Quantum Dynamics Experienced by a Single Molecular Eigenstate Excited by Incoherent Light

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Contrary to conventional wisdom that all dynamics are a result of interference (or "dephasing") between many (at least two) energy eigenstates, we show that when a continuum of states is present, even a single molecular eigenstate undergoes "steady-state" quantum dynamics. Moreover, this type of dynamics can be initiated by incoherent (e.g., solar) light sources. Continua are invariably involved in molecular systems due to a variety of sources such as the ever present bath modes, spontaneously emitted photons; the detachment of electrons, or the dissociation of chemical bonds. Contrary to a single bound energy eigenfunction which is a real ("standing-waves") function that carries no flux and, hence, has no dynamics, a single (complex) continuum energy eigenfunction carries "steady-state" flux given by the group velocity of the energetically narrow wave packet it represents. When this energy eigenfunction is a multimode resonance embedded in a continuum via a chain of intramolecular couplings, this dynamics may be initiated by any (light) source, and is controlled, contrary to coherent wave packet dynamics, by the position of the resonance rather than its width.

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Introduction.—There is now growing evidence [1,2] that the coherent wave packet dynamics induced by ultrashort coherent pulses is quite different from the dynamics induced by incoherent sources, which in the long time limit results in the excitation of a multitude of phase-unrelated molecular eigenstate(s) (ME) [1–3]. Therefore, experiments using ultrafast coherent pulses that excite coherent wave packets and display long-lived electronic coherences [4–9], do not really tell us what happens when naturally occurring biological systems are excited by incoherent light, such as solar radiation.

Given this point of view, the origin and nature of the dynamics observed when incoherent sources, such as solar radiation, excite ME, become a bit of a mystery. This is because a single ME is expected to have no dynamics. Yet, quite clearly dynamical processes do occur under conditions of incoherent excitation of isolated ME, e.g., photosynthesis.

In this paper we show that the quantum dynamics of a single ME can be naturally explained when the ME is "dressed" by a continuum of states. Such a continuum may be due, for example, to the ever-present environment [10,11], or to the spontaneous emission of a photon [12] (or electron [13]) following the excitation, or to the breakage of a chemical bond [13–15], or to a combination of all of the above. Contrary to a bound-ME, which is a real (standing-waves) function and carries no flux and, hence, has no dynamics, a continuum-ME may be a complex function which carries ("steady-state") flux [16]. We show that resonances which arise when bound states are coupled to such flux carrying continua of states also carry flux and, therefore, exhibit dynamics under the action of incoherent light sources.

A brief review of scattering resonances theory.—We consider $|E, n^-\rangle$ the individual continuum energy eigenstates whose accumulation forms a *scattering resonance*. Each such state is a solution of the time independent Schrödinger equation

$$[E - i\epsilon - H]|E, n^-\rangle = 0, \tag{1}$$

where the $-i\epsilon$ serves to remind us of the incoming boundary conditions,

$$\lim_{t\to\infty} e^{-i(E-i\epsilon)t/\hbar}|E, n^-\rangle = N_n e^{-i(E-i\epsilon)t/\hbar} e^{i\mathbf{k}_n\cdot\mathbf{r}}, \tag{2}$$

where n denotes the internal states of the collision fragments—the "channel" index, and $\mathbf{k}_n$—the momentum in that channel.

We solve the problem using the "partitioning technique" [17–21], which is a general method for constructing the solutions of an interaction-containing Schrödinger equation from its (assumed known) noninteracting parts, represented by two orthogonal projection operators Q and P, which span the entire space $P + Q = I$, where I is the identity operator.

Multiplying Eq. (1) once by P and once by Q, we obtain

$$\begin{aligned}[E - i\epsilon - PHP]P|E, n^-\rangle &= PHQ|E, n^-\rangle,\\ [E - i\epsilon - QHQ]Q|E, n^-\rangle &= QHP|E, n^-\rangle.\end{aligned} \tag{3}$$

We now define P and Q as

$$P = \sum_n \int dE|E, n^-; 1\rangle\langle E, n^-; 1|, \quad Q = \sum_s |\phi_s\rangle\langle\phi_s|, \tag{4}$$

where $|E, n^-; 1\rangle$ are continuum states and $|\phi_s\rangle$ are bound states which solve the decoupled parts of the above equations,

$$[E - i\epsilon - PHP]|E, n^-; 1\rangle = [E_s - QHQ]|\phi_s\rangle = 0. \quad (5)$$

We first solve for $P|E, n^-\rangle$ as the sum of the homogeneous solution ($|E, n^-; 1\rangle$) and a particular solution of Eq. (3) obtained by inverting $[E - i\epsilon - PHP]$,

$$P|E, n^-\rangle = P|E, n^-; 1\rangle + [E - i\epsilon - PHP]^{-1} PHQ|E, n^-\rangle. \quad (6)$$

Substituting this solution into Eq. (3) and reordering terms, we obtain that

$$[E - i\epsilon - Q\mathcal{H}Q]Q|E, n^-\rangle = QHP|E, n^-; 1\rangle, \quad (7)$$

where $Q\mathcal{H}Q \equiv QHQ + QHP[E - i\epsilon - PHP]^{-1}PHQ$.

We obtain from Eq. (7) that

$$Q|E, n^-\rangle = [E - i\epsilon - Q\mathcal{H}Q]^{-1} QHP|E, n^-; 1\rangle. \quad (8)$$

Once $Q|E, n^-\rangle$ is known, $P|E, n^-\rangle$ can be computed from Eq. (6). We have thus managed to construct the solution of the full Schrödinger equation from the decoupled solutions. This, contrary to the Lippmann Schwinger formal solutions [22], is a it practical solution. To make this aspect even more obvious, we now present an explicit representation of $Q\mathcal{H}Q$ using the well-known identity

$$[E - i\epsilon - PHP]^{-1} = \mathsf{P}_v[E - PHP]^{-1} + i\pi\delta(E - PHP), \quad (9)$$

with P_v denoting Cauchy's *Principal Value* integration. With the aid of the above, $\mathsf{P}_v[E - PHP]^{-1}$ is given, using the spectral resolution of an operator, as

$$\mathsf{P}_v[E - PHP]^{-1} \equiv \sum_n \mathsf{P}_v \int \frac{dE'}{E - E'} |E', n^-; 1\rangle\langle E', n^-; 1|. \quad (10)$$

Assuming for simplicity that we are dealing with an isolated resonance for which $Q\mathcal{H}Q$ is a single matrix element, we can write $[E - i\epsilon - Q\mathcal{H}Q]$ as

$$\langle\phi_s|[E - i\epsilon - Q\mathcal{H}Q]|\phi_s\rangle = [E - E_s - \Delta_s(E) - i\Gamma_s(E)/2], \quad (11)$$

where $\Gamma_s(E) \equiv \sum_n 2\pi|V(s|E, n)|^2$,

$$\Delta_s(E) \equiv \mathsf{P}_v \sum_n \int dE' |V(s|E', n)|^2/(E - E')$$

with $V(s|E, n) \equiv \langle\phi_s|H|E, n^-; 1\rangle$.

It follows that the $A(s|E, n) \equiv \langle\phi_s|E, n^-\rangle$ bound states expansion coefficients are given as

$$A(s|E, n) = \frac{V(s|E, n)}{E - E_s - \Delta_s(E) - i\Gamma_s(E)/2}, \quad (12)$$

giving rise to the typical "resonance" line shape. Using Eqs. (6) and (9) we obtain an expression for the continuum expansion coefficients,

$$\langle E, m^-; 1|E', n^-\rangle = \delta(E - E')\delta_{n,m} + V(E, m|s)\left[\mathsf{P}_v \frac{1}{E - E'} + i\pi\delta(E - E')\right] \times \langle\phi_s|E', n^-\rangle.$$

Hence,

$$P|E, m^-\rangle = \sum_n \Big\{ |E, n^-; 1\rangle B_{m,n}(E) + \mathsf{P}_v \int dE' |E', n^-; 1\rangle C_{m,n}(E, E') \Big\},$$

where

$$B_{m,n}(E) \equiv \delta_{n,m} + i\pi V(E, m|s)A(s|E, n)$$
$$C_{m,n}(E, E') \equiv V(E, m|s)A(s|E', n)/(E - E'). \quad (13)$$

The single mode flux associated with a set of bound states coupled to a set of continua.—We assume for simplicity that the decoupled continuum states $\langle\mathbf{r}|E, n^-; 1\rangle$, are given as energy normalized $\langle E, n^-; 1|E', n^-; 1\rangle = \delta(E - E')$, plane waves,

$$\langle\mathbf{r}|E, n^-; 1\rangle = N_n e^{i\mathbf{k}_n\cdot\mathbf{r}}, \quad \text{where } N_n = \{\mu/(2\pi k_n)\}^{1/2}, \quad (14)$$

with μ being the reduced mass of the continuum mode. With this normalization the magnitude of the flux density per unit energy of $\langle\mathbf{r}|E, n^-; 1\rangle$ is given as $\mathcal{F}[E, n; 1] = \frac{1}{2\pi}$. The fully interacting continuum wave functions are now given as

$$\langle\mathbf{r}|E, m^-\rangle = \langle\mathbf{r}|\phi_s\rangle A(s|E, n) + \Big\{ N_n \exp(i\mathbf{k}_n\cdot\mathbf{r}) B_{m,n}(E) + \mathsf{P}_v \int dE' N_n \exp(i\mathbf{k}_n\cdot\mathbf{r}) C_{m,n}(E, E') \Big\}.$$

The flux associated with these functions is given as

$$\frac{\mathcal{I}m}{\mu}\langle E, m^-|\mathbf{r}\rangle \frac{d}{d\mathbf{r}}\langle\mathbf{r}|E, m^-\rangle = \frac{\mathcal{I}m}{\mu}[\langle\phi_s|\mathbf{r}\rangle A^*(s|E, m) + \sum_n N_n e^{-i\mathbf{k}_n\cdot\mathbf{r}} B^*_{m,n}(E) + \mathsf{P}_v \int dE' N'_n e^{-i\mathbf{k}'_n\cdot\mathbf{r}} C^*_{m,n}(E, E')] \times \left[\frac{d\langle\mathbf{r}|\phi_s\rangle}{d\mathbf{r}} A(s|E, m) + i\sum_{n'} N_{n'}\mathbf{k}_{n'} e^{i\mathbf{k}_{n'}\cdot\mathbf{r}} B_{m,n'}(E) + \mathsf{P}_v \int dE' N'_{n'}\mathbf{k}'_{n'} e^{i\mathbf{k}'_{n'}\cdot\mathbf{r}} C_{m,n'}(E, E')\right]. \quad (15)$$

When we execute the multiplication in Eq. (15) we obtain four terms: the first (Bound-Bound) term is zero,

$$\mathcal{F}_{B-B} = \frac{Im}{\mu}|A(s|E,m)|^2\langle\phi_s|\mathbf{r}\rangle\frac{d}{d\mathbf{r}}\langle\mathbf{r}|\phi_s\rangle = 0,$$

because it is associated with a real term. It is the second and third Bound-Continuum interference terms, given as

$$\mathcal{F}_{B-C} = \frac{Im}{\mu}i\langle\phi_s|\mathbf{r}\rangle A^*(s|E,m)\left\{\sum_n N_n\mathbf{k}_n, e^{i\mathbf{k_n}\cdot\mathbf{r}}B_{m,n}(E) + \mathsf{P}_v\int dE' N'_n\mathbf{k}'_n e^{i\mathbf{k}'_n\cdot\mathbf{r}}C_{m,n}(E,E')\right\},$$

that contain the flux imparted to the bound states due to their interaction with the continuum. However, because $\langle\mathbf{r}|\phi_s\rangle\overset{r\to\infty}{\longrightarrow}0$, $\mathcal{F}_{B-C}$ does not contribute to the asymptotic (e.g., bond-breaking) flux.

It is the fourth term,

$$\mathcal{F}_{C-C} = \frac{Im}{\mu}i\sum_{n,n'}\left[N_n e^{-i\mathbf{k_n}\cdot\mathbf{r}}B^*_{m,n}(E) + \mathsf{P}_v\int dE' N'_n, e^{-i\mathbf{k}'_n\cdot\mathbf{r}}C^*_{m,n}(E,E')\right]$$
$$\times\left[N_{n'}\mathbf{k}_{n'}\cdot e^{i\mathbf{k}_{n'}\cdot\mathbf{r}}B_{m,n'}(E) + \mathsf{P}_v\int dE' N'_{n'}\mathbf{k}'_{n'}e^{i\mathbf{k}'_{n'}\cdot\mathbf{r}}C_{m,n'}(E,E')\right], \quad (16)$$

that directly tells us the flux associated with the dissociation, or exchange, or isomerization, to form the final photo-products.

Equation (16) has a very simple interpretation: taking into account the form of N_n [Eq. (14)] we see that the asymptotic flux is essentially the $\frac{1}{2\pi}$ classical flux associated with the energy normalized densities of Eq. (14), modulated by the probability of the bound states transiting to the continuum, as embodied in the $B_{m,n}(E)$ and $C_{m,n'}(E,E')$ coefficients of Eqs. (13) and (16).

Contrary to coherent dynamics, it is not the width of the resonance that determines the flux: it is the energetic position of the resonance (via the height of the $B_{m,n}(E)$ and $C_{m,n}(E,E')$ coefficients at that energy) that modulates the incoherent asymptotic flux. Therefore, some levels will have much higher fluxes associated with them relative to other levels. We note that whereas the Lorentzian-like $B_{m,n}(E)$ contributes mostly to levels near the resonance center, $\mathsf{P}_v\int dE' C_{m,n}(E,E')/(E-E')$ has a dispersion-like shape and is minimal near the resonance center, thus contributing to the flux of "off-resonance" levels.

Equation (16) is devoid of any attribute of the light that initiated the photochemical process of interest and, therefore, has nothing to do with the de-phasing dynamics between various eigenstates of the energetically broad wave packets prepared by coherent pulsed excitations [4–9]. However, it can be easily generalized to include both coherent and incoherent dynamics by realizing that a coherent pulse creates a wave packet of $|E,n^-\rangle$ resonances,

$$\Phi_n(t) = \int dE a_E|E,n^-\rangle\exp(-iEt), \quad (17)$$

where a_E are the pulse-dependent preparation coefficients of the initial wave packet. The asymptotic flux in this case is given as

$$\mathcal{F}_{C-C}(t) = \frac{Im}{\mu}i\sum_{n,n'}\int dE dE'' a^*_E a_{E''}e^{-i(E''-E)t}\left[N_n e^{-i\mathbf{k_n}\cdot\mathbf{r}}B^*_{m,n}(E) + \mathsf{P}_v\int dE' N'_n e^{-i\mathbf{k}'_n\cdot\mathbf{r}}C^*_{m,n}(E,E')\right]$$
$$\times\left[N_{n'}\mathbf{k}''_{n'}e^{i\mathbf{k}''_{n'}\cdot\mathbf{r}}B_{m,n'}(E'') + \mathsf{P}_v\int dE' N'_{n'}\mathbf{k}'_{n'}e^{i\mathbf{k}'_{n'}\cdot\mathbf{r}}C_{m,n'}(E'',E')\right]. \quad (18)$$

Equation (18) contains *all* of the coherent and incoherent dynamics for a single mode consisting of a set of bound states coupled to a set of continua. We now generalize it to the multimode case.

The multimode fluxes.—So far we have obtained expressions for the flux carried by a single mode in which a bound state is coupled to a continuum of plane waves. We now wish to extend this theory to a nested chain of N coupled modes,

$$(((1\leftrightarrow 2)\leftrightarrow 3)\leftrightarrow\cdots N).$$

The above diagram implies that we first consider (as in the previous section) a space composed of mode 1. We then augment the space by considering a product space composed of two modes, $|\mathbf{r}_1\rangle|\mathbf{r}_2\rangle$. The Hamiltonian is now written as $H = H_1 + H_2 + V_{1,2}$, where H_1 is the full Hamiltonian of mode 1 (i.e., the total Hamiltonian of the previous section), and H_2 is the full Hamiltonian of mode 2 (assumed to have only bound states). $V_{1,2}$ is the interaction term between the two modes satisfying, per definition, the asymptotic condition

$$\lim_{(r_1 \text{ or } r_2)\to\infty} V_{1,2} = 0.$$

Denoting by $E^{(2)}_s$ and $\phi^{(2)}_s$ the eigenenergies and bound eigenstates of H_2,

$$[E_s^{(2)} - H_2]|\phi_s^{(2)}\rangle = 0,$$

and by $|E, n^-; 2\rangle$ the mode-1 fully interacting states of the previous section,

$$[E - H_1]|E, n^-; 2\rangle = 0,$$

we define the Q and P projectors as

$$Q = |0\rangle|\phi_s^{(2)}\rangle \cdot \langle 0|\langle\phi_s^{(2)}|,$$
$$P = \sum_{s' \neq s, n} \int dE |E - E_{s'}^{(2)}, n^-; 2\rangle|\phi_{s'}^{(2)}\rangle \cdot \langle E - E_{s'}^{(2)}, n^-; 2|\langle\phi_{s'}^{(2)}; 2|,$$

with $|0\rangle$ signifying the ground state in the 1 mode.

We now define a compound index $\mathbf{n}$ to includes the mode-1 continuum channel index n and the index s' used in the definition of $|E - E_{s'}^{(2)}, n^-; 2\rangle$ state. Explicitly,

$$|E, \mathbf{n}^-; 2\rangle \equiv |E - E_{s'}^{(2)}, n^-; 2\rangle. \tag{19}$$

Designating as $|E, \mathbf{n}^-\rangle$ the full solution of the $1 + 2$ modes space, we expand this state as

$$|E, \mathbf{m}^-\rangle = |0\rangle|\phi_s^{(2)}\rangle\langle 0|\langle\phi_s^{(2)}|E, \mathbf{m}^-\rangle + \sum_{\mathbf{n}(s' \neq s)} \int dE' |E', \mathbf{n}^-; 2\rangle|\phi_{s'}^{(2)}\rangle \times \langle E', \mathbf{n}^-; 2|\langle\phi_{s'}^{(2)}|E, \mathbf{m}^-\rangle,$$

whose solution in coordinate representation is

$$\langle \mathbf{r}_1, \mathbf{r}_2|E, \mathbf{m}^-\rangle = \sum_s \langle \mathbf{r}_1|0\rangle\langle \mathbf{r}_2|\phi_s^{(2)}\rangle A(s|E, m) + \sum_{\mathbf{n}} \langle \mathbf{r}_1|E, \mathbf{n}^-; 2\rangle\langle \mathbf{r}_2|\phi_{s'}^{(2)}\rangle B_{\mathbf{m},\mathbf{n}}(E) + \mathsf{P}_v \int dE' \langle \mathbf{r}_1|E', \mathbf{n}^-; 2\rangle\langle \mathbf{r}_2|\phi_{s'}^{(2)}\rangle C_{\mathbf{m},\mathbf{n}}(E, E'),$$

where

$$A(s|E, \mathbf{n}) \equiv \langle 0|\langle\phi_s^{(2)}|E, \mathbf{n}^-\rangle = \frac{V(s|E, \mathbf{n})}{E - E_s^{(2)} - \Delta_s(E) - \frac{i\Gamma_s(E)}{2}},$$
$$B_{\mathbf{m},\mathbf{n}}(E) \equiv \delta_{\mathbf{n},\mathbf{m}} + i\pi V(E, \mathbf{m}; 2|s) A(s|E, \mathbf{n}),$$
$$C_{\mathbf{m},\mathbf{n}}(E, E') \equiv V(E, \mathbf{m}|s) A(s|E', \mathbf{n})/(E - E'), \tag{20}$$

with

$$V(s|E, \mathbf{n}) \equiv \langle 0|\langle\phi_s^{(2)}|H|E, \mathbf{n}^-; 2\rangle|\phi_{s'}^{(2)}\rangle,$$
$$\Gamma_s(E) \equiv \sum_{\mathbf{n}} 2\pi |V(s|E, \mathbf{n}; 2)|^2,$$
$$\Delta_s(E) \equiv \mathsf{P}_v \sum_{\mathbf{n}} \int dE' |V(s|E', \mathbf{n})|^2/(E - E').$$

Extending the formula of Eq. (16), the asymptotic flux associated with the bound states of mode 2 in the augmented $(1 + 2)$ space is given as

$$\mathcal{F}_{C-C}^{(2)} = \frac{Im}{\mu} i \sum_{\mathbf{n},\mathbf{n}'} [\langle E, \mathbf{n}^-; 2|\mathbf{r}_1\rangle\langle\phi_{s'}^{(2)}|\mathbf{r}_2\rangle B_{\mathbf{m},\mathbf{n}}^*(E) + \mathsf{P}_v \int dE' \langle E', \mathbf{n}^-; 2|\mathbf{r}_1\rangle\langle\phi_{s'}^{(2)}|\mathbf{r}_2\rangle C_{\mathbf{m},\mathbf{n}}^*(E, E')] \cdot \left[\frac{d}{d\mathbf{r}}\langle \mathbf{r}_1|E, \mathbf{n}'^-; 2\rangle\langle \mathbf{r}_2|\phi_{s'}^{(2)}\rangle B_{\mathbf{m},\mathbf{n}'}(E) + \mathsf{P}_v \int dE' \frac{d}{d\mathbf{r}}\langle \mathbf{r}_1|E', \mathbf{n}'^-; 2\rangle\langle \mathbf{r}_2|\phi_{s'}^{(2)}\rangle C_{\mathbf{m},\mathbf{n}'}(E, E')\right], \tag{21}$$

where the $d/d\mathbf{r}$ operation can be performed with respect to $\mathbf{r} = \mathbf{r}_1$ or $\mathbf{r} = \mathbf{r}_2$.

Given the solution of the $(1 + 2)$ problem we can now add mode 3 with the total Hamiltonian given as

$$H = (H_1 + H_2 + V_{1,2}) + H_3 + V_{1,2,3},$$

where

$$\lim_{(r_1 \text{ or } r_2 \text{ or } r_3) \to \infty} V_{1,2,3} = 0,$$

and repeat the procedure outlined in this section. The result is a simple iterative procedure for obtaining multimode resonant states and the fluxes associated with them for each of these modes. We see from Eq. (21) that although the expressions for the flux are more complicated than in the single mode case, they clearly show that one mode being coupled to a continuum is enough to permeate *all* other modes with flux carrying continuum character. As in Eqs. (17) and (18) of the previous section, we can generalize Eq. (21) to include, in addition to the present incoherent case, the coherent ultrashort pulse preparation case, thereby obtaining a very attractive method for generating a complete quantum solution of intramolecular dynamics.

Conclusions.—We have introduced a new general method for solving the quantum intramolecular dynamics for multimode systems. We have shown that the existence of a flux-carrying continuum coupled to even 1 mode permeates all other modes, even those that are very far removed in the intramolecular coupling scheme from the continuum. By deriving a formula for the flux carried by a single multimode molecular eigenstate we have demonstrated the existence of incoherent dynamics, which is unrelated to the existence, or coherence with respect to other ME. As shown in Refs. [1,2], the initial conditions for excitation with an incoherent light source such as the sun are the productions of a set of individual phase-unrelated eigenstates. Hence, the incoherent dynamics discussed here always exists and is being induced by all light sources.

The present discussion may be viewed as supplementing Einstein's incoherent rate equations for absorption or emission of radiation which account for population changes due to external fields, in that we discuss the possibility that a single ME whose population is fixed can have dynamics. In addition to this type of incoherent dynamics, there are coherent dynamics which follow excitations with coherent pulses, arising from the de-phasing of each ME with respect to all others. Such coherent pulsed excitations tell us, however, nothing about the situation with incoherent sources, where no coherent dynamics is exhibited [1,2].

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