ON A RANDOM COUPLING MODEL FOR INTRAMOLECULAR DYNAMICS†

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The time evolution of a system involving separable random coupling between quasi-continuous manifolds is studied. The problem is solved using ensemble averages. In the strong coupling maximum randomness case the continua are found to be effectively uncoupled on the experimentally relevant time scale.

1. Introduction

In the last few years some attention has been given [1–5] to the application of random coupling models (RCM's) in theories of intramolecular processes. Such processes may be described in terms of matrix elements between zero order molecular states which are wildly varying as functions of state energy or state index. In spectral regions of high density of states such coupling may be modeled by some random distribution.

The study of Heller and Rice (HR) [3] is of particular interest as it provides a possible mathematical basis for the treatment of time evolution in systems of several interacting continua (fig. 1). However, these authors have restricted themselves to a case characterized by a low density of states in the intermediate quasicontinua (the manifold $\{|l\rangle\}$, fig. 1). As discussed below this raises some questions regarding the implications of their results.

It should be mentioned that solutions of time evolution problems involving several interacting quasicontinua in the constant coupling model (CCM) exists in the literature for some time [6–8]. The CCM solution is characterized by a simultaneous (nonsequential) branching behavior, where all continua coupled to the initial discrete level are populated simultaneously. This behavior results from the quantum-mechanical interference between the mutually coupled continua and may disappear in the RCM [3].

In the present note we study the HR model without restricting ourselves to low density of states in the intermediate quasicontinuum. We limit ourselves to the two continua model (fig. 1) in order to establish a working approximation scheme that may later be generalized to the multicontinuum case (relevant for the multiphoton excitation

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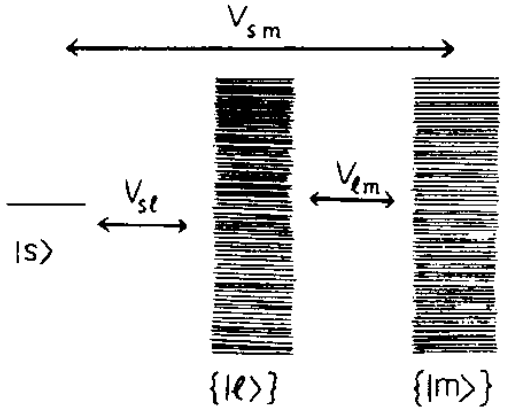

Fig. 1. Energy level scheme for the model studied. The initial level $|s\rangle$ is coupled to the continua (or quasicontinua) $\{|l\rangle\}$ and $\{|m\rangle\}$ (also denoted L and M in the text). In the constant coupling model (CCM) V_{sl}, V_{ml} and V_{sm} are taken to be independent of the level indices l and m. In the random coupling model (RCM) they are taken as random functions of these indices.

problem [5]). We also limit ourselves to the HR coupling model (to be described below). Our final results, given by eqs. (23), (25)–(32) look very different than those obtained by Heller and Rice [eqs. (4)–(9)]; however, both solutions coincide in the (relatively uninteresting) case where their ranges of validity coincide. The physical significance of these results is discussed in the last section of this note.

2. The Heller–Rice (HR) model

The HR model [3] is essentially described by fig. 1, provided V_{sm} is set equal to zero. V_{sl} and V_{lm} are taken to be random functions of the indices l and m and their averages are assumed to be zero††. Two additional assumptions characterize this model:

(a) The coupling V_{lm} is assumed to take the separable form

$$V_{lm} = V_l V_m \,, \tag{1}$$

so that the theory is characterized by three random functions V_{sl}, V_l (of the index l) and V_m (of the index m), with $\langle V_{sl}\rangle = \langle V_l\rangle = \langle V_m\rangle = 0$††.

(b) The intermediate manifold $\{|l\rangle\}$ is sparse so that the spacings ΔE_l of levels $|l\rangle$ greatly exceed their width. However, it is assumed to be much smaller than the width of the level $|s\rangle$

$$\hbar\Gamma_s \equiv 2\pi\langle V_{sl}^2\rangle\rho_L \gg \langle\Delta E_l\rangle \gg \hbar\langle\Gamma_l^M\rangle = 2\pi\langle V_{lm}^2\rangle\rho_M = 2\pi\langle V_l^2\rangle\langle V_m^2\rangle\rho_M \,, \tag{2}$$

where ρ_j, the density of states in $\{|j\rangle\}$ is assumed to be a smooth function of the energy E_j. Maximum randomness is also assumed and this assumption is used essentially in the following way: If a_j is any of the random functions involved then

$$\Big(\sum_j a_j\Big)^2 = \sum_j\sum_{j'} a_j a_{j'} = \sum_j a_j^2 = \int \mathrm{d}E_j\,\rho(E_j)\langle a_j^2\rangle \,. \tag{3}$$

With these assumptions Heller and Rice obtain the following kinetic equations for the time evolution of the population of the state s and the continua $\{l\}$ and $\{m\}$

$$\dot{P}_s = -\Gamma_s P_s, \quad \dot{P}_L = \Gamma_s P_s - \langle\Gamma_l^M\rangle P_L, \quad \dot{P}_M = \langle\Gamma_l^M\rangle P_L \,, \tag{4}$$

where $P_L = \Sigma_l P_l$ and $P_M = \Sigma_m P_m$, P_l and P_m being the probabilities for states l and m, and where $\langle\Gamma_l^M\rangle$ is an average Γ_l^M taken over the manifold $\{|l\rangle\}$. Identical results were obtained before for the model employed by Nitzan, Jortner and Rentzepis (NJR) [10] in which each of the levels $|l\rangle$ is coupled to its own continuum. This feature of the NJR model implies that the levels $|l\rangle$ evolve essentially independently of each other and the similar HR results was interpreted as a washout of interference effects due to the random coupling. This conclusion stands in accord with the recent results of Druger [4]. The HR results however are restricted by the model assumption stated by eq. (2) which limit their usefulness:

(a) The assumption (2), if made within the CCM would imply an upper time limit on the validity of the results. This is the Bixon–Jortner condition [11]

$$t < \hbar/\langle\Delta E_l\rangle \,. \tag{5}$$

Eq. (2) then implies that this time is long relative to the lifetime $1/\Gamma_s$ of the state $|s\rangle$ but short relative to the time-scale $1/\langle\Gamma_l^M\rangle$ which characterizes the transition between the $\{|l\rangle\}$ and $\{|m\rangle\}$ continua. In the time range defined by (5), eqs. (4) yield (using also $\Gamma_s \gg \langle\Gamma_l^M\rangle$)

$$P_L(t) = 1 - \exp(-\Gamma_s t), \quad P_M(t) = 0 \,. \tag{6}$$

†† When $V_{sm} = 0$ the nature of V_m does not affect the solution. In the HR model V_m was taken constant [9].

In the RCM the restriction on time may be weaker than that given by eq. (5) [2]. However on the time scale of order $1/\Gamma_l$ recurrences may occur and the validity of the results (4) on such time scale is not clear.

(b) Assuming the solution (4) to be valid for $t > \hbar/\langle \Delta E_l \rangle$, the condition $\langle \Delta E_l \rangle \gg \langle \Gamma_l^M \rangle$ implies that in some sense (in the long time limit), each level $|l\rangle$ is coupled to its own piece of the $\{|m\rangle\}$ continuum. This makes the HR model (for $t > \hbar/\langle \Delta E_l \rangle$) similar to the NJR model. The HR results cannot therefore be taken as an implication of the RCM alone, and cannot be contrasted with the simultaneous decay results [6–8] obtained in the CCM without invoking any assumption similar to (2).

(c) For the application of the RCM in the theory of multiphoton excitation of large molecules [5] condition (2) is too restrictive and may be unphysical.

In view of these observations it becomes worthwhile to reopen the question and to consider multicontinua decay models within the RCM with $\langle \Gamma_l^M \rangle$ allowed to be equal to or to exceed the mean level spacing $\langle \Delta E_l \rangle$. An approach to this problem is described next.

3. The ensemble average method

Here we investigate the time evolution of a system whose level and coupling structure are displayed in fig. 1. We adopt the HR model without the assumption (2). Thus we take $V_{lm} = V_l V_m$ and take V_{sm}, V_{sl}, V_l and V_m to be random functions of the parameters l and m. Unlike Heller and Rice we do not require maximum randomness and we investigate the effects of short range correlations in the random coupling functions.

The main idea behind the present calculation is the introduction of *ensemble averages*. We consider a set of identical molecules, each characterized by the same random distribution of coupling parameters, and we take averages of the calculated observables over this ensemble. We make the "ergodic" assumption that averages like in eq. (3) may be equally taken over the ensemble.

We define our ensemble by choosing (for a_j being a random function of the index j)

$$\langle a_j \rangle = 0 \tag{7}$$

and

$$\langle a_j a_{j'} \rangle = \langle a_j^2 \rangle \mathcal{C}_J / [(E_j - E_{j'})^2 + \mathcal{C}_J^2] \ , \tag{8}$$

where $\langle\ \rangle$ denotes an ensemble average, E_j is the energy of the state j and $\mathcal{C}_J$ is a correlation length. While eq. (7) reflects the observation that the relevant random functions V_{sl}, V_{sm}, V_m, V_l can take equally likely positive and negative values, eq. (8) constitutes a rather specific choice of model, suggested by the ease of evaluating lorentzian integrals. We do not expect that the gross features of the solution obtained below will be affected by the particular choice of the correlation form. Eq. (8) offers the advantage of ability to consider the almost constant coupling case (large $\mathcal{C}_J$) as well as large randomness (small $\mathcal{C}_J$) and intermediate cases. However, the ensemble average method makes physical sense in the present context only for large randomness. It should be realized that when we convert sums Σ_j to integrals $\int \mathrm{d}E_j \rho(E_j)$, $\mathcal{C}_J$ has a lower bound of order $[\rho(E_j)]^{-1}$. This reflects the fact that as the quasi-continuum is smeared to give an approximate continuum, the correlation length cannot be less than the distance between adjacent levels. Mathematically this is seen starting from (for maximum randomness)

$$\langle a_j a_{j'} \rangle = \langle a_j^2 \rangle \delta_{jj'} \tag{9}$$

and summing over all j'

$$\sum_{j'} \langle a_j a_{j'} \rangle = \langle a_j^2 \rangle = \langle a_j^2 \rangle \sum_{j'} \frac{\mathcal{C}_J^2}{(E_j - E_{j'})^2 + \mathcal{C}_J^2} = \langle a_j^2 \rangle \rho(E_j)\, \mathcal{C}_J^2 \int \mathrm{d}E_{j'} \frac{1}{(E_j - E_{j'})^2 + \mathcal{C}_J^2} = \pi \rho_J \mathcal{C}_J \langle a_j^2 \rangle \ .$$

Therefore the minimum value for $\mathcal{E}_J$ is

$$\mathcal{E}_J^{\min} = (\pi\rho_J)^{-1} \,. \tag{10}$$

In addition we shall, for simplicity, disregard levels shifts and repeatedly make the approximation

$$\lim_{\eta\to 0} \sum_j \frac{a_j^2}{E - E_j + \mathrm{i}\eta} \approx -\pi\mathrm{i}\rho_J \langle a_j^2 \rangle \,, \tag{11}$$

when summing over the $\{l\}$ or $\{m\}$ continua.

Eqs. (1), (7), (8) and (11) are the basic assumptions of our model. The assumption (1) enables us to obtain simple explicit forms for the relevant elements of the Green's function [3,7]. Using also (11) we obtain

$$G_{ss} = (E - E_s + \tfrac{1}{2}\,\mathrm{i}\Gamma_s)^{-1} \,, \tag{12}$$

where

$$\Gamma_s = -\pi\mathrm{i}\rho_l \langle V_{sl}^2 \rangle \left(1 - \frac{N}{1+N}\, Q_L\right) - \pi\mathrm{i}\rho_M \langle V_{sm}^2 \rangle \left(1 - \frac{N}{1+N}\, Q_M\right) + \frac{2}{1+N}\, Q_{LM} \,, \tag{13}$$

$$N = \pi^2 \rho_L \rho_M \langle V_m^2 \rangle \langle V_l^2 \rangle = \pi^2 \rho_L \rho_M \langle V_{lm}^2 \rangle \tag{14}$$

is the intercontinuum coupling parameter, and where Q_L, Q_M and Q_{ML} are functions which take simple values in the extreme limits

$$Q_M = Q_L = -\frac{Q_{ML}}{\pi^2 \rho_M \rho_L V_{lm} V_{ls} V_{ms}} \begin{array}{l} \approx 0 \text{ (maximum randomness);} \\ = 1 \text{ (CCM).} \end{array} \tag{15}$$

Also

$$G_{ls} = \left\{ \frac{V_{ls}}{E - E_l + \mathrm{i}\eta} + \frac{1}{1+N} \frac{V_l}{E - E_l + \mathrm{i}\eta} \left[\sum_m \frac{V_m V_{ms}}{E - E_m + \mathrm{i}\eta} - \pi\mathrm{i}\rho_M \langle V_m^2 \rangle \sum_{l'} \frac{V_{l'} V_{l's}}{E - E_{l'} + \mathrm{i}\eta} \right] \right\} G_{ss} \,, \tag{16}$$

$$G_{ms} = \left\{ \frac{V_{ms}}{E - E_m + \mathrm{i}\eta} + \frac{1}{1+N} \frac{V_m}{E - E_m + \mathrm{i}\eta} \left[\sum_l \frac{V_l V_{ls}}{E - E_l + \mathrm{i}\eta} - \pi\mathrm{i}\rho_L \langle V_l^2 \rangle \sum_{m'} \frac{V_{m'} V_{m's}}{E - E_{m'} + \mathrm{i}\eta} \right] \right\} G_{ss} \,. \tag{17}$$

The populations of the level $|s\rangle$ and the continua $\{|l\rangle\}$ and $\{|m\rangle\}$ are obtained from

$$P_s(t) \exp(-\Gamma_s t) \,, \tag{18}$$

$$P_J(t) = \sum_j |c_{js}(t)|^2 = \sum_j \langle |c_{js}(t)|^2 \rangle$$

$$= \frac{1}{4\pi^2} \int \mathrm{d}E\, \mathrm{e}^{-\mathrm{i}Et} \int \mathrm{d}u \sum_j \langle G_{js}(E + u + \mathrm{i}\eta) G_{js}^*(u + \mathrm{i}\eta) \rangle \qquad (j = m,l;\, J = M,L). \tag{19}$$

Inserting eqs. (16) or (17) into (19) and using eq. (8) we obtain after some algebra†

† Eq. (8) is used with random $a_l = V_l V_{ls}$ or $b_m = V_m V_{ms}$. When $V_{ms} \neq 0$ we encounter also terms of the form $\langle a_l b_m \rangle$ which are taken to be zero. This makes it impossible to take the constant coupling limit in this case. The asymmetric case ($V_{ms} = 0$) is not so restricted.

$$P_L(t) = \frac{\Gamma_s^L}{\Gamma_s}\left\{[1 - \exp(-\Gamma_s t)] - \frac{2N}{(1+N)^2}\left[1 + \frac{\mathcal{E}_L}{\Gamma_s - \mathcal{E}_L}\exp(-\Gamma_s t) - \frac{\Gamma_s}{\Gamma_s - \mathcal{E}_L}\exp(-\mathcal{E}_L t)\right]\right\}$$

$$+ \frac{2N}{(1+N)^2}\frac{\Gamma_s^M}{\Gamma_s}\left[1 + \frac{\mathcal{E}_M}{\Gamma_s - \mathcal{E}_M}\exp(-\Gamma_s t) - \frac{\Gamma_s}{\Gamma_s - \mathcal{E}_M}\exp(-\mathcal{E}_M t)\right], \tag{20}$$

$$P_M(t) = \frac{\Gamma_s^L}{\Gamma_s}\left\{[1 - \exp(-\Gamma_s t)] - \frac{2N}{(1+N)^2}\left[1 + \frac{\mathcal{E}_M}{\Gamma_s - \mathcal{E}_M}\exp(-\Gamma_s t) - \frac{\Gamma_s}{\Gamma_s - \mathcal{E}_M}\exp(-\mathcal{E}_M t)\right]\right\}$$

$$+ \frac{2N}{(1+N)^2}\frac{\Gamma_s^M}{\Gamma_s}\left[1 + \frac{\mathcal{E}_L}{\Gamma_s - \mathcal{E}_L}\exp(-\Gamma_s t) - \frac{\Gamma_s}{\Gamma_s - \mathcal{E}_L}\exp(-\mathcal{E}_L t)\right]. \tag{21}$$

Here $\Gamma_s^L = 2\pi\langle V_{sl}^2\rangle\rho_L$, $\Gamma_s^M = 2\pi\langle V_{sm}^2\rangle\rho_M$ and for large randomness $\Gamma_s \approx \Gamma_s^L + \Gamma_s^M$.

In the asymmetric model with $V_{sm} = 0$ (considered by Heller and Rice), eqs. (20) and (21) lead to

$$P_L(t) = [1 - \exp(-\Gamma_s t)] - \frac{2N}{(1+N)^2}\left[1 - \frac{\Gamma_s\exp(-\mathcal{E}_L t) - \mathcal{E}_s\exp(-\Gamma_s t)}{\Gamma_s - \mathcal{E}_L}\right], \tag{22}$$

$$P_M(t) = \frac{2N}{(1+N)^2}\left[1 - \frac{\Gamma_s\exp(-\mathcal{E}_L t) - \mathcal{E}_L\exp(-\Gamma_s t)}{\Gamma_s - \mathcal{E}_L}\right]. \tag{23}$$

Here we used again the large randomness limit $\Gamma_s \approx \Gamma_s^L$. Eqs. (18), (22) and (23) are solutions of the following kinetic equations.

$$\dot{P}_s = -\Gamma_s P_s\,, \tag{24}$$

$$\dot{P}_L = \Gamma_s P_s - k_{L\to M}P_L + k_{M\to L}P_M\,, \tag{25}$$

$$\dot{P}_M = k_{L\to M}P_L - k_{M\to L}P_M\,, \tag{26}$$

where

$$k_{L\to M} = \mathcal{E}_L\,2N/(1+N)^2\,, \quad k_{M\to L} = \mathcal{E}_L(1+N^2)/(1+N)^2\,, \tag{27}$$

which should be compared to the results of the HR model, eq. (4).

4. Discussion and conclusions

Eqs. (18)–(27) provide the solution to the two continua decay model with random coupling coefficients. The following points concerning this solution should be pointed out

(a) The solution conserves unitarity: $P_s + P_L + P_M = 1$ at all times.

(b) Strong randomness (small $\mathcal{E}$) was assumed in taking $\Gamma_s \approx \Gamma_s^L + \Gamma_s^M$ and (for the symmetric case) in taking $\langle V_{sl}V_{sm}\rangle = \langle V_{sl}V_{lm}\rangle = \langle V_{sm}V_{lm}\rangle = 0$.

(c) The asymmetric model ($V_{sm} = 0$) yields a simple kinetic scheme, eqs. (24)–(27) which unlike the HR result, contains bidirectional transition rates between the continua L and M.

(d) Consider now the different limits for the intercontinuum coupling strength N in the maximum randomness case. In the weak coupling limit $N \ll 1$ which is typical of the coupling between radiative and dissociative continua [12], eq. (27) yields $k_{l\to M} = \langle \Gamma_l^M \rangle$ and $k_{M\to L} = \mathcal{C}_L = (\pi\rho_L)^{-1}$. It should be noted that in this limit

$$N \ll 1 \to \langle \Gamma_l^M \rangle \ll \rho_L^{-1} = \pi \mathcal{C}_L \ . \tag{28}$$

This corresponds to the HR model. Our solution in this limit thus yields $k_{M\to L} \gg k_{L\to M}$, in apparent contradiction of the HR result, eq. (4). This discrepancy is resolved by realizing that our solution was obtained by converting sums over the L manifold (as well as over the M manifold) to integrals and is thus limited to times $t \ll \hbar\rho_L$. On this time scale the $L \leftrightarrow M$ transition does not occur and our solution is identical to the HR solution (see also comment (f) below). For longer times our solution is not valid; the different l levels evolve essentially independently of each other and the NJR or the HR result, eq. (4) should be used.

In the strong coupling limit (realised in later stages of multiphoton excitation of large molecules) $N \gg 1$ implies $\langle \Gamma_l \rangle \gg \rho_L^{-1} = \pi \mathcal{C}_L$. The validity of the results (18), (20)–(27) is still restricted to times shorter than $\hbar\rho_L$ (and $\hbar\rho_M$), however this may now cover all experimentally relevant times. Eq. (27) again implies that the $L \rightleftharpoons M$ transition does not take place on the relevant time scale. In other words, even for strong coupling under maximum randomness, the decay $S \to L$ takes place as if the continua M and L were uncoupled from each other.

(e) Another way to elucidate the nature of the solution is to consider in eqs. (20)–(27) the relevant time scale for which $\mathcal{C}_L t, \mathcal{C}_M t \ll 1$. On this time scale eqs. (20) and (21) yield

$$P_J(t) \approx (\Gamma_s^J/\Gamma_s)\ [1 - \exp(-\Gamma_s t)], \quad J = L, M \ , \tag{29}$$

with similar results (with $\Gamma_s^M = 0$) corresponding to eqs. (22) and (23). Again we see that the continua L and M are effectively uncoupled on the relevant time scale.

(f) Another case of interest is one where the levels $\{|l\rangle\}$ and/or $\{|m\rangle\}$ have additional widths due to decay to other channels (e.g. spontaneous IR emission or collision induced transitions). In this case the same treatment yields

$$P_L(t) = \frac{\Gamma_s}{\Gamma_s - \gamma_L}\left\{\exp(-\gamma_L t) - \exp(-\Gamma_s t) - \frac{2N}{(1+N)^2}\left[\exp(-\gamma_L t) - \frac{(\Gamma_s - \gamma_L)\exp[-(\gamma_L + \mathcal{C}_L)t] - \mathcal{C}_L \exp(-\Gamma_s t)}{\Gamma_s - \gamma_L - \mathcal{C}_L}\right]\right\} , \tag{30}$$

$$P_M(t) = \frac{2N}{(1+N)^2}\ \frac{\Gamma_s}{\Gamma_s - \gamma_M}\left[\exp(-\gamma_M t) - \frac{(\Gamma_s - \gamma_M)\exp[-(\gamma_M + \mathcal{C}_L)t] - \mathcal{C}_L \exp(-\Gamma_s t)}{\Gamma_s - \gamma_M - \mathcal{C}_L}\right], \tag{31}$$

where γ_M and γ_L are the (assumed constant over the manifolds) decay widths of levels in the manifolds M and L. When $\gamma_J \gtrsim \rho_J^{-1}$ $(J = L, M)$ these results are valid at all times; γ_L^{-1} and γ_M^{-1} set the relevant time scales, on which our former conclusions remain unchanged.

(g) The discussion in points (e) and (f) refers to the maximum randomness limit. It is interesting to note that a larger correlation $\mathcal{C}$ implies an effective non-zero $L \leftrightarrow M$ coupling.

The implications of these results to the molecular dissociation problem, when such process occurs via an intermediate intramolecular quasicontinuum, is that the initial intramolecular relaxation and the subsequent molecular dissociation are uncoupled from each other. This conclusion fits well the results obtained by Houston and Moore on the photodissociation of formaldehyde [13]. Regarding the multiphoton excitation process in large molecules we must conclude that the model, at least in the maximum randomness limit cannot be useful for this problem. This probably results from the unphysical assumption (1). It is also possible that correlations in the random coupling play an essential role. These interesting questions are currently under study.

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