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Resonant Vibrational-Electronic Coupling between Photosynthetic Excitons is Inadequately Described by Reduced Basis Sets

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Abstract

Ultrafast internal conversion between excited states of photosynthetic pigments has been a subject of intense spectroscopic interest owing to its near unity quantum yield. Of particular interest is the possibility of strong non-adiabatic mixing between vibrational and electronic degrees of freedom, termed as vibronic mixing, caused by resonances between exciton energy gaps and dense low-frequency vibrational spectrum of photosynthetic pigments. Several reports have implicated coherent superpositions of vibronically mixed excitons to explain experimental signatures, and vibronic exciton quantum dynamical simulations have further suggested a possible functional role for quantum superpositions in enhancing the rates of energy and charge delocalization. A key question which arises in this context is -- *what are the unique properties of excitons coupled through resonant vibronic coupling, and whether these properties could be well approximated in basis sets with reduced vibrational dimensionality without over-simplifying the expected excited state dynamics?* The above question will be the main theme of this presentation.

Using a dimer model for a typical photosynthetic protein, we show when exciton energy gaps and vibrational quanta become resonant, presence of vibrational excitations on electronically excited as well as unexcited sites causes vibronic interactions between donor-acceptor excitons to become progressively stronger with increasing quanta of vibrational excitation. The above mixing leads to three unique features of excitons coupled through a vibronic resonance which are not captured in basis sets with reduced vibrational dimensionality - 1. the vibronic resonance criterion itself, 2. synergistic effect of energetic disorder and vibrations in enhancing exciton delocalization by overcoming disorder, 3. progressively larger molecular distortions away from the site of electronic excitation for higher vibrational quanta.

Fig. 1: Increasing molecular distortions for states with higher vibrational quanta caused by non-adiabatic vibronic mixing. Reduced basis sets cannot capture such molecular distortions.

In terms of spectroscopic observables, limitations of reduced basis set descriptions of vibronic resonance, may be obscured in linear spectra on account of overwhelming line broadening. However, we show that several features which ultimately dictate the excited state wavepacket motions and relaxation processes, are fundamentally not described under reduced basis set descriptions of vibronic resonance.

Keywords: Vibrational-Electronic Coupling, Two-dimensional Electronic Spectroscopy, Photosynthesis, Exciton Delocalization

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