

Transitions Between Stationary States (Adapted from *Harris and Bertolucci*, p. 130)

We need to consider the means by which matter absorbs radiation, i.e., the manner in which radiation perturbs a system described by one stationary state (say, the ground state) so that it is at some later time in another stationary state (an excited state). The total wavefunction of the system is symbolized by Ψ (capital psi, a function of position and time, $\Psi = \Psi(\mathbf{r}, t)$) and will reserve ψ 's (lowercase psi's) to symbolize time-independent wavefunctions. We seek an expression for the probability that a system in its ground state, ψ_0 can be stimulated by radiation into an excited state, ψ_1 .

We will assume that only the two states are important so the wavefunction will take the form

$$\Psi(\mathbf{r}, t) = c_0(t)\Psi_0(\mathbf{r}, t) + c_1(t)\Psi_1(\mathbf{r}, t) \quad (1)$$

where it has been made explicit that the coefficients of the two states, $c_0(t)$ and $c_1(t)$, will change over time. We will assume that the system starts out in the ground state, so that at $t = 0$, $c_0 = 1$ and $c_1 = 0$. Furthermore, it is anticipated that probability for absorption is low enough that $c_0 \gg c_1$ so that $\Psi \approx \Psi_0 + c_1\Psi_1$ for the time periods of interest (i.e., the normalization constant, $[|c_0|^2 + |c_1|^2]^{-1/2}$, is sufficiently close to 1 that $c_0 \approx 1$). What we seek is the probability of finding the system in the excited state, Ψ_1 , after the system is irradiated. That probability is given by $|c_1|^2 = c_1^*c_1$.

If the Schrödinger equation contained no time dependent potential, the system would remain in its ground state forever. However, when a photon impinges on matter it introduces an electromagnetic field that varies in space and time, which means that in the presence of radiation, the Hamiltonian of the system is perturbed; the electromagnetic field of the photon subject the particles that make up matter to a potential energy:

$$\mathcal{H}(\mathbf{r}, t) = \mathcal{H}_0(\mathbf{r}) + \mathcal{H}'(\mathbf{r}, t) \quad (2)$$

where $\mathcal{H}_0(\mathbf{r})$ is the Hamiltonian for the system in the absence of the electromagnetic field. The potential energy term, $\mathcal{H}'(\mathbf{r}, t)$, introduced by the electromagnetic field will be more carefully discussed below.

Before we consider the system's changes in the presence of the electromagnetic field, let us recall that we can write the time dependent Schrödinger equation and apply it even in the absence of the field:

$$\mathcal{H}_0(\mathbf{r})\Psi(\mathbf{r}, t) = i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} \quad (3)$$

ψ_0 and ψ_1 are solutions of the time-independent Schrödinger equation, $\mathcal{H}_0 \psi_i = E_i \psi_i$, with energies E_0 and E_1 , and the solutions Ψ_0 and Ψ_1 are

$$\Psi_0(\mathbf{r},t) = \psi_0(\mathbf{r})e^{-iE_0t/\hbar} \quad \text{and} \quad \Psi_1(\mathbf{r},t) = \psi_1(\mathbf{r})e^{-iE_1t/\hbar}. \quad (4)$$

The time-dependent terms multiplying these wavefunctions are not significant when the potential isn't time-dependent because these terms just multiply the time-independent wavefunctions by 'phase factors' with magnitude unity (so they don't affect $|\Psi|^2 = \Psi^*\Psi$, for example, and therefore don't affect our probabilities of finding the particles in the system in any given location.) Substituting equations (4) into Equation (1):

$$\Psi(\mathbf{r},t) = c_0(t)\psi_0(\mathbf{r})e^{-iE_0t/\hbar} + c_1(t)\psi_1(\mathbf{r})e^{-iE_1t/\hbar}. \quad (5)$$

Now we consider how the system changes with time using the time-dependent Schrödinger equation with the electric field present:

$$[\mathcal{H}_0(\mathbf{r}) + \mathcal{H}'(\mathbf{r},t)]\Psi(\mathbf{r},t) = i\hbar \frac{\partial \Psi(\mathbf{r},t)}{\partial t}. \quad (6)$$

Before substituting Equation (5) into (6), we note that

$$[\mathcal{H}_0(\mathbf{r}) + \mathcal{H}'(\mathbf{r},t)]\Psi(\mathbf{r},t) = \mathcal{H}'(\mathbf{r},t)\Psi(\mathbf{r},t) + c_0E_0\Psi_0 + c_1E_1\Psi_1 \quad (7)$$

and

$$\begin{aligned} i\hbar \frac{\partial \Psi(\mathbf{r},t)}{\partial t} &= i\hbar \frac{\partial}{\partial t} \left(c_0(t)\psi_0(\mathbf{r})e^{-iE_0t/\hbar} + c_1(t)\psi_1(\mathbf{r})e^{-iE_1t/\hbar} \right) \\ &= i\hbar \left(\Psi_0 \frac{\partial c_0}{\partial t} + \Psi_1 \frac{\partial c_1}{\partial t} \right) + c_0E_0\Psi_0 + c_1E_1\Psi_1 \end{aligned} \quad (8)$$

The last two terms in (7) and (8) are the same, so when we plug (5) into (6), we get

$$\mathcal{H}'(\mathbf{r},t)(c_0\Psi_0 + c_1\Psi_1) = i\hbar \left(\Psi_0 \frac{\partial c_0}{\partial t} + \Psi_1 \frac{\partial c_1}{\partial t} \right). \quad (9)$$

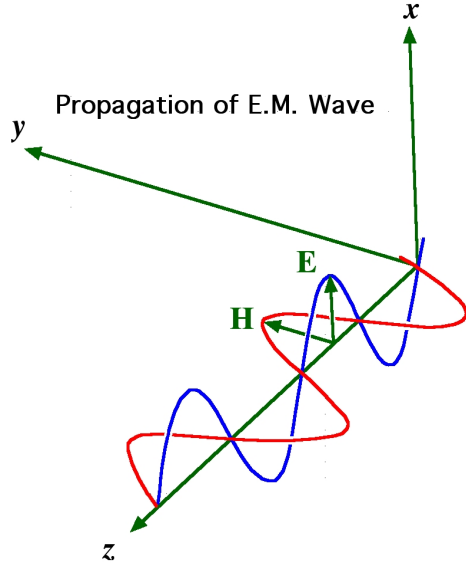
If we multiply on the left of both sides of (9) by Ψ_1^* and integrate over all space, we get

$$\int_{\text{all space}} \Psi_1^* \mathcal{H}'(\mathbf{r},t) (c_0\Psi_0 + c_1\Psi_1) d\tau = i\hbar \left(\frac{\partial c_0}{\partial t} \int_{\text{all space}} \Psi_1^* \Psi_0 d\tau + \frac{\partial c_1}{\partial t} \int_{\text{all space}} \Psi_1^* \Psi_1 d\tau \right), \quad (10)$$

but since Ψ_0 and Ψ_1 are orthogonal and Ψ_1 is normalized, the first term on the right hand side vanishes and the second integral is unity, so

$$\int_{\text{all space}} \Psi_1^* \mathcal{H}'(\mathbf{r},t) (c_0\Psi_0 + c_1\Psi_1) d\tau = i\hbar \frac{\partial c_1}{\partial t}. \quad (11)$$

At this point, we must turn our attention to actual nature of the electromagnetic field. In general, we can write the following for electric and magnetic fields, \mathcal{E} and \mathcal{H} , of an electromagnetic wave propagating along the direction of the *wavevector* \mathbf{k} ,



$$\begin{aligned}\mathcal{E} &= \mathcal{E}_0 \cos\{2\pi i(\mathbf{k} \cdot \mathbf{r} - vt)\}; \\ \mathcal{H} &= \mathcal{H}_0 \cos\{2\pi i(\mathbf{k} \cdot \mathbf{r} - vt)\}\end{aligned}\quad (12)$$

If the wave is propagating in the z -direction, then the electric field oscillates in the x -direction and the magnetic field oscillates in the y -direction (see Figure),

$$\begin{aligned}\mathbf{k} &= k\hat{\mathbf{z}}; \quad \mathcal{E}_0 = \mathcal{E}_0\hat{\mathbf{x}}; \quad \mathcal{H}_0 = \mathcal{H}_0\hat{\mathbf{y}} \\ (\hat{\mathcal{E}}_0 \times \hat{\mathcal{H}}_0 &= \hat{\mathbf{k}}) \\ \mathcal{E} &= \mathcal{E}_0 \cos\{2\pi(kz - vt)\}\hat{\mathbf{x}}; \\ \mathcal{H} &= \mathcal{H}_0 \cos\{2\pi(kz - vt)\}\hat{\mathbf{y}}\end{aligned}\quad (13)$$

Moving along the z -direction at fixed time, we can see that cosine function goes through one period (its argument changes by 2π) if $k = 1/\lambda$, so another way to write \mathcal{E} and \mathcal{H} is

$$\mathcal{E} = \mathcal{E}_0 \cos\left\{\frac{2\pi}{\lambda}(z - ct)\right\}\hat{\mathbf{x}} \quad ; \quad \mathcal{H} = \mathcal{H}_0 \cos\left\{\frac{2\pi}{\lambda}(z - ct)\right\}\hat{\mathbf{y}}, \quad (14)$$

where we have used $v = c/\lambda$. This form reveals most clearly that the photon “wave” function shifts the position of any crest or trough at the speed of light, c , but we shall use the forms given in Eq. (13) and we will neglect the effects of the magnetic field. In an electric field \mathcal{E} , an electron with a charge $-e$ is subject to a force, $\mathbf{F} = -e\mathcal{E}$. A force acting in a given direction can be viewed as the gradient of a potential energy – which is our perturbation, $\mathcal{H}'(\mathbf{r}, t)$,

$$\begin{aligned}\mathbf{F} &= -\bar{\nabla}V \quad \text{so} \quad -e\mathcal{E} = -e\mathcal{E}_0 \cos\{2\pi(kz - vt)\}\hat{\mathbf{x}} = \left(\frac{dV}{dx}\right)\hat{\mathbf{x}} \\ V &= -ex\mathcal{E}_0 \cos\{2\pi(kz - vt)\} + C = \mathcal{H}'(\mathbf{r}, t)\end{aligned}\quad (15)$$

where the second equation follows by integration of the first. We can choose the constant of integration, C , to be zero (which is equivalent of making a choice for our zero of potential energy). For the purpose of calculation, it is convenient to use an exponential form for the cosine function, $\cos \theta = (e^{i\theta} + e^{-i\theta})/2$,

$$\mathcal{H}'(\mathbf{r}, t) = \frac{-ex\mathcal{E}_0}{2} \left\{ e^{2\pi i(kz-vt)} + e^{-2\pi i(kz-vt)} \right\} = \frac{-ex\mathcal{E}_0}{2} \left\{ e^{2\pi ikz} e^{-i\omega t} + e^{-2\pi ikz} e^{i\omega t} \right\} \quad (16)$$

where $\omega = 2\pi\nu$. Now, upon inserting this perturbing field into equation (11), we recall that our interest lies in how c_1 is changing near $t = 0$, at which time $c_1 = 0$ and $c_0 = 1$. We can therefore throw out the term in (11) containing c_1 on the left side:

$$\frac{-e\mathcal{E}_0}{2} \int_{\substack{\text{all} \\ \text{space}}} \psi_1^* e^{iE_1 t/\hbar} x \left\{ e^{2\pi ikz} e^{-i\omega t} + e^{-2\pi ikz} e^{i\omega t} \right\} \psi_0 e^{-iE_0 t/\hbar} d\tau = i\hbar \frac{\partial c_1}{\partial t} \quad \text{or}$$

$$\boxed{\frac{\partial c_1}{\partial t} = \frac{-e\mathcal{E}_0}{2i\hbar} e^{i(E_1-E_0)t/\hbar} \left\{ \begin{array}{l} e^{-i\omega t} \int e^{2\pi ikz} \psi_1^* x \psi_0 d\tau \\ + e^{i\omega t} \int e^{-2\pi ikz} \psi_1^* x \psi_0 d\tau \end{array} \right\}} \quad (17)$$

Eq. (17) is useful when considering transitions in crystals, as we shall see later on. Values of z typical for molecular dimensions are much smaller than the wavelength of the radiation impinging on it, i.e., $z \ll \lambda$ (or $kz \ll 1$). We can therefore expand the exponentials inside the integrals in a rapidly convergent series, i.e., $e^{\pm 2\pi ikz} \approx 1 \pm 2\pi ikz - 4(\pi kz)^2$. Truncating the expansion at the first (constant) term is called the *electric dipole approximation*. With *all three* the terms shown, we have

$$\frac{\partial c_1}{\partial t} = \frac{-e\mathcal{E}_0}{2i\hbar} e^{i(E_1-E_0)t/\hbar} \left\{ \begin{array}{l} e^{-i\omega t} \int (1 + 2\pi ikz - 2(\pi kz)^2) \psi_1^* x \psi_0 d\tau \\ + e^{i\omega t} \int (1 - 2\pi ikz - 2(\pi kz)^2) \psi_1^* x \psi_0 d\tau \end{array} \right\}$$

$$= \frac{-e\mathcal{E}_0}{2i\hbar} e^{i(E_1-E_0)t/\hbar} \left\{ \begin{array}{l} (e^{-i\omega t} + e^{i\omega t}) \left(\boxed{\int \psi_1^* x \psi_0 d\tau} + 2(\pi k)^2 \int \psi_1^* x z^2 \psi_0 d\tau \right) \\ + 2\pi ik (e^{-i\omega t} - e^{i\omega t}) \int \psi_1^* x z \psi_0 d\tau \end{array} \right\}$$

but we will retain only the first integral (in the box). If we retain the other much smaller integrals, we can obtain *electric-quadrupole transitions*, etc. Without them, we get

$$\frac{\partial c_1}{\partial t} = \frac{-\mathcal{E}_0}{2i\hbar} (e^{i(E_1-E_0+h\nu)t/\hbar} + e^{i(E_1-E_0-h\nu)t/\hbar}) \int \psi_1^* ex \psi_0 d\tau. \quad (18)$$

The integral in this expression is called the *transition moment integral*, between state 0 and state 1, which we will denote as μ_{01}^x . Since this expression applies for *short times* after $t = 0$, we integrate the expression under this assumption to obtain

$$c_1 = \frac{-E_0}{2} \mu_{01}^x \left[\frac{1 - e^{i(E_1 - E_0 + h\nu)t/\hbar}}{E_1 - E_0 + h\nu} + \frac{1 - e^{i(E_1 - E_0 - h\nu)t/\hbar}}{E_1 - E_0 - h\nu} \right] \quad (19)$$

When $h\nu \cong E_1 - E_0$, the first term is much smaller than the second and can be neglected. As indicated at the beginning of this section, the probability of being in the excited state is given by $c_1^* c_1$,

$$c_1^* c_1 = \frac{\mathcal{E}_0^2}{4} \mu_{01}^{x^2} \left[\frac{2 - e^{i(E_1 - E_0 + h\nu)t/\hbar} - e^{-i(E_1 - E_0 - h\nu)t/\hbar}}{(E_1 - E_0 - h\nu)^2} \right]$$

or
$$c_1^* c_1 = \frac{\mu_{01}^{x^2} \mathcal{E}_0^2 \sin^2 \left[(E_1 - E_0 - h\nu)t/2\hbar \right]}{(E_1 - E_0 - h\nu)^2} \quad (20)$$

where the substitution $\sin^2 \theta = (2 - e^{2i\theta} - e^{-2i\theta})/4$ has been used. If we integrate over all frequencies of radiation (assuming the incident radiation is white light), this gives,

$$c_1^* c_1 = \frac{\mathcal{E}_0^2 \mu_{01}^{x^2} t}{4\hbar^2} \quad \text{or, taking account of } x, y, \text{ or } z \text{ polarizations}$$

$$\boxed{\frac{d(c_1^* c_1)}{dt} \propto \mathcal{E}_0^2 (\mu_{01}^{x^2} + \mu_{01}^{y^2} + \mu_{01}^{z^2})} \quad (21)$$

The initial rate at which the excited state is generated when the light is turned on is proportional the square of the amplitude of the radiation and to the square of the transition moment integral(s). Because the intensity of the light is also proportional the square of the amplitude of the radiation, rate at which the excited state is populated in proportional to the intensity of the incident radiation. *Of fundamental significance as far as symmetry is concerned is the fact that absorption does not occur in the dipole approximation if transition moments are zero by symmetry.*