The semi classical approaches for the comparison of time dependent Schrödinger equation with experimental quantities

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Abstract

The time dependent Schrödinger equations have been solved to show the equivalence of the theoretical expressions, the transition probabilities with the experimental quantities that are important in UV-Vis spectroscopy. The theoretical expressions are derived by semi classical approach in which the radiation of incident upon an atom is described by classical electromagnetic plane wave and the atom on the other hand treated quantum mechanically. The mathematical derivations are useful for qualitative and quantitative understanding of how transition induced in molecular systems.

Keywords: Rate of Transition, Molar Extinction Coefficient, Time Dependent Schrödinger equation.

Resumen

Las ecuaciones de Schrödinger dependientes del tiempo se han resuelto para mostrar la equivalencia de las expresiones teóricas, las probabilidades de transición con las cantidades experimental, el coeficiente de extinción molar que son importantes en la espectroscopia UV-Vis. Las expresiones teóricas se derivan de una aproximación semi clásica en la que se describe que la radiación incide sobre un átomo por la onda electromagnética clásica de un avión y el átomo de la otra parte trata de la mecánica cuántica. Las derivaciones matemáticas también son útiles para la comprensión cualitativa y cuantitativa de la transición inducida en los sistemas moleculares.

Palabras clave: La tasa de transición, coeficiente de extinción molar, función del tiempo S ecuación de Schrödinger.

I. INTRODUCTION

Absorption and emission are the phenomena in which the electromagnetic radiation interacts with matter. When this process is taking place in an atom or molecule it is said to be transition [1, 2, 3, 4]. Transition is a quantum mechanical process expressed in molecular states by deriving the time-dependent Schrodinger equation which allows calculating the atomic scale phenomena as a function of time as well as space. In this research, by semi classical approach, the transition dipole moment of the molecule are derived from time dependent Schrodinger equation in which the radiation of incident upon an atom is described by classical electromagnetic plane wave and the atom on the other hand treated quantum mechanically and this equation has been compared with the experimentally measured quantities.

II. THE TIME DEPENDENT SCHRÖDINGER EQUATION

Transition of the molecules is no longer stationary and need the time dependent Schrodinger equation, including the description of the system under the influence of a time dependent perturbation. So, if a system that is initially in some stationary state of definite energy, exposed to electromagnetic radiation for a limited time, then it undergoes transition to some other stationary states. Let $\hat{H}^0$ be the Hamiltonian of the molecular system in the absence of radiation field thus, the time independent equation becomes [1, 2, 3, 4],

$$i\hbar \frac{\partial \psi_k^{(0)}(x,t)}{\partial t} = \hat{H}^0 \psi_k^{(0)}(x,t), \qquad (1)$$

Where, the eigen function of the unperturbed atom expressed as, $\psi_k^{(0)}(x,t) = \psi_k^{(0)}(x)e^{-i\omega_k t}$ and the spatial parts, $\psi_k^{(0)}(x)$ of these eigen functions are solution of the time independent Schrodinger equation and satisfy the orthogonality relation $\int \psi_m^{(0)}\psi_k^{(0)}d\tau = \delta_{mk}$ [5]. On the other hand, if $\hat{H}'$ be the Hamiltonian due to interaction between the system and radiation, the time dependent Schrodinger equation can be written as follows to indicate the state change with time [5, 6]:

$$ i\hbar \frac{\partial \psi}{\partial t} = \hat{H}'\psi. \tag{2}$$

During the time interval the perturbation becomes, the sum of unperturbed Hamiltonian of the free atom plus the perturbation operator [5, 6]:

$$ i\hbar \frac{\partial \psi}{\partial t} = (\hat{H}^0 + \hat{H}')\psi. \tag{3}$$

Where the general state function expressed as a linear superposition of

$$ \psi(x,t) = \sum c_k \exp(-iE_k^{(0)}t/\hbar)\psi_k^{(0)}(x). \tag{4}$$

For two level system Eq. (4) reduced to a sum of two terms, according to the following

$$ \psi(x,t) = c_k(t)\psi_k^{(0)}e^{-\frac{iE_k t}{\hbar}} + c_m(t)\psi_m^{(0)}e^{-\frac{iE_m t}{\hbar}}. \tag{5}$$

The coefficients $c_k(t)$ and $c_m(t)$ are the time dependent probability amplitudes of the two atomic states of k and m [5]. This means that the value $|c_k(t)|^2$ gives the probability of finding the system in level $|k\rangle$ at time t. In addition, the relation of $|c_k(t)|^2 + |c_m(t)|^2 = 1$, holds at all times t, if the decay into other level is neglected.

If we substituting Eq. (4) in to Eq. (3) yields

$$ i\hbar \frac{d}{dt}(\sum c_k(t)\exp(-\frac{iE_k t}{\hbar})\psi_k^{(0)}) = (\hat{H}^0 + \hat{H}')\sum c_k(t)\exp(-\frac{iE_k^{(0)}t}{\hbar}). \tag{6}$$

For two level states Eq. (6) becomes the following, where the relation in Eq. (1) has been used to cancel equal terms on both sides and a multiplication by conjugate with $\psi_n^*(n=k,m)$ and spatial integration result in the following two equations:

$$ \frac{d(c_k(t))}{dt} = -\frac{i}{\hbar}(c_k(t)\hat{H}'_{kk} + c_m(t)\hat{H}'_{km}e^{i(\frac{E_k-E_m}{\hbar})t}), \tag{7}$$

$$ \frac{d(c_m(t))}{dt} = -\frac{i}{\hbar}(c_m(t)\hat{H}'_{mm} + c_k(t)\hat{H}'_{mk}e^{-i(\frac{E_k-E_m}{\hbar})t}), \tag{8}$$

with the spatial integral

$$ \hat{H}'_{kn} = \int \psi_k^* \hat{H}'\psi_m d\tau. \tag{9}$$

Where,

$$ \vec{\mu}_{mk} = -e\int \psi_k^* \vec{r}\psi_m d\tau. \tag{10}$$

The above equation is the atomic transition dipole moment. It depends on the wave functions ψ_k and ψ_m of the two states and are determined by charge distribution in these states [4, 5]. Eqs. (7) and (8) show the rate at which a system can be changed from one stationary to another under the influence of perturbing effect. They are the basic equations, which must be solved to obtain the probability amplitudes of $c_k(t)$ and $c_m(t)$ [4, 5]. To further proceed with Eqs. (7) and (8), it is necessary to be more specific about the perturbation. Thus in the next section some features of the interaction between the electric field and molecular system would be treated.

III. INTERACTION OF EMR WITH MOLECULAR SYSTEM

When electromagnetic radiation falls on a molecule the oscillating electric field of the radiation can disturb the energy of the molecule and allow it to escape from its initial stationary state, which is characterized by quantum number k [2, 4, 5]. The classical expression of the electromagnetic radiation obtained from Maxwell's equations can be describe as follows:

$$ \vec{E}_x = \vec{E}_x^{(0)}(\frac{e^{i\omega t} + e^{-i\omega t}}{2}). \tag{11}$$

When this field acts on a dipole moment component it produces a change in energy and is responsible for the change in Hamiltonian that occurs when radiation falls on the system. The change in the Hamiltonian therefore, is given by,

$$ \hat{H}' = -\vec{E}_x\vec{\mu}. \tag{12}$$

Substituting Eq. (11) into (12), the perturbed Hamiltonian becomes

$$ \hat{H}' = -\vec{E}_x^{(0)}(\frac{e^{i\omega t} + e^{-i\omega t}}{2})\vec{\mu}_x \tag{13}$$

If a weak-field approximation were considered for Eq. (7) and (8), in which at time t=0, the atoms are in the lower

state which implies $c_k(t) = 1$ and $c_m(t) = 0$. And further by the assumption that the field amplitude to be sufficiently small for the time $t<T$ and the population of E_m remains small compared with that of E_k. Therefore with this assumption the first approximation of Eq. (7) and (8) become

$$\frac{dc_k(t)}{dt} = 0, \qquad (14)$$

$$\frac{dc_m(t)}{dt} = \frac{i}{\hbar} E_x^{(0)} \left\langle \psi_m^{(0)} \left| \mu_x \right| \psi_k^{(0)} \right\rangle \left[e^{it(\omega+\omega_{mk})} + e^{it(\omega_{mk-\omega})} \right] \quad (15)$$

Where

$$\left| \mu_{xkm} \right| = \int (\left\langle \psi_m^{(0)} \left| \mu_x \right| \psi_k^{(0)} \right\rangle) dx. \qquad (16)$$

With the initial condition of $c_k(0) = 1$ and $c_m(0) = 0$ the integration over the time interval 0 to t will give

$$c_k(t) = 0, \qquad (17)$$

$$c_m(t) = \frac{E_x^{(0)} \left| \mu_{xkm} \right|}{2} \left[\frac{e^{it(E_m-E_k-h\upsilon)} - 1}{E_m - E_k - h\upsilon} + \frac{e^{it(E_m-E+h\upsilon)_k} - 1}{E_m - E_k + h\upsilon} \right]. \qquad (18)$$

The process of interest here is the process in which the system goes from lower energy level k to higher level m. For such arrangement of energies, the denominator of the first term of Eq. (18) will go to zero when the radiation frequency is such that $h\upsilon = E_m - E_k$. On the other hand for emission case the second term is important since the energy in sate m is greater than that of state K. Thus, for assumed energy level pattern Eq. (18) reduces to

$$c_m(t) = \frac{E_x^{(0)} \left| \mu_{xkm} \right|}{2} \left[\frac{e^{it(E_m-E_k-h\upsilon)} - 1}{E_m - E_k - h\upsilon} \right]. \qquad (19)$$

Thus, the transition probability of absorption from k to m state becomes

$$c_m^*(t)c_m(t) = E_0^2 \left| \mu_{xkm} \right|^2 \frac{\sin^2(\frac{E_m - E_k - h\upsilon)t}{2\hbar})}{(E_m - E_k - h\upsilon)^2}. \qquad (20)$$

The total probability of a transition to state m is found by summing the infinitesimal probabilities over the various frequencies. Since the energy density in an electromagnetic wave is given by $u = \frac{E_0^2 \varepsilon_0}{2}$, the transition probabilities

calculated proportional to the energy density of the incoming radiation. If we consider a situation in which the in coming radiation is electromagnetic waves of many frequencies, it is the best to replace u with energy density in the range $d\omega$ (that means $u \to d\omega\rho(\omega)$) and integrate over the frequency spectrum. Moreover since the term in the bracket is sharply peaked about $\omega \approx \omega_{mk}$ while $\rho(\omega)$ is slowly varying we can move ρ outside of the integral.

$$c_m^*(t)c_m(t) = \frac{2\rho(\omega)}{\varepsilon_0\hbar^2} \left| \mu_{xkm} \right|^2 \int \sin^2(\frac{\frac{\omega_{mk} - \omega}{2}}{(\omega_{mk} - \omega)^2} t) d\omega, \quad (21)$$

after integration Eq. (21) becomes

$$c_m^*(t)c_m(t) = \frac{\pi\rho(\omega)}{\varepsilon_0\hbar^2} \left| \mu_{xkm} \right|^2 t. \qquad (22)$$

Eq. (22), gives the probability that any molecule will make a transition to sate m after having been illuminated for a time *t*. The transition probability here after no longer oscillating with time, but instead increasing monotonically. Therefore, the number of transition to m per second or rate of transition probability becomes

$$\frac{d}{dt}(c_m^*(t)c_m(t)) = \frac{\pi\rho(\omega)}{\varepsilon_0\hbar^2} \left| \mu_{xkm} \right|^2. \qquad (23)$$

For isotropic radiation the three components of the radiation dipole interaction are equal and one can write

$$\frac{d}{dt}(c_m^*(t)c_m(t)) = \frac{\pi\rho(\omega)}{3\varepsilon_0\hbar^2} \left| \mu_{xkm} \right|^2. \qquad (24)$$

This is the rate of change of the system as a result of absorption under the perturbing effect of the electric field of the radiation and it is usually written with Einstein's coefficient of induced absorption so that Eq. (24) becomes,

$$\frac{d}{dt}(c_m^*(t)c_m(t)) = B_{km}\rho. \qquad (25)$$

From the Eq. (25) it is obvious that the rate of transition depends on transition moment and energy density of the radiation.

To complete the general study of the process by which radiation is absorbed, it remains only to compare this derived expression with the quantities usually encountered in the experimental determination of the absorption of radiation. Thus in the next sections, the experimentally observable quantities, the molar extinction coefficient, are related to the parameter which reflects the detail molecular properties of the system, namely the transition integral.

IV. COMPARISON THE THEORETICAL RESULTS WITH EXPERIMENTAL QUANTITIES

Now, let us relate the measurable quantities, the molar decadic absorption coefficient, ε to quantum mechanical expression that means the theoretical expression for the rate of transfer of molecules from state k to m of Eq. (24). The molar decadic absorption coefficient, related to the absorption coefficient by the following [4, 5]:

$$\alpha(\upsilon) = \ln(10)\varepsilon(\upsilon)cl. \qquad (26)$$

Substituting this equation to Beerr-Lambert's law, for diluted and short path length it becomes

$$I = I_0(1 - \ln(10)\varepsilon(\upsilon)cl). \qquad (27)$$

Taking differential of the both sides of the above equation

$$-dI = I_0 \ln(10)\varepsilon(\upsilon)cdl. \qquad (28)$$

Where the concentration $c = \dfrac{N}{N_a}$, s substituting this into (28), leads to

$$-dI = \varepsilon(\upsilon)\frac{N}{N_a}I_0 \ln(10)dl \cdot \qquad (29)$$

From theoretical expression, if $\dfrac{d}{dt}(c_m{}^*(t)c_m(t))$ is the rate of probability for a single molecule changes as a result of absorption of radiation under perturbing effect of electric field radiation then $\dfrac{d}{dt}(c_m{}^*(t)c_m(t))Ndl$ is the number of molecules excited in a layer dl with energy absorption $h\upsilon_{mk}$, so the loss in intensity becomes [4, 7].

$$-dI = \frac{d}{dt}(c_m{}^*(t)c_m(t))Nh\upsilon_{mk}dl \cdot \qquad (30)$$

Comparing Eq. (29), containing an experimental quantities with Eq. (30) the theoretical expression, the rate of probability can be expressed as follows,

$$\frac{d}{dt}(c_m{}^*(t)c_m(t)) = \frac{\varepsilon(\upsilon)c\rho \ln(10)}{N_a h\upsilon}, \qquad (31)$$

where, $I_0 = \rho c$.

If the energy density is assumed to be constant through out the bands the total rate of probability for the entire absorption band is obtained by integrating over the entire frequency range. Therefore, the total rate of transition probability [4, 8, 9] is given by

$$\frac{c\rho \ln(10}{Nah}\int \frac{\varepsilon(\upsilon)}{\upsilon}d\upsilon = \frac{|\mu_{km}|^2}{6\varepsilon_0 \hbar^2}. \qquad (32)$$

The total intensity of the band is obtained by measuring $\varepsilon(\upsilon)$ in the region of absorption and usually determined by integrating the area under the graph. So the integrated absorption coefficient due to transition can be expressed as [4, 8, 9]

$$I_A = \int \frac{\varepsilon(\upsilon)}{\upsilon}d\upsilon = S\frac{|\mu_{km}|^2}{3} = \frac{2\pi^2 N_a |\mu_{mk}|^2}{3\ln(10)c\varepsilon_0 h}, \qquad (33)$$

where, $S=2.9352 \times 10^{60} C^{-2}$ mol^{-1}. Eq. (33) relates the experimentally measured molar decadic absorption coefficient with the quantum mechanical expression the transition dipole moment. The transition dipole moment is a vector that depends on both ground state and excited state wave function and couples the transition to the electric field of light. The above equation clearly shows the equivalence of theoretical expression obtained from deriving the time dependent Schrodinger equation with the experimentally measured quantities.

On the other hand, oscillator strength was considered the other useful parameter providing the intensity of transition; it expresses the relative strength of electron transition [10, 11, 12]. It is one of the most fundamental quantities in analytical spectroscopy. In practice, it determines the sensitivity of a given atomic resonance line and needs to be accurately known if one needs to relate the magnitude of the absorption signal to its concentration. Oscillator strength can be determined directly through absolute emission, absorption or dispersion measurement. Oscillator strength is related to the molar decadic absorption coefficient by the following equation [10, 13, 14]:

$$f = 4.32 \times 10^{-9} \frac{molcm}{L} \int \varepsilon d\upsilon \cdot \qquad (34)$$

Measurements of emission, absorption and dispersion intensities of the molecules give their number density and oscillator strength. Absorption and dispersion measurement involves the number density of the lower level of the transition, and emission measurement involves that of the upper level. An equation relating integrated absorption coefficient with number density and oscillator strength for the Gaussian shaped spectrum is given by [10, 11]:

$$\int \alpha(\upsilon)d\upsilon = 2.65 \times 10^{-6} Nf, \qquad (35)$$

where N is number density in molecules cm^{-3}, integrated absorption coefficient in m^{-1} and f is oscillator strength of the transition molecule.

REFERENCES

[1] Piepho, S. B. and Schatz, P. N., *Group theory in spectroscopy with applications to magnetic circular dichroism*, (John Wiley and Sons, New York, 1983).

[2] Levine, N., *Molecular Spectroscopy*, (John Wiley and Sons, New York, 1975).

[3] Bauman, R. P., *Absorption spectroscopy*, (John Wiley and Sons, New York, 1962).

[4] Barrow, G. M., *Introduction to molecular spectroscopy*, (Mc Graw-Hill, New York, 1962).

[5] Demtroder, W., *Laser spectroscopy*, (Springer, Berline, Germany, 1995).

[6] Svanberg, S., *Atomic and molecular spectroscopy: Basic aspects and practical applications*, (Springer-verlag, Berlin, Germany, 1991).

[7] Banwell, C. N., *Fundamental of molecular spectroscopy*, (Mc Graw-Hill, New York, 1972).

[8] Michale, J. L., *Molecular spectroscopy*, (Prentice-Hall, Inc., USA, 1999).

[9] Lipty, W., *Angewandte Chemie,* International Edition **8**, 177-187 (1969).

[10] Radwan, R. M., *Electron induced modification in optical properties of polypropylene*, J Phys D: Appl. Phys. **40**, 374-379 (2007).

[11] Thorne, A. P., *Spectrophysics*, (Chapman and Hall Ltd, London, 1988).

[12] Rao, C. N. R., *Ultra-violet and visible spectroscopy chemical applications*, (Butterworth and Co Ltd, England, 1975).

[13] Georgakopoulous, S., Grondelle, R. V., Zwan, G. V. D., *Circular dichroism of carotenoids in bacterial light-harvesting complexes: Experimental modeling* Biophysical Journal **87**, 3010-3022 (2004).

[14] Forsman, E. N., Clark, K. C., *measurement of the oscillator strength of the O(IS-IPO) transition at 1217.6 A* Physical Review A. **7**, 1203-1208 (1973).