

KINETIC EQUATIONS FOR COLLISIONLESS MULTIPHOTON EXCITATION OF LARGE MOLECULES

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Most of the multiphoton absorption steps in a large molecule excited by an intense radiation field may be viewed as transitions between quasicontinuous manifolds of exact molecular levels. It is shown that the assumption that the radiative coupling varies randomly with level indices leads to simple kinetic schemes. Coherent phenomena are absent if the average coupling vanishes, but may persist otherwise.

1. Introduction

The continued interest in multiphoton processes in atomic and molecular systems [1,2] has produced a substantial amount of experimental and theoretical studies into the nature of these phenomena. Of particular interest is the question "when can the Schrödinger equation be reduced to a simple kinetic equation for populations, and when do coherent phenomena persist whereupon the full quantum-mechanical description has to be maintained?" In atoms and in small molecules it has been shown that the Schrödinger equation may be reduced to a classical master equation under conditions which imply a unidirectional flow of energy [3]. In large molecules experimental evidence (ref. [2], section 4; see also ref. [4]) suggests that a classical master equation provides a good description of the collisionless multiphoton excitation process in the continuous and quasicontinuous parts of the molecular vibrational manifold while coherent phenomena underline the excitation within the few discrete bottom levels.

So far, attempts to explain the non-coherent nature of the multiphoton excitation through the upper vibrational spectrum of large molecules have mostly been based on the idea of rapid intramolecular dephasing processes [5]. The non-optically active modes are assumed to provide a thermal bath which acts to dephase the optically active system. This implies that

coherent effects should appear at low temperature where proper dephasing rates vanish. Also, selection rules which single out the optically active modes break down for high vibrational excitation.

A different model [6,7] considers the multiphoton absorption within the dense molecular manifold as transitions between (quasi) continua of exact \ddagger molecular levels, each characterized by a different number of photons. This picture in the rotating wave approximation is displayed in fig. 1. Each level in a given manifold is radiatively coupled to each level in the two neighbouring manifolds. Because of the highly oscillatory nature of high vibrational wavefunctions, such coupling matrix elements vary wildly between

\ddagger By "exact" we mean diagonalised in the anharmonic interaction.

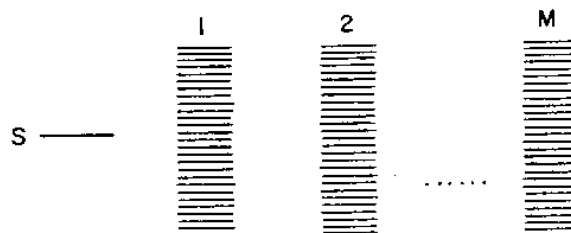


Fig. 1. A schematic representation of multiphoton excitation of a large molecule. Each manifold $L = 1, 2, \dots, M$ represents the molecular levels with a different number ($M-L$) of photons. The few initial discrete levels are represented for simplicity by a single level $|s\rangle$.

different levels. Also, if the bandwidth of the exciting beam is small relative to the width of vibrational absorption resonances (resulting from zero-order selection rules) there will be no systematic variation in the coupling elements over the range of energetically relevant levels. The intercontinua radiative coupling matrix elements may thus be considered as random functions of the level indices. Such random coupling models, most commonly used for disordered solids have also been used in the theories of nuclear spectra [8] and in intramolecular dynamics [6,7,9]. It should be noted that conventional derivations of the Pauli master equations for isolated systems [10] [‡] involve a weak coupling assumption and are not applicable in the present context.

In this communication we solve the random coupling model for multiphoton excitation of large molecules by an infinite order resummation of a perturbation series for the averaged tetradic Green's function. The result is valid in the strong coupling limit and yields a classical master equation when the average coupling vanishes, with coherent contributions when it does not. Corrections are of order $(\tau/h\rho)$ where τ is the experimental time scale and ρ is the density of states in a molecular quasicontinuum.

2. Model

For simplicity we take a single discrete level $|s\rangle$ and assume $P_s(t=0) = 1$ where P_s is the probability of finding the molecule in this level. The following manifolds $L = 1, 2, \dots, M$ (fig. 1) consist of molecular levels with different population numbers for the radiation field. The coupling between $|s\rangle$ and its neighboring manifold, and between each pair of levels belonging to neighboring manifolds is the radiative coupling $S(t)V_{ij}$, where $S(t) \neq 0$ only during the irradiation time. For our purpose it is enough to note that V_{ij} is a random function of i and j . As the simplest possible model we take $V_{ij} = u_{ij} + v_{ij}$ where $u_{ij} = \langle V_{ij} \rangle$ and with v_{ij} a gaussian random variable satisfying $\langle v_{ij} \rangle = 0$ and $\langle v_{ij} v_{i'j'} \rangle = \langle v_{ij}^2 \rangle \delta_{ii'} \delta_{jj'}$. Here $i, i' \in I$; $j, j' \in J$, I and J being two neighboring manifolds. Each manifold J is further characterized by its density of levels ρ_J .

[‡] For a recent application to multiphoton absorption see ref. [11].

The calculation is facilitated by introducing two ideas: (a) It is assumed that the dynamics is determined by the distribution of the random v elements rather than by their specific values. (b) Each level in the manifold J is assigned a width γ_J and we assume $\rho_J \gamma_J \gg 1$. For quasi-continua below the dissociation threshold γ_J is taken to be much smaller than the inverse experimental timescale. For continua above it γ_J is the dissociation rate from the J th energy range.

3. Calculation and results

The method is demonstrated for a single initial level $|s\rangle$ coupled to a manifold $L \equiv \{|l\rangle\}$ which is coupled to $M \equiv \{|m\rangle\}$, and for the purely random case $u_{IJ} = 0$ for all I, J . The objective is to calculate the quantities $\langle \mathcal{G}_{ss,ss}(E) \rangle$, $\sum_l \langle \mathcal{G}_{ll,ss}(E) \rangle$, $\sum_m \langle \mathcal{G}_{mm,ss}(E) \rangle$ where

$$\mathcal{G}_{bb,aa}(E) = (2\pi i)^{-1} \int_{-\infty}^{\infty} d\bar{u} G_{ba}(\bar{u} + i\epsilon) \times G_{ba}^+(\bar{u} - E + i(\epsilon' - \epsilon)), \quad \epsilon, \epsilon' \rightarrow 0, \quad \epsilon' > \epsilon \quad (1)$$

is an element of the tetradic Green's function, G_{ab} being elements of the diadic Green's function. The probability of finding the system in state $|b\rangle$ at time t starting from state $|a\rangle$ at $t = 0$ is given by

$$P_b(t) = (2\pi i)^{-1} \int_{-\infty}^{\infty} dE \exp(-iEt) \langle \mathcal{G}_{bb,aa}(E) \rangle. \quad (2)$$

$\langle \quad \rangle$ denotes an average over the distribution of random v elements. Putting $H = H_0 + v$ where H_0 is the sum of free-molecule and radiation-field hamiltonians we expand each of the diadic Green's functions in the r.h.s. of (1) using Dyson's equation. We introduce the diagram elements shown in fig. 2. A diagrammatic expansion of the product $G_{ba}(u) G_{ba}^+(u-E)$ is obtained by forming all relevant combinations of free propagators and vertices and combining them in pairs of upper and lower branches. The upper branch belongs to $(u - H + \frac{1}{2}i\gamma)^{-1}$ while the lower one results from $(u - E - H - \frac{1}{2}i\gamma)^{-1}$ where γ represents the width associated with the particular propagator. A diagram is calculated as a product of its elements with intermediate propagators summed over their index. Thus the

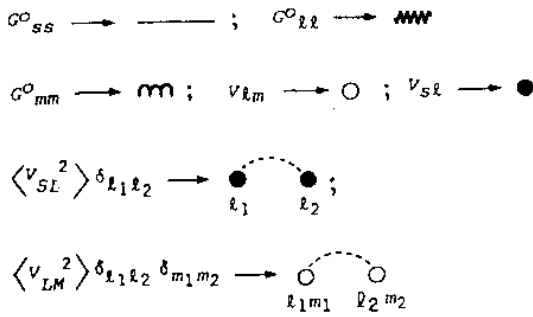


Fig. 2. Notation for diagram components.

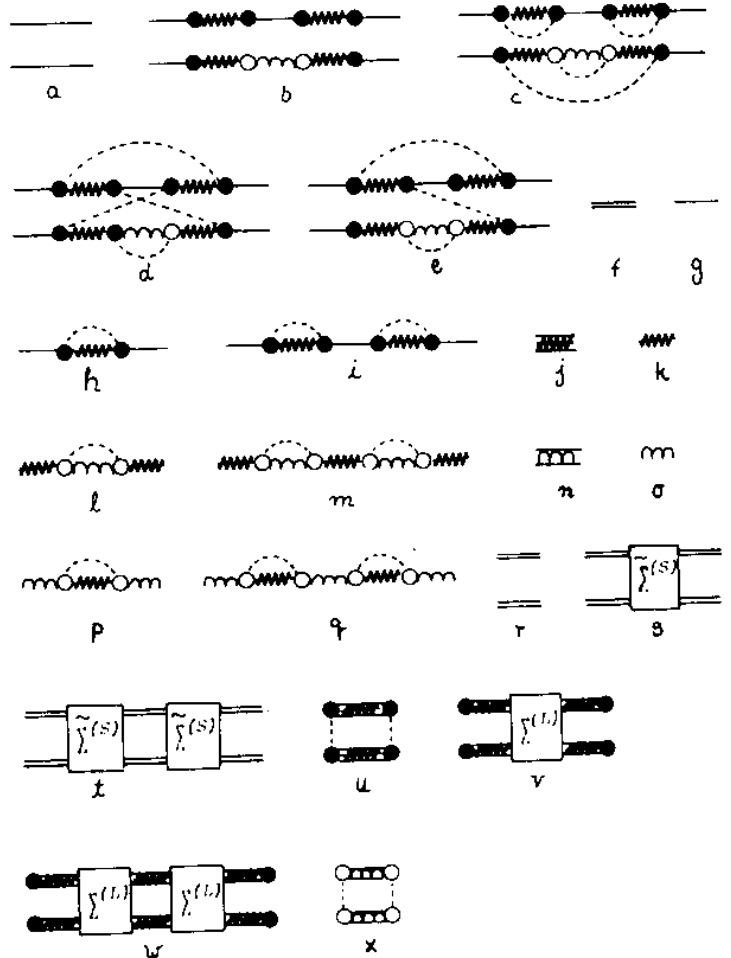


Fig. 3. Diagrams referred to in the text.

diagram in fig. 3a stands for $[(u-E_s + \frac{1}{2}i\gamma)(u-E-E_s - \frac{1}{2}i\gamma)]^{-1}$ while fig. 3b represents the term (belonging to $\mathcal{G}_{ss,ss}(E)$)

$$\sum_{l_1} \sum_{l_2} \sum_{l_3} \sum_{l_4} \sum_m v_{l_1 s}^2 v_{l_2 s}^2 v_{l_3 s} v_{l_4 s} v_{l_3 m} v_{m l_4} \times (u-E_{l_1} + \frac{1}{2}i\gamma_L)^{-1} (u-E_{l_2} + \frac{1}{2}i\gamma_L)^{-1} \times (u-E-E_{l_3} - \frac{1}{2}i\gamma_L)^{-1} (u-E-E_{l_4} - \frac{1}{2}i\gamma_L)^{-1} \times (u-E-E_m - \frac{1}{2}i\gamma_M)^{-1} (u-E_s + \frac{1}{2}i\gamma_s)^{-3} \times (u-E-E_s - \frac{1}{2}i\gamma_s)^{-2}.$$

Next, an average of each diagram is taken by combining pairs of the same kind of vertices by dotted lines in all possible combinations. Thus the diagram (3b) yields a sum of fifteen terms, three of which are represented by figs. 3c, d, e. Studying these diagrams we realize that 3c vanishes and that 3d is of higher power in $(\gamma\rho)^{-1}$ than 3e. Keeping in each order only diagrams of lowest power in $(\gamma\rho)^{-1}$ we follow the usual resummation technique by defining renormalized propagators: The diagrams 3f, 3j and 3n are infinite sums of terms starting from 3g, h, i; 3k, l, m and 3o, p, q respectively. We also encounter self-energy terms: $\Sigma^{(s)}$ is defined as the geometric series starting with the diagrams 3u, v, w where $\Sigma^{(L)}$ is given by the diagram 3x. These summations yield (with small energy shifts disregarded)

$$(3f) = [u-E_s + \frac{1}{2}i(\Gamma_s^L + \gamma_s)]^{-1}, \quad (3)$$

$$(3j) = [u-E_l + \frac{1}{2}i(\Gamma_L^M + \gamma_L)]^{-1}, \quad (4)$$

$$(3n) = [u-E_m + \frac{1}{2}i(\Gamma_M^L + \gamma_M)]^{-1}, \quad (5)$$

where Γ are golden-rule rates

$$\Gamma_s^L = 2\pi \langle v_{sL}^2 \rangle \rho_L, \quad \Gamma_L^M = 2\pi \langle v_{LM}^2 \rangle \rho_M, \quad \Gamma_M^L = 2\pi \langle v_{LM}^2 \rangle \rho_L. \quad (6)$$

Eqs. (3)–(5) are for upper-branch propagators. Lower-branch terms are obtained by replacing u by $u-E$ and taking complex conjugates. Also

$$\Sigma^{(L)} = i\Gamma_L^M \langle v_{LM}^2 \rangle [E + i(\Gamma_M^L + \gamma_M)]^{-1}, \quad (7)$$

$$\Sigma^{(s)} = i\Gamma_s^L \langle v_{sL}^2 \rangle \{E + i(\Gamma_L^M + \gamma_L) + \Gamma_L^M \Gamma_M^L [E + i(\Gamma_M^L + \gamma_M)]^{-1}\}^{-1}. \quad (8)$$

Expressions for the desired average tetrads are obtained in terms of such renormalized propagators and self-energies. For example $\langle G_{ss}(u)G_{ss}^+(u-E) \rangle$ is given by the infinite series starting with diagrams 3r, s, t where $\tilde{\Sigma}^{(s)} = 2[\Sigma^{(s)} - i\Gamma_s^L \langle v_{sL}^2 \rangle (E + i\gamma_L)^{-1}]$. ($\tilde{\Sigma}^{(s)}$ however is of higher order in $(\gamma\rho)^{-1}$ than the free tetradic propagator (3r) and the latter gives the main contribution.) Similar summable series are obtained for $\Sigma_j \langle G_{js}(u)G_{js}^+(u-E) \rangle$ ($j = l, m$). With eq. (1) they yield

$$\langle \mathcal{G}_{ss,ss}(E) \rangle = [E + i(\Gamma_s^L + \gamma_s)]^{-1},$$

$$\sum_l \langle \mathcal{G}_{ll,ss}(E) \rangle = i\Gamma_s^L \{E + i(\Gamma_L^M + \gamma_L) + \Gamma_L^M \Gamma_M^L [E + i(\Gamma_M^L + \gamma_M)]^{-1}\}^{-1} \langle \mathcal{G}_{ss,ss}(E) \rangle$$

and

$$\sum_m \langle \mathcal{G}_{mm,ss}(E) \rangle = i\Gamma_L^M [E + i(\Gamma_M^L + \gamma_M)]^{-1} \sum_l \langle \mathcal{G}_{ll,ss}(E) \rangle,$$

which are the Fourier Laplace transforms (eq. (2)) of the rate equations

$$\dot{P}_s = -\Gamma_s^L P_s,$$

$$\dot{P}_L = \Gamma_s^L P_s + \Gamma_M^L P_M - (\Gamma_L^M + \gamma_L) P_L$$

and

$$\dot{P}_M = \Gamma_L^M P_L - (\Gamma_M^L + \gamma_M) P_M,$$

with $P_s = 1, P_L = P_M = 0$ at $t = 0$.

When the average coupling elements are different from zero each vertex in the former diagrams has to be replaced by two, corresponding to the u and v parts. The expansion and resummation procedure is similar, averaging is performed by connecting v vertices. The final result is identical to the solution of the kinetic equation $\dot{P}(t) = \mathbf{D}P(t)$ where $P \equiv (P_0, P_1, \dots, P_M)$ are the populations of the different manifolds (P_0 corresponds to the initial $|s\rangle$ state) and the kinetic matrix \mathbf{D} is given by $\mathbf{D} = \mathbf{D}_{IC} + \mathbf{D}_C$. The incoherent component \mathbf{D}_{IC} is the tridiagonal matrix

$$(\mathbf{D}_{IC})_{JJ} = -(\Gamma_J^{J-1} + \Gamma_J^{J+1} + \gamma_J), (\mathbf{D}_{IC})_{J,J+1} = \Gamma_{J+1}^J,$$

$$\Gamma_K^L = 2\pi \langle v_{KL}^2 \rangle \rho_L, \Gamma_0^{-1} = \Gamma_{-1}^0 = \Gamma_1^0 = \Gamma_M^{M+1} = \Gamma_{M+1}^M = 0, \quad (9)$$

which corresponds to a classical master equation. γ_J may be disregarded for manifolds below the dissociation limit. The coherent component \mathbf{D}_C is nonzero only when $\langle V \rangle \equiv u \neq 0$ and is given by

$$(\mathbf{D}_C)_{00} = -C_1 (2\pi u_{s1}^2 \rho_1), (\mathbf{D}_C)_{10} = C_1^2 (2\pi u_{s1}^2 \rho_1),$$

$$(\mathbf{D}_C)_{J0} = C_J \left[\prod_{j=1}^{J-1} (1 - C_j) \right] C_1 (2\pi u_{s1}^2 \rho_1), \quad (10)$$

where all other elements vanish and where the coefficients C_j are defined by

$$C_M = 1, \quad C_J = (1 + N_J C_{J+1})^{-1}, \quad J = 1, 2, \dots, M-1, \quad (11)$$

with $N_J = \pi^2 u_{J,J+1}^2 \rho_J \rho_{J+1}$.

4. Conclusions

For vanishing average coupling the time evolution of the intercontinuum random coupling model is incoherent, with consecutive steps and golden-rule rates. $\langle V \rangle \neq 0$ leads to a coherent evolution component characterized by direct transitions from the discrete level to all the coupled manifolds. A purely coherent evolution of this form has been previously obtained [12] for an intercontinuum constant-coupling model.

Analysis of multiphoton excitation of large molecules is usually done with the incoherent rate model for which the present results provide a proper justification. The coherent component is expected to be small because probably $u_{s1}^2 \ll \langle v_{s1}^2 \rangle$ and also $C_1 < 1$. Its contribution should mainly affect the branching ratio for different excitation levels of the molecule (different manifolds L in fig. 1) which was shown to be a strongly oscillating function of L in the constant-coupling model. Experiments aimed to yield such information are therefore highly desirable.

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