The Interaction of Atoms and Electromagnetic Waves

Time Dependent Perturbation Theory

Until now, we only studied static perturbations. But in the case of applying an oscillating electric field to an atom, our perturbation varies with time. So we need to use the full Time dependent Schrodinger equation.

The general solution to the time dependent SE is:

$$\psi(\underline{r}, t) = \sum_n a_n^{(0)} \psi_n(\underline{r}) e^{-iE_n t/\hbar}$$

To find a specific solution, we would need to find a_n using properties of orthonormality.

We now want to introduce the time dependent perturbation $\lambda \hat{H}_p(t)$

Once again we use a power law expansion: $\psi_j' = \psi_j + \lambda \psi_j^{(1)} + \lambda^2 \psi_j^{(2)} + \dots$

so $\psi(\underline{r}, t) = \sum_n (a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) \dots) \psi_n(\underline{r}) e^{-iE_n t/\hbar}$

Substituting this into the time dependent Schrodinger eqn:

$$[\hat{H} + \lambda \hat{H}_p] \psi(\underline{r}, t) = i\hbar \frac{\partial}{\partial t} \psi(\underline{r}, t)$$

we will find that $\dfrac{\partial a_n^{(0)}}{\partial t} = 0$

and $$\frac{\partial a_n^{(1)}}{\partial t} = -\frac{i}{\hbar} \sum_j a_j^{(0)} \int \psi_n^*(\underline{r}) \hat{H}_p(t) \psi_j(\underline{r}) \, d\Gamma \, \exp\left(-i \frac{(E_j - E_n)t}{\hbar}\right).$$

We can also obtain higher order terms but often they are not required.

Einstein A and B coefficients

We know Planck's law from other modules as:

$$\rho(\nu) = \underbrace{\frac{2h\nu^3}{c^3}}\ \underbrace{\frac{1}{\exp(h\nu/k_BT)-1}}$$

where $\rho(\nu)$ is energy density per unit volume

$$= \sigma(\nu)\,\bar{n}_p$$

$\sigma(\nu)$ is the density of states per unit volume and

$\bar{n}_p$ is the average photon occupancy number for one of the modes. (below)

$\sigma(\nu)d\nu$ gives the number of em vibrational modes per unit volume in this $d\nu$ frequency band.

Einstein reasoned, using thermodynamics, that the number of atoms N_1 in the ground state energy level E_1 is maintained in thermal equilibrium with the population of atoms N_2 in the excited energy level E_2, through emission and absorption of photons with appropriate frequency ν

$$\Delta E = E_2 - E_1 = h\nu$$

If the intrinsic rate an atom falls to ground state is $\alpha_\downarrow$ and the intrinsic rate an atom is excited to a higher state is $\alpha_\uparrow$ then to be in equilibrium:

$$N_1\alpha_\uparrow = N_2\alpha_\downarrow$$

called the detailed balance equation.

On the other hand Boltzmann's law is: $\frac{N_2}{N_1} = \exp\left(\frac{-h\nu}{k_BT}\right)$

Note, the LHS $= \frac{N_2}{N_1} = \frac{\alpha_\uparrow}{\alpha_\downarrow}$ and the RHS $= \frac{\bar{n}_p}{\bar{n}_p + 1}$

$$\therefore \quad \frac{\alpha_\uparrow}{\alpha_\downarrow} = \frac{\bar{n}_p}{\bar{n}_p + 1}$$

We know that $\alpha_\uparrow \propto \rho(\nu)$ so let's say $\alpha_\uparrow = B_{12}\,\rho(\nu)$ where B_{12} is some constant.

so $\frac{\alpha_\uparrow}{\alpha_\downarrow} = \frac{\bar{n}_p}{\bar{n}_p + 1}$ and $\alpha_\uparrow = B_{12}\,\rho(\nu) = B_{12}\,\sigma(\nu)\,\bar{n}_p$

$$= B_{12}\,\frac{2h\nu^3}{c^3}\,\bar{n}_p$$

$$\therefore \quad B_{12}\,\frac{2h\nu^3}{c^3}\,\frac{1}{\alpha_\downarrow} = \frac{1}{\bar{n}_p + 1} \quad \Rightarrow \quad \alpha_\downarrow = B_{12}\,\sigma(\nu)\,(\bar{n}_p + 1)$$

$$= B_{12}\,\rho(\nu) + B_{12}\,\sigma(\nu)$$

let's call $B_{12}\,\sigma(\nu)$ as A_{21}

And since this is for the $\alpha_\downarrow$, let's say $B_{12} = B_{21}$. So:

$$\alpha_\downarrow = B_{21}\,\rho(\nu) + A_{21} \qquad \frac{A_{21}}{B_{21}} = \frac{2h\nu^3}{c^3}$$

Here we have introduced the Einstein A and B coefficients. B_{ij} is the stimulated transition rate (probability per unit time) for moving up from state i to state j, per unit energy density of the EM field. $B_{ij} = B_{ji}$. A_{ji} is the spontaneous transition rate for moving down from state j to state i. You might know this better if you did the "Photons in Astrophysics" Module. B tells you how likely it is for a particle to excite or de-excite when stimulated by an electric field. A tells you how likely it is for a particle to spontaneously de-excite.

Fermi's Golden Rule

Since quantum electrodynamics is hard, in this section we will use a semi-classical approach. We will treat the atom with QM but the electromagnetic field with classical mechanics. In this way we can model absorption and stimulated emission, but we cannot model spontaneous emission. But we can find B and use it to predict A.

We will assume an EM field interacts with the atom with its E field only. The correction to the energy of an electron is given by the dipole correction: $-e\underline{r}\cdot\underline{E}(t)$ So the perturbation hamiltonian is:

$$\hat{H}_p = -e\underline{r}\cdot\underline{E}(t) = -e\underline{r}\cdot\underline{E}\cos\omega t$$

so $\hat{H}_p(t) = -e\underline{r}\cdot\underline{E}\cos\omega t = -e\underline{r}\cdot\underline{E}\,\frac{1}{2}(\exp(i\omega t) + \exp(-i\omega t))$

we will assume the atom starts in either the ground state or an excited state (the eigenstates of the unperturbed system) we will call this the j^{th} state.

In this case, all the zeroth order amplitude coefficients $a_n^{(0)}$ are 0 except for $a_j^{(0)} = 1$ and the time dependence of other coefficients is given to the first order by:

$$\frac{\partial a_n^{(1)}}{\partial t} = -\frac{i}{\hbar}\underbrace{\int \psi_n^*(\underline{r})\,\hat{H}_p(t)\,\psi_j(\underline{r})\,dV}\exp\left(-i\frac{(E_j - E_n)t}{\hbar}\right)$$

we will call this D_{nj}, the dipole matrix element

so $$\frac{\partial a_n^{(1)}}{\partial t} = \frac{-i\,D_{nj}\cdot\underline{E}}{2\hbar}\left(\exp(i\omega t) + \exp(-i\omega t)\right)\exp\left(-i\frac{(E_j - E_n)t}{\hbar}\right)$$

let $\omega_{jn} = \frac{E_n - E_j}{\hbar}$ the transition frequency from j^{th} state to n^{th} state.

if we integrate over time:

$$a_n^{(1)} = \frac{D_{nj}\cdot\underline{E}}{2\hbar}\left[\frac{1 - \exp(i(\omega_{jn}+\omega)t)}{\omega_{jn}+\omega} + \frac{1 - \exp(i(\omega_{jn}-\omega)t)}{\omega_{jn}-\omega}\right]$$

let this be modelling absorption so j^{th} state is lower than n^{th} state. And let's assume $\omega_{jn} \approx \omega$, i.e the radiation is resonant with the transition. So the second term in brackets is much larger than the first, so we ignore the first. This is the rotating wave approximation. The fast oscillations "wash out" and the slow oscillations dominate. So:

$$|a_n^{(1)}(t)|^2 = |D_{nj}\cdot\underline{E}|^2\,\frac{\sin^2\left((\omega_{jn}-\omega)\frac{t}{2}\right)}{(\hbar(\omega_{jn}-\omega))^2}$$

This is the probability of finding the system in the n^{th} state

Unfortunately, this doesn't behave well for $\omega_{jn} = \omega$. This problem has happened because we assumed the spectral lines are perfectly sharp and EM radiation is perfectly monochromatic

So let's replace the E field in the expression. We know from electromagnetism that the power density of an EM wave is:

$$\rho(\omega)\,d\omega = \tfrac{1}{2}\varepsilon_0 |\underline{E}|^2 \quad \Rightarrow \quad |\underline{E}|^2 = \frac{2\rho(\omega)\,d\omega}{\varepsilon_0}$$

So let's put this into the expression and integrate.

$$P_n(t) = \frac{2}{\varepsilon_0}\int_0^\infty |D_{nj}\cdot\hat{\underline{e}}|^2 \frac{\sin^2\left((\omega_{jn}-\omega)\frac{t}{2}\right)}{(\hbar(\omega_{jn}-\omega))^2}\,\rho(\omega)\,d\omega$$

where $\hat{\underline{e}}$ is the unit vector direction of the electric field.

so $$P_n(t) = \frac{\pi|\underline{D}_{nj}\cdot\hat{\underline{e}}|^2}{\varepsilon_0\hbar^2}\rho(\omega_{jn})\,t$$

This is the probability of finding the system in the n^{th} (excited) state.

$\rho(\nu) = 2\pi\,\rho(\omega_{jn}t)$ so $$P_n(t) = \frac{|\underline{D}_{nj}\cdot\hat{\underline{e}}|^2}{2\varepsilon_0\hbar^2}\rho(\nu_{jn})\,t$$

the absorption rate is $\frac{\text{probability}}{\text{time}}$ so:

$$\boxed{W_{nj} = \frac{|\underline{D}_{nj}\cdot\hat{\underline{e}}|^2}{2\varepsilon_0\hbar^2}\rho(\nu_{jn})}$$

where W_{nj} is absorption rate.

This is Fermi's Golden Rule.

This let's us work out:

$$B_{nj} = \frac{|\underline{D}_{nj}\cdot\hat{\underline{e}}|^2}{2\varepsilon_0\hbar^2}$$

And we can thus also work out A_{nj}.

Selection Rules

We stated that the absorption rate is proportional to the vector matrix element D_{ij}:

$$D_{ij} = \int \psi_i^*(\underline{r})\,[-e\underline{r}]\,\psi_j(\underline{r})\,dV$$

if all the components of this matrix element are 0, then EM waves cannot cause a transition between i^{th} and j^{th} state, either through absorption or stimulated emission.

Actually, for most pairs of states, the matrix element is 0 and the transitions are called forbidden. Let's come up with some rules to work out which transitions are forbidden.

Let's split D_{ij} into the x, y and z components.

$x = r\sin\theta\cos\varphi$ so:

$$D_{ij}^{x} = \int_0^\infty\int_0^{2\pi}\int_0^{\pi} \psi_i^*(\underline{r})\,(-er\sin\theta\cos\varphi)\,\psi_j(\underline{r})\,r^2\sin\theta\,dr\,d\theta\,d\varphi$$

Let's split $\psi_i(r,\theta,\varphi) = R_{n'l'}(r)\,Y_{l'm'}(\theta,\varphi)$ and $\psi_j = R_{nl}Y_{lm}$

$$\therefore\ D_{ij}^{x} = \underbrace{-e\int_0^\infty R_{n'l'}^*\,R_{nl}\,r^3\,dr}_{\text{This will never be 0}}\ \underbrace{\int_0^{\pi}\int_0^{2\pi} Y_{l'm'}^*\,\sin\theta\cos\varphi\,Y_{lm}\,\sin\theta\,d\theta\,d\varphi}_{\text{This can be 0}}$$

We will use some relations to help us calculate the angular integral

$$\sin\theta\cos\varphi = \sqrt{\frac{2\pi}{3}}\,(Y_{1,-1} - Y_{1,1}) \qquad \sin\theta\sin\varphi = i\sqrt{\frac{2\pi}{3}}\,(Y_{1,-1} + Y_{1,1})$$

$$\cos\theta = \sqrt{\frac{4\pi}{3}}\,(Y_{1,0}) \qquad Y_{1,m}Y_{l,m'} = AY_{l+1,m+m'} + BY_{l-1,m+m'}$$

where A and B are constants whose value is not important to this calculation.

We can now work out the integral.

$$D_{ij}^{(x)} = -e \int_0^{2\pi}\int_0^{\pi} Y_{l'm'}^{*}(\theta,\varphi)\sqrt{\frac{2\pi}{3}}\,(Y_{1,-1} - Y_{1,1})\,Y_{l,m}(\theta,\varphi)\sin\theta\, d\theta\, d\varphi$$

$$\Rightarrow D_{ij}^{(x)} \propto \int_0^{\pi}\int_0^{2\pi} Y_{l'm'}^{*}(AY_{l+1,m-1} + BY_{l-1,m-1} - AY_{l+1,m+1} - BY_{l-1,m+1})\sin\theta\, d\theta\, d\varphi$$

So from orthogonality, we will find that this will be 0 unless:

$$\left.\begin{array}{l} l' = l+1,\ m' = m-1 \\ l' = l-1,\ m' = m-1 \\ l' = l+1,\ m' = m+1 \\ l' = l-1,\ m' = m+1 \end{array}\right\} \quad \text{so } \Delta l = \pm 1 \text{ and } \Delta m_l = \pm 1$$

Repeating all this for $D_{ij}^{(y)}$, $D_{ij}^{(z)}$, we find the rules for D_{ij}^{y} to be $\Delta l = \pm 1$, $\Delta m_l = \pm 1$ and for D_{ij}^{z} $\Delta l = \pm 1$, $\Delta m_l = 0$

So our selection rules for unforbidden transitions are:

$$\underline{\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1}$$

Assuming that the z direction in space is not defined by any external perturbation. If we had a magnetic field defining the z direction, the polarisation of light travelling in different directions will have slightly different selection rules.

Forbidden Transitions

Consider the state $(n=2, l=0)$ There is only one state lower than this $(n=1, l=0)$, but this is a forbidden transition since we require $\Delta l = \pm 1$. So, if we excite atomic hydrogen, any electrons that relax into $(n=2, l=0)$ will become stuck there forever.

This is not reasonable. There must be some perturbation we have not discovered that allows for the electrons to relax into the ground state. The problem in our model is that we assumed the E field is uniform in space and we neglected the effect of the magnetic field.

If we don't make this approximation, we find a hierarchy of perturbations, split into dipoles, quadrupoles, octapoles and higher multipoles. Each of these has its own selection rules but they are very unlikely which is why we can usually safely ignore them. But in this particular case, their selection rules would allow for the electron to relax into the ground state (after a <u>long</u> time since it is so unlikely).