Self-consistent approach to quantum dynamics of photoinduced electronic excitations in molecular aggregates

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Further progress in fundamental understanding of the initial steps of solar-energy conversion in both natural and artificial systems requires computationally inexpensive yet reasonably accurate methods for quantum dynamics of photoinduced electronic excitations in molecular aggregates immersed in structured bosonic environments.

Starting from the memory kernel in Born approximation, and recognizing the quantum master equation as the Dyson equation of Green's functions theory, we formulate the self-consistent Born approximation (SCBA) to resum the memory-kernel perturbation series in powers of the exciton–environment interaction [1]. Our SCBA is formulated in the Liouville space and frequency domain, and it handles arbitrary spectral densities of the interaction.

In a molecular dimer coupled to an overdamped oscillator environment, we find that the SCBA reproduces the true dynamics of excitons generated by an ultrashort laser pulse very well even in the most challenging regimes of strong interactions, slow environments, and low temperatures. While the SCBA is good (poor) at describing energy transfer modulated by an underdamped vibration resonant (off-resonant) with the exciton energy gap, we find it reasonably describes light-triggered exciton dynamics in the seven-site model of the Fenna–Matthews–Olson complex in a realistic environment comprising both an overdamped continuum and underdamped vibrations.

REFERENCES

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