The interaction of radiation with a molecule

The time-dependent model

A molecule has a set of electronic states, defined by *known* wave functions ψ_0, ψ_1, ψ_2, . . . and energies $E_0, E_1, E_2, \ldots$ satisfying the Schrödinger equations

$$\begin{aligned} H^0\psi_0 &= E_0\ \psi_0 \\ H^0\psi_1 &= E_1\ \psi_1 \\ H^0\psi_2 &= E_2\ \psi_2 \qquad \text{etc.} \end{aligned} \tag{1}$$

The set of functions $\{\psi_j\}$ are eigenfunctions of H_0, so they enjoy their usual relationships:

$$\int \psi_j^* \psi_j \, d\tau = 1 \text{ (normalization)} \quad \text{and} \quad \int \psi_j^* \psi_k \, d\tau = 0 \text{ for } j \neq k \text{ (orthogonality)}$$

which can be combined into the statement

$$\int \psi_j^* \psi_k \, d\tau = \delta_{jk}$$

where δ_{jk} is the 'Kronecker delta' – a 'function' which takes only two values, 0 and 1: it is 0 if $j \neq k$ and 1 if $j = k$.

Now suppose that by the flick of a switch we shine light (or any type of electromagnetic radiation) on the molecule. Even if, prior to switching on, the molecule were known to be in its ground state ψ_0 with energy E_0, after a short time interval it would not be known what energy state the molecule would be in. In order to investigate it, consider just how the light and the molecule interact.

By virtue of their electrons, atoms and molecules are *polarizable.* That means that the electrons respond to the light's electric field component fluctuating with frequency ν by being displaced through the molecule in the direction of the field. The resulting *induced electric dipole moment* also fluctuates with frequency ν of the light. But any electric dipole moment $\boldsymbol{\mu}$ (induced or permanent) undergoes an energy coupling with an electric field **F** which is given by

$$\begin{aligned} E &= -\boldsymbol{\mu} \cdot \mathbf{F} \\ &= -\mu F \end{aligned}$$

if the field and dipole moment are along a single direction arbitrarily chosen to be the *x* axis. Since **F** fluctuates with frequency ν (angular frequency ω) its time dependence is $F(t) = F^0 cos\ \omega t$ and so the energy coupling *V* (a hamiltonian term) is written

$$V(t) = -\mu F^0 cos\ \omega t$$

Recognising that the dipole moment results from the displacement of an electron with charge $-e$ by a distance *x*, then $\mu = -e\ x$ and so the fluctuation is $e\ x\ F^0 cos\ \omega t$**.** Including this term with the molecule's stationary state hamiltonian H^0 appearing in eqs. (1), the time-dependent hamiltonian $H(t) = H^0 + H'(t)$ is now

$$H(t) \equiv H^0 + V(t) = H^0 + e\ x\ F^0 cos\ \omega t \qquad (2)$$

The hamiltonian H^0 appearing in eqs. (1) is independent of time; the functions $\psi_0, \psi_1, \psi_2, \ldots$ therefore describe the *stationary states* of the system, i.e. they are *time-independent.* So how do we get a wave function that describes the fluctuating behaviour of the electrons when light shines on the molecule? Let us call this wave function, which must contain time as a variable, by the symbol $\Psi(t)$. To calculate Ψ we invoke Schrödinger's time-dependent equation

$$H(t)\Psi(t) = -\frac{\hbar}{i}\frac{\partial}{\partial t}\Psi(t) \qquad (3)$$

Any stationary state wave function , ψ can be extended to include a time dependence by the factor $e^{-iE_i t/\hbar}$. You can easily check that the resulting function $\Psi(t) \equiv \psi\ e^{-iE_i t/\hbar}$ satisfies eq. (3). Moreover the inclusion of $e^{-iE_i t/\hbar}$ does not affect any of the stationary state quantities e.g. $\Psi^*\Psi$ or $\int \Psi^* H \Psi d\tau$ for which we previously used ψ rather than Ψ.

At a time *t* after switching on the radiation we do not know which of the functions $\psi_0, \psi_1, \psi_2, \ldots$ describes the state of our molecule. This ignorance can be expressed as

$$\Psi(t) = a_0(t)\ \psi_0 + a_1(t)\ \psi_1 + a_2(t)\ \psi_2 + \ldots + a_j(t)\ \psi_j + \ldots \qquad (4)$$

where the time dependence is carried by the coefficients $a_0, a_1, a_2, \ldots,$

i.e. $a_j \equiv a_j(t)$

The functions $\psi_0, \psi_1, \psi_2, \ldots$ of the stationary states of the molecule are of course independent of time.

We wish to monitor the behaviour of the j^{th} state as a function of time t after switching on the light, and do this by deriving the time dependence of a_j.

The calculation of $a_j(t)$

Substituting eq. (4) into eq. (3) gives

$$\sum_i a_i H \psi_i = -\frac{\hbar}{i} \sum_i \psi_i \frac{da_i}{dt}$$

and substituting for the 'perturbed Hamiltonian H from (2) we get

$$\sum_i a_i H_0 \psi_i + \sum_i a_i \psi_i F^0 ex \cos(\omega t) = -\frac{\hbar}{i} \sum_i \psi_i \frac{da_i}{dt}$$

$$\sum_i a_i E_i \psi_i + \sum_i a_i \psi_i F^0 ex \cos(\omega t) = -\frac{\hbar}{i} \sum_i \psi_i \frac{da_i}{dt}$$

The summations are over all the states.

We wish to consider how the j^{th} state evolves in time in the radiation field.

Multiply by ψ_j* from the left, and integrate:

$$\sum_i a_i E_i \int \psi^*_j \psi_i d\tau + F^0 e \cos(\omega t) \sum_i a_i \int \psi^*_j x \psi_i d\tau = -\frac{\hbar}{i} \sum_i \frac{da_i}{dt} \int \psi^*_j \psi_i d\tau$$

δ_{ij} — *Kronecker delta*

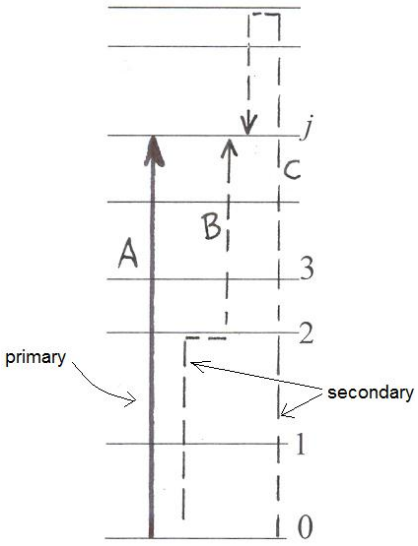
M^x_{ij} — *Transition moment integral*

δ_{ij} — *Kronecker delta*

The Kronecker delta δ_{ij} has the meaning that when i and j are the same then $\delta_{ii} = 1$; when different it equals zero: $\delta_{ij} = \begin{cases} 1 & (i=j) \\ 0 & (i \neq j) \end{cases}$. Because of this, δ_{ij} kills all the terms in the first summation on the left hand side except the j^{th} term. Similarly all the terms in the summation on the right hand side are liquidated except the j^{th}. We benefit from the massacre because the surviving (j^{th}) term of each summation are just the ones we want. The equation is now

$$a_j E_j + F^0 e \cos(\omega t) \sum_i a_i M^x_{ij} = -\frac{\hbar}{i} \frac{da_j}{dt} \qquad (5)$$

But there is a snag with it: we wish to calculate $a_j(t)$, but in order to do so the summation term over i means that all the other coefficients a_i are required! This problem



can be overcome if we agree to make an approximation. Let us specify that we want to know about the development of the j^{th} state over a *very short time interval* τ seconds after switching on the radiation. In this scenario transitions initially occur from the lowest energy state E_0 to all the others. This are the *primary processes*, when the occupation of our state of interest E_j begins to happen. This is shown by transition **A** in the figure. At a later stage the *secondary process* occur, when transitions may take place between any pair of states, some of which include E_j. The primary process which we consider is that like **A** in the sketch, which goes directly from state 0 to state *j* and *not* those involving intermediate states as in **B** and **C**. By limiting the time interval to that defining the primary processes *t* will be so short that $a_1 \approx a_2 \approx a_3 \approx \ldots \approx 0$. At the end of this time interval τ the coefficient a_0 will be $a_0 \approx e^{-iE_0\tau/\hbar}$. Of the surviving summation terms in eq. (5) all except $j = 0$ are eliminated, so that we can now consider the time-evolution of level *j* by confining our attention to the pair of levels $i = 0$ and $i = j$ only. Putting $i = 0$ and dropping the summation in (5), the only term in the summation is that for $i = 0$. The equation thus reduces to

$$a_j E_j + F^0 e M^x_{0j} \cos(\omega\tau) e^{iE_0 t/\hbar} = -\frac{\hbar}{i}\frac{da_j}{dt}.$$

Let us multiply this equation by $e^{i\omega_j\tau}$:

$$F^0 e M^x_{0j} \cos(\omega t) e^{i\omega_j t/\hbar} = -\left[a_j E_j + \frac{\hbar}{i}\frac{da_j}{dt}\right] e^{i\omega_j t}$$

The factor $(E_j - E_0)/\hbar$ in the exponent on the left of the equation is the E_0 to E_j gap expressed as a frequency ω_j. And the entire right hand side of the equation is the time-derivative of

$$-\left[\frac{\hbar}{i} a_j e^{iE_j t/\hbar}\right],$$

(check out the differentiation!)

So now $$\frac{d}{dt}\left[\frac{\hbar}{i} a_j e^{iE_j t/\hbar}\right] = -F^0 e M^x_{0j} \cos(\omega t) e^{i(E_j - E_0)t/\hbar}$$

where a_j appears only once. Now we have finally (yes, really!) got what we strove to achieve, namely the time evolution of the j^{th} energy level in the presence of radiation with frequency ω_j. The integration limits will be $t = 0$ and $t = \tau$ (the short duration of the light pulse):

$$a_j(\omega) = -\frac{i}{\hbar} e^{-iE_j\tau/\hbar} eF^0 M^x_{0j} \int_0^\tau e^{i\omega_j t} \cos(\omega t) dt$$

Note that ω_j is a constant – it's the frequency associated with the $0 \rightarrow$ j transition, but ω is a variable which appears in the question 'What is the probability of a transition with frequency ω?'. (We are going to 'sweep' the frequency ω to see how it affects $|a_j|^2$.) The integral on the RHS of the equation is the Fourier transformation of the *time-domain* cosine function cos ωt and as a definite integral, it produces a function a_j which (although it depends on the time interval τ) is in the *frequency domain*.

Transition probabilities

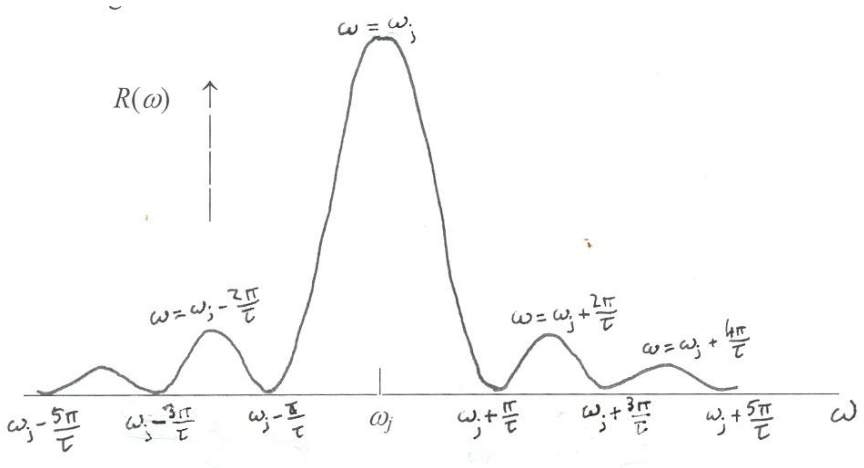
The probability of the occupation of the j^{th} state is $a_j^* a_j$. The probability of a transition from the ground state to the j^{th} state depends on (a) the rate R at which the energy $E_j - E_0$ is absorbed, and (b) since there may be several energy states in the neighbourhood of E_j, on the density of states $n(E_j)$ at E_j. The resulting quantity $R(\omega)$ describes the shape of the spectrum when the frequency ω of the radiation is close to the 'resonant' frequency ω_j :

i.e. $$R(\omega) = \frac{(E_j - E_0) a_j^* a_j}{\tau} \times n(E_j) = \frac{\hbar\omega_j}{\tau} a_j^* a_j \times n(E)$$

$$R(\omega) = \frac{\omega_j}{\hbar}(M^x_{0j} eF^0)^2 n(E) \frac{\sin^2[\frac{1}{2}(\omega_j - \omega)\tau]}{(\omega_j - \omega)^2 \tau} \qquad (6)$$

Eqn. (6) was derived by Fermi and the science community were so elated with it that the equation has become known as **Fermi's Golden Rule**. Although derived using time-dependent theory the equation has no explicit time dependence. It expresses the average rate of energy absorption during the τ seconds lifetime of the radiation pulse. We shall presently use this fact to get the uncertainty in the lifetimes of the quantum states while the radiation is interacting with the molecule.

Try Excel on a PC to plot the function $\frac{\sin^2 \frac{1}{2}x}{x^2}$ against *x*. The shape of $R(\omega)$ is an interesting one:



Discussion

The shape of the spectral absorption curve deserves comment.

1. Eqn. (6) has no explicit time dependence. Energy is absorbed over the brief time interval τ. This interval τ therefore constitutes a time uncertainty δt.
2. The absorption is a maximum when the energy $\hbar\omega$ of the supplied photon is equal to the separation $E_j - E_0$ of the levels (i.e. when ω is equal to the 'resonant frequency' ω_j). But there are also satellite peaks at $\omega_j \pm \frac{n\pi}{\tau}$ where n = 2, 4, 6, . . .
3. The existence of *(a)* finite line width and *(b)* satellite peaks shows that energy can be absorbed from the light <u>even if the resonance condition is not obeyed precisely</u>.
4. All the peaks can be seen to have width $2\pi/\tau$. Now although the time τ was defined as that for which the light interacted with the molecule, it can also be interpreted as the *lifetime* of the energy states involved in the transition. (Clearly if the molecule is undergoing reaction its energy levels will change; τ is then the lifetime of the molecule.) The shorter is τ, the broader is the absorption line. The Uncertainty Principle $\delta E.\delta t \approx \hbar$ predicts that the width of a spectral line associated with a species of lifetime τ is $\hbar/\tau$. The width of the above line in energy units is $(2\pi/\tau)\hbar$ which is consistent with the Principle within a factor of 2π.
5. Since the sample in a typical spectroscopic experiment will contain a large number of molecules with different lifetimes τ the satellite wiggles from different molecules usually interfere and annihilate[1]. The result is a single bell-shaped absorption peak, under which the area is proportional to the number of molecules undergoing transitions at frequency ω_j.
6. The absorption will also be affected by the spectrometer's inherent bandwidth, i.e. its lack of monochromatic resolution ω. The satellite peaks might then be eliminated by interference between those for the different frequencies in the bandwidth.

[1] But not always. Sometimes in NMR spectra the proton spin relaxation times are in a sufficiently narrow range that the wiggles can be seen as 'side-bands' or 'satellites' of the main peaks.