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A quantum model of almost perfect energy transfer

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Abstract. The Wigner-Weisskopf-type model describing the energy transfer between two centers mediated by a continuum of energy levels is studied. This work is motivated by the recent interest in transport phenomena at nanoscale in biology and quantum engineering. The analytical estimation for the energy transfer efficiency is derived in the weak coupling regime and the conditions for the almost perfect transfer are discussed. The embedding of the standard tight-binding model into Wigner-Weisskopf one which includes the environmental noise is presented.

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1. Introduction

The almost perfect energy transfer (APET) in biologically relevant molecular systems attracts attention of physicists in the recent years [1]. Similar phenomena should be observed also in the engineered systems relevant for information processing like arrays of quantum dots or Josephson junctions [2]. Most of the theoretical analysis is performed using tight-binding Hamiltonian for an interacting N-body system in the single excitation regime. The influence of environment is usually modeled by Markovian master equations with phenomenological decay parameters. The numerical computations show the interplay between quantum propagation, quantum localization, decoherence and dissipation [4, 3, 5]. The aim of this paper is to present a simple, essentially exactly solvable model which describes a generic class of such phenomena and allows to derive analytical bounds on the efficiency of energy transfer processes. The motivation for the applied formalism comes from the particular model of two identical atoms placed in the focuses of two parabolic mirrors separated by a distance ℓ , see Fig.1. We assume that the dipole moments of both atoms are parallel to the symmetry axis of the system. If initially the first atom is excited and the second is in the ground state

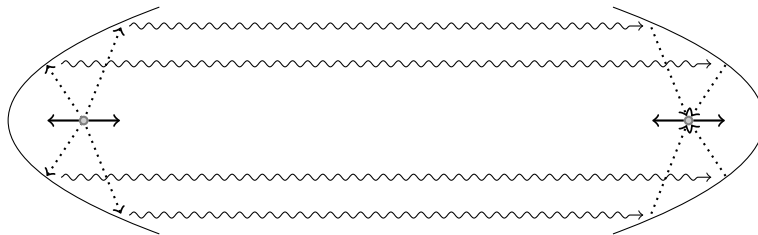


Figure 1. The APET for two atoms places in the focuses of two parabolic mirrors. Radiating dipoles are parallel to the axis.

we expect that roughly after time $t \simeq \ell/c + \mathcal{O}(\tau)$, where τ is a mean life-time of the excited state, the energy quantum carried by a photon is almost perfectly transferred to the second atom. Obviously APET demands fine-tuning conditions: the atoms should be identical, placed exactly at the focuses of perfectly aligned mirrors and the dipoles should be parallel to the symmetry axis.

The simple description of such a system can be given in terms of the Wigner-Weisskopf (W-W) Hamiltonian (compare the case of a single mirror and a single atom [7]). The conditions which allows for APET are encoded entirely in the structure of the Hamiltonian which is determined by the details of the model. Treating W-W model as a generic one of a large class of energy transfer phenomena between two localized centers one can try to find a general bound for the efficiency of such process and determine the sufficient conditions for APET.

2. Wigner-Weisskopf model

In order to introduce a 2-state W-W model we consider a quantum system of two 2-level atoms interacting with an electromagnetic field which can be described by the standard Hamiltonian in the rotating wave approximation

$$H = \frac{\omega_1}{2}\sigma_1^z + \frac{\omega_2}{2}\sigma_2^z + \int d^3\mathbf{k} \omega(\mathbf{k}) a^\dagger(\mathbf{k})a(\mathbf{k}) + \sigma_1^+ a(g_1) + \sigma_1^- a^\dagger(g_1) + \sigma_2^+ a(g_2) + \sigma_2^- a^\dagger(g_2). \quad (1)$$

The operators $a(g)$ and $a^\dagger(g)$ are smeared annihilation and creation operators for the electromagnetic field given by $a^\dagger(g) = \int d^3\mathbf{k} g(\mathbf{k})a^\dagger(\mathbf{k})$, $g_j(\mathbf{k}), j = 1, 2$, are suitable formfactors, and the quantum fields satisfy $[a(\mathbf{k}), a^\dagger(\mathbf{k}')] = \delta(\mathbf{k} - \mathbf{k}')$ (we omit for simplicity the polarization degrees of freedom). The standard 2×2 Pauli matrices $\sigma_{1,2}^{\pm,z}$ refer to 2-level atoms. In the case of identical atoms with relative position described by the vector \mathbf{r} the formfactors differ by the relative phase $L(\mathbf{k}) = \mathbf{k} \cdot \mathbf{r}$

$$g_2(\mathbf{k}) = e^{-iL(\mathbf{k})}g_1(\mathbf{k}). \quad (2)$$

The crucial property of the Hamiltonian (1) is the commutation with the excitation number operator defined as

$$N_{ex} = \int d^3\mathbf{k} a^\dagger(\mathbf{k})a(\mathbf{k}) + (\sigma_1^z + 1/2) + (\sigma_2^z + 1/2). \quad (3)$$

The total Hilbert space of the system possesses a tensor product structure

$$\mathcal{H}_{tot} = \mathbb{C}^2 \otimes \mathcal{F}_{ph} \otimes \mathbb{C}^2 \quad (4)$$

with the bosonic Fock space \mathcal{F}_{ph} describing an electromagnetic field. As a consequence of the commutation $[H, N_{ex}] = 0$ the subspace corresponding to the eigenvalue 1 of N_{ex} , which can be called single exciton Hilbert space is invariant under the evolution. It possesses a direct orthogonal sum structure, i.e., is spanned by the following vectors

$$\begin{aligned} |1\rangle &\equiv |\uparrow; 1\rangle \otimes |\text{vac}\rangle \otimes |\downarrow; 2\rangle, \\ |2\rangle &\equiv |\downarrow; 1\rangle \otimes |\text{vac}\rangle \otimes |\uparrow; 2\rangle, \\ |f\rangle &\equiv |\downarrow; 1\rangle \otimes a^\dagger(f)|\text{vac}\rangle \otimes |\downarrow; 2\rangle \text{ for any wave - packet } f. \end{aligned} \quad (5)$$

Here, $|\uparrow; j\rangle$ and $|\downarrow; j\rangle$ denote excited and ground state of the j -th atom, respectively, and $|\text{vac}\rangle$ is the vacuum state of an electromagnetic field. This mathematical construction, which has been used frequently in quantum optics [6], will be called the 2-state W-W model.

The 2-state W-W model is suitable for the following generic physical situation. We restrict ourselves to physical systems which can be described in terms of the single-exciton Hilbert space \mathcal{H}_{ex} . In this Hilbert space we choose two orthogonal vectors $|1\rangle, |2\rangle$ which are determined by the initial state preparation and the measurement procedures. Namely, the initial state ("donor") of the system at time $t_0 = 0$ is denoted by $|1\rangle$, while the measurement at time $t > 0$ after preparation is a von Neumann projection on the state $|2\rangle$ ("acceptor").

The Hilbert space of the model system is decomposed into a direct sum (compare with (5))

$$\mathcal{H}_{ex} = \mathbb{C} \oplus \mathbf{L}^2(\Omega) \oplus \mathbb{C} \quad (6)$$

where the one-dimensional subspaces \mathbb{C} are generated by the states $|1\rangle, |2\rangle$ and the Hilbert space $\mathbf{L}^2(\Omega)$ is their orthogonal supplement. For the convenience we represent this Hilbert space as the space of wave packets $f(k), g(k), k \in \Omega$ denoted by $|f\rangle, |g\rangle$ with the scalar product

$$\langle f|g\rangle = \int_{\Omega} \overline{f(k)}g(k) dk. \quad (7)$$

One should stress that the notation of above is used for convenience only. One can always replace the continuous variable k by a joint set of continuous variables ω and discrete quantum numbers m such that $|k\rangle$ is replaced by $|\omega, m\rangle$ and

$$\langle \omega, m|\omega', m'\rangle = \delta(\omega - \omega')\delta_{mm'}, \text{ and } \int_{\Omega} dk \mapsto \sum_m \int d\omega. \quad (8)$$

The 2-state W-W Hamiltonian, which can be seen as the restriction of (1) to the single-exciton space, reads

$$\begin{aligned} H &= H_0 + V, \\ H_0 &= \omega_1|1\rangle\langle 1| + \omega_2|2\rangle\langle 2| + \int_{\Omega} dk \omega(k)|k\rangle\langle k|, \\ V &= (|1\rangle\langle g_1| + |g_1\rangle\langle 1|) + (|2\rangle\langle g_2| + |g_2\rangle\langle 2|) \end{aligned} \quad (9)$$

where $g_{1,2} \in \mathbf{L}^2(\Omega)$. All details of the model are hidden in the form of formfactors $g_{1,2}$ and the spectral resolution of the part of the Hamiltonian denoted here by $\int_{\Omega} dk \omega(k)|k\rangle\langle k|$.

Remarks The presented model should be treated as an open quantum system where the system consists of donor and acceptor and the continuous modes form a reservoir. Notice that strictly speaking for the 2-atom model presented in the Introduction the cavity formed by the mirrors is finite and hence the modes are discrete. Therefore the W-W Hamiltonian applies to the case of a large enough cavity such that the Heisenberg time $t_H = 1/\delta\omega$ ($\hbar\delta\omega$ - characteristic energy level splitting of modes) is much longer than any relevant time scale. Alternatively, the continuous spectrum can be used if the modes themselves are unstable, due to environmental effects, and have finite life-times comparable to t_H .

3. Efficiency of energy transfer

The system begins its evolution in the excited state $|1\rangle$ and after time t can be found in the state $|2\rangle$ with the probability

$$\mathcal{P}_{12}(t) = |\mathcal{A}_{12}(t)|^2, \quad \mathcal{A}_{12} = \langle 2|e^{-iHt}|1\rangle. \quad (10)$$

The APET holds if $\omega_1 \simeq \omega_2$ and for a certain time t_0 the transfer probability $\mathcal{P}_{12}(t_0) \simeq 1$. To find the sufficient conditions for APET in terms of the Hamiltonian (9) notice that

the (complex) probability amplitude $\mathcal{A}_{12}(t)$ is a scalar product of two states, $e^{-iHt/2}|1\rangle$ and $e^{iHt/2}|2\rangle$ which evolve forward and backward in time, respectively. For $t \gg \tau$ where τ is the life-time of the excited states one expects that the following approximation holds

$$e^{-iHt/2}|1\rangle \simeq e^{-iH_0t/2}|f_1\rangle, \quad e^{iHt/2}|2\rangle \simeq e^{iH_0t/2}|f_2\rangle \quad (11)$$

where $f_1(k)$, $f_2(k)$ are certain wave packets from the Hilbert space component $\mathbf{L}^2(\Omega)$ describing intermediate excitonic states. The estimation (11) is equivalent to the existence of wave operators defined as

$$W_+ = \lim_{t \rightarrow +\infty} e^{iH_0t} e^{-iHt}, \quad W_- = \lim_{t \rightarrow +\infty} e^{-iH_0t} e^{iHt} \quad (12)$$

which holds under mild conditions on the formfactors $g_{1,2}$ and exciton's dispersion relation $\omega(k)$, at least in the weak sense of convergence of matrix elements. Combining (11) with (12) one obtains

$$f_1(k) = \langle k|W_+|1\rangle, \quad f_2(k) = \langle k|W_-|2\rangle \quad (13)$$

and finally

$$\mathcal{A}_{12}(t) = \int_{k \in \Omega} dk e^{-i\omega(k)t} \langle k|W_+|1\rangle \overline{\langle k|W_-|2\rangle}. \quad (14)$$

The advantage of the Wigner-Weisskopf model is the fact that the matrix elements $\langle 1|W_-|k\rangle$ and $\langle 2|W_+|k\rangle$ can be exactly computed using Laplace transforms (see the next Section).

4. The computation of matrix elements

The basic tools used for the computation of the probability amplitude (14) are: the identity

$$\begin{aligned} e^{-iHt} &= e^{-iH_0t} - i \int_0^t ds [e^{-i\omega_1(t-s)}|1\rangle\langle g_1| + |g_1(t-s)\rangle\langle 1| \\ &\quad + e^{-i\omega_2(t-s)}|2\rangle\langle g_2| + |g_2(t-s)\rangle\langle 2|] e^{-iHs} \end{aligned} \quad (15)$$

where $|g_j(t)\rangle \equiv e^{-iH_0t}|g_j\rangle$, and the Laplace transform

$$\tilde{f}(z) = \int_0^\infty e^{-zt} f(t) dt. \quad (16)$$

Introducing the notation ($j, j' = 1, 2$):

$$\begin{aligned} S_{jj'}(t) &= \langle j|e^{-iHt}|j'\rangle \\ F_{jj'}(t) &= \langle g_j|e^{-iHt}|j'\rangle \\ G_{jj'}(t) &= \langle g_j|e^{-iH_0t}|g_{j'}\rangle. \end{aligned} \quad (17)$$

and using the identity (15), the definition of the wave operators (12), the notation (17) and the Laplace transform we have

$$\begin{aligned} f_1(k) &= \langle k|W_+|1\rangle = -i \left[g_1(k) \tilde{S}_{11}(-i\omega(k)) + g_2(k) \tilde{S}_{21}(-i\omega(k)) \right] \\ f_2(k) &= \langle k|W_-|2\rangle = i \left[g_1(k) \overline{\tilde{S}_{21}(-i\omega(k))} + g_2(k) \overline{\tilde{S}_{22}(-i\omega(k))} \right]. \end{aligned} \quad (18)$$

Combining the identity (15) with the definitions (17) we obtain a series of equations

$$\begin{aligned}
 S_{11}(t) &= e^{-i\omega_1 t} - i \int_0^t e^{-i\omega_1(t-s)} F_{11}(s) ds, \\
 S_{22}(t) &= e^{-i\omega_2 t} - i \int_0^t e^{-i\omega_2(t-s)} F_{22}(s) ds, \\
 S_{12}(t) &= -i \int_0^t e^{-i\omega_1(t-s)} F_{12}(s) ds, \\
 F_{11}(t) &= -i \int_0^t G_{11}(t-s) S_{11}(s) ds - i \int_0^t G_{12}(t-s) S_{21}(s) ds, \\
 F_{22}(t) &= -i \int_0^t G_{22}(t-s) S_{22}(s) ds - i \int_0^t G_{21}(t-s) S_{12}(s) ds, \\
 F_{12}(t) &= -i \int_0^t [G_{11}(t-s) S_{12}(s) + G_{12}(t-s) S_{22}(s)] ds,
 \end{aligned} \tag{19}$$

which can be converted into equations for Laplace transforms

$$\begin{aligned}
 \tilde{S}_{11}(z) &= \frac{1}{z + i\omega_1} [1 - i\tilde{F}_{11}(z)], \\
 \tilde{S}_{22}(z) &= \frac{1}{z + i\omega_2} [1 - i\tilde{F}_{22}(z)], \\
 \tilde{S}_{12}(z) &= \frac{-i}{z + i\omega_1} \tilde{F}_{12}(z), \\
 \tilde{S}_{21}(z) &= \frac{-i}{z + i\omega_2} \tilde{F}_{21}(z), \\
 \tilde{F}_{11}(z) &= -i\tilde{G}_{11}(z)\tilde{S}_{11}(z) - i\tilde{G}_{12}(z)\tilde{S}_{21}(z), \\
 \tilde{F}_{22}(z) &= -i\tilde{G}_{22}(z)\tilde{S}_{22}(z) - i\tilde{G}_{21}(z)\tilde{S}_{12}(z), \\
 \tilde{F}_{12}(z) &= -i[\tilde{G}_{11}(z)\tilde{S}_{12}(z) + \tilde{G}_{12}(z)\tilde{S}_{22}(z)] \\
 \tilde{F}_{21}(z) &= -i[\tilde{G}_{21}(z)\tilde{S}_{11}(z) + \tilde{G}_{22}(z)\tilde{S}_{21}(z)].
 \end{aligned} \tag{20}$$

The system of equations (20) can be solved yielding the relevant Laplace transforms

$$\begin{aligned}
 \tilde{S}_{11}(z) &= \frac{1}{z + i\omega_1 + \tilde{G}_{11}(z)} \left[1 + \frac{\tilde{G}_{12}(z)\tilde{G}_{21}(z)}{W(z)} \right] \\
 \tilde{S}_{12}(z) &= \frac{-\tilde{G}_{12}(z)}{W(z)} \\
 \tilde{S}_{21}(z) &= \frac{-\tilde{G}_{21}(z)}{W(z)} \\
 \tilde{S}_{22}(z) &= \frac{1}{z + i\omega_2 + \tilde{G}_{22}(z)} \left[1 + \frac{\tilde{G}_{12}(z)\tilde{G}_{21}(z)}{W(z)} \right]
 \end{aligned} \tag{21}$$

where

$$W(z) = (z + i\omega_1 + \tilde{G}_{11}(z))(z + i\omega_2 + \tilde{G}_{22}(z)) - \tilde{G}_{12}(z)\tilde{G}_{21}(z). \tag{22}$$

Combining (21) with (18) and (14) one can obtain the exact final formula for the transition amplitude which can be used for numerical calculations. The formulas

can be essentially simplified if one neglects all terms containing $\tilde{G}_{12}(z), \tilde{G}_{21}(z)$. This approximation means that the interaction between donor and acceptor mediated by the reservoir is neglected as well as the collective contribution to their relaxation processes. In the case of two atoms in a large cavity it means that the dipole-dipole interaction and the "superradiance/subradiance" effects [10] are neglected.

5. Markovian approximation

In order to continue analytical analysis of the problem we consider the case of weak coupling or Markovian approximation and neglect the collective effects as discussed above. The further approximation concerns Laplace transforms $\tilde{G}_{jj}(z)$. The real part of $\tilde{G}_{jj}(-i\omega)$, taken at the physical frequency is the standard *Fermi Golden Rule* approximation for the decay rate of the state $|j\rangle$ ($j = 1, 2$) given by

$$\gamma_j = \pi \int_{\Omega} dk |g_j(k)|^2 \delta(\omega(k) - \omega_j^{ren}), \quad (23)$$

while the imaginary part is a "radiative correction" to the bare frequencies ω_j yielding a physical renormalized frequency

$$\omega_j^{ren} = \omega_j - \int_{\Omega} dk |g_j(k)|^2 \mathcal{P} \left(\frac{1}{\omega(k) - \omega_j^{ren}} \right). \quad (24)$$

Notice, that the equation (24) has a self-consistent character because ω_j^{ren} appears on both sides of it. It is due to the fact that we cannot expect that the "radiative correction" is small and hence it is not justified to put the bare value ω_j on the RHS of (24) and (23).

Summarizing, the Markovian approximation means that

$$\tilde{S}_{21}(-i\omega(k)) \simeq 0, \quad \tilde{S}_{jj}(-i\omega(k)) \simeq [i(\omega_j^{ren} - \omega(k)) + \gamma_j]^{-1}, \quad \gamma_j \ll \omega_j. \quad (25)$$

Therefore using Eqs. 18) and (25) one obtains

$$f_1(k) = \frac{g_1(k)}{\omega(k) - \omega_1^{ren} + i\gamma_1}, \quad f_2(k) = \frac{g_2(k)}{\omega(k) - \omega_2^{ren} - i\gamma_2} \quad (26)$$

and

$$\mathcal{A}_{12}(t) = \int_{k \in \Omega} dk e^{-i\omega(k)t} \frac{g_1(k) \overline{g_2(k)}}{(\omega(k) - \omega_1^{ren} + i\gamma_1)(\omega(k) - \omega_2^{ren} + i\gamma_2)} \quad (27)$$

One can estimate the upper bound for $\mathcal{P}_{12}(t)$ using (27) to get

$$\mathcal{P}_{12}(t) = |\mathcal{A}_{12}(t)|^2 \leq \|f_2\|^2 \|f_1\|^2. \quad (28)$$

The equality $\int_{-\infty}^{\infty} \gamma [x^2 + \gamma^2]^{-1} dx = \pi$ implies for example

$$\begin{aligned} \|f_1\|^2 &= \int_{\Omega} |f_1(k)|^2 dk = \int_{\Omega} dk \frac{|g_1(k)|^2}{(\omega_1^{ren} - \omega(k))^2 + \gamma_1^2} \\ &\simeq \frac{1}{\pi} \int_0^{\infty} \frac{\gamma_1}{(\omega_1^{ren} - \omega)^2 + \gamma_1^2} d\omega \simeq 1 - \frac{\gamma_1}{\pi\omega_1} \end{aligned} \quad (29)$$

what finally gives the bound (compare with [8])

$$\mathcal{P}_{12}(t) \leq \left(1 - \frac{\gamma_1}{\pi\omega_1^{ren}}\right) \left(1 - \frac{\gamma_2}{\pi\omega_2^{ren}}\right) < 1. \quad (30)$$

In the weak coupling regime the upper bound is close to one.

6. Conditions for APET

In order to approach the bound (30) and achieve APET certain matching conditions implied directly by the formula (27) must be satisfied. To present them in a transparent form we introduce certain additional assumptions in a convenient parametrization. There are satisfied by the two-mirror system discussed in the Introduction.

Assume that the intermediate Hilbert space $\mathbf{L}^2(\Omega)$ is spanned by the basis $|\omega, m\rangle$ and the corresponding part of the Hamiltonian reads

$$H_1 = \sum_m \int d\omega \omega |\omega, m\rangle \langle \omega, m|. \quad (31)$$

The formfactors possess the following structure

$$|g_1\rangle = \int d\omega g(\omega) |\omega, m_0\rangle, \quad |g_2\rangle = \int d\omega e^{-iL(\omega)} g(\omega) |\omega, m_0\rangle. \quad (32)$$

where $g(\omega)$ is a smooth enough formfactor and $L(\omega)$ accounts for the spatial separation of donor and acceptor similarly to (2). Now the mechanism leading to APET can be illustrated. We have to put the resonance condition

$$\omega_1^{ren} = \omega_2^{ren} \equiv \omega_0, \quad (33)$$

which by (23) implies also the equality of decay rates

$$\gamma_1 = \gamma_2 \equiv \gamma. \quad (34)$$

Then we have the approximative expression

$$\mathcal{A}_{12}(t) \simeq \frac{1}{\pi} \int d\omega \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} \left(\frac{\omega - \omega_0 - i\gamma}{\omega - \omega_0 + i\gamma} \right) e^{i(L(\omega) - \omega t)}. \quad (35)$$

Further approximations valid for $|\omega - \omega_0| \leq \gamma$

$$\left(\frac{\omega - \omega_0 - i\gamma}{\omega - \omega_0 + i\gamma} \right) \simeq -e^{i2(\omega - \omega_0)/\gamma}, \quad L(\omega) \simeq L(\omega_0) + L'(\omega_0)(\omega - \omega_0) \quad (36)$$

lead to

$$|\mathcal{A}_{12}(t)| \simeq \frac{1}{\pi} \left| \int d\omega \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2} \exp\{i[L'(\omega_0) + 2\tau - t](\omega - \omega_0)\} \right| \quad (37)$$

where $\tau = 1/\gamma$. The transition probability is maximal and close to one if the oscillating factor in the integral of above vanishes what happens for the time

$$t_0 = L'(\omega_0) + 2\tau \quad (38)$$

which can be called the optimal transfer time.

7. Transport in quantum networks

The standard tight-binding model of energy transport in quantum networks which is applicable both to molecular systems and engineered ones consist of N 2-level "atoms" described by the Hilbert space \mathbb{C}^{2^N} and the Hamiltonian written in terms of Pauli matrices

$$H_N = \sum_{k=1}^N \omega_k \sigma_k^z + \sum_{k<l=2}^N (h_{kl} \sigma_k^+ \sigma_l^- + h.c.) \quad (39)$$

where $\{\omega_k\}$ are energies of the sites and $\{h_{kl}; k < l\}$ are hopping amplitudes. Similarly to the example in the Section 2 the exciton number operator

$$N_{ex} = \sum_{k=1}^N (\sigma_k^z + 1/2) \quad (40)$$

commutes with H_N .

Again a single exciton N -dimensional Hilbert space \mathbb{C}^N is invariant with respect to the dynamics and the corresponding restriction of the Hamiltonian H_N is given by the $N \times N$ hermitian matrix $[h_{kl}]$ with the diagonal elements $h_{kk} = \omega_k$. We attribute to the donor site an index "1" and to the acceptor site an index "2". The famous example of such a model is the standard description of the exciton transfer in the Fenna-Matthews-Olson (FMO) complex which involves $N = 7$ centers and the experimentally determined 7×7 single-exciton Hamiltonian [11, 12]. To describe the influence of environment different schemes have been proposed mainly based on the Markovian master equations for the reduced density matrix of the exciton system [3, 4, 5, 9]. Here we propose a different approach based on the W-W model where only donor and acceptor form an open system while the other sites are included into a bath.

We assume that the direct hopping $1 \leftrightarrow 2$ is negligible, i.e. $h_{12} = h_{21} = 0$. We have to add also the site $N + 1$ with the energy ϵ_{N+1} which represents a sink coupled only to the acceptor by the matrix element $h_{2(N+1)}$. Under these conditions the extended Hamiltonian can be recast into the discrete version of the W-W Hamiltonian

$$H^{(d)} = \omega_1 |e_1\rangle\langle e_1| + \omega_2 |e_2\rangle\langle e_2| + (|e_1\rangle\langle g_1| + |e_2\rangle\langle g_2| + h.c.) + H_1^{(d)}. \quad (41)$$

Here $|e_1\rangle = [1, 0, \dots, 0]$, $|e_2\rangle = [0, 1, \dots, 0]$, $|g_1\rangle = [0, 0, h_{13}, \dots, h_{1N}, 0]$, $|g_2\rangle = [0, 0, h_{23}, \dots, h_{2N}, h_{2(N+1)}]$ and $H_1^{(d)}$ is a submatrix of $H^{(d)}$ with indices $k, l = 3, 4, \dots, N, N+1$. $H_1^{(d)}$ can be written in its spectral decomposition form

$$H_1^{(d)} = \sum_{\alpha=3}^{N+1} \epsilon_\alpha |\alpha\rangle\langle\alpha| \quad (42)$$

where $|N+1\rangle = [0, \dots, 0, 1]$. The energies ϵ_α are chosen in a decreasing order what is consistent with the intuition that the energy of a sink ϵ_{N+1} should be the lowest one. Notice that (41),(42) can be treated as a discrete version of the continuous spectrum Hamiltonian (9). In the next step we embed the discrete model into a continuous one. Physically, it means that the interaction with other (environmental) degrees of freedom

is taken into account. This interaction transforms the eigenstates $|\alpha\rangle$ into resonances with finite spectral widths. The Hilbert space spanned by $\{|\alpha\rangle\}$ is replaced by $L^2(\mathbb{R})$ and the Hamiltonian (42) by the multiplication operator by ω which can be formally written as $H_1 = \int d\omega \omega |\omega\rangle\langle\omega|$. Consider the correlation functions characterizing the interaction of the donor-acceptor system with the bath consisting of other sites including a sink site

$$G_{jj}^{(d)}(t) = \langle g_j | e^{-iH_1 t} | g_j \rangle = \sum_{\alpha=3}^{N+1} |\langle \alpha | g_j \rangle|^2 e^{-i\epsilon_\alpha t}, j = 1, 2. \quad (43)$$

In order to include the interaction with the other degrees of freedom, e.g. vibrational modes for molecular systems like FMO, we assume that the discrete modes $|\alpha\rangle$ are unstable and the correlations decay with the decoherence rates Γ_α . The modified correlation functions corresponding to the continuous model read

$$G_{jj}(t) = \sum_{\alpha=3}^{N+1} |\langle \alpha | g_j \rangle|^2 e^{-i\epsilon_\alpha t} e^{-\Gamma_\alpha |t|}, j = 1, 2. \quad (44)$$

One can replace the discrete formactors $\langle \alpha | g_j \rangle$ by the suitable wave functions $g_j(\omega)$ from $L^2(\mathbb{R})$ satisfying

$$\text{Re} \left(\int_0^\infty e^{i\omega t} G_{jj}(t) dt \right) = \sum_{\alpha=3}^{N+1} |\langle \alpha | g_j \rangle|^2 \frac{\Gamma_\alpha}{(\omega - \epsilon_\alpha)^2 + \Gamma_\alpha^2} = \pi |g_j(\omega)|^2. \quad (45)$$

The condition (45) determines only the modulus of $g_j(\omega)$. The relative phase $L(\omega)$ should be constructed as an interpolation between discrete relative phases for $\langle \alpha | g_1 \rangle$ and $\langle \alpha | g_2 \rangle$ defined at the points $\{\omega = \epsilon_\alpha\}$.

8. Energy transfer controlled by decoherence

The search for the condition which should be satisfied to achieve APET in quantum networks can be treated as a control problem for quantum open systems. One of the possible settings is to treat the tight-binding Hamiltonian (39) as given and optimize the choice of decoherence rates $\{\Gamma_\alpha\}$, acceptor-sink coupling $h_{2(N+1)}$ and the sink energy ϵ_{N+1} to maximize the transition probability $\mathcal{P}_{12}(t_0)$. The advantage of the presented model is a deeper insight into the mechanism of APET based on the discussion in the Section 6 where analytical formulas are used.

The first condition for APET is a fine-tuning one, namely the resonance condition (33). It can be discussed using the following formula for the renormalized frequencies obtained by putting (44) into (24)

$$\omega_j^{ren} = \omega_j - \sum_{\alpha=3}^{N+1} |\langle \alpha | g_j \rangle|^2 \frac{\epsilon_\alpha - \omega_j^{(ren)}}{(\omega_j^{ren} - \epsilon_\alpha)^2 + \Gamma_\alpha^2}. \quad (46)$$

Another condition follows from (34) which implies that $|g_1(\omega)|$ and $|g_2(\omega)|$ should essentially coincide in the neighborhood of ω_0 of the width $\gamma \simeq \pi |g_1(\omega_0)|^2 \simeq \pi |g_2(\omega_0)|^2$. One can expect that this condition can be satisfied generically for the widths of the resonances comparable to the typical nearest neighbor energy spacing.

The optimal transfer time estimated from the formula (38) reads

$$t_0 \simeq \frac{\pi}{\epsilon_{\alpha_0} - \epsilon_{\alpha_0+1}} + \frac{2}{\pi |g_{1,2}(\omega_0)|^2} \quad (47)$$

where $\epsilon_{\alpha_0} \geq \omega_0 \geq \epsilon_{\alpha_0+1}$.

9. Concluding remarks

The 2-state Wigner-Weisskopf model provides a versatile mathematical tool to study, within the single exciton approach, the transport properties in complex molecular systems or engineered networks relevant for quantum information processing, both in the weak coupling (Markovian) and strong coupling (non-Markovian) regimes. The preliminary results for the FMO model (work in progress) show that the presented here APET conditions can be achieved under realistic assumptions concerning the decoherence rates and sink parameters. The necessity of fine-tuning to achieve APET in disordered molecular networks has been already noticed in [9] where sampling over many molecular configurations has been performed. However, the presented here formalism allows to design the optimal parameters and shows the details of the physical mechanisms leading to APET. In the case of engineered networks the fine-tuning conditions imply a careful design while for biologically relevant systems one can imagine that the natural selection mechanism plays a crucial role.

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