 have attained their steady state values) the radiation emitted is distributed in a small range of frequencies close to ω_{21}, and the shape of the distribution is a function dependent on the spontaneous decay lifetime of the upper state.

Not to be interpreted as "a certain frequency ω near ω_{21} is emitted at time t and this line shape emerges in time, or that different frequencies under this distribution are emitted at different times"

Had τ been infinite, i.e. there were no spontaneous emission, then $C_2(t) \simeq 1$ for $t > 0$ and $C_1(t, \omega)$ would be delta-function in ω.

This hybrid calculation of $C_2(t)$ allows for the existence of a spontaneous emission channel, which manifests as a non-delta-function distribution of the emitted radiation.

This hybrid calculation is also consistent with the uncertainty principle: if E_2 were sharply defined, $\Delta E \to 0$ so the corresponding time uncertainty $\Delta t \to \infty$, which implies that the upper state stays for an infinitely long time. If [$\Delta E \Delta t$ is finite $\sim \hbar$] on the other hand if this state does not stay indefinitely (i.e. $C_2(t) \sim e^{-t/2\tau}$ type), then Δt is finite [$\sim O(\tau)$] and $\Delta E \sim \hbar/\tau$ which is the finite spread in the value of E_2, hence the value of ω of the emitted radiation.

ABSORPTION RATE AND ABSORPTION CROSS-SECTION

The amplitude of the upper state in the perturbative treatment of absorption is given by $c_2(t)$. The corresponding transition probability is

$$|c_2(t)|^2 = \left(\frac{\Omega}{2}\right)^2 \left[\frac{\sin[(\omega-\omega_{21})t/2]}{(\omega-\omega_{21})/2}\right]^2 \rightarrow \{\text{function of } \omega \text{ also}\}$$

Ω contains the electric field $\mathcal{E}(\omega)$. We can integrate over ω to get the total transition probability.
Due to the $[\ ]^2$ function, which behaves like a delta function in the limit $t \to \infty$, we can write

$$|c_2(t,\omega)|^2 \rightarrow c(\infty, \omega_{21})$$

NOTE

$$\lim_{t\to\infty} \frac{\sin^2 \alpha t}{\pi t \alpha^2} = \delta(\alpha)$$

$$|c_2(\infty, \omega_{21})|^2 = \left(\frac{\Omega}{2}\right)^2 2\pi t\ \delta(\omega-\omega_{21})$$

$$\{\mathcal{E} \text{ is also a function of } \omega\} = \frac{e^2 \mathcal{E}^2(\omega_{21}) 2\pi \langle z_{21}\rangle^2 t}{4\hbar^2} = \boxed{\frac{\pi e^2 \mathcal{E}^2(\omega_{21}) \langle z_{21}\rangle^2 t}{2\hbar^2}}$$

The transition rate for absorption

$$R_{12} = d/dt\ |c_2|^2$$

$$= \frac{\pi e^2 \mathcal{E}^2(\omega_{21}) |z_{21}|^2}{2\hbar^2} \qquad \frac{1}{2}\epsilon_0 \mathcal{E}^2(\omega) = \rho(\omega)$$

$$= \frac{\pi e^2}{\epsilon_0 \hbar^2} \rho(\omega_{21}) \langle z_{21}\rangle^2 \qquad \hat{\mathcal{E}} \text{ polarised along } \hat{z}$$

$$= \frac{\pi e^2}{3\epsilon_0 \hbar^2} \rho(\omega_{21}) \langle z_{21}\rangle^2 \qquad \hat{\mathcal{E}} \text{ unpolarised}$$

We also define an absorption cross-section:

$\sigma(\omega)$ = rate of absorption of energy per atom per unit Intensity per unit ang. freq.

$$= R_{12} \cdot \hbar\omega_{21} \,/\, c\rho(\omega_{21}) \,/\, \omega_{21}$$

$$= \frac{\pi e^2}{\epsilon_0 \hbar^2} \rho(\omega_{21}) \langle z_{21}\rangle^2 \hbar\omega_{21} \cdot \frac{1}{c\,\rho(\omega_{21})} \cdot$$

$$\sigma_{21}(\omega) = 4\pi^2 \left(\frac{e^2}{4\pi\epsilon_0 ch}\right) \langle z_{21}\rangle^2 \omega_{21} \checkmark$$

σ_{21} has units of $L^2 T^{-1}$

If we take account of the fact that the absorption profile is not a delta function but a Lorentzian, we get

$$\sigma(\omega) = 4\pi^2 \alpha^R \langle z_{21} \rangle^2 \omega \cdot a(\omega) \; ;$$

or simply $\sigma = 4\pi^2 \alpha^R \langle z_{21} \rangle^2 \omega_{21} \delta(\omega - \omega_{21})$

$$a(\omega) = \frac{1}{\pi} \left[\frac{\Gamma/2\hbar}{(\omega-\omega_{21})^2 + \Gamma^2/4\hbar^2} \right]$$

and $\int a(\omega) d\omega = 1$

UPPER STATE IN THE CONTNUUM

$E_f = \hbar^2 k_f^2 / 2m$ $\quad$ $E_i \equiv E_1$.

we assume $E_f \ll mc^2$ and $E_f \gg |E_i|$

The equation to be solved is the Schrödinger equation for a coulomb field with a positive energy:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} - E_f \right] \psi_f(\vec{k}_f, \vec{r}) = 0 \qquad (\text{where } E_f > 0)$$

when $E_f \gg |E_1|$ the Ze^2/r term can be neglected. and we have

$$\left(\nabla^2 + \frac{2m}{\hbar^2} E_f \right) \psi_f(\vec{k}_f, \vec{r})$$

$$\Rightarrow \quad \psi_f(\vec{k}_f, \vec{r}) = (2\pi)^{-3/2} \exp(i\vec{k}_f \cdot \vec{r})$$

The cross-section for this process is obtained by using this ψ_f in calculating $\langle z_{21} \rangle$ or $\langle z_{fi} \rangle$ and integrating over all final states k_f

$$\sigma = 4\pi^2 \alpha \int_{k_f} d\vec{k}_f \langle z_{fi} \rangle^2 \omega \, \delta(\omega - \omega_{fi})$$

where now $\omega_{fi} = (E_f - E_i)/\hbar$

and $d\vec{k}_f = k_f^2 \, dk_f \, d\Omega$; since $E_f = \hbar^2 k_f^2 / 2m$,

$$d\vec{k}_f = \frac{k_f m}{\hbar^2} dE_f \, d\Omega$$

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one integral over K_f, other over Ω

$$\therefore \quad \sigma = 4\pi^2\alpha \iint \frac{m\,K_f}{\hbar^2}\, dE_f\, d\Omega\, \langle z_{fi}\rangle^2\, \omega\, \delta(\omega-\omega_{fi})$$

$$= 4\pi^2\alpha \frac{m}{\hbar^2} \iint \omega_{fi}\, K_f\, \langle z_{fi}\rangle^2\, \hbar\, d\omega_f \cdot \omega \cdot \delta(\omega-\omega_f+\omega_i)\, d\Omega$$

$$= 4\pi^2\alpha \int \frac{m}{\hbar} K_f\, \omega_{fi} \langle z_{fi}\rangle^2\, d\Omega$$

$$\boxed{\frac{d\sigma}{d\Omega} = 4\pi^2\alpha\, \frac{m}{\hbar}\, K_f\, \omega_{fi}\, \langle z_{fi}\rangle^2}$$

~~CALCULATION OF $\langle z_{fi}\rangle$~~

~~$\langle z_{fi}\rangle = \langle f|z|i\rangle = \langle k|z|1s\rangle$~~

~~$= \int e^{i\vec{K}_f\cdot\vec{r}}\, z\, e^{-r/a}\, d^3\vec{r}$~~

~~$= \int e^{iK_f r\cos\theta}\, r\cos\theta\, e^{-r/a}\, r^2\, dr\, (d\cos\theta)\, d\phi$~~

EMISSION PROFILE OF A COLLECTION OF ATOMS

The distribution $|c_1(t\to\infty, \omega)|^2$, [which we will label $a(\omega)$] gives the natural lineshape of a stationary atom. [↖]
For a collection of atoms (or molecules), e.g. in a gas, when the atoms are in motion, the distribution will appear to have broadened
[to an observer w.r.t. whom the gas is stationary on average]

To this observer, the emission from an atom moving with a velocity $\vec{v}$ will appear to have shifted to a freq.

$$\omega = \omega_0 + \vec{K}\cdot\vec{v}$$

where ω_0 is the rest frame emission freq. and $\vec{K}$ is the rest frame propagation vector.

Thus $\omega_e = \omega_0 + K_z v_z$

- ω_e: observed emission freq
- ω_0: rest frame emission freq
- v_z: velocity along line of sight

$$\omega_e = \omega_0 (1 + v_z/c)$$

The natural lineshape in the rest frame of the emitter is given by

$$a(\omega') = \frac{\gamma/2\pi}{(\omega-\omega')^2 + (\gamma/2)^2} \qquad (\gamma = \Gamma/\hbar)$$

ABSORPTION PROFILE OF A COLLECTION OF ATOMS

If a plane wave with rest frame frequency ω and wavevector $\vec{k}$ is incident on an atom moving with a velocity $\vec{v}$ then it sees the frequency to have shifted to a frequency ω' given by

$$\omega' = \omega - \vec{k}\cdot\vec{v}$$

This means that resonant absorption at ω_0 if the incident freq ω is

$$\omega = \omega_0 + \vec{k}\cdot\vec{v}$$

If we call ω_a the frequency that is being absorbed, then

$$\omega_a = \omega_0 + k_z v_z$$
$$= \omega_0 (1 + v_z/c)$$

ω_a: observed absorption freq. ω_0: this is absorption / emission freq in rest frame.

In a collection of absorbers (gas molecules, for example), the population of atoms moving at a particular v_z is given by

$$n(v_z)\,dv_z = \frac{N}{\tilde{v}\sqrt{\pi}} \exp(-v_z^2/\tilde{v}^2)$$

where

$$\tilde{v} = [2kT/m]^{1/2}$$
$$N = \int_{-\infty}^{\infty} n(v_z)\,dv_z$$

Written as a function of the absorbed freq ω and rest frame absorption / emission freq ω_0,

$$v_z = c(\omega - \omega_0)/\omega_0$$
$$dv_z = (c/\omega_0)\,d\omega$$

Hence

$$n(\omega)\,d\omega = \frac{cN}{\tilde{v}\sqrt{\pi}} \exp\left[-c^2(\omega-\omega_0)^2/\omega_0^2\tilde{v}^2\right]$$

$n(\omega)$: number of atoms absorbing at ω w.r.t. a stationary observer

ω_0 = rest frame absorption freq

$\tilde{v}$ = most probable velocity in the rest frame of observer

So far we have assumed that the emission / absorption frequency in the rest frame is single valued. However this is a simplification of the fact that there is a natural linewidth / lineshape, $a(\omega')$

The natural line shape ~~does~~ of a moving atom is given by

$$L(\omega, \omega') = \frac{\gamma/2\pi}{(\omega-\omega')^2 + (\gamma/2)^2}$$

where ω' is the central frequency of emission ~~is~~ of the moving atom seen by a stationary observer. If the moving atom has a velocity v_z w.r.t. the observer,

$$\omega' = \omega_0 (1 + v_z/c)$$

[$\omega_0 \equiv$ emis/absorp. freq in rest frame]

If $n^*(\omega')\,d\omega'$ is the number of atoms emitting/absorbing at ω', then the frequency distribution of the radiation emitted by the entire collection is given by a convolution of $L(\omega, \omega')$ and $n(\omega')$:

$$I(\omega) = \int_{\omega'=0}^{\infty} n(\omega')\, L(\omega, \omega')\, d\omega'$$

observed

This distribution is called the VOIGT distribution and is the most commonly observed line shape for a collection of atoms/molecules as a low pressure gas