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Letter

Explaining the Efficiency of Photosynthesis: Quantum Uncertainty or Classical Vibrations?

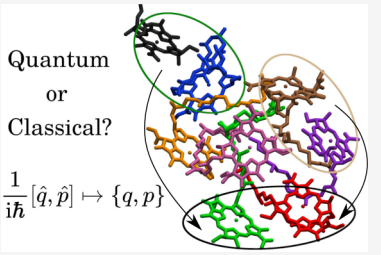
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ABSTRACT: Photosynthetic organisms are known to use a mechanism of vibrationally assisted exciton energy transfer to efficiently harvest energy from light. The importance of quantum effects in this mechanism is a long-standing topic of debate, which has traditionally focused on the role of excitonic coherences. Here, we address another recent claim: that the efficient energy transfer in the Fenna−Matthews−Olson complex relies on nuclear quantum uncertainty and would not function if the vibrations were classical. We present a counter-example to this claim, showing by trajectory-based simulations that a description in terms of quantum electrons and classical nuclei is indeed sufficient to describe the funneling of energy to the reaction center. We analyze and compare these findings to previous classical-nuclear approximations that predicted the absence of an energy funnel and conclude that the key difference and the reason for the discrepancy is the ability of the trajectories to properly account for Newton's third law.



Photosynthesis provides the energy that underpins nearly all life on Earth. Its remarkable efficiency is partly due to the success of light-harvesting antenna complexes at funneling the excitation energy from captured photons to a reaction center, where conversion to chemical energy takes place.[1,2] A question that remains controversial is whether or not this "energy funnel" has an exclusively quantum-mechanical mechanism. In particular, it has been proposed that the vibrations that mediate the flow of energy between pigments exhibit nontrivial quantum effects, suggesting that the Heisenberg uncertainty principle plays a key role in explaining the efficiency of photosynthesis. It is the aim of the present article to examine this hypothesis in a typical light-harvesting complex.

The idea that nontrivial quantum-mechanical effects, such as tunneling, delocalization, and entanglement, could play a vital role in explaining biological function, has attracted scientists since the early days of quantum theory.[3,4] In recent decades, the development of specialized experimental and theoretical tools has allowed scientists to seriously investigate this question. Much of the recent debate in the area of photosynthetic light harvesting was stimulated by experimentally observed oscillations in 2D-spectroscopic studies of the Fenna−Matthews−Olson (FMO) complex found in green sulfur bacteria.[5] Originally, it was suggested that these oscillations were indicative of long-lived quantum coherences, which were thought to be responsible for the efficient energy transfer in FMO. This hypothesis instigated over a decade of extensive debate about the quantum nature of these coherences[6−8] and was recently reviewed by Cao et al.[9] The review summarizes the progress that has been made to reach the current consensus: that the oscillations observed in electronic 2D spectra of the FMO complex are now no longer believed to indicate interexcitonic coherences and that such coherences are too short-lived to contribute to the efficiency of photosynthesis.

However, the review highlights the vibrational motion as another area where uniquely quantum-mechanical effects are nevertheless believed to be essential.[9] The vibrational motion is responsible for site-energy fluctuations of the same order of magnitude as the energy gaps and is therefore clearly a crucial part of the energy-transfer mechanism irrespective of the importance of quantum-mechanical effects. The quantum nature of these vibrations and their relevance for efficient exciton energy transfer have been extensively discussed in the literature.[10−13] Here, we focus on the specific claim that quantum uncertainty between the nuclear positions and momenta is necessary to ensure the directed flow of energy after photoexcitation.[9,14,15] This conclusion is based on an interpretation of secular Redfield theory,[16] which is a commonly used theoretical tool for describing excitonic systems such as FMO. In this interpretation, certain contributions to the rate of excitonic population transfer are associated with quantum uncertainty between the nuclear coordinates and momenta, and it is argued that in the absence of these contributions, the energy funnel that is essential to light-harvesting systems breaks down. Thus, the review concludes that in a world of quantum electrons and classical nuclei, there would be no preferential "downhill" flow of energy in light-harvesting complexes.[9]

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This conclusion is perhaps surprising, in particular given the success of models that use classical nuclei to both qualitatively and quantitatively describe many chemical and biological systems.[17,18] It would seem to imply that light harvesting is an anomalous case where the quantum-mechanical properties of nuclei play a more important role than in many other biological systems. Such a conclusion needs to be carefully analyzed, since it risks creating the impression that a full simulation (beyond the perturbative approximation inherent in Redfield theory) may require expensive computational resources, such as quantum computers.[19−21] However, in reality, the same may well be achievable with simpler algorithms on classical computers.

It is therefore important to clarify the role of quantum uncertainty in light harvesting. Behind the discussion, there is an even deeper question: what does it actually mean to say that a process is fundamentally quantum mechanical? The difficulty one faces in answering this question is that quantum mechanics forms the foundation of our theoretical understanding of the world at the molecular level. Hence, in a sense, all of biology could be described as fundamentally quantum mechanical. However, this is clearly not a useful description. Instead, we work on the basis that it is only meaningful to say that something is fundamentally quantum mechanical, if it cannot be explained using a classical model.

In this article, we investigate whether the energy funnel in light-harvesting complexes can be described using an entirely classical model of nuclear motion, with no need to invoke quantum uncertainty in the nuclear degrees of freedom. We begin by reviewing previous arguments in favor of the importance of quantum uncertainty, although we show that the conclusion depends on how one performs the analysis. We then discuss alternative approaches to answer the question in the context of mixed quantum−classical dynamics, focusing on a recently developed technique based purely on Newtonian mechanics. With this method, we explicitly simulate the same physical model of the FMO complex as Cao et al.[9] Using the results of these simulations, in conjunction with a detailed analysis of Redfield theory, we demonstrate that the energy funnel can indeed be described classically and show that the inability of previous classical methods to describe the energy funnel is due to an extra approximation that breaks Newton's third law. We conclude with a discussion of the additional physical insight provided by our explicit simulation method, with particular focus on the accuracy of the common assumptions of weak coupling between the excitonic states and the nuclear environment as well as the Markovian relaxation of the environment.

Model. In order to provide a concrete example to illustrate our discussion, we consider a specific application to the same model of the FMO complex that was studied by Cao et al. in ref 9. While our findings regarding the quantitative importance of nuclear quantum effects are necessarily system-dependent, our conclusions regarding the role of quantum uncertainty in obtaining an appropriate classical limit apply more generally.

The FMO complex is known to efficiently transfer excitation energy from the baseplate, where photoexcitation takes place, to the reaction center, where the subsequent steps of photosynthesis ensue. The model (see Figure 1) consists of eight excitonic states coupled to a bath of nuclear vibrational degrees of freedom whose spectral density has been determined experimentally (the model is fully defined in Section S1 of the Supporting Information). We are interested in the relaxation dynamics of the excitonic populations, given an initial state of

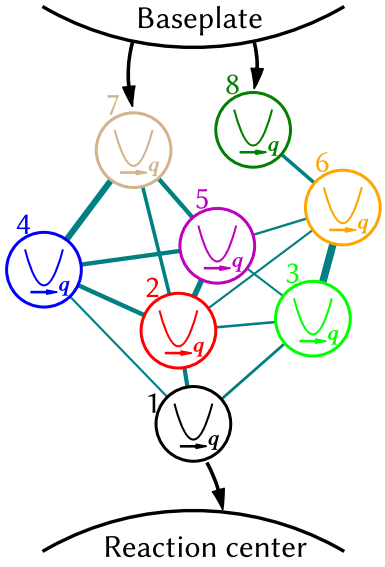


Figure 1. Schematic depiction of energy transfer through the FMO complex. The complex is modeled by eight excitonic states (colored circles) that are coupled through a set of vibrational modes. The vertical positions of the circles represent the exciton energies. To quantify the effective interexciton couplings (teal lines), the line thickness indicates the root-mean-square of the corresponding exciton−bath coupling, where the bath modes follow a classical Boltzmann distribution, and only the dominant couplings are shown. Following an initial transfer from the baseplate, principally to the high-energy excitons 8 and 7, the excitation energy is funneled toward the low-energy excitons by means of the vibronic couplings. Eventually, the excitation undergoes a transfer to the reaction center; this trapping step is not included in the present simulation, as it occurs on a much slower time scale.

the system that corresponds to the state of the complex after incoherent exciton transfer from the baseplate. To facilitate reproducibility, we have fixed the initial populations by their disorder-averaged values, which is a minor simplification compared to ref 9 but one that does not result in a significant change to the dynamics and hence does not affect any of the conclusions drawn. The interplay between vibrational and excitonic motion creates a "funnel" from high- to low-energy excitons and thereby from the baseplate to the reaction center. The question of debate is whether or not quantum effects in the vibrational motion are important for this energy transfer.

To address this question, we analyze two different strategies for simulating the dynamics in the FMO model. First, we discuss Redfield theory, whose classical limit according to previous studies does not correctly describe the energy funnel.[9,14,15] Second, we consider a mixed quantum−classical trajectory approach, which (as we demonstrate) is able to capture the energy funnel even though classical vibrational motion is treated explicitly with Newtonian equations of motion. We then compare the approximations behind the two strategies and discuss how to define a more appropriate classical limit of Redfield theory that is free from the previous problems.

Redfield theory. The conclusion reached by previous studies, that light-harvesting complexes would not function in a world with classical nuclei, is based on an interpretation of analytical rate theories.[9,14,15,22] Here, we concentrate on Redfield theory,[9,14] for which this analysis was first made, although note that similar arguments have been made in the context of Förster theory[22] and modified Redfield theory.[15] To derive the

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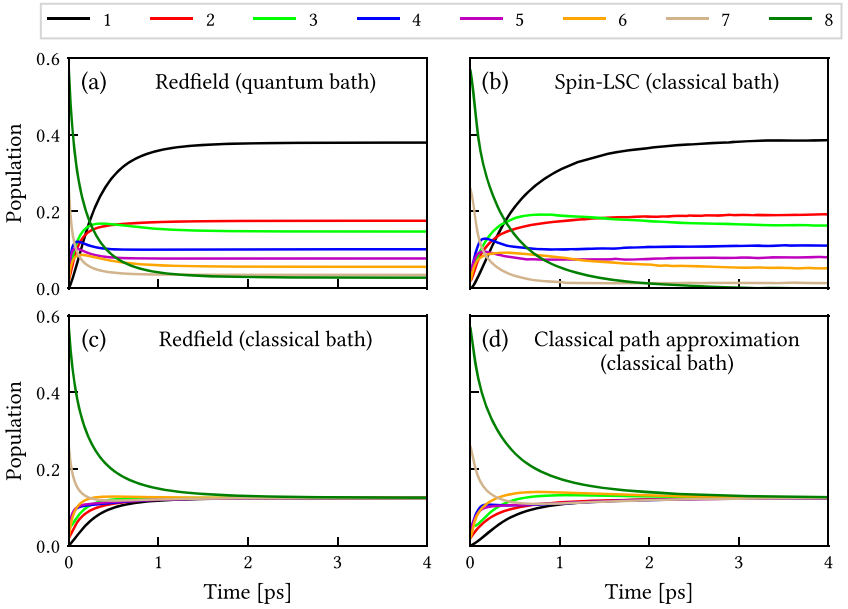


Figure 2. Exciton population dynamics in FMO following an initial incoherent transfer from the baseplate. Previous studies based on Redfield theory[9] have reported a decisive difference between quantum (a) and classical (c) treatments of the bath. Using a mixed quantum−classical description of the full dynamics, it is possible to describe the correct thermalization using a classical bath (b). The failure observed in (c) is explained by the ground-state classical path approximation (d) rather than a lack of quantum uncertainty.

Redfield master equation from a fully quantum-mechanical expression for the time-dependence of the excitonic populations,[23−26] one makes two approximations: (i) the Markov approximation, which amounts to assuming that the dynamics can be described using rate constants; (ii) the Born approximation, which treats the coupling between the (electronic) system and (nuclear) bath as a weak parameter and uses second-order perturbation theory to obtain explicit expressions for the rate constants in terms of time integrals of bath correlation functions.

By analyzing the Redfield rate constants, it has been argued that quantum uncertainty is necessary for the biological function of light-harvesting complexes.[9,14] In this analysis, a "classical" approximation to Redfield theory is defined by replacing quantum expectation values of the nuclear degrees of freedom, such as $\langle \hat{q}_\xi^2 \rangle$, by their classical counterparts, i.e., phase-space averages. Importantly, the conclusion relies on identifying a term in the Redfield rate expression containing $\langle [\hat{q}_\xi, \hat{p}_\xi] \rangle$ (the expectation value of the commutator between nuclear coordinates and momenta) as originating from the Heisenberg uncertainty principle and hence being fundamentally quantum mechanical. It is thus proposed to neglect this term in the classical case, which results in classical rate constants that do not obey detailed balance.

Panels (a) and (c) of Figure 2 show the results of applying the quantum Redfield theory and the "classical" theory described above. The exciton dynamics we obtain closely match those of ref 9 in both cases, confirming that the simplified initial conditions used here do not make a significant difference to the results. One sees that quantum Redfield theory correctly predicts transfer of excitonic population through the energy funnel from the high-energy exciton states close to the baseplate (states 7 and 8) to the low-energy exciton state close to the reaction center (state 1). In contrast, the "classical" Redfield theory predicts equal population of all exciton states at long time. This illustrates that taking the classical limit

$$\langle [\hat{q}_\xi, \hat{p}_\xi] \rangle \overset{\text{cl}}{=} 0 \tag{1}$$

results in a breakdown of the energy funnel and hence seems to support the argument that quantum uncertainty in the nuclear degrees of freedom is essential to the function of light-harvesting complexes.[9,14] A similar analysis based on Förster theory has led to the same conclusion.[22]

Crucially, this conclusion rests on the identification of the classical limit with eq 1. This may seem perfectly natural when one identifies a nonzero commutator with quantum uncertainty. However, this is not the only possible classical limit one could take. If one instead uses Dirac's famous correspondence between quantum-mechanical commutators and classical Poisson brackets[27] $\frac{1}{i\hbar}[\hat{A}, \hat{B}] \overset{\text{cl}}{=} \{A, B\}$, one arrives at a very different conclusion. In this case, the expectation value remains unchanged between quantum and classical mechanics

$$\frac{1}{i\hbar}\langle [\hat{q}_\xi, \hat{p}_\xi] \rangle \overset{\text{cl}}{=} \langle \{q_\xi, p_\xi\} \rangle_{\text{cl}} = 1 \tag{2}$$

The first of these two choices (eq 1) makes more sense when one thinks about $\langle [\hat{q}_\xi, \hat{p}_\xi] \rangle$ in terms of the quantum uncertainty principle. However, the second (eq 2) is more natural if one considers this term as arising from a time derivative. Since all the equations of motion in quantum mechanics can be written in terms of commutators of quantum observables, we clearly cannot set them all to zero, as this would result in a classical limit where everything was stationary! It is not immediately obvious which of these two interpretations is appropriate in our particular case, and this illustrates the difficulty that can arise when trying to determine whether a phenomenon is fundamentally quantum mechanical by analysis of the quantum mechanics alone. In the following section, we resolve this ambiguity by considering a microscopic description of the system in which the vibrations are treated entirely classically.

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Mixed quantum−classical dynamics. At this point, it is important to discuss what constitutes a classical, rather than quantum, description of the nuclear vibrations in photosynthetic energy transfer. A natural requirement for a classical description of the nuclei is that it should consist of a single position and momentum variable per nuclear degree of freedom and that these should evolve under Newtonian equations of motion.

It is, however, a delicate issue to rigorously unify the classical motion of the nuclei with the quantum dynamics of the electrons.[28] A wide range of approximate techniques have been developed that can be broadly classified into *surface-hopping methods* and *mapping methods*. The former involves stochastic hops between potential-energy surfaces, reminiscent of the Copenhagen interpretation of the collapsing wave function.[18,29,30] However, one might argue that, due to the stochastic nature of the hopping, this type of description is not entirely classical. In contrast, mapping approaches effectively utilize the equivalence of the dynamics of the electronic wave function with the linear equations of motion of a set of classical harmonic oscillators,[6,31−33] allowing both electronic and nuclear motion to be treated with Newtonian equations of motion. It has been demonstrated that several classical mapping approaches accurately describe the dynamics of light-harvesting complexes (although typically simpler models than the one examined in this work were used, with only seven sites coupled to Debye baths without static disorder).[34−43] In light of these findings, it appears contradictory that quantum uncertainty of the nuclei would be essential for the functioning of the energy funnel. In the following, we resolve this apparent paradox by carefully analyzing the properties of a mapping-based approach and comparing these to the assumptions behind the classical approximation to Redfield theory.

Another requirement of a classical description is that the positions and momenta obey classical Boltzmann statistics. This is in contrast to the use of the Wigner distribution, which includes some of the effects of quantum uncertainty and is commonly used to initialize mixed quantum−classical simulations of FMO.[36,37,39−41] Since we want to treat the vibrations fully classically, we shall in this paper instead initialize the simulation from a classical Boltzmann distribution.

There exist a range of different mapping approaches that can all be considered classical, since they consist only of Newtonian trajectories. However, these methods do not necessarily give comparably accurate results, for reasons that will be discussed in detail later. Discrepancies between the classical and quantum results may either indicate that the process is inherently quantum mechanical or simply that the accuracy of the mapping approach is not sufficient. It is therefore important to employ one of the classical mapping methods that demonstrates a higher accuracy.

The method we will make use of in the following is called the "generalized spin-mapping" approach.[40] In this approach, the nuclear operators are replaced by phase-space variables, and the Hilbert space of electronic states is mapped to a phase space of "electronic" positions and momenta. The latter are proportional to the real and imaginary parts of the coefficients of the electronic wave function, and the proportionality factor is chosen such that classical phase-space integrals agree with quantum-mechanical traces according to the Stratonovich−Weyl correspondence rules.[44] For a two-level system, one can interpret this procedure in terms of a classical spin $S = \frac{1}{2}$ with the quantum magnitude $\sqrt{S(S+1)} = \frac{\sqrt{3}}{2}$,[45,46] and the idea behind generalized spin mapping is to extend the spin analogy to multiple levels (for details, see Section S3 of the Supporting Information).

The mapping leads to a classical Hamiltonian for both the nuclear and electronic phase-space variables, which is used to propagate trajectories of the mixed electronic−nuclear problem. As with other mapping approaches, the classical dynamics of these trajectories constitute an approximation that can be derived from a linearization of the quantum propagator.[41,47,48] There are two main ways to make this approximation: the "fully linearized" spin-LSC (linearized semiclassical), which leads to entirely classical dynamics, and the "partially linearized" spin-PLDM (partially linearized density matrix), which retains interferences between forward and backward paths in the electronic variables, beyond a classical description. Since we want to assess the applicability of classical dynamics to light-harvesting complexes, we will in the following concentrate on the fully linearized approximation.

Figure 2(b) shows the population dynamics for the FMO model calculated using spin-LSC. One can immediately see that, unlike the "classical" Redfield results in panel (c), the spin-LSC approach correctly captures the transfer of excitonic population from the high-energy exciton states to the low-energy exciton states in the long-time limit. It is clear that this entirely classical description of the nuclei agrees at least qualitatively with the quantum Redfield dynamics in panel (a), apart from a slight difference in the time scales that we shall come back to later. This finding stands in stark contrast to the claim that there could be no energy funnel in a world of classical nuclei and quantum electrons and demonstrates that quantum uncertainty in the nuclei is not necessary to explain the energy funnel.

While the success of the mapping results in describing the energy funnel in the FMO complex is compelling evidence that quantum uncertainty is not necessary, it raises the question: why does the "classical" Redfield theory (panel (c)) fail to capture this phenomenon? If we are correct that quantum uncertainty in the nuclei is not necessary to capture the phenomenon, then this implies that there must be an additional approximation that is being made in the "classical" Redfield theory. A detailed theoretical analysis is given in the Supporting Information (Section S2), and here, we simply summarize the results.

The Redfield master equation is (within the secular approximation) simply a system of first-order rate equations between the excitonic states. Starting from the full expression for the population dynamics and applying the Born and Markov approximations, one finds that the expression for the rate constants consists of two terms. The first term involves the correlation of the time derivative of an initial system population with a time derivative of a system population at later time. The second term involves the correlation of the time derivative of the initial bath density with the time derivative of a system population at later time. Importantly, because this second term involves the time derivative of the bath density, it gives rise to a commutator between bath variables. It is precisely this resulting commutator that is set to zero in the "classical" Redfield theory. Neglecting this term is equivalent to assuming that the bath density does not change with time and hence feels no effect of interaction with the system. Hence, in addition to treating the nuclei classically, the "classical" Redfield theory effectively assumes that the nuclei move as if they were on the ground state rather than responding to changes in the electronic state.

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It is this additional approximation that is responsible for the lack of proper thermalization in "classical" Redfield theory. To see this, we have reproduced the problem numerically by neglecting the analogous terms in the mapping framework. The resulting theory is formally equivalent to the so-called ground-state classical path approximation,[49−52] which has been frequently used in QM/MM simulations of FMO and other light-harvesting complexes.[53−56] Figure 2(d) shows the results of applying this method to describe the exciton dynamics. It can be seen that it leads to the same failure as "classical" Redfield theory, with all excitonic states becoming equally populated in the long-time limit. By ignoring the effect of the system on the bath, the bath acts as an infinite source of energy that drives the system to the maximally mixed state. The results demonstrate the importance of correctly capturing the resulting "back" reaction of the nuclear environment on the excitonic system when describing population transfer—or in other words, the importance of respecting Newton's third law, that "every action has an equal and opposite reaction".

Based on the discussion above, one may define an alternative classical limit of Redfield theory by instead replacing commutators by Poisson brackets (as in eq 2), while still approximating $\langle \hat{q}_\xi^2 \rangle$ by a classical phase-space average. This satisfies detailed balance to first order in $\beta = 1/k_B T$ (Section S2.3), which is sufficient to recover the correct qualitative behavior in the FMO case (Figure S3). Our conclusions about the energy funnel can therefore also be understood in the context of Redfield theory, provided that this alternative classical limit is used.

We now return to the difference in time scale between panels (a) and (b), which one may note is similar to the difference between panels (c) and (d). This suggests that the faster transfer rate observed in Redfield theory is not, as one might have first thought, a matter of quantum vibrations either. Instead, it can be attributed predominantly to the weak-coupling approximation made by Redfield theory that is not present in the spin-mapping framework. To show this, we apply the partially linearized spin-PLDM method (defined in Section S4) initialized by a Wigner distribution, which is exact in the weak-coupling limit (Section S4.1). In a scenario where the system−bath coupling is reduced, spin-PLDM and Redfield indeed approach the same result (Figure S5). However, spin-PLDM and Redfield give different results for the original coupling, which implies that the weak-coupling assumption is not valid in this case. This observation is in line with previous discussions about the validity of perturbative approaches in systems like FMO.[57] Note that the Markovian approximation *is* valid, as demonstrated by the similarity of the results of a (non-Markovian) generalized master equation (Figure S2). Since spin-PLDM agrees closely with spin-LSC (Figure S6), and spin-PLDM is known to be close to full quantum accuracy for similar systems,[41,42] we expect panel (b) to be a more accurate approximation of the full quantum dynamics than panel (a).

Although mixed quantum−classical approaches can provide an accurate description of exciton dynamics, they do not necessarily reproduce all features of a fully quantum description. For example, it is well-known that such approaches lead to the wrong thermalization of the bath,[58,59] at least for high-frequency modes ($\hbar\omega \gg k_B T$) where classical and quantum statistics differ. The importance of quantum statistics can be assessed by starting the classical simulation from a Wigner initial distribution of coordinates and momenta, which includes quantum uncertainty. However, we observe that this barely changes the population dynamics compared to a classical Boltzmann distribution at room temperature (Figure S4).

Note that not all mixed quantum−classical methods can treat detailed balance as accurately as spin-LSC does and may therefore lead to less accurate results than seen in Figure 2(b). This error is associated with the inconsistency between the evolution of classical trajectories and the appropriate phase-space representation of the quantum system.[60,61] For example, the commonly used Ehrenfest approximation is also known to give inadequate thermalization,[62,63] as shown for the present model in Figure 3. In fact, one can show that Ehrenfest predicts

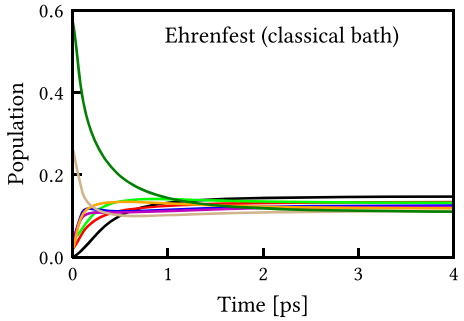


Figure 3. Same situation as in Figure 2 computed with Ehrenfest dynamics.

final population differences that are approximately a factor $F + 1$ too small (Section S3.1 of the Supporting Information), where F is the number of levels ($F = 8$ in the present model). Since the classical initial distribution of the nuclei is identical in Ehrenfest and spin-LSC, and the equations of motion have the same form, it is clear that the difference has nothing to do with the quantum-mechanical nature of the nuclei but of the ability of the nonadiabatic method to describe the "back" reaction. The advantage of the spin-LSC method is that its long-time limit is at least correct to first order in β (Section S3.1).

Conversely, spin-LSC is likely not the only mixed quantum−classical method that would be able to describe the energy funnel in this model. A few other mapping-based methods have proven to be comparably accurate, such as the symmetric quasiclassical (SQC) windowing approach,[33,36,63] modified linearized approaches for the Meyer−Miller−Stock−Thoss mapping,[39] partially linearized density matrix (PLDM) dynamics,[37,64,65] and even Ehrenfest dynamics when used in conjunction with the generalized quantum master equation.[66] Like us, previous studies using simulations of a different mapping approach (based on non-Hamiltonian trajectories) found negligible differences between Boltzmann and Wigner sampling on the dynamics in exciton transfer models at room temperature.[38] Since these other methods have reported results of comparable accuracy for simpler FMO models, we expect that they would lead to the same conclusion also for the more realistic model considered in this article.

Discussion. In this article, we have analyzed the importance of nuclear quantum uncertainty for the energy funnel in photosynthesis. With the example of FMO, we have demonstrated that an entirely classical description of vibrational motion is sufficient to explain the functionality of light-harvesting complexes. However, not all classical approximations are equally valid, especially in how accurately they describe the "back" reaction. The mapping framework provides a tool to systematically define the classical limit of quantum dynamics. Fully linearized

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dynamics, such as spin-LSC, constitute a classical description where both nuclear and electronic motion are treated on the same footing, and their accuracy can be further improved by partially linearized methods such as spin-PLDM. Crucially, the mapping framework leads to a qualitatively different classical limit than had previously been proposed on the grounds of Redfield theory. We have resolved this apparent paradox by noting that, within the original classical Redfield theory, the nuclei do not respond to changes in the electronic state, whereas in the mapping approach they do. By a careful analysis, we have shown how to define an alternative classical limit of Redfield theory that removes this additional approximation and, hence, is also able to recover the energy funnel.

The analysis demonstrates that the energy funnel in photosynthesis requires detailed balance between the quantized electronic states but not necessarily nuclear quantum uncertainty. Although the simulations in this paper concerned the particular example of FMO, the main conclusion, that the commutator $\langle[\hat{q}_\xi, \hat{p}_\xi]\rangle$ should not be interpreted as nuclear quantum uncertainty, applies more generally to other light-harvesting complexes. Note, however, that nuclear quantum effects (for instance in the term $\langle\hat{q}_\xi^2\rangle$) may still be important for quantitatively describing the dynamics of light-harvesting complexes in certain cases. According to Redfield theory, the relevant vibrations are those that are close to resonance with the interexciton energy gaps. For FMO, these gaps are on the order of k_BT, which is why the bath can be well approximated using classical statistics. For complexes with larger energy gaps, such as LH2[67] or PE545,[68] quantum features such as nuclear zero-point energy are likely to play a more important role. The development of trajectory-based methods that can properly treat nuclear quantum effects is an area of ongoing research.

METHODS

The Frenkel-exciton model parameters (Section S1) were chosen as in ref 9 and consisted of eight chromophoric sites coupled to independent and identical baths with an experimentally measured spectral density.[69] The site energies and couplings refer to the holo form of the FMO protein found in *P. aestuarii* determined by Schmidt am Busch et al.[70] Static disorder was included in the Hamiltonian by sampling normally distributed site energies based on spectral fits from ref 71. The initial state describing the incoherent transfer from the baseplate was assumed to be the same for all samples, which is a simplification compared to ref 9 that leads to similar qualitative behavior and facilitates reproducibility of the results. All simulations used a temperature of 300 K.

The spin-mapping dynamics (Section S3) were generated using a bath discretized into 100 modes per site, following the discretization scheme in ref 72, and a time step of 1 fs. This discretization included bath frequencies up to 500 cm^{-1}; higher frequencies are known to have a negligible impact on the dynamics.[73] The results in Figure 2(b) use fully linearized dynamics that were validated against more accurate partially linearized dynamics (Figure S6). To assess the weak-coupling limit, partially linearized dynamics were compared against Redfield theory for a reduced system−bath coupling (Figure S5). To minimize statistical errors, the spin-LSC simulation was averaged over 10^6 trajectories, but the qualitative behavior can be seen already with 10^3. The average is taken over both initial electronic and nuclear variables as well as static disorder in the Hamiltonian. The initial nuclear variables were sampled from a classical Boltzmann distribution of the ground state. The electronic variables were sampled from full-sphere initial conditions for linearized dynamics (although focused initial conditions were found to give the same result) and focused initial conditions for partially linearized dynamics.[40,42] It was verified that the simulations are converged with respect to time step, number of modes, and number of trajectories. The Redfield simulations (Section S2) used a Markovian and secular approximation in the exciton basis and were averaged over 10^4 samples of static disorder in the Hamiltonian.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c00538.

File containing the employed discretization of the spectral density and files containing the raw population data plotted in each figure (ZIP)

Additional details on the FMO model, Redfield theory and the employed methods (PDF)

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Notes

The authors declare no competing financial interest.

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