

The Intensity of Absorption

Derivation of an Expression for the Intensity as Function of the Transition Probability per Unit Time

The time dependent Schrödinger equation is

$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

The formal solution is

$$\Psi(t) = e^{-iHt/\hbar}\Psi = e^{-iEt/\hbar}\Psi$$

where the following definitions apply

$\hbar \equiv$ Planck's constant

$H \equiv$ hamiltonian (an operator)

$E \equiv$ energy eigenvalue (a constant)

$\Psi \equiv$ wave function

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We can treat an applied electromagnetic field as a perturbation to the hamiltonian. The zeroth order hamiltonian (that of system without the field) is H_0 . The field hamiltonian is $H_1 = -\mu \cdot E$. The total hamiltonian is $H = H_0 + H_1 = H_0 - \mu \cdot E$

We consider two states, an initial state i and a final state f . The transition probability between the two states is

$$W_{if} = \frac{\pi}{2\hbar^2} \langle f | \mu \cdot E | i \rangle^2 \left\{ \delta(\omega_{fi} - \omega) + \delta(\omega_{fi} + \omega) \right\}$$

This expression is an approximate solution known as the Fermi Golden Rule. The Golden Rule gives the transition probability per unit time for transitions from $i \rightarrow f$. The above expression is also valid for transitions from $f \rightarrow i$ if we interchange the indices. The same inherent transition rate applies for the absorption probability.

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We wish to relate the transition rate to the intensity of absorbed radiation. It is the intensity that we will use to define the time-correlator for spectroscopy. First, we determine the net energy change in the radiation field:

$$-\frac{du}{dt} = -\dot{u} = \frac{N}{V} \sum_{i,f} p_i w_{if} \hbar \omega_{fi} \quad p_i = \frac{e^{-\hbar \omega_i / kT}}{Q}$$

The energy density is u . There are N molecules in volume V . The p_i is the probability that the i th initial state is occupied. Q is the partition function. (Note that McHale calls the partition function z). w_{if} is the transition probability per unit time from above and $\hbar \omega_{fi}$ is the energy of an absorbed photon. We now substitute in the explicit Golden Rule transition probability per unit time for w_{if} .

$$-\dot{u} = \frac{\pi}{2\hbar} \frac{N}{V} \sum_{i,f} \left\{ p_i \omega_{fi} \langle f | \mu \cdot E | i \rangle^2 \delta(\omega_{fi} - \omega) + p_i \omega_{fi} \langle f | \mu \cdot E | i \rangle^2 \delta(\omega_{fi} + \omega) \right\}$$

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Since i and f are dummy indices we can interchange them in the second sum. Further we use the fact that $\omega_{fi} = -\omega_{if}$.

$$-\dot{u} = \frac{\pi}{2\hbar} \frac{N}{V} \sum_{i,f} \left\{ (p_i - p_f) \omega_{fi} \langle f | \mu \cdot E | i \rangle^2 \delta(\omega_{fi} - \omega) \right\}$$

Note that

$$p_f = p_i e^{-\hbar\omega_{fi}/kT}$$

The time derivative of the energy density becomes:

$$-\dot{u} = \frac{\pi}{2\hbar} \frac{N}{V} \left(1 - e^{-\hbar\omega_{fi}/kT} \right) \sum_{i,f} \left\{ p_i \omega_{fi} \langle f | \mu \cdot E | i \rangle^2 \delta(\omega_{fi} - \omega) \right\}$$

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Our goal is to relate the transition probability to the intensity of absorbed radiation. Recall that we have shown that the absorption coefficient is obtained from the intensity reduction as electromagnetic radiation travels through a medium:

$$I = I_0 \exp \{-\gamma x\} = I_0 \exp \left\{ -\frac{4\pi\kappa x}{\lambda} \right\}$$

From the definition of the imaginary part of the dielectric constant

$$\varepsilon_r''(\omega) = 2n_r(\omega)\kappa(\omega)$$

we have:

$$\gamma(\omega) = \frac{\omega\varepsilon_r''(\omega)}{n_r(\omega)c}$$

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We also saw that by comparison with Beer's law

$$I = I_0 \exp \left\{ - 2.303 \epsilon Cx \right\} = I_0 10^{-\epsilon Cx}$$

we can express the familiar extinction coefficient in terms of the imaginary part of the dielectric constant (relative permittivity):

$$\epsilon = \frac{\omega \epsilon_r''(\omega) N_A V}{2303 c n_r N}$$

By reestablishing the connection between $\epsilon_r''(\omega)$ and $I(\omega)$ the relative intensity we can see that it is necessary to determine the imaginary part of the relative permittivity before we proceed. We can express $\epsilon_r''(\omega)$ in terms of the energy density u .

$$\epsilon_r''(\omega) = - \frac{\dot{u}}{\omega u} \quad \text{where } u = \frac{1}{2} \epsilon_0 E_0^2$$

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Using the relation

$$\varepsilon_r''(\omega) = \frac{\pi}{\varepsilon_0 \hbar} \frac{N}{V} \left(1 - e^{-\hbar\omega_{fi}/kT} \right) \sum_{i,f} \left\{ \rho_i \langle f | \mu \cdot e | i \rangle^2 \delta(\omega_{fi} - \omega) \right\}$$

we can express the imaginary part of the permittivity in terms of the transition probability. Note that the amplitude of the radiation E_0 has been factored out and instead there remains a unit vector pointed in the direction of the polarization of the radiation. We can choose any direction for the incident radiation (in the absence of applied static fields). Suppose we choose x-polarization. The square of the transition moment $(\mu_{if})^2$ can be replaced by $1/3 \mu_{fi} \times \mu_{if}$. For a given polarization:

$$\varepsilon_r''(\omega) = \frac{\pi}{3\varepsilon_0 \hbar} \frac{N}{V} \left(1 - e^{-\hbar\omega_{fi}/kT} \right) \sum_{i,f} \left\{ \rho_i \langle f | \mu | i \rangle \langle i | \mu | f \rangle \delta(\omega_{fi} - \omega) \right\}$$

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The relative absorption intensity is:

$$I(\omega) = \frac{3\hbar\epsilon_0\epsilon_r''(\omega)V}{\pi(1 - e^{-\hbar\omega/kT})N} = \sum_{i,f} p_i \langle f|\mu|i\rangle \langle i|\mu|f\rangle \delta(\omega_{fi} - \omega)$$

It is the expression on the right that is used to derive a time-correlator.