

Reference: Brand, J.C.D.; Speakman, J.C. "Molecular Structure The Physical Approach", Arnold, London, 1960.

The time-dependent Schrodinger Equation, described early in the course, is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = \mathcal{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (1)$$

where  $\Psi(x, t) = \psi(x)\phi(t)$  is the time dependent wave function describing a system. Note that the time dependent wave function includes a spatial wave function multiplied by a time-dependent wave function. Also note, for simplicity, that we are using a 1D spatial problem. In general, however, the time-dependent wave function can be written as:

$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t)$  where  $\mathbf{r}$  is a general position in a problem of any dimension.

The time dependent part of the function can be written as:  $\phi(t) = e^{-iEt/\hbar}$  Although a general proof of this will not be given, we can use the fairly general standing wave expression developed in the first unit of the course:

$$\Psi(x, t) = Ae^{2\pi i \left( \frac{x}{\lambda} - \nu t \right)} = Ae^{2\pi i \frac{x}{\lambda}} e^{-2\pi i \nu t} = A \left[ \cos 2\pi \left( \frac{x}{\lambda} - \nu t \right) + i \sin 2\pi \left( \frac{x}{\lambda} - \nu t \right) \right] \quad (2)$$

along with the expression  $E = h\nu$  to show that

$$\Psi(x, t) = Ae^{2\pi i \left( \frac{x}{\lambda} - \nu t \right)} = Ae^{2\pi i \frac{x}{\lambda}} e^{-2\pi i \nu t} = Ae^{2\pi i \frac{x}{\lambda}} e^{-it/\hbar} = \psi(x)\phi(t) \quad (3)$$

This is a good point to note that:  $\Psi^*(\mathbf{r}, t) = \psi^*(\mathbf{r})\phi^*(t) = \psi^*(\mathbf{r})(e^{-iEt/\hbar})^* = \psi^*(\mathbf{r})e^{iEt/\hbar}$  (4)

Because of this result for the complex conjugate, we have:  $\Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t) = \psi^*(\mathbf{r})\psi(\mathbf{r})e^{-iEt/\hbar}e^{iEt/\hbar} = \psi^*\psi$  (5)

that is, in wave function products of this sort, the time dependence drops out.

We will now consider the general transition between two states  $\Psi_n(x, t)$  and  $\Psi_m(x, t)$ . When both wave functions are solutions of (1), it follows that a general combination form:

$$\Psi = c_n \Psi_n(x, t) + c_m \Psi_m(x, t) \quad (6)$$

is also a solution to (1). This equation describes a system which can fluctuate in time between the two component states. The  $c_i$  are time dependent. We now modify (1) by a small perturbation, obtaining:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi + v\Psi = i\hbar \frac{\partial \Psi}{\partial t} = c_n E_n \Psi_n + c_m E_m \Psi_m + v\Psi = \\ i\hbar \left[ \Psi_n \frac{\partial c_n}{\partial t} + c_n \frac{\partial \Psi_n}{\partial t} + \Psi_m \frac{\partial c_m}{\partial t} + c_m \frac{\partial \Psi_m}{\partial t} \right] = i\hbar \left[ \Psi_n \frac{\partial c_n}{\partial t} + \Psi_m \frac{\partial c_m}{\partial t} \right] + c_n E_n \Psi_n + c_m E_m \Psi_m \end{aligned} \quad (7)$$

Simplifying, we have:  $v\Psi = i\hbar \left[ \Psi_n \frac{\partial c_n}{\partial t} + \Psi_m \frac{\partial c_m}{\partial t} \right]$  (9)

Now multiply from the left by  $\Psi_m$  and integrate:  $\int \Psi_m v\Psi = i\hbar \left[ \frac{\partial c_n}{\partial t} \int \Psi_m \Psi_n + \frac{\partial c_m}{\partial t} \int \Psi_m \Psi_m \right] = i\hbar \frac{\partial c_m}{\partial t}$  (10)

Now  $\int \Psi_m v\Psi = c_m \int \Psi_m v\Psi_m + c_n \int \Psi_m v\Psi_n$  giving (11)

$$i\hbar \frac{\partial c_m}{\partial t} = c_m \int \Psi_m^* v \Psi_m d\tau + c_n \int \Psi_m^* v \Psi_n d\tau \quad (12)$$

We can simplify our assessment of transitions a bit now by assuming that at an initial time  $c_m = 0$  and that the system is initially in state  $\psi_n$ . We now try to find an expression for  $\frac{\partial c_m}{\partial t}$  as a way of determining the transition likelihood for going from  $\psi_n$  to  $\psi_m$ :

$$i\hbar \frac{\partial c_m}{\partial t} = c_n \int \Psi_m^* v \Psi_n d\tau \quad (13)$$

Now imagine that the perturbing potential  $v$  results from the interaction of an electromagnetic field with the dipole moment  $ex$  of an absorbing molecule. The electromagnetic field can be described by:

$$E_x = 2E_x^o \cos 2\pi\nu t = E_x^o (e^{i2\pi\nu t} + e^{-i2\pi\nu t}) \text{ and } v = E_x ex \quad (14)$$

Now starting with (13),

$$\begin{aligned} i\hbar \frac{\partial c_m}{\partial t} &= c_n \int \Psi_m^* v \Psi_n d\tau = c_n \int \Psi_m^* ex E_x^o \Psi_n d\tau (e^{i2\pi\nu t} + e^{-i2\pi\nu t}) e^{iE_m t/\hbar} e^{-iE_n t/\hbar} = \\ &= c_n e E_x^o \left[ \int \Psi_m^* x \Psi_n d\tau \right] (e^{i2\pi(E_m - E_n + h\nu)t/\hbar} + e^{i2\pi(E_m - E_n - h\nu)t/\hbar}) \end{aligned} \quad (15)$$

In this expression, the time terms are not involved in the integral, which includes only position terms. The term in brackets is called the *transition moment*  $M$ , and is the key to whether transitions are possible (*allowed*) or not (*forbidden*). We note that  $M$  will be a constant, and so the time dependence of  $c_m$  is given by:

$$\frac{\partial c_m}{\partial t} = \frac{-ic_n e E_x^o M}{\hbar} (e^{(i/\hbar)(E_m - E_n + h\nu)t} + e^{(i/\hbar)(E_m - E_n - h\nu)t}) \quad (16)$$

Let us assume that a molecule starts out in state  $n$ , so that  $c_n = 1$ . The initial rate of change of  $c_m$  is then given by integrating (16) from  $t = 0$  to  $t = t$ . Approximating  $c_n = 1$  in this initial process, we have:

$$c_m = \frac{-ie E_x^o M}{\hbar} (\hbar/i) \left[ \frac{e^{(i/\hbar)(E_m - E_n + h\nu)t} - 1}{E_m - E_n + h\nu} + \frac{e^{(i/\hbar)(E_m - E_n - h\nu)t} - 1}{E_m - E_n - h\nu} \right] = e E_x^o M \left[ \frac{1 - e^{(i/\hbar)(E_m - E_n + h\nu)t}}{E_m - E_n + h\nu} + \frac{1 - e^{(i/\hbar)(E_m - E_n - h\nu)t}}{E_m - E_n - h\nu} \right] \quad (17)$$

In addition to the importance of the transition moment  $M$ , it is also clear that the last two terms will be very large when  $E_m - E_n = h\nu$  (absorption of radiation, second term) or when  $E_m - E_n = -h\nu$  (emission of radiation, first term). We also note that  $c_m$  is still a complex number. Neglecting the emission term and multiplying both sides of (17) by  $c_m^*$  gives the probability of the higher state  $m$  at the end of the time integration period::

$$\begin{aligned} c_m^* c_m = |c_m|^2 &= (e E_x^o M)^2 \left[ \frac{1 - \cos 2\alpha + i \sin 2\alpha}{E_m - E_n - h\nu} \right] \left[ \frac{1 - \cos 2\alpha - i \sin 2\alpha}{E_m - E_n - h\nu} \right] = (e E_x^o M)^2 \frac{(1 - \cos 2\alpha)^2 - \sin^2 2\alpha}{(E_m - E_n - h\nu)^2} = \\ &= (e E_x^o M)^2 \frac{(1 - \cos 2\alpha)^2 + \sin^2 2\alpha}{(E_m - E_n - h\nu)^2} = (e E_x^o M)^2 \frac{2 - 2 \cos 2\alpha}{(E_m - E_n - h\nu)^2} = \\ &= (e E_x^o M)^2 \frac{2 - 2(1 - 2 \sin^2 \alpha)}{(E_m - E_n - h\nu)^2} = 4 (e E_x^o M)^2 \frac{\sin^2 \alpha}{(E_m - E_n - h\nu)^2} \text{ where } \alpha = \pi (E_m - E_n - h\nu)t/h \end{aligned} \quad (18)$$

This expression is valid for monochromatic light.