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Interpreting Coherence Beats in Numerically Exact Simulations of 2D Electronic Spectra

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Abstract: Coherence beats are simulated in a numerically exact hierarchy method treatment of an electronic heterodimer coupled to a vibration and bath. We vary coupling parameters to analyze the lifetimes and contributions from different Liouville pathways.

1. Introduction and Motivation

The mechanisms of electronic energy transfer (EET) in biological systems depend on an interplay of pigment-pigment and pigment-bath interactions [1]. Strong electronic coupling creates delocalized excitons, helping to avoid trapping at local energy minima. Coupling to pigment or protein nuclear modes generally counteracts this effect by dephasing the site superpositions, effectively localizing the excitation on the pigment sites. While localization prevents wavelike transfer, it may be important in accumulating energy at the reaction center for subsequent charge separation. 2D electronic spectroscopy is a versatile tool for investigating the time and energy resolved dynamics in photosynthetic pigment protein complexes and other EET systems. However, oscillatory signals that emerge over the coherence time T can result from several different processes involving both nuclear and electronic degrees of freedom [2, 3].
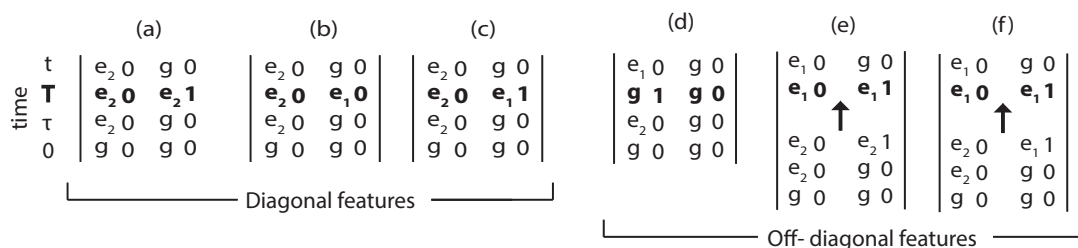

Fig. 1. Selected nonrephasing Liouville pathways contributing to beats in a 2D spectrum. States are written in a product basis of eigenstates, where subscripted letters denote electronic eigenstates and 0 or 1 is the vibrational occupation number at one of the two sites. Coherences observed over waiting time T are in bold.

For instance, pathway (a) in Fig 1 represents a vibrational coherence. While this will produce beats in a 2D spectrum, the superposition of states differs mainly in the nuclear degrees of freedom, and an extended beating lifetime is not a sign of electronic delocalization. In contrast, pathways (b) and (c) contain coherences between states that differ significantly in the electronic portion of the wavefunction. If the oscillations due to these pathways are long lived, it is because the electronic states are delocalized over the same sites and are exposed to correlated bath fluctuations. We are especially interested to analyze the dephasing of the vibronic coherence in (c). In this coherence the electronic and nuclear degrees of freedom are strongly correlated and it is difficult to predict their lifetime, though it is likely closer to that for the coherence in (b) than in (a). Knowing how much of the vibronic coherence lifetime is due to exciton delocalization vs. due to entanglement with slow-moving, localized nuclear modes will help determine how we can best use multidimensional spectroscopy to study the incidence of wavelike states in EET. Here we present a numerically exact model for use in interpretations of experimental observations. We moreover hope to use the model as a testbed for different experimental techniques (e.g. polarization selective measurements) for isolating the pathways that contribute to beats.

2.   Model

Our model consists of an electronic heterodimer with site energies 200 cm^{-1} apart and coupling $J = 50$ cm^{-1}. Each site is coupled to an independent bath of harmonic oscillators and to a vibrational mode with a dephasing time of $\tau_{vib} = 2$ ps. The vibrational frequency is chosen either on resonance with the gap between electronic eigenstates ($\omega = 223$ cm^{-1}), or off-resonance by detuning Δ. The bath reorganization energy and correlation time, which describe the magnitude and rapidity of the bath's response to electronic excitation, are $\lambda = 35$ cm^{-1} and $\tau_{bath} = 50$ fs respectively. These parameters are used to construct a Drude-Lorentz spectral density at each site. While in principle we may define bath correlations as a function of site separation, we assume here that the baths and vibrations are uncorrelated between sites. Defining environmental properties in the molecular coordinate basis allows us to incorporate enviromental stochasticity and correlations in a physically intuitive manner. Since $J \sim \lambda$ in the intermediate coupling regime typical of photosynthetic pigment complexes, neither site-site nor site-bath interactions are small enough to be treated perturbatively, and non-Markovian effects are important in the action of the bath. Here we use a second order time nonlocal master equation, solved using the hierarchy equation of motion method [4], to propagate both the reduced density matrix and the time-dependent system-bath interactions. Having defined a dipole matrix for the dimer system, we use the computed propagator to calculate system responses and obtain frequency-frequency correlation plots as a function of waiting time T.

3.   Initial Discussion

We initially consider oscillations observed in the real portion of calculated nonrephasing spectra. Absent coupling to the intramolecular vibration, we see small, rapidly dephased beats on the diagonal peaks and no oscillation in the crosspeak. As the Huang-Rhys factor S increases (Fig. 2, panels i - iii), longer-lived beats appear both on and off the diagonal. We ascribe the on-diagonal beats at late time to vibrational coherences as in Fig. 1(a). The new off-diagonal beats are partly due to a stimulated Raman pathway (d), but may also appear if vibrational phase is preserved through an electronic population (e) or coherence transfer (f). Analyzing these cross peak specific signals in the nonrephasing spectra will provide insight into contributions of (b) and (c) to the diagonal beats.
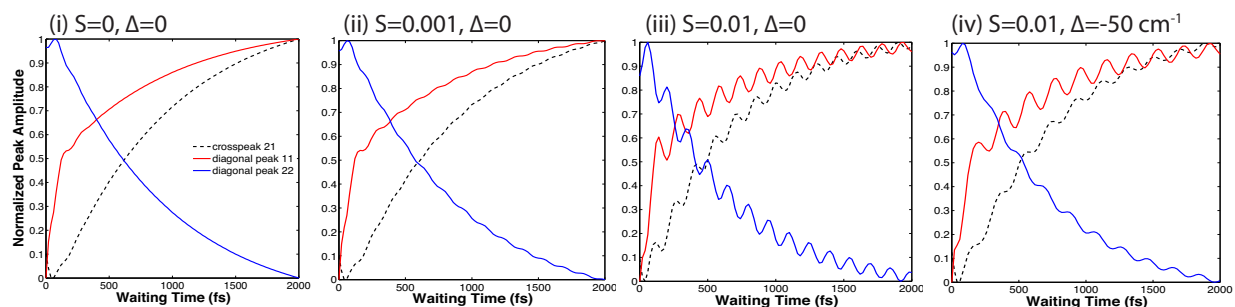

Fig. 2. Beats in simulated 2D spectra.

As the frequency of vibration is detuned from the excitonic energy gap, the vibronic coherence (c) will oscillate at a higher frequency and quickly dephase. Indeed, we see in Fig. 2 (iv) that when $\Delta > \lambda$ and the induced bath oscillations are slow compared to the coherence oscillations, the late-time beats seen at large S are more effectively damped.

References

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