FIG. 1: Schematic of the EET mechanism from pigment 1 to pigment 2 in Förster theory. In Förster theory, the de-excitation (down-pointing arrow) and excitation (up-pointing arrow) occur from the equilibrium phonons of the initial state $|1\rangle = |\varphi_{1e}\rangle|\varphi_{2g}\rangle$ to the nonequilibrium phonons of the final state $|2\rangle = |\varphi_{1g}\rangle|\varphi_{2e}\rangle$ in accordance to the vertical Franck-Condon transition.

I. FÖRSTER THEORY: PRELUDE TO NON-MARKOVIAN DYNAMICS

Förster theory [1] still has a significant impact on wide areas of physics, chemistry, and biology. The theory is employed to describe incoherent diffusive motion of electronic excitation localized on individual pigments and is not capable of describing quantum coherent EET. [2] Nevertheless, the theory is thought-provoking regarding the interplay between electronic excitation and its associated phonons. In this section, we give a brief review of Förster theory with a specific account of its intrinsic non-Markovian features, i.e. site-dependent reorganization and the nature of optical lineshapes involved in the theory, which play a crucial role in exploring rigorous theories of quantum coherent EET in photosynthetic PPCs. [3–5]

Förster derived the EET rate expression with the use of the Fermi golden rule approach with a second-order perturbative treatment of the excitonic coupling between the pigments. [1] The resultant rate constant is expressed as the overlap integral between the fluorescence spectrum of a donor and the absorption spectrum of an acceptor as follows:

$$k_{m\leftarrow n}^{\mathrm{F}} = J_{mn}^2 \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{Re}\, A_m[\omega]\, \mathrm{Re}\, F_n[\omega]. \qquad (1.1)$$

Here, $A_m[\omega]$ and $F_m[\omega]$ are the absorption and fluorescence lineshapes of the mth pigment expressed as

$$A_m[\omega] = \int_0^{\infty} \mathrm{d}t\, e^{i\omega t} e^{-i\Omega_m t - g_m(t)}, \qquad (1.2)$$

$$F_m[\omega] = \int_0^{\infty} \mathrm{d}t\, e^{i\omega t} e^{-i(\Omega_m - 2\lambda_m)t - g_m^*(t)}, \qquad (1.3)$$

respectively, where $g_m(t)$ is the line-broadening function [6, 7] defined by

$$g_m(t) = \frac{1}{\hbar^2} \int_0^t \mathrm{d}s_1 \int_0^{s_1} \mathrm{d}s_2 \left[S_m(s_2) - i\frac{\hbar}{2}\chi_m(s_2) \right]. \qquad (1.4)$$

It should be noticed that the derivations of eqns (1.2)-(1.4) are based on the Gaussian property given in eqn (??).

The expression of Förster rate implies the following: First, the reorganization of the initial state, $|n\rangle = |\varphi_{ne}\rangle \prod_{k\neq n}|\varphi_{kg}\rangle$,

takes place *instantaneously*. *Subsequently*, the electronic de-excitation of the nth pigment and the excitation of the mth pigment occur from the equilibrium phonons of the initial state to the nonequilibrium phonons or hot phonons of the final state, $|m\rangle = |\varphi_{me}\rangle \prod_{k\neq m}|\varphi_{kg}\rangle$, in accordance to the Franck-Condon principle, as depicted in Fig. 1. This sequential process involving the site-dependent reorganization is the key assumption of Förster theory. This transfer process through hot phonons associated with the acceptor state is the physics of the so-called multiphonon transition process. [8] Extensions of Förster theory also have been explored to treat finite timescales of the reorganization, i.e. hot transfer mechanism or nonequilibrium effects. [9–13]

For later discussion of quantum coherent dynamics influenced by the surrounding environment, it is advisable to consider the mathematical structure of the lineshapes in eqns (1.2)-(1.4) since the lineshapes provide important insights into the dynamic interactions of a system of interest and its environment. For the sake of simplicity, we employ the so-called Kubo-Anderson stochastic model, [14, 15]

$$S_m(t) = \hbar^2 \Delta_m^2 e^{-\gamma_m t} \quad \text{and} \quad \chi_m(t) = 0, \qquad (1.5)$$

where $\hbar\Delta_m$ is the root-mean-squared amplitude of the energy gap fluctuations. It should be noticed that eqn (1.5) neglects the inherent dissipative effects described by the response function $\chi_m(t)$; thus, the Stokes shift does not exist and the absorption and fluorescence lineshapes coincide. For this model, the lineshape can be represented by a continued fraction, [16]

$$A_m[\omega] = \cfrac{1}{-i\tilde{\omega} + \cfrac{\Delta_m^2}{-i\tilde{\omega} + \gamma_m + \cfrac{2\Delta_m^2}{-i\tilde{\omega} + 2\gamma_m + \cfrac{3\Delta_m^2}{\ddots}}}}, \qquad (1.6)$$

where $\tilde{\omega} \equiv \omega - \Omega_m$. Takagahara, Hanamura and Kubo gave a comprehensible proof of this expression by introducing auxiliary functions, [17]

$$A_m^{(n)}[\omega] = \int_0^{\infty} \mathrm{d}t \left(\int_0^t \mathrm{d}s\, e^{-\gamma_m s} \right)^n e^{i\tilde{\omega}t - g_m(t)}, \qquad (1.7)$$

for $n = 0, 1, 2, \ldots$, and $A_m^{(0)}[\omega] = A_m[\omega]$. Integrating eqn (1.7) by parts, we obtain a set of hierarchically coupled equations of $A_m^{(n)}[\omega]$, which constructs the continued fraction. By creating a fusion of this treatment and Caldeira-Leggett theory concerning quantum Brownian motion, [18] Tanimura and Kubo derived a nonperturbative quantum master equation. [19] However, these theories invoked a high-temperature approximation, and hence cannot be applied to low temperature systems where quantum effects play a role. Thus, low-temperature corrections [20] were explored and summarized as a rigorous but convenient form for practical calculations by Ishizaki and Tanimura. [21] Extensions of the theories to various spectral densities were also studied. [22–25]

The continued fraction representation in eqn (1.6) is convenient not only for numerical computations but also for understanding properties of the lineshape. In the fast modulation

limit characterized by $\Delta_m/\gamma_m \ll 1$ (a Markovian regime), the continued fraction converges at first order and thus the lineshape becomes Lorentzian as

$$A_m[\omega] \simeq \frac{1}{-i(\omega - \Omega_m) + \dfrac{\Delta_m^2}{\gamma_m}}. \tag{1.8}$$

This phenomenon is the well-known motional narrowing. [26] In the slow modulation limit of $\Delta_m/\gamma_m \gg 1$ (a strong non-Markovian regime), on the other hand, the fraction in eqn (1.6) continues to infinity. However, a continued fraction representation of the complementary error function,[19, 27] $\mathrm{erfc}\, z = (2/\sqrt{\pi})\int_z^\infty \mathrm{d}t\, e^{-t^2}$, allows us to approximate eqn (1.6) by a Gaussian function as follows:

$$\mathrm{Re}\, A_m[\omega] \simeq \sqrt{\frac{\pi}{2\Delta_m^2}} \exp\left[-\frac{(\omega - \Omega_m)^2}{2\Delta_m^2} \right]. \tag{1.9}$$

This case is known as the limit of inhomogeneous broadening, where the timescale for nuclear motion is such that the nuclei can be considered to be frozen. In the intermediate regime of $\Delta_m/\gamma_m \sim 1$ (a typical situation in photosynthetic EET), the continuous fraction converges at a finite depth, and thus the lineshape presents a mixed profile of Lorentzian and Gaussian forms. In this manner, the ratio of Δ_m/γ_m, lineshape, and depth of the continued fraction provide information concerning the extent of the non-Markovian character of the dynamic interaction of a system of interest and its environment. Note that the depth of the continued fraction is essentially unrelated to the order of perturbative expansion with respect to electron-phonon coupling.

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