# Semiclassical Description of Electronic Excitation Population Transfer in a Model Photosynthetic System

Guohua Tao and William H. Miller*

Department of Chemistry and Kenneth S. Pitzer Center for Theoretical Chemistry, University of California, Berkeley, California 94720-1460, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

ABSTRACT Recently, Fleming's group observed direct evidence that the electronic excitation energy (and population) transfers coherently rather than through incoherent hopping motions in the Fenna−Mathews−Olson pigment−protein complex. Ishizaki and Fleming further developed a hierarchy equation approach to describe this excitation population transfer dynamics in a model photosynthetic system. Here, we treat this same model system via the linearized approximation to the semiclassical (SC) initial value representation (IVR) for time correlation functions, in combination with the Meyer−Miller−Stock−Thoss model for the electronic degrees of freedom. Our approach is able to describe the long-lived quantum coherent dynamics, in excellent agreement with Ishizaki−Fleming's results. Moreover, the advantage of the linearized SC-IVR approach is that it can be applied to any molecular model for which classical MD simulations are feasible, all the way up to a full all-atom MD simulation, while at the same time treating the electronic and nuclear dynamics in a consistent fashion.

SECTION Dynamics, Clusters, Excited States
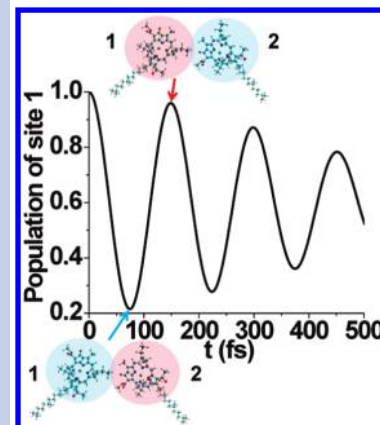
By capturing sunlight and converting solar energy into chemical energy, photosynthesis is the greenest resolution for energy consumption.[1] Despite a long history of extensive studies, the molecular mechanisms for the highly efficient light-harvesting and excitation energy transfer (EET) in photosynthesis are elusive. For example, electronic quantum coherence is often assumed to decay rapidly, so that the excitation energy transfer can be well-described by semiclassical hopping models.[2] Recently, however, Fleming's group has observed long-lived electronic coherence[3] in the Fenna−Mathews−Olson (FMO) pigment−protein complex,[4] suggesting that one needs to reconsider the significant role of quantum coherence in photosynthetic systems. The Redfield equation[5] is perhaps the simplest theoretical approach available for describing quantum coherence in photosynthetic EET; however, in Redfield theory, the reorganization energy is assumed to be small in comparison with the electronic couplings, and the electron environment is treated perturbatively. These assumptions are often not valid in typical photosynthetic EET systems; therefore, it may be problematic[6] using it to describe quantum coherent dynamics in these systems. In fact, Ishizaki and Fleming developed a reduced hierarchy equation approach[7,8] that predicted several times longer-lived electronic coherence than does Redfield theory in a pigment dimer system.

The initial value representation (IVR) of semiclassical (SC) theory,[9−11] which successfully adds quantum effects to classical molecular dynamics (MD) simulations, is an alternative choice for the study of quantum coherence in photosynthetic EET. It has also been shown[12−15] that the SC-IVR can describe

quantum coherence in electronically nonadiabatic dynamics by using the Meyer−Miller−Stock−Thoss (MMST)[16−18] classical analogue model for electronic degrees of freedom. In this work, we apply the linearized SC-IVR method[19] (LSC-IVR) and the MMST model to treat the specific photosynthetic model system used by Ishizaki and Fleming.[7,8] Our methods predict much longer lived electronic coherence than does Redfield theory, in excellent agreement with Ishizaki and Fleming's approach. The advantage of our approach is that it is, in principle, possible to apply it to a full molecular model of the photosynthetic system of interest, that is, a complete molecular dynamics simulation. In the meanwhile, we have many opportunities of investigating molecular mechanisms in EET in other simpler multichromophoric systems, such as conjugated polymers.[20]

In SC-IVR theory, the time propagator is approximated by an *f*-dimensional phase space integral over classical trajectories

$$e^{-i\hat{H}t/\hbar} =$$

$$\int d\boldsymbol{q}_0 \int d\boldsymbol{p}_0 \left[\det\left(\frac{\partial \boldsymbol{q}_t}{\partial \boldsymbol{p}_0}\right) / (2i\pi\hbar)^f \right]^{1/2} e^{iS_t(\boldsymbol{q}_0, \boldsymbol{p}_0)/\hbar} |\boldsymbol{q}_t\rangle\langle\boldsymbol{q}_0|$$

$$(1)$$

where $\boldsymbol{q}_t(\boldsymbol{q}_0,\boldsymbol{p}_0)$ is the time-dependent classical trajectory with the initial condition of $(\boldsymbol{q}_0,\boldsymbol{p}_0)$ and $S_t(\boldsymbol{q}_0,\boldsymbol{p}_0)$ is the classical action integral along this trajectory. The linearized approximation to the two time propagators involved in a typical time correlation function[19] leads to the Wigner form[21]

$$C_{AB}(t) = \mathrm{tr}[\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}]$$

$$= (2\pi\hbar)^{-f} \int d\boldsymbol{q}_0 \int d\boldsymbol{p}_0 A^{\mathrm{w}}(\boldsymbol{q}_0,\boldsymbol{p}_0)B^{\mathrm{w}}(\boldsymbol{q}_0,\boldsymbol{p}_0)^* \quad (2)$$

where A^{w} and B^{w} are the Wigner functions of the corresponding operators, defined by

$$O^{\mathrm{w}}(\boldsymbol{q}_0,\boldsymbol{p}_0) = \int d\Delta\boldsymbol{q}\, e^{-i\Delta\boldsymbol{q}\cdot\boldsymbol{p}_0}\langle\boldsymbol{q}_0+\Delta\boldsymbol{q}/2|\hat{O}|\boldsymbol{q}_0-\Delta\boldsymbol{q}/2\rangle$$

$$(O = A, B)$$

We use the MMST theory to model discrete electronic states, in which each electronic state is modeled by a harmonic oscillator, so that both electronic and nuclear degrees of freedom are treated consistently in the semiclassical description, eq 1. The MMST Hamiltonian for the case of n electronic states (in the Cartesian representation) is

$$H(\boldsymbol{x},\boldsymbol{p},\boldsymbol{Q},\boldsymbol{P}) = \sum_{k=1}^{n} \frac{1}{2}(x_k^2 + p_k^2 - 1)H_{kk}$$

$$+ \sum_{k=1}^{n}\sum_{l=k+1}^{n}(x_kx_l + p_kp_l)H_{kl} \quad (3)$$

where $H_{kk}(\boldsymbol{Q})$ is the electronic potential energy surface for diabatic state k and $H_{kl}(\boldsymbol{Q})$ is the electronic coupling between state k and state l; $(\boldsymbol{x},\boldsymbol{p})$ and $(\boldsymbol{Q},\boldsymbol{P})$ are classical electronic and nuclear coordinates and momenta, respectively. If the system is in the electronic state k, the action variable $n_k = (1/2)(x_k^2 + p_k^2 - 1)$ equals 1 and all other action variables are 0, that is, $n_l = 0$ $(l \neq k)$. The classical (i.e., Hamilton) equations of motion are derived from eq 3 for all electronic and nuclear degrees of freedom.[14] Note the sum of all action variables, that is, the total electronic population, is a constant of the motion and equals 1. We use this conservation of the total electronic population in our calculations.[22]

To study the excitation energy transfer dynamics, we use the same photosynthetic model system as that in Ishizaki and Fleming's work.[7,8] The system Hamiltonian is a spin–boson-type one, in which each Bacteriochlorophyll (Bchl) molecule is modeled by a two-level site and is coupled with an independent harmonic phonon bath, that is, the fluctuations of electronic–phonon couplings for different Bchl molecules are uncorrelated. We evaluate electronic population functions for each site, which can be calculated by using eq 2.

$$P_i(t) = \mathrm{tr}[\hat{\rho}(0)e^{-\beta\hat{H}_{\mathrm{b}}}e^{i\hat{H}t/\hbar}\hat{\rho}_{ii}e^{-i\hat{H}t/\hbar}]$$

$$= \frac{1}{(2\pi\hbar)^{N+n}Q_{\mathrm{B}}} \int d\boldsymbol{Q}_0 \int d\boldsymbol{P}_0 \int d\boldsymbol{x}_0$$

$$\times \int d\boldsymbol{p}_0 \rho^{\mathrm{w}}(\boldsymbol{x}_0,\boldsymbol{p}_0)\rho_{\mathrm{B}}^{\mathrm{w}}(\boldsymbol{Q}_0,\boldsymbol{P}_0)\rho_{ii}^{\mathrm{w}}(\boldsymbol{x}_t,\boldsymbol{p}_t) \quad (4)$$
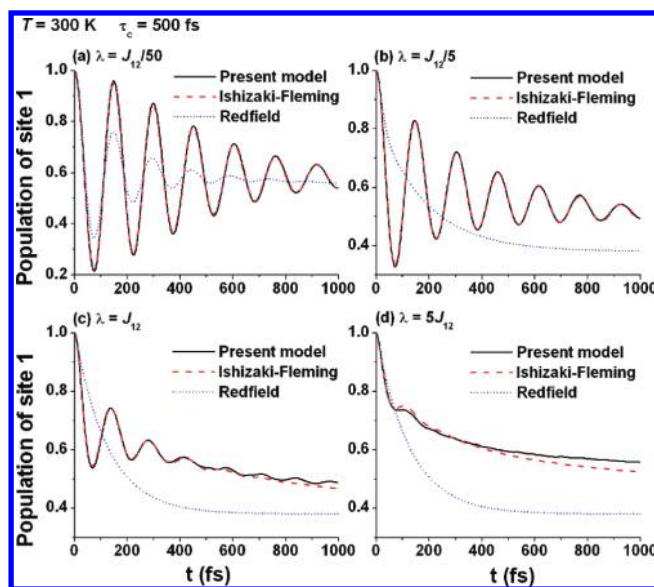

Figure 1. Electronic population dynamics of site 1. The results are calculated by the present semiclassical model for various reorganization energies, in comparison with those by using Ishizaki and Fleming's hierarchy equation approach and Redfield theory taken from ref 7.

The Wigner transform of the density matrix element $\rho_{ii}^{\mathrm{w}}(\boldsymbol{x}_t, \boldsymbol{p}_t)$ and of the Boltzmann operator $\rho_{\mathrm{B}}^{w}(\boldsymbol{Q}_0,\boldsymbol{P}_0)$ can be found in ref 14. We assume the spectra density of phonon modes (for all sites) to be of Debye form

$$J(\omega) = 2\lambda\frac{\omega\tau_{\mathrm{c}}^{-1}}{\omega^2 + \tau_{\mathrm{c}}^{-2}} \quad (5)$$

where the reorganization energy λ represents the coupling strength between the Bchl molecule and phonon bath and τ_{c} is the characteristic time of the phonon bath. We discretize the continuous phonon spectra density eq 5 as done in ref 23; 200 phonon modes are used for each site. Typically 50 000–500 000 trajectories are necessary to obtain converged results in the current applications.

We first consider the simplest model system which contains only two sites plus uncorrelated phonon baths for each site. The difference of the excited electronic energy between two free sites is $\varepsilon_1^0 - \varepsilon_2^0 = 100\ \mathrm{cm}^{-1}$, the site–site electronic coupling is $J_{12} = 100\ \mathrm{cm}^{-1}$, and the bath temperature is 300 K. At time $t = 0$, site 1 is in its excited electronic state, and site 2 is in its ground electronic state, and the time-dependent electronic population of site 1 is calculated for different phonon bath conditions. Figure 1 shows the results for the case in which the characteristic time of the phonon bath is 500 fs, with various reorganization energies. For small reorganization energy, the excitation energy transfers back and forth between two sites, and we observe long-lived electronic coherence. Redfield theory, which is supposed to be valid for small reorganization energies, still underestimates the magnitude of the electronic coherence. Our semiclassical treatment predicts much longer lived quantum coherence than does Redfield theory, in excellent agreement with Ishizaki and Fleming's reduced hierarchy equation approach.[7] Similar
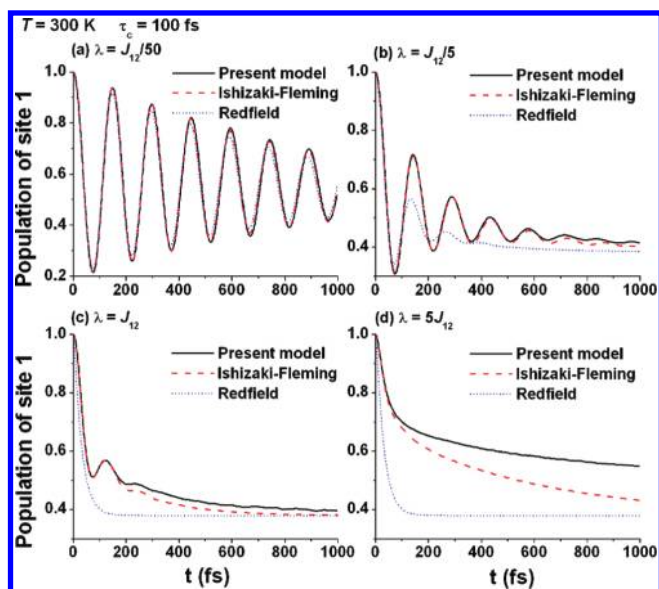
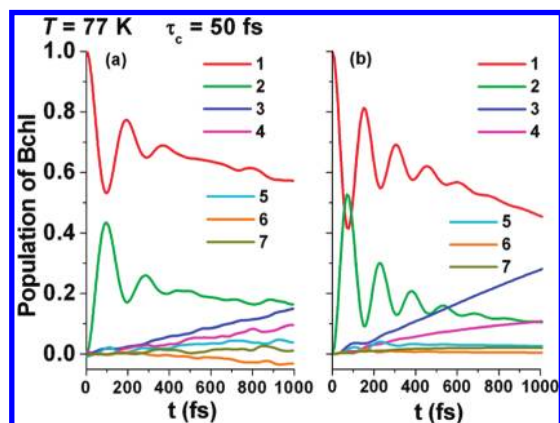**Figure 2.** The same as Figure 1, except for $\tau_c = 100$ fs.

Figure 3. Electronic population dynamics of Bchl molecules. The results are calculated for the seven-site system at $T = 77$ K by using LSC-IVR and the MMST models (a) in comparison with Ishizaki and Fleming's hierarchy equation approach (b) (taken from ref 8). All parameters are the same as those in ref 8.

on negative values at the longest times; this is a typical problem within the LSC-IVR and is an indication of the error given by this approximate version of the SC theory. Further investigation is underway to resolve the origin of these remaining differences.

Quantum coherence appears to play a role in EET in photosynthesis even at physiological temperature. Conventional Redfield theory seems to be insufficient for describing this long-lived coherent dynamics in EET (which is perhaps not unexpected since the time scale of the bath is not faster than that of the system). In this paper, we have demonstrated the feasibility of the LSC-IVR and MMST models for treating quantum coherence in photosynthetic EET. The attractiveness of this approach is that it can be applied to any model for which classical MD simulations are possible, all the way up to a full all-atom MD simulation of the molecular system, treating the electronic and nuclear dynamics on an equivalent basis.

AUTHOR INFORMATION

Corresponding Author:
*To whom correspondence should be addressed. E-mail: millerwh@berkeley.edu.

trends can be found for a faster phonon bath with $\tau_c = 100$ fs (see Figure 2). In all coherent regimes, our results agree very well with those of Ishizaki and Fleming's, though there are some noticeable differences in the incoherent hopping regime (Figure 2d).

We have also carried out preliminary calculations using our approach for the larger system consisting of seven two-state Bchl molecules, all parameters for this model system being the same as those in Figure 1 of ref 8. The initial excitation is at site 1 and the time evolution of the electronic populations of Bchl molecules are shown in Figure 3. (About 50 000 trajectories were sufficient to obtain converged results in this case.) The preliminary results from the semiclassical approach are seen to describe the electronic coherence in this multiple-state system in qualitative agreement with the results in ref 8, though there are some noticeable differences. We also note in Figure 3a that the population of some electronic states takes

REFERENCES

(1) Blankenship, R. E. *Molecular Mechanisms of Photosynthesis*; World Scientific: London, 2002.

(2) van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Scientific: Singapore, 2000.

(3) Engel, G. S.; Calhoun, T. R.; Read, E. L.; Ahn, T.-K.; Mancal, T.; Cheng, Y.-C.; Blankenship, R. E.; Fleming, G. R. Evidence for Wavelike Energy Transfer through Quantum Coherence in Photosynthetic Systems. *Nature* **2007**, *446*, 782–786.

(4) Fenna, R. E.; Matthews, B. W. Chlorophyll Arrangement in a Bacteriochlorophyll Protein from Chlorobium Limicola. *Nature* **1975**, *258*, 573–577.

(5) Redfield, A. G. On the Theory of Relaxation Processes. *IBM J. Res. Dev.* **1957**, *1*, 19–31.

(6) Ishizaki, A.; Fleming, G. R. On the Adequacy of the Redfield Equation and Related Approaches to the Study of Quantum Dynamics in Electronic Energy Transfer. *J. Chem. Phys.* **2009**, *130*, 234110/1–234110/8.

(7) Ishizaki, A.; Fleming, G. R. Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equations Approach. *J. Chem. Phys.* **2009**, *130*, 234111/1–234111/10.

(8) Ishizaki, A.; Fleming, G. R. Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 17255–17260.

(9) Miller, W. H. Spiers Memorial Lecture: Quantum and Semi-classical Theory of Chemical Reaction Rates. *Faraday Discuss. Chem. Soc.* **1998**, *110*, 1–21.

(10) Miller, W. H. The Semiclassical Initial Value Representation: A Potentially Practical Way for Adding Quantum Effects to Classical Molecular Dynamics Simulations. *J. Phys. Chem. A* **2001**, *105*, 2942–2955.

(11) Miller, W. H. Electronically Nonadiabatic Dynamics via Semi-classical Initial Value Methods. *J. Phys. Chem. A* **2009**, *113*, 1405–1415.

(12) Sun, X.; Miller, W. H. Semiclassical Initial Value Representation for Electronically Nonadiabatic Molecular Dynamics. *J. Chem. Phys.* **1997**, *106*, 6346–6353.

(13) Sun, X.; Wang, H.; Miller, W. H. Semiclassical Theory of Electronically Nonadiabatic Dynamics: Results of a Linear-ized Approximation to the Initial Value Representation. *J. Chem. Phys.* **1998**, *109*, 7064–7074.

(14) Wang, H.; Song, X.; Chandler, D.; Miller, W. H. Semiclassical Study of Electronically Nonadiabatic Dynamics in the Con-densed-Phase: Spin-Boson Problem with Debye Spectral Density. *J. Chem. Phys.* **1999**, *110*, 4828–4840.

(15) Ananth, N.; Venkataraman, C.; Miller, W. H. Semiclassical Description of Electronically Nonadiabatic Dynamics via the Initial Value Representation. *J. Chem. Phys.* **2007**, *127*, 084114/1–084114/9.

(16) Meyer, H. D.; Miller, W. H. A Classical Analog for Electronic Degrees of Freedom in Nonadiabatic Collision Processes. *J. Chem. Phys.* **1979**, *70*, 3214–3223.

(17) Stock, G.; Thoss, M. Semiclassical Description of Nonadia-batic Quantum Dynamics. *Phys. Rev. Lett.* **1997**, *78*, 578–581.

(18) Thoss, M.; Stock, G. Mapping Approach to the Semiclassical Description of Nonadiabatic Quantum Dynamics. *Phys. Rev. A* **1999**, *59*, 64–79.

(19) Wang, H.; Sun, X.; Miller, W. H. Semiclassical Approximations for the Calculation of Thermal Rate Constants for Chemical Reactions in Complex Molecular Systems. *J. Chem. Phys.* **1998**, *108*, 9726–9736.

(20) Collini, E.; Scholes, G. D. Coherent Intrachain Energy Migra-tion in a Conjugated Polymer at Room Temperature. *Science* **2009**, *323*, 369–373.

(21) Wigner, E. On the Quantum Correction for Thermodynamic Equilibrium. *Phys. Rev.* **1932**, *40*, 749–759.

(22) Golosov, A. A.; Reichman, D. R. Classical Mapping Ap-proaches for Nonadiabatic Dynamics: Short Time Analysis. *J. Chem. Phys.* **2001**, *114*, 1065–1074.

(23) Wang, H.; Thoss, M.; Sorge, K.; Gelabert, R.; Gimenez, X.; Miller, W. H. Semiclassical Description of Quantum Coherence Effects and Their Quenching: A Forward—Back-ward Initial Value Representation Study. *J. Chem. Phys.* **2001**, *114*, 2562–2571.