

Dissertation

**Light-Driven Dynamics in Molecular Aggregates:
Energy Transfer and Charge-Separation Processes**

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Light-Driven Dynamics in Molecular Aggregates: Energy Transfer and Charge-Separation Processes

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Abstract

Converting light into usable chemical or electrical energy remains a central challenge for a clean and sustainable future. Nature uses photosynthesis in sophisticated molecular architectures to accomplish this process, whereas most human-made organic photovoltaics process light using donor–acceptor systems. In both cases, molecular mechanisms are exploited that involve energy transfer and charge-separation processes in complex molecular aggregates. Understanding the physical principles underlying these phenomena requires a theoretical framework capable of describing excitation dynamics with microscopic precision.

The real-time formulation of time-dependent density functional theory (TDDFT) provides the computational efficiency needed to simulate light-driven dynamics in large-scale supramolecular systems with atomic-scale spatial and temporal resolution. Since this theoretical framework, however, propagates the time-dependent electron density rather than the many-body wavefunction, wavefunction-based observables cannot be used to trace the evolution of the excitation energy. We circumvent this limitation by proposing several measures based on the time-dependent density that allow us to analyze the spatial distribution of excitation energy on a first-principles basis, i.e., without requiring an a priori partitioning of the system. Using chains of sodium dimers as proof-of-concept systems, we validate these measures and additionally demonstrate how nuclear motion within Ehrenfest dynamics can drive directed excitation-energy transfer.

Building on the insights of this concept study, we investigate the coupled electron-nuclear dynamics of a real-world system—the B850 light-harvesting antenna ring of the purple bacterium *Rhodoblastus acidophilus*. This supramolecular ring is an assembly of 18 bacteriochlorophylls. An analysis of excitation dynamics in systems of this size poses a significant computational challenge, which is now within reach using real-time TDDFT. We simulate the dynamics within the B850 ring upon excitation by a short laser pulse and reveal that this pulse initially triggers a delocalized excitation with characteristics similar to those of the exciton states that are also the most relevant in the natural sunlight-driven process. On a time scale of about 40 fs, however, transient patterns appear in which the excitation energy is localized on ring segments of just a few bacteriochlorophylls. Simulations with and without nuclear dynamics reveal that quantum interference of multiple exciton states gives rise to these localization patterns, and on the same time scale, nuclear motion further enhances this localization effect. These results shed light on the time-resolved dynamics in the B850 ring upon excitation and highlight the interplay between electronic excitation and nuclear motion.

The focus of this thesis then shifts from biological systems to artificial materials for light conversion. We investigate a novel organic donor–acceptor combination using phenothiazine and naphthalenediimide derivatives and assess its potential for organic photovoltaic devices. Using linear-response TDDFT, we calculate the optoelectronic properties of the donor–acceptor interface using molecular models. Our simulations reveal multiple charge-transfer excitations with varying electron-hole separations; the lowest-energy excited state (≈ 1.5 eV) is optically accessible and

shows a charge transfer directly at the donor–acceptor interface, while other states show charge transfer across multiple molecules. Born–Oppenheimer molecular dynamics simulations of the complex demonstrate that ambient structural fluctuations lead to a significant energetic overlap between the states, thereby suggesting a viable pathway for charge dissociation away from the interface.

Finally, we implement a computational framework that interfaces semiclassical dynamics with electronic structure calculations to access nonadiabatic dynamics simulations for such complex donor–acceptor systems. Its capabilities are demonstrated in a charge-transfer system in which a photoexcited zinc phthalocyanine molecule donates charge to a buckminsterfullerene. This tool paves the way for future computational studies of excitation dynamics in large-scale molecular aggregates, offering insights for the design of robust artificial light-harvesting systems.

Kurzdarstellung

Die Umwandlung von Licht in nutzbare chemische oder elektrische Energie ist eine der zentralen Herausforderungen für eine saubere und nachhaltige Zukunft. Die Natur führt diese Umwandlung mit Photosynthese durch und verwendet dafür komplexe molekulare Architekturen, wohingegen menschengemachte organische Photovoltaiksysteme diesen Prozess mit Donor-Akzeptor-Komplexen durchführen. In beiden Fällen werden molekulare Mechanismen benutzt, die Energietransfer und Ladungsseparation in komplexen Molekülaggregaten involvieren. Um die unterliegenden physikalischen Prinzipien dieser Phänomene zu verstehen, wird ein theoretisches Framework benötigt, mit dem man die Anregungsdynamik mit mikroskopischer Genauigkeit untersuchen kann.

Die Echtzeitformulierung der zeitabhängigen Dichtefunktionaltheorie (TDDFT) liefert die rechnerische Effizienz, um lichtgetriebene Dynamiken in großskaligen Supramolekülen mit atomarer Raum- und Zeitauflösung zu simulieren. Da dieses Framework allerdings nur die elektronische Dichte statt einer Vielteilchen-Wellenfunktion propagiert, können keine wellenfunktionsbasierten Observablen verwendet werden, um die Evolution der Anregungsenergie zu verfolgen. Um diese Limitierung zu umgehen, stellen wir mehrere dichtebasierte Anregungsenergiemaße in dieser Arbeit vor, mit denen wir die räumliche Verteilung der Anregungsenergie quantifizieren können, ohne Annahmen über die Struktur, wie zum Beispiel eine Partitionierung der Moleküle, zu treffen. Wir validieren diese Maße mit Konzeptstudien von Ketten aus Natriumdimeren und zeigen, wie die Kerndynamik im Rahmen von Ehrenfest-Dynamik directionalen Energietransfer treiben kann.

Basierend auf der Konzeptstudie simulieren wir die gekoppelte Elektron-Kern-Dynamik in einem realen System – dem B850-Antennenring des lichtsammelnden Purpurbakteriums *Rhodoblastus acidophilus*. Die Analyse der Anregungsdynamik auf quantenmechanischer Skala in solch einem supramolekularen Ring, bestehend aus 18 Bakteriochlorophyllen, stellt eine erhebliche rechnerische Herausforderung dar, die nun mit Echtzeit-TDDFT und einer Gitterdarstellung in numerische Reichweite kommt. Wir simulieren die Dynamik im B850-Ring nach Anregung mit einem kurzen Laserpuls und zeigen auf, dass dieser delokalisierte Zustände anregt, deren Charakteristik den relevanten Exzitonenzuständen unter natürlicher Sonnenlichteinstrahlung entspricht. Auf einer Zeitskala von circa 40 fs werden dann transiente Muster sichtbar, bei denen die Anregungsenergie auf ein paar wenige Bakteriochlorophyllen lokalisiert. Vergleicht man Simulationen mit und ohne Kerndynamik, wird sichtbar, dass diese Lokalisierungsmuster einerseits durch Quanteninterferenz verschiedener Exzitonenzustände entsteht und andererseits führt die Kerndynamik zusätzlich zu einer Verstärkung des Lokalisierungseffekts auf der gleichen ultraschnellen Zeitskala. Diese Ergebnisse geben Einblicke in die zeitliche Dynamik der Anregung und verdeutlichen, wie wichtig das Wechselspiel zwischen Elektronen- und Kerndynamik für den Anregungsenergietransfer ist.

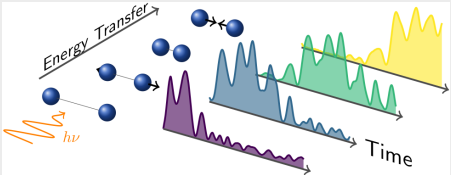
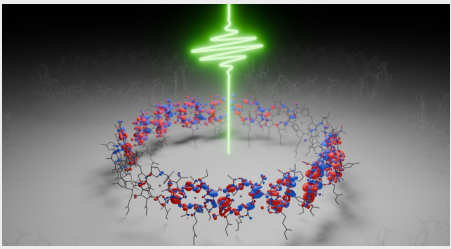
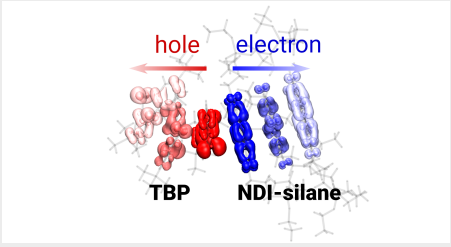
Anknüpfend an die Untersuchung biologischer Systeme widmet sich diese Dissertation der

Entwicklung künstlicher Materialien zur Lichtumwandlung. Wir untersuchen eine neue Donor-Akzeptor-Kombination aus Derivaten von Phenothiazin und Naphthalenediimid auf ihr Potential in organischen Photovoltaikgeräten. Unter Verwendung von *linear-response* Dichtefunktionaltheorie berechnen wir die optoelektronischen Eigenschaften der Donor-Akzeptor-Grenzschicht mit molekularen Modellen. Unsere Simulationen zeigen mehrere Ladungstransferzustände auf, bei denen das Elektron und das Loch der Anregung unterschiedlich weit entfernt sind, wobei die energetisch niedrigste Anregung bei circa 1.5 eV liegt und einen Ladungstransfer direkt an der Grenzschicht aufweist. Born-Oppenheimer Molekulardynamik-Simulationen des Komplexes zeigen, dass die strukturellen Fluktuationen bei Raumtemperatur zu deutlichen energetischen Überlappungen der Zustände führen und damit einen möglichen Pfad aufzeigen, wie Ladung von der Grenzschicht wegdiffundiert werden kann.

Abschließend präsentieren wir eine neue Software, die eine Schnittstelle zwischen semiklassischer Dynamik und Berechnungen der elektronischen Struktur realisiert, um nichtadiabatische Simulationen für solche Donor-Akzeptorsysteme durchzuführen. Die Software wird an einem Ladungstransfersystem exemplarisch gezeigt, in dem ein optisch angeregtes Zinkphthalocyanin Ladung an ein Fullerenmolekül überträgt. Dieser Code eröffnet die Möglichkeit für zukünftige computergestützte Studien der Anregungsdynamik in molekularen Aggregaten, um die Entwicklung robuster künstlicher Photovoltaik-Systeme voranzutreiben.

List of Publications

This cumulative dissertation is based on my publications [Pub. 1], [Pub. 2], [Pub. 3], and [Pub. 4] listed below. Reprints of the papers are provided on pages 81–172.

Publication 1	Analyzing Excitation-Energy Transfer Based on the Time-Dependent Density Functional Theory in Real Time <u>T. Trepl</u>, I. Schelter, and S. Kümmel <i>J. Chem. Theory Comput.</i> 18, 6577 (2022) Reprint on pages 81–110 
Publication 2	Time-Resolved Ultrafast Excitation Dynamics in the B850 Light-Harvesting Antenna from Density Functional Theory <u>T. Trepl</u>, I. Schelter, and S. Kümmel <i>J. Phys. Chem. Lett.</i> 16, 10891 (2025) Reprint on pages 111–136 
Publication 3	Optically Induced Charge Separation at the Naphthalenediimide-Phenothiazine interface <u>T. Trepl</u>, R. G. De Assis, C. M. Isborn, T. B. De Queiroz, and S. Kümmel <i>Phys. Chem. Chem. Phys.</i> 27, 24806 (2025) Reprint on pages 137–159 
Publication 4	GPU-Accelerated On-The-Fly Nonadiabatic Semiclassical Dynamics C. A. Myers, K. Miyazaki, <u>T. Trepl</u>, C. M. Isborn, and N. Ananth <i>J. Chem. Phys.</i> 161, 084114 (2024) Reprint on pages 159–172

All publications included in this thesis were produced with co-authors; therefore, the plural form “we” is used in the main text of this dissertation.

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CHAPTER 1

Introduction

Sunlight delivers more energy to Earth in one hour than the entire humanity consumes in one year [1]. However, despite this abundant resource, our global energy supply still relies heavily on fossil fuels—a system that is not only vulnerable to geopolitical instabilities but also severely harms the environment [2, 3]. In contrast, solar radiation is clean, virtually limitless, and globally available, thus representing an attractive, environmentally friendly energy source. A central challenge of our time, therefore, lies in developing efficient ways to convert sunlight into useful forms of energy in order to meet humankind’s growing demand for renewable energy. In this respect, means to utilize solar radiation that are robust, cheap, and flexible on the one hand, while not requiring rare or toxic materials on the other hand, are of particular relevance and interest.

Natural photosynthesis constitutes a fascinating example of solar-energy conversion that sustains virtually all life on the planet’s surface [4, 5]. These light-harvesting systems are found in plants, algae, and certain bacteria. Among them, purple bacteria are some of the most studied and best characterized photosynthetic organisms since their light-harvesting apparatus is one of the simplest of its kind, providing access to the basic principles of photosynthesis [6–8]. In such photosystems, most solar radiation is absorbed by supramolecular antenna complexes. The associated excitation energy is then funneled within the complex and subsequently through the network of structurally organized antenna complexes before finally being delivered to the reaction center, where charge is separated to drive further biochemical processes [9, 10]. A remarkable feature of this energy-transfer chain is that it operates at near-unit quantum efficiency [3]. This observation has fueled an intense debate about whether quantum effects plays a role in natural light harvesting [11–16]. In the energy-transfer step, the molecular structure and dynamics of the antenna complex play a key role in achieving this efficiency [17, 18]. However, it remains an open question which fundamental quantum-mechanical processes govern the excitation dynamics after light absorption and direct the flow of excitation energy.

Getting insight into the excitation-energy transfer with simulations poses substantial challenges, since it requires a quantum mechanical description of a system containing thousands of atoms. In this work, we focus on the excitation dynamics of the so-called B850 ring of the light-harvesting complex 2 of the purple bacterium *Rhodoblastus acidophilus*, a fundamental element in the chain of excitation-energy transport [19, 20]. The B850 ring consists of 18 bacteriochlorophyll pigments that are strongly coupled and held in place by a protein scaffold. For a realistic description, simultaneous treatment of electronic and nuclear motion is required, which induces dynamics and interactions across various length and time scales [21–23]. Thus, describing the underlying

processes with atomic resolution is particularly demanding. The standard theoretical approach to describe the excitation relies on model Hamiltonians that simplify the system to reduce the computational burden [8, 24, 25]. However, the outcomes of such approaches depend decisively on which interactions are included in the model [26, 27]. Therefore, an unbiased insight into the B850 excitation dynamics requires simulations based on first principles, which avoid the a priori assumptions and parameter dependencies inherent in simplified model Hamiltonians.

This dissertation aims to address this research gap. Solving the Kohn–Sham equations of real-time time-dependent density functional theory (TDDFT) provides a first-principles framework for accessing excitation dynamics with atomic-scale spatial and temporal resolution [28–42]. The efficient parallelizability and favorable scaling of the real-time approach with a real-space grid representation, combined with modern high-performance clusters, enable simulations of the coupled electron-nuclear dynamics of large-scale, multichromophoric complexes [43–47]. This framework gives us access to simulate the ultrafast excitation dynamics in the B850 ring [Pub. 2]. We follow the dynamics after a pulsed excitation for the first 100 fs and investigate the length and time scales of localization and delocalization effects. Importantly, we identify whether—and if so, how—nuclear dynamics influences the excitation on that time scale, a decisive first step towards a qualitative understanding of the efficiency of natural light harvesting.

An inherent limitation of real-time TDDFT is that the only directly accessible physical observable is the time-dependent electron density. Consequently, all other observables of interest must be extracted from the density. While established protocols exist for computation, for example, the photoabsorption spectrum or the amount of charge transferred in a charge-transfer process, to the best of our knowledge, no measure based solely on the density is available that describes excitation-energy transfer [30, 31, 48–53]. Additional conceptual and computational hurdles arise from coupling the electron dynamics within TDDFT to nuclear motion [54–59]. We develop an approach compatible with coupled electron-nuclear dynamics that allows us to track excitation-energy transfer from first principles in real-time TDDFT without resorting to model assumptions [Pub. 1]. As proof of concept, we trace the excitation-energy transfer through a chain of sodium dimers. This transparent system allows us to systematically study the individual contributions of electron and nuclear dynamics that lead to the transfer. The concepts, therefore, provide insight into the elementary processes that also underlie the significantly more complex excitation dynamics of light-harvesting systems.

To make practical use of solar energy and ultimately generate electricity for human needs, an effective charge-separation process is essential. While nature typically uses similar chromophores in its reaction centers for the initial charge-transfer step, most human-made organic solar cells use distinct electron donors and electron acceptors [60]. With their low cost, flexibility, and light weight, such organic solar cells are promising candidates to become the cornerstone of the next generation of photovoltaic devices [61, 62]. Although their potential for inexpensive power generation is great, the physical mechanisms that govern the charge-separation process are remarkably complex. Despite this complexity, considerable progress in understanding these processes has been achieved over the past decades [63–66].

Organic donor–acceptor systems combining fullerene derivatives with low-bandgap polymers

have been studied extensively in the past [67–69]. In recent years, however, non-fullerene systems have attracted increasing interest because they offer tunable light absorption, favorable energy-level alignment, and structural stability [68, 70–73]. Driven by the search for new materials for organic solar cells, we investigate a novel donor–acceptor combination using derivatives of naphthalenediimide and phenothiazine [Pub. 3]. Phenothiazine provides excellent donor properties and naphthalenediimide has favorable acceptor properties, making the pair a promising candidate for the development of efficient organic photovoltaic devices [74–77].

A central research question addressed in this thesis is whether charge-transfer excitations emerge at the interface of the donor and acceptor molecules and how charge can dissociate. We construct molecular models of the interface to investigate the optical properties using the linear-response formulation of TDDFT and aim to predict the excited states that potentially participate in the charge separation [78]. Because organic solar cells are intended to operate at ambient temperature, we also examine how the statistical deviations in the nuclear configurations at room temperature influence the energetic landscape. We thereby explore possible transition pathways for electron-hole separation after the excitation.

To establish a computational framework for simulating such charge-separation processes in real-time, we introduce a new software implementation [Pub. 4]. The implementation’s capabilities are demonstrated through a benchmark calculation of a well-studied organic donor–acceptor complex, highlighting its potential for future applications.

This dissertation provides a coherent path of insights through fascinating areas of photophysics, ranging from the excitation-energy transfer in natural photosynthesis to charge separation in organic donor–acceptor complexes. At the heart of this thesis lies the overarching question of how the light-induced excitations in complex molecular aggregates evolve and how nuclear motion influences this process. This thesis is organized as follows. Chapter 2 introduces the fundamental concepts of the underlying theory, providing an overview of (TD)DFT together with molecular dynamics approaches. Chapter 3 outlines the path through the results of the four publications [Pub. 1, Pub. 2, Pub. 3, Pub. 4]. In Section 3.1, the excitation-energy measures for real-time TDDFT and the sodium dimer concept study of Publication 1 are presented. Building on this foundation, Section 3.2 reports the excitation dynamics in the B850 ring of the light-harvesting complex 2 (Publication 2). Section 3.3 then examines the novel organic donor–acceptor system based on a naphthalenediimide–phenothiazine combination (Publication 3), and finally Section 3.4 presents coupled electron-nuclear dynamics in a benchmark donor–acceptor system (part of Publication 4).

CHAPTER 2

Theoretical Framework

Quantum mechanics provides the theoretical framework to understand the physics underlying light absorption and subsequent dynamics on atomic time and length scales. Ideally, it is desirable to describe the whole molecular system entirely within quantum mechanics. This includes the dynamics of both electrons and nuclei, which are coupled and influence each other. Formally, electrons and nuclei can be described by the molecular wavefunction Ψ , which follows from the molecular Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\{\mathbf{r}\},\{\mathbf{R}\},t) = \hat{H}_{\text{mol}}\Psi(\{\mathbf{r}\},\{\mathbf{R}\},t), \quad (2.1)$$

where $\{\mathbf{r}\}$ and $\{\mathbf{R}\}$ are the electronic and nuclear coordinates, respectively. Atomic units are used throughout this thesis unless specified otherwise. The molecular Hamiltonian

$$\hat{H}_{\text{mol}} = T_{\text{elec}} + T_{\text{nuc}} + V_{\text{elec-elec}} + V_{\text{nuc-nuc}} + V_{\text{elec-nuc}} \quad (2.2)$$

comprises the kinetic energy operators T_{elec} and T_{nuc} for electrons and nuclei, respectively, and the interaction terms $V_{\text{elec-elec}}$, $V_{\text{nuc-nuc}}$, and $V_{\text{elec-nuc}}$, which correspond to the Coulomb interaction of electrons and electrons, nuclei and nuclei, and electrons and nuclei, respectively.

The wavefunction encodes the full electron-nuclear dynamics. In principle, solving the molecular Schrödinger equation (2.1) would allow us to model light-driven processes computationally on a molecular scale and get insight into the fundamental molecular mechanisms. Despite the beauty of the equation, its exact solution is beyond analytical or computational feasibility for any chemically or biologically relevant system. This complexity arises from the high dimensionality of the underlying wavefunction. For each electron and each nucleus, three spatial dimensions must be resolved, resulting in an exponential scaling of the computational effort with the number of particles.

While calculating the exact wavefunction already exceeds the capabilities of state-of-the-art supercomputers for systems of just a few atoms [79], molecular aggregates investigated in this thesis include assemblies of well over a thousand atoms. Therefore, we use density functional theory (DFT) and its time-dependent (TD) variant TDDFT for the electronic subsystem [80, 81]. This framework provides an (in principle) exact reformulation of quantum mechanics in terms of the density, reducing the many-body problem to computationally feasible single-particle equations. The key concepts underlying (TD)DFT and the approximations necessary for practical

applications are detailed in Section 2.1 in which we initially assume fixed nuclei. In Section 2.2 we then describe the molecular dynamics approaches used in [Publications 1–4](#), in which the electrons are coupled to the motion of the nuclei.

2.1 Electrons

In this section, we provide a brief introduction to the key concepts of DFT at the ground-state level and in its time-dependent version TDDFT. For a comprehensive review of (TD)DFT, we refer the reader to refs [78, 82–88]. Here, we treat only electrons explicitly; nuclei are assumed to be fixed and are included only implicitly via an external potential that acts on the electrons.

2.1.1 Electronic Structure with Density Functional Theory

DFT is the method of choice for describing quantum effects in molecules and solid-state materials and has become the workhorse of electronic structure theory [79, 89, 90].

DFT is based on the insight that the electronic one-body density contains all information about a many-body ground state. The Hohenberg–Kohn theorems [80] provide an exact reformulation of the many-body problem by establishing two key results: (i) there is a unique mapping between the ground-state density and the external potential (up to a constant) and (ii) the ground-state energy is a functional of the density, which is minimized by the ground-state density [91, 92]. While ref [80] provides evidence of the existence of a universal ground-state energy functional, it offers only little guidance on how to determine its exact analytical form. Therefore, approximations have to be used for practical applications.

DFT only became truly successful with the Kohn–Sham (KS) formalism [93]. The concept of the KS scheme is to replace the electronic many-body system with an auxiliary system of non-interacting fermionic particles that yield the same density as the many-body system. In the KS scheme, the many-body problem is mapped to a set of single-particle Schrödinger equations¹

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{KS}}[n](\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) \quad (2.3)$$

that have to be solved, where the density is calculated as

$$n(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2. \quad (2.4)$$

Equations 2.3 are called KS equations, with the kinetic energy operator $-\nabla^2/2$, KS potential v_{KS} , KS eigenvalues ε_i , and KS orbitals φ_i . The electronic ground-state energy reads

$$E^{\text{elec}} = T_{\text{s}}[n] + E_{\text{H}}[n] + E_{\text{ext}} + E_{\text{xc}}[n], \quad (2.5)$$

with kinetic energy of the KS system

$$T_{\text{s}}[n] = T_{\text{s}}[\{\varphi_i[n]\}] = -\frac{1}{2} \sum_i \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) d^3r, \quad (2.6)$$

¹For the sake of simplicity, spin degrees of freedom are omitted in the following.

the classical Hartree energy

$$E_H[n] = \int v_H(\mathbf{r})n(\mathbf{r})d^3r = \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r', \quad (2.7)$$

the external energy

$$E_{\text{ext}} = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r})d^3r, \quad (2.8)$$

and E_{xc} , which is the so-called exchange correlation energy. Using the KS orbitals (which are a functional of the density) to derive a kinetic-energy term allows for a more accurate approximation of the true kinetic energy than purely density-based approaches. The exchange-correlation (xc) energy is formally defined by eq 2.5 and accounts for the difference between the many-body kinetic energy and the kinetic energy of the KS system, as well as the difference between the many-body Coulomb interaction energy and the Hartree energy. The effective KS potential follows from the different energy contributions

$$v_{\text{KS}}[n] = v_{\text{ext}} + v_H[n] + v_{\text{xc}}[n]. \quad (2.9)$$

The external potential v_{ext} includes external fields as well as the electrostatic potential created by the nuclei. The xc potential is defined as the functional derivative of the xc energy with respect to the density,

$$v_{\text{xc}} = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (2.10)$$

Both the Hartree potential and the xc potential implicitly depend on the KS orbitals via the density, making the KS equations (2.3) non-linear. Within the scheme, the actual electron–electron interaction of the many-body system is incorporated into the density-dependent KS potential.

The main benefit of DFT is the significant reduction of the dimensionality. Instead of solving for a $3N$ -dimensional many-body wavefunction (where N is the number of particles), the problem reduces to solving for a set of 3-dimensional KS orbitals. The price to pay for this simplification, however, is that the many-body interaction is now encoded in the xc functional—a universal quantity whose exact form is unknown. Finding good approximations for the xc functional remains a scientific challenge. The choice of approximation to the functional critically defines both the accuracy of the theoretical predictions and the computational burden. Specific functionals used in this work are detailed in Section 2.1.3.

2.1.2 Time-Dependent Density Functional Theory

While DFT is ideally suited to describe ground-state properties, it cannot capture dynamical phenomena such as the excitation dynamics after photoabsorption. TDDFT addresses this and extends the DFT formalism to time-dependent densities, allowing for the computation of excitation dynamics and theoretical spectroscopy [29–40].

In 1984, the cornerstone of TDDFT was established by Runge and Gross [81]. The Runge–Gross theorem establishes a one-to-one correspondence between the time-dependent external potential

and the time-dependent density for a given non-degenerate initial state Φ_0 . This framework serves as the theoretical foundation for TDDFT, establishing a rigorous reformulation of time-dependent quantum mechanics in terms of the time-dependent density.

As in the ground-state case, this one-to-one correspondence allows us to use a KS approach, providing a computationally feasible framework for investigating time-dependent phenomena. In the time-dependent KS approach, we rely on a non-interacting reference system that is constructed such that its density evolves identically to the interacting many-body system. The time-dependent KS equations read

$$i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) = \underbrace{\left(-\frac{1}{2} \nabla^2 + v_{\text{KS}}[n; \Phi_0](\mathbf{r}, t) \right)}_{\hat{h}_{\text{KS}}} \varphi_i(\mathbf{r}, t), \quad (2.11)$$

with the time-dependent KS potential

$$v_{\text{KS}}(\mathbf{r}, t) = v_{\text{H}}(\mathbf{r}, t) + v_{\text{ext}}(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t). \quad (2.12)$$

The time-dependent density

$$n(\mathbf{r}, t) = \sum_i |\varphi_i(\mathbf{r}, t)|^2 \quad (2.13)$$

is evaluated using the KS orbitals and provides the fundamental connection between the fictitious KS system and the many-body system.

The xc potential is now also a functional of the initial state Φ_0 and depends on the whole history of the density [94]. Due to its computational simplicity, practically all TDDFT calculations employ an adiabatic approximation to this dependence. Within this approximation, the time-dependent density is plugged into the ground-state xc functional to obtain the time-dependent xc potential

$$v_{\text{xc}}[n](\mathbf{r}, t) \approx v_{\text{xc}}^{\text{adiab}}[n](\mathbf{r}, t) = v_{\text{xc}}^{\text{gs}}[n(t)](\mathbf{r}) = \left. \frac{\delta E_{\text{xc}}[n]}{\delta n} \right|_{n=n(\mathbf{r}, t)}. \quad (2.14)$$

It is therefore assumed that the xc potential is local in time and the dependency on the history of the density is neglected. In frequency space, this assumption corresponds to dropping the frequency dependence of the xc kernel, see below. To compute excitation properties, there are two common paths within TDDFT: real-time TDDFT and linear-response TDDFT—both are elaborated in the following.

Real-Time TDDFT

In real-time TDDFT, the time-dependent KS equations 2.11 are used to propagate the KS orbitals directly [95]. Starting from an initial set of KS orbitals $\{\varphi_i(\mathbf{r}, t_0)\}$, we apply the time-evolution operator $\hat{U}$ to trace the orbitals' dynamics at times $t > t_0$ [96, 97] as

$$\varphi_i(\mathbf{r}, t) = \hat{U}(t, t_0) \varphi_i(\mathbf{r}, t_0) = \mathcal{T} \exp \left(-i \int_{t_0}^t \hat{h}_{\text{KS}}(t') dt' \right) \varphi_i(\mathbf{r}, t_0), \quad (2.15)$$

where $\mathcal{T}$ is the time-ordering operator. To solve eq 2.15 numerically, the time variable is discretized to time steps $(t_0, t_1, t_2, t_3 \dots)$ with an equidistant increment Δt . The time-dependent KS equations are then solved step by step using the time-evolution operator, $\varphi(\mathbf{r}, t_{k+1}) = \hat{U}(t_{k+1}, t_k) \varphi(\mathbf{r}, t_k)$. The step size has to be chosen small enough to ensure that the KS Hamiltonian $\hat{h}_{\text{KS}}$ can be approximated as constant during the time step [96, 97]. Typical time-stepping algorithms, such as the Crank–Nicolson scheme used in Publication 1 and Publication 2, exploit a Taylor expansion of the exponential term on the right-hand side of eq 2.15, leading to numerically solvable matrix equations. With this, the time-dependent KS equations are iteratively propagated until the desired simulation time is reached.

In real-time TDDFT, the excited-state information is not directly provided by the solution of the equations but rather encoded in the time-dependent density. A representative workflow for accessing excited-state information is briefly exemplified in Figure 2.1, guiding the reader from the initial ground-state calculation to the analysis of excited-state data. The procedure runs as

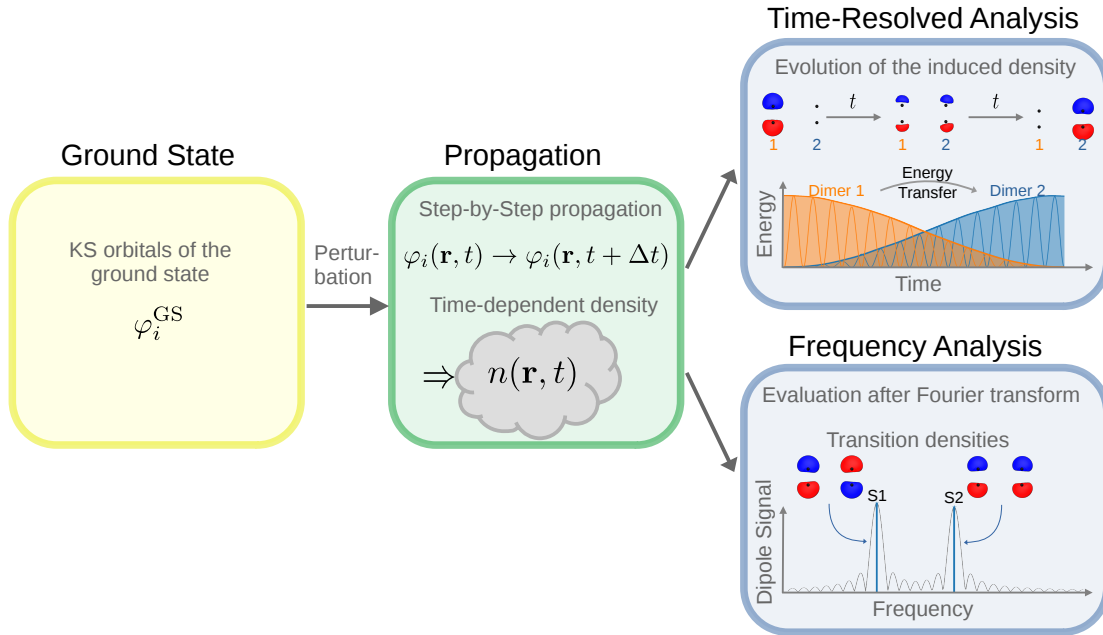


Figure 2.1: Workflow of the procedure of a real-time TDDFT calculation. Initially, the ground-state KS orbitals are calculated (yellow box). Then, a perturbation is applied and the KS orbitals are propagated (green box). Excitation information can then be extracted from the time-dependent density in either time domain or frequency domain (blue boxes). Presented is an example of two sodium dimers of which the left one is initially excited. See text for details.

follows: First, a ground state without perturbation is calculated (Figure 2.1 yellow box). This is achieved by applying a self-consistent energy minimization scheme within standard DFT. To then trigger dynamics, a perturbation is applied. One common technique is to give the ground-state KS orbitals a very short, delta-like kick and use the resulting state as a starting point for the simulation

[33, 42, 50, 95]. This instantaneous perturbation triggers a spectrally broad excitation. An alternative is to perturb the system by applying an additional time-dependent external field. This provides a more natural way to mimic, e.g., the excitation by a laser pulse as in an experimental setup. In the dipole approximation, such an external field reads [78]

$$v_{\text{ext}} = E f(t) \sin(\omega t) \mathbf{r} \cdot \boldsymbol{\alpha}, \quad (2.16)$$

where E is the amplitude, ω is the carrier frequency, $\boldsymbol{\alpha}$ is the polarization, and $f(t)$ models the envelope of the temporal shape of the laser pulse. The laser can be approximated reasonably well as a linear dipole field since the wavelength of visible light is usually much larger than the size of the molecule. With typical intensities of laser pulses in pump-probe experiments or the intensity of solar radiation, a tremendous amount of photons are involved justifying a classical description of the electromagnetic field.

During propagation (Figure 2.1 green box), the electron density is evaluated in every time step from the KS orbitals using eq 2.13. Within TDDFT, the time-dependent density is the fundamental observable, and therefore, excitations are analyzed via the time evolution of the density during and after the perturbation. An observable directly accessible from the time-dependent density is the induced density

$$\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n^{\text{gs}}(\mathbf{r}) \quad (2.17)$$

that renders the time- and space-resolved response of the density due to the perturbation. The induced density provides qualitative insight into the underlying excitation dynamics and relevant time scales. In Figure 2.1 (top blue box) the simulation of two sodium dimers (of which the left one is initially excited) is depicted. The time evolution of the induced density reveals that during the propagation the system changes from a state in which only dimer 1 is excited to a state in which the excitation is shared between dimer 1 and dimer 2 and finally a state in which only dimer 2 is excited. The excitation information can also be extracted from observables, which contain an integration over the spatial dependency. Using, e.g., the induced dipole moment

$$\delta \boldsymbol{\mu}(t) = \int \mathbf{r} \delta n(\mathbf{r}, t) d^3r, \quad (2.18)$$

the excitation-energy transfer can also be analyzed quantitatively in this example. Such reduced quantities can be used, e.g., as quantitative measure of energy and for computing time scales [Pub. 1, Pub. 2]. The analysis can be further extended by Fourier transforming quantities from the time domain to the frequency domain. This allows us to assess the optical absorption spectrum with its excitation energies [33, 50, 51, 98]. For the sodium dimer system, using an evaluation technique of ref [42] gives insight into the transition densities of the involved excited states (see Figure 2.1 bottom blue box). Real-time TDDFT is, of course, not limited to the quantities presented in this workflow example. In literature, plenty of quantities derived from propagation methods are available, depending on the excitation information of interest: excitation-energy densities [Pub. 1, 42], (hyper)polarizabilities [99, 100], partition charges [30, 31], hole densities [101], and particle-hole orbitals [102], to name just a few.

The real-time formulation of TDDFT has attracted growing interest over the past decades, and remarkable progress has been made in getting insight into a wide variety of phenomena across different classes of systems [88]. Applications include strong-excitation phenomena in atoms, molecules, clusters, and solids [29, 103–110], charge-transfer dynamics [30, 31, 52], excitations in biological systems [43, 111–114], electron transfer [115–119], photoemission processes [120–126], and pump-probe spectroscopy [127, 128]. This success is based on three key aspects. First, real-time TDDFT captures the electronic response of molecules and materials across both weak (linear) and strong (non-linear) interaction regimes [129]. Second, only occupied KS orbitals need to be propagated, so the computational effort scales favorably with the number of electrons [28]. Third, the approach supports extensive parallelization. On the first level, the orbitals can be distributed across compute units. At a second level, when combined with a real-space implementation, the workload can be efficiently shared further by partitioning the simulation box into subdomains. These advantages have motivated the development of numerous real-time TDDFT codes [44–47, 50, 130–134]. For the real-time studies in Publications 1 and 2, we use the program package BTDDFT [50].

Alongside these advantages, three challenges persist. First, a fundamental limitation of real-time TDDFT lies in its very nature: it yields only the time-dependent density rather than a wavefunction. This requires observables such as photoabsorption spectra to be obtained through postprocessing techniques using Fourier analyses [42, 50]. Real-time TDDFT, however, often fails to reveal dark states. Second, the selection of the xc functional determines the accuracy of the predictions—a general TDDFT constraint discussed in Section 2.1.3. For real-time TDDFT implementations on a real-space grid, this choice is further restricted by parallelization efficiency. Specifically, the grid parallelization can only be efficiently applied with the use of (semi-)local functionals, whose accuracy for the phenomena of interest has to be carefully tested beforehand (as in Publication 2). Third, while real-time TDDFT’s favorable scaling allows for studying large-scale systems, its computational efficiency does not come into play for small systems with few states involved due to the necessary initialization of the real-space grid. These advantages and limitations motivate the complementary use of both real-time TDDFT and linear-response TDDFT, depending on the system size and phenomena of interest.

Linear-Response TDDFT

An alternative to the real-time propagation is a formulation in the frequency domain, namely, linear-response TDDFT. This is a common way to obtain excitation energies and oscillator strengths for small- to medium-sized systems, as done in [Pub. 3]. Following ref [78] and [135], this section offers insight into the fundamental linear-response equations of TDDFT and a brief overview of how optical properties are accessed.

Starting from the ground state, a weak perturbation is switched on in the external potential

$$v_{\text{ext}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, 0) + \delta v_{\text{ext}}(\mathbf{r}, t), \quad (2.19)$$

at time $t = 0$ with $\delta v_{\text{ext}}(\mathbf{r}, t \leq 0) = 0$. The reaction of the electronic system to this perturbation is represented by the change in the density. Expanded in orders of δv_{ext} , the density can be written as a series

$$n(\mathbf{r}, t) = n^{\text{gs}}(\mathbf{r}) + n_1(\mathbf{r}, t) + n_2(\mathbf{r}, t) + \dots \quad (2.20)$$

Linear-response TDDFT considers the density response linear in the perturbation, $n_1(\mathbf{r}, t)$. If one seeks a higher-order response, real-time TDDFT or higher-order response formalisms [78, 84] are available. Within the linear regime, the perturbation and the density response can be connected with

$$n_1(\mathbf{r}, t) = \int_0^\infty dt' \int d^3 r' \chi(\mathbf{r}, t, \mathbf{r}', t') \delta v_{\text{ext}}(\mathbf{r}, t), \quad (2.21)$$

in which

$$\chi(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}', t')} \right|_{v_{\text{ext},0}} \quad (2.22)$$

is the density–density response function. Within the KS system, the density response can also be written as

$$n_1(\mathbf{r}, t) = \int_0^\infty dt' \int d^3 r' \chi_{\text{KS}}(\mathbf{r}, t, \mathbf{r}', t') \delta v_{\text{KS}}(\mathbf{r}, t). \quad (2.23)$$

with the first-order change of the KS potential due to the perturbation δv_{KS} . This change contains the perturbation of the external potential as well as the change in the Hartree and xc potential due to the disturbed density. Equivalently to eq 2.22, one can write the density–density response function of the KS system as

$$\chi_{\text{KS}}(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{KS}}(\mathbf{r}', t')} \right|_{v_{\text{KS}}[n^{\text{gs}}]}. \quad (2.24)$$

Using eq 2.21 and eq 2.23 and Fourier transforming to frequency space, one can obtain a Dyson-like equation that connects the responses of the systems

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) + \iint \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}_1, \omega) \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{\text{Hxc}}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right) \chi(\mathbf{r}_2, \mathbf{r}', \omega) d^3 r_1 d^3 r_2, \quad (2.25)$$

with the Hartree-xc kernel $f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) = |\mathbf{r} - \mathbf{r}'|^{-1} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega)$, where the xc kernel is defined as [88]

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) = \int e^{i\omega(t-t')} \frac{\delta v_{\text{xc}}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t)} d(t-t'). \quad (2.26)$$

Equation 2.25 can be reformulated as an eigenvalue problem that yields the excitation energies of the many-body system. When expanded in the KS orbital basis, this yields the Casida equations

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (2.27)$$

with the matrices $\mathbf{A}$ and $\mathbf{B}$ defined as

$$A_{ia,jb}(\omega) = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ia|f_{\text{Hxc}}(\omega)|jb), \quad (2.28)$$

$$B_{ia,jb}(\omega) = (ia|f_{\text{Hxc}}(\omega)|bj). \quad (2.29)$$

For brevity, we used the Mulliken notation

$$(ia|f_{\text{Hxc}}(\omega)|jb) = \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \varphi_a(\mathbf{r}) f_{\text{Hxc}}(\mathbf{r}, \mathbf{r}', \omega) \varphi_b^*(\mathbf{r}') \varphi_j(\mathbf{r}') \quad (2.30)$$

The indices i, j run over all occupied KS orbitals and indices a, b run over all unoccupied (“virtual”) KS orbitals. For hybrid and range-separated hybrid functionals, the KS formalism has to be expanded to generalized KS, which comes with additional terms to account for non-local parts of the xc functional. For further information regarding generalized KS, we refer the reader to refs [136] and [137]. For practical applications of the Casida equations, typically the adiabatic approximation is applied, which drops the frequency dependency of the xc kernel in standard KS-DFT.

A noteworthy approximation commonly applied is the Tamm–Dancoff approximation. Within the Tamm–Dancoff approximation, the excitations (contained in matrix $\mathbf{A}$) are being decoupled from the deexcitations (contained in matrix $\mathbf{B}$), i.e., $\mathbf{B} = 0$. The to-be-solved eigenvalue problem then reduces to $\mathbf{A}\mathbf{X} = \omega\mathbf{x}$. The Tamm–Dancoff approximation can even improve the accuracy of excitations when instabilities are involved [138].

2.1.3 Exchange-Correlation Functionals

The choice of the xc functional is not simply a technical detail, but it fundamentally determines which physical phenomena can be described reliably in a simulation. In literature, there is a whole hierarchy of density functional approximations, which can be categorized following the metaphor of a Jacob’s ladder [139]. Each rung of the ladder corresponds to a class of functionals of different accuracy and complexity. At the lowest rung, there is the local density approximation (LDA) [93, 140] using a spatially local dependency on the density. Using the gradient of the density in addition leads to generalized gradient approximations [141–145] on the second rung, followed by meta-generalized gradient approximations [146–153] on the third rung, which additionally make use of the kinetic energy density. Hybrid approximations on the fourth rung make use of exact exchange [154] and mix it with functionals of lower rungs (typically mixed globally [155–159] or in a range-separated manner [160–164]). As one climbs the ladder towards chemical heaven, the gain in accuracy comes at the expense of increased computational costs. For each application, a balance must be struck between the required accuracy and the computational resources available. We introduce two classes of functionals in this section: LDA and range-separated hybrids, which have been used in Publications 1,2 and Publications 3,4, respectively.

Local Density Approximation

LDA, the mother of all functionals, relies purely on the value of the electron density at each point in space. It is already rooted in the original KS paper [93], and its simplicity allowed for the first practical DFT calculations just some years later. The mathematical form is based on the homogeneous electron gas, for which an analytical expression for the exchange term can be derived as [82, 83]

$$E_x^{\text{LDA}} = - \int d^3r \frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} n^{\frac{4}{3}}. \quad (2.31)$$

For the correlation component, no exact analytical form is available. Through reliable Quantum Monte Carlo data [165], numerical access to the correlation energy is gained, which can then be modeled and parameterized under limiting constraints [166–168]. For the LDA, one takes the xc energy of the homogeneous electron gas and substitutes the homogeneous electron gas density with the actual density. Surprisingly, LDA has not only shown success for systems with slow varying density, but also for systems with rapidly varying densities [79]. Given its conceptual simplicity, LDA has often been shown to make reasonably accurate predictions of experimental results [154]. One reason for the success is that some exact constraints of xc functionals (see, e.g., ref [169]) are accounted for, leading to an error cancellation [139, 170]. Due to the local dependence on the density, computationally efficient parallelizations in real-time TDDFT codes are possible [43, 44, 46, 47] and allow propagation of systems with more than a thousand atoms, as done in Publication 2. However, care has to be taken in systems for which the self-interaction error of LDA [167] or its incorrect asymptotics [87, 169] of the potential for large distances play a major role. For sodium dimers and bacteriochlorophyll compounds, as in Publications 1 and 2, LDA yields qualitatively correct results, and the shortcomings are of minor concern. Charge-transfer excitations (as investigated in Publications 3 and 4) are, however, systematically underestimated [171], calling for the use of higher-rank functionals for such applications.

Range-Separated Hybrids

Charge-transfer states play an important role in organic solar cells (as investigated in Publication 3 and partly in Publication 4), in which an electron is transferred from a donor species to an acceptor species at the interface. Charge-transfer excitations proposed a major challenge for density functionals, and one step to meet this challenge was the development of range-separated hybrids. Making use of the exact-exchange term of Hartree-Fock theory [172, 173] turned out to be advantageous for the description of long-range charge-transfer states [174]. Depending on the functional design, this exact exchange is either mixed globally with a (semi-)local functional (e.g., in the M06-2X functional [159]) or mixed using a range-separation function. The core idea of range-separated hybrids lies in the splitting of the electron–electron interaction into a short-range part and a long-range part. Using a Gaussian basis set (as most TDDFT codes do), this can be

computationally efficiently done using the error function [175]

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \underbrace{\frac{\text{erf}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}}_{\text{long range}} + \underbrace{\frac{1-\text{erf}(\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}}_{\text{short range}}. \quad (2.32)$$

The first term on the right-hand side of eq 2.32 corresponds to the long-range part and the second term to the short-range part, with ω controlling the effective distance at which the transition between the regimes occurs. This framework allows us to make use of the complementary strengths of distinct functionals within specific interaction regimes.

In Publication 3, the range-separated hybrid optimally-tuned ω PBE was employed, using the semilocal generalized gradient approximation PBE [142] for the short-range component and exact exchange in the long-range regime. Using exact exchange for $r \rightarrow \infty$ yields the correct asymptotics of the xc potential. Following the idea of first-principle methods, the range-separation parameter is determined self-consistently via a tuning procedure [176]. The parameter adjustment is based on fulfilling the IP theorem

$$-\epsilon_{\text{HOMO}} = \text{IP} \quad (2.33)$$

as good as possible, which is an exact condition in DFT [177–179], though not fulfilled by most density functional approximations. It relates the eigenvalue of the highest occupied molecular orbital (HOMO) to the ionization potential ($\text{IP} = E(N) - E(N-1)$). In the optimally tuning procedure, ω is iteratively determined to best satisfy this condition for the N -electron system (or simultaneously for the N and $N+1$ system). Numerous studies have demonstrated highly accurate results for properties relevant to charge transfer, such as ionization energies and excitation energies [176, 180–182].

In contrast, CAM-B3LYP (used in Publication 4) follows an alternative approach [162]. The mixing of different functionals at varying interaction ranges is generalized to three parameters, allowing for more flexible adjustments. Instead of tuning the parameters prior to each TDDFT calculation, the parameters are universally fixed. This approach eliminates the computationally costly tuning procedure at the cost of making the functional empirical. The parameter set is chosen such that simultaneously atomization energies, ionization potentials, total atomic energies, and excitation energies are reasonably well described in a large set of molecules, making CAM-B3LYP a versatile functional for many chemical and physical problems [162].

Both functional approaches employ the same concept of range-separation to predict charge-transfer states accurately, but they have fundamental differences in their parameterizations. While CAM-B3LYP can be used out-of-the-box and is robust for a variety of electronic properties through the empirical adjustments, optimally-tuned ω PBE follows a first-principles approach by utilizing a system-specific parameter, enabling high spectroscopic accuracy at the computational cost of the prior tuning procedure.

2.2 Nuclei: Molecular Dynamics

Classical nuclei with fixed positions, as assumed in the previous section, are an adequate approximation for many electronic properties. In such a clamped-ion approximation, the electrons move in the static potential that is generated by the nuclei. This approximation is based on the fact that nuclei are three orders of magnitude heavier than electrons and therefore move on a slower scale. Neglecting the nuclei's movement entirely corresponds to classical nuclei at zero temperature. In real-world scenarios, however, room temperature is ubiquitous. Nature's photosystems work remarkably well at ambient temperatures, and human-made solar cells are designed to operate at room temperature. Generally, nuclear motion plays a decisive role in a broad range of photochemical and photophysical phenomena, as in isomerization reactions [183–185], photodissociation [186], excitation-energy transfer, and charge transfer in photosynthetic molecular aggregates [Pub. 2, Pub. 3, 30, 31]. Thus, to describe such processes adequately, nuclear motion must be accounted for in our simulations, which leads us to the realm of molecular dynamics [25].

For our molecular dynamics simulations, the theoretical framework must resolve the rapid electronic dynamics with TDDFT while also providing an accurate approximation for the slower nuclear motion, for which a full quantum-mechanical treatment would be too cumbersome. Furthermore, the framework must be reliable enough to simulate dynamics over a time scale of hundreds of femtoseconds, and the implementation must be efficient enough to reach such time scales with the available cluster architecture. A related challenge one faces when choosing a coupled electron-nuclear dynamics framework is that, for many applications, nonadiabaticity must be considered.² In the adiabatic (so-called Born–Oppenheimer) approximation, the electrons are assumed to instantaneously and adiabatically adjust to the nuclear geometry. However, in many photochemical processes, electronic states become energetically close, and the Born–Oppenheimer approximation breaks down. In such cases, nonadiabatic coupling terms (arising beyond the Born–Oppenheimer regime) give a dominant contribution to the dynamics. Including such dynamical coupling leads to nonadiabatic dynamics. A further decision to be made when choosing a method for electron-nuclear dynamics is whether the quantum nature of the nuclei is important. In principle, multicomponent TDDFT would be capable of a simultaneous quantum treatment of electrons and nuclei on equal footing based on their densities [187–189]. However, as finding reliable xc functional approximations for the nuclear degrees of freedom remains difficult, practical applications are yet limited [190]. Therefore, most approaches combined with (electronic) TDDFT approximate the nuclei as classical point particles while preserving the quantum nature of the electrons.

The above challenges are particularly relevant when studying light-harvesting systems, such as natural photosynthetic complexes or organic donor–acceptor systems. For an accurate description of excitation-energy transfer and charge-transfer excitations, electron-nuclear dynamics approaches are necessary that can simulate large and complex molecular aggregates on the

²Note: In the context of molecular dynamics the term (*non*)*adiabatic* has a different use than in the TDDFT adiabatic approximation of the xc functional.

relevant time scale. The most prominent electron-nuclear dynamics approaches include Born–Oppenheimer molecular dynamics (BOMD) [59], Ehrenfest dynamics [191, 192], surface hopping [192, 193], multiple spawning [194, 195], path-integral based methods [196, 197], and exact factorization [198]. While all methods contribute valuable perspectives, our selection focuses on frameworks that ensure sufficient accuracy for our purposes, offer computational scalability for large multichromophoric complexes, and remain grounded in first principles. In this work, we use three complementary first-principles approaches. For the charge-transfer excitations in the donor–acceptor system in Publication 3, we use BOMD combined with linear-response TDDFT. For the excitation-energy transfer in the B850 ring (Publication 2) and the preceding concept study (Publication 1), nonadiabaticity is required, and therefore we use Ehrenfest Dynamics combined with real-time TDDFT. For the computational project Publication 4, which enables real-time simulations of charge-transfer excitations within nonadiabatic dynamics, we implemented the linearized semiclassical initial value representation (LSC-IVR) formalism. We select the molecular dynamics approach (BOMD, Ehrenfest dynamics, and LSC-IVR) and the applied electronic structure method (real-time TDDFT, linear-response TDDFT) based on the specific photophysical process and system size to ensure a well-balanced trade-off between the accurate treatment of key physical effects and computational feasibility.

2.2.1 Born–Oppenheimer Molecular Dynamics

BOMD is a standard approach for simulating electron-nuclear dynamics in systems where nonadiabatic effects are negligible [59]. Its primary advantage is computational efficiency, as the costly evaluation of nonadiabatic couplings is avoided, making the framework ideally suited for simulating thermal fluctuations of molecular geometries on time scales up to picoseconds or even nanoseconds.

BOMD rests on an adiabatic approximation, which assumes that the (fast) electrons instantaneously adapt to the (slow) motion of the nuclei due to their mass difference. This separation of time scales is realized by nuclei that move classically on a (chosen) single potential energy surface generated by the electronic structure. While BOMD can be applied on any potential energy surface, in the following, we restrict ourselves to the electronic ground state. The nuclear equations of motion arise from the gradient of the potential energy surface according to Newton’s second law

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I = -\nabla_{\mathbf{R}_I} E_{\text{gs}} \quad (2.34)$$

with the mass M_I and position $\mathbf{R}_I$ of the I th nucleus, and the force $\mathbf{F}_I$ acting on it, which is determined by the gradient of the ground-state energy of the electron-nuclear system E_{gs} with respect to the nucleus’ position. To determine the energy in eq 2.34 on-the-fly at every nuclear time step, the ground-state KS equations (eq 2.3) are solved, in which the updated nuclear positions are used in the KS Hamiltonian. As the electronic structure follows from solving the ground-state KS equations, no explicit propagation of the electrons is required. As the fast electron dynamics therefore does not need to be resolved, the time step can be chosen on the nuclear time scale (typically in the range 0.1 fs to 3.0 fs [59, 199, 200]). The computational effort of the electronic

subsystem is therefore reduced to solving the static electronic structure problem using ground-state DFT for the nuclear configuration at each nuclear time step.

BOMD is widely used to sample the thermal fluctuations of the nuclear configuration at finite temperature to obtain ensemble spectra [200–202]. BOMD allows us to track how nuclear motion modulates vertical excitation energies via applying linear-response TDDFT calculations to the resulting nuclear structures along the trajectory in the postprocessing (see Section 3.3 for application in Publication 3).

Due to the adiabatic limit, BOMD, however, fails to describe dynamical phenomena involving multiple potential energy surfaces or situations in which the Born–Oppenheimer approximation itself breaks down.

2.2.2 Ehrenfest Dynamics

In energy transfer processes within light-harvesting complexes, as the B850 ring studied in Publication 2, multiple electronic states are involved. This regime cannot be captured by BOMD, which assumes a single adiabatic surface. Ehrenfest dynamics overcomes this limitation of BOMD and provides a framework that captures coupled electron-nuclear dynamics at the nonadiabatic level in a computationally efficient manner, making it ideally suited for investigating excitation-energy transfer in the B850 ring.

In Ehrenfest dynamics, the molecular system is treated within a mixed quantum-classical framework. The nuclear degrees of freedom evolve classically along a single trajectory on the mean-field potential created by the electronic subsystem. At the same time, the electronic subsystem is propagated quantum mechanically using the time-dependent electronic Hamiltonian, which is parameterically dependent on the nuclear coordinates. In contrast to the Born–Oppenheimer approximation discussed previously, the electronic state is generally not confined to a single adiabatic eigenstate of the electronic Hamiltonian but allows for a superposition of multiple electronic states. This formalism thereby goes beyond the adiabatic (Born–Oppenheimer) approximation and allows for transitions between electronic states through the time-dependent electronic Hamiltonian. For the photoinduced dynamics of the B850 ring, this approach is well-suited to include nuclear dynamics, as the ultrafast energy transfer following photoexcitation involves excitation dynamics across numerous coupled excited states.

Formally, the Ehrenfest dynamics equations can be derived from a time-dependent self-consistent field ansatz for the molecular wavefunction. For a rigorous derivation of the governing equations of motion, we refer the reader to refs [59, 135, 203]. The nuclear trajectories are obtained by integrating the equations of motion

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F}_I = -\nabla_{\mathbf{R}_I} \langle E \rangle, \quad (2.35)$$

determined from Newton’s second law, where $\langle E \rangle$ is the expectation value of the system’s total energy. In this approach, the energy consists of the classical energy of the nuclei and the energy of the electronic subsystem, the latter being the expectation value of the electronic Hamiltonian

(including the electron-nucleus interaction) evaluated with the current electronic structure. Using adiabatic eigenstates of the electronic Hamiltonian as a basis, the electronic state can be written as a superposition of multiple eigenstates, and the resulting force on the nuclei arises from an average of the potential energy surfaces of the eigenstates. Concurrently with the nuclei, the electrons are explicitly propagated in this scheme, which is realized by solving the time-dependent KS equations

$$i\frac{\partial}{\partial t}\varphi_i(\mathbf{r},t) = \hat{h}_{\text{KS}}(\mathbf{r},\{\mathbf{R}(t)\},t)\varphi_i(\mathbf{r},t), \quad (2.36)$$

in the TDDFT formalism (as eq 2.11), where the KS Hamiltonian parameterically depends on the coordinates of the nuclei $\{\mathbf{R}(t)\}$ at time t . Equations 2.35 and 2.36 are solved simultaneously, leading to a coupled dynamics of electrons and nuclei. The electrons are coupled to nuclear motion through the dependence of the KS Hamiltonian on nuclear coordinates, and the nuclei are coupled to the electron dynamics by evaluating the energy expectation value with the current electronic structure. This dynamics contains nonadiabatic coupling terms, which allow the occupation numbers of the excited states to change during the evolution of the molecular system. Thus, energy can also be transferred between the electronic and nuclear systems.

The implementation of Ehrenfest-TDDFT in the software package BTDDFT (used in [Publication 1](#) and [Publication 2](#)) employs a real-space grid as a basis to represent spatial quantities. Due to the grid discretization, the translational invariance is formally broken, which poses numerical challenges for molecular dynamics simulations. With a grid spacing that is chosen too coarse, integrated observables (as the energy in eq 2.35) can strongly depend on the molecule’s position with respect to the grid, as the integration happens over the KS orbitals, which are represented on that grid. Therefore, such observables artificially oscillate when the molecule is positioned differently relative to the grid, the resulting integration errors are known as the *egg-box* effect. To mitigate this effect in BTDDFT, we implemented an evaluation of the nuclear forces without explicitly calculating the energy (see ref [204]) and furthermore implemented a filtering scheme for the ionic potentials that reduces artificial oscillations. Our numerical implementations are essential for running Ehrenfest-TDDFT efficiently with a grid representation, explaining the numerical details, however, would be beyond the scope here. Therefore, we refer interested readers to Section A.2, which documents several numerical details to address the grid-space challenges.

Ehrenfest dynamics has well-known limitations, such as the mean-field approximation, arising from the product ansatz for the molecular wavefunction in the derivation of the equations of motion [205]. This approximation can yield unphysical trajectories in systems where distinct electronic states exert significantly different forces on the nuclei [192]. Such shortcomings can be demonstrated with simplified model systems, where Ehrenfest dynamics fails to correctly capture decoherence effects [55, 206], a phenomenon that describes the “collapse” of the electronic subsystem to a single adiabatic state when the system runs through a region of strong nonadiabatic coupling [207]. For real-world applications, however, recent studies [208] have demonstrated that Ehrenfest dynamics gives the qualitatively correct picture of the dynamics. For the B850 ring studied in [Publication 2](#), nuclear motion mainly consists of room-temperature vibrations on the

investigated 100 fs time scale, therefore inducing only marginal structural perturbations. Given the harmonic nature of vibronic displacements, the potential energy surfaces are not expected to undergo abrupt topological changes. Consequently, the forces acting on the nuclei are expected to remain comparable across the relevant electronic states. The mean-field approximation is therefore justified for the dynamics of the B850 ring, given the short investigated time scale (~ 100 fs) and the limited extent of the structural changes at room temperature.

For systems with strong nonadiabatic couplings, e.g., at conical intersections, decoherence corrections can be applied to Ehrenfest dynamics [209]. While such corrections recover the decoherence within Ehrenfest dynamics, their implementation typically requires explicit knowledge of potential energy surfaces of all occupied electronic states [210], rendering them prohibitively cumbersome for large-scale systems. The mean-field deficiency is particularly relevant for the dynamics of systems that branch into significantly different potential energy surfaces.

Ehrenfest dynamics' limitations have motivated the development of alternative semiclassical approaches that retain the efficiency of propagating classical trajectories. Among these, LSC-IVR (as in Publication 4) has emerged as a powerful approach, which we now shortly outline.

2.2.3 Linearized Semiclassical Initial Value Representation

Note: Publication 4 originated from a three-month research stay at the University of California Merced as part of the Elite Study Program Biological Physics. Given the limited timeframe, the focus was on the technical implementation of PYSCES [Pub. 4]. The underlying theory, established in prior work, is therefore summarized only briefly.

LSC-IVR is a nonadiabatic dynamics method based on the path-integral formulation of quantum mechanics [211]. For a comprehensive overview of the framework, we refer the reader to refs [135, 196, 212–214]. Miyazaki and Ananth recently applied the LSC-IVR framework to study nonadiabatic dynamics in ethylene [215]. This molecule is frequently used in such studies because it is small, computationally accessible, and has a conical intersection, where nonadiabatic couplings govern the dynamics. Building on the code implementation by Miyazaki and Ananth, we implemented the framework in PYSCES [Pub. 4], a Python code that interfaces TERAChem [216] to leverage GPU acceleration for on-the-fly electronic structure calculations.

Formally, nonadiabatic dynamics can be described exactly by the path-integral approach, and approximations allow for practical simulations [135]. Many experimental observables, as the vibronic spectrum [217, 218] and the rate of nonadiabatic processes [219, 220], are derived from theory by evaluating real-time quantum correlation functions. In the path-integral formalism, real-time quantum correlation functions involve a double integral over all possible forward and backward paths. The overall phase within the integral corresponds to the difference in action between the two paths, and truncating the terms to the first order yields a linearized semiclassical approximation [215]. Furthermore, key to the approach is the Meyer–Miller–Stock–Thoss mapping, which represents the discrete electronic states as classical phase-space variables (x, p) [221, 222]. This places both electronic and nuclear degrees of freedom on an equivalent

dynamical footing in a classical phase space [212]. Using a Wigner transformation for the operators, the correlation function is represented by a phase-space integral over a product of Wigner functions evaluated at the initial time and classically time-evolved phase-space coordinates at time t , respectively. In practice, initial conditions are sampled from the first Wigner function, and each trajectory is propagated independently according to the classical equations of motion until time t , at which the second Wigner function is evaluated. Calculating correlation functions using the LSC-IVR approach allows for efficient on-the-fly simulations, and the method is exact at time zero and for harmonic potentials [215].

An important point when implementing the numerics in PYSCES—and in general propagation methods in an adiabatic basis representation—is the sign convention of the electronic states. Electronic structure programs (e.g., TERACHEM used in Publication 4) calculate states up to a global phase factor, which is not uniquely defined. Using adiabatic states as a basis for propagating nonadiabatic dynamics can therefore lead to phase inconsistencies between time steps [223]. In practice, most electronic structure programs select real-valued phase factors, meaning the phase factor is typically either $+1$ or -1 . While this choice has no influence on, e.g. the energy eigenvalues of the excited states, it becomes a decisive difference when calculating quantities that involve multiple states. This is especially relevant for the equations of motion in nonadiabatic dynamics, where nonadiabatic coupling vectors $\langle \psi_i | \nabla_{\mathbf{R}_k} \psi_j \rangle$ depend on two states ψ_i and ψ_j . If one phase factor changes sign unexpectedly between time steps, the nonadiabatic coupling vector would flip the sign accordingly, adversely influencing the dynamics.

We designed the numerical algorithm such that a consistent sign convention is used. To ensure phase consistency throughout the propagation, we employ a two-level criterion to reliably detect and correct artificial sign swaps in all nonadiabatic coupling vectors. First, we monitor whether the nonadiabatic coupling vectors have unexpectedly flipped sign by estimating their expected signs via linear extrapolation from previous time steps. Second, we verify this detection by checking whether the transition dipole moment between the corresponding states has also artificially swapped sign, using a similar extrapolation-based estimate. This second check is particularly insightful because if the phase of an adiabatic state has flipped, both the nonadiabatic coupling vector and the transition dipole moment change sign. By combining both criteria, we can identify most artificial sign swaps and apply the necessary corrections to the nonadiabatic coupling vectors, thereby restoring phase consistency. An alternative algorithm to preserve phase consistency is to detect sign flips by calculating the overlap of the states between time steps [223], which, however, comes with demanding computational effort. Our algorithm has minimal computational overhead and pays off significantly in terms of numerical stability (see Publication 4 for an example).

CHAPTER 3

Results and Overview

3.1 Density-Based Measures for Excitation Energy

Natural light-harvesting complexes convert solar energy into chemically useful energy. A key step within this process is the transport of electronic excitation energy across a network of chromophores. Real-time TDDFT provides the framework for simulating these energy-transfer pathways with atomic-scale spatial and temporal resolution. Before we turn to the excitation dynamics in the light-harvesting complex 2 in Section 3.2, a fundamental question must, however, be addressed: How do we actually measure the excitation-energy distribution in our simulation? This question arises because real-time TDDFT provides only the time-dependent electron density $n(\mathbf{r}, t)$ and observables derived from it. For energy-transfer processes involving charge transfer between molecules, the density can simply be integrated over predefined regions to monitor the movement of charge and, consequently, the associated energy [35]. However, excitation-energy transfer typically occurs without any net charge displacement. Consequently, a more sophisticated approach is required to extract meaningful energy distributions from density oscillations alone. In [Publication 1](#), we address this challenge by developing density-based measures of excitation energy that do not rely on model assumptions about the system.

To this end, we start from a physically intuitive perspective: a weak excitation of a molecule induces a redistribution of its electron density, resulting in density oscillations. Density oscillations in one molecule of an assembly may induce oscillations on a neighboring molecule, which can be understood as a mechanism of excitation-energy transfer. Figure 3.1 schematically illustrates this idea for a prototypical system of two dimers, where the sequence of induced density snapshots makes intuitively evident that excitation energy flows from the left molecule to the right molecule. The central challenge is to translate these density fluctuations into a spatial representation that determines where the excitation energy resides. Consequently, we sought measures that satisfy three criteria: (i) they can be derived from $n(\mathbf{r}, t)$ and do not require an explicit model Hamiltonian, (ii) they are positive definite, allowing an interpretation as excitation-energy densities, and (iii) they are compatible with Ehrenfest dynamics, so that nuclear motion can be incorporated in later simulations. These measures are therefore designed to provide an interpretable description of how the excitation energy is distributed throughout the system at every time step.

In [Publication 1](#), we propose three density-based measures to localize excitation energy.¹

¹Note that the numbering of the measures differs from [Publication 1](#), where we initially considered a fourth measure based on the KS energy density, but disregarded it for reasons explained in the article.

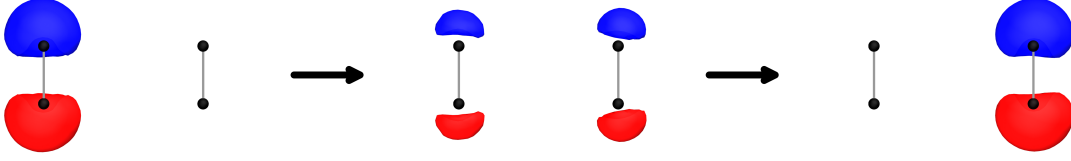


Figure 3.1: Schematic excitation-energy transfer in a real-time propagation of two sodium dimers with the left dimer initially excited. Snapshots display the induced density $\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n(\mathbf{r}, 0)$ as isosurfaces, red for positive and blue for negative values. The sequence illustrates that the excitation is first localized on the left dimer, subsequently shared equally between both fragments, and finally resides primarily on the right dimer, thereby visualizing the excitation-energy transfer from left to right using the density fluctuation.

The first measure is motivated by the intuitive physics of dipole oscillations as underlying the well-known Förster-type energy transfer [25, 224]. Here, we partition the system into molecular sites indexed by l . For each site, we evaluate the induced dipole moment $\delta\mu^{(l)}$ by restricting the integration in eq 2.18 to the volume $V^{(l)}$ associated with the molecular site. Formally, the measure can be written as

$$\mathcal{E}_\mu^{(l)} \propto |\delta\mu^{(l)}(t)|^2, \quad (3.1)$$

where the time evolution of the amplitude of $|\delta\mu^{(l)}(t)|^2$ directly reflects the magnitude of the density oscillation on the molecular site l . While this definition is physically intuitive and easy to compute, it has two clear limitations. First, it only works for dipole-active excitations, and second, it requires partitioning the system into fragments for the volume integration, making the results also sensitive to the specific partition definition. Such a partitioning is straightforward for systems like sodium dimer chains (Publication 1) or the bacteriochlorophyll (BChl) units in the light-harvesting complex 2 (Publication 2). However, for more general supramolecular architectures, where entities are less obvious, a partition-free excitation-energy density is preferable. To overcome these shortcomings, we therefore introduce two additional measures.

The second and third measures for excitation energy are based on the density fluctuation itself and are defined as

$$\mathcal{E}_{\delta n}^{(l)} = \int_{V^{(l)}} \epsilon_{\delta n}(\mathbf{r}, t) \, d^3r \quad \text{with} \quad \epsilon_{\delta n}(\mathbf{r}, t) \propto \delta n(\mathbf{r}, t)^2 \quad \text{and} \quad (3.2)$$

$$\mathcal{E}_{\dot{n}}^{(l)} = \int_{V^{(l)}} \epsilon_{\dot{n}}(\mathbf{r}, t) \, d^3r \quad \text{with} \quad \epsilon_{\dot{n}}(\mathbf{r}, t) \propto \dot{n}(\mathbf{r}, t)^2. \quad (3.3)$$

The proportionality factors in eqs 3.2 and 3.3 required for proper energy-density units are omitted here for simplicity (see Publication 1 for details). To study the relative distribution of the excitation energy within the investigated systems, knowledge of the proportionality factors is not required, and we thus directly analyze $\delta n(\mathbf{r}, t)^2$ and $\dot{n}(\mathbf{r}, t)^2$ in the following. The induced

density $\delta n = n(\mathbf{r}, t) - n(\mathbf{r}, 0)$ entering eq 3.2 measures the deviation of the time-dependent density from its initial value (usually the ground-state density). Thus, $\varepsilon_{\delta n}(\mathbf{r}, t)$ effectively reflects the “elongation” of the density fluctuation, analogously to the displacement from the equilibrium position in a classical harmonic oscillator. The induced density has also been used in prior studies by Rozzi et al. [30] to analyze the excitation dynamics in an organic donor–acceptor system. The time derivative of the density $\dot{n}(\mathbf{r}, t)$ entering eq 3.3 represents the magnitude of the density change. Through the continuity equation $\dot{n} = -\nabla \cdot \mathbf{j}$, it is directly related to the electronic current $\mathbf{j}$ and therefore carries information on how quickly the electrons move, similar to the momentum in the harmonic oscillator example. Both approaches (eqs 3.2 and 3.3) provide spatially resolved densities of excitation energy that allow the energy to be followed without the need to partition the system into subunits. If we *do* want subunit-specific energies (e.g., per molecule), $\mathcal{E}_{\delta n}^{(l)}$ and $\mathcal{E}_{\dot{n}}^{(l)}$ are available, which integrate the excitation-energy density over the volume of the respective subunit $V^{(l)}$. In addition to the physical motivation behind the measures, [Publication 1](#) also provides an analytical validation showing that the three measures are equivalent to the time-dependent state-occupation numbers in a model-Hamiltonian system in a limiting case.

To test the measures in practice, we performed real-time TDDFT simulations of molecular model systems built from sodium dimers. Chains of sodium dimers enable the analysis of excitation-energy transfer using first-principles simulations, while remaining simple and transparent. There are several reasons why sodium dimers are particularly attractive for constructing prototype excitation-energy transfer systems. First, their lowest excitation is a dipole-active oscillation oriented along the internuclear axis [225, 226], and it is energetically isolated from higher-energy states. Consequently, a pair of such dimers can be regarded as coupled two-level systems—the canonical model of excitation-energy transfer [25, 50, 227]. Second, the excitation energy of a dimer can be controlled by varying its bond length, thereby allowing us to set dimers either in resonance (identical excitation energies) or out of resonance (mismatched excitation energies). Third, the inter-dimer coupling can be tuned by adjusting the relative orientation and the separation of the dimers. Fourth and finally, the small molecular size of sodium dimers makes them computationally cheap. Within grid-based real-time TDDFT, a modest grid spacing is already sufficient to achieve high-accuracy results.

The first model that we study consists of two non-resonant sodium dimers. The molecular arrangement (with values for the dimer distances) is illustrated in Figure 3.2a. In this geometry, the first dimer (donor D) is oriented with its symmetry axis along the z direction, whereas the second dimer (acceptor A) is rotated by 20° around the inter-dimer connection axis. For simplicity, the nuclei’s positions are fixed throughout the simulation in this case; the effects of nuclear motion are discussed later in this section. We excite the donor with a weak laser pulse with a temporal width of 10 fs, modeled as an electric dipole field spatially focused on the donor dimer (see [Publication 1](#) for the pulse parameters).

Throughout the simulation, we monitor the three excitation-energy measures. In addition to the excitation-energy signal, the raw measures also contain a high-frequency oscillation not related to the excitation-energy transfer. To isolate the excitation-energy signal from the data, we smooth the signal as explained in detail in Section A.1. The resulting smoothed quantities are

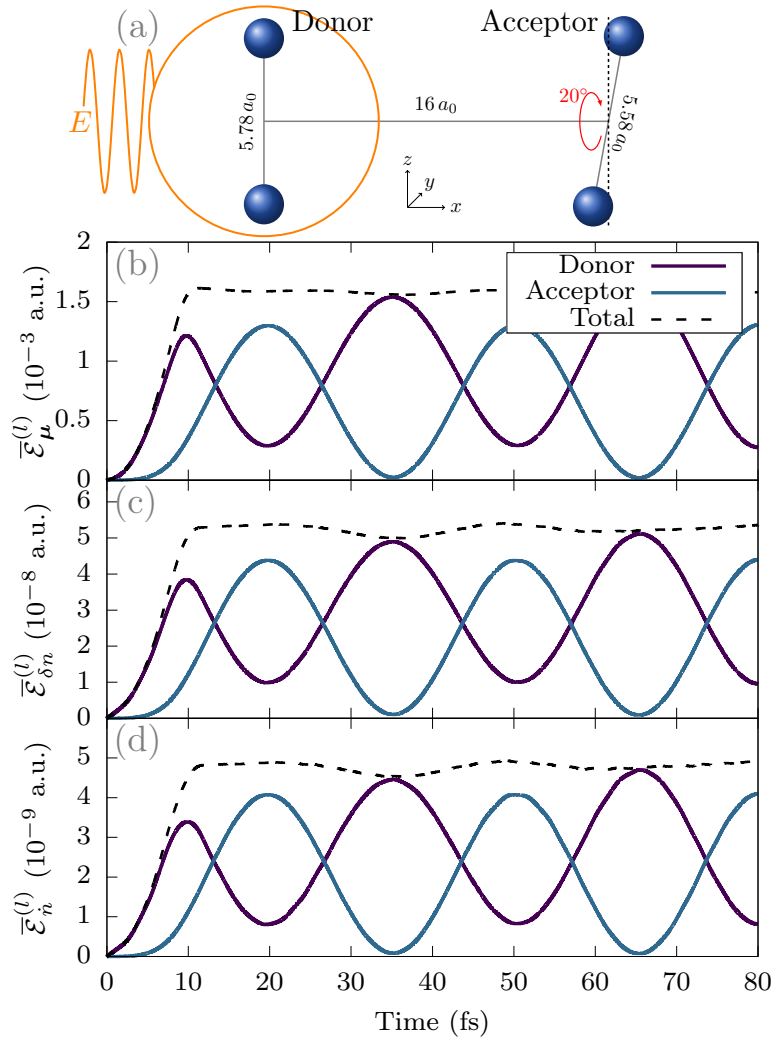


Figure 3.2: (a) Illustration of the donor–acceptor model setup to study excitation-energy transfer between two sodium dimers. (b–d) Time-dependent (smoothed) excitation-energy measures $\overline{\mathcal{E}}_{\mu}^{(l)}$, $\overline{\mathcal{E}}_{\delta n}^{(l)}$, and $\overline{\mathcal{E}}_n^{(l)}$, respectively. In each panel, the purple (solid), blue (solid), and black (dashed) line correspond to the donor ($l = D$), acceptor ($l = A$), and their sum (“Total”). Note that these measures are designed to quantify the relative excitation-energy distribution; thus, absolute values across different measures are not directly comparable.

denoted by an overline, as, e.g., $\overline{\mathcal{E}}_{\mu}^{(l)}$. The three (smoothed) excitation-energy measures for the two-sodium-dimer system are displayed in Figure 3.2b–d.

The measure using the induced dipole moment presented in Figure 3.2b reveals a back-and-forth flow of excitation energy. Because the dimers are off-resonant, the transfer is incomplete, and thus the average excitation energy on the donor remains at a higher level than on the acceptor. The sum of both contributions (donor and acceptor) is essentially constant, with only a slight deviation

that appears due to the different geometry of the two dimers (which leads to slightly different single-molecule excitations). With the different geometries of the molecules, a model Hamiltonian (as in the supporting information of [Publication 1](#)) also predicts an incomplete energy transfer. Hence, the squared dipole moment constitutes a reliable indicator of how the excitation energy is distributed across the system.

The smoothed measures $\overline{\mathcal{E}}_{\delta n}^{(l)}$ and $\overline{\mathcal{E}}_{\dot{n}}^{(l)}$ are shown in Figure 3.2c,d. Both reproduce the same back-and-forth energy-transfer dynamics as visible in $\overline{\mathcal{E}}_{\mu}^{(l)}$. As with the dipole-based measure, the sum of the donor and acceptor contributions remains nearly constant throughout the propagation with only minor deviations that originate from the slightly different bond lengths of the dimers. These results demonstrate that the measures defined by eqs 3.2–3.3 provide two additional consistent measures for quantifying excitation energy within real-time TDDFT.

So far, the discussion has been restricted to the clamped-ion approximation. In real-world systems at ambient temperature, however, nuclear motion plays a decisive role in energy-transfer processes [25]. The concepts introduced above can be transferred directly to a coupled electron-nuclear dynamics description by combining real-time TDDFT with Ehrenfest dynamics.

With nuclear motion, the excitation-energy measure based on $\dot{n}$ can offer advantages over the measures based on δn and $\delta\mu$. In a real-time propagation with moving nuclei, the electron density carries two distinct features: (i) the electronic response to the excitation and (ii) the effect of the electron density being dragged along with the moving nuclei. Our primary interest lies in the former, as it contains the excitation-energy transfer signal. Once the molecular geometry has changed noticeably in the propagation, a comparison of the density (or dipole moment) with its initial value primarily reflects how far the electron density has been displaced by the nuclear motion. Therefore, using the time derivative of the density $\dot{n}$ is better suited for monitoring the excitation energy, as the measure does not rely on the initial state by construction. Moreover, the time derivative applied on the density amplifies high-frequency contributions associated with the electronic excitations rather than the low-frequency components related to nuclear motion.

We study a linear arrangement of four sodium dimers as a proof-of-principle model for a chain of repetitive structural units—inspired by natural light-harvesting complexes, in which excitation energy is often transferred through identical molecular building blocks [8]. Figure 3.3 shows the molecular arrangement of the chain, with all dimers aligned in parallel and separated by an inter-dimer distance of $16a_0$. The dimers are numbered from left to right (1–4) and have bond lengths $d_1 = 6.40a_0$, $d_2 = 5.55a_0$, $d_3 = 4.90a_0$, and $d_4 = 5.55a_0$. Dimer 2 and dimer 4 have the equilibrium bond length, dimer 1 is stretched, and dimer 3 is squeezed. As in the previous example, we excite the left-most dimer (dimer 1) and monitor the excitation energy of the subunits as a function of time. We first simulate the system with fixed atom coordinates as a reference, and then revisit the identical configuration with nuclear motion. In this situation, $\overline{\mathcal{E}}_{\mu}^{(l)}$, $\overline{\mathcal{E}}_{\delta n}^{(l)}$, and $\overline{\mathcal{E}}_{\dot{n}}^{(l)}$ give identical energy-transfer dynamics, so for clarity we only show the latter explicitly.

Figure 3.3 demonstrates that the excitation energy remains largely localized on dimer 1 throughout the simulation, since the magnitude of $\overline{\mathcal{E}}_{\dot{n}}^{(1)}$ remains consistently higher than that of the other dimers. The observed trapping of energy stems from dimer 1 being off-resonant with

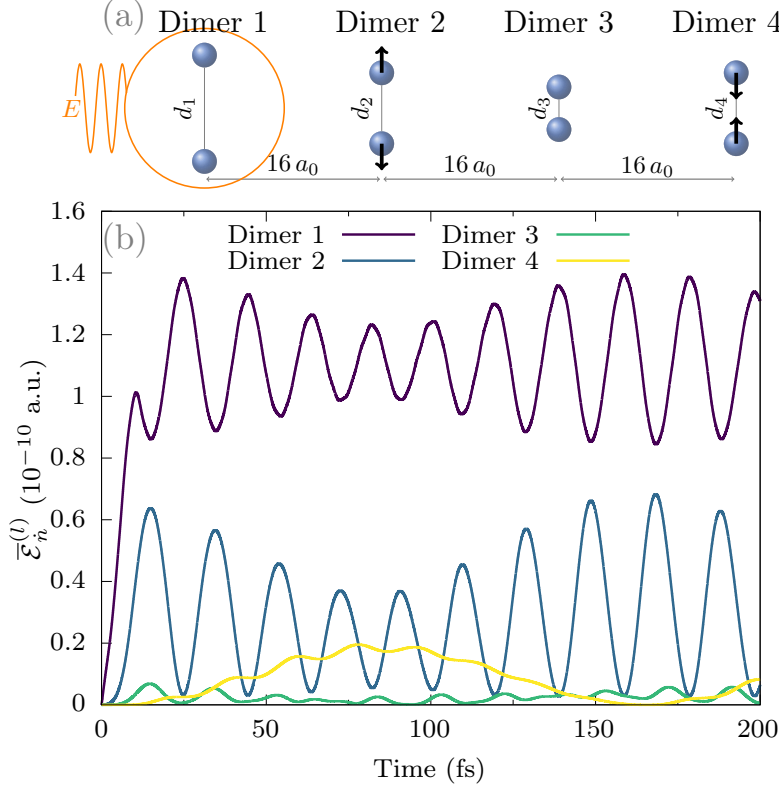


Figure 3.3: (a) Initial geometry of the four-dimer chain. Arrows indicate the assigned initial velocities for the simulation in which nuclear dynamics is switched on. (b) Smoothed $\overline{\mathcal{E}}_n^{(l)}$ excitation-energy signal for all dimers ($l = 1-4$) obtained from the fixed-nuclei simulation after excitation of dimer 1.

other dimers because its bond length differs from the other dimers. Therefore, the corresponding excitation energies do not exactly match, resulting in only a slight back-and-forth excitation-energy transfer between dimer 1 and the neighboring dimer 2, accompanied by minor participation of dimer 3.

This picture changes when nuclear motion is included. We keep the inter-dimer distances fixed and confine the nuclear motion to vibrations along the intra-dimer axes. Moreover, we assign initial velocities to the atoms of dimers 2 and 4, as indicated by arrows in Figure 3.3a. With the given positions and initial velocities, all four dimers undergo identical vibrational motions, with a phase shift of $-\pi/2$ from dimer 1 to dimer 4. Panel (a) of Figure 3.4 displays the time evolution of the dimer bond lengths during the propagation, thereby illustrating the vibrational motion.

Figure 3.4b shows the processed excitation-energy measures $\overline{\mathcal{E}}_n^{(l)}$ for the four dimers that now shows excitation-energy transfer as the dimers show vibrational motion. Note that including nuclear motion requires a further signal-processing step for the measures detailed in Appendix A.1. Whenever two lines intersect in the bond-length plot (Figure 3.4a), the corresponding dimers have identical bond lengths and therefore become resonant. For instance, at roughly 30 fs, dimer 1 and

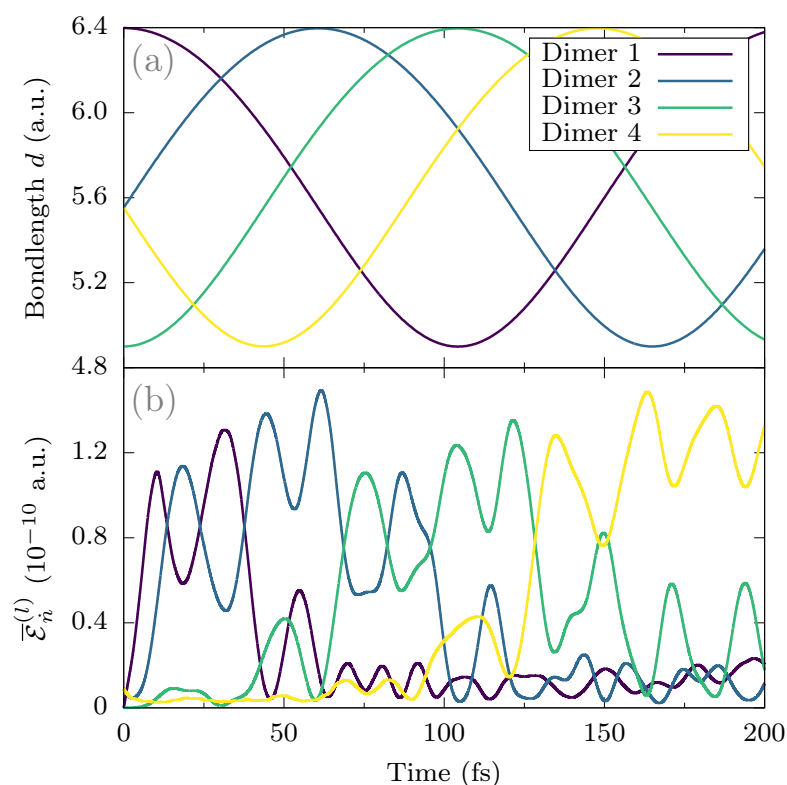


Figure 3.4: Results of an Ehrenfest-dynamics simulation for the four-dimer chain. (a) Time-dependent bond lengths of the four dimers, illustrating the vibrational motion. (b) Excitation energy evaluated with $\bar{\mathcal{E}}_n^{(l)}(t)$ for all four dimers.

dimer 2 have identical bond lengths, which makes them resonant. The excitation-energy measure shown in Figure 3.4b clearly indicates a transfer of energy from dimer 1 to dimer 2 at that time. Later, at around 80 fs, dimer 2 and dimer 3 become resonant and at 130 fs, dimer 3 and dimer 4 do so. Consequently, by switching on nuclear dynamics, excitation-energy transfer through the chain is enabled. While the excitation-energy signals also contain smaller oscillations reflecting the general coupling between the dimers, the overall trend is clearly evident: excitation energy propagates stepwise from dimer 1 to dimer 2, then to dimer 3, and finally to dimer 4. After the transfer, a direct back transfer from dimer 4 is not observed because the other dimers either have different bond lengths or are located farther apart. Thus, the excitation energy remains temporarily trapped at the end of the dimer chain.

For this concept study of a system with only a few nuclear degrees of freedom, a fully quantum-nuclear treatment would arguably be required to capture every subtlety of the dynamics. Nevertheless, the classical approximation inherent to Ehrenfest dynamics becomes justified when we investigate much larger multichromophoric assemblies, as discussed in the next section. Still, this sodium-dimer model provides a transparent view of how coupled electron-nuclear dynamics enables directional energy transfer through the molecular chain. In addition, the model

demonstrates that nuclear motion can induce a temporary trapping of excitation energy at specific molecular sites. Comparing the energy transfer in the static-nuclei and moving-nuclei simulations reveals the substantial impact nuclear motion can have on excitation-energy transfer.

3.2 Excitation Dynamics in the B850 Light-Harvesting Antenna

In natural light-harvesting systems, the excitation-energy transfer within the antenna complex is a key element in the solar-energy conversion. To gain insight into the molecular mechanisms of this process, [Publication 2](#) investigates the excitation dynamics of the B850 ring in the light-harvesting complex 2 of the purple bacterium *Rhodoblastus acidophilus*. The central questions that we aim to address in this study are focused on understanding the excitation dynamics and the interplay of electronic and nuclear dynamics in the B850 ring. Generally, we are interested in how the dynamics evolves in real time in the first tens of femtoseconds after the excitation. Specifically, we investigate whether nuclear motion has a decisive influence on the excitation dynamics on this time scale. Additionally, experimental studies often use laser pulses with an intensity much higher than sunlight [15, 228, 229]. Therefore, we discuss if such pulses trigger the same excited states of the B850 ring as the ones relevant in natural photosynthesis.

The B850 ring of *Rhodoblastus acidophilus* consists of 18 bacteriochlorophylls (BChls), as depicted in Figure 3.5. The center-to-center distance between neighboring BChls is only

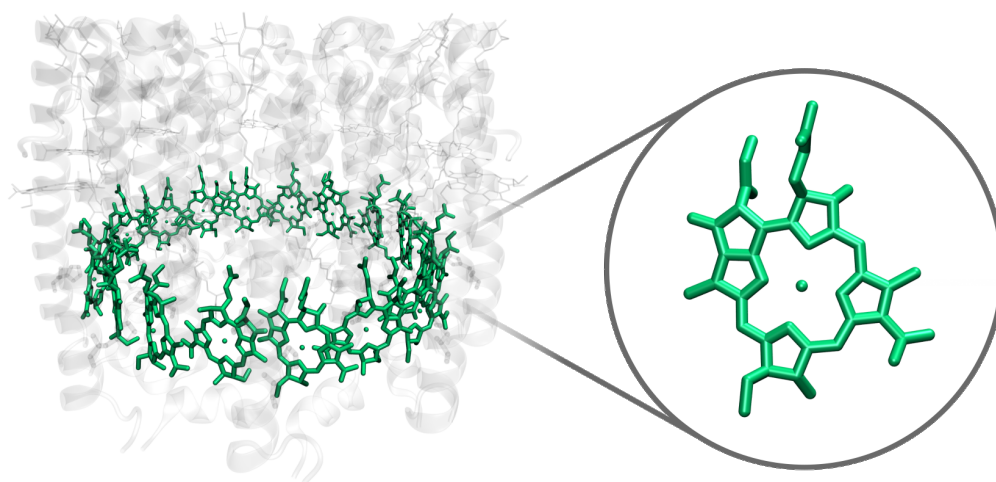


Figure 3.5: Left panel: B850 antenna ring (green) comprising 18 BChls and its environment (gray) inside the light-harvesting complex 2 of *Rhodoblastus acidophilus*. Right panel: Close-up of a single BChl without environment.

about $17a_0$ ($\approx 9\text{ \AA}$). Therefore, their coupling significantly determines the excitation dynamics. A key challenge when studying the B850 ring is that the molecular interactions are in the so-called intermediate coupling regime [22]. In this regime, the magnitude of the electronic coupling between the chromophores is of the same order as the coupling to the nuclei and

environment (in literature often referred to as “bath”). This proposes a fundamental challenge for perturbation-based theoretical descriptions, as neither the electronic coupling nor the coupling between excitation and nuclei can be considered as a small perturbation [230]. Thus, the standard approach in the literature is to apply a Frenkel exciton Hamiltonian and include the coupling to the bath in a parameterized manner [26, 27].²

In contrast to investigations based on exciton Hamiltonians, we employ real-time TDDFT with the Ehrenfest approach to simulate the coupled electron-nuclear dynamics without relying on exciton-model assumptions. The sheer size of the B850 ring, which includes almost 2000 nuclei and 5000 valence electrons, poses a significant computational challenge. We meet this challenge with our software package BTDDFT [50], which uses a real-space grid representation and massive parallelization to run the simulations. We embed the B850 ring in an electrostatic potential that mimics the environment, and we use LDA as the DFT functional, which is computationally light-weight and gives qualitatively reliable results for BChl systems when used with an environment potential (see Publication 1 and ref [43]).

We start our simulation from a thermally equilibrated geometry of the B850 ring and excite the molecule complex with a short, intense laser pulse. The pulse parameters are chosen such that they reproduce similar excitation conditions as in the experimental study of ref [231]. In the simulation, the laser pulse is modeled as an external dipole field with temporal shape and polarization as depicted in Figure 3.6a,b, respectively. The real-time propagation of the KS orbitals yields the time-dependent electron density $n(\mathbf{r}, t)$, from which we compute the induced density $\delta n(\mathbf{r}, t)$ for a qualitative view on the excitation dynamics and the induced dipole moments $\delta\mu^{(l)}(t)$ of the 18 individual BChl pigments for a later phase analysis of the density oscillations.³ We use Ehrenfest dynamics to propagate the nuclei along with the electrons in a nonadiabatic fashion. As discussed in Section 2.2.2, the Ehrenfest dynamics framework is ideally suited for this supramolecular structure due to the large number of electrons and nuclei, the short simulation window ($\lesssim 100$ fs), and the moderate nuclear movement at room temperature.

Figure 3.6 shows representative snapshots of the induced density during the propagation, thereby providing qualitative insight into the excitation dynamics during and after the laser pulse. The complete spatio-temporal evolution for an extended time window is available as a video in the Supporting Information of Publication 2 on the publisher’s website. We systematically analyze the excitation dynamics in a two-step protocol. First, we compare our dynamics to the excited states of a Frenkel exciton Hamiltonian. Second, we analyze the phase relations of the oscillations on the BChl sites using $\delta\mu^{(l)}(t)$.

To establish a connection between our real-time simulations and established exciton theory, we set up a Frenkel exciton Hamiltonian that models the electronic structure features of the B850 ring consistent with our time-dependent setup. We partition the ring into 18 BChl subsystems using an experimentally determined geometry [232] as used in ref [43]. Each BChl is individually modeled as a two-level system using the ground state and the excited state Q_y (both calculated on

²We use the term “exciton” to describe excited states of the B850 ring that are delocalized over multiple BChl units.

³The other proposed measures of Section 3.1 could also be used, giving similar results. Here, we present the analysis with the dipole moment, as it is more established in the literature.

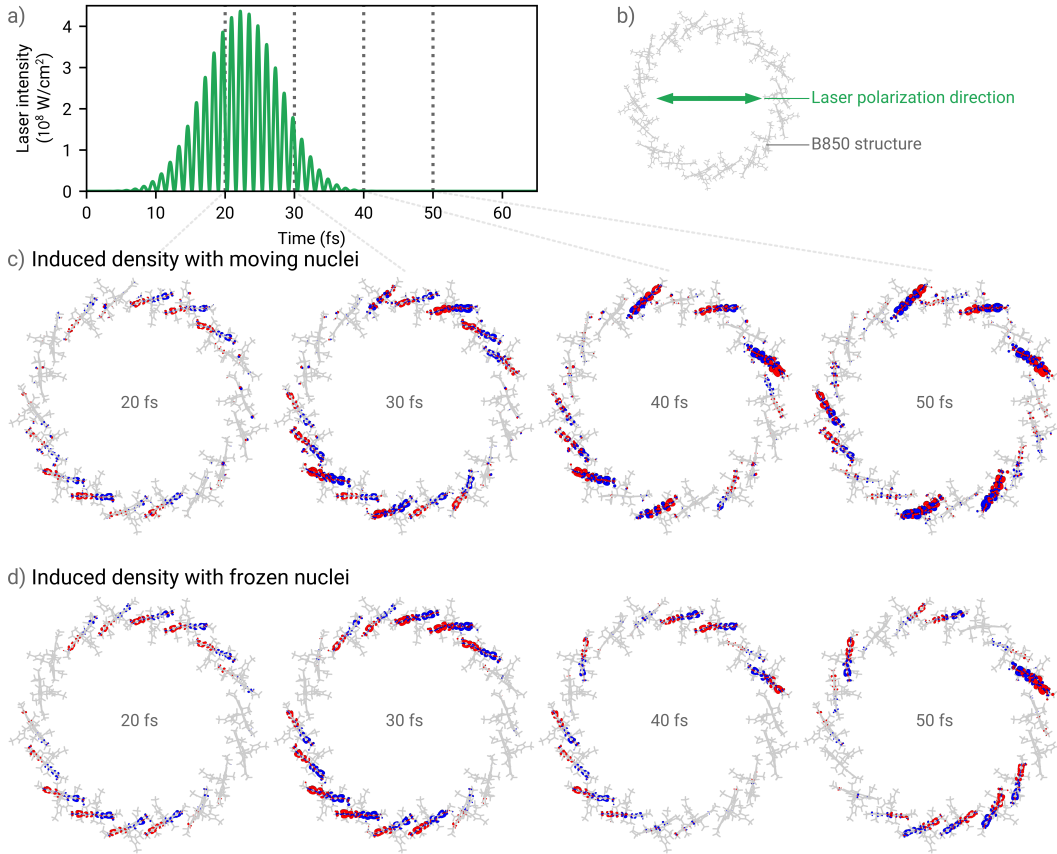


Figure 3.6: Real-time excitation dynamics of the B850 ring after an external laser pulse. (a) Intensity of the laser as a function of time depicted in green. (b) Top view of the B850 structure (gray) and polarization of the laser field (green) in the B850 plane. (c) Dynamics of the induced electronic density (after high-pass filtering, see Section A.1) with moving nuclei visualized for 4 snapshots at 20 fs, 30 fs, 40 fs, and 50 fs. These time stamps are indicated by dotted vertical gray lines in panel (a). Positive and negative values of the induced density are rendered in red and blue, respectively, using isosurfaces with isovalues $\pm 0.0002 a_0^{-3}$. For comparison, (d) shows the same quantity for a propagation with frozen nuclei.

the same level of (TD)DFT as described previously). The Q_y excitation is primarily responsible for the B850 band in the spectrum, when the BChls are assembled to the ring. In each single-BChl calculation, the other pigments and the surrounding proteins are included through an electrostatic environment potential. We compute the site energies E_i (Q_y excitation energy) and the transition densities n_i^{td} between ground state and Q_y excitation from the real-time TDDFT simulations according to the protocol of refs [50] and [42]. For the model Hamiltonian, the BChl–BChl couplings $V_{i,j}$ are computed with the transition density cube method [233],

$$V_{i,j} = \iint \frac{n_i^{\text{td}}(\mathbf{r})n_j^{\text{td}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r'. \quad (3.4)$$

Using E_i and $V_{i,j}$, we construct the Frenkel exciton Hamiltonian

$$\hat{H}_{\text{ex}} = \begin{pmatrix} E_1 & V_{1,2} & V_{1,3} & \dots & V_{1,18} \\ V_{2,1} & E_2 & V_{2,3} & \dots & V_{2,18} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ V_{18,1} & V_{18,2} & V_{18,3} & \dots & E_{18} \end{pmatrix}, \quad (3.5)$$

whose eigenvectors represent the ring's excited states in the Frenkel exciton picture using the two-level approximated BChls as basis. Figure 3.7 visualizes the transition densities of the first seven excited states. Figure 3.7 demonstrates that every excited state is delocalized over the ring, yet each with a different spatial pattern. The quantum number k categorizes these states by their symmetry, with $|k| = 0 - 3$ states visualized in panels (a–d), respectively. In the $k = 0$ exciton state, the individual transition-dipole moments of the BChls all point in the same angular direction, meaning the pigments oscillate in phase when this state is excited. For the energetically higher $k = \pm 1$ states, the transition-dipole moments undergo a full 2π phase twist across the ring, producing two nodes where the angular direction reverses. With higher values for $|k|$, the exciton states show progressively more nodes.

A comparison of the early real-time TDDFT excitation dynamics with the eigenstates of the exciton Hamiltonian reveals an interesting similarity. The collective oscillation at about 30 fs in the real-time simulation (second panel from the left in Figure 3.6c) displays the same spatial pattern as the $k = \pm 1$ exciton states (Figure 3.7). Consequently, the dynamics within the first 30 fs can be interpreted predominantly by the population from the ground state to the $k = \pm 1$ states. At later times (≈ 40 fs to 50 fs), the initially delocalized excitation starts to fragment into smaller segments, confining the density oscillations to regions that contain only a few chromophores. This effect may arise from two effects: (i) quantum mechanical interference between multiple excited states, which generate transient beating patterns, and (ii) coupling of the electron dynamics to the nuclear motion, which can lead to the localization of excitation energy.

To disentangle these contributions, we perform a reference real-time simulation with clamped nuclei. To make both simulations comparable, we start from the electronic ground state of the same initial nuclear geometry. We furthermore use the same laser pulse and simulation parameters so that the only modification is that the nuclei are now kept at their initial coordinates throughout the simulation. The induced densities of the excitation dynamics in this reference calculation are displayed in Figure 3.6d at the same time stamps as for the moving-nuclei simulation. For the first ~ 30 fs, the induced densities of the two simulations differ only marginally, both mainly showing the characteristics of the $k = \pm 1$ excitations. Beyond 30 fs, however, the initially collective oscillation starts to break up into smaller segments that span only a few BChls. In the frozen-nuclei simulation, this effect can now be entirely attributed to the interference of multiple excited states. As the short laser pulse is spectrally broad, not only the $|k| = 1$ states are excited, but also states with higher $|k|$ values. This superposition of multiple exciton states causes a beating pattern in the time-dependent density that manifests as the spatially localized (transient) patterns in Figure 3.6d.

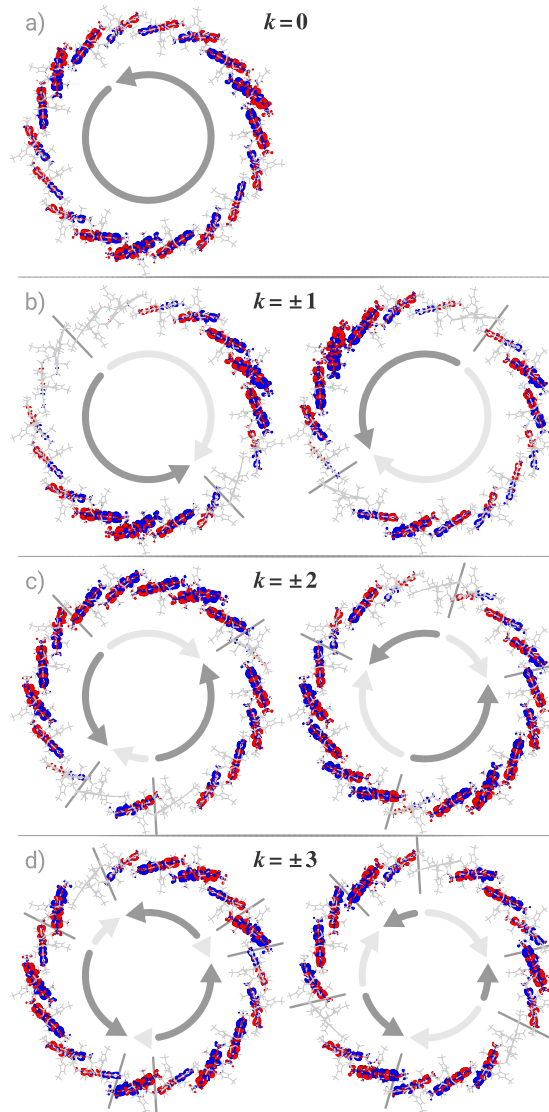


Figure 3.7: Transition densities of the first seven eigenstates of the exciton Hamiltonian visualized with isosurfaces (isovalue $\pm 0.0002 a_0^{-3}$, red: positive, blue: negative) set up on the geometry as determined crystallographically [232]. Gray segmentations and arrows indicate regions in which the BChls' individual transition dipole moments point in the same circular direction. The eigenstates are categorized by their $|k|$ value with (a–d) showing $|k| = 0 - 3$, respectively.

Comparing the moving-nuclei simulation (Figure 3.6c) with the frozen-nuclei simulation (Figure 3.6d) reveals that the dynamics begin to differ after roughly 40 fs. This trend continues so that at 50 fs, the excitation patterns are clearly distinct in both cases with the localization being slightly more pronounced in the moving-nuclei simulation. Two effects are therefore apparent in the moving-nuclei simulation. First, the short laser pulse populates several excited states, producing similar interference effects as they are also present in the frozen-nuclei simulation.

Second, including nuclear motion leads to a noticeable change in the spatial pattern of the induced density. Therefore, both the multi-state interference and the influence of the nuclear motion shape the excitation dynamics. We stress that both effects act on the same time scale and together determine how the excitation energy is distributed across the B850 ring.

Thus far, our investigation has relied primarily on visual inspection of induced-density snapshots. To present a more detailed analysis of the dynamics, we switch to an analysis of the induced dipole moments $\delta\mu^{(l)}$ of the BChls that are derived from the induced density. For each BChl l , we project its time-dependent induced dipole moment onto its approximate Q_y transition direction, yielding the scalar quantity $p^{(l)}(t) = \delta\mu^{(l)}(t) \cdot \mathbf{e}_{Q_y}^{(l)}$. The Q_y transition direction is approximately tangential to the ring, and we define the unit vector $\mathbf{e}_{Q_y}^{(l)}$ pointing in clockwise direction from a top view. When a BChl is excited, its dipole moment oscillates primarily along the Q_y direction. This causes an oscillation in $p^{(l)}(t)$ that encodes the amplitude and phase of this BChl's dipole-moment oscillation due to the excitation. We use these projected quantities for all BChls to determine (i) the times at which the dipole oscillations have a positive or negative extremum and (ii) the magnitude of each extremum. Thus, a positive extremum corresponds to a dipole moment elongated in clockwise direction, while a negative extremum indicates an elongation in counter-clockwise direction. Figure 3.8 visualizes the temporal positions of the extrema of $p^{(l)}(t)$ for all BChls. Blue

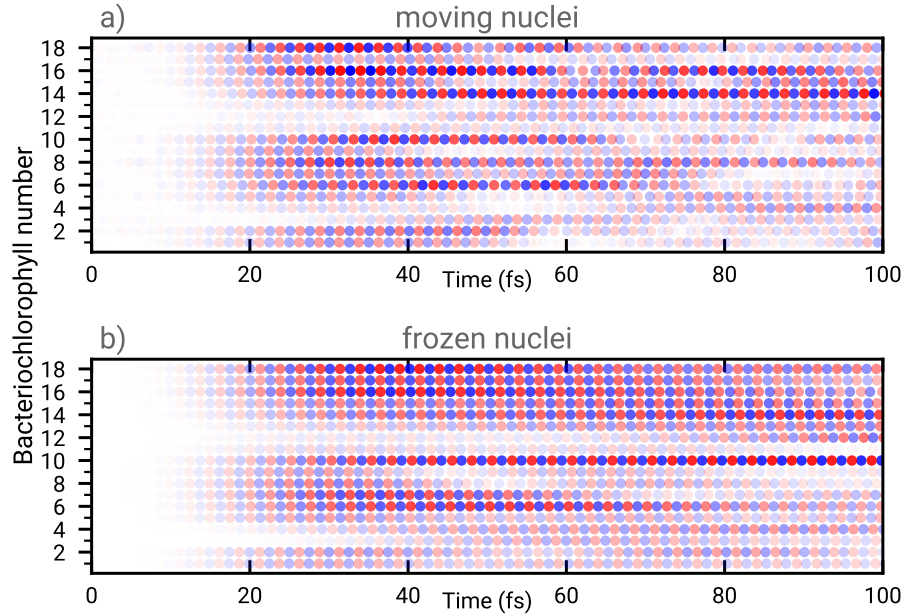


Figure 3.8: Phase analysis of the excitation dynamics for simulations with moving nuclei (a) and frozen nuclei (b). For each BChl (vertical axis), the times (horizontal axis) at which local maxima and minima of the projected dipole moment $p^{(l)}(t)$ occur are indicated by blue and red dots, respectively. The magnitude of these extrema is encoded by the color saturation.

dots denote local maxima, red dots local minima, and the color saturation of the dots encodes

the magnitude of the extremum. The figure contains two panels for two simulations: (a) with moving nuclei and (b) with frozen nuclei. The intensity of the extrema provides information about the amount of excitation energy (with the dipole moment being directly related to it, see Section 3.1), whereas the timing of the dots allows for the analysis of the phase relation of the dipole oscillations of the BChls.

Figure 3.8b (frozen nuclei) shows that at about 20fs the dots align to a vertical line. The extrema therefore occur simultaneously, which indicates that all BChls oscillate collectively. In each vertical line, there is a contiguous group of red dots and a contiguous group of blue dots, representing that the induced dipole moments in one group point clockwise while those in the other group point counter-clockwise, similar to the pattern in the $k \pm 1$ exciton states. At later times, starting around 30fs to 40fs, the perfect vertical alignment disappears and the collective character of the excitation fades progressively. In some segments, the dots still form a line, now slightly diagonal, indicating a temporal delay of the oscillations from one BChl to the next. These diagonal patterns appear within several different groups of BChls, and they reflect a wave-like propagation of a dipole oscillation around the ring. A direct comparison of panel (a) (moving nuclei) with panel (b) (frozen nuclei) shows that the coherent oscillations and wave-like patterns persist for a longer duration in the frozen-nuclei simulation than in the moving-nuclei case.

From these results, several important conclusions can be drawn. First, the analyses of the excitation dynamics demonstrate that the initial excitation (up to about 30fs) can be understood in terms of the $k \pm 1$ exciton states. This is supported by the visual inspection of the induced density (Figure 3.6) as well as the vertical lines in the dipole moment analysis (Figure 3.8). The ultrashort laser pulse therefore excites those delocalized states, which give the primary contribution in the absorption of sunlight and provide a main contribution in the excitation-energy transfer chain [234]. Therefore, although such a pulse clearly differs from natural sunlight, it predominantly triggers the same dynamics as present in natural light-harvesting. This supports the experimental insights obtained with such pulses to study the natural process.

In addition, the evolution of the excitation after the pulse offers insight into the delocalization and localization effects. The static-nuclei simulation demonstrates that already the pure electron dynamics show transient localization of the excitation energy, which arises from quantum interference between several excited states. Although the nuclei move on a significantly slower time scale than the electrons, our results demonstrate that nuclear motion has a significant impact on the excitation dynamics. Nuclear motion modulates the excitation on the same time scale as the quantum-interference effects and furthermore enhances the localization of excitation energy. Thus, for the excitation-energy transfer within the B850 ring, the interplay between electronic excitation and nuclear dynamics is decisive.

In the broader context of the photosynthetic process in *Rhodoblastus acidophilus*, the excitation-energy transfer within the B850 ring is only one of many steps to transport the energy through the chromatophore. While our focus is limited to this single step, the insights gained are nonetheless fascinating. They highlight the remarkable way how nature utilizes the arrangement and motion of the BChls within the B850 ring to control the excitation dynamics. The interplay of collective density oscillations across the ring and localization effects on individual BChls give initial hints

for further studies on how the excitation finds its optimal route to the reaction center, where it can undergo charge separation in a subsequent process.

3.3 Optically Induced Charge Separation at a Novel Donor–Acceptor Interface

Most human-made organic solar cells designed to absorb sunlight and separate charge for electricity generation rely on donor–acceptor systems. These materials are recognized to have tremendous potential in photovoltaic devices for generating green energy [63–66]. In [Publication 3](#), we investigate a novel organic donor–acceptor material combination to access its potential for photovoltaic applications. Our donor material is 3,7-di-*t*-butylphenothiazine (TBP). Phenothiazine dyes are known for their good light-absorption properties and their ability to donate electrons from their aromatic rings, and moreover, they are chemically flexible [76, 77, 235]. As an electron-acceptor molecule, we use *N,N'*-bis[3-(triethoxysilyl)propyl]-1,4,5,8-naphthalenediimide, which we abbreviate as NDI for simplicity. Naphthalenediimides possess an electron-deficient conjugated ring system and their high electron affinity thus enables efficient electron acceptance in donor–acceptor compounds [74, 75, 236, 237]. The skeletal structures of donor and acceptor molecules are illustrated in Figure 3.9a, which also presents a photograph of solutions of the single molecules and their mixture in panel (b). The subtle light-green color that appears when TBP and NDI

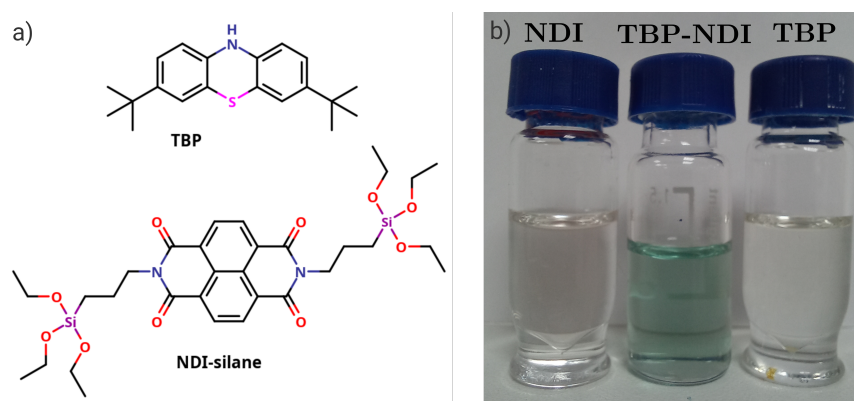


Figure 3.9: (a) Skeletal structures of TBP and NDI. (b) Photograph of TBP (left flask), NDI (right flask), and a TBP–NDI mixture (middle flask) in solution.

are mixed (middle flask in Figure 3.9b) already hints at an interaction between the molecules that changes their optical properties. Furthermore, considering the properties of the individual molecules, their combination appears promising for efficient and durable photovoltaic devices.

In this section, we analyze the optical properties of the chosen material combination using *ab initio* simulations, while [Publication 3](#) additionally provides initial experimental data from a collaborating author. For insights from theoretical perspective, we use TBP and NDI as building blocks to construct a series of molecular models that approximate the donor–acceptor interface of a

bulk heterojunction. To explore the structural and spectroscopic properties, we use different model sizes. First, we access the intermolecular binding with a single TBP and a single NDI (hereafter named the 1×1 system). This tests whether the molecules can form stacked arrangements and whether they retain their donor/acceptor character when combined. Subsequently, we investigate the excited-state properties for our largest model, containing three TBPs and three NDIs (the 3×3 system), as well as of a reduced 2×2 system (2 TBPs and 2 NDIs). The energies and character of the excited states shed light on the ability of the molecular compound to absorb light and separate charge. Finally, for the 2×2 system, we adiabatically incorporate nuclear motion to evaluate its impacts on the excited-state properties.

We verify whether the molecules stack on one another by examining the 1×1 system. As shown in the chemical structures in Figure 3.9a, both TBP and NDI have aromatic rings. These rings have delocalized π electrons that enable π – π interactions between TBP and NDI and thus potentially lead to stacking. First, we optimize the geometries of TBP and NDI independently and subsequently optimize the combined 1×1 complex. In this context, optimization means searching for the nuclear structure that yields the lowest total energy. All calculations in this project line are performed using the software packages QCHEM [133] and TERACHEM [216], which both primarily use Gaussian basis sets to represent the spatial electronic structure. To obtain the total energies in the optimization procedure, we use ground-state DFT with the global hybrid functional M06-2X that has been shown to describe intermolecular distances and binding energies accurately for this class of systems [159]. The resulting equilibrium distance between the two molecules is 3.18 Å with a binding energy of –21 kcal/mol. Compared with other π -stacked donor–acceptor pairs (as, e.g., in ref [238]), these values indicate strong binding between donor and acceptor. Therefore, our simulation confirms that the molecules bind, which is also approved experimentally in Publication 3 by the observation of long-living TBP–NDI aggregates.

For the calculation of electron affinities, ionization potentials, and later excited-state properties, we resort to the density-functional approximation optimally-tuned ω PBE (see Section 2.1.3) [176, 182]. This functional provides the high level of accuracy required to describe charge-transfer processes and has proven reliable in many cases, although it is computationally more demanding than (semi-)local functionals [73, 200, 239, 240]. Because the range-separation parameter ω is tuned separately for each molecular system, we first verify whether the optimal ω for TBP agrees with that for NDI. A similar ω of both molecules is essential so that a simulation of a combined TBP–NDI complex can be reasonably well described with one common ω . For each system, the tuning is performed at the ground-state geometry, and the resulting ω_{opt} values are shown in Figure 3.10. The ω_{opt} values for TBP and NDI are indeed very similar, confirming that a common range-separation parameter can be used for the combined system. For the combined 1×1 , 2×2 , and 3×3 systems, the tuning yields low values for the optimization cost function (numbers are presented in Publication 3). Consequently, optimally-tuned ω PBE is expected to provide reliable results for our further simulations.

Figure 3.10 also reports the eigenvalues of the HOMO and the lowest unoccupied molecular orbital (LUMO), which correspond to the negative value of the ionization potential and the electron affinity, respectively. For NDI we obtain an ionization potential of 8.61 eV and an electron affinity

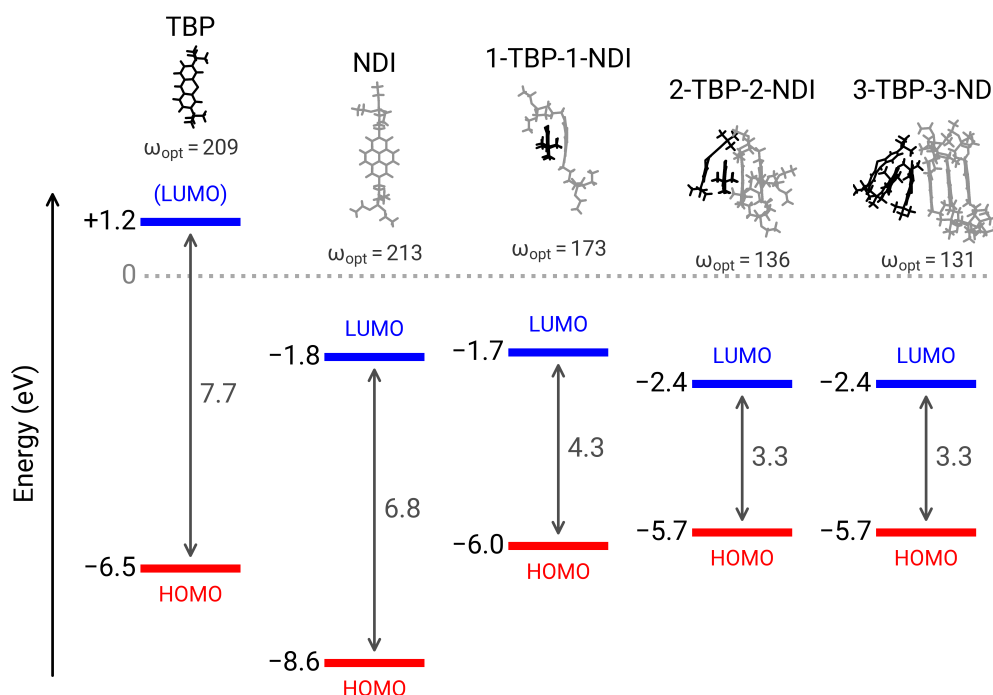


Figure 3.10: Diagram of the energy levels based on the KS eigenvalues. From left to right we show TBP, NDI, 1-TBP–1-NDI, 2-TBP–2-NDI, and 3-TBP–3-NDI. For each system, we display the geometry-optimized structure (TBPs: black, NDIs: gray), the optimal-tuned ω in $10^{-3} a_0^{-1}$, the LUMO eigenvalue (blue), the HOMO eigenvalue (red), and the HOMO–LUMO gap. The vacuum level is indicated by a horizontal dotted gray line.

of 1.80 eV, and for TBP we get values 6.55 eV and -1.23 eV.⁴ When combining both molecules into the 1×1 system, the ionization potential remains close to that of NDI and the electron affinity aligns with that of TBP. This indicates that the donor properties of TBP and the acceptor properties of NDI are retained when both molecules are combined, confirming our concept of combining these two molecules. Comparing the 1×1 , 2×2 , and 3×3 systems, a slight reduction of the band gap is observed with increasing model size. From the 2×2 system to the 3×3 system, the gap, however, changes only marginally, indicating that the band gap changes saturate. Thus, the 2×2 and 3×3 systems are within this accuracy already a reasonably large enough model for the interface. This saturation confirms our approach to mimic the bulk interface with our multimolecular models.

The 3×3 system, our largest model with 417 atoms and 1584 electrons, comes closest to capturing the properties of the bulk interface. This molecular size already represents the upper limit of what is computationally feasible with ω PBE as a high-accuracy density functional. For

⁴The negative electron affinity for TBP signifies that the molecule does not accept electrons, consistent with its donor role. The precise numerical value has no physical interpretation; it stems from the numerics using a finite basis set.

the geometry-optimized structure of the 3×3 system, we investigate its optical properties by calculating the excitation energy and the corresponding oscillator strengths. The resulting values are listed in Table 3.1.

Table 3.1: Excitation energies and oscillator strengths of the first eight excited states (S1–S8) of the 3-TBP–3-NDI system.

State	Excitation Energy (eV)	O.S.
S1	1.47	0.1039
S2	1.73	0.0285
S3	1.78	0.0011
S4	2.05	0.0004
S5	2.25	0.0001
S6	2.42	0.0003
S7	2.46	0.0008
S8	2.52	0.0109

Interesting results emerge from these calculations. The lowest-energy excited state, S1, has a non-negligible oscillator strength, making it optically accessible. Furthermore, the excitation energy of S1 is 1.47 eV, which is close to the value 1.4 eV often referred to as most efficient for single junction organic solar cells [241]. This is a promising finding for our material, which is supposed to be used in photovoltaic devices. The excited states higher in energy remain within the visible range, but show significantly lower oscillator strengths.

We now characterize the electronic structure of the individual excited states using difference densities, which show the difference between the excited-state and ground-state densities. Figure 3.11 visualizes these difference densities for the first eight excited states. Blue regions indicate increased electron density upon excitation, while red regions show decreased electron density. For charge-transfer excitations, this means the transferred electron leaves behind a positive charge, referred to as “hole”, and the additional negative charge referred to as “electron”. All excitations in Figure 3.11 show charge-transfer character from the donor molecules to the acceptor molecules, though the specific molecules involved vary from excitation to excitation. Therefore, the electron-hole distances differ across the excited states. In S1, charge is being transferred directly from the interface TBP to the neighboring interface NDI. In S2, the electron and hole are farther apart as the interface TBP donates charge to the second (middle) NDI molecule, with one molecule in between non-participating in the excitation. S3 shows an electron-hole distance similar to that of S2, but transfers charge from the middle TBP to the interface NDI. For S4–S7, the electron-hole distance increases further with two rather uninvolved molecules between the electron and the hole. Overall, a trend is apparent for the states: states with higher excitation energies are associated with larger electron-hole separation. Since S1 has the smallest electron-hole separation, its electron and hole orbitals have the greatest overlap, likely explaining its higher oscillator strength compared to those of higher states.

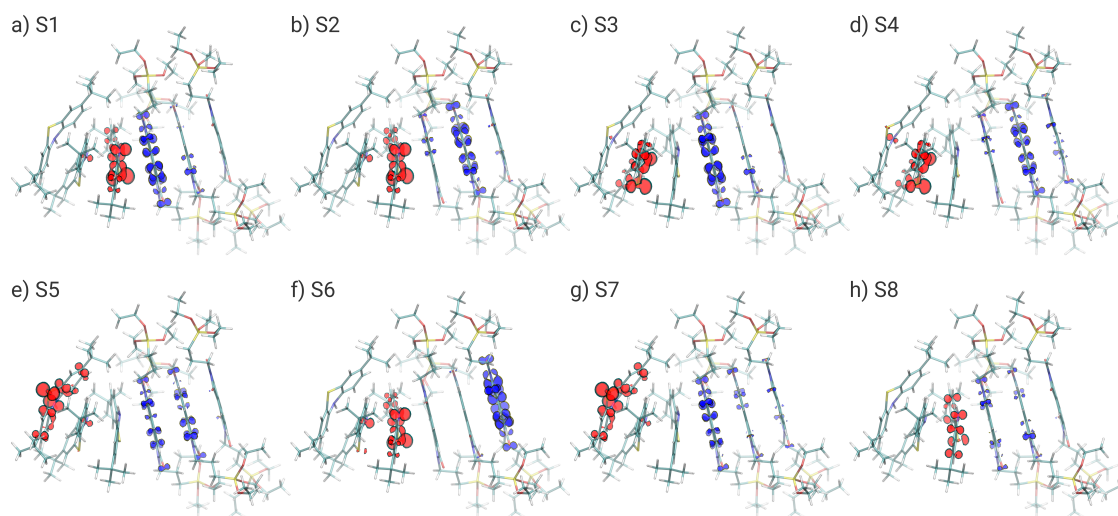


Figure 3.11: (a–h): Difference densities of the first eight excited states (S1–S8) with respect to the ground state for the 3-TBP–3-NDI system visualized with isosurfaces (isovalues $\pm 0.0002 a_0^{-3}$). Red surfaces denote electron-deficient regions (“hole”) and blue surfaces denote regions with increased electronic charge after excitation (“electron”).

To convert incident light to free charge for electric current in organic donor–acceptor combinations, the following steps typically occur [60, 62, 242]: (i) incident light is absorbed, creating a local excitation on one molecule, (ii) the excitation diffuses through the supramolecular complex and eventually reaches the interface, (iii) charge transfer occurs at the interface via a charge-transfer excitation, (iv) the opposite charges separate away from the interface until their Coulomb interaction becomes negligible, after which they diffuse to the electrodes. In our material combination, however, the situation is different. The charge-transfer excitation S1 is already located at the interface and is optically accessible. Therefore, it can be directly excited by light without requiring steps (i) and (ii), which could enhance overall efficiency.

A so far unresolved question for the TBP–NDI system is whether charge separates from the interface as in step (iv). To address this, the exciton-binding energy must be overcome—the energy required to dissociate the bound electron-hole pair into free charge carriers. This energy is defined as the difference between the fundamental gap (calculated here from the frontier eigenvalues) and the optical gap. For the 3×3 system, a direct calculation results in an exciton-binding energy of 1.66 eV. However, this value must be treated with caution, as exciton-binding energies resulting from such simulations strongly depend on the number of units included in the molecular structure [73]. For a quantitatively reliable value comparable to bulk conditions, either larger molecular assemblies should be used or dielectric screening through the environment should be considered. Adding more molecules would significantly increase the computational effort, while incorporating dielectric screening is difficult given the distinct donor and acceptor regions, which are difficult to model without introducing empirical parameters. Therefore, the reported excitation-binding

energy should rather be interpreted as an upper limit for the value in bulk conditions.

The spatial structure of the excited states provides insight into possible mechanisms of charge separation. The presented states (Figure 3.11) all show charge-transfer character, with S2–S7 having larger electron hole distances than the (optically accessible) interface charge-transfer excitation S1. Those states suggest a possible dissociation pathway in the 3×3 system, highlighting the potential usefulness of this material combination for photovoltaic devices. Transitions to states with larger electron-hole distances could represent early steps in the dissociation under bulk conditions. Whether such transitions happen at ambient conditions raises new questions. Our findings so far were based on geometry-optimized structures, prompting the question of whether our results remain valid in the presence of room-temperature nuclear motion. Furthermore, the energetic ordering of the states is not ideal for a self-driven charge separation. In our calculations, the strongest bound electron-hole excitation is the lowest in energy, whereas a more favorable scenario would have charge-transfer states with larger electron-hole separation at lower energies, enabling electronic relaxation to a charge-separated state. Considering nuclear motion, however, could change this picture by inducing strong couplings between states and driving charge separation.

Changes in the geometry due to nuclear motion modulate the excited states, which we examine for the first excited states below. To enable computationally feasible molecular dynamics, we need to drastically reduce the molecular size while preserving the excitations' characteristics. This reduction is achieved, on the one hand, by replacing the silyl residues of the NDIs with methyl groups. For ease of readability, we still abbreviate those molecules as NDIs. Although the silyl residues are important for experimental thin-film fabrication, they play a minor role in our analysis focused on the first excited states [Pub. 3]. On the other hand, we additionally remove the outer units from the 3×3 system, yielding a 2×2 system.

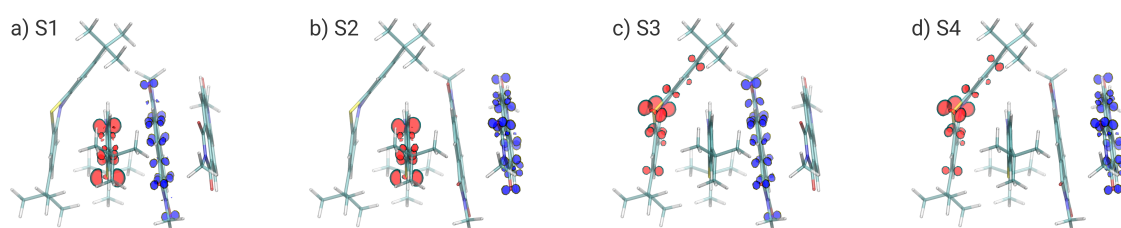
Before incorporating nuclear dynamics, we first verify whether the reduced 2×2 system retains the charge-transfer characteristic of the larger 3×3 system. We optimize the resulting 2×2 geometry and compute its first excited states. To be consistent with later molecular dynamics simulations, we use optimally-tuned ω PBE with the D3 dispersion correction [243] to maintain accurate π stacking. Table 3.2 reports the excitation energies and oscillator strengths, with the difference densities presented in Figure 3.12.

The characteristics of the first excited states of the 2×2 system mirror those of the 3×3 system: All states show donor-to-acceptor charge transfer; S1 remains an interface charge transfer; S2 and S3 show larger electron-hole distances with one non-participating molecule in between; and S4 confirms the similarity with a charge transfer beyond two uninvolved molecules. These results validate that our reduced 2×2 system reproduces the excited-state physics of the 3×3 system, enabling us to study nuclear motion effects on the excited states using the reduced 2×2 model.

To model nuclear structural changes at ambient conditions, we perform Born–Oppenheimer molecular dynamics (cf. Section 2.2.1). We sample initial positions and velocities for the nuclei from a 300 K probability distribution and couple the nuclei to a thermostat [244]. The system is propagated on the electronic ground state for approximately 2 ps. Thermal equilibrium is reached after about 0.5 ps, from which we begin our excited-state analysis. Along the trajectory, we extract

Table 3.2: Excitation energies and oscillator strength for the first six excited states (S1–S6) of the 2-TBP–2-NDI system.

State	Excitation Energy (eV)	O.S.
S1	1.21	0.0576
S2	1.63	0.0001
S3	2.03	0.0020
S4	2.42	0.0006
S5	2.44	0.0243
S6	2.73	0.0007

Figure 3.12: (a–d): Difference densities of the first four excited states (S1–S4) with respect to the ground state for the 2-TBP–2-NDI system visualized with isosurfaces. Red regions (isovalue $0.0002 a_0^{-3}$) indicate the hole, blue regions (isovalue $-0.0002 a_0^{-3}$) indicate the electron.

nuclear geometries every 4 fs and compute the adiabatic excitation energies for these structures.

Figure 3.13a shows the evolution of the excitation energies along the nuclear trajectory. This time-domain presentation already reveals that the excitation energies approach each other as closely as 10 meV. The individual excitation energies fluctuate by over 100 meV. Figure 3.13b,c provide statistical analyses of the data. Panel (b) plots the excitation energies and oscillator strengths for each geometry snapshot and shows statistical averages. Panel (c) shows the excitation-energy distributions as probability histograms. A key insight from the analyses, especially apparent in panel (c), is that the excitations reveal substantial energetic overlap. This overlap occurs between S1 and S2, S2 and S3, and also S3 and S4. This energetic proximity can indicate strong coupling between the states necessary for population transfer. While adiabatic excitation energies alone cannot prove such population transfer, the analysis demonstrates that the states are getting close in energy, suggesting a pathway for potential population transfer in a nonadiabatic description.

Our molecular dynamics results demonstrate that the earlier conclusions about the charge-transfer states are not limited to geometry-optimized structures, they remain valid for realistic, room-temperature geometries. In this context, we also emphasize the optical accessibility of S1. S1 has an average oscillator strength of 0.7, and for individual geometry snapshots, the oscillator strength reaches values up to 0.14. This indicates that the interface excitation remains optically accessible under ambient conditions. Consistent with the earlier analysis, the mean oscillator

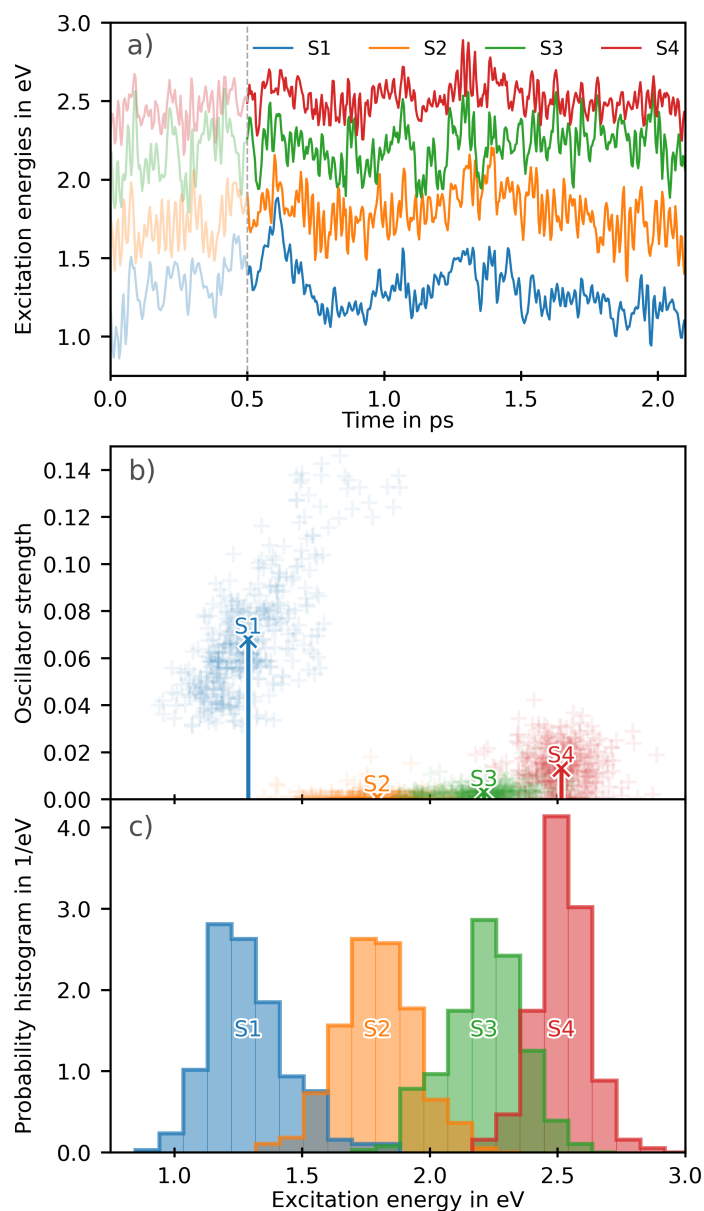


Figure 3.13: (a) Adiabatic excitation energies of the first four excited states (S1–S4) along the Born–Oppenheimer trajectory as a function of time. (b) Scatter plot of the excitation energies and oscillator strengths for all snapshots with $t > 0.5$ ps. Individual points are shown with “+” markers, and the mean values are indicated by an “x” and a vertical line. (c) Probability distribution of the excitation energies (for $t > 0.5$ ps snapshots) displayed as a histogram.

strengths of S2–S4 are lower than those of S1.

Possible coupling of the states at room-temperature nuclear configurations offers a plausible pathway for charge separation. Light can generate a charge-transfer state at the interface,

after which nuclear motion may drive transitions to states with a larger electron-hole distance, effectively separating electron and hole. In an organic solar cell, this charge-separation path could complement the traditional route, in which a local excitation of higher energy relaxes to a charge-separated state.

It is also noteworthy that [Publication 3](#) briefly explores recombination once S1 is accessed. When the geometry is relaxed on S1, the coupling to the ground state S0 has a rather small magnitude (≈ 0.01 eV) and is significantly smaller than the coupling to higher electronic states. This is a reassuring result, as the low S1–S0 coupling contributes to suppressing an undesired recombination.

Overall, the TBP–NDI combination appears to be a promising candidate for organic photovoltaic devices. Both the 3×3 and 2×2 systems show an optically accessible state with an excitation energy in a favorable spectral region, confirming the material’s potential photovoltaic efficiency. Higher-energy states also show charge-transfer character with larger electron-hole distances, suggesting a possible pathway for charge separation. Additional room-temperature molecular dynamics reveal the proximity of the excitation energies. This makes it plausible that the charge-separation pathway represents the first steps towards free charge carriers. Ideally, one would like to study the dynamics nonadiabatically to explicitly demonstrate which transitions actually occur from S1 and on what time scale. However, performing nonadiabatic dynamics with range-separated hybrid functionals on picosecond time scales is a serious computational challenge (see also Section A.3). On the qualitative level, our adiabatic analysis shows first steps how the electronic transitions could be driven by nuclear dynamics, potentially leading to efficient excitation dissociation in the material.

3.4 Nonadiabatic Dynamics in a Charge-Transfer System

The computational challenge of simulating nonadiabatic dynamics motivated our development of the software interface PYSCES [[Pub. 4](#)]. This tool addresses the need to explicitly track real-time population transfer in nonadiabatic processes like the charge separation discussed in the previous section.⁵ [Publication 4](#) presents the computational workflow and showcases PYSCES’ capabilities for two systems—a molecule in solution and an organic donor-acceptor pair—of which we briefly discuss the latter in this section.

We applied PYSCES to simulate charge-transfer dynamics at the donor–acceptor interface of Zinc phthalocyanine (ZnPc) and Buckminsterfullerene (C₆₀), a combination of potential interest for organic photovoltaic devices [[245–247](#)]. ZnPc is a planar molecule whose porphyrin-like ring shares structural similarities with BChl chromophores. Fullerenes are prototypical acceptors that are widely studied in organic photovoltaic research due to their high electron affinity [[30, 31, 67–69, 248](#)]. Prior studies [[249, 250](#)] have shown charge-separation dynamics in the face-on ZnPc–C₆₀ pair, with a higher-energy locally excited state on the ZnPc relaxing to a lower-energy charge-transfer state where an electron is transferred to the C₆₀. This donor–acceptor combination

⁵A benchmark simulation of a TBP–NDI system is provided in Section A.3.

thus provides a well-characterized test case for our software implementation, offering established photophysics while remaining computationally feasible.

We optimize the ZnPc–C₆₀ geometry and compute the excited states using CAM-B3LYP within (TD)DFT [162]. Consistent with ref [250], our excited-state characterization confirmed that the transition from the ground state to S4 is a bright, localized transition on ZnPc. For the molecular dynamics trajectory, we sample nuclear velocities from a thermal distribution, initialize the electronic system in the bright S4 state, and propagate the coupled electron-nuclear dynamics.⁶ To keep the calculations feasible while capturing the essential physics of the excitation dynamics, we explicitly included only the states S0–S4 in the dynamics.

Figure 3.14 illustrates the dynamics. To visualize the excitation dynamics, we plot a weighted

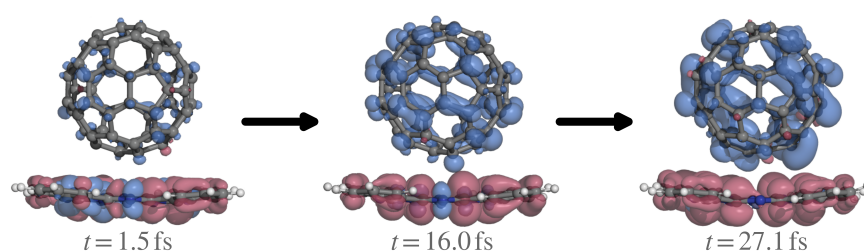


Figure 3.14: Charge-transfer dynamics of the ZnPc–C₆₀ pair at three different times ($t = 1.5$ fs, 16.0 fs and 27.1 fs from left to right) along the molecular dynamics trajectory. The isosurface representation shows the sum of the excited-state difference densities (with respect to the ground state) weighted by their time-dependent occupation numbers. Red surfaces correspond to negative values (hole); blue surfaces to positive values (electron). C₆₀ acts as the electron acceptor after a local excitation of the ZnPc.

sum of ground-to-excited-state difference densities for three snapshots along the trajectory, with weights determined by the time-dependent occupation numbers. While Publication 4 provides a more detailed analysis of the evolution of the occupation number, here we analyze the dynamics on a qualitative level. At about 1.5 fs, the excitation is localized on the ZnPc, as initialized. By 16 fs, nuclear motion has already induced partial electron transfer, yielding a state with a mixed character of a local excitation and a charge-transfer state. Finally, at about 27.1 fs, the electronic structure is completely relaxed to a state with charge-transfer character from ZnPc to C₆₀. The simulations thus demonstrate that the transfer from a locally excited state to a charge-transfer state occurs within 30 fs in this trajectory.

Simulating such medium-sized systems at a nonadiabatic level comes with significant computational costs. To resolve the fast electron dynamics, sub-femtosecond time steps are required. At each step, energy eigenvalues, state gradients, and nonadiabatic couplings have to be calculated in the adiabatic basis, which demands substantial computational effort. Consequently, the ZnPc–C₆₀

⁶Note that we only investigate a single trajectory here. For a quantitatively reliable population function, an ensemble of trajectories should be considered.

system represents the upper size limit of what can be studied nonadiabatically on this level of accuracy with the given cluster architecture. Nevertheless, PYSCES' parallelization capabilities allow distributing the workload across multiple nodes. Coupled with the ongoing development of graphics processing units, this software opens a path for future projects to study larger systems on a high-performance cluster.

The investigated excitation dynamics trajectory represents a fundamental step in the traditional procedure of energy conversion in organic solar cells—a paradigm example of a nuclear-motion driven energy transfer. The observed time scale for the local excitation to transition to a charge-separated state highlights the importance of nuclear dynamics in the investigation of such systems and how fast the nuclei can drive energy transfer.

APPENDIX A

Complementary Work

The appendix provides technical information relevant for the results presented in the main text. In this section, I briefly note some of my important implementations in the BTDDFT software package and explain the postprocessing scheme for the excitation-energy measures developed in this work. Furthermore, this section contains benchmarks and tests that may prove valuable for future work building on my findings.

A.1 Postprocessing of the Excitation-Energy Signal

To extract meaningful excitation-energy measures in an Ehrenfest dynamics simulation within real-time TDDFT on a real-space grid, several numerical challenges must be met. To isolate the excitation-energy signal from raw simulation data, two Fourier filtering steps are essential. The first step is only required when nuclear motion is active, while the second filtering is required in frozen-nuclei and moving-nuclei simulations. This section explains the data processing using the four-sodium-dimer chain from Section 3.1 as a representative example. We illustrate the workflow for dimer 1 of the sodium-dimer chain using the excitation-energy measure based on $\hat{n}$, while the procedure is similar for all three measures introduced in Section 3.1.

Figure A.1 shows the two-step filtering procedure. Panel (a) shows the raw, unmodified excitation-energy measure $\mathcal{E}_n^{(1)}$ for dimer 1, which contains three features: (i) a very fast oscillation with a frequency of ca. 1 fs^{-1} , (ii) the slower energy-transfer signal with a frequency of ca. $1/18 \text{ fs}^{-1}$, and (iii) a third modulation with a frequency of ca. $1/104 \text{ fs}^{-1}$ that appears as an oscillatory offset. The offset originates from the nuclear motion slowly dragging the electrons, an effect that has to be removed to isolate the excitation-energy transfer signal.

We remove this component by applying a high-pass Fourier filter to the time-dependent density before the excitation-energy measures are computed. This filtering is applied either on-the-fly (i.e., during runtime) in BTDDFT or in the postprocessing. In BTDDFT, a τ -filter is applied that computes the time average of the density over a time window τ and subtracts it from the time-dependent density. For the sodium dimer chain, a value of $\tau = 4 \text{ fs}$ is efficient to remove the nuclear-drag contribution from the signal. Figure A.1b shows that this step successfully removes the offset while preserving the energy-transfer signal.

For larger systems like the B850 ring, this filtering step is significantly more demanding. The huge number of nuclei introduces many low-frequency signals and the large number of electrons introduces an excitation signal that contains many high-frequency components, which requires

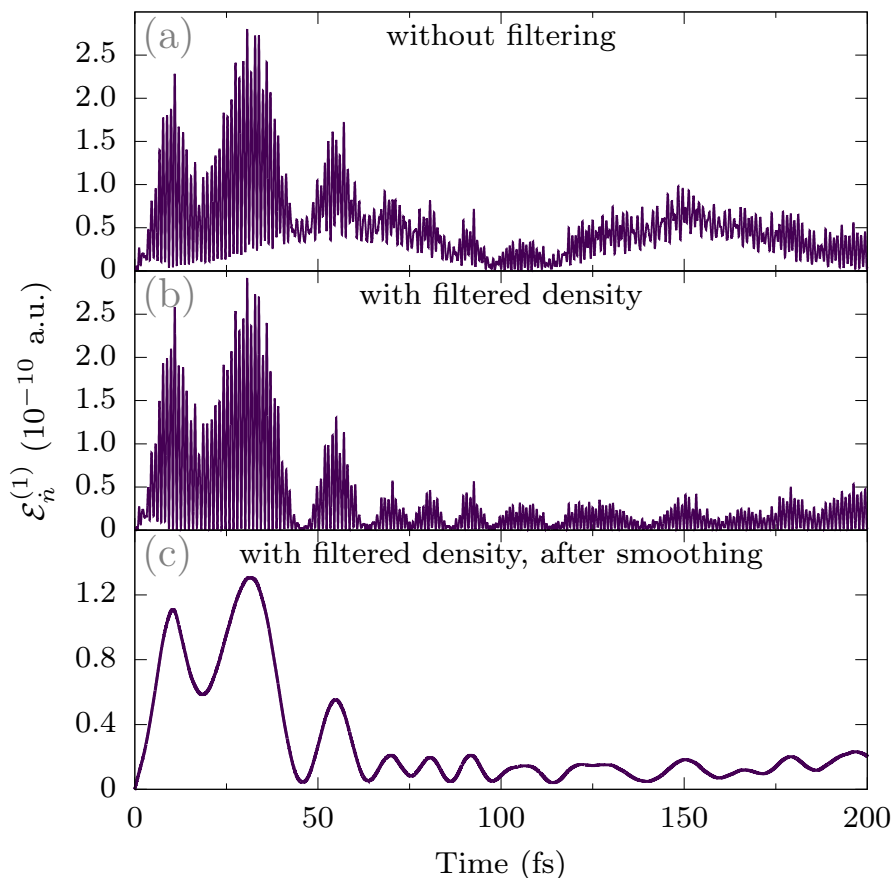


Figure A.1: Signal-processing workflow for the excitation-energy measure. The processing steps are illustrated exemplarily for dimer 1 in the sodium-dimer-chain simulation presented in Section 3.1. (a) Measure obtained from the raw simulation data (no filtering). (b) Measure evaluated with the τ -filtered electron density. (c) Measure evaluated with the τ -filtered density after Jacobi smoothing. See the main text for the processing details.

a sharper filtering than the τ -filter provides. Moreover, the spatial extent of the ring structure generates a massive amount of data—for example, storing the time-dependent density every time step in a 100 fs simulation requires ~ 570 GB of disk space. We therefore output the time-dependent density in BTDFT during the propagation and perform the subsequent analysis in the postprocessing. To this end, we developed a Python implementation within the BTDFT package that uses distributed-memory parallelization to process the time-dependent density. For each grid point, the script loads all time steps and applies a zero-phase Butterworth high-pass filter [251]. This approach efficiently removes the nuclear-drag contribution from the time-dependent density and isolates the relevant excitation dynamics as presented in Section 3.2.

To obtain the excitation-energy measures as in Section 3.1, a second filtering step is applied. While the high-pass filter on the density removed the nuclear-drag effects, the signal shown in Figure A.1 still contains the high-frequency oscillations that are related to the molecules’

excitation energies [Pub. 2, 50, 252]. To isolate the envelope of the signal, which is the excitation-energy signal, we apply a Jacobi smoothing to the (scalar) excitation-energy measure. This step is computationally less demanding than the first filtering step as it is applied on a scalar function rather than on volumetric data. For the sodium-dimer chain, the resulting smoothed signal (Figure A.1c) finally enables an analysis of the excitation-energy distribution in the chain as presented in Section 3.1.

A.2 BTDFT Implementations and Tests

Building on the Ehrenfest dynamics that I originally implemented in BTDFT during my master’s thesis, we have optimized code’s performance as part of this doctoral thesis and added a number of molecular dynamics related routines, three of which are presented below.

Pseudopotential Filtering

The representation of a function on a real-space grid is not invariant under arbitrary translations of the underlying function. For example, the numerically calculated ground-state energy of an atom depends on whether the nucleus is placed exactly on a grid point or between grid points. Shifting the atom relative to the grid leads to artificial oscillations in the energy, a phenomenon commonly referred to as egg-box effect. The size of this error depends on the chosen grid spacing and on the observable that is evaluated. This effect is particularly relevant for simulations where nuclear motion is switched on, as the forces determining the dynamics of the nuclei can be contaminated by the egg-box effect [204, 253].

A straightforward remedy is to reduce the grid spacing until the error becomes negligible. For larger multichromophoric systems this approach, however, would make calculations even more computationally cumbersome. For the calculation of the forces on the nuclei, one step to reduce the egg-box effect is to use an analytical reformulation of the energy gradient, as we have implemented it in BTDFT [204, 254]. An additional step is to remove high-frequency Fourier components of the atoms’ pseudopotentials that are beyond the grid’s resolution.

To this end we implemented the pseudopotential-filtering scheme by Tafipolsky and Schmid [255] and the algorithm to numerically calculate the *mask* function that is used in the filtering scheme [256]. We refer the reader to refs [255] and [256] for the details of these procedures. The BTDFT user can select which atom types are filtered, and for each atom type the two parameters α (default value: 1.1) and γ (default value: 2.0) must be chosen. α is the ratio between the Nyquist critical frequency (maximum frequency representable on the grid without aliasing) [257] and the cut-off frequency of the filter in Fourier space. γ determines the radial extent of the filtered real-space function relative to the cut-off radius of the projection functions used in the pseudopotential. Because γ modifies the size of the sphere around the atoms in which the non-local part of the pseudopotential enters the Hamiltonian, it also has an influence on the runtime of BTDFT propagations.

We test the impact of the filter on the position dependence of the ground-state energy in

BTDF. The test is performed for the five elements that occur in bacteriochlorophylls: carbon, hydrogen, oxygen, nitrogen, and magnesium. For each element, we calculate the ground-state energy with the atom placed exactly on a grid point and with the atom displaced by half a grid spacing (Δx) in diagonal direction (i.e., shifted by $(\Delta x/2, \Delta x/2, \Delta x/2)$). This artificial energy deviation $\Delta E = E_{\text{on-gridpoint}} - E_{\text{displaced}}$ is used here to quantify the magnitude of the egg-box effect. We sample ΔE for several grid spacings ranging from $0.20a_0$ to $0.50a_0$ and respectively perform unfiltered calculations and filtered calculations (with default filter parameters).

Figure A.2 shows the absolute values of ΔE for the five elements as a function of the grid spacing, and respectively for unfiltered (blue) and filtered (orange) calculations. As expected, the data shows that larger grid spacings lead to larger artificial energy deviations because fewer frequencies can be represented on the grid. The pseudopotential filter evidently reduces the artificial energy deviation for all elements as the blue lines lie above the orange lines for most grid spacings. In many cases the reduction exceeds even an order of magnitude. For hydrogen and magnesium, the artificial energy deviations are comparatively small, whereas carbon, oxygen, and nitrogen show larger egg-box errors.

In practice one should always benchmark different grid spacings for the observable of interest to test the impact of the egg-box effect, and one should check how much the pseudopotential filter improves the results. Based on the data shown here, we recommend using the pseudopotential filtering for molecular dynamics simulations for the atom types carbon, oxygen, and nitrogen to reduce the egg-box effect. Filtering the hydrogen and magnesium atoms yields only modest benefits and can be omitted to save computational time during the propagation.

Thermostat

The thermalization of the B850 ring in [Publication 2](#) is carried out with Nosé–Hoover chain dynamics. For this purpose, we implemented the reversible VV-1 algorithm of ref [258] in BTDF and adapted the velocity-Verlet integration accordingly. BTDF users can specify the target temperature, the chain length, and the time scale of the first chain link of the thermostat chain. Following ref [259], the time scales of the remaining chain links are chosen relative to that of the first link. Because the thermostat involves only classical variables, its computational cost is negligible compared to the coupled electron-nuclear dynamics.

Tricubic Interpolation

Before the implementation of nuclear motion, the spatial functions required evaluation only at the grid points. With the inclusion of nuclear motion, values (or spatial derivatives) of these functions are also needed at arbitrary positions between the grid points. For instance, computing the force on a nucleus from the environment potential (which is defined on the grid) demands an evaluation of potential's gradient at the nucleus' position, which typically lies between the grid points.

We therefore implemented a tricubic interpolation scheme as described by Lekien and Marsden [260]. This approach provides an interpolation that is continuously differentiable and isotropic. To determine a function value at an arbitrary position, function values together with selected

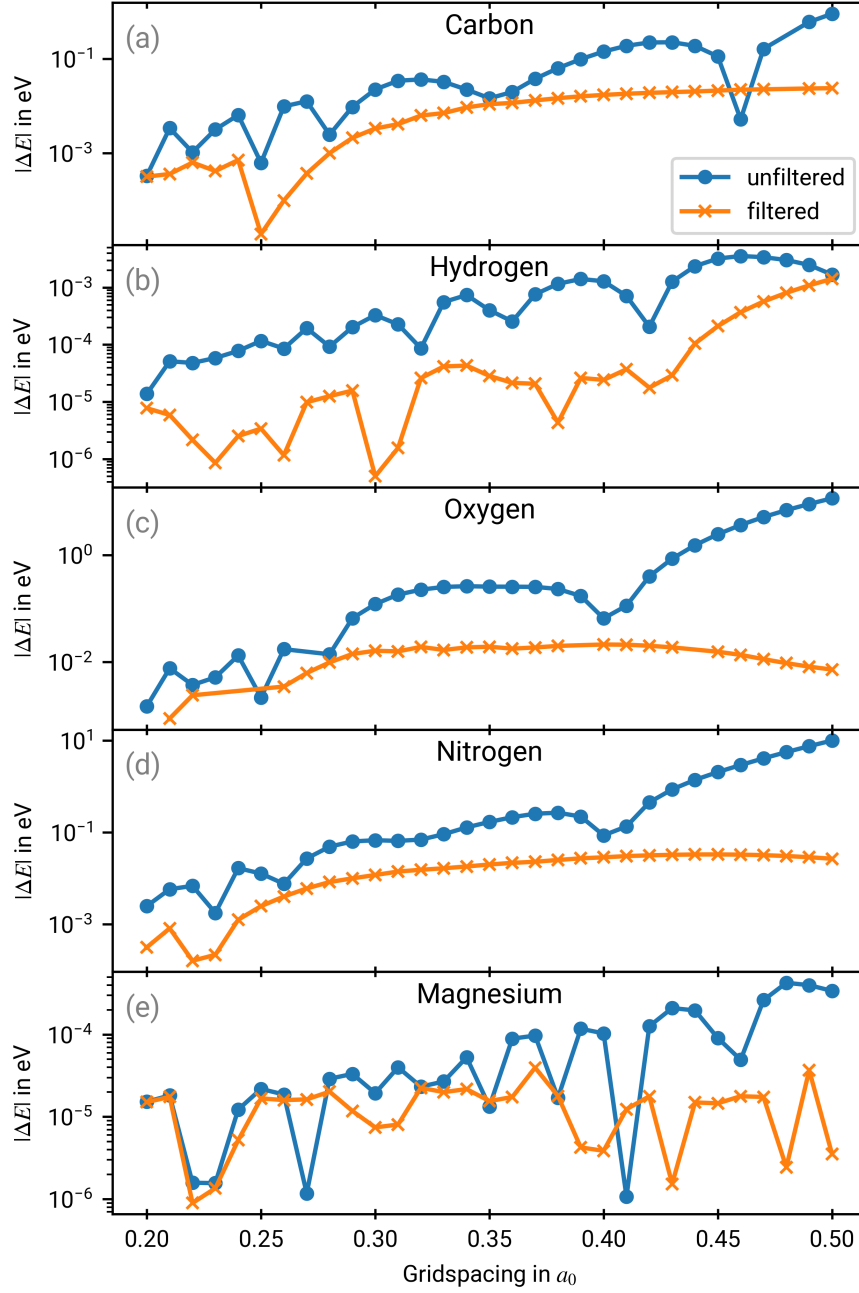


Figure A.2: Absolute value of the energy deviation ΔE between the calculated ground-state energy with the atom on a grid point and in between the grid points shown as a function of the grid spacing. (a–e) Illustration of the data for carbon, hydrogen, oxygen, nitrogen, and magnesium, respectively. Blue markers represent values without filtering and orange markers represent values from simulations in which the Tafipolsky–Schmid filtering was applied to the pseudopotentials.

derivatives at the eight closest grid points of the surrounding cell are used to construct a polynomial that is cubic in each spatial direction.

To ensure reproducibility of the implemented BTDFT code, we provide a MATHEMATICA script in our research group’s GitLab instance that generates the Fortran code needed to compute the polynomial’s coefficients from the supplied function values and derivatives. Although the implementation in BTDFT is currently only used for the environment potential, the subroutine is written in a generic fashion, making it readily applicable also to future projects.

A.3 Nonadiabatic Dynamics Simulation of a TBP–NDI system

To describe the time-resolved charge-separation dynamics in the TBP–NDI assembly, a nonadiabatic framework is required. One of the aims of the software project reported in [Publication 4](#) was to implement such a framework. Consequently, we also carried out a first benchmark simulation of a combination of TBP and NDI molecules.

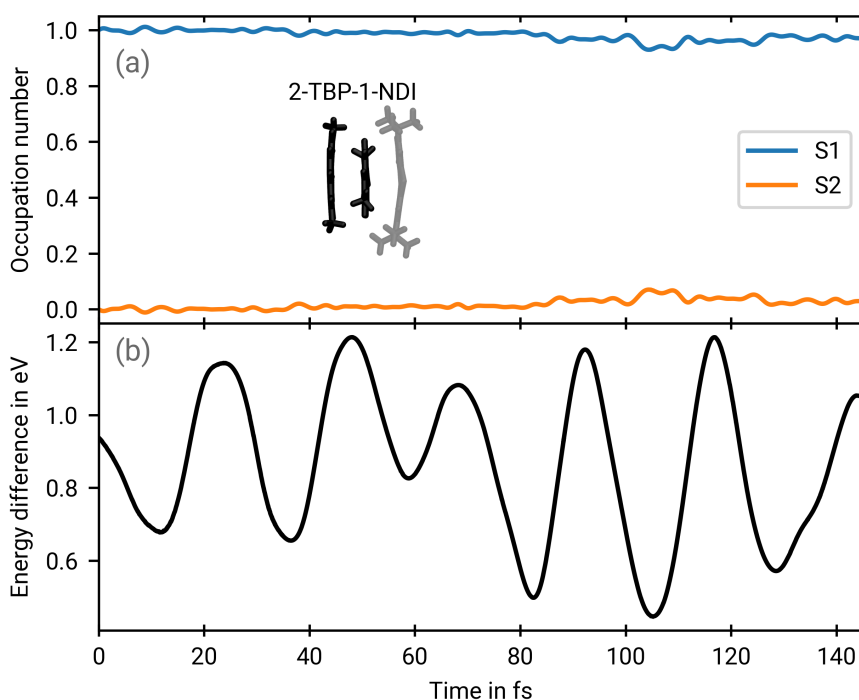


Figure A.3: Nonadiabatic dynamics trajectory of a 2-TBP–1-NDI system using ω PBE with a 6-31g basis set. (a) State-occupation numbers of S1 (blue) and S2 (orange) as function of time; the inset shows the molecular structure. (b) Energy difference between S1 and S2.

The smallest model that is computationally feasible and still contains multiple charge-transfer states consists of two TBP molecules and one NDI molecule (without residues). In this system

the S1 state corresponds to a charge transfer from the interface TBP to the NDI, whereas the S2 involves a charge transfer from the outer TBP to the NDI. Therefore, a transition from S1 to S2 represents a charge-separation step in which the excitation hole moves away from the interface towards the outer TBP. Figure A.3a shows the time-dependent occupation numbers obtained from a nonadiabatic trajectory performed with the method described in Section 2.2.3. Figure A.3b presents the difference of the S1–S2 energy gap along the trajectory. At the beginning, S1 is populated and only marginal transitions to S2 occur during the investigated time scale. The two energies do not approach each other as closely as they do in the Born–Oppenheimer trajectory reported in Section 3.3.

Drawing conclusions about the dynamics in a bulk scenario from the data presented here should be done with caution. To quantitatively determine whether charge separation occurs and on which time scale, multiple trajectories and larger molecular assemblies should be considered. Running this single trajectory already required a walltime of five days on one cluster node equipped with two NVIDIA Tesla A100 GPUs, with each time step taking about 74 s. Simulating, for example, the 3-TBP–3-NDI system in a similar nonadiabatic fashion is computationally prohibitive for the present time scale because the linear-response calculation becomes dramatically more expensive and the required number of nonadiabatic coupling vectors scales quadratically with the number of included states. Thus, given the performance limits of the code, one should rather rely on the findings presented in Section 3.3 to make estimations about possible charge separation in a bulk scenario.

List of Abbreviations

BChl bacteriochlorophyll	24
BOMD Born–Oppenheimer molecular dynamics	18
BTDFT Bayreuth Density Functional Theory: pseudopotential and real-space grid based TDDFT code [50]	12
C₆₀ Buckminsterfullerene	45
DFT density functional theory	5
HOMO highest occupied molecular orbital	16
KS Kohn–Sham, usually referring to the KS scheme, orbitals, eigenvalues, potential, or equation [93]	7
LDA local-density approximation xc functional	14
LSC-IVR linearized semiclassical initial value representation	18
LUMO lowest unoccupied molecular orbital	38
NDI N,N'-bis[3-(triethoxysilyl)propyl]-1,4,5,8-naphthalenediimide	37
TBP 3,7-di-t-butylphenothiazine	37
TDDFT time-dependent density functional theory	2
xc exchange-correlation	8
ZnPc Zinc phthalocyanine	45

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Auxiliary Tools

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Analyzing Excitation-Energy Transfer Based on the Time-Dependent Density Functional Theory in Real Time

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T.T. and I.S. contributed equally to this work. All authors conceptualized the work. T.T. performed the presented DFT and TDDFT simulations. I.S. technically supported the (TD)DFT simulations and performed initial clamped-ion simulations of the two-sodium-dimer system. T.T. implemented the nuclear dynamics and pseudo-potential filtering into the BTDDFT code. I.S. supported the implementation and developed the tau filter. S.K. structured the discussion about energy densities. T.T. prepared all graphics for the manuscript. I.S. conceptualized Fig. 1. I.S. did all analytical model calculations. All authors discussed the results. All authors wrote the main manuscript. I.S. wrote the Supporting Information. T.T. and S.K. proofread the Supporting Information and gave comments. S.K. supervised the project and acquired the funding.

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Analyzing Excitation-Energy Transfer Based on the Time-Dependent Density Functional Theory in Real Time

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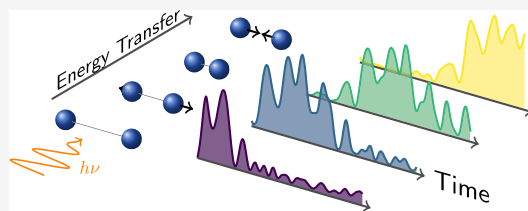


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ABSTRACT: Excitation-energy transfer is a key step in processes such as photosynthesis that convert light into other forms of energy. Time-dependent density functional theory (DFT) in real time is ideal for the first-principles simulation of such processes due to its computational efficiency. We here demonstrate how real-time DFT can be used for analyzing excitation-energy transfer from first-principles. We discuss several measures of energy transfer that are based solely on the time-dependent density, are well founded in the DFT framework, allow for intuitive understanding and visualization, and reproduce important limiting cases of an analytical model. We demonstrate their usefulness in calculations for model systems, both with static nuclei and in the context of DFT-based Ehrenfest dynamics.



1. INTRODUCTION

Time-dependent (TD) density functional theory (DFT) using propagation of the Kohn–Sham orbitals in real time is ideally suited for studying large-scale problems of electronic structure and dynamics and is used in different technical realizations.^{1–13} As a theory, it is attractive because with the exchange–correlation (xc) approximation properly chosen, it is a first-principles approach, it allows one to follow electron dynamics with temporal and atomistic resolution, and it allows one to study all kinds of excitations within and beyond the linear-response regime. On the technical level, it is very attractive because the computational effort for the propagation scales favorably with the particle number¹⁴ and the calculations parallelize excellently. When combined with real-space techniques, a further level of efficient parallelization can be exploited.^{9,15–17} The power of modern computer systems can thus be brought to bear on complex, large-scale problems. Real-time DFT has been used successfully, for example, for studying strong-excitation phenomena in finite systems, such as atoms, molecules, clusters,^{15,18–25} and solids,^{26–28} charge-transfer dynamics in molecular systems,^{29–31} electronic excitations in biological systems,^{32–36} electron transport,^{37–41} photoemission processes,^{5,42–48} pump–probe spectroscopy,^{49,50} and exciton dynamics,^{26,51,52} to name just a few examples from a body of literature that is too vast to cite in completeness.

It lies in the very nature of real-time DFT that it yields just the TD density $n(\mathbf{r}, t)$ (or the spin densities) and not a wavefunction. One must therefore obtain the observables of interest from the density. This means that in addition to the usual question of which functional to employ for describing the xc effects, one must also know the density functionals for the observables of interest. For some observables, these are well known. The photoabsorption spectrum, for example, is readily

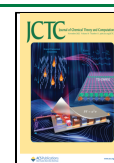
accessible as the imaginary part of the Fourier-transformed dipole moment, which is an explicit functional of the density. Special algorithms allow one to evaluate this observable with high accuracy.^{9,53,54} There are also situations in which one can directly compute the information of interest from the density itself. This is the case, for example, for questions of charge transfer, where direct integration of the density over certain regions of space yields the desired information.^{30,31,40,55} In a similar vein, one can study the conductance through molecular wires based on the density,³⁷ and absorbing and anti-absorbing boundaries can make such calculations particularly efficient.⁴¹

However, there are also well-known challenges associated with real-time propagation. Linear-response techniques, such as the Casida-approach,⁵⁶ for example, yield excitation energies and oscillator strengths separately, and thus easily reveal both dipole active and inactive transitions, whereas real-time simulations using the above-mentioned Fourier technique have difficulties revealing dark transitions. Another well-known example for an observable for which no exact explicit density functional representation is known is the double ionization probability.^{57–60}

In this work, we focus on a further physical phenomenon for which a description based solely on the TD density is challenging, namely, excitation-energy transfer. Excitation-energy transfer is of great relevance in many processes that convert sunlight into other forms of energy, especially in

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natural light-harvesting processes.^{61,62} Its theoretical description is often based on models, such as the famous one by Förster,⁶³ and on model Hamiltonians, for example, the exciton Hamiltonian.^{61,64,65} TDDFT has often and successfully been used in calculations of energy transfer.^{66,67} However, in many cases, it is only being used as a means to calculate parameters that go into the above-mentioned models. On the other hand, it has also been realized that excitation-energy-transfer processes can also be directly studied within TDDFT.^{68–74} Our work falls into the latter line of thinking. In this article, we develop an approach that allows for simulating excitation-energy transfer fully from first-principles in the framework of real-time DFT without resorting to model Hamiltonians. We first review the basic equations of real-time DFT and DFT-based Ehrenfest dynamics in Section 2 and then discuss excitation-energy transfer from different perspectives in Section 3: first, from the one of the exact TD wavefunction and then from the one of the exciton model Hamiltonian. The comparison leads to a set of requirements for the definition of excitation-energy transfer in TDDFT. Section 4 builds on these insights and looks at four different measures for excitation-energy transfer that one can define based on the TD density. A detailed analysis reveals particular advantages for one of them, which we therefore recommend for future work. Finally, Section 5 is devoted to proof-of-concept calculations that demonstrate the real-time simulation of excitation-energy transfer in transparent model systems. It highlights the relevance of coupled electronic and nuclear motion. The main paper is complemented by the Supporting Information,⁷⁵ which presents analytical and numerical considerations in great detail. We close with a summary and outlook in Section 6.

2. REVIEWING THE BASIC EQUATIONS OF TDDFT

In TDDFT, one describes the system of interest by the electron density

$$n(\mathbf{r}, t) = \sum_{\sigma=\uparrow,\downarrow} n_{\sigma}(\mathbf{r}, t) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_{\sigma}} |\varphi_{j\sigma}(\mathbf{r}, t)|^2 \quad (1)$$

where N_{σ} is the number of electrons with spin σ , n_{σ} is the spin density, and $\varphi_{j\sigma}$ are the TD Kohn–Sham orbitals. The latter are the solutions of the initial value problem

$$i\hbar \frac{\partial}{\partial t} \varphi_{j\sigma}(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{KS},\sigma}(\mathbf{r}, t) \right] \varphi_{j\sigma}(\mathbf{r}, t) \quad (2)$$

where m is the electron mass and $\hbar$ is the reduced Planck constant. The expression in the square brackets defines the Kohn–Sham Hamiltonian $h_{\text{KS},\sigma}$. The initial state is usually the ground state with density n_{GS} . The Kohn–Sham potential is given by

$$v_{\text{KS},\sigma}[n] = v_{\text{ion}} + v_{\text{H}}[n] + v_{\text{xc},\sigma}[n] + v_{\text{ext}} \quad (3)$$

where the terms on the right-hand side are the potential generated by the nuclei, the Hartree potential, the xc potential, and further contributions to the external potential, which can, for example, model an external perturbation. In eq 3, we dropped the space and time arguments for clarity of the notation. Because the focus of this paper is on developing methods for analyzing energy transfer, the specific nature of the employed xc approximation is not decisive: the approaches that we discuss can be used with any approximation for $v_{\text{xc},\sigma}[n]$

that can stably be propagated. For the proof-of-principle examples that we present in Sections 4 and 5, we keep the computational effort low and use the adiabatic local-density approximation (ALDA) in the parametrization of ref 76.

In addition to the electron dynamics, we also take the nuclear motion into account in the form of TDDFT-based Ehrenfest dynamics.² The nuclear equation of motion follows from Newton's second law

$$M_J \ddot{\mathbf{R}}_J = \mathbf{F}_J = -\nabla_{\mathbf{R}_J} E \quad (4)$$

where M_J is the mass, $\mathbf{R}_J$ is the coordinate, and $\mathbf{F}_J$ is the force acting on nucleus J . The spatial derivative with respect to $\mathbf{R}_J$ is denoted by $\nabla_{\mathbf{R}_J}$ and E is the system's total energy.

Evaluating the resulting terms requires special care, and the option for Ehrenfest dynamics is a new feature⁷⁷ of the Bayreuth TDDFT program package⁹ (BTDDFT) that we use for our calculations. For the propagation of the nuclei via eq 4, we use the velocity-Verlet scheme⁷⁸ at every electronic time step. The Ehrenfest dynamics is very sensitive to the grid spacing, as the nuclei's relative positions with respect to the grid points influence the energy and especially the forces acting on the nuclei. If the grid spacing is chosen too coarse, artificial oscillations appear in the observables, inducing the so-called eggbox effect. To mitigate this effect, one rewrites the derivative of the energy with respect to the nuclear positions such that it only contains derivatives of the Kohn–Sham orbitals with respect to the electronic coordinates, see ref 16 for details. Furthermore, BTDDFT features the option to Fourier filter the pseudopotentials^{79,80} with the method of Tafipolsky and Schmid,⁸¹ which is recommended for atoms with more valence electrons.

Finally, we introduce and explain our notation for the density fluctuation and the dipole moment, which we use in the following sections. The density fluctuation is defined by

$$\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n_{\text{GS}}(\mathbf{r}) \quad (5)$$

A frequently used observable that is directly related to δn is the induced dipole moment. We evaluate the latter in the form

$$\delta \boldsymbol{\mu}^{(l)}(t) = -e \int_{V^{(l)}} \mathbf{r} \delta n(\mathbf{r}, t) d^3r + \sum_{\mathbf{R}_J \in V^{(l)}} Z_J [\mathbf{R}_J(t) - \mathbf{R}_J(0)] \quad (6)$$

where Z_J denotes the charge of nucleus J . The notation in this equation indicates that we restrict the integral to the volume $V^{(l)}$, and the sum runs only over nuclei within this volume. Thus, eq 6 defines the contribution of the volume $V^{(l)}$ to the induced dipole moment. This notation is useful because in the subsequent sections, we look at ensembles of molecules. Dividing the space into the volumes $V^{(l)}$ allows one to obtain, for example, the dipole moment that is associated with a specific molecule. We always ensure that $\mathbb{R}^3 = \bigcup_l V^{(l)}$ and $V^{(l)} \cap V^{(k)} = \emptyset$ for all $l \neq k$. Consequently, the net dipole moment of the total system is given by $\delta \boldsymbol{\mu} = \sum_l \delta \boldsymbol{\mu}^{(l)}$.

3. EXCITATION-ENERGY TRANSFER

With the equations of TDDFT in mind, we proceed to elucidate why a density-based definition of excitation-energy transfer requires special care. To this end, we take a look at the definition of excitation-energy transfer from different perspectives. We start by thinking about how one could define excitation-energy transfer based on the exact wavefunction

$\Psi(r_1, r_2, \dots, r_N, t)$ for an N -particle system, omitting spin indices here for simplicity of the notation. One can define the system's total excitation energy by

$$\mathcal{E}(t) = \langle \Psi(t) | H | \Psi(t) \rangle - \langle \Psi_0 | H | \Psi_0 \rangle \quad (7)$$

where Ψ_0 denotes the ground state of the system and as usually the expectation value is defined by

$$\langle \Psi | H | \Psi \rangle = \int d^3r_1 \dots \int d^3r_N \Psi^*(r_1, r_2, \dots, r_N, t) H \Psi(r_1, r_2, \dots, r_N, t) \quad (8)$$

When the time dependence of Ψ is caused by a finite initial perturbation that ends at $t = t_0$ and the many-particle Hamiltonian H is thus independent of t for $t > t_0$, then $\mathcal{E}(t)$ is a time-independent constant energy for $t > t_0$. In practice, for example, when trying to unravel the mechanism of a light-harvesting system, one is typically interested in how the excitation energy is spatially distributed within the system as a function of time, that is, one is more interested in an excitation-energy density than the excitation energy as such. When the exact wavefunction is known, an excitation-energy density can be defined by

$$\begin{aligned} \varepsilon(r, t) &= \int d^3r_2 \dots \int d^3r_N [\Psi^*(r, r_2, \dots, r_N, t) \\ &\quad H \Psi(r, r_2, \dots, r_N, t) - \Psi_0^*(r, r_2, \dots, r_N) \\ &\quad H \Psi_0(r, r_2, \dots, r_N)] \end{aligned} \quad (9)$$

Because in this way, $\mathcal{E}(t) = \int \varepsilon(r, t) d^3r$. Besides, we note that one can add to $\varepsilon(r, t)$ any function that integrates to zero and still obtain the same $\mathcal{E}(t)$, that is, different energy densities can lead to the same energy. As the definition of eq 9 is straightforward when the exact wavefunction is used, this poses no problem here. However, a related issue will appear in Section 4.2.1 below. When one is in the special situation that a system is clearly separated into different parts, for example, two well separated molecules of which one is the energy donor and the other the energy acceptor, one can integrate the excitation-energy density over a given volume, for example, the one associated with the donor (D) or acceptor (A), respectively. In this way, we can define the excitation-energy content within that volume by

$$\mathcal{E}^{(l)}(t) = \int_V \varepsilon(r, t) d^3r \quad (10)$$

where l stands for D or A, respectively.

As the exact wavefunction, $\Psi(r_1, r_2, \dots, r_N, t)$ is almost impossible to compute for real-world systems with more than a few particles, excitation-energy transfer is typically analyzed from a different perspective, namely, using a model Hamiltonian. For the paradigm case of excitation-energy transfer from a donor molecule D to an acceptor molecule A that is well separated from the donor, the two-level system approximation is frequently used.⁶⁵ In this model, D and A are described as two-level systems, each with a ground state $|D\rangle$ and $|A\rangle$ and an excited state $|D^*\rangle$ and $|A^*\rangle$, respectively. One further defines the following states of the combined system, called site basis, as antisymmetrized product states (see the Supporting Information,⁷⁵ for detailed definitions): The ground state $|AD\rangle$, the state $|AD^*\rangle$ in which D is excited and A in the ground state, and the state $|A^*D\rangle$ in which A is excited and D in the ground state. A general TD state of the

combined system with one of the molecules possibly excited can then be written in the form

$$|\psi(t)\rangle = c_{AD}(t)|AD\rangle + c_{AD^*}(t)|AD^*\rangle + c_{A^*D}(t)|A^*D\rangle \quad (11)$$

where $|c_{AD}(t)|^2 + |c_{AD^*}(t)|^2 + |c_{A^*D}(t)|^2 = 1$. In this model, and other models of a similar kind, the information about the excitation-energy transfer is contained in the dimensionless coefficients. For example, if one wants to know whether the acceptor is excited at time t , one evaluates the coefficients $c_{A^*D}(t)$ and $c_{AD^*}(t)$. When all excitation energy has been transferred from the donor to the acceptor at t , then $|c_{AD^*}(t)|^2 = 0$ and $|c_{A^*D}(t)|^2 = 1 - |c_{AD}(t)|^2$.

It is important to realize the different implications of eqs 9 and 11. The former defines an excitation-energy density for every point in space and thus in principle does not require one to make a distinction between the donor and acceptor. By plotting $\varepsilon(r, t)$ on a grid in space and in time, one could directly follow the flow of energy in a first-principles simulation. The model Hamiltonian, on the other hand intrinsically requires one to distinguish between donor and acceptor, and information about the spatial distribution of the excitation energy is conveyed only indirectly: When the excitation energy has been transferred from the donor to the acceptor, it has been transferred from the volume of space that is occupied by the donor to the volume of space occupied by the acceptor. The widespread use of the model Hamiltonian approach, in which the dimensionless coefficients, such as $c_{A^*D}(t)$ and $c_{AD^*}(t)$, carry the information about the excitation-energy transfer, confirms that typically one is interested just in the relative distribution of the excitation energy, and absolute measures such as in eq 10 are of secondary relevance.

Based on this analysis of the ab initio wavefunction-based definition of excitation-energy transfer and the model Hamiltonian definition of excitation-energy transfer, it becomes clear what the aim of a TDDFT-based calculation of excitation-energy transfer should be. It should yield a quantity similar to $\varepsilon(r, t)$, allowing one to analyze and visualize the spatio-temporal distribution of excitation energy in a system without having to make an a priori distinction between different parts of the system, for example, donor and acceptor molecules. However, in the case that a system can be well separated into a donor and an acceptor similar to the model Hamiltonian, the TDDFT-based definition should lead to results that correspond to the results that one obtains in the model Hamiltonian approach.

4. EXCITATION-ENERGY MEASURES IN REAL-TIME DFT

4.1. Model Systems for First-Principles Energy-Transfer Simulations. Before proceeding to define density-based measures of excitation energy, we discuss the systems that we use for validating the measures. For this purpose, we rely on molecular model systems built from sodium dimers. These allow us to study energy transfer in setups that are first-principles, yet at the same time transparent, intuitively understandable, and can well be related to the above-discussed model Hamiltonian. There are several reasons why Na_2 is ideally suited as a building block for model energy-transfer systems. First, its lowest excitation corresponds to a dipole-like oscillation along the internuclear axis^{82,83} that is energetically well separated from other excitations. Thus, two sodium

dimers approximately realize a coupled two-level system,^{9,70} that is, the paradigm model of energy-transfer studies.⁶⁵ Second, one can simply tune the excitation energy by changing the internuclear separation in the dimer.

Thus, it is easy to realize situations with several dimers that either have the same excitation energy (resonant) or different ones (off-resonant). One can further change the coupling readily and in a well-controlled way by changing the relative orientation and the separation between the dimers. Finally, when treated in the pseudopotential approximation,⁸² Na₂ is just a two-electron system that can well be represented on a grid of relatively modest spacing, that is, high accuracy can be gained at modest computational cost. This is beneficial for the proof-of-principle, benchmark-type studies that we present here.

The first model that we study consists of two non-resonant sodium dimers with fixed nuclei, bond lengths (in Bohr radii a_0) of 5.78 a_0 and 5.58 a_0 , respectively, and an interdimer distance of 16 a_0 along the x -axis, as shown in Figure 1a. The first dimer (donor D) is aligned with its symmetry axis along the z -direction while the second dimer (acceptor A) is rotated by 20° around the interdimer connection axis (x -axis). We excite the donor by a weak laser pulse. The pulse is modeled as an electric dipole field that we restrict to the donor via a Gaussian spatial profile with a full width at half maximum of 6 a_0 centered around the donor. The intensity maximum is 10⁹ W/cm², the polarization is aligned with the donor axis (z -axis), and the frequency corresponds to 2.07 eV. With these parameters, the excitation matches the dominant dipole-active excitation of the isolated donor sodium dimer. Beginning at $t = 0$, we ramp the amplitude of the electric field up for 1 fs, stay at full amplitude for 8 fs, and ramp it down again for another 1 fs so that the excitation ends at $t_1 = 10$ fs. This excites the dimer in the upper linear-response range. By assigning each grid point to its closest atom, we split the whole space into a donor ($l = D$) and an acceptor ($l = A$) region and label all quantities accordingly, for example, $V^{(D)}$ and $V^{(A)}$. We give further numerical details in the Supporting Information.⁷⁵

4.2. Measures for a System's Excitation-Energy

Content. Our aim is to define a measure of excitation energy with spatio-temporal resolution in analogy to eq 9, that is, we seek for a measure that does not require to a priori define subunits, such as the donor and acceptor. At the same time, for the case of well-separated subunits that are two-level like, the measure should be in line with the model Hamiltonian results. Furthermore, the measure should be based on quantities that can be evaluated from only the occupied orbitals. This latter requirement comes about because first, the unoccupied Kohn–Sham orbitals do not have rigorous physical meaning and second, we want to keep the high computational efficiency that real-time DFT gains by relying on only the TD-occupied orbitals. Therefore, we are seeking for measures that do not require, for example, to calculate unoccupied orbitals and project onto them.

Such measures can be defined in different ways, and one may think about employing the concepts of density-based quantum hydrodynamics, which have been successfully used in different contexts.^{84–88} However, our aim here is to develop an approach that can be used for systems with a complex electronic structure, for example, organic semiconductors or light-harvesting antenna complexes. Such systems typically require an accuracy beyond the one that can be reached with hydrodynamics or Thomas–Fermi theory⁸⁹ concepts. Fur-

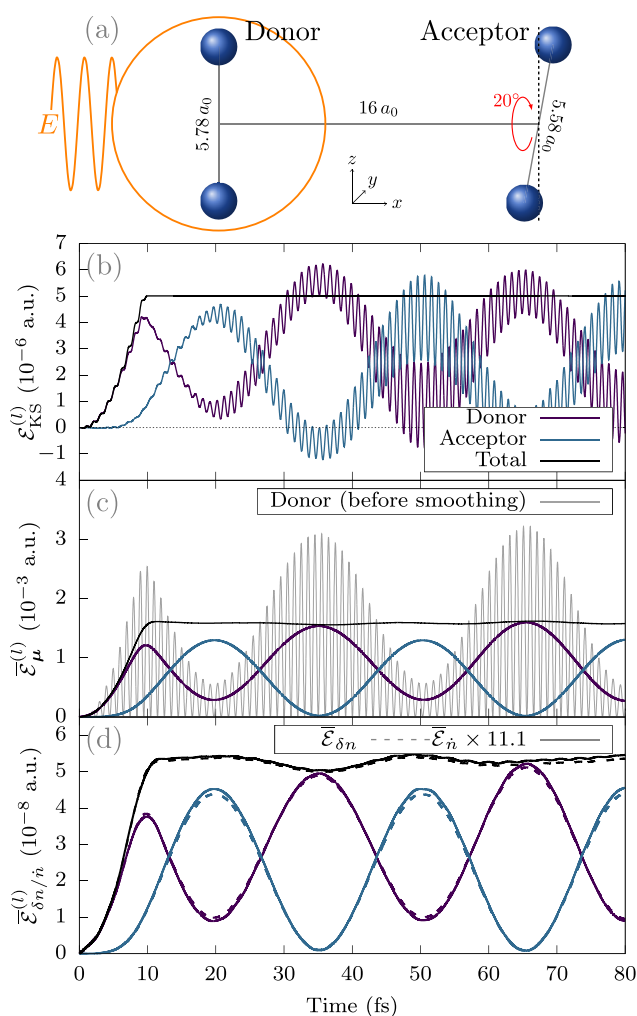


Figure 1. Panel (a): sketch of a model setup to study energy transfer between two Na₂ molecules. Panels (b–d) show as a function of time the different measures for the excitation energy that are discussed in Sections 4.2.1–4.2.1: Panel (b) shows $E_{KS}^{(l)}(t)$, where the lines of different color designate donor (i.e., $l = D$), acceptor (i.e., $l = A$), and total energy. Panel (c) shows $\bar{E}_{\mu}^{(l)}(t)$, again distinguishing between the donor, acceptor, and total. Here, the signals have been smoothed (denoted by the overline) as discussed in the main text, and one unsmoothed signal is also shown for reference. Panel (d) shows $\bar{E}_{\delta n}^{(l)}$ (full lines) and $\bar{E}_{\delta n}^{(l)}$ (dashed lines) for the donor, acceptor, and total. $\bar{E}_{\delta n}^{(l)}$ was multiplied by a factor of 11.1 a.u. to ease the visual comparison with $\bar{E}_{\delta n}^{(l)}$ by ensuring the same amplitude. See the main text for a detailed discussion.

thermore, when using ideas from hydrodynamics in the context of Kohn–Sham TDDFT, one must keep in mind that the Kohn–Sham and the true current density are equivalent only with respect to their longitudinal parts.^{90–92}

The question of how to define measures of excitation energy has some similarity to the problem of characterizing charge-carrier dynamics that was studied by Jannis Krumland et al.⁹³ They also investigated how to define observables in real-time DFT-based Ehrenfest-dynamics simulations. However, whereas the amount of transferred charge can directly be obtained from the density, the situation is more subtle for the transfer of excitation energy.

4.2.1. Measure 1: $\mathcal{E}_{\text{KS}}$. One obvious and straightforward option to define an excitation-energy density is based on the Kohn–Sham energy density in the form that one usually uses in ground-state DFT but evaluate it with the TD density and orbitals, that is, one can define an excitation-energy density by

$$\varepsilon_{\text{KS}}(\mathbf{r}, t) = e_{\text{KS}}[n(\mathbf{r}, t)] - e_{\text{KS}}[n_{\text{GS}}(\mathbf{r})] \quad (12)$$

where

$$e_{\text{KS}} = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_{\text{r}}} \varphi_{j\sigma}^* h_{\text{KS},\sigma} \varphi_{j\sigma} - \frac{1}{2} n v_{\text{H}} - \sum_{\sigma=\uparrow,\downarrow} n_{\sigma} v_{\text{xc},\sigma} + e_{\text{xc}} \quad (13)$$

In the latter equation, e_{xc} is the xc energy density, the asterisk denotes complex conjugation, and we once more dropped the time and space arguments for clarity. This is essentially the approach that has been explored in the recent work by Yang et al.⁷² Using this definition, one can assign an excitation energy to each molecule by integrating

$$\mathcal{E}_{\text{KS}}^{(l)}(t) = \int_{V^{(l)}} \varepsilon_{\text{KS}}(\mathbf{r}, t) d^3r \quad (14)$$

over the respective molecule's volume.

One might be tempted to regard these definitions as the straightforward TDDFT analogy to eqs 9 and 10. In line with this expectation one finds that ε_{KS} and $\mathcal{E}_{\text{KS}}^{(l)}$ integrate to an (adiabatically defined) energy that should be constant after an initial perturbation. On the conceptual level, however, using eq 13 as a measure for energy transfer leaves one with an unresolved problem: the Kohn–Sham energy density is not uniquely defined because one can add to e_{KS} any function that integrates to zero and still obtain the same Kohn–Sham energy, while substantially changing the energy density. In difference to the previously discussed similar situation that occurs for the exact wavefunction, cf. eq 9, this issue has considerable importance in the DFT context, for example, for the definition of the xc energy density e_{xc} ^{94,95} and cannot be ignored. The numerical results from the simulation of the energy transfer between the two sodium dimers demonstrate this explicitly.

Panel (b) of Figure 1 shows the donor and acceptor contributions $\mathcal{E}_{\text{KS}}^{(l)}$ for the sodium dimer energy-transfer setup as well as their sum (denoted as “total”). During the excitation period (the first 10 fs), the molecular excitation energy defined via eq 14 increases at the donor site. Thereafter, most of the energy is transferred to the acceptor and subsequently oscillates back and forth between the two. Note that the total excitation energy remains constant as expected as soon as the external perturbation ends. The energy transfer to the acceptor is incomplete because the two sodium dimers are not perfectly resonant due to their different bond lengths, and their non-parallel orientation. Thus, on the one hand, $\mathcal{E}_{\text{KS}}^{(l)}$ seems to describe the energy transfer reasonably well in agreement with common sense expectations. A closer look, on the other hand, reveals difficulties. First, the signal is modulated by a fast oscillation that originates directly in eq 13 and complicates the interpretation. One might argue that signal filtering, as discussed below, may reduce this problem. However, apart from the fast oscillations, one observes a further and more fundamental problem: The signal falls below zero at some points in time. A quantity that measures the excitation energy relative to the ground-state energy in a subsystem that does not lose charge should always be positive. The sub-zero values are

therefore a significant hurdle for a consistent interpretation. For this reason, we do not consider $\mathcal{E}_{\text{KS}}$ any further.

4.2.2. Measure 2: $\mathcal{E}_{\mu}$. As an alternative to eq 12, one can think about defining a measure for excitation energy in a way that is inspired by the physics of dipole oscillations that is underlying the famous Förster energy-transfer mechanism.^{63,65} In this spirit, one can define a measure for the excitation energy that is present at a molecular site in terms of the amplitude of the dipole moment $\delta\mu^{(l)}$ that is induced in the molecule (i.e., its associated volume) during an excitation. Within this concept, one identifies energy transfer with a dipole oscillation at one site of a donor–acceptor system that induces a dipole oscillation at the other site. The changes in the dipole amplitudes at both sites indicate the energy transfer.

Our motivation for using the dipole moment for a definition of excitation-energy transfer is on the one hand the intuitively appealing concept of dipole oscillation physics that is readily accessible based on the density. On the other hand, we show below in Section 4.3 that a definition of energy transfer in terms of the dipole moment can be justified rigorously in the context of the model Hamiltonian because the square of the donor and acceptor dipole moment is proportional to the probabilities $|c_{\text{AD}}|^2$ and $|c_{\text{A}^*\text{D}}|^2$, respectively. Therefore, it is reasonable to define

$$\mathcal{E}_{\mu}^{(l)}(t) \propto |\delta\mu^{(l)}(t)|^2 \quad (15)$$

as a second measure of the excitation energy that is associated with $V^{(l)}$, cf. eq 6. This definition is of a quite different nature than eqs 9 and 12: it does not define an excitation-energy density at every point in space but defines it for a certain entity such as a donor or an acceptor molecule that occupies a certain region of space $V^{(l)}$. It also does not have the unit of energy but is only proportional to the excitation energy. In this sense, eq 15 in spirit corresponds to how one thinks about excitation-energy transfer in the model Hamiltonian, cf. eq 11. In the following, we analyze the results that one finds for the model setup of Figure 1a with this definition.

The squared induced dipole moment shows rapid oscillations that have first been explained in ref 9 and are not related to energy transfer, as discussed in detail in the Supporting Information.⁷⁵ These rapid oscillations are clearly visible, for example, in the plot of $\mathcal{E}_{\mu}^{(l)}$ in Figure 1c (the gray wiggly line). The actual energy transfer between the donor and acceptor is seen in the beating signal that has a much lower frequency. It is, therefore, useful to remove all high-frequency components by smoothing the signal, for example, by using a Jacobi-relaxation-based iteration (for details see the Supporting Information^{75,96}) or more advanced Fourier-filtering techniques. We further discuss this smoothing step in Section 4.3 and denote all quantities that were smoothed by an overline, for example, $\overline{\mathcal{E}_{\mu}^{(l)}}$.

The resulting molecular excitation-energy measures for our donor–acceptor system are shown in panel (c) of Figure 1 as smooth lines. The overall pattern and beating signal are very similar to the ones seen in $\mathcal{E}_{\text{KS}}^{(l)}$, but the signal is smoother and strictly positive by construction. Moreover, donor and acceptor contributions sum up to almost a constant. The reason for the small deviation from a constant is explained in Section 4.3. Equation 15 thus appears as a reasonable definition for measuring excitation-energy transfer in real-time simulations.

It however also has drawbacks. The first is that it obviously only works for dipole-active excitations. The second is that, as already discussed above, the scheme does not define an excitation-energy density that one can integrate over any given volume but requires to assign a dipole moment to some “entity”. In our two- Na_2 setup, the definition of the entities is obvious, as one naturally assigns a dipole moment to each of the Na_2 molecules. Also in biological structures such as the light-harvesting complex 2 of purple bacteria,⁶¹ one can readily choose each bacteriochlorophyll molecule as an entity to which one can assign a dipole moment. However, the choice of proper entities might be less obvious in general supramolecular architectures.

4.2.3. Measures 3 and 4: $\mathcal{E}_{\delta n}$ and $\mathcal{E}_{\dot{n}}$. We therefore introduce two further measures that allow one to specify an excitation-energy density without referring to a specific subsystem. As a third option for an excitation-energy density and a molecule’s excitation energy, respectively, we define

$$\varepsilon_{\delta n}(\mathbf{r}, t) = c_{\delta n}[\delta n(\mathbf{r}, t)]^2 \quad (16)$$

with

$$\mathcal{E}_{\delta n}^{(l)}(t) = \int_{V^{(l)}} \varepsilon_{\delta n}(\mathbf{r}, t) \, d^3r \quad (17)$$

and as a fourth one

$$\varepsilon_{\dot{n}}(\mathbf{r}, t) = c_{\dot{n}}[\dot{n}(\mathbf{r}, t)]^2 \quad (18)$$

with

$$\mathcal{E}_{\dot{n}}^{(l)}(t) = \int_{V^{(l)}} \varepsilon_{\dot{n}}(\mathbf{r}, t) \, d^3r \quad (19)$$

where $\dot{n} = \partial n / \partial t$. The density fluctuation δn was also used, for example, in the work of Andrea Rozzi et al.³⁰ to visualize excitation dynamics, and it allows for an intuitive and transparent interpretation. An intuitive interpretation can also be found for $\varepsilon_{\dot{n}}$ and $\mathcal{E}_{\dot{n}}^{(l)}$: the latter are directly related to the quantum mechanical probability current $\mathbf{j}$ through the continuity equation $\dot{n} = -\nabla \cdot \mathbf{j}$, that is, they measure the source and drain strengths of the electron current density $\mathbf{j}$.

Equations 16 and 18 define energy densities that can be analyzed and visualized independent of the definition of specific subunits such as donor and acceptor molecules, and in this sense are analogues of eq 9. When one is interested in the excitation energy associated with, for example, an acceptor molecule, then the integrals of eqs 17 and 19 allow one to calculate it. The proportionality factor $c_{\delta n}$ in eq 16 has the unit energy times volume, and the factor $c_{\dot{n}}$ in eq 18 has the unit energy times volume times time squared. Section 4.3 and the Supporting Information⁷⁵ discuss in detail how one can obtain excitation-energy densities based on eqs 16 and 18 including the proper units. We stress, however, that an analysis of the relative distribution of the excitation energy does not require knowledge of these factors and can be obtained by just plotting and analyzing $[\delta n(\mathbf{r}, t)]^2$ and $[\dot{n}(\mathbf{r}, t)]^2$, respectively. This is what we do in the following.

Panel (d) of Figure 1 shows the smoothed measures $\bar{\mathcal{E}}_{\dot{n}}^{(l)}$ (solid) and $\bar{\mathcal{E}}_{\delta n}^{(l)}$ (dashed) for the system of two sodium dimers. Note that we scaled the former by an auxiliary factor of 11.1 a.u. that was chosen to ensure the same amplitude for both systems to ease the visual comparison between the two data sets. The reason for the difference in the absolute numbers is

detailed in Section 4.3. One readily notes that panel (d) shows the same energy-transfer dynamics as panels (b) and (c), yet without the previously discussed difficulties. Again, the donor and acceptor contributions sum up to almost a constant, with the deviation being explained in Section 4.3. Thus, eqs 16–19 are two further ways for defining valid measures of excitation energy. Both have the advantage that they can be used either without referring to subunits such as donor and acceptor molecules by directly analyzing the quantities of eqs 16 and 18 with their spatio-temporal resolution, or one can refer to subsystems such as donor and acceptor molecules by using eqs 17 and 19.

4.3. Excitation-Energy Measures in an Analytical Model. The definitions of excitation energy given in the previous section were so far based on intuitive physics arguments. One can also put them on a more formal footing by relating them to the previously mentioned model Hamiltonian in which a donor (D) and an acceptor (A) molecule are described as two-level systems that are coupled with a coupling strength V .⁶⁵ In previous works,⁹ we extended this model to include the system’s ground state. In this way, one can understand the high-frequency oscillations that are found in typical real-time-propagation results for coupled systems, for example, in Figure 1c. The two sodium dimers realize such a model in a very good approximation, as explained in Section 4.1.

In the framework of this model Hamiltonian, one can also show that each of the above defined excitation energy measures $\mathcal{E}_{\mu}^{(l)}(t)$, $\mathcal{E}_{\delta n}^{(l)}(t)$, and $\mathcal{E}_{\dot{n}}^{(l)}(t)$, where the superscript l again denotes either the donor ($l = \text{D}$) or acceptor ($l = \text{A}$) molecule, is directly related to the probabilities $|c_{\text{AD}}^*(t)|^2$ and $|c_{\text{AD}}^*(t)|^2$ with which the coupled donor–acceptor system at time t after an excitation is in a state in which the excitation energy is on the donor or acceptor, respectively. Thus, the definitions $\mathcal{E}_{\mu}^{(l)}(t)$, $\mathcal{E}_{\delta n}^{(l)}(t)$, and $\mathcal{E}_{\dot{n}}^{(l)}(t)$ that we arrived at from the perspective of real-time propagation correspond in a well defined way to the usual way of measuring excitation-energy transfer in terms of excited-state populations. The three measures just differ in their prefactor, that is,

$$\begin{aligned} \bar{\mathcal{E}}_{\xi}^{(\text{D})}(t) &= A_{\xi}^{(\text{D})} |c_{\text{AD}}^*(t)|^2 \\ \bar{\mathcal{E}}_{\xi}^{(\text{A})}(t) &= A_{\xi}^{(\text{A})} |c_{\text{AD}}^*(t)|^2 \end{aligned} \quad (20)$$

where $\xi \in \{\mu, \delta n, \dot{n}\}$. In the Supporting Information, we show that the specific prefactors are

$$A_{\mu}^{(l)} = 2(\boldsymbol{\mu}_l^T)^2 \quad (21)$$

$$A_{\delta n}^{(l)} = 2 \int_{V^{(l)}} (\rho_l^T)^2 \, d^3r \quad (22)$$

$$A_{\dot{n}}^{(l)} = \bar{\omega}^2 A_{\delta n}^{(l)} \quad (23)$$

where ρ_l^T denotes the transition densities of the single acceptor or donor excitation, $\boldsymbol{\mu}_l^T$ the transition dipoles associated with these excitations, and $\bar{\omega}$ is the mean value of the excitation frequencies of the donor and the acceptor (cf. the Supporting Information⁷⁵ for precise definitions and details).

Thus, the excitation-energy measures defined by eqs 15, 17, and 19 are not only physically plausible and intuitively understandable but also match the established definition of excitation-energy transfer via state occupation probabilities in

the model Hamiltonian. Equations 21–23 also explain some of the details that we observed in Figure 1. First, it is now clear why we had to introduce the scaling factor in panel (d) when comparing $\mathcal{E}_{\delta n}^{(l)}(t)$ and $\mathcal{E}_n^{(l)}(t)$: the factor corresponds to the ratio $A_n^{(l)}/A_{\delta n}^{(l)}$. Second, we see that the sum of donor and acceptor contributions becomes constant if the coefficients $A_{\delta}^{(D)}$ and $A_{\delta}^{(A)}$ are equal. This happens especially when donor and acceptor are identical. In our trial setup, however, we deliberately chose slightly different bond lengths for the two Na₂ molecules, and therefore panels (c) and (d) show a slight fluctuation in the total (sum of donor and acceptor) signal.

The equations also reveal a third insight. In practice and especially when also taking nuclear motion into account, $\bar{\mathcal{E}}_n^{(l)}(t)$ has an advantage over $\bar{\mathcal{E}}_{\delta n}^{(l)}(t)$ for the following reason. When one studies electronic excitations in a system in which also the nuclei are moving, the electron density reflects two different effects: On the one hand, it has a time dependence due to the electronic excitation; on the other hand, it has a time dependence because electron density is being dragged along with the moving nuclei. For revealing electronic excitation-energy transfer, one is predominantly interested in the former. Equation 23 shows that particularly $\mathcal{E}_n^{(l)}(t)$ is well suited for this purpose because the additional weighting with the square of the mean excitation frequency that $A_n^{(l)}$ features pronounces the signals related to electronic excitations over the signals related to nuclear movement. Furthermore, frequency filtering can be used to disentangle the two types of signals when the frequencies of the electronic excitation and the nuclear movement are separated well enough. Section 5 will discuss the influence of nuclear movement explicitly.

In summary of this section, we can state that the model Hamiltonian analysis supports the definition of the introduced excitation-energy measures, and the insights gained from the analysis fall well into line with the numerical observations in the two-dimer simulations. The actual analytical derivation of eqs 20–23 is, however, lengthy and fraught with a lot of detail. Therefore, we provide it as a separate text in the Supporting Information.⁷⁵

5. ENERGY TRANSFER AND EHRENFEST DYNAMICS

Our examples so far were based on static nuclei, but in real-world systems, nuclear motion plays a decisive role in energy transfer.⁶⁵ TDDFT-based Ehrenfest dynamics offers a natural way to take nuclear motion into account. In the following, we demonstrate that the previously introduced concepts can readily be used also in Ehrenfest simulations.

For this proof-of-principle demonstration, we use a linear arrangement of four sodium dimers, as shown in panel (a) of Figure 2. The dimers are numbered by 1 to 4 from left to right along the *x*-axis. The interdimer distance is 16 *a*₀ and we aligned all dimers parallel to the *z*-axis. Moreover, we chose the initial bond length *d* differently for each dimer, namely, *d*₁ = 6.40 *a*₀, *d*₂ = 5.55 *a*₀, *d*₃ = 4.90 *a*₀, and *d*₄ = 5.55 *a*₀. With this choice, dimers 2 and 4 are in their equilibrium distance (within LDA), while the ground-state energies of the isolated dimers 1 (stretched) and 3 (squeezed) are about 0.09 eV larger than that of the isolated equilibrium structure. For the TD simulation, we excite the left-most dimer (1) with a field that simulates a laser as described in Section 4.1. Moreover, we again define a dimer's volume *V*⁽¹⁾ as the set of grid points that are closer to the atoms of this dimer than to the others at the

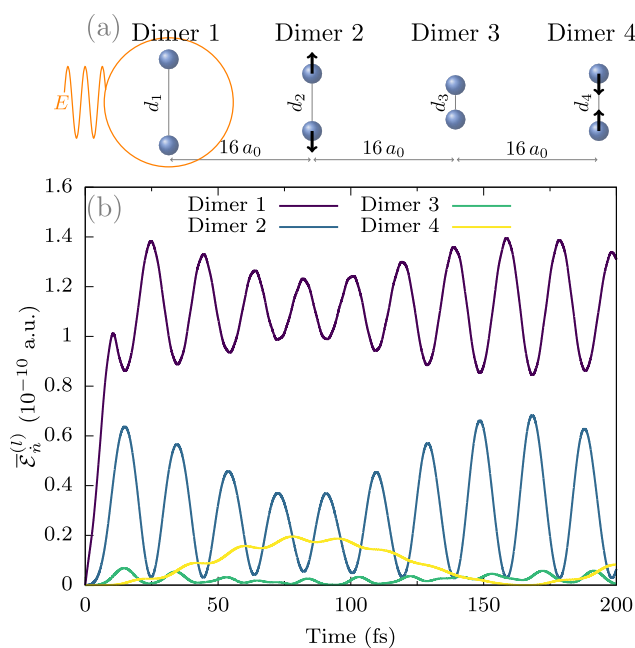


Figure 2. (a) Initial setup of the chain of four sodium dimers and (b) $\bar{\mathcal{E}}_n^{(l)}(t)$ for all four dimers, that is, *l* = 1–4 in different colors, for fixed nuclear positions after an initial laser excitation of dimer 1. Black arrows in (a) indicate initial velocities in the later discussed case with enabled nuclear dynamics.

initial time. As a reference, we do a first simulation with fixed atom coordinates (clamped-ion approximation). Panel (b) of Figure 2 shows the corresponding excitation-energy dynamics using $\bar{\mathcal{E}}_n^{(l)}$. In the present situation, $\bar{\mathcal{E}}_{\mu}^{(l)}$ and $\bar{\mathcal{E}}_{\delta n}^{(l)}$ lead to equivalent results and are therefore not shown explicitly. As the neighboring dimers are significantly off-resonant, only a small fraction of excitation energy is transferred and most of the excitation energy stays on dimer 1, as indicated by the dark purple line staying at a significantly higher level than the other three lines at all times.

In a second calculation, we enable nuclear motion but restrict the movement to the *z*-axis, that is, we only allow intradimer oscillations along the bond axis and keep the interdimer distances fixed. Additionally, we give initial momenta to the nuclei of dimers 2 and 4 with a magnitude of 11.6 a.u. and with directions as indicated by the arrows in Figure 2a. This choice for the initial bond lengths and momenta makes all dimers perform the same oscillation but with an incremental phase shift of $-\pi/2$ from left to right.

Panel (a) of Figure 3 shows the TD bond lengths of the four dimers during the propagation. Crossing lines indicate that the respective two dimers have the same bond length at that point in time and, thus, become resonant. Panel (b) shows $\mathcal{E}_n^{(1)}$ as a function of time, that is, the excitation energy on dimer 1 as measured by the criterion of eq 19. The plot demonstrates the influence that the nuclear motion has on the signal, as mentioned toward the end of Section 4.3: in addition to the very rapid oscillations with a frequency of ca. 1 fs^{−1} [that were smoothed out in panel (d) of Figure 1], and the energy-transfer signal with a frequency of ca. 1/18 fs^{−1}, it also shows a signal with a frequency of ca. 1/104 fs^{−1} that modulates the two other signals in the form of an oscillating offset. This low-frequency signal is caused by the previously mentioned effect

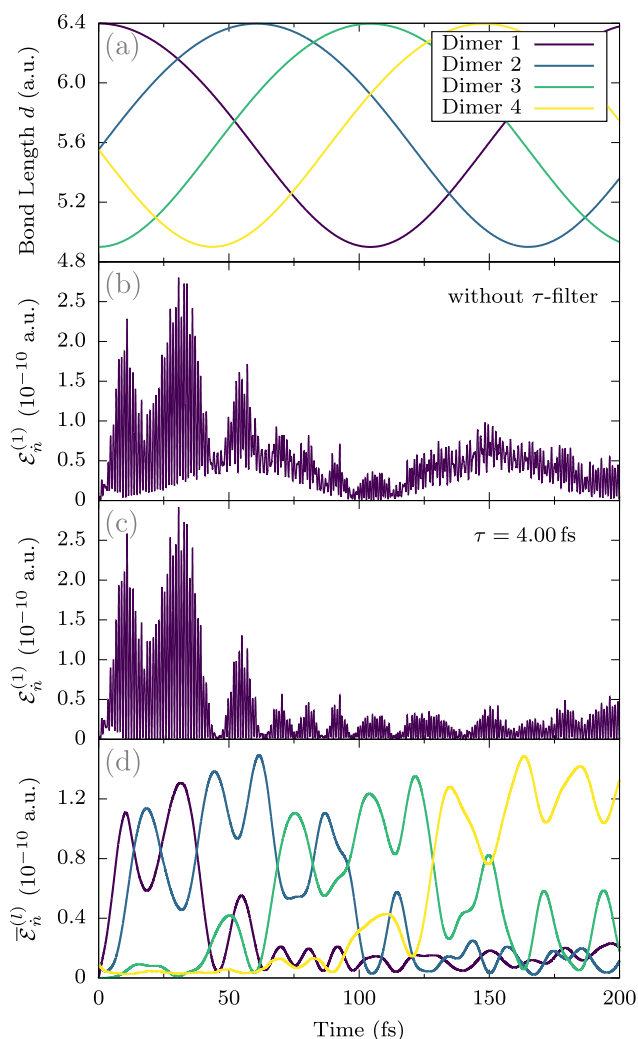


Figure 3. Results of an Ehrenfest-dynamics simulation of the chain of four sodium dimers. (a) TD bond lengths of the four dimers, (b) $\mathcal{E}_n^{(1)}(t)$, that is, excitation energy on dimer 1 as a function of time without filtering and smoothing, (c) excitation energy on dimer 1 after the nuclear signal has been removed by τ -filtering, and (d) $\bar{\mathcal{E}}_n^{(l)}$ for all dimers, after τ -filtering and Jacobi smoothing. See the main text for details.

of the electron density being dragged along with the nuclei. While this disturbing contribution is relatively small for $\mathcal{E}_n^{(l)}$ in this specific example, it completely dominates $\mathcal{E}_{dn}^{(l)}$ (not shown) from eq 17 because the latter explicitly refers to the system's initial density n_{GS} , cf. eq 5. In general, $\mathcal{E}_\mu^{(l)}$ (also not shown) suffers from the same effect. However, because the symmetric oscillations in our setup do not induce dipole moments in the excitation direction z , $\mathcal{E}_\mu^{(l)}$ in the present special case constitutes a qualitative energy measure if evaluated only with the z components of the dimers' dipole moments.

The unwanted nuclear signal can be removed by exploiting the fact that electronic and vibrational frequencies are well separated. Thus, a high-pass Fourier filter can be applied to the density before computing the energy measures. In our case, the τ -filtering method explained in the Supporting Information,⁷⁵ with $\tau = 4$ fs works perfectly while being efficient to evaluate on-the-fly during the propagation, that is, with this filtering we can avoid storing the whole time-evolution of the density,

which would be required for typical filtering schemes. Panel (c) of Figure 3 shows the resulting signal. One can clearly see that it corresponds to the signal of panel (b) but with the slowly oscillating offset removed. We note in passing that if the vibrational and electronic frequencies should lie closer together, the observables may benefit from using more advanced Fourier-filtering algorithms. Finally, panel (d) of Figure 3 shows $\bar{\mathcal{E}}_n^{(l)}$ for $l = 1-4$ in different colors, that is, the signal with τ -filtering of the density and subsequent Jacobi smoothing for each of the dimers. This plot now allows for a transparent discussion of the excitation-energy transfer in the chain of dimers.

Panel (a) of Figure 3 shows that the bond lengths of dimers 1 and 2 are similar at about 30 fs, that is, they become resonant so that an excitation-energy transfer from the initially excited dimer 1 to dimer 2 can occur. Panel (a) also shows that in the further course of the propagation, dimer 2 becomes resonant with dimer 3 at about 80 fs, and dimer 3 becomes resonant with dimer 4 at around 130 fs. As a consequence, the excitation energy can migrate through the chain from one dimer to the next. This is confirmed with striking clarity by the plot of the excitation-energy measure $\bar{\mathcal{E}}_n^{(l)}$ shown in panel (d): there are some overall small oscillations that reflect the general quantum mechanical coupling of the dimers, but the dominant feature is clearly that the excitation energy initially resides on dimer 1 and then moves over dimer 2 and 3 to dimer 4. We also see that even though dimer 4 becomes resonant with dimer 1 at about 180 fs, the energy stays at dimer 4 until the end of the shown time frame. One reason for why one does not observe immediate backwards energy transfer from dimer 4 to dimer 1 at this point in time is the relatively large distance between dimer 1 and dimer 4. Another reason is that the two non-resonant dimers between 1 and 4 can hinder the backwards energy transfer.⁷¹

This model calculation thus exemplifies in a transparent setup how the interplay between electron and nuclear dynamics can lead to directional energy transfer along a chain of molecules. Also the trapping of the excitation energy at a specific site for a certain interval of time, for example, on dimer 4 towards the end of the simulation, can be induced in this way. The comparison between panel (b) of Figure 2 and panel (d) of Figure 3 strikingly shows the huge impact that nuclear motion can have on energy-transfer dynamics.

6. CONCLUSIONS

We introduced the three transparent, density-based quantities $\mathcal{E}_\mu$, $\mathcal{E}_{dn}$, and $\mathcal{E}_n$ as meaningful measures for molecular excitation energy. These quantities can be evaluated straightforwardly in real-time DFT simulations and allow one to analyze and visualize excitation-energy transfer from first-principles. They are directly rooted in the density-based formalism of TDDFT and do not require the evaluation of unoccupied orbitals or the interpretation of Kohn–Sham orbitals as physical states. The three quantities were, on the one hand, justified by intuitive physics arguments. On the other hand, we showed that they are rigorously related to the definition of excitation-energy transfer in terms of state populations as used in the paradigm, state-based donor–acceptor model Hamiltonian. If one wants to study excitation-energy transfer without referring to subunits such as, for example, donor and acceptor, one can do so by analyzing the excitation-energy density measures of eqs 16 and 18 directly as

functions of space and time. Overall, our analysis suggests eq 18 as the most general and reliable measure.

We further discussed numerical procedures that allow for obtaining more transparent energy-transfer signatures. On the one hand, we applied a Jacobi-smoothing step that acts as a low-pass Fourier filter to remove the high-frequency modulations that stem from high-frequency electron dynamics that is not related to energy transfer. On the other hand, we showed that applying a high-pass Fourier filter to the electron density before evaluating the actual excitation-energy measures allows for removing signals that are caused by nuclear movement. This becomes relevant especially in the case of TDDFT-based Ehrenfest dynamics, where the moving nuclei drag along electron density and thus induce electron dynamics that is not related to excitation-energy transfer. We showed that in the present examples, a modest quality but efficient on-the-fly τ -filtering method,⁷⁵ which we discuss in detail in the Supporting Information,⁷⁵ was sufficient. Both filtering steps are optional, that is, one can also work with the unfiltered versions of $\mathcal{E}_\mu$, $\mathcal{E}_{\delta\mu}$, and $\mathcal{E}_{\delta\mu}$, if this is better suited for the application at hand.

Finally, we demonstrated in a worked example how these concepts can be used to study excitation-energy transfer. For a chain of four dimer molecules, we demonstrated how nuclear dynamics can drive directional energy transfer and can also lead to the trapping of excitation energy on molecular sites for a certain interval of time. The here developed methods are expected to unfold considerable relevance in future real-time simulations of light-harvesting systems.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jctc.2c00600>.

Detailed presentation of the analytical calculations that relate the real-time excitation-energy measures to the donor–acceptor model Hamiltonian; derivation of eqs 20–23 explaining all of the steps, underlying assumptions, and inherent approximations; discussion of alternative energy measures; detailed explanation of the filtering; and numerical details and simulation parameters (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information:

Analyzing excitation-energy transfer based on time-dependent density functional theory in real time

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In Section S.1 of this Supporting Information, we present the detailed derivation that complements Section 4.3 of the main paper. We study the electronic excitations and excitation-energy transfer in the paradigm model Hamiltonian that describes a donor-acceptor system as two coupled two-level systems subjected to a weak external perturbation. In extension of the typical version of this model, we here explicitly include the system's ground state into the analysis. This allows for connecting the results from the model Hamiltonian to the results from real-time DFT. We introduce the model Hamiltonian in Section S.1.1 and discuss the eigenstates of the system. Thereafter, we apply a weak external perturbation and calculate the time-dependent occupation of the excited donor and acceptor states in Section S.1.2. Finally, we derive the time-dependent density in Section S.1.3 and relate the latter to the state occupations in Section S.1.4. We thus explicitly demonstrate that the energy measures $\mathcal{E}_\mu$, $\mathcal{E}_{\delta n}$, and $\mathcal{E}_n$ of the main article can be interpreted as an excitation energy per molecule. In the course of this derivation we discuss the special cases of a resonant, a non-interacting, and a special non-resonant setup. Finally, in Section S.2 we present and discuss thoughts about alternative energy measures mentioned in the main article, in Section S.3 we detail the used Fourier-filtering algorithms, Jacobi smoothing and τ -filtering, and in Section S.4 we discuss the parameters used in the simulations, and other numerical details.

S.1 DONOR-ACCEPTOR ENERGY-TRANSFER MODEL

S.1.1 The model Hamiltonian

We consider a donor (D) and an acceptor (A) molecule that are separated well enough so that one can think about D and A as distinct, separate molecules. Each of them is described as a two-level system with a ground state $|D\rangle$ and $|A\rangle$, and an excited state $|D^*\rangle$ and $|A^*\rangle$, respectively. We further define the following states of the combined system consisting of D and A, called site basis:

a. Site basis

$$\begin{aligned} |AD\rangle & \text{ Ground state with energy } E_{AD} \\ |AD^*\rangle & \text{ Excitation on the donor with energy } E_{AD^*} \\ |A^*D\rangle & \text{ Excitation on the acceptor with energy } E_{A^*D}. \end{aligned} \tag{S.1}$$

These states are the antisymmetrized product states of the eigenstates of the single donor and acceptor systems, e.g., $|AD^*\rangle = (|A\rangle|D^*\rangle - |D^*\rangle|A\rangle)/\sqrt{2}$. We further assume that D and A are coupled to each other via the Coulomb interaction $\hat{V}^C$. See, e.g., Ref. 1 or Ref. 2 for discussions of this model.

b. Model Hamiltonian We describe the coupled system by the model Hamiltonian

$$\hat{H}_{\text{ex}} = \begin{pmatrix} E_{AD} & 0 & 0 \\ 0 & E_{A^*D} & V \\ 0 & V & E_{AD^*} \end{pmatrix}. \tag{S.2}$$

$V = \langle A^*D|\hat{V}^C|AD^*\rangle = \langle AD^*|\hat{V}^C|A^*D\rangle$ is the coupling strength between the excited donor and acceptor states. Note that eq. (S.2) is an extension of the typical model Hamiltonian [3], as the latter does not include the ground state and has the donor and acceptor excitation energies (site energies) on the diagonal:

$$\hat{H}_{\text{ex}}^{\text{typical}} = \begin{pmatrix} E_{A^*D} - E_{AD} & V \\ V & E_{AD^*} - E_{AD} \end{pmatrix}. \tag{S.3}$$

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c. *Definitions* To keep the notation transparent, we define the abbreviations

$$\bar{E} = \frac{E_{A^*D} + E_{AD^*}}{2} \quad (\text{Mean value}), \quad \Delta E = \frac{E_{A^*D} - E_{AD^*}}{2} \quad (\text{Off-Resonance}) \quad (\text{S.4})$$

$$\oplus = 1 + \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}}, \quad \ominus = 1 - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} \quad (\text{S.5})$$

where $\oplus, \ominus \in [0, 2]$ compare the off-resonance ΔE to the coupling strength V . We assume that $(\Delta E)^2 + V^2 > 0$. Further below, we will also use

$$\oplus + \ominus = 2 \quad \text{and} \quad (\text{S.6})$$

$$\sqrt{\oplus}\sqrt{\ominus} = \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}}. \quad (\text{S.7})$$

d. *Eigen basis* By diagonalizing the model Hamiltonian from eq. (S.2), one can relate the eigen basis to the site basis

$$|0\rangle = |AD\rangle \quad \text{with energy} \quad E_0 = E_{AD} \quad (\text{S.8})$$

$$|1\rangle = \frac{1}{\sqrt{2}} [\sqrt{\ominus}|AD^*\rangle + \text{sgn}(V)\sqrt{\oplus}|A^*D\rangle] \quad \text{with energy} \quad E_1 = \bar{E} + \sqrt{(\Delta E)^2 + V^2}$$

$$|2\rangle = \frac{1}{\sqrt{2}} [\sqrt{\oplus}|AD^*\rangle - \text{sgn}(V)\sqrt{\ominus}|A^*D\rangle] \quad \text{with energy} \quad E_2 = \bar{E} - \sqrt{(\Delta E)^2 + V^2},$$

where $|1\rangle$ is always the excited state with higher energy. Vice versa, the inversion of eq. (S.8) gives

$$|AD\rangle = |0\rangle \quad (\text{S.9})$$

$$|A^*D\rangle = \frac{1}{\sqrt{2}} \text{sgn}(V) [\sqrt{\oplus}|1\rangle - \sqrt{\ominus}|2\rangle]$$

$$|AD^*\rangle = \frac{1}{\sqrt{2}} [\sqrt{\ominus}|1\rangle + \sqrt{\oplus}|2\rangle].$$

e. *Assumptions* The following derivation uses some main assumptions that we summarize here:

- Donor and acceptor are well separated so that the overlap of donor and acceptor states is negligible, i.e., $\bar{E} \gg V$.
- In line with the first assumption, we assume that the transition densities of the coupled system are well approximated by the transition densities of the separate donor and acceptor excitations.
- The external perturbation is weak.
- The excitation energies are close to each other, i.e., $\bar{E} \gg \Delta E$.

In the following, we will explicitly point out when we make approximations that are based on these assumptions.

f. *Special cases* In order to keep the derivation general but transparent, we frequently discuss the two limiting cases, i.e., the resonant and the non-interacting systems. As a further special case, we discuss a specific non-resonantly coupled system.

$\Delta E = 0$: (Resonant system)

In this case, the eigenstates are symmetric and anti-symmetric superpositions of the site-basis states. If the separate D and A excitations are optically active, the symmetric state combines the oscillator strengths of donor and acceptor constructively, the anti-symmetric state destructively. This is extremal if the transition dipoles of the D and A excitations are equal in direction and magnitude, e.g., if donor and acceptor are the same molecules with a parallel alignment. The sign of the interaction strength $\text{sgn}(V)$ determines the energetic ordering and leads to a blue shift ($V > 0$, H-aggregate) or red shift ($V < 0$, J-aggregate) of the absorption.

$V > 0$: (H-aggregate)

$$\begin{aligned}\oplus = \ominus &= 1, \quad \text{sgn}(V) = 1 \\ |1\rangle &= \frac{1}{\sqrt{2}} [|AD^*\rangle + |A^*D\rangle] \quad \text{with energy} \quad E_1 = \bar{E} + |V| \\ &\quad \text{(delocalized, symmetric)} \\ |2\rangle &= \frac{1}{\sqrt{2}} [|AD^*\rangle - |A^*D\rangle] \quad \text{with energy} \quad E_2 = \bar{E} - |V| \\ &\quad \text{(delocalized, anti-symmetric)}\end{aligned}$$

$V < 0$: (J-aggregate)

$$\begin{aligned}\oplus = \ominus &= 1, \quad \text{sgn}(V) = -1 \\ |1\rangle &= \frac{1}{\sqrt{2}} [|AD^*\rangle - |A^*D\rangle] \quad \text{with energy} \quad E_1 = \bar{E} + |V| \\ &\quad \text{(delocalized, anti-symmetric)} \\ |2\rangle &= \frac{1}{\sqrt{2}} [|AD^*\rangle + |A^*D\rangle] \quad \text{with energy} \quad E_2 = \bar{E} - |V| \\ &\quad \text{(delocalized, symmetric)}\end{aligned}$$

$V = 0$: (Non-interacting system)

If donor and acceptor are not coupled, the Hamiltonian is already diagonal in the site basis. According to our definitions, state $|1\rangle$ ($|2\rangle$) is the site state with respective higher (lower) site energy. Since $\text{sgn}(V)$ is not well defined in this case, we arbitrarily choose $\text{sgn}(V) = 1$ for this example without further substantial consequences for the results.

$\Delta E > 0$: (Acceptor with larger site energy)

$$\begin{aligned}\oplus &= 2, \quad \ominus = 0 \\ |1\rangle &= |A^*D\rangle \quad \text{with energy} \quad E_1 = \bar{E} + |\Delta E| = E_{A^*D} \quad \text{(localized on A)} \\ |2\rangle &= |AD^*\rangle \quad \text{with energy} \quad E_2 = \bar{E} - |\Delta E| = E_{AD^*} \quad \text{(localized on D)}\end{aligned}$$

$\Delta E < 0$: (Donor with larger site energy)

$$\begin{aligned}\oplus &= 0, \quad \ominus = 2 \\ |1\rangle &= |AD^*\rangle \quad \text{with energy} \quad E_1 = \bar{E} + |\Delta E| = E_{AD^*} \quad \text{(localized on D)} \\ |2\rangle &= -|A^*D\rangle \quad \text{with energy} \quad E_2 = \bar{E} - |\Delta E| = E_{A^*D} \quad \text{(localized on A)}\end{aligned}$$

$V = \sqrt{3}\Delta E > 0$: (Non-resonant system)

In the general, non-resonantly coupled case, the eigenstates are superpositions of the site-basis states, with the different superpositions having larger weight on either one or the other site state. In this case, the system is an imperfect H-aggregate with larger acceptor site energy,

$$\begin{aligned}\oplus &= \frac{3}{2}, \quad \ominus = \frac{1}{2}, \quad \text{sgn}(V) = 1 \\ |1\rangle &= \frac{1}{2} [|AD^*\rangle + \sqrt{3}|A^*D\rangle] \quad \text{with energy} \quad E_1 = \bar{E} + \frac{2}{\sqrt{3}}|V| = \bar{E} + 2|\Delta E| \\ &\quad \text{(delocalized, A-dominant)} \\ |2\rangle &= \frac{1}{2} [\sqrt{3}|AD^*\rangle - |A^*D\rangle] \quad \text{with energy} \quad E_2 = \bar{E} - \frac{2}{\sqrt{3}}|V| = \bar{E} - 2|\Delta E| \\ &\quad \text{(delocalized, D-dominant)}\end{aligned}$$

S.1.2 Free propagation after a weak excitation

g. Time-dependent state After a weak excitation of the ground state, we allow the system to evolve without further perturbation for $t \geq 0$. One can express the time-dependent wave function for $t > 0$ in terms of the eigenstates or the site states

$$\begin{aligned} |\psi(t)\rangle &= \sum_{j=0}^2 c_j e^{-\frac{i}{\hbar} E_j t} |j\rangle \\ &= c_{AD}(t) |AD\rangle + c_{AD^*}(t) |AD^*\rangle + c_{A^*D}(t) |A^*D\rangle \end{aligned} \quad (S.10)$$

so that $\sum_{j=0}^2 |c_j|^2 = |c_{AD}(t)|^2 + |c_{AD^*}(t)|^2 + |c_{A^*D}(t)|^2 = 1$. Since the propagation is free, the coefficients c_j of the eigenstates are time-independent for $t > 0$.

h. Initial state One way to define the initial state of the system is to directly set the coefficients c_1 , c_2 , and c_0 . Without further restriction, we chose c_0 to be real valued. Alternatively, it can be more intuitive to define the initial state in the site basis

$$|\psi(t=0)\rangle = c_{AD}(t=0) |AD\rangle + C_{D^*} |AD^*\rangle + C_{A^*} |A^*D\rangle \quad (S.11)$$

with $|C_{D^*}|, |C_{A^*}| \ll |c_{AD}|$. C_{D^*} and C_{A^*} are, therefore, the coefficients with which $|AD^*\rangle$ and $|A^*D\rangle$ contribute to the initial state, i.e., using eq. (S.9)

$$\begin{aligned} c_{AD}(t=0) &= c_0 = \sqrt{1 - |C_{D^*}|^2 - |C_{A^*}|^2} \\ c_{A^*D}(t=0) &= C_{A^*} = \frac{1}{\sqrt{2}} \text{sgn}(V) [\sqrt{\oplus} c_1 - \sqrt{\ominus} c_2] \\ c_{AD^*}(t=0) &= C_{D^*} = \frac{1}{\sqrt{2}} [\sqrt{\ominus} c_1 + \sqrt{\oplus} c_2] \end{aligned} \quad (S.12)$$

and, vice versa,

$$\begin{aligned} c_1 &= \frac{1}{\sqrt{2}} [\sqrt{\ominus} C_{D^*} + \text{sgn}(V) \sqrt{\oplus} C_{A^*}] \\ c_2 &= \frac{1}{\sqrt{2}} [\sqrt{\oplus} C_{D^*} - \text{sgn}(V) \sqrt{\ominus} C_{A^*}] . \end{aligned} \quad (S.13)$$

In the course of the general derivation below, we will usually use the coefficients in the eigenbasis. When we discuss special cases, we may express the excitation in the site basis (e.g., we initially excite the donor only) and derive c_1 and c_2 according to eq. (S.13).

i. Time-dependent state in the site basis By replacing the eigenstates in eq. (S.10) by the site states with the help of eq. (S.8), one can express the time-dependent state in the site basis

$$\begin{aligned} |\psi(t)\rangle &= c_0 e^{-\frac{i}{\hbar} E_0 t} |0\rangle + c_1 e^{-\frac{i}{\hbar} E_1 t} |1\rangle + c_2 e^{-\frac{i}{\hbar} E_2 t} |2\rangle \\ &= c_0 e^{-\frac{i}{\hbar} E_0 t} |0\rangle + c_1 e^{-\frac{i}{\hbar} E_1 t} \frac{1}{\sqrt{2}} [\sqrt{\ominus} |AD^*\rangle + \text{sgn}(V) \sqrt{\oplus} |A^*D\rangle] \\ &\quad + c_2 e^{-\frac{i}{\hbar} E_2 t} \frac{1}{\sqrt{2}} [\sqrt{\oplus} |AD^*\rangle - \text{sgn}(V) \sqrt{\ominus} |A^*D\rangle] \\ &= c_0 e^{-\frac{i}{\hbar} E_0 t} |0\rangle + \left[\frac{1}{\sqrt{2}} \sqrt{\ominus} c_1 e^{-\frac{i}{\hbar} E_1 t} + \frac{1}{\sqrt{2}} \sqrt{\oplus} c_2 e^{-\frac{i}{\hbar} E_2 t} \right] |AD^*\rangle \\ &\quad + \left[\frac{1}{\sqrt{2}} \sqrt{\oplus} \text{sgn}(V) c_1 e^{-\frac{i}{\hbar} E_1 t} - \frac{1}{\sqrt{2}} \sqrt{\ominus} \text{sgn}(V) c_2 e^{-\frac{i}{\hbar} E_2 t} \right] |A^*D\rangle \\ &= \underbrace{c_0 e^{-\frac{i}{\hbar} E_0 t} |0\rangle}_{=c_{AD}(t)} + \underbrace{\left[d_{AD^*}^{(1)} e^{-\frac{i}{\hbar} E_1 t} + d_{AD^*}^{(2)} e^{-\frac{i}{\hbar} E_2 t} \right]}_{=c_{AD^*}(t)} |AD^*\rangle \\ &\quad + \underbrace{\left[d_{A^*D}^{(1)} e^{-\frac{i}{\hbar} E_1 t} + d_{A^*D}^{(2)} e^{-\frac{i}{\hbar} E_2 t} \right]}_{=c_{A^*D}(t)} |A^*D\rangle \end{aligned} \quad (S.14)$$

where

$$\begin{aligned}
d_{\text{AD}^*}^{(1)} &= \frac{1}{\sqrt{2}} & \sqrt{\ominus}c_1 &= \frac{1}{2} [\ominus C_{\text{D}^*} + \text{sgn}(V)\sqrt{\oplus}\sqrt{\ominus}C_{\text{A}^*}] \\
d_{\text{AD}^*}^{(2)} &= \frac{1}{\sqrt{2}} & \sqrt{\oplus}c_2 &= \frac{1}{2} [\oplus C_{\text{D}^*} - \text{sgn}(V)\sqrt{\oplus}\sqrt{\ominus}C_{\text{A}^*}] \\
d_{\text{A}^*\text{D}}^{(1)} &= \frac{1}{\sqrt{2}}\text{sgn}(V)\sqrt{\oplus}c_1 & &= \frac{1}{2} [\oplus C_{\text{A}^*} + \text{sgn}(V)\sqrt{\oplus}\sqrt{\ominus}C_{\text{D}^*}] \\
d_{\text{A}^*\text{D}}^{(2)} &= -\frac{1}{\sqrt{2}}\text{sgn}(V)\sqrt{\ominus}c_2 & &= \frac{1}{2} [\ominus C_{\text{A}^*} - \text{sgn}(V)\sqrt{\oplus}\sqrt{\ominus}C_{\text{D}^*}] .
\end{aligned} \tag{S.15}$$

For later reference, we further compute

$$\begin{aligned}
d_{\text{AD}^*}^{(1)} \left(d_{\text{AD}^*}^{(2)} \right)^* &= \frac{1}{2} \sqrt{\oplus}\sqrt{\ominus}c_1c_2^* = \frac{1}{2} \sqrt{1 + \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}}} \sqrt{1 - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}}} c_1c_2^* \\
&= \frac{|V|}{2\sqrt{(\Delta E)^2 + V^2}} c_1c_2^* = \frac{|V|}{2\sqrt{(\Delta E)^2 + V^2}} |c_1||c_2| e^{i(\varphi_1 - \varphi_2)} \\
&= -d_{\text{A}^*\text{D}}^{(1)} \left(d_{\text{A}^*\text{D}}^{(2)} \right)^* = |d| e^{2i\tilde{\varphi}} ,
\end{aligned} \tag{S.16}$$

where we wrote the coefficients using $c_j = |c_j|e^{i\varphi_j}$ and introduced $2\tilde{\varphi} = \varphi_1 - \varphi_2$. Moreover,

$$\begin{aligned}
\left| d_{\text{AD}^*}^{(1)} \right|^2 + \left| d_{\text{AD}^*}^{(2)} \right|^2 &= \frac{1}{2} |c_1|^2 \ominus + \frac{1}{2} |c_2|^2 \oplus \\
&= \frac{1}{2} |c_1|^2 \left(1 - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} \right) + \frac{1}{2} |c_2|^2 \left(1 + \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} \right) \\
&= \frac{1}{2} \left[(|c_1|^2 + |c_2|^2) - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} (|c_1|^2 - |c_2|^2) \right] \\
\left| d_{\text{A}^*\text{D}}^{(1)} \right|^2 + \left| d_{\text{A}^*\text{D}}^{(2)} \right|^2 &= \frac{1}{2} |c_1|^2 \oplus + \frac{1}{2} |c_2|^2 \ominus \\
&= \frac{1}{2} \left[(|c_1|^2 + |c_2|^2) + \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} (|c_1|^2 - |c_2|^2) \right] .
\end{aligned} \tag{S.17}$$

j. Time-dependent occupation of excited D- and A- states The probabilities to find the system in the state $|\text{AD}^*\rangle$ or $|\text{A}^*\text{D}\rangle$, using the definition $2\hbar\tilde{\omega} = E_1 - E_2 = 2\sqrt{(\Delta E)^2 + V^2} > 0$, are

$$|c_{\text{AD}^*}(t)|^2 = |\langle \text{AD}^* | \psi(t) \rangle|^2 \tag{S.19}$$

$$\begin{aligned}
&= \left| d_{\text{AD}^*}^{(1)} e^{-\frac{i}{\hbar} E_1 t} + d_{\text{AD}^*}^{(2)} e^{-\frac{i}{\hbar} E_2 t} \right|^2 \\
&= \left| d_{\text{AD}^*}^{(1)} \right|^2 + \left| d_{\text{AD}^*}^{(2)} \right|^2 + \left[d_{\text{AD}^*}^{(1)} \left(d_{\text{AD}^*}^{(2)} \right)^* e^{-\frac{i}{\hbar} (E_1 - E_2) t} + c.c. \right] \\
&= \frac{1}{2} |c_1|^2 \ominus + \frac{1}{2} |c_2|^2 \oplus + \frac{1}{2} \sqrt{\oplus}\sqrt{\ominus} |c_1||c_2| \left[e^{-2i(\tilde{\omega}t - \tilde{\varphi})} + c.c. \right] \\
&= \underbrace{\frac{1}{2} (|c_1|^2 + |c_2|^2)}_A - \underbrace{\frac{1}{2} \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} (|c_1|^2 - |c_2|^2)}_B \\
&\quad + \underbrace{|c_1||c_2| \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} \cos(2(\tilde{\omega}t - \tilde{\varphi}))}_C \\
&= A - B + C \cos(2(\tilde{\omega}t - \tilde{\varphi})) \\
|c_{\text{A}^*\text{D}}(t)|^2 &= |\langle \text{A}^*\text{D} | \psi(t) \rangle|^2 \\
&= A + B - C \cos(2(\tilde{\omega}t - \tilde{\varphi})) .
\end{aligned} \tag{S.20}$$

k. Special cases In the following, we discuss the situation that only the donor is excited at $t = 0$, i.e., $C_{A^*} = 0$, which always leads to $c_1 c_2^* \stackrel{\text{eq. (S.13)}}{=} 1/2\sqrt{\oplus}\sqrt{\ominus}|C_{D^*}|^2 \in \mathbb{R}$ and, thus, $\tilde{\varphi} = 0$. In a real-time propagation, an instantaneous boost excitation [4] in the donor's associated volume produces this situation with $C_{D^*} = i\mathbf{k} \cdot \mathbf{r}$ [5], where the boost vector $\mathbf{k}$ determines the boost strength and polarization. A laser pulse applied to the donor's associated volume, however, in general leads to $C_{A^*} \neq 0$ and, thus, $\tilde{\varphi} \neq 0$ since the energy transfer already starts during the excitation time ($t < 0$).

$\Delta E = 0$: (Resonant system)

$V > 0/V < 0$: (H/J-aggregate, complete energy transfer)

$$\begin{aligned} c_1 = c_2 &= \frac{1}{\sqrt{2}}C_{D^*} \quad |1\rangle \text{ and } |2\rangle \text{ are equally excited} \\ A &= \frac{1}{2}|C_{D^*}|^2, \quad B = 0, \quad C = \frac{1}{2}|C_{D^*}|^2 \\ \Rightarrow |c_{AD^*}(t)|^2 &= \frac{1}{2}|C_{D^*}|^2 [1 + \cos(2\tilde{\omega}t)], \quad |c_{A^*D}(t)|^2 = \frac{1}{2}|C_{D^*}|^2 [1 - \cos(2\tilde{\omega}t)] \end{aligned} \quad (\text{S.21})$$

$V = 0$: (Non-interacting system, no energy transfer, we set $\text{sgn}(V) = 1$)

$\Delta E > 0/\Delta E < 0$:

$$\begin{aligned} c_1 = 0, c_2 &= C_{D^*} \quad (\Delta E > 0) \quad \text{D-localized state is excited} \\ c_1 &= C_{D^*}, c_2 = 0 \quad (\Delta E < 0) \\ A &= \frac{1}{2}|C_{D^*}|^2, \quad B = -\frac{1}{2}|C_{D^*}|^2, \quad C = 0 \\ \Rightarrow |c_{AD^*}(t)|^2 &= |C_{D^*}|^2, \quad |c_{A^*D}(t)|^2 = 0 \end{aligned} \quad (\text{S.22})$$

$V = \sqrt{3}\Delta E > 0$: (Non-resonant system, incomplete energy transfer)

$$\begin{aligned} c_1 &= \frac{1}{2}C_{D^*}, c_2 = \frac{\sqrt{3}}{2}C_{D^*} \quad \text{D-dominant state is stronger excited} \\ A &= \frac{1}{2}|C_{D^*}|^2, \quad B = -\frac{1}{8}|C_{D^*}|^2, \quad C = \frac{3}{8}|C_{D^*}|^2 \\ \Rightarrow |c_{AD^*}(t)|^2 &= |C_{D^*}|^2 \left[\frac{5}{8} + \frac{3}{8}\cos(2\tilde{\omega}t) \right] \in \left[\frac{2}{8}|C_{D^*}|^2, |C_{D^*}|^2 \right] \\ |c_{A^*D}(t)|^2 &= |C_{D^*}|^2 \left[\frac{3}{8} - \frac{3}{8}\cos(2\tilde{\omega}t) \right] \in \left[0, \frac{3}{4}|C_{D^*}|^2 \right] \end{aligned} \quad (\text{S.23})$$

S.1.3 Time-dependent density

So far, the results correspond to the ones of the typical model Hamiltonian that does not take the ground state of the system explicitly into account. In the following, including the system's ground state becomes important because we now compute the time-dependent density from the model, so that we can compare it to the density from an actual real-time propagation. In the following, we drop the $\mathbf{r}$ -argument for clarity of the notation. Moreover, since the external perturbation is weak, $|c_1|, |c_2| = \mathcal{O}(\lambda)$ and $|c_0| = 1 + \mathcal{O}(\lambda^2)$ where λ is a small parameter. We can, therefore, approximate $|c_0||c_j| \approx |c_j|$ for $j \in \{1, 2\}$, $|c_0|^2 \approx 1$, and $|c_1||c_2| \approx 0$ by neglecting $\mathcal{O}(\lambda^2)$ -terms. Since we further assume that the densities of donor and acceptor states do not overlap and the transition densities of the donor and acceptor excitations remain unperturbed, we can further approximate $\langle AD | \hat{n} | AD^* \rangle \approx \langle D | \hat{n} | D^* \rangle = \rho_{D^*}$ and $\langle AD | \hat{n} | A^*D \rangle \approx \langle A | \hat{n} | A^* \rangle = \rho_{A^*}$ which are the (real-valued) transition densities of the single donor and acceptor excitations. In the previous equations, $\hat{n}$ denotes the density operator. The transition dipole moments are $\boldsymbol{\mu}_{D^*}$ and $\boldsymbol{\mu}_{A^*}$, respectively.

l. Definitions and notation We use the following notation

$$\begin{aligned}
\hbar\omega_{0j} &= E_j - E_0 && \text{Excitation energies} \\
\varphi_{0j} &= \varphi_j - \varphi_0 && \text{Respective phases} \\
\rho_{0j} &= \langle 0|\hat{n}|j\rangle = \langle j|\hat{n}|0\rangle && \text{Respective (real-valued) transition densities} \\
\tilde{\omega} &= \frac{1}{2}(\omega_{01} - \omega_{02}) && \text{Beat frequency between } |1\rangle \text{ and } |2\rangle \\
\tilde{\varphi} &= \frac{1}{2}(\varphi_{01} - \varphi_{02}) && \text{Respective phase} \\
\bar{\omega} &= \frac{1}{2}(\omega_{01} + \omega_{02}) && \text{Mean excitation energy} \\
\bar{\varphi} &= \frac{1}{2}(\varphi_{01} + \varphi_{02}) && \text{Respective phase} \\
[j] &= \omega_{0j}t - \varphi_{0j} && \text{Short notation} \\
[\sim] &= \tilde{\omega}t - \tilde{\varphi} && \text{Short notation} \\
[-] &= \bar{\omega}t - \bar{\varphi} && \text{Short notation,}
\end{aligned}$$

where we already introduced $\tilde{\omega}$ and $\tilde{\varphi}$ before.

m. Time-dependent density Using these conventions and eq. (S.14), the induced density fluctuation for $t \geq 0$ reads

$$\begin{aligned}
\delta n(t) &= \langle \psi(t) | \hat{n} | \psi(t) \rangle - \langle 0 | \hat{n} | 0 \rangle \\
&= 2|c_1|\rho_{01}\cos([1]) + 2|c_2|\rho_{02}\cos([2]) + \mathcal{O}(\lambda^2) \\
&\approx 2|c_1|\frac{1}{\sqrt{2}} [\sqrt{\ominus}\rho_{D^*} + \text{sgn}(V)\sqrt{\oplus}\rho_{A^*}] \cos([1]) \\
&\quad + 2|c_2|\frac{1}{\sqrt{2}} [\sqrt{\oplus}\rho_{D^*} - \text{sgn}(V)\sqrt{\ominus}\rho_{A^*}] \cos([2]) \\
&= \underbrace{\sqrt{2} [|c_1|\sqrt{\ominus}\cos([1]) + |c_2|\sqrt{\oplus}\cos([2])] \rho_{D^*}}_{=\delta n_D} \\
&\quad + \underbrace{\sqrt{2}\text{sgn}(V) [|c_1|\sqrt{\oplus}\cos([1]) - |c_2|\sqrt{\ominus}\cos([2])] \rho_{A^*}}_{=\delta n_A}
\end{aligned} \tag{S.24}$$

Since, again, the donor and acceptor states and, therefore, the donor and acceptor transition densities do not overlap, we can split the density fluctuation δn into independent contributions from the donor (δn_D) and the acceptor (δn_A). For the discussion of the energy measures from the main article, we further need the time derivative

$$\begin{aligned}
\dot{n}(t) &= \frac{\partial}{\partial t} n(t) = \frac{\partial}{\partial t} \delta n(t) \\
&= \underbrace{\sqrt{2} [-|c_1|\omega_{01}\sqrt{\ominus}\sin([1]) - |c_2|\omega_{02}\sqrt{\oplus}\sin([2])] \rho_{D^*}}_{=\dot{n}_D} \\
&\quad + \underbrace{\sqrt{2}\text{sgn}(V) [-|c_1|\omega_{01}\sqrt{\oplus}\sin([1]) + |c_2|\omega_{02}\sqrt{\ominus}\sin([2])] \rho_{A^*}}_{=\dot{n}_A}
\end{aligned} \tag{S.25}$$

and the induced dipole moment

$$\begin{aligned}
\delta \boldsymbol{\mu}(t) &= \int \delta n(\mathbf{r}, t) \mathbf{r} d^3r \\
&= \underbrace{\sqrt{2} [|c_1|\sqrt{\ominus}\cos([1]) + |c_2|\sqrt{\oplus}\cos([2])] \boldsymbol{\mu}_{D^*}}_{=\delta \boldsymbol{\mu}_D} \\
&\quad + \underbrace{\sqrt{2}\text{sgn}(V) [|c_1|\sqrt{\oplus}\cos([1]) - |c_2|\sqrt{\ominus}\cos([2])] \boldsymbol{\mu}_{A^*}}_{=\delta \boldsymbol{\mu}_A} .
\end{aligned} \tag{S.26}$$

n. Special case If, as in our former examples, only the donor is excited at $t = 0$ so that $C_{A^*} = 0$, eq. (S.24) can be simplified to

$$\begin{aligned}
\delta n(t)^{(C_{A^*}=0)} &\approx |C_{D^*}| [\ominus \cos([1]) + \oplus \cos([2])] \rho_{D^*} \\
&\quad + \text{sgn}(V) |C_{D^*}| [\sqrt{\oplus} \sqrt{\ominus} \cos([1]) - \sqrt{\oplus} \sqrt{\ominus} \cos([2])] \rho_{A^*} \\
&= |C_{D^*}| \left\{ [\cos([1]) + \cos([2])] - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [\cos([1]) - \cos([2])] \right\} \rho_{D^*} \\
&\quad + |C_{D^*}| \frac{V}{\sqrt{(\Delta E)^2 + V^2}} [\cos([1]) - \cos([2])] \rho_{A^*} \\
&= 2|C_{D^*}| \left\{ \cos([\sim]) \cos([-]) + \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} \sin([\sim]) \sin([-]) \right\} \rho_{D^*} \\
&\quad - 2|C_{D^*}| \frac{V}{\sqrt{(\Delta E)^2 + V^2}} \sin([\sim]) \sin([-]) \rho_{A^*}
\end{aligned}$$

In this special case, the interpretation of the density fluctuation becomes relatively transparent and intuitively understandable: The density fluctuation consists of a high-frequency component $\bar{\omega}$ that is modulated by the low-frequency beating signal $\tilde{\omega}$.

S.1.4 Energy measures

Under the assumption that the densities of the donor and acceptor states do not overlap, we further approximate $\delta n^2 \approx \delta n_D^2 + \delta n_A^2$.

$$\begin{aligned}
\delta n_D^2 &\approx 2\rho_{D^*}^2 [|c_1| \sqrt{\ominus} \cos([1]) + |c_2| \sqrt{\oplus} \cos([2])]^2 \\
&= 2\rho_{D^*}^2 [|c_1|^2 \ominus \cos^2([1]) + |c_2|^2 \oplus \cos^2([2]) + 2|c_1||c_2| \sqrt{\oplus} \sqrt{\ominus} \cos([1]) \cos([2])] \\
&= 2\rho_{D^*}^2 \left\{ [|c_1|^2 \cos^2([1]) + |c_2|^2 \cos^2([2])] - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2 \cos^2([1]) - |c_2|^2 \cos^2([2])] \right. \\
&\quad \left. + 2|c_1||c_2| \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} \cos([1]) \cos([2]) \right\} \\
&= \rho_{D^*}^2 \left\{ [|c_1|^2 + |c_2|^2] [1 + \cos(2[-]) \cos(2[\sim])] - [|c_1|^2 - |c_2|^2] \sin(2[-]) \sin(2[\sim]) \right. \\
&\quad - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2 - |c_2|^2] [1 + \cos(2[-]) \cos(2[\sim])] \\
&\quad - [|c_1|^2 + |c_2|^2] \sin(2[-]) \sin(2[\sim])] \\
&\quad \left. + 2|c_1||c_2| \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} [\cos(2[\sim]) + \cos(2[-])] \right\},
\end{aligned} \tag{S.27}$$

where we used

$$\begin{aligned}
|c_1|^2 \cos^2([1]) \pm |c_2|^2 \cos^2([2]) &= \frac{1}{2} [|c_1|^2 \pm |c_2|^2] [1 + \cos(2[-]) \cos(2[\sim])] \\
&\quad - \frac{1}{2} [|c_1|^2 \mp |c_2|^2] \sin(2[-]) \sin(2[\sim])
\end{aligned} \tag{S.28}$$

and

$$\begin{aligned}
\cos([1]) \cos([2]) &= \frac{1}{2} [\cos([1] + [2]) + \cos([1] - [2])] \\
&= \frac{1}{2} [\cos(2[\sim]) + \cos(2[-])]
\end{aligned} \tag{S.29}$$

The squared density fluctuation in eq. (S.27) shows several high-frequency components with frequencies $2(\bar{\omega} + k\tilde{\omega})$, where $k \in \{-1, 0, 1\}$. To extract the relevant information about the energy-transfer dynamics, we filter these high-frequency components so that

$$\begin{aligned}\cos(2[-]) &\rightarrow 0 \\ \cos(2[-]) \cos(2[\sim]) &\rightarrow 0 \\ \sin(2[-]) \sin(2[\sim]) &\rightarrow 0\end{aligned}\tag{S.30}$$

The thus filtered quantities (denoted by an overline) become

$$\begin{aligned}\bar{\mathcal{E}}_{\delta n}^{(D)}(t) &= \int_{V^{(D)}} \overline{(\delta n_D)^2}(t) d^3r \\ &= 2 \int_{V^{(D)}} \rho_{D*}^2 d^3r \left\{ \underbrace{\frac{1}{2} [|c_1|^2 + |c_2|^2]}_{=A} - \underbrace{\frac{1}{2} \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2 - |c_2|^2]}_{=B} \right. \\ &\quad \left. + \underbrace{|c_1||c_2| \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} \cos(2[\sim])}_{=C} \right\} \\ &= 2 \int_{V^{(D)}} \rho_{D*}^2 d^3r |c_{AD*}(t)|^2\end{aligned}\tag{S.31}$$

and, in analogy

$$\bar{\mathcal{E}}_{\delta n}^{(A)}(t) = \int_{V^{(D)}} \overline{(\delta n_A)^2}(t) d^3r = 2 \int_{V^{(A)}} \rho_{A*}^2 d^3r |c_{A*D}(t)|^2.\tag{S.32}$$

In the same way, one finds

$$\bar{\mathcal{E}}_{\mu}^{(D)}(t) = 2\mu_{D*}^2 |c_{AD*}(t)|^2 \quad \text{and} \quad \bar{\mathcal{E}}_{\mu}^{(A)}(t) = 2\mu_{A*}^2 |c_{A*D}(t)|^2,\tag{S.33}$$

where the donor and acceptor transition densities are just replaced by their respective transition dipoles. Finally,

$$\begin{aligned}\dot{n}_D^2 &\approx 2\rho_{D*}^2 [-|c_1|\omega_{01}\sqrt{\ominus}\sin([1]) - |c_2|\omega_{02}\sqrt{\oplus}\sin([2])]^2 \\ &= 2\rho_{D*}^2 [|c_1|^2\omega_{01}^2 \ominus \sin^2([1]) + |c_2|^2\omega_{02}^2 \oplus \sin^2([2]) + 2|c_1||c_2|\omega_{01}\omega_{02}\sqrt{\oplus}\sqrt{\ominus}\sin([1])\sin([2])] \\ &= 2\rho_{D*}^2 \left\{ [|c_1|^2\omega_{01}^2 \sin^2([1]) + |c_2|^2\omega_{02}^2 \sin^2([2])] \right. \\ &\quad - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2\omega_{01}^2 \sin^2([1]) - |c_2|^2\omega_{02}^2 \sin^2([2])] \\ &\quad \left. + 2|c_1||c_2|\omega_{01}\omega_{02} \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} \sin([1])\sin([2]) \right\} \\ &= \rho_{D*}^2 \left\{ [|c_1|^2\omega_{01}^2 + |c_2|^2\omega_{02}^2] [1 - \cos(2[-]) \cos(2[\sim])] \right. \\ &\quad + [|c_1|^2\omega_{01}^2 - |c_2|^2\omega_{02}^2] \sin(2[-]) \sin(2[\sim]) \\ &\quad - \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2\omega_{01}^2 - |c_2|^2\omega_{02}^2] [1 - \cos(2[-]) \cos(2[\sim])] \\ &\quad + [|c_1|^2\omega_{01}^2 + |c_2|^2\omega_{02}^2] \sin(2[-]) \sin(2[\sim])] \\ &\quad \left. + 2|c_1||c_2|\omega_{01}\omega_{02} \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} [\cos(2[\sim]) - \cos(2[-])] \right\}.\end{aligned}\tag{S.34}$$

After the filtering step, one obtains

$$\begin{aligned}
\bar{\mathcal{E}}_{\dot{n}}^{(D)}(t) &= \int_{V^{(D)}} \overline{(\dot{n}_D)^2}(t) d^3r \\
&= 2 \int_{V^{(D)}} \rho_{D^*}^2 d^3r \left\{ \frac{1}{2} [|c_1|^2 \omega_{01}^2 + |c_2|^2 \omega_{02}^2] - \frac{1}{2} \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2 \omega_{01}^2 - |c_2|^2 \omega_{02}^2] \right. \\
&\quad \left. + |c_1| |c_2| \omega_{01} \omega_{02} \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} \cos(2[\sim]) \right\} \\
&\approx 2\bar{\omega}^2 \int_{V^{(D)}} \rho_{D^*}^2 d^3r \left\{ \underbrace{\frac{1}{2} [|c_1|^2 + |c_2|^2]}_{=A} - \underbrace{\frac{1}{2} \frac{\Delta E}{\sqrt{(\Delta E)^2 + V^2}} [|c_1|^2 - |c_2|^2]}_{=B} \right. \\
&\quad \left. + \underbrace{|c_1| |c_2| \frac{|V|}{\sqrt{(\Delta E)^2 + V^2}} \cos(2[\sim])}_{=C} \right\} \\
&= 2\bar{\omega}^2 \int_{V^{(D)}} \rho_{D^*}^2 d^3r |c_{AD^*}(t)|^2,
\end{aligned} \tag{S.35}$$

where we further used $\bar{\omega} \gg \tilde{\omega}$ to approximate $\omega_{01/02} = \bar{\omega} \pm \tilde{\omega} \approx \bar{\omega}$ and $\omega_{01}\omega_{02} = \bar{\omega}^2 - \tilde{\omega}^2 \approx \bar{\omega}^2$. Accordingly,

$$\bar{\mathcal{E}}_{\dot{n}}^{(A)}(t) = 2\bar{\omega}^2 \int_{V^{(A)}} \rho_{A^*}^2 d^3r |c_{A^*D}(t)|^2. \tag{S.36}$$

S.2 DISCUSSION OF ALTERNATIVE ENERGY MEASURES

In the context of the donor-acceptor model, the excitation-energy measures that we derived in the preceding Section S.1.4 (eqs. (S.31) – (S.36)), i. e., eqs. (20) – (23) in the main article, have the form

$$\begin{aligned}
\bar{\mathcal{E}}_{\xi}^{(D)}(t) &= A_{\xi}^{(D)} |c_{AD^*}(t)|^2 \\
\bar{\mathcal{E}}_{\xi}^{(A)}(t) &= A_{\xi}^{(A)} |c_{A^*D}(t)|^2.
\end{aligned} \tag{S.37}$$

While we associated the energy content of an entity (donor or acceptor in this case) with $|c_{AD^*}|^2$ and $|c_{A^*D}|^2$, the coefficients $A_{\xi}^{(l)}$ are determined by the specific measures $\xi \in \{\mu, \delta n, \dot{n}\}$ and may be different for different entities l . In this section, we discuss three ideas for alternative excitation-energy measures that do not rely on single-entity quantities and feature the correct units of an energy or energy density, respectively.

We again assume that there is no external excitation after $t = 0$ and that one can derive an expression for a meaningful (time-local) total excitation energy $\mathcal{E}(t)$ of the system from the underlying theory. One possibility is to define

$$\mathcal{E}(t) = \int \varepsilon_{KS}(\mathbf{r}, t) d^3r, \tag{S.38}$$

in analogy to Section 4.2.1 of the main article, but in difference to eq. (14) in Section 4.2.1, the integral here runs over all space and therefore, as the ground-state density is a variational minimum, it cannot fall below zero.

1. As a first alternative measure, one can define

$$\bar{\varepsilon}_{\xi}^{\text{alt1}}(\mathbf{r}, t) = \frac{\mathcal{E}(t=0)}{\int \bar{\varepsilon}_{\xi}(\mathbf{r}, t=0) d^3r} \bar{\varepsilon}_{\xi}(\mathbf{r}, t), \tag{S.39}$$

which scales the original measure with a constant. The disadvantage is that the prefactor at $t = 0$ is not a well defined quantity since its value is influenced by $\varepsilon_{\xi}(\mathbf{r}, t)$ at times $t < 0$ via the smoothing procedure. Therefore, the resulting energy values strongly depend on the smoothing algorithm. Taking the constants at a reference time $t > 0$ leads to equivalent problems since $\int \bar{\varepsilon}_{\xi}(\mathbf{r}, t) d^3r$ is usually not perfectly constant over time, as discussed in the main article.

2. A second alternative measure, defined by

$$\bar{\varepsilon}_{\xi}^{\text{alt2}}(\mathbf{r}, t) = \frac{\frac{1}{\Delta t} \int_0^{\Delta t} \mathcal{E}(t) dt}{\frac{1}{\Delta t} \int_0^{\Delta t} \int \bar{\varepsilon}_{\xi}(\mathbf{r}, t) d^3r dt} \bar{\varepsilon}_{\xi}(\mathbf{r}, t), \quad (\text{S.40})$$

is similar to alternative 1 but uses a time integral to generate a mean scaling factor. It shows a similar degree of arbitrariness since it depends on the chosen averaging interval.

3. Finally,

$$\bar{\varepsilon}_{\xi}^{\text{alt3}}(\mathbf{r}, t) = \mathcal{E}(t) \frac{\bar{\varepsilon}_{\xi}(\mathbf{r}, t)}{\int \bar{\varepsilon}_{\xi}(\mathbf{r}, t) d^3r} \quad (\text{S.41})$$

looks similar to alternative 1 (apart from the ordering of terms) with the only but important difference that the scaling factor is taken to be time dependent (note that $\mathcal{E}(t)$ is constant for $t > 0$). The beauty of this expression is that the time-local normalization ensures that the measure always integrates to the total excitation energy as determined by $\mathcal{E}(t)$. We show this measure in Figure 1, complementing Figure 1 (d) of the main article. In the context of the donor-acceptor model, by integrating over donor and acceptor volumes, this translates to

$$\begin{aligned} \bar{\mathcal{E}}_{\xi}^{(\text{D}), \text{alt3}}(t) &= \mathcal{E}(t) \frac{A_{\xi}^{(\text{D})} |c_{\text{AD}^*}(t)|^2}{A_{\xi}^{(\text{D})} |c_{\text{AD}^*}(t)|^2 + A_{\xi}^{(\text{A})} |c_{\text{A}^* \text{D}}(t)|^2} \\ \bar{\mathcal{E}}_{\xi}^{(\text{A}), \text{alt3}}(t) &= \mathcal{E}(t) \frac{A_{\xi}^{(\text{A})} |c_{\text{A}^* \text{D}}(t)|^2}{A_{\xi}^{(\text{D})} |c_{\text{AD}^*}(t)|^2 + A_{\xi}^{(\text{A})} |c_{\text{A}^* \text{D}}(t)|^2}, \end{aligned} \quad (\text{S.42})$$

i.e., this variant compensates for the effect of the different entity-specific $A_{\xi}^{(l)}$. This leads to beneficial properties. E.g., if the energy is completely located on one entity, this entity's momentary excitation energy equals the total excitation energy irrespective of its $A_{\xi}^{(l)}$.

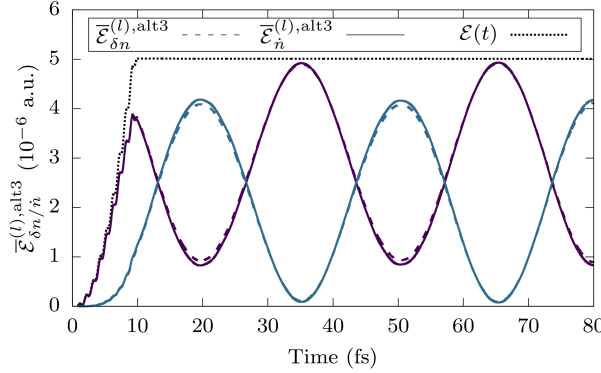


FIG. 1. The dark purple lines show $\bar{\varepsilon}_{\delta n}^{\text{alt3}}$ (full line) and $\bar{\varepsilon}_{\delta n}^{\text{alt3}}$ (dashed line) as a function of time for the donor, the blue lines show the same quantities for the acceptor. The total excitation energy $\mathcal{E}(t)$ is shown as black dotted line.

All three alternatives feature the correct units of an energy density. Alternative 3 also integrates to the total excitation energy $\mathcal{E}(t)$. However, all three alternatives have the drawback that the signal filtering, which is just a technical aid for evaluating the measures of excitation energy that we discuss in the main article, becomes a fundamental ingredient for the definition of the alternative measures. As a consequence, the alternative measures are less transparent, and the layers of physical interpretation and technical evaluation are intermixed. A further disadvantage regarding the use of the alternative measures in Ehrenfest simulations is that $\mathcal{E}(t)$ strongly suffers from the Eggbox effect. However, it should be noted that $\bar{\varepsilon}_{\xi}^{\text{alt}[1-3]}(\mathbf{r}, t)/\mathcal{E}(t)$ remain good measures for the relative energy distribution in the system.

In a nutshell we conclude that eqs. (S.39) – (S.41) define valid measures for the relative energy distribution in the system, but in practice, eqs. (16) – (19) of the main paper are the measures that we regard to be of greater practical relevance.

S.3 FOURIER-FILTERING ALGORITHMS

S.3.1 Jacobi smoothing

o. Method The iterative Jacobi-relaxation [6, 7] based smoothing algorithm discussed below can be used to smooth a signal that consists of two well separated frequency domains. It acts as a simple Fourier filter that is applied in the time domain.

It founds on the Jacobi relaxation [6, 7], which is an iterative algorithm to find the solution of a system of linear equations $Df = y$ starting from an initial function $f^{(0)}$. The system of equations may result from the discretization of a differential equation, e.g., in which a function $f(t)$ of time is discretized on an equidistant grid $f_k = f(t_k)$ for $k \in [0, N_t - 1]$ and $t_k = k\Delta t$, where Δt is the time-step size. The general recursion to solve the equations reads

$$f_k^{(n+1)} = \frac{1}{d_{kk}} \left(y_k - \sum_{l \neq k} d_{kl} f_l^{(n)} \right), \quad (\text{S.43})$$

where d_{kl} denote the matrix elements of the matrix representation of the operator D .

One can use this scheme to smooth an initial signal $f^{(0)}$ by attempting to solve the differential equation $\Delta f = 0$ with the Laplacian represented by second-order central finite differences

$$D = \frac{1}{2\Delta t} \begin{pmatrix} -2 & 1 & 0 & 0 & \cdots \\ 1 & -2 & 1 & 0 & \ddots \\ 0 & 1 & -2 & 1 & \ddots \\ \vdots & \ddots & \ddots & \ddots & \ddots \\ \cdots & 0 & 0 & 1 & -2 \end{pmatrix} \quad (\text{S.44})$$

In this special case, one iteration $(n) \rightarrow (n+1)$ of the recursion reads

$$f_k^{(n)} = \frac{1}{2} \left[f_{k-1}^{(n-1)} + f_{k+1}^{(n-1)} \right], \quad (\text{S.45})$$

i.e., the value at t_k is assigned the mean value of its neighboring points from the previous iteration. At the two boundaries, one may either apply (i) von Neumann boundary conditions (fix the values, e.g., $f_0^{(n)} = f_0^{(0)}$ and $f_{N_t-1}^{(n)} = f_{N_t-1}^{(0)}$), which can lead to artifacts if the boundary values of $f^{(0)}$ are not meaningful, or (ii) Dirichlet boundary conditions (fix the derivative, e.g., by assigning $f_{-1}^{(n)} = f_1^{(n)}$ and $f_{N_t}^{(n)} = f_{N_t-2}^{(n)}$), which leads to a smooth connection with zero derivative at the boundaries. Iterative application of the recursion above works as a smoothing algorithm as long as the condition $\omega_{\text{lf}} \ll \omega_{\text{hf}} \ll \omega_{\text{Ny}}$ is fulfilled, where ω_{lf} are the low- and ω_{hf} high-frequency contributions to the initial signal, and $\omega_{\text{Ny}} = \pi/\Delta t$ is the Nyquist frequency. Note that the smoothing properties depend on the time-step size Δt , as shown below.

p. Theory One can investigate the smoothing properties by a von Neumann stability analysis [7] that describes the evolution of the frequency-dependent amplification factor from one iteration to the next. To this end, one decomposes $f^{(n)}$ into its frequency components

$$f_k^{(n)} = \int e^{i\omega k \Delta t} g_{\omega}^{(n)} d\omega \quad (\text{S.46})$$

and inserts the recursion from eq. (S.45) into this expression for $f^{(n+1)}$

$$f_k^{(n+1)} = \int e^{i\omega k \Delta t} g_{\omega}^{(n+1)} d\omega \quad (\text{S.47})$$

$$\begin{aligned} &= \frac{1}{2} \int \left[e^{i\omega(k-1)\Delta t} + e^{i\omega(k+1)\Delta t} \right] g_{\omega}^{(n)} d\omega \\ &= \frac{1}{2} \int e^{i\omega k \Delta t} g_{\omega}^{(n)} \underbrace{\left[e^{-i\omega \Delta t} + e^{i\omega \Delta t} \right]}_{=2 \cos(\omega \Delta t)} d\omega \\ &= \int e^{i\omega k \Delta t} g_{\omega}^{(n)} \cos(\omega \Delta t) d\omega. \end{aligned} \quad (\text{S.48})$$

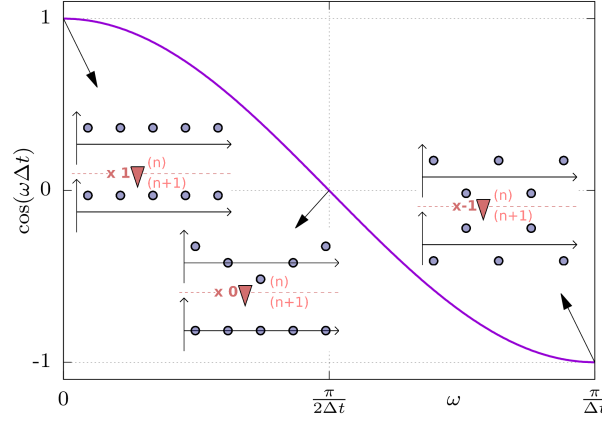


FIG. 2. Frequency-dependent amplification factor for one iteration of the Jacobi smoother and illustration of what one smoothing step achieves in the three special cases $\omega = 0$, $\omega = \omega_{Ny} = \pi/\Delta t$ and $\omega = \omega_{Ny}/2$.

The comparison between the first and the last line provides the frequency-dependent amplification factor

$$\frac{g_{\omega}^{(n+1)}}{g_{\omega}^{(n)}} = \cos(\omega \Delta t). \quad (\text{S.49})$$

The latter is shown in Figure 2 together with three special cases:

$\omega = 0$: A constant function with only a zero-frequency contribution remains unchanged by averaging respective neighboring values (amplification factor +1).

$\omega = \omega_{Ny}$: A function that oscillates with the Nyquist frequency, i.e., the highest frequency that can be represented with Δt sampling, is inverted (amplification factor -1).

$\omega = \omega_{Ny}/2$: A function that oscillates with half the Nyquist frequency is perfectly removed (amplification factor 0).

Thus, the algorithm acts as a smoother if the requested signal's frequency is close to zero while all frequencies to be filtered are much larger (but still much smaller than the Nyquist frequency). From eq. (S.49) it also becomes clear that the smoothing properties directly depend on the time-step size Δt .

S.3.2 τ -filtering

The τ -filtering method is a simple but numerically efficient Fourier-filtering scheme applied in the time domain. It can be used as a high or low pass filter with acceptable quality in situations where the spectrum contains two well separated bands of which one is at low frequencies. Even though the τ -filtering method is of limited quality, it is useful if a more advanced Fourier-filtering scheme is not feasible. A typical example for such a situation is a time-dependent function on a multidimensional real-space grid that results from a numerical propagation. In such a case storing the complete time line of the function or computing its complete Fourier transform may take too much storage or time resources.

q. Method Given a function $f(t)$ that oscillates with certain frequencies, the τ -filtered function is given by

$$\bar{f}^{\tau}(t) = \frac{1}{\tau} \int_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} f(t') dt' \quad (\text{S.50})$$

with a given time constant τ . Thus, the filtered function at a given time t is the mean value of the original function in a symmetric interval of extension τ around t . Intuitively, it is clear that Fourier components with circular frequencies close to $\omega_{\tau} = 2\pi/\tau$ as well as ones with very large frequencies are filtered out, while Fourier components with frequencies close to zero remain almost unaltered. A good choice for the time constant τ is usually the mean time

period of signals in the high-frequency band. Equation (S.50) can therefore be used as a low-pass Fourier filter. Vice versa,

$$\tilde{f}^\tau(t) = f(t) - \frac{1}{\tau} \int_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} f(t') dt' \quad (\text{S.51})$$

can be used as high-pass filter.

r. Theory The Fourier transform of $f(t)$ is

$$g(\omega) = \frac{1}{2\pi} \int e^{-i\omega t} f(t) dt. \quad (\text{S.52})$$

The Fourier transform of the (low-pass) filtered function $\bar{f}^\tau(t)$ is

$$\bar{g}^\tau(\omega) = \frac{1}{2\pi} \int e^{-i\omega t} \bar{f}^\tau(t) dt \quad (\text{S.53})$$

$$= \frac{1}{2\pi} \int e^{-i\omega t} \frac{1}{\tau} \int_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} f(t') dt' dt \quad (\text{S.54})$$

$$\begin{aligned} &= \frac{1}{2\pi} \int e^{-i\omega t} \frac{1}{\tau} \int_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} \int e^{i\omega' t'} g(\omega') d\omega' dt' dt \\ &= \frac{1}{2\pi} \int e^{-i\omega t} \left\{ \int g(\omega') \left[\frac{1}{\tau} \int_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} e^{i\omega' t'} dt' \right] d\omega' \right\} dt \\ &= \frac{1}{2\pi} \int e^{-i\omega t} \left\{ \int \underbrace{e^{i\omega' t} g(\omega') \text{sinc}\left(\frac{\omega' \tau}{2}\right)}_{=\bar{g}^\tau(\omega')} d\omega' \right\} dt \end{aligned}$$

with

$$\begin{aligned} \frac{1}{\tau} \int_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} e^{i\omega' t'} dt' &= \frac{1}{i\omega' \tau} \left[e^{i\omega' (t+\frac{\tau}{2})} - e^{i\omega' (t-\frac{\tau}{2})} \right]_{t-\frac{\tau}{2}}^{t+\frac{\tau}{2}} \\ &= \frac{1}{i\omega' \tau} e^{i\omega' t} \left[e^{i\frac{\omega' \tau}{2}} - e^{-i\frac{\omega' \tau}{2}} \right] \\ &= \frac{2}{\omega' \tau} e^{i\omega' t} \sin\left(\frac{\omega' \tau}{2}\right) \\ &= e^{i\omega' t} \text{sinc}\left(\frac{\omega' \tau}{2}\right). \end{aligned}$$

One thus finds

$$\bar{g}^\tau(\omega) = g(\omega) \text{sinc}\left(\frac{\omega \tau}{2}\right) \quad (\text{S.55})$$

as the Fourier transform of the filtered function. Thus, the τ -filter works as a sine-cardinal filter in Fourier space centered at $\omega = 0$ and with its first root at $\omega = 2\pi/\tau$. Therefore, as expected, frequencies around $2\pi/\tau$ and larger ones are filtered while frequencies close to zero are hardly influenced.

s. Implementation The numerical computation in a propagation calculation can be done efficiently on-the-fly as illustrated in Figure 3. At a given time $t_j = j\Delta t$, one can compute $\bar{f}_{j-N_\tau/2}^\tau$ with $N_\tau = \tau/\Delta t$ using all f_k within the given τ interval $k \in [j - N_\tau, j]$. A good choice for negative k (occurring during the first $N_{\tau/2}$ time steps) is setting $f_{k<0}$ to $f_{k=0}$. Having $\bar{f}_{j-N_\tau/2}^\tau$ at hand, one can compute $\bar{f}_{j-N_\tau/2+1}^\tau$ in the next time step $(j+1)$ simply using

$$\bar{f}_{j-N_\tau/2+1}^\tau = \bar{f}_{j-N_\tau/2}^\tau - f_{j-N_\tau} + f_{j+1} \quad (\text{S.56})$$

by replacing the oldest with the latest value of f .

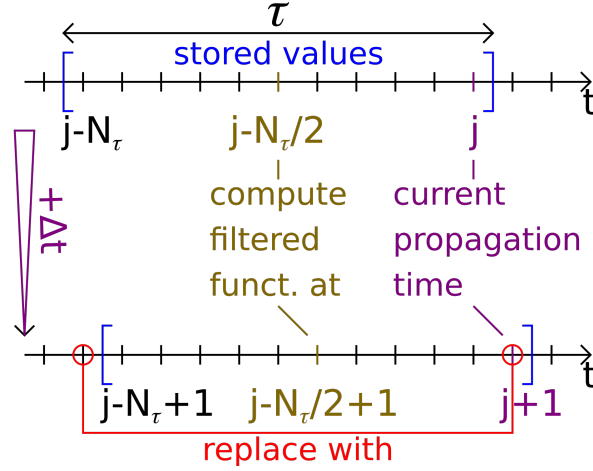


FIG. 3. Illustration of the efficient on-the-fly computation of the τ -filtering scheme as described in the text.

S.4 NUMERICAL DETAILS

All our simulations were done with our own grid-based real-time code Bayreuth DFT (BTDF) [5]. For all systems, we used a grid spacing of $0.5 a_0$ and a time-step size of $\Delta t = 0.01$ fs. The whole grid volume was defined by the union of atom-centered spheres with a radius of $20.38 a_0$ around all sodium nuclei so that the pseudopotential valence density falls below $10^{-10} a_0^{-3}$ at the boundaries. We described the sodium nuclei (i.e., nuclei and core electrons) by a norm-conserving Troullier-Martins pseudopotential [8] with a cutoff radius of $3.09 a_0$ for the s and p component and chose the s component as the local component in the Kleinman-Bylander [9] transformation. BTDF solves the Poisson equation for the Hartree potential using a 9^{th} order multipole expansion for the boundary conditions on a larger ellipsoidal grid with halfaxes of $(35, 30, 30) a_0$ (two dimers) or $(50, 30, 30) a_0$ (four dimers), respectively. For the propagation of the Kohn-Sham orbitals, we used a Crank-Nicolson propagator [7] with a predictor-corrector scheme with one corrector step. For the τ -filtering (high-pass) of the density in Section 5 of the main article, we used $\tau = 4$ fs to remove the low-frequency nuclear signals.

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Publication 2

Time-Resolved Excitation Dynamics in the B850 Light-Harvesting Antenna from Real-Time Density Functional Theory

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Pub. 2

Author contributions

All authors conceptualized the work. T.T. did all DFT and TDDFT simulations, constructed the exciton Hamiltonian, and did the data processing. I.S. technically supported the (TD)DFT simulations. The environment potential was generated by I.S. for the whole B850 ring and by T.T. for the single BChls for the exciton Hamiltonian. All authors discussed the results. S.K. led the interpretation of the results, with support from T.T. and I.S. S.K. structured the results and the manuscript. T.T. and S.K. wrote the manuscript; I.S. proofread it and gave comments; T.T. prepared the graphics for the manuscript. All authors equally wrote the Supporting Information. T.T. and I.S. prepared the graphics and videos for the Supporting Information. S.K. supervised the project and acquired the funding.

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Time-Resolved Ultrafast Excitation Dynamics in the B850 Light-Harvesting Antenna from Density Functional Theory

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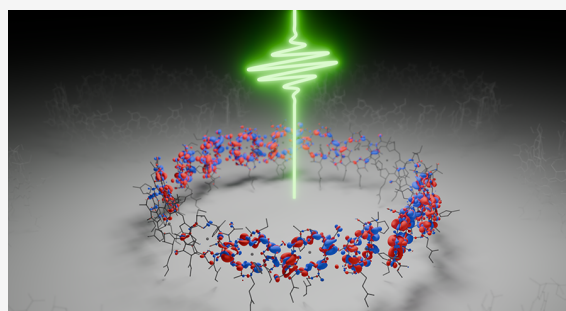


Article Recommendations



Supporting Information

ABSTRACT: Antenna complexes absorb sunlight and transfer the harvested energy with remarkable quantum efficiency. In spectroscopic experiments, they are typically excited with laser pulses that differ substantially from sunlight. Using density functional theory calculations in real time, we reveal the excitation dynamics that results in the B850 antenna ring of the purple bacterium *Rhodoblastus acidophilus* upon excitation by a short, strong pulse as typically used in experiments. The pulse dominantly triggers the exciton modes that are also the most relevant ones in the natural process. Quantum mechanical interference patterns noticeably influence the electronic density distribution after about 40 fs, and on the same time scale, the effects of nuclear motion start to have a noticeable influence on the excitation dynamics. About 20 fs after the laser peak, the B850 ring transitions into dynamics in which the excitation energy is mostly localized on segments that comprise just a few bacteriochlorophyll molecules.



The importance of photosynthesis can hardly be overestimated, as it provides the chemical energy for life. The harvesting of light is one of the most fascinating natural processes, with supramolecular antenna complexes¹ transferring collected energy first to neighboring complexes, and ultimately to a reaction center.² There, the harvested energy generates a charge-transfer state^{3–7} that initiates the further biochemical processes by which sunlight is converted into chemical energy.^{8–10}

One of the most fascinating aspects of this process is its remarkable quantum efficiency,¹¹ and this has fueled an intense debate about the role that quantum coherence plays in the light-harvesting process.^{12–16} The excitation-energy transfer within the antenna structure plays a key role for this efficiency. Experimentally, this process is typically probed by pulsed intense lasers,^{15,17,18} and remarkable insights have been obtained in this way. However, the electromagnetic field of a strong pulse is very different from the one of natural sunlight. It is a so far open question whether the excitation dynamics that is triggered by the typical pulses is similar to the one that is triggered by sunlight.

Solving the Kohn–Sham equations in real time allows for obtaining insight into the evolution of excitation dynamics with spatial and temporal resolution on the atomic scale.^{19–34} Here, we combine the natural strengths of the real-time approach with an efficient parallelization on a real-space grid to determine, without input from spectroscopic experiments and fully based on first-principles, the electronic and nuclear dynamics that realizes the excitation-energy transfer in the B850 ring of the light-harvesting complex 2 of the purple

bacterium *Rhodoblastus acidophilus*. We simulate the pulsed excitation of the complete B850 ring without any a priori assumptions about the linearity of the excitation and the nature of the coupling between the chromophores. We account for the coupling between the electronic and the nuclear degrees of freedom on a nonadiabatic level by propagating classical nuclei according to the forces derived from the excited electronic system, which is propagated in real time.

The B850 ring consists of 18 bacteriochlorophyll (BChl) molecules, held in place by a protein scaffold of which at least parts must be taken into account explicitly for a realistic description of the electron dynamics. With almost 5000 valence electrons and 2000 atoms the B850 ring is of a size and complexity that is a serious challenge for first-principles methods. However, exploiting the naturally excellent scaling of time-dependent density functional theory (TDDFT) in real time³⁵ and combining it with the additional efficient parallelization that a real-space grid allows for^{26,31,36,37} makes the present calculations possible.

The time-dependent Kohn–Sham equations are solved on an equidistant grid in time and space. The interaction between the valence electrons and the atomic cores is described by

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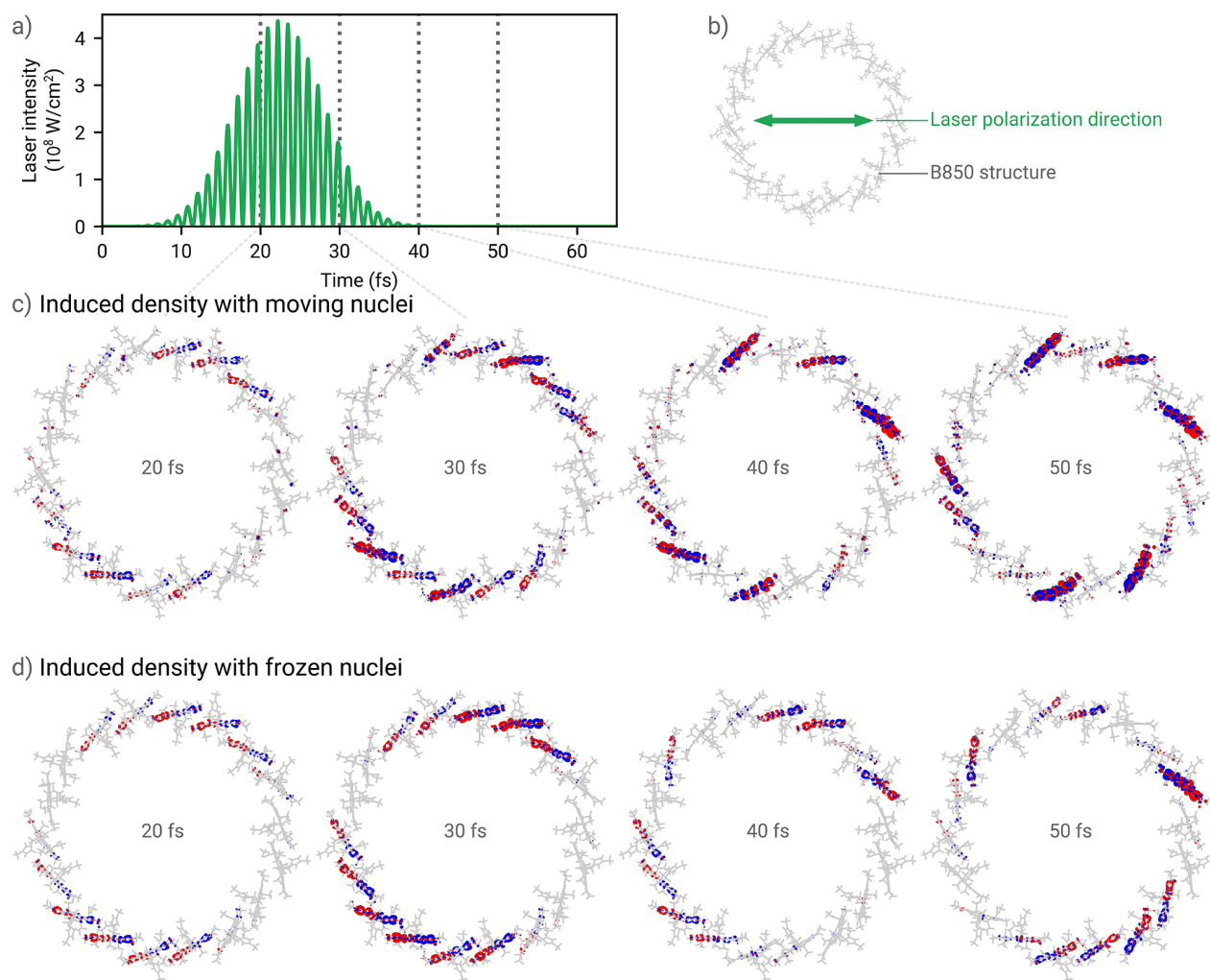


Figure 1. Real-time excitation dynamics of the B850 ring after an external laser pulse. (a) The intensity of the laser as a function of time is depicted in green. (b) A top view of the B850 nuclear structure (gray) and the polarization of the laser field (green) in the B850 plane. (c) The dynamics of the induced electronic density (after high-pass filtering, see text) with moving nuclei is visualized for 4 snapshots at 20, 30, 40, and 50 fs. These time stamps are indicated by dotted vertical gray lines in (a). Positive and negative values of the induced density are rendered in red and blue, respectively, using isosurfaces with isovalues $\pm 0.0002 a_0^{-3}$. For comparison, (d) shows the same quantity for a propagation with frozen nuclei.

norm-conserving pseudopotentials.³⁸ All BChl molecules and their coordinating histidines were simulated explicitly. The other parts of the surrounding protein and environment were described by an electrostatic potential,^{37,39,40} see the [Supporting Information](#). For the exchange correlation potential, we used the adiabatic local density approximation.⁴¹ On first sight, this approximation might appear very inadequate due its well-known shortcomings, in the present context most notably its serious underestimation of charge-transfer excitation energies.⁴² However, as demonstrated in a previous study that compared to very reliable optimally tuned range-separated hybrid calculations,³⁷ and as detailed in the [Supporting Information](#), the combined effects of the histidines and the environment potential tend to shift the spurious charge-transfer excitations away from the energetic range that is the most relevant one for the excitation-energy transfer. Therefore, for the special case of excitation-energy transfer in the B850 ring, qualitatively trustworthy results can be expected with this approximation.

The decisive advantage of the present setup is that it requires no a priori assumptions about the coupling between

the chromophores, e.g., truncation of the interaction at certain distances or model interactions. Whereas the results obtained with model Hamiltonians can depend decisively on which couplings are taken into account, as convincingly demonstrated in refs 43 and 44, the B850 ring is here treated as one united, complete quantum mechanical system in which all couplings are inherently included via the time-dependent Kohn–Sham equations. The real-time approach furthermore allows to obtain insight into the time scales of the excitation-energy transfer.

In our simulations, we start from a thermalized geometry (298 K) for the B850 ring. At time $t = 0$, an electric dipole field is switched on, and the time evolution of the time-dependent Kohn–Sham orbitals is computed to obtain the time-dependent electron density $n(\mathbf{r}, t)$. Different strategies exist to extract excitation-energy transfer dynamics from $n(\mathbf{r}, t)$.⁴⁵ For the sake of transparency, we here focus on analyzing the induced time-dependent electron density $\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n(\mathbf{r}, 0)$ and the induced dipole moment $\delta\mu$ of the complete B850 ring as well as its constituent BChls. Concurrently with the orbitals, the atom cores are propagated as classical particles,

driven by the forces derived from the time-dependent electronic structure via the gradient of the total energy.^{45,46} The coupled propagation of orbitals and classical nuclei in this Ehrenfest-like approach goes beyond the adiabatic approximation. Ehrenfest dynamics has well-known shortcomings, such as the averaging over potential energy surfaces.⁴⁷ However, given the large number of electrons and nuclei in the B850 ring, the short simulation time scale (~ 100 fs), and the relatively limited extent of the nuclear room-temperature motion, the mean-field approximation underlying this coupled electron–nuclear dynamics framework is reasonably well justified in the present case. Furthermore, while failures of the Ehrenfest approximations have been shown for model systems,⁴⁸ recent studies demonstrated its qualitative reliability in real-world applications,⁴⁹ and valuable insights have been obtained with this method.^{20,21,50,51}

Based on this framework, we study the excitation dynamics triggered in the B850 ring by a laser pulse chosen similar to typical experimental conditions. The pulse has a 13 fs full width at half-maximum of the intensity (see Figure 1a), comparable to the experimental setup in ref 52. The polarization was chosen as displayed in Figure 1b. Alternative pulse parameters are discussed in the Supporting Information. To separate the electronic excitation dynamics from the traces of nuclear motion in the electron density, we apply a high-pass filter during the postprocessing (see ref 45). This filters out the low-frequency signals of electrons adiabatically following the nuclear displacements, and we thus obtain sharper signatures of the signals that are relevant for excitation-energy transfer.

The resulting time evolution of the induced electron density $\delta n(r, t)$, depicted in Figure 1c, reveals distinct features of the excitation dynamics during and after the laser pulse. The Supporting Information additionally provides a video visualization of the evolution of the induced density for the entire simulation time of 100 fs, offering intuitive insight into the dynamics. To systematically understand the excitation dynamics we proceed in three steps: First, we connect our results to the standard model system for the interpretation of light-harvesting systems, the Frenkel exciton Hamiltonian.^{10,53} Second, we analyze the real-time signals from our simulations with respect to their magnitude, and third, with respect to their phase relations.

We constructed an exciton Hamiltonian that mirrors the decisive elements of the electronic structure setup used in the real-time approach. Starting from the experimentally determined geometry we partition the B850 ring into 18 BChl subsystems. Each of these BChls is individually treated as a two-level system (ground state and Q_y level calculated at the previously described level of TDDFT), with the other pigments and constituents of the antenna complex being treated as parts of the electrostatic environment. Using the real-time TDDFT analysis of ref 54, we extract the site energies E_i and transition densities n_i^{td} of the 18 subsystems. The intersite couplings V_{ij} are computed using the transition density cube method,⁵⁵ i.e., (in atomic units)

$$V_{ij} = \iint \frac{n_i^{\text{td}}(\mathbf{r})n_j^{\text{td}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \quad (1)$$

The Hamiltonian

$$\hat{H}_{\text{ex}} = \begin{pmatrix} E_1 & V_{1,2} & V_{1,3} & \dots & V_{1,18} \\ V_{2,1} & E_2 & V_{2,3} & \dots & V_{2,18} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ V_{18,1} & V_{18,2} & V_{18,3} & \dots & E_{18} \end{pmatrix} \quad (2)$$

then captures the information about the excited states of the B850 ring in the Frenkel exciton picture. The transition densities of the first 7 excited states are visualized in Figure 2.

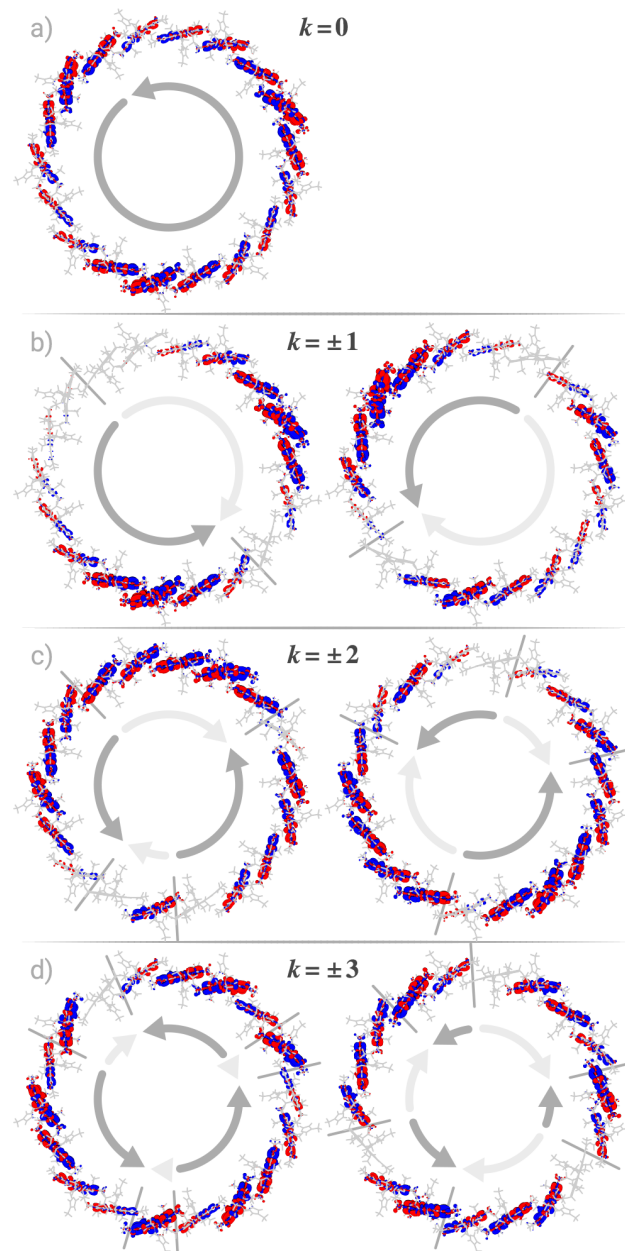


Figure 2. Transition densities of the first seven eigenstates of the exciton Hamiltonian visualized with isosurfaces (isovalue $\pm 0.0002 a_0^{-3}$; red, positive; blue, negative) set up on the geometry as determined crystallographically. Gray segmentations and arrows indicate regions in which the BChls' individual transition dipole moments point in the same circular direction. The eigenstates are categorized by their $|k|$ value with (a–d) showing $|k| = 0–3$, respectively.

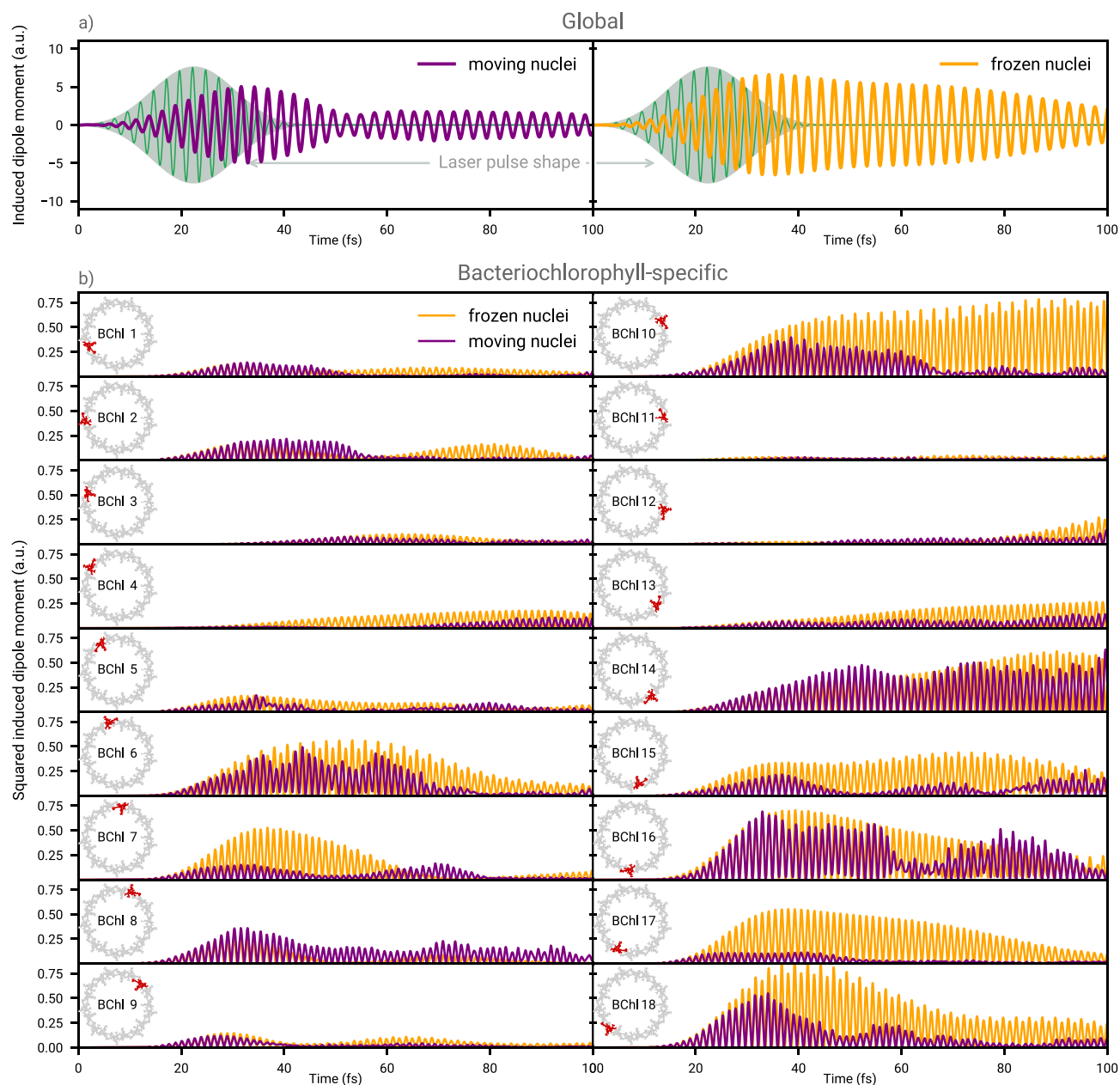


Figure 3. (a) Time-resolved total dipole moment projected onto the direction of the laser polarization for the simulation with moving nuclei (left) and frozen nuclei (right). Both plots also show the laser pulse (arbitrary scale). (b) Time-resolved squared induced dipole moments for the 18 BChls of the B850 ring (orange lines, frozen-nuclei simulation; purple lines, moving-nuclei simulation). Each subplot has a small inset illustrating to which BChl (red) of the B850 ring (gray) the data set refers.

The categorization with quantum numbers k follows the common naming convention, see, e.g., refs 1, 14, 43, and 53.

Comparing the initial real-time TDDFT excitation dynamics and the exciton Hamiltonian eigenstates reveals a remarkable similarity: The collective dipole-like oscillation observed at 30 fs in the laser-driven simulation, cf. the second panel from the left in Figure 1c, shows the spatial structure that is characteristic for the $k = \pm 1$ exciton states, cf. the transition densities in Figure 2b. Thus, the real time excitation dynamics within the first 30 fs can dominantly be understood in terms of transitions from the ground state to the $k = \pm 1$ states.

Looking at Figure 1c at later times, 40–50 fs, shows that the excitation evolves from a fully delocalized pattern to a more segmented one, with density oscillations that only extend over

considerably smaller segments of the B850 ring, down to regions that comprise only about one chromophore. Two different effects could be responsible for this apparent localization of the excitation energy: On the one hand, the interference between different electronic states can lead to (transient) beating patterns, and on the other hand the coupling between electrons and nuclei can lead to a redistribution of the excitation energy.

To disentangle the two effects we do a second real-time simulation in which we eliminate the effects of the nuclear motion. To this end, we keep all the physical and simulation parameters as before, in particular we start from the electronic ground state of the same nuclear geometry, and we again excite the system with the pulse and propagate the electrons.

However, now the nuclear positions are held fixed at their initial values at all times. Figure 1d shows the induced density at the same time stamps as Figure 1c.

At 20 fs, there are only minute differences in the induced densities from the two simulations. Also at 30 fs, the densities are still quite similar and the dominant pattern in both excitations corresponds to the $k = \pm 1$ exciton states. Beyond 30 fs, however, the situation changes. The simulations show an increasing fragmentation of the initial collective, dipole-like oscillation into smaller patterns spanning just a few chromophores. In the clamped-nuclei simulation, this transition can now completely be attributed to the excitation of states with higher $|k|$ values by the spectrally broad laser pulse. As the states with higher $|k|$ have transition densities that are more strongly modulated than the $k = \pm 1$ states (see Figure 2), a superposition of excited states generates a beating in the induced time-dependent density that leads to spatially localized, transient maxima and minima of the induced charge density. It is important to realize, however, that the spatial structure of the patterns in the simulation with clamped nuclei starts to noticeably differ from the one that is observed in the simulation with the moving nuclei at about 40 fs. This trend continues, and after 50 fs the excitation energy is clearly distributed differently in the two simulations, with the localization effects being more pronounced in the simulation that includes the nuclear dynamics.

This analysis, which so far largely relied on visual inspection of the induced densities, can further be quantified. Figure 3a shows the induced dipole moment in the direction of the laser polarization for the whole B850 ring from both simulations as a function of time. When the nuclear motion is included, the dipole moment fades much more quickly. A more detailed view of the excitation dynamics is provided by Figure 3b, which shows the squared induced dipole moments of the individual BChls. Comparing the envelopes of the fast oscillations reveals that the nuclear motion leads to a faster modulation. Differences between the simulations with clamped and moving nuclei become visible already during the laser pulse, and the differences are quite significant after about 30 fs.

The movies of the time-dependent induced densities show that the energy-transfer signal is modulated by a fast wave-like oscillation that travels around the B850 ring in counterclockwise direction. To quantify this wave-like motion, we projected the time-dependent induced dipole moment of each BChl onto the direction of its Q_y transition, i.e., $\delta\mu^{(i)}(t) \cdot \mathbf{e}_{Q_y}^{(i)}$, approximately tangential to the ring. Here, $\mathbf{e}_{Q_y}^{(i)}$ denotes a unit vector approximately in the direction of the transition dipole moment, see Supporting Information, section S3. We then, for each BChl, recorded the temporal position of the local extrema of its projected dipole moment. Figure 4 shows the times at which maxima (blue dots) and minima (red dots) of the dipole moment appear for each BChl (vertical axis). Part a reports the data for the simulation with moving nuclei, part b with frozen nuclei. The relative magnitude of the extremum is reflected in the color saturation: The extremum with the largest absolute value has maximum intensity, whereas very small extrema are almost white. Looking at the pattern at ca. 20 fs in part b shows that initially, all maxima and minima occur at the same time, leading to a pattern of vertical lines. However, looking at, e.g., BChl 1–6 at later times (after ca. 50 fs), the pattern changes: The extrema at BChl 5 occur slightly later than the ones at 6, the ones at 4 slightly later than the ones at 5, and so on, leading

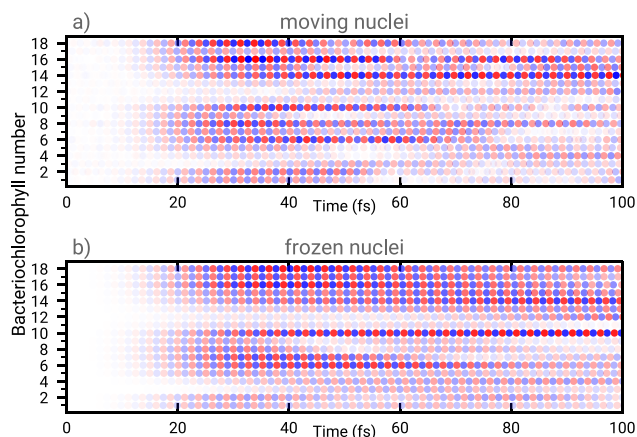


Figure 4. Phase analysis of the excitation for the simulation with moving nuclei (a) and frozen nuclei (b). For each BChl (vertical axis), the times (horizontal axis) at which maxima and minima of the projected dipole moment occur are marked by blue and red dots, respectively. The color saturation represents the magnitude of the extrema. See main text for details.

to diagonal lines. Such wave-like patterns can be observed within different groups of BChls, and they reflect extrema of the dipole moment traveling within the B850 ring in counterclockwise direction. The effect is seen both with and without nuclear movement. However, the comparison of parts a and b reveals that with nuclear movement, the coherent patterns are fragmented much more rapidly and after ca. 70 fs, the relative amplitudes have faded significantly.

Important insights emerge from these results. First, the simulations clearly show that the changes in the electron density that the pulse triggers during the first 30 fs can be well interpreted in terms of the fewest low-lying exciton states that yield the primary contribution to the excitation-energy transfer between multiple B850 rings, and that are the most relevant ones in the natural light-harvesting process.⁵⁶ Therefore, the ultrashort pulse, despite being very different from natural light and spectrally very broad, dominantly triggers the dynamics that is the relevant one for the natural process. This underlines the relevance of the insights gained from short-pulse experiments, despite their substantial difference from natural light.

The calculations further show a transient localization of the excitation energy about 20 fs after the laser pulse that arises from coherent quantum interference between excited states. Nuclear motion starts to noticeably influence the excitation dynamics on a very similar time scale and enhances the localization. The B850 light-harvesting system thus operates in a regime where the interplay of these different phenomena is decisive. Analyzing the relative phases of the dipole oscillations of the individual BChls in the B850 ring further supports this conclusion. These findings here emerged from first-principles simulations that are independent of any experimental spectroscopic input and did not make any a priori assumptions about the electronic coupling. They forcefully underpin experimental and model-Hamiltonian observations.^{15,57} Real-time TDDFT thus emerges as a powerful technique to obtain insight into the complex excitation dynamics that governs light-harvesting processes, and further insights will become possible when future work can use improved approximations for the exchange-correlation functional.

■ COMPUTATIONAL METHODS

All simulations have been done with the program package BTDDFT,⁵⁴ which solves the equations of the ground-state calculations and real-time TDDFT calculations on a real-space grid. The grid is equidistant in all Cartesian directions with a grid spacing of $0.30 a_0$. The grid volume is defined in the ground-state calculation by the union of atom-centered spheres. The radius of each sphere is defined by the distance at which the pseudo potential valence density of the respective atom falls below $10^{-7} a_0^{-3}$. To calculate the electronic ground state, Chebyshev-filtered subspace acceleration⁵⁸ is used. The supramolecular geometry is adapted from previous work^{37,59} and based on the experimentally resolved crystal structure at 1.85 Å resolution by Gardiner, Roszak, and Cogdell. We cut the phytyl chains and truncated the histidines from the protein backbone as described in the [Supporting Information](#). There, we also detail the construction of the environment potential. The coordinating histidines are explicitly taken into account together with all BChls. Details about how we evaluate the BChl-specific dipole moments from the total density are described in the [Supporting Information](#). The laser is modeled as an oscillating electric dipole field with a carrier frequency of 1.63 eV, and an envelope of a blackman window. The frequency and orientation were chosen to be in line with the dominant excitations. The window parameters are chosen such that the full-width at half-maximum of the intensity is 13 fs and the maximum intensity is $4.38 \times 10^8 \text{ W/cm}^2$, which we have checked to be in the linear-response regime for one BChl. The time-dependent Kohn–Sham equations are propagated with a Crank–Nicolson scheme and a time step of $\Delta t = 0.02 \text{ fs}$. Newton's equations for the nuclear motion were propagated with a velocity Verlet algorithm⁶⁰ and the same time step as the electronic time step. To prepare the initial state of the coupled electron–nuclear dynamics, we start from the atomic coordinates corresponding to the crystal structure and calculate the electronic ground state; then, the initial velocities of the nuclei were chosen according to a Boltzmann distribution at 298 K with a random number generator and every nucleus' motion is individually coupled to a Nosé–Hoover thermostat with chain length 3 at 298 K with time scales of 20, 24, and 30 fs for the chain. The thermalization procedure is done for 276 fs until the strong initial thermostat effects have vanished and a Boltzmann velocity distribution is achieved. The resulting electronic and nuclear structure is used as the input for the excited state dynamics with moving nuclei as described in the main text. In all simulations with moving nuclei, a few specific nuclei have been fixed at their position, see [Supporting Information](#) for details. The atom cores are described using norm-conserving Troullier–Martins pseudopotentials³⁸ with all local components chosen to be the *s* component in the Kleinman–Bylander transformation.⁶¹ For the cutoff radii of the pseudopotentials we chose for the elements: H $1.39 a_0$ (*s*), C $1.47 a_0$ (*s* and *p*), N $0.99 a_0$ (*s* and *p*), O $1.39 a_0$ (*s* and *p*), and Mg $2.18 a_0$ (*s*) and $2.56 a_0$ (*p* and *d*). We additionally applied a Tafipolsky–Schmid Fourier filter on the pseudopotentials of C, N, and O with parameters $\alpha = 1.1$ and $\gamma = 2.0$ to reduce the egg-box effect on the nuclei.⁶² The high-pass filtering on the time-dependent density was done with a frequency cutoff at 1.02 eV with a zero-phase Butterworth filter. For consistency, the high-pass filter was applied to the simulation with moving nuclei as well as the

frozen-nuclei simulation, yet for the latter no significant change was observed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.5c02108>.

Evaluation of BChl-specific observables; environment potential details; fixed nuclei in the molecular dynamics; exciton Hamiltonian details; laser pulse parameter test (PDF)

Video 1: induced electronic density with moving nuclei (MP4)

Video 2: induced electronic density with frozen nuclei (MP4)

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Notes

The authors declare no competing financial interest.

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Supporting Information for

Time-Resolved Ultrafast Excitation Dynamics in the B850 Light-Harvesting Antenna from Density Functional Theory

The Journal of Physical Chemistry Letters

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S1 Evaluation of bacteriochlorophyll-specific observables

The B850 ring, composed of 18 bacteriochlorophyll (BChl) molecules and their coordinating histidine (HIS) residues, is simulated entirely on a real-space grid. The grid contains about ~ 14 million grid points on which the equations of Kohn-Sham density functional theory (DFT) are solved for the 4896 orbitals that represent the valence electrons.

To analyze properties specific to individual BChl molecules while preserving the united electronic structure of the full ring, we partition the grid into 18 subspaces. Each subspace corresponds to one BChl-HIS pair. The subspaces are defined at the beginning of the ground-state calculation by assigning each grid point to the nearest BChl-HIS unit. Figure S1 shows a two dimensional illustration of the spatial partitioning. The 18 color-coded areas with white borders in between indicate the subspaces, with the black

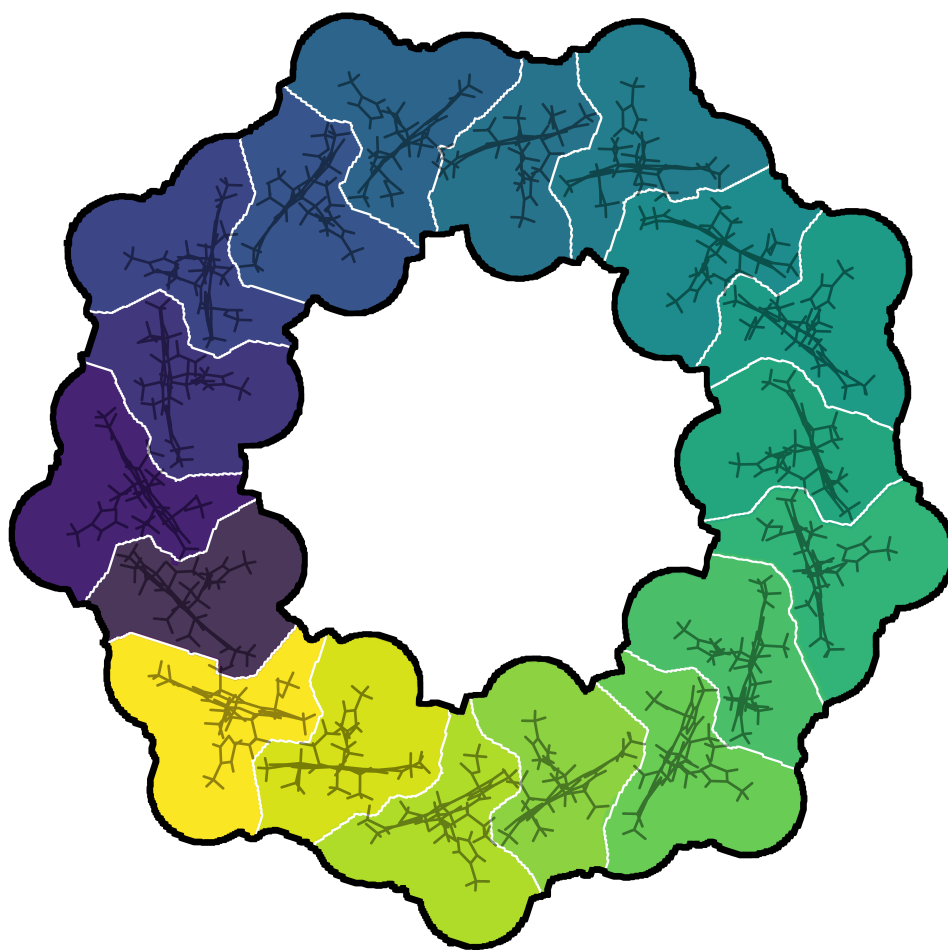


Figure S1: A two-dimensional illustration of the real-space partitioning for the evaluation of BChl-specific observables. The differently colored areas (separated with white lines) visualize the 18 subspaces. Black borders show the simulation grid borders.

border denoting the simulation grid boundaries. We emphasize that the partitioning serves only as a tool to evaluate subsystem-specific observables, while the electronic and nuclear structure remains fully coupled during the simulation.

One subsystem-specific observable used in this study (cf. Figure 3, main text) is the time-dependent dipole moment. We evaluate the time-dependent induced dipole moment $\delta\boldsymbol{\mu}^{(i)}$ for the i -th BChl by integrating contributions from both electrons and nuclei within their subspace $V^{(i)}$:

$$\delta\boldsymbol{\mu}^{(i)}(t) = -e \int_{V^{(i)}} \mathbf{r} \delta n(\mathbf{r}, t) d^3r + \sum_{\mathbf{R}_I \in V^{(i)}} Z_I (\mathbf{R}_I(t) - \mathbf{R}_I(0)), \quad (\text{S1})$$

where $\delta n(\mathbf{r}, t)$ is the induced electron density, Z_I is the charge of nucleus I , and $\mathbf{R}_I(t)$ its position. The first term on the right hand side of eq (S1) accounts for the electronic contribution and the second term for the nuclear contribution to the total dipole moment.

S2 Environment potential

In the following, we briefly explain the construction of the environment potential and verify its influence on the Q-band of a single BChl with our simulation parameter set. We furthermore elucidate the numerical assembly process of the environment potential for large systems such as the B850 ring.

Construction of the environment potential and its influence on the electronic excitations

We account for the static electric field generated by the environmental pigments, proteins, and the solvent. The environment potential comprises two components. The first originates from the electrostatic potential generated by (i) the partial charges on the atoms in the light-harvesting complex that are not incorporated in the explicit time-dependent density functional theory (TDDFT) region and (ii) the free ions in the surrounding solvent. Solving a linearized Poisson-Boltzmann equation with the charge distributions yields the corresponding electrostatic potential. The second component is the reaction field representing the polarization of the environment induced by the explicitly treated molecules. Reference 1 gives a comprehensive overview of the construction procedure.

This earlier work¹ also demonstrated that the environment potential can have a noteworthy influence on the electronic excitations. In the following, we check and confirm these findings for the specific computational parameter setup that we use in the present work (described in the main article). We calculate the absorption spectra for the BChl α B302 from the B850 ring once with the environment potential and once without it, using a grid spacing of $0.30 a_0$ and the pseudopotential parameters given in the main text. Both calculations were done with BTDDFT and the spectra were evaluated as described in ref 2. Figure 2 visualizes the results. First, consistent with ref 1, the environment potential slightly red-shifts the Q_y and Q_x excitation energies. Second and more importantly, a charge-transfer (CT) excitation is seen within the Q-band region in the vacuum case. The spuriously low energy at which this CT excitation appears is a consequence of using the adiabatic CT local density approximation (LDA) and reflects one of the well known limitations that (semi-)local functionals suffer from. However, when the BChl is embedded in the environment potential, the environment shifts this spurious CT excitation out of the spectral range of the Q-band. Thus, including the protein environment leads to a qualitatively correct spectrum in the energy range that is the relevant one for excitation energy transfer in the B850 ring. This has also been verified explicitly for the coupling between two BChl by comparing to accurate optimally-tuned range-separated hybrid calculations.¹

Assembling the B850 environment potential from different focus grids

The calculation of the environment potential is based on the *Adaptive Poisson-Boltzmann Solver* (APBS) software,³ as described in ref 1. In APBS, the calculation of the potential

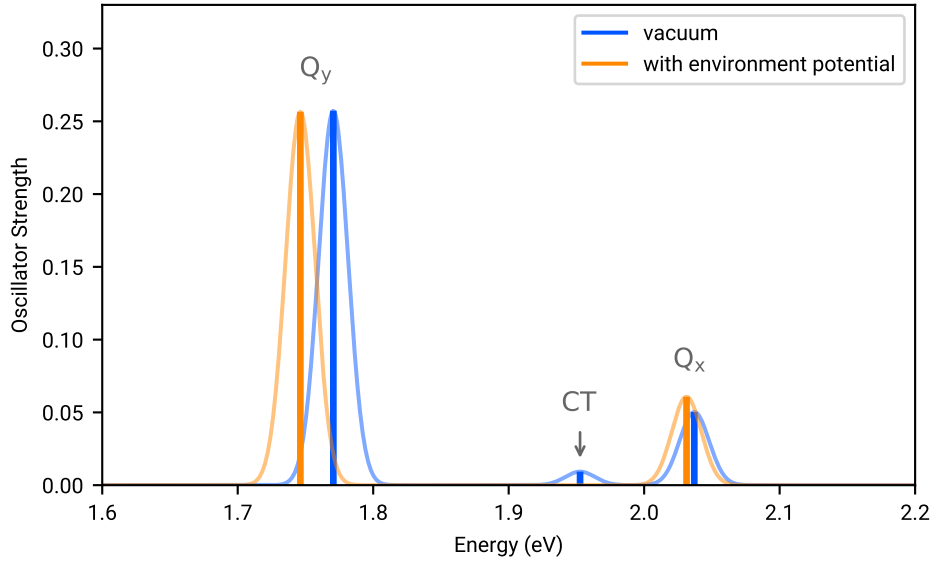


Figure S2: Absorption spectrum of B302 from real-time TDDFT in vacuum (blue) and with electrostatic environment (orange). The excitations are represented by vertical lines, and as guide to the eye, we also show the spectrum broadened with Gaussian functions, using a room-temperature energy width.

consists of two steps: (i) the computation of the potential on a large coarse grid (grid spacing $0.76 a_0$) that covers the whole light-harvesting 2 complex followed by a (ii) computation on a smaller focus grid with finer grid spacing matching the BTDDFT simulation grid ($0.30 a_0$). The first calculation on the coarse grid is used to define the boundary conditions for the subsequent calculation on the focus grid.

In version 1.5 of APBS, which we employed in this work, one can only use up to 512 grid points in each direction. This is not sufficient for the focus grid to cover the whole BTDDFT grid that is required for simulating the B850 ring. This situation is sketched in the top (left and right) and bottom left panels of Figure S3, in which the B850 ring is not entirely covered by the (central) focus grid (called $FG^{(0,0,0)}$).

To solve this issue and ultimately calculate the environment potential on a sufficiently large grid with the fine grid spacing, we proceeded in the following way: First, we computed several environment potentials on different focus grids, which slightly overlap. For consistency, all focus-grid calculations were based on the same coarse-grid potential (also shown in the figure). For the B850 ring, we used one focus grid that is centered with respect to the B850 ring ($FG^{(0,0,0)}$ with an edge length of 512 grid points) and eight additional focus grids of the same size that are shifted by 128 grid points (one quarter of the edge length) in $(\pm x, \pm y, \pm z)$ -direction, respectively, called $FG^{(\pm 1, \pm 1, \pm 1)}$. In the top (left and right) and bottom left panels of Figure S3, $FG^{(+1, +1, +1)}$, which is shifted in $(+x, +y, +z)$ direction, is shown as representative example. By construction, it covers an additional part of the B850 ring.

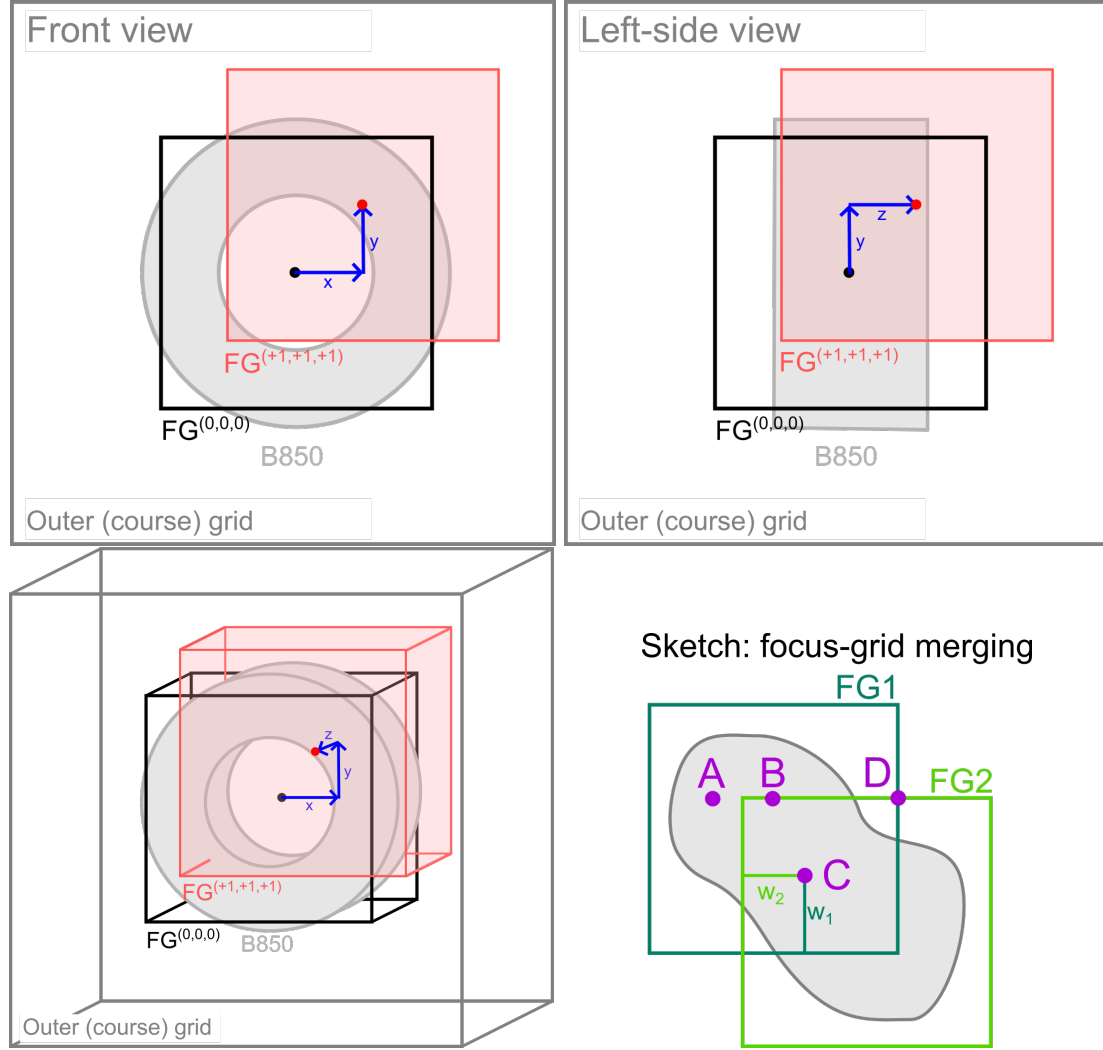


Figure S3: Schematic visualization of the procedure for assembling the environment potentials from different focus grids. Top row and bottom left: minimal sketch for the B850 ring in 3D (bottom left) and as front and left-side view (top left and right, respectively). The B850 ring does not entirely fit into a single focus grid in the center $FG^{(0,0,0)}$ (black). Therefore, the center focus grid is combined with eight additional focus grids that are shifted by 128 grid points (one quarter of the edge length) in $(\pm x, \pm y, \pm z)$ directions. $FG^{(+1,+1,+1)}$, which covers an additional part of the B850 ring, is shown as a representative example. Bottom right: schematic 2D sketch showing two focus grids (FG1 and FG2), the BTDFT grid (filled gray) in the center, and four points (A, B, C, and D) for which the algorithm is explained in the main text.

Second, we assemble the potentials of the different focus grids into a smooth potential on the joint grid. The procedure is explained by means of the bottom right panel of Figure S3, which shows a simplified two-dimensional sketch with two focus grids and the BTDFT grid in the middle. To explain all possible scenarios, we picked out four

representative points (A, B, C, and D), which are shown in the sketch. Some grid points (e.g. point A) are only covered by a single focus grid. Others are covered by multiple focus grids (e.g. points B, C, and D), whereas some lie on a focus-grid boundary (e.g., point B) or even on the intersection of different focus-grid boundaries (e.g., point D).

To assemble the potential, we go through each grid point of the joint grid and compute the respective potential value as a weighted sum over the corresponding potential values from the focus grids

$$v_{\text{env}}(\mathbf{r}) = \frac{1}{\sum_j w_j(\mathbf{r})} \sum_j w_j(\mathbf{r}) v_{\text{env}}^{\text{FG}(j)}(\mathbf{r}). \quad (\text{S2})$$

In the latter equation, $\mathbf{r}$ is the grid point's position and the sum over j runs over all focus grids that cover that grid point. To find appropriate weighting coefficients $w_j(\mathbf{r})$, we followed these guidelines: (i) The potential values close to a grid's boundary are less accurate due to the less accurate boundary conditions from the courser grid. Therefore, focus grids in which the current grid point is close to this grid's boundary should have a lower weight in eq S2. (ii) To ensure a smooth transition between the potentials, the weighting coefficient within a focus grid should follow a continuous function and approach 0 at its boundary. With these principles in mind, we chose the weighting coefficients $w_j(\mathbf{r})$ to be equal to the minimum distance between the grid-point's position $\mathbf{r}$ and the boundary of the respective focus grid. This ensures that the weights on a focus grid approach zero at its boundary while increasing towards the focus grid's center.

For transparency, we demonstrate the weighting for four representative grid points (cf. Figure S3 bottom right). For point C, which is covered by both focus grids, the respective weights are depicted as straight lines measuring the distance from that point to the boundaries of the two focus grids. The weight w_1 for the focus grid FG1 is slightly larger than w_2 for FG2 since C is closer to FG2's boundary. The potential value at points A and B is purely determined by FG1 since A is only covered by FG1 and B is covered by FG1 and on the boundary of FG2 (at which the weight from this focus grid vanishes). At point D, all weights are zero and eq S2 is ill defined. To prevent this situation at singular grid points where only focus-grid boundaries intersect, we added a very small constant to the weights. This ensures that all intersecting focus grids contribute equally to the resulting value.

In Figure S4, we show how the method works in practice for the present B850 simulation. The figure shows the environment potential along the y -axis close to the upper boundary of the focus grids that were shifted in the $-y$ direction. This boundary is indicated by the dashed vertical line. The purple line in Figure S4 represents the potential values from focus grids that are shifted in $-y$ direction. As the values of those focus grids are indistinguishable on this scale, they are depicted with a single line. Similarly, the green line represents the potential values from all $+y$ shifted focus grids and the center focus grid. The values of those grids align in this range, as the shown region is far from their boundaries. In regions close to the boundary of the $-y$ -shifted focus grids ($y \approx 50.5 - 53.6 a_0$ in the figure), the corresponding potentials deviate from the potentials

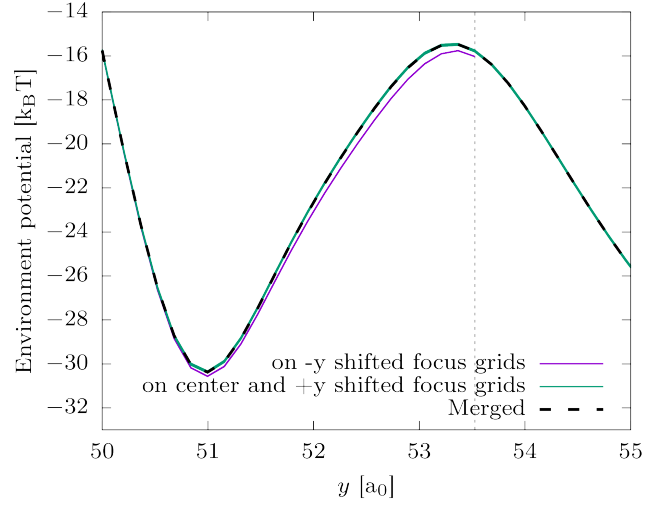


Figure S4: Values along the y -axis of the B850 environment potentials from different focus grids as well as the assembled potential ("Merged"). The values are shown in the range around the upper y boundary ($y \approx 53.6 a_0$, indicated by the gray dashed line) of the focus grids that were shifted in $-y$ direction. The potential values on those focus grids deviate from the potentials on the other focus grids that completely cover the shown y -range in their center region. Dominant weights of focus grids fully covering the displayed y -range ensure that the merged potential matches their potentials over those of $-y$ -shifted focus grids.

on the other grids. In this about $3 a_0$ wide layer, the weights of the $-y$ -shifted grids are small compared to the other grids (since the weight is the distance to the respective grid's boundary). The resulting combined potential (shown as "Merged" in the figure) is thus dominated by the center and the $+y$ -shifted grids and crosses the boundary of the $-y$ -shifted grids smoothly. Further than about $3 a_0$ away from the boundary of the $-y$ -shifted grids (below $50.5 a_0$ in the figure), all potentials coincide again so that the precise weighting values are not decisive.

S3 Fixed nuclei in the molecular dynamics

During the coupled electron-nuclear dynamics and the thermalization procedure, some of the nuclei have been fixed at their crystal-structure position. This involves 6 nuclei of each BChl and 5 nuclei of their coordinating HISs. The affected nuclei are marked with

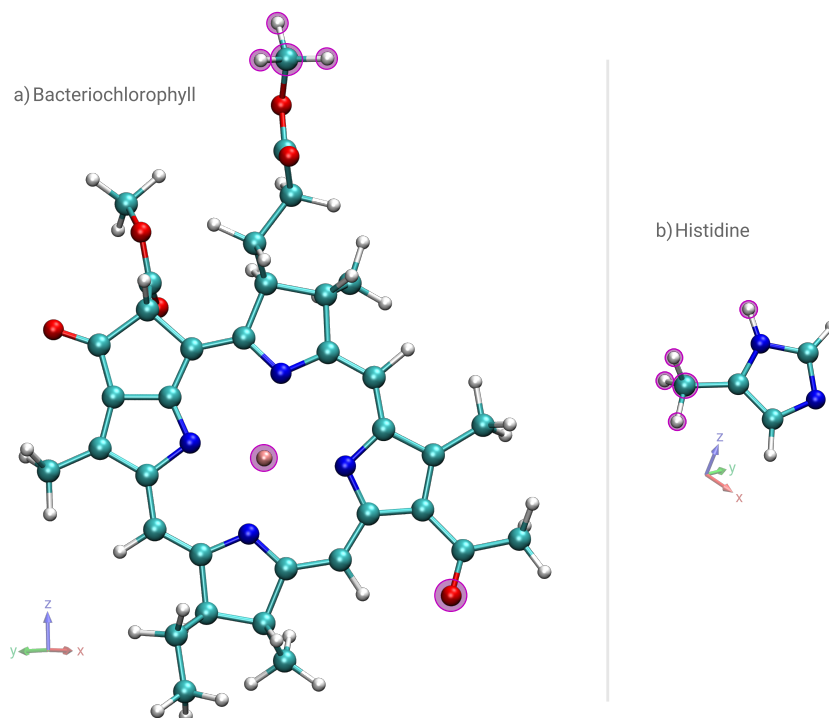


Figure S5: Crystal structure of a BChl (a) and a HIS (b) of the B850 ring visualized with a ball-and-stick model (cyan: Carbon, red: Oxygen, white: Hydrogen, blue: Nitrogen, pink: Magnesium). Nuclei that are fixed in the molecular dynamics are each marked with a purple circle.

purple circles in Figure S5 for a BChl and the corresponding HIS of the B850 ring.

The methyl groups (at the top of Figure S5a) of the BChls are held fixed for the following reason: The phytol tail of the BChls structurally stabilizes the BChl in the protein environment.⁴ To save computation time but retain the stabilization of the structure, the phytol tail is cut off and replaced with a methyl group that is held at a fixed position. Similarly, the amino acid HIS is anchored in the protein backbone. For the same reasons as described for the BChl phytol tail, the protein backbone is left out of the TDDFT region and we replace the bridge with a fixed methyl group (left side of Figure S5b). Furthermore, one oxygen atom (bottom right in Figure S5a) and one hydrogen atom (middle top in Figure S5b) are held fixed because they undergo a (polar) hydrogen-water

bond with a hydrogen or oxygen atom in the environment, respectively. Finally, also the partially charged magnesium atom in the center of the BChl is held fixed for overall structural stability and consistency with the environment.

Fixing these atoms is expected to play a subordinate role in the Q_y excitation. For orientation, in Figure S5a, the transition dipole moment is approximately oriented horizontally through the left and right nitrogen atoms (e_{Q_y}). The Q_y transition density is not located around the fixed atoms. Therefore, the coupling of the electronic excitation to the BChls' nuclear movement is not significantly altered by fixing the above mentioned few atomic positions.

S4 Exciton Hamiltonian details

In the following, we list details about the calculation of the exciton Hamiltonian

$$\hat{H}_{\text{ex}} = (h_{i,j}) = \begin{pmatrix} E_1 & V_{1,2} & V_{1,3} & \dots & V_{1,18} \\ V_{2,1} & E_2 & V_{2,3} & \dots & V_{2,18} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ V_{18,1} & V_{18,2} & V_{18,3} & \dots & E_{18} \end{pmatrix}, \quad (\text{S3})$$

as in eq 2 in the main text and tabulate all matrix elements.

The site energy E_i is the Q_y excitation energy of BChl i and is obtained from a 100 fs boost propagation.⁵ We chose 1.4×10^{-3} eV as the boost energy, thus exciting the system in the linear-response regime. The boost direction for the B302 (see Figure S5) is chosen as $(1, -1, -1)$, such that it will excite the Q_y and Q_x excitation. For the other BChls we rotated the boost direction by a multiple of $1/18$ of a unit circle around the ring axis according to the position of the BChl with respect to the B302. In the spectral analysis, we identify the Q_y and Q_x excitation in each spectrum and obtain the transition density n_i^{td} between the Q_y excitation and the ground state. The transition density is obtained by decoupling the Fourier transformed density into Q_y and Q_x transition densities according to ref 1. To model the coupling $V_{i,j}$ between the subsystems, we use the transition density cube method⁶ as in eq (2) (main text). In practice, we circumvent the explicit calculation of the double integral in eq (2) by evaluating the energy of n_j^{td} in the Coulomb potential generated by n_i^{td} . We furthermore use $V_{i,j} = V_{j,i}$. All matrix elements are tabulated in Table S1.

Table S1: Exciton Hamiltonian matrix elements in eV split into two subtables. For orientation, the site energies on the matrix diagonal are printed in boldface.

	$h_{i,1}$	$h_{i,2}$	$h_{i,3}$	$h_{i,4}$	$h_{i,5}$	$h_{i,6}$	$h_{i,7}$	$h_{i,8}$	$h_{i,9}$
$h_{1,j}$	1.7628	-0.0183	-0.0066	-0.0017	-0.0008	-0.0004	-0.0002	-0.0001	-0.0001
$h_{2,j}$	-0.0183	1.7470	-0.0183	-0.0049	-0.0017	-0.0006	-0.0003	-0.0002	-0.0001
$h_{3,j}$	-0.0066	-0.0183	1.7445	-0.0196	-0.0066	-0.0017	-0.0008	-0.0004	-0.0002
$h_{4,j}$	-0.0017	-0.0049	-0.0196	1.7094	-0.0191	-0.0049	-0.0018	-0.0006	-0.0004
$h_{5,j}$	-0.0008	-0.0017	-0.0066	-0.0191	1.7241	-0.0203	-0.0064	-0.0016	-0.0008
$h_{6,j}$	-0.0004	-0.0006	-0.0017	-0.0049	-0.0203	1.7784	-0.0186	-0.0048	-0.0019
$h_{7,j}$	-0.0002	-0.0003	-0.0008	-0.0018	-0.0064	-0.0186	1.7600	-0.0183	-0.0066
$h_{8,j}$	-0.0001	-0.0002	-0.0004	-0.0006	-0.0016	-0.0048	-0.0183	1.7449	-0.0184
$h_{9,j}$	-0.0001	-0.0001	-0.0002	-0.0004	-0.0008	-0.0019	-0.0066	-0.0184	1.7445
$h_{10,j}$	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004	-0.0006	-0.0017	-0.0049	-0.0197
$h_{11,j}$	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004	-0.0008	-0.0017	-0.0066
$h_{12,j}$	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004	-0.0006	-0.0017
$h_{13,j}$	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0003	-0.0008
$h_{14,j}$	-0.0003	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004
$h_{15,j}$	-0.0008	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002
$h_{16,j}$	-0.0018	-0.0006	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001
$h_{17,j}$	-0.0064	-0.0016	-0.0008	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001
$h_{18,j}$	-0.0185	-0.0048	-0.0019	-0.0006	-0.0003	-0.0002	-0.0001	-0.0001	-0.0001

	$h_{i,10}$	$h_{i,11}$	$h_{i,12}$	$h_{i,13}$	$h_{i,14}$	$h_{i,15}$	$h_{i,16}$	$h_{i,17}$	$h_{i,18}$
$h_{1,j}$	-0.0001	-0.0001	-0.0001	-0.0002	-0.0003	-0.0008	-0.0018	-0.0064	-0.0185
$h_{2,j}$	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004	-0.0006	-0.0016	-0.0048
$h_{3,j}$	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004	-0.0008	-0.0019
$h_{4,j}$	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0004	-0.0006
$h_{5,j}$	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002	-0.0003
$h_{6,j}$	-0.0006	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001	-0.0002
$h_{7,j}$	-0.0017	-0.0008	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001	-0.0001
$h_{8,j}$	-0.0049	-0.0017	-0.0006	-0.0003	-0.0002	-0.0001	-0.0001	-0.0001	-0.0001
$h_{9,j}$	-0.0197	-0.0066	-0.0017	-0.0008	-0.0004	-0.0002	-0.0001	-0.0001	-0.0001
$h_{10,j}$	1.7055	-0.0190	-0.0049	-0.0018	-0.0006	-0.0004	-0.0002	-0.0001	-0.0001
$h_{11,j}$	-0.0190	1.7259	-0.0203	-0.0065	-0.0016	-0.0008	-0.0004	-0.0002	-0.0001
$h_{12,j}$	-0.0049	-0.0203	1.7760	-0.0186	-0.0048	-0.0019	-0.0006	-0.0004	-0.0002
$h_{13,j}$	-0.0018	-0.0065	-0.0186	1.7622	-0.0184	-0.0066	-0.0017	-0.0008	-0.0004
$h_{14,j}$	-0.0006	-0.0016	-0.0048	-0.0184	1.7466	-0.0185	-0.0049	-0.0017	-0.0006
$h_{15,j}$	-0.0004	-0.0008	-0.0019	-0.0066	-0.0185	1.7455	-0.0198	-0.0066	-0.0017
$h_{16,j}$	-0.0002	-0.0004	-0.0006	-0.0017	-0.0049	-0.0198	1.7057	-0.0190	-0.0049
$h_{17,j}$	-0.0001	-0.0002	-0.0004	-0.0008	-0.0017	-0.0066	-0.0190	1.7263	-0.0202
$h_{18,j}$	-0.0001	-0.0001	-0.0002	-0.0004	-0.0006	-0.0017	-0.0049	-0.0202	1.7783

S5 Laser pulse parameter test

In the following we verify that the decisive features of the density dynamics reported in the main article remain the same when the pulse length is somewhat modified. To this end, we here report an additional simulation in which the temporal width of the pulse was increased by 25%, i.e., to a full width at half maximum (FWHM) of the intensity of 16 fs. Figure S6a displays the intensity of both laser pulses as a function of time. We evaluate

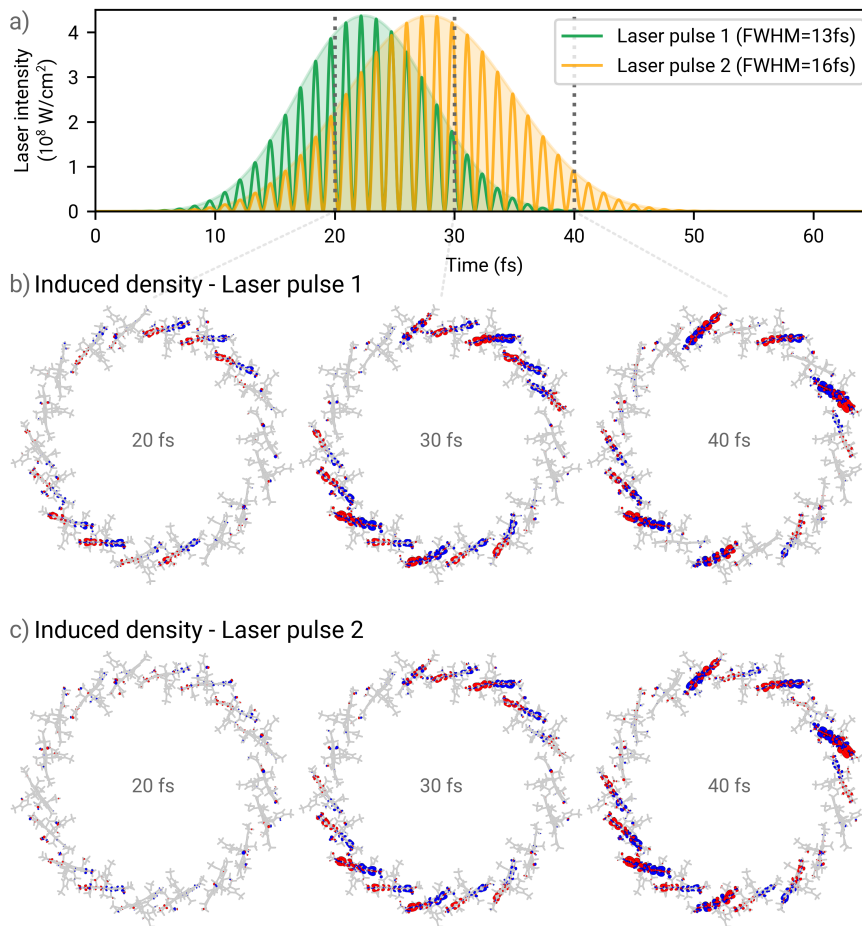


Figure S6: Real-time excitation dynamics of the B850 ring for two different laser pulse simulations. Panel a) shows the time-resolved laser intensity for both pulses. In panel b), snapshots of the induced density are depicted for the simulation with the pulse from the main article. Panel c) shows the corresponding snapshots for the simulation with the 16 fs pulse. The time stamps are marked with vertical dotted lines in panel a).

the induced density (after high-pass filtering) with moving nuclei for both simulations. Figure S6b displays the snapshots taken from Figure 1c of the main article at times 20 fs, 30 fs, and 40 fs. We show the corresponding snapshots for the 16 fs pulse simulation in Figure S6c. While slight differences between the simulations are visible, the overall

excitation dynamics is quite similar. In both simulations, the same distinct features (as discussed in the main article for the 13 fs pulse simulation) are observed. First, the initial excitation is delocalized across the whole B850 ring, reflecting a collective dipole-like oscillation. Second, after the pulse peak, a transient localization pattern appears on a ten-femtosecond time scale. This similarity of the excitation dynamics confirms that our observations are not a coincidence occurring for a specific set of laser pulse parameters.

Author contribution statement

All authors conceptualized the work. T.T. did all DFT and TDDFT simulations, constructed the exciton Hamiltonian, and did the data processing. I.S. technically supported the (TD)DFT simulations. The environment potential was generated by I.S. for the whole B850 ring and by T.T. for the single BChls for the exciton Hamiltonian. All authors discussed the results. S.K. led the interpretation of the results, with support from T.T. and I.S. S.K. structured the results and the manuscript. T.T. and S.K. wrote the manuscript; I.S. proofread it and gave comments; T.T. prepared the graphics for the manuscript. All authors equally wrote the Supporting Information. T.T. and I.S. prepared the graphics and videos for the Supporting Information. S.K. supervised the project and acquired the funding.

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Publication 3

Optically Induced Charge Separation at the Naphthalenediimide-Phenothiazine Interface

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Author contributions

T.T. ran the calculations of Section 2.1 (partly; geometry optimization and optimal tuning of 2-TBP–2-NDI-silane), Section 2.2 (excited-state calculation on 3-TBP–3-NDI-silane), and Section 2.3 (excited-state calculations and Born–Oppenheimer molecular dynamics of 2-TBP–2-NDI), prepared Fig. 2–6 and Table 1 (partly), 2, and 3, and contributed to the results shown in Section 2.3.3, e.g., via excited-state geometry optimizations. R.A. synthesized NDI-silane and performed and discussed the experiments presented in Section 2.4. C.M.I. discussed with T.T. and supervised all TeraChem calculations. S.K. conceptualized the steps of the theoretical approach, structured the analysis of the data, and structured the first manuscript draft. T.B. suggested to study this material combination, initiated the project, did part of the calculations presented in Section 2.1, calculated the couplings in Section 2.3.3, and guided and discussed the experiments discussed in Section 2.4. T.T., S.K., and T.B. together wrote the final manuscript. All authors commented on and discussed the final manuscript.

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Optically induced charge separation at the naphthalenediimide–phenothiazine interface

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Naphthalenediimide (NDI) is stable under ambient air and an efficient electron acceptor due to its high electron affinity. Phenothiazine derivatives are paradigm electron donors due to their relatively low oxidation potentials and cations of high stability. Combining these two system classes therefore appears as a promising strategy for obtaining a material with attractive optoelectronic properties. We here investigate molecular models of π -coupled junctions of *N,N'*-bis[3-(triethoxysilyl)propyl]-1,4,5,8-naphthalenediimide (NDI-silane) and 3,7-di-*t*-butylphenothiazine (TBP) using time-dependent density functional theory. We calculate the electronic excitations for systems with frozen nuclei, and in a second step also investigate the influence that the dynamics of the nuclei has on the electronic excitations. We find optically active excitations around 1.5 eV that are associated with a charge transfer at the interface. We further calculate the electronic couplings between the states that are the most relevant ones for charge separation. Our findings can be seen as indicators for these materials' suitability for photovoltaic applications. First experimental results are in line with the theoretical conclusions.

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1 Introduction

During the past years, the quest for sustainable sources of energy has led to remarkable advances in the development of photovoltaic materials.¹ Donor–acceptor molecular systems for photoinduced charge separation hold the promise to become key actors in clean energy generation, particularly in the context of organic photovoltaic devices.^{2–5} Traditionally, fullerene derivatives, such as PCBM-60 and PCBM-70, have been used in combination with low-bandgap polymers to form the active layers of organic photovoltaic materials.^{6–8} However, non-fullerenes are finding increasing interest as they can offer important advantages, *e.g.*, in terms of light absorption, level alignment, and possibly structural stability.^{9–19}

Time-dependent density functional theory (TDDFT) is ideally suited for obtaining insight into the electronic structure and excitations of molecules and solids, and can thus support the search for new energy converting materials.^{20–25} With modern functionals, such as optimally-tuned range-separated hybrids, the limitations of traditional semilocal functionals in the accuracy of the prediction of relative electronic levels, band

gaps, and charge-transfer excitations can be overcome.^{22,26–29} Here, we employ DFT and TDDFT to check a combination of materials for potential suitability in photovoltaic devices. Naphthalenediimide (NDI) is an electron-deficient ring system that has been proposed as a backbone or skeleton for electron acceptor applications due to its relatively high electron affinity and ambient air stability.^{30–33} It is chemically flexible and can be functionalized with siloxyl groups to permit sol–gel chemistry in device fabrication,^{34,35} and can be attached to electron withdrawing groups to manipulate its electronic properties.³⁶ On the other hand, phenothiazine dyes are excellent light absorbers, good electron donors and also chemically flexible.^{37–41} Consequently, the combination of these materials holds potential for the development of efficient and durable photo-induced charge-separating devices.

In this article, we investigate the combination of 3,7-di-*t*-butylphenothiazine (TBP) as a donor molecule and *N,N'*-bis[3-(triethoxysilyl)propyl]-1,4,5,8-naphthalenediimide (NDI-silane) as an acceptor molecule. Fig. 1 shows a sketch of the chemical structure of these molecules.

From these building blocks we construct molecular models that allow us to investigate the excited state properties of the donor–acceptor interface with the help of (TD)DFT.^{42,43} We explore possible charge-separation pathways and investigate the influence of nuclear motion on the excited-state properties. The calculations are complemented by experiments that demonstrate the successful synthesis of these molecular systems and the first steps in their spectroscopic characterization.

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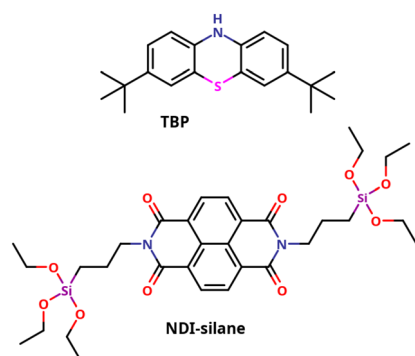


Fig. 1 2D representation of the TBP and NDI-silane molecules.

2 Results and discussions

2.1 The interface models – 1×1 , 2×2 , and 3×3 TBP/NDI-silane molecular systems

Our aim is the prediction of possible material properties from first principles. DFT and TDDFT allow for the quantitative prediction of both the structure and the excitations of multi-chromophoric systems and are therefore our methods of choice.

We modeled three π -stacked interfaces for the following purposes: (i) By 1-TBP-1-NDI-silane we denote a 1×1 molecular system, *i.e.*, a combination of one TBP with one NDI-silane molecule. We use this dimer system to estimate the binding energy between the molecules and to predict, *a priori*, their roles as donor and acceptor entities from their ionization energies and electron affinities. (ii) The 2-TBP-2-NDI-silane is a 2×2 molecular system. We use it to investigate the excited states, especially how they are influenced by the motion of the atomic nuclei which we take into account *via* DFT-based *ab initio* molecular dynamics. (iii) The 3-TBP-3-NDI-silane is a 3×3 molecular system. It is the largest model that we study here in order to explore the properties of the excitations and possible charge-transfer at the TBP-NDI-silane interface.

For the geometry optimization of the model interfaces, the single molecules are optimized individually and placed in an arbitrary plane-to-plane orientation with a distance of about 4 Å, which is the typical range in which dispersive interactions are significant for these conjugated molecules.⁴⁴ Then, DFT-based geometry optimizations are performed. For the latter we use the M06-2X⁴⁵ functional because it has been shown to accurately predict intermolecular distances and binding energies of similar molecular systems.⁴⁴

For the 1-TBP-1-NDI-silane system, the plane-to-plane equilibrium distance between the molecules is 3.18 Å and their binding energy is $-21.3 \text{ kcal mol}^{-1}$ (calculated with the M06-2X functional⁴⁵ and 6-311++G** basis set). This value reveals significant coupling between the molecules. For comparison, Kumar *et al.* have investigated the charge-transfer performance of several combinations of π -stacked donor-acceptor systems and found substantial binding and frontier orbital congruence for the pyrene-NDI pair.⁴⁶ For this system, the optimal interplanar distance is about 3.35 Å and the binding energy is about $-18 \text{ kcal mol}^{-1}$.⁴⁴

For the calculation of charge-transfer excitations with TDDFT, care must be taken. Local or semi-local approximations yield the computationally most efficient exchange–correlation functionals, but they systematically underestimate charge-transfer excitation energies. Therefore, one typically resorts to range-separated hybrid functionals, potentially in combination with optimal tuning of the range-separation parameter.²⁶ We here use the range-separated hybrid functional ω PBE⁴⁷ with a range-separation parameter determined by optimal tuning according to the J_2 criterion.⁴⁸ In this procedure, the exchange term of the functional is split into short-range and long-range parts. The short-range component is represented by a semi-local approximation while the long-range component is represented by the exact Fock exchange. The range-separation parameter ω is chosen such that the frontier eigenvalues are as close as possible to the ionization potential and the electron affinity as determined from total energy differences. This is achieved by minimizing the function $J^2(\omega) = (e_{\text{HOMO}}^N(\omega) + \text{IP}^N(\omega))^2 + (e_{\text{HOMO}}^{N+1}(\omega) + \text{IP}^{N+1}(\omega))^2$, where N is the number of electrons of the molecule's most stable oxidation state. This strategy of optimal tuning, and also variants of it, has proven its reliability in many cases.^{21,22,25,27,28} However, it comes at an unavoidable computational cost. Our largest interface model, the 3×3 molecular system consisting of 417 atoms with 1584 electrons, is at the upper end of the system size that can reasonably be studied with this relatively high level of accuracy.

Table 1 lists the optimally tuned ω , generalized Kohn–Sham orbital eigenvalues, ionization energies, and $J(\omega)$ (where $J = \sqrt{J^2}$) evaluated at ω_{opt} for the optimized geometries. While the optimal range-separation parameter is system-dependent, especially in systems in which the extension of the effective conjugation depends on the system size, we find that ω_{opt} is similar for both isolated molecules. This is a reassuring result because it indicates that also the combined systems, *i.e.*, the interface models, can be reasonably well described with one common value of ω_{opt} . The reliability of the optimal tuning is confirmed by the low values that we find for $J(\omega_{\text{opt}})$ when we do the tuning for the interface models, *cf.* Table 1.

We note that the ionization energy and electron affinity of the NDI-silane are about 8.61 eV and 1.80 eV, respectively. For TBP, we find the values 6.55 and -1.23 eV . The negative value of the electron affinity, which corresponds to a positive LUMO eigenvalue, only indicates that TBP does not accept an additional electron, in line with the donor character of the molecule, but the value itself does not have physical meaning. It just

Table 1 Optimal ω , HOMO eigenvalues (ϵ), ionization energies, and $J(\omega_{\text{opt}})$ for the structures as calculated with optimally tuning

System	ω_{opt} ($10^{-3} a_0^{-1}$)	ϵ_{HOMO}^N (eV)	IP^N (eV)	$\epsilon_{\text{HOMO}}^{N+1}$ (eV)	IP^{N+1} (eV)	$J(\omega_{\text{opt}})$ (meV)
TBP	209	−6.54	6.55	1.22	−1.23	14
NDI-silane	213	−8.62	8.61	−1.79	1.80	21
1-TBP-1-NDI-silane	173	−6.06	6.04	−1.65	1.68	33
2-TBP-2-NDI-silane	136	−5.67	5.71	−2.35	2.32	50
3-TBP-3-NDI-silane	131	−5.67	5.68	−2.37	2.37	9

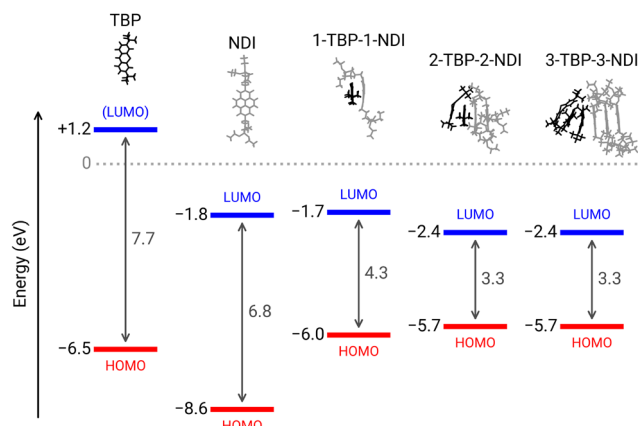


Fig. 2 Energy level diagram (based on the generalized Kohn–Sham eigenvalues) of TBP and NDI-silane as single molecules and their interfaces. From left to right, we display TBP, NDI-silane, 1-TBP–1-NDI-silane, 2-TBP–2-NDI-silane, and 3-TBP–3-NDI-silane. For each structure we display the optimized geometry (TBPs: black, NDI-silanes: gray), the eigenvalue of the lowest unoccupied molecular orbital (LUMO) in blue, the eigenvalue of the highest occupied molecular orbital (HOMO) in red, and the value for the HOMO–LUMO gap. The vacuum level is indicated by a vertical dotted line. The LUMO eigenvalue reported for TBP is the value that we find with the basis set 6-31G**. The positive eigenvalue does not have much physical meaning, as discussed in the main text, therefore it is set in parentheses.

results from the use of a finite, localized basis set. The relevant eigenvalues show a typical donor–acceptor “cascade” alignment, as illustrated in Fig. 2. For the coupled 1-TBP–1-NDI-silane the ionization energy is close to that of the isolated donor (6.55 eV) and the electron affinity is close to that of the isolated acceptor (1.80 eV). This shows that also in the combined system, the distinct donor and acceptor properties are retained. Similar observations are made for the 2-TBP–2-NDI-silane and 3-TBP–3-NDI-silane systems, but there one sees an additional narrowing of the gap from 4.36 eV to 3.39 eV and 3.31 eV. The onset of the saturation of the gap confirms the consistency of our multimolecular approach. Altogether, these results confirm that TBP–NDI-silane is a promising model structure for photoinduced charge separation, which motivated us to proceed further with its evaluation.

2.2 Electronic excitations in the 3-TBP–3-NDI-silane interface

Within our set of molecular models, the 3×3 system comes closest to capturing the properties of an interface, therefore we start by presenting these results. The geometry optimization of the 3×3 systems leads to a stable configuration in which all 6 molecules are bound to each other by π -stacking of the molecules' aromatic rings. Table 2 reports the energies and oscillator strengths for the lowest eight singlet excitations. For completeness we also calculated the lowest-lying triplet excitation energies. They are found at 1.19 eV, 1.70 eV, 1.77 eV, 1.99 eV, 2.05 eV, 2.21 eV, 2.25 eV, and 2.28 eV. These states are not directly optically accessible, and we see that the triplet energies are not in the energetic range that could be relevant for fission of the lowest singlet. As triplet states are therefore not expected to

Table 2 Excitation energies, oscillator strengths, and exciton binding energies for the first eight excited states of the 3-TBP–3-NDI-silane interface model

State	Excitation energy (eV)	O.S.	Exciton binding energy (eV)
S1	1.47	0.1039	1.66
S2	1.73	0.0285	1.40
S3	1.78	0.0011	1.35
S4	2.05	0.0004	1.08
S5	2.25	0.0001	0.88
S6	2.42	0.0003	0.71
S7	2.46	0.0008	0.68
S8	2.52	0.0109	0.61

participate in the initial photophysics of the system, the subsequent discussion will focus on the singlet excitations.

Several important insights emerge from the singlet excitation data. First, the lowest excitation appears at 1.47 eV. This is close to the value 1.4 eV that is considered as the optimal gap for single junction organic solar cells.⁴⁹ Second, the S1 excitation carries oscillator strength, *i.e.*, it can be directly accessed optically. Third, several further excitations appear within a few tenths of an eV above the S1 energy. Their oscillator strengths vary, but are lower than that of S1. Finally, S8 appears at 2.52 eV, *i.e.*, still in the visible range.

Further understanding of these findings can be gained by analyzing the excitations in terms of their difference density, *i.e.*, the difference between the excited-state density and the ground-state density. Fig. 3 depicts the difference densities for S1–S8 by visualizing regions where the electron density in the excited state is higher than the ground-state density in blue, and regions where it is lower in red, *i.e.*, red regions can be interpreted as “holes”.

The plots show that all of the excitations are associated with a (partial) charge-transfer from the region of the TBP molecules on the left to the region of the NDI-silane molecules on the right. The extension of the charge transfer is different in the different excitations. The difference densities of S1 and S8 show a charge transfer from the innermost TBP molecule to the innermost NDI-silane molecule, *i.e.*, the particle and hole densities are directly neighboring at the interface and the charge transfer is thus relatively short ranged. In S2, the charge separation is larger as the hole density is still on the TBP molecule at the interface, but the particle density is mostly on the second, middle NDI-silane molecule. In S3, the situation is reversed, *i.e.*, the particle density is on the NDI-silane molecule at the interface, but the hole density is on the second, middle TBP molecule. In S4, both particle and hole density have moved to the second layer, and for the yet higher excitations these trends continue, with particle and hole densities then also involving the outermost molecules and delocalizing over several molecules within the donor or acceptor region, respectively.

The typical situation that one thinks about in organic solar cells^{20,50} is that light is absorbed *via* an optically active non-charge transfer excitation. The excitation energy then goes over to a (dark) charge-transfer state, and further steps then lead to the charge-separated state and the collection of charges at the

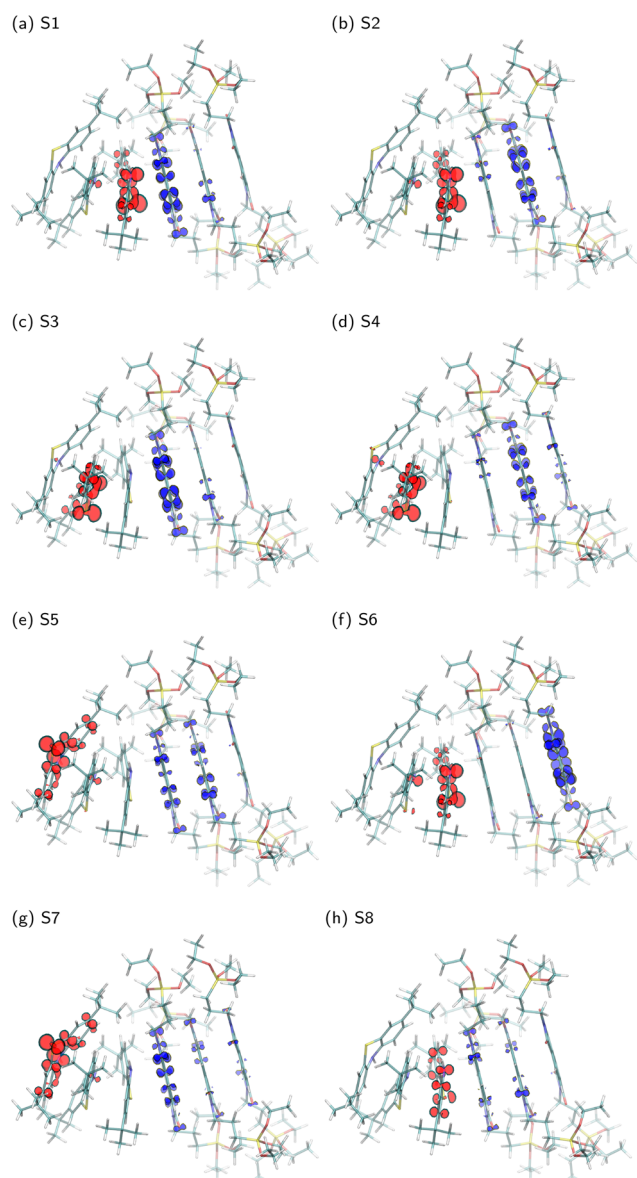


Fig. 3 Difference densities for the first eight excited states, labeled (a)–(h), of the 3-TBP–3-NDI-silane interface model. In all excitations, charge is transferred from the TBP molecules on the left (electron deficient “hole” regions in red; isosurface with isovalue $-0.0002a_0^{-1}$) to the NDI-silane molecules on the right (electron gaining “particle” regions in blue; isosurface with isovalue $0.0002a_0^{-1}$).

electrodes. In the TBP–NDI-silane system the situation is different: The (partial) charge-transfer state is optically active, *i.e.*, carries oscillator strength, and at the same time is the first (lowest in energy) excitation. Thus, the charge-transfer state is not reached from a bright non-charge transfer state *via* a transition of the type that is often described by Marcus theory, but is directly accessed by the optical excitation. This difference is discussed in detail in Section 2.3.3.

For the further process of carrier generation, the electron and hole densities need to decouple, *i.e.*, the exciton binding energy has to be overcome. In Table 2 we report the exciton binding energies for the first eight excitations. They were

calculated as the difference between the fundamental gap as obtained from the frontier eigenvalues of the optimally-tuned range-separated hybrid calculations, and the excitation energies from Table 2. When interpreting the calculated exciton binding energies, the number of molecules explicitly included in the calculation must be kept in mind: our finite-system calculation only includes 3 molecules of each species. In a film, there will be many more molecules, and these can lead to additional dielectric screening. When one takes this effect into account, *e.g.*, *via* a screened range-separated hybrid approach, the exciton binding energy typically is further reduced, and the effect can be substantial, as discussed in detail in ref. 25. Here, we refrain from using a screened range-separated hybrid, as an interface with different electrostatics on each side would be hard to include, and the approach would also introduce empirical elements, *e.g.*, for estimating the effective dielectric constants. Therefore, while it is thus clear that the absolute values for the exciton binding energy that we present here only represent an upper limit, it is encouraging to see that as expected, the exciton binding energies are lower for the higher excitations. This confirms the impression from the visual inspection of Fig. 3, *i.e.*, the higher excited states correspond to electron–hole pairs that are more weakly bound.

The optically active excitations, the multitude of states that exhibit charge-transfer character, and the existence of states in which the electron and hole are well separated offer a promising view on the potential usefulness of the interface for photovoltaic purposes. However, there are also open questions. The first is that the results so far were obtained for one molecular geometry. Further, different geometries should be checked to safeguard against drawing conclusions based on just one geometry that by chance might have particular properties. Second, the energetic ordering of the states, with the most tightly bound exciton lowest in energy, is not ideal for charge separation: if the charge-transfer states in which electron and hole densities are largely separated would be lower in energy than the ones in which they are close together, the excitation would naturally relax into a completely charge-separated state.²⁰ Changes in geometry and nuclear motion might change the picture or might lead to a coupling of the excitations. Therefore, we examine these effects in the following.

2.3 The 2-TBP–2-NDI interface

2.3.1 Excited states. For studying how nuclear vibrations affect the excited-state energetics, and a more detailed analysis of the interface charge-transfer states, the computational costs need to be decreased considerably. At the same time, however, the important physical characteristics of the model need to be retained. As a first step to reach this goal, we drop the outermost TBP and NDI-silane from the simulation. This leaves us with 2 TBPs and 2 NDI-silanes. As a second step, we replace the silyl residues at the NDIs' endings by methyl residues. This system in the following is designated as 2-TBP–2-NDI. This simplification is justified by the observation that the difference densities in the 3×3 system (*cf.* Fig. 3) show that the electronic excitations predominantly involve the molecules' aromatic

Table 3 Excitation energies and oscillator strength for the first 6 excited states of the 2-TBP–2-NDI system

State	Excitation energy (eV)	O.S.
S1	1.21	0.0576
S2	1.63	0.0001
S3	2.03	0.0020
S4	2.42	0.0006
S5	2.44	0.0243
S6	2.73	0.0007

rings, while the silyl residues play a subordinate role. We optimally tune the range-separation parameter ($\omega_{\text{opt}} = 0.15a_0^{-1}$) for this system and optimize the geometry with ω PBE and a D3 dispersion correction.⁵¹ See the SI for computational details. We calculate the excited states at the geometry-optimized structure to test whether the reduced system reproduces the characteristics of the excited states of the 3-TBP–3-NDI-silane system. Table 3 lists the excitation energies and oscillator strengths of the first 6 excited states, and their difference densities with respect to the ground state are depicted in Fig. 4.

The first excited states of the reduced 2-TBP–2-NDI system show similar charge-transfer character as the excitations in the larger 3-TBP–3-NDI-silane system. All calculated excited states show charge-transfer character, with an electron being transferred from the TBP region to the NDI region. Comparing the difference densities of the 2-TBP–2-NDI system in Fig. 4 with the 3-TBP–3-NDI-silane system in Fig. 3 shows that the same type of molecules is involved. In both cases, the lowest excited state S1 is a charge transfer directly at the interface and with non-negligible oscillator strength. Similarly, S2 and S3 show charge transfers over a larger distance across one rather inactive molecule and even across two rather inactive molecules for S4.

2.3.2 Born–Oppenheimer molecular dynamics. Since organic solar cells are intended to operate at room temperature, nuclear motion has to be taken into account in the excitation analysis. Here, the nuclei are modeled as classical particles that propagate according to Born–Oppenheimer molecular dynamics. We investigate how the adiabatically calculated excited states change along the trajectory and whether their energies overlap. In both the ground-state DFT-based *ab initio* molecular dynamics and the excitation energy calculations, the electrons are treated at the same ω PBE($\omega = 0.15a_0^{-1}$) level of theory.

To model realistic structural changes at room temperature, we run Langevin dynamics with the algorithm of ref. 52 at 300 K on the electronic ground state for 2128 fs. Detailed information about the simulation parameters are listed in the SI. Initial conditions for the atom coordinates and velocities are sampled from a Wigner distribution at 300 K. The molecular dynamics are performed within a canonical ensemble.

After *ca.* 0.5 ps the system has reached room temperature and is at equilibrium. We start our analysis from this time onward. Every 4 fs we take a snapshot of the nuclear geometry and calculate the adiabatic excitation energies on that geometry. The resulting excitation energies for the first 4 excited

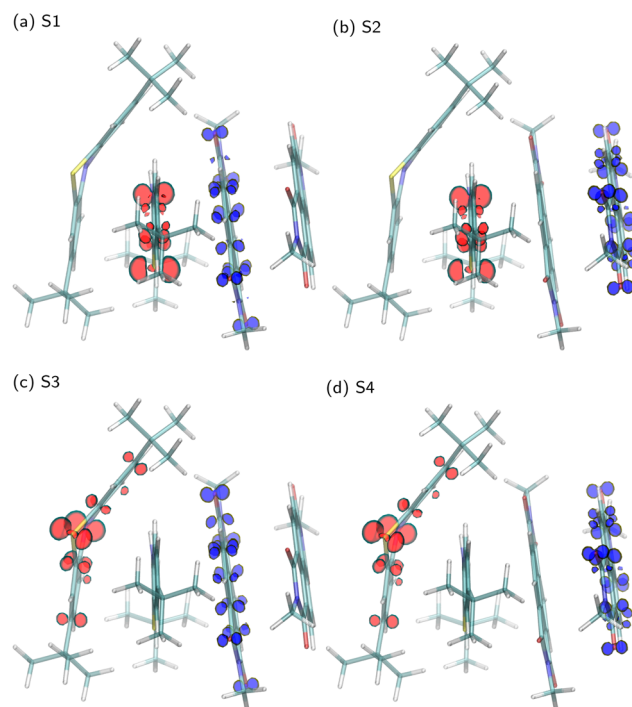


Fig. 4 Difference densities with respect to S0 of S1–S4, labeled (a)–(d), for the 2-TBP–2-NDI system. For all excitations, the “hole” (red isosurface; isovalue $-0.0002a_0^{-3}$) is located in the TBP domain and the “electron” (blue isosurface; isovalue $0.0002a_0^{-3}$) in the NDI domain.

states and the temperature along the trajectory are depicted in Fig. 5. It shows that each excited-state energy fluctuates about half an electron volt along the trajectory. As a consequence of these substantial fluctuations, the different excitation energies get as close as ten millielectronvolts in the course of the simulation.

For clarity, we look at the trajectory data also from a different point of view by presenting a statistical analysis of the excitation energies and oscillator strengths in Fig. 6. The excitation energies and oscillator strengths for all snapshots along the trajectory with their average values are depicted in Fig. 6(a). In Fig. 6(b), the excitation energies are condensed to a probability distribution with a histogram. The decisive insight that emerges from these figures is that the excitation energies clearly overlap. This is particularly well seen in Fig. 6(b) for the excitation energy distributions of S1 and S2. Similar overlaps are observed between S2 and S3, as well as between S3 and S4. Although adiabatic excitation energies do not provide information about the coupling between excited states or population transfer, the observed energetic overlap suggests that excited state population transfer between these states is plausible.

Furthermore, the calculations indicate that the observed electronic states are not specific to the initial geometry but consistently appear across a wide range of geometries, *i.e.*, the (charge-transfer) character of the states is an inherent property of the system. In this context it is also noteworthy to take a look at the oscillator strengths. The mean oscillator strength of S1 is 0.07 and for some molecular geometries along the trajectory the

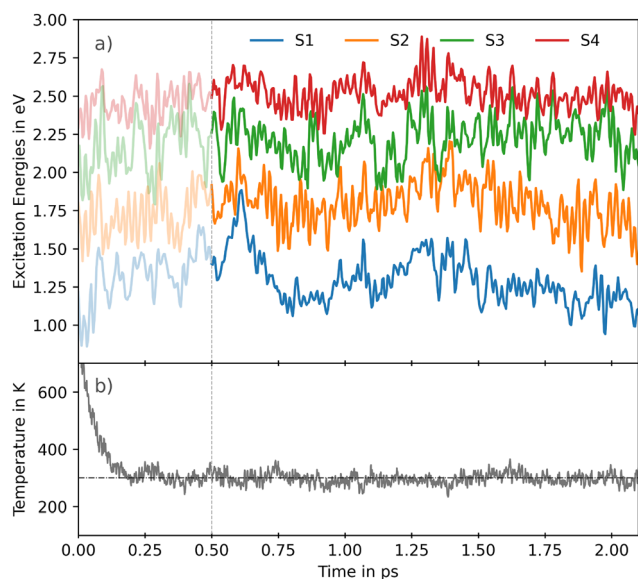


Fig. 5 (a) Adiabatic excitation energies of S1–S4 as function of time along the nuclear trajectory. (b) Instantaneous temperature during the molecular dynamics in dark gray. The horizontal dot-dashed line indicates the thermostat temperature (300 K). The beginning time for the trajectory analysis is marked with a vertical line at 0.5 ps, after which the temperature has stabilized.

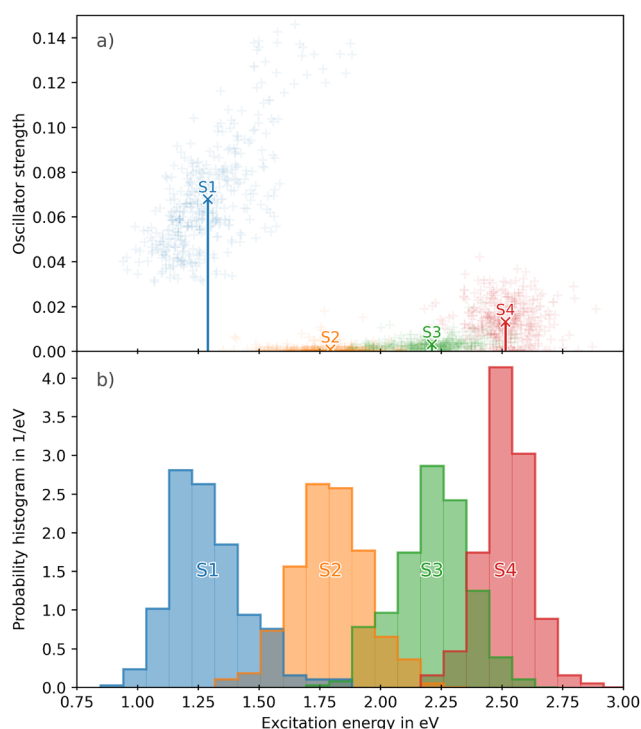


Fig. 6 (a) Excitation energies of S1–S4 with their oscillator strength along the Born–Oppenheimer trajectory. Each “+” marker corresponds to one trajectory snapshot, the average values are depicted with “x” markers and vertical lines. (b) Probability histogram of S1–S4 evaluated from the excitation energies for the molecular structures taken from the Born–Oppenheimer molecular dynamics trajectories.

oscillator strength even reaches values of about 0.14. This average value therefore strongly suggests that this interface excitation is optically accessible under room temperature conditions. A notably weaker optical response is consistently observed for S2–S4. This can be attributed to the increased electron–hole distance, *i.e.*, the reduced overlap of electron and hole orbitals is likely responsible for the reduced intensity of the transitions.

The oscillator strength of S1 together with the indicated coupling to higher states establish a possible pathway for charge separation. After optical excitation of the interface charge-transfer state, nuclear dynamics could drive the transfer to other excited states, leading to the separation of electron and hole. This pathway could be combined with the more traditional pathway of excitation to a higher lying bright state followed by relaxation to lower lying charge-transfer states.

2.3.3 Charge separation and recombination. In this section, we take a closer look at the coupling between the different states of the 2-TBP-2-NDI system that can be involved in the processes of charge transfer, charge separation, and charge recombination. This is motivated by the observation – as already mentioned in Section 2.2 – that the present system differs noticeably from the situation that is typically discussed for molecular donor–acceptor systems:²⁰ typically, the optical excitation leads to a state in which electron and hole are localized on the same molecular unit. In a second step, this excitation is then followed by a transition to a charge-transfer state, which can subsequently lead to the desired charge separation, or an undesired charge recombination.^{53,54} The transition is often evaluated using Marcus theory^{55–57} or the complementary Marcus–Levich–Jortner (MLJ) theory.^{58,59} However, the TBP–NDI system investigated here is characterized by a direct optical excitation of a state with substantial charge-transfer character, *i.e.*, the optically excited state and the charge-transfer state coincide. Furthermore, the system shows a cascade of additional charge-transfer states that are progressively more delocalized and are associated with decreasing exciton binding energies. Therefore, the traditional perspective has to be adjusted.

In order to obtain some first insight into how the charge-separation and charge recombination processes might evolve, we calculate the couplings between different states. The electronic coupling between the states of a donor–acceptor system can be obtained from fragment charge difference (FCD) calculations.⁶⁰ In our case, the two TBP molecules define the donor fragment and the two NDI molecules the acceptor. The coupling is obtained from⁶⁰

$$V_{i \rightarrow f}^{(Q_i)} = \frac{(E_f - E_i) \Delta q_{if}}{\sqrt{(\Delta q_i - \Delta q_f)^2 + 4 \Delta q_{if}^2}}, \quad (1)$$

where $\Delta q_{i,f}$ are the donor–acceptor charge differences between the final and initial states and Δq_{if} is the symmetrized off-diagonal donor–acceptor charge population term (see details in ref. 60). The square of the electronic coupling is the quantity that scales the transition between the states in the

framework of Marcus theory or, more generally, the Fermi's golden rule.^{55–57,61}

For these calculations the geometry that the system assumes in each of the respective states must be known. We show results for the relaxed geometries at the ground state S0 and the first excited state S1, labeled Q0 and Q1, respectively. The Q1 geometry is obtained by finding the energetic minimum of the Born–Oppenheimer surface of the first excited state as calculated by linear-response TDDFT. For reasons of computational practicability, the optimized geometries are calculated with the M06-2X functional, while, for consistency, total energies and excited-state energies are obtained with the ω PBE functional ($\omega = 0.15 a_0^{-1}$). For computational details and calculated values see the SI. Obtaining the optimized geometries for higher excited states turns out to be extremely challenging and shows indications of state crossings, and could therefore not be pursued further. However, some of the most relevant insights can already be obtained based on just Q0 and Q1.

Table 4 shows the charge-displacement parameters and the electronic coupling for the transitions of interest as obtained from eqn (1). A first insight gained from Table 4 is that the charge displacements from the donor fragment to the acceptor fragment for the first four excited states are all about $2e$, confirming the character of complete charge separation for these states at both the Q0 and the Q1 geometry. Next, we note that the states S2 to S4, which have pronounced charge-transfer character, are relatively well coupled to S1 at the ground-state geometry, with couplings V of about 0.1 eV. Furthermore, S2 and S4 are significantly coupled to S1 at the S1 excited state geometry, with V s of about 0.3 and 0.6 eV. These high coupling constants indicate that a vibronically mediated interchange between these states^{62,63} could be possible. Finally, the last line of Table 4 shows that the coupling for the transfer from S1 (in the excited-state relaxed geometry Q1) back to S0 comes with a coupling of a rather small magnitude, ≈ 0.01 eV. This is a reassuring finding in so far as this transition is associated with charge recombination, *i.e.*, the low coupling here contributes to suppressing the undesired recombination process.

Table 4 Last number in each line: the electronic coupling, *cf.* eqn (1), for different transitions as indicated by the first entry in each line. The superscript Q0 indicates that the states were calculated based on the geometry optimized in the ground state, whereas the index Q1 denotes states based on the geometry optimized for the first excited state; see main text. The second to fifth number in each line report the parameters that enter eqn (1), where $\Delta E = E_f - E_i$, and *i* and *f* refer to the states indicated by the first entry in the line

Transition	Δq_i	Δq_f	Δq_{if}	ΔE (eV)	V (eV)
S1 ^(Q0) $\rightarrow$ S2 ^(Q0)	1.960	2.010	−0.007	0.579	−0.078
S1 ^(Q0) $\rightarrow$ S3 ^(Q0)	1.960	2.012	0.006	1.076	0.121
S1 ^(Q0) $\rightarrow$ S4 ^(Q0)	1.960	2.078	0.008	1.462	0.098
S1 ^(Q1) $\rightarrow$ S2 ^(Q1)	1.905	1.928	0.008	1.010	−0.288
S1 ^(Q1) $\rightarrow$ S3 ^(Q1)	1.905	1.934	0.000	1.332	0.020
S1 ^(Q1) $\rightarrow$ S4 ^(Q1)	1.905	1.872	0.009	1.817	0.572
S1 ^(Q1) $\rightarrow$ S0 ^(Q1)	1.905	0.008	0.076	−0.351	−0.014

It would be interesting to analyze not only the couplings, but also reorganization energies and transition rates.⁶⁴ However, due to the nature of the charge-transfer states in the system, and the size and the complexity of our multi-molecular TBP–NDI system, this is a very challenging task and beyond the scope of the present work. It is reassuring to see, though, that the analysis of the couplings supports the point of view that charge separation can occur at the TBP–NDI interface.

2.4 Experimental insights

As an evaluation of our theoretical predictions, we address the experimental spectroscopic assignment of the charge-transfer states at the interface. Thus, we synthesized the compounds, as described in ref. 35 and 65, and measured their optical absorption. However, measuring charge-transfer states is not straightforward, since it has inherently low oscillator strength in solution and the species responsible for such optical response are only the ones at the donor–acceptor interface. Our approach was to perform vis-NIR absorption measurements in highly concentrated tetrahydrofuran (THF) solutions (30 g L^{-1}), in order to increase the existence probability of TBP–NDI-silane bound species without compromising optical quality (see Methods in the SI).

Fig. 7 (left) shows the THF solution of the single molecules and their 1:2 molar mixture. The solution of the single molecules are transparent. Their absorption bands are only observed above 3 eV ($\lambda > 400 \text{ nm}$). On the other hand, the mixed solution is light green, showing an absorption band in the red-NIR. Fig. 7 (right) shows the contrast between the NIR-absorption spectrum and the vertical excitations guided by a Gaussian overlap calculated for the 1-TBP–1-NDI-silane configuration. A broad band around 1.8 eV is observed, while the calculated first transition is predicted at 1.46 eV. Considering the large difference between the geometries of dynamic aggregates formed in the concentrated solution at room temperature and the optimized geometry in our calculation, this is a quite reasonable agreement between experimental and calculated data. When comparing experiment and theory here, one

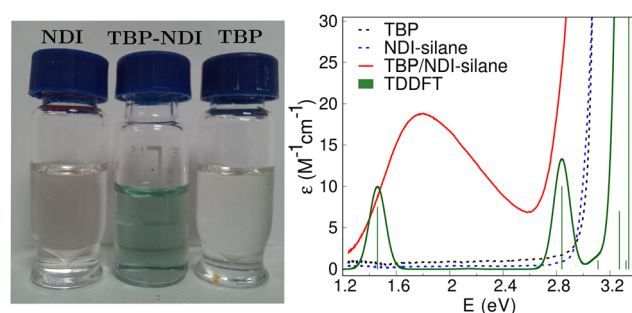


Fig. 7 (left) Photograph of the THF solutions of TBP, NDI-silane and TBP/NDI-silane 2:1 solutions at a concentration of 30 g L^{-1} (right) and their vis-NIR absorption spectra. Dashed lines are the spectra of the single molecules and the solid red line is the spectrum of the TBP/NDI-silane 2:1 solution. For comparison, TDDFT calculated excitation energies for 1-TBP–1-NDI-silane configuration are presented below the experimental data as green bars and convoluted Gaussian curves.

must also take into account that in the solution on which the experiments are based, aggregates of different sizes and complexity might be forming. This can lead to a distribution of excited states that can contribute to the lowest absorption band. For instance, the contrasts between the lower excited states in Tables 2 and 3 for the 3×3 and 2×2 interface models shows that the excitation spectrum is sensitive to the aggregation.

In order to confirm that the absorption in the NIR region comes from TBP/NDI-silane interfaces, we probed the existence of the long-living TBP/NDI-silane aggregates in the concentrated THF solutions. This was done by dipolar-correlated nuclear magnetic resonance (NMR) spectroscopy using the 1D selective rotating-frame Overhauser effect spectroscopy (1D-ROESY).^{66–69} In this technique, a proton species is selectively excited and its magnetic moment transferred through space by dipole–dipole interaction that is averaged out by molecular motion. The resulting spectrum shows the signal due to the selectively excited species plus the ones cross-correlated to the former.⁷⁰ In our case, we performed 1D ROESY experiments selectively exciting the aromatic H₃ and H₅ of the TBP (see labeled structure in Fig. S2c), observed close together around 6.9 ppm. As a result, the aromatic protons H₂ of TBP are observed at 6.4 ppm, as expected, and also the ones of the NDI-silane (Fig. S3). This demonstrates that these molecules in THF solution are stacked together transferring magnetization, at least, in the NMR time-scale of milliseconds to seconds. Finally, the compounds and their mixture are stable over many weeks at ambient conditions, either in THF solution or as solid powders, as probed by NMR spectroscopy. The details of the NMR study are described in the SI.

3 Conclusions

In this study, we have investigated the electronic properties of a TBP–NDI interface, a promising system for organic photovoltaics. We found that the lowest excited state, S1, is a charge transfer state at the interface with a favorable excitation energy and oscillator strength. This confirms that this material class has the potential for efficient light-driven charge separation. Higher excited states, S2–S8, also show charge-transfer characteristics with larger electron–hole distances, extending over several molecular units. At room temperature conditions, *ab initio* molecular dynamics simulations showed general optical accessibility of the lowest interfacial charge-transfer state. Furthermore, it revealed energetic overlap between different excited states. We furthermore evaluated the electronic couplings between different states explicitly. In future work, one might think about non-adiabatic simulations that allow for the quantitative analysis of non-adiabatic couplings, *e.g.*, using the methods from ref. 71 and 72. The computational costs of such calculations will be a serious challenge, though. On a qualitative level, the statistical analysis that we presented in the present article can already be seen as a strong hint that coupling between different electronic excitations can be

mediated by nuclear vibrations. This can open a pathway for efficient exciton dissociation. We presented first data on the experimental realization of this material class and a first spectroscopic analysis that is qualitatively in line with the theoretical predictions. Thus, our study confirms the significant potential that the TBP–NDI-silane material class holds for organic photovoltaics.

Author contributions

T. T. ran the calculations of Section 2.1 (partly; geometry optimization and optimal tuning of 2-TBP–2-NDI-silane), Section 2.2 (excited-state calculation on 3-TBP–3-NDI-silane), and Section 2.3 (excited-state calculations and Born–Oppenheimer molecular dynamics of 2-TBP–2-NDI), prepared Fig. 2–6 and Table 1 (partly), 2, and 3, and contributed to the results shown in Section 2.3.3, *e.g.*, via excited-state geometry optimizations. R. A. synthesized NDI-silane and performed and discussed the experiments presented in Section 2.4. C. M. I. discussed with T. T. and supervised all TeraChem calculations. S. K. conceptualized the steps of the theoretical approach, structured the analysis of the data, and structured the first manuscript draft. T. B. suggested to study this material combination, initiated the project, did part of the calculations presented in Section 2.1, calculated the couplings in Section 2.3.3, and guided and discussed the experiments discussed in Section 2.4. T. T., S. K., and T. B. together wrote the final manuscript. All authors commented on and discussed the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5cp02934a>.

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Supplementary Information for

Optically induced charge separation at the naphthalenediimide-phenothiazine interface

Physical Chemistry Chemical Physics

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S1 Detailed simulation information

In this section we give detailed information about the simulation parameters and list the electronic structure programs.

TBP, NDI-silane

Geometry Optimization

Software: Q-Chem¹, Functional: M06-2X², Basis set: 6-31G**

Optimization thresholds: Gradient-Max $< 3 \cdot 10^{-4}$ a.u. & $\Delta E < 1 \cdot 10^{-6}$ a.u.

Optimal tuning

Software: Q-Chem, Functional: ω PBE³, Basis set: 6-31G**

We sample over different values of ω with a step size of $0.01 a_0^{-1}$ and calculate the HOMO eigenvalues ($\epsilon_{\text{HOMO}}(\omega)$) and ionization potential ($\text{IP}(\omega)$) for both the neutral system (N) and the anion (N+1). For each system, we fit a quadratic function into the difference between $\epsilon_{\text{HOMO}}(\omega)$ and $-\text{IP}(\omega)$. Those parabolas are used to evaluate $J^2(\omega)$ and we determine the value of ω that minimizes $J^2(\omega)$, yielding ω_{opt} . The minimum found by this procedure can vary by a few $\text{mili } a_0^{-1}$ depending on the details of the fit, but such tiny differences in ω do not have a relevant impact on the physical observables.

1-TBP-1-NDI-silane

Geometry Optimization

Software: Q-Chem, Functional: M06-2X, Basis set: 6-31G**

Optimization thresholds: Gradient-Max $< 3 \cdot 10^{-4}$ a.u. & $\Delta E < 1 \cdot 10^{-6}$ a.u.

Binding energy

Software: Q-Chem, Functional: M06-2X, Basis set: 6-311++G**

Optimal tuning

Software: Q-Chem, Functional: ω PBE, Basis set: 6-31G**

We sample over different values of ω with a step size of $0.01 a_0^{-1}$ and evaluate $J^2(\omega)$ according to the procedure described above and determine the optimal ω_{opt} that minimizes J^2 .

Excited states

Software: Q-Chem, Functional: ω PBE, Basis set: 6-31G**

3-TBP–3-NDI-silane

Geometry Optimization

Software: Q-Chem, Functional: M06-2X, Basis set: 6-31G**

Optimization thresholds: Gradient-Max $< 3 \cdot 10^{-4}$ a.u. & $\Delta E < 1 \cdot 10^{-6}$ a.u.

Optimal tuning

Software: Q-Chem, Functional: ω PBE, Basis set: 6-31G**

We sample over different values of ω with a step size of $0.01 a_0^{-1}$ and evaluate $J^2(\omega)$ according to the procedure described above and determine the value ω_{opt} that minimizes $J^2(\omega)$.

Excited states with difference densities

Software: TeraChem⁴ (singlets), QChem (triplets), Functional: OT- ω PBE, Basis set: 6-31G*, Tamm-Dancoff approximation

2-TBP–2-NDI

Initial Geometry Optimization for the Optimal Tuning

Software: Q-Chem, Functional: M06-2X, Basis set: 6-31G**

Optimization thresholds: Gradient-Max $< 3 \cdot 10^{-4}$ a.u. & $\Delta E < 1 \cdot 10^{-6}$ a.u.

Optimal tuning

Software: Q-Chem, Functional: ω PBE, Basis set: 6-31G**

We sample over different values of ω with a step size of $0.01 a_0^{-1}$ and evaluate the $J^2(\omega)$ value with ω PBE. The minimal value for $J^2(\omega)$ is achieved for $\omega = 0.15 a_0^{-1}$.

The sampling rate is chosen comparatively coarse. The resulting physics, however, are expected to be reliable within this accuracy.

Refined Geometry Optimization for Excited States and Initial Born-Oppenheimer Dynamics Structure

Software: TeraChem, Functional: OT- ω PBE, Dispersion correction: D3⁵, Basis set: 6-31G

Optimization thresholds: $\Delta E < 1 \cdot 10^{-6}$ a.u. & Gradient-RMS $< 3 \cdot 10^{-4}$ a.u. & Gradient-Max $< 4.5 \cdot 10^{-4}$ a.u. & Displace-RMS $< 1.2 \cdot 10^{-3}$ a.u. & Displace-Max $< 1.8 \cdot 10^{-3}$ a.u.

Excited states with difference densities

Software: TeraChem, Functional: OT- ω PBE, Dispersion correction: D3, Basis set: 6-31G*, Tamm-Dancoff approximation

Born-Oppenheimer Molecular Dynamics

Software: TeraChem, Functional: OT- ω PBE, Dispersion correction: D3, Basis set: 6-31G*, Tamm-Dancoff approximation

Charge separation and recombination

Software: QChem, Functional: OT- ω PBE (total energies, excited-state energies, and couplings) and M06-2X (geometry optimization), Basis set: 6-31G**, Tamm-Dancoff approximation (only for the S1 geometry optimization)

S2 Charge separation and recombination

For the calculations presented in the Section 2.3.3, the optimized geometries of the ground state (Q0) and first excited state (Q1) were obtained by DFT and TDDFT/TDA calculations, respectively, using the M06-2X functional and 6-31G(d,p) basis set. Both optimizations had as initial guess the DFT optimized geometry performed with the ω PBE+D3 functional and 6-31G(d,p) basis set presented in Section 2.3.1. The energies reported here and the FCD parameters listed in the main manuscript were obtained from full TDDFT calculations with the ω PBE functional and 6-31G(d,p) basis set using $\omega = 0.150 \text{ bohr}^{-1}$.

Table S1: Energy shifts with respect to $E_{S_0}^{Q_0} = -122680.575 \text{ eV}$ of the ground state and first four excited states for optimized geometries at S0 and S1. The small differences between the excited states energies reported for Q0 here and in Tab. 3 of the main manuscript are due to minor distinctions between the optimized geometries obtained with the ω PBE+D3 and M06-2X functionals.

Geometry	$\Delta E(S_0)$ (eV)	$\Delta E(S_1)$ (eV)	$\Delta E(S_2)$ (eV)	$\Delta E(S_3)$ (eV)	$\Delta E(S_4)$ (eV)
Q0	0.000	1.116	1.695	2.192	2.578
Q1	0.326	0.677	1.687	2.009	2.494

Fig. 1 presents the Huang-Rhys spectrum of the $S_1 \rightarrow S_0$ transition for 2-TBP-2-NDI system, dominated by high frequency vibrational modes ($\nu > 400 \text{ cm}^{-1}$). The Huang-Rhys factors are calculated by:

$$S_k = \frac{\omega_k \Delta Q_k^2}{2\hbar} \quad (1)$$

where ΔQ_k is the mass-weighted projection between two electronic states along mode k , given by:

$$\Delta Q_k = \sum_{\mu=1}^{3N} L_{\mu k} \Delta R_{\mu} \quad (2)$$

where L_{μ} is the mass-weighted normalized frequency eigenvectors obtained at Q0 and ΔR_{μ} is the geometry displacement between Q0 and Q1. The vibrational frequencies and corresponding mass-weighted normalized frequency eigenvectors were obtained from harmonic vibrational DFT calculations performed in Q-Chem¹ using the M06-2X functional² and 6-31G(d,p) basis set.

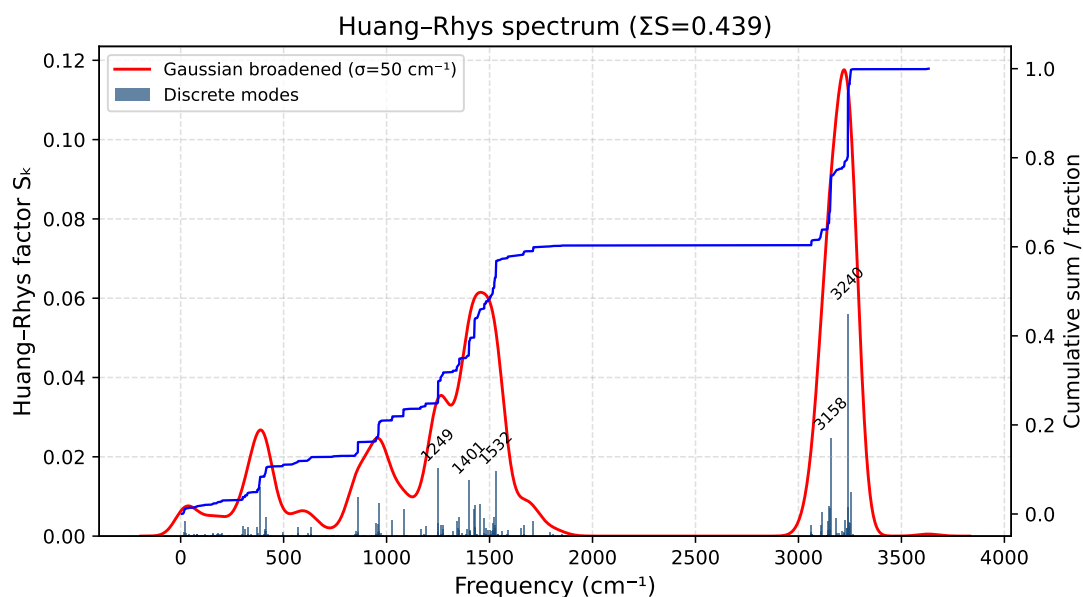


Figure S1: Huang-Rhys spectrum of the S1→S0 transition for the 2-TBP-2-NDI system.

S3 Experimental details

S3a NIR absorption spectroscopy

The vis-NIR absorption spectra were performed in a UV-M51 UV-vis-NIR single beam spectrometer (Bel Engineering) equipped with a tungsten and deuterium lamp and a silicon photodiode detector. The equipment can measure the absorption spectrum in the range of 190-1000 nm with 1 nm bandwidth. The measurements were performed in 2 mm thick quartz cuvettes.

S3b NMR spectroscopy

The NMR spectra were obtained in a Avance Neo 600 MHz Bruker spectrometer with magnetic flux of 14.1 T with a iProbe TBO 5mm BBF/19F/1H. The measurements were performed at 298 K with an acquisition time of 5 s collecting 12k points in the time dimension. The spectra were averaged over 32 scans. Further acquisition parameters are $\pi/2$ pulse of 12 μ s (nutating frequency of 20.8 kHz). The ^1H single pulse experiments were performed applying a 30° flip angle. The selective gradient-enhanced 1D ROESY experiments (selrogp Bruker protocol from - avance-version 21/09/15) were performed following an excitation $\pi/2$ pulse of 12 μ s, a selective π gradient pulse of 12.2 ms and a spinlock ROESY pulse during (P15) 0, 200, and 900 ms. This methodology based on refs.

6–9 has been developed to contain no subtraction artifacts, such that NOE enhancements are detected with complete confidence.

Fig. 2 shows selected regions of the ^1H NMR spectra of the TBP, NDI-silane and TBP/NDI-silane 2:1 THF- d_8 solutions at a concentration of 30 g.L^{-1} . The frame c) shows the aromatic region (Ar), the frame a) the region around 8.56 ppm where the proton H4 of the NDI-silane is observed, and the frame b) shows the region around 6.8 ppm where the protons H3 and H5 of TBP are observed. The assigned peaks are labeled in correspondence to the structures presented in the inset of Fig. 2-c). For the NDI-silane in THF- d_8 the assigned spectrum in δ (ppm) is: 0.59 (4H, H_α , m); 1.07 (18H, CH_3 , t), 1.71 (4H, C_β , m), 3.69 (12H, OCH_2 , q), 4.02 (4H, C_γ , t), and 8.57 (2H, Ar/ H_4 , s). For the TBP in THF- d_8 the assigned spectrum in δ (ppm) is: 1.12 (18H, CH_3 , s), 6.37 (2H, Ar/ H_2 , d), 6.81 (2H, Ar/ H_5 , d), 6.83 (2H, Ar/ H_3 , dd), and 7.33 (1H, NH, s). Tetramethylsilane (TMS) is used as internal reference at 0.0000 ppm.

The singlet peaks due to THF are observed at 3.47 and 1.61 ppm with a maximum variation between the samples of 0.1 ppm (3 Hz). Interestingly, in the 2:1 TBP:NDI-silane mixture the peaks related to the Ar/ H_4 of NDI-silane and Ar/ H_5 of the TBP are about 12 Hz downshifted in comparison with the solutions of the separated molecules, which is beyond the variation in the chemical shift of the solvent. This is a result of an up-shielding effect on these sites, which is the first indication of their spatial interaction in the 2:1 TBP:NDI-silane THF solution.

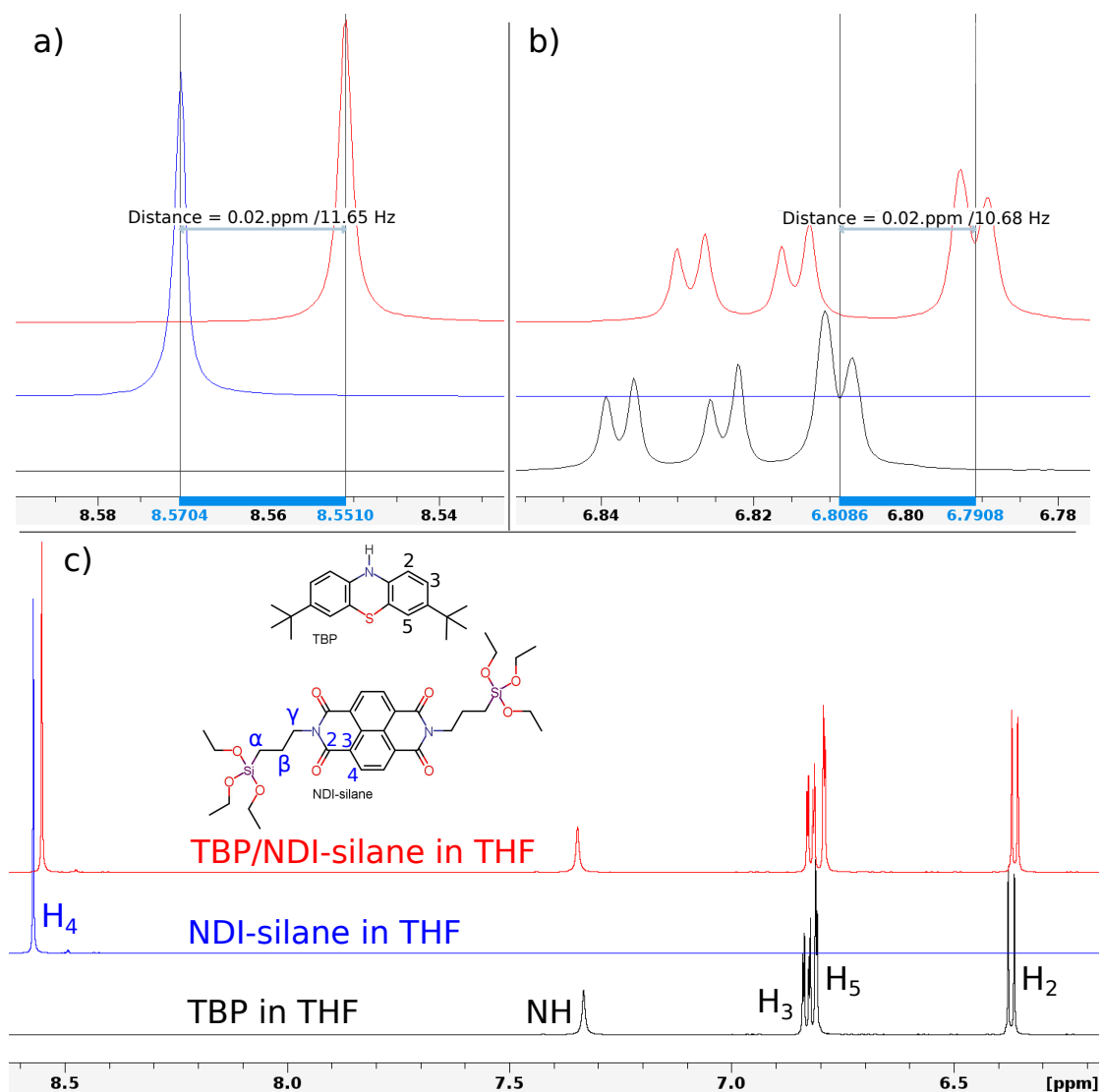


Figure S2: ^1H NMR spectra of the TBP, NDI-silane and TBP/NDI-silane 2:1 THF- d_8 solutions, from bottom to top, at a concentration of 30 g.L^{-1} . Frame a) shows the region of the Ar/ H_4 of the NDI-silane, frame b) the region of the Ar/ H_3 and Ar/ H_5 of the TBP, and frame c) shows the aromatic region.

Fig. 3 shows the ^1H selective 1D ROESY NMR spectra of the TBP/NDI-silane 2:1 THF- d_8 concentrated solution with spin lock pulse duration of 0, 200, and 900 ms. The selective pulse is placed at 6.9 ppm, which excites only the protons Ar/H₃ and Ar/H₅ of the TBP molecule. The spectrum without spinlock pulse has no trace of signals due to NOE or spin-diffusion (as expected), neither zero-quantum coherence of a single pulse experiment, except for a tiny peak at 6.37 ppm corresponding to the (2H, Ar/H₂, d) site of the TBP molecule. The spectrum obtained with spin lock pulse with duration of 200 ms has a significant negative-phase signal at 1.12 and 6.37 ppm, corresponding to the (18H, CH₃, s) and (2H, Ar/H₂, d) protons of the TBP molecule, due to the NOE. Some traces of signal due to the NDI-silane could be observed already. The spectrum obtained with the spin lock pulse duration of 900 ms shows negative-phase peaks attributed to the TBP, due to NOE, and positive-phase peaks attributed to the NDI-silane. The positive-phase peaks are due to either chemical exchange or spin-diffusion (multiple spins cross correlation).¹⁰ In the case of the TBP with NDI-silane aggregates, it is reasonable to assume that chemical exchange is not relevant and that spin-diffusion is taking place.

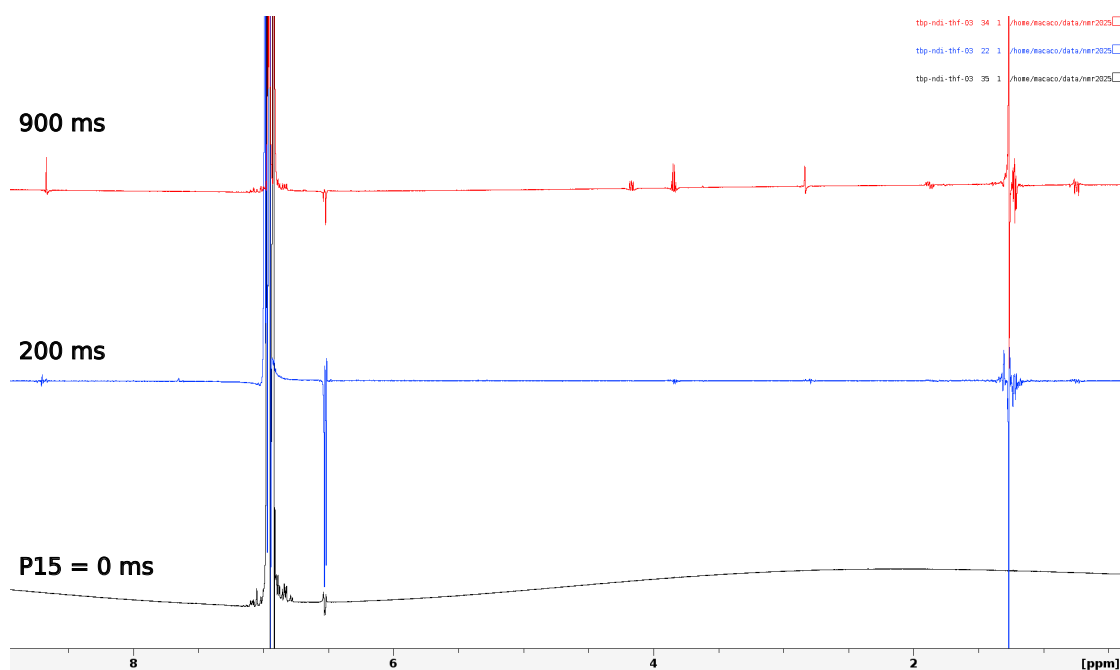


Figure S3: ^1H selective 1D ROESY NMR spectra of the TBP/NDI-silane 2:1 THF- d_8 solution at a concentration of 30 g.L^{-1} . The spectra were taken with spin lock pulse duration of 0, 200, and 900 ms, from bottom to top, as indicated.

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Publication 4

GPU-Accelerated On-The-Fly Nonadiabatic Semiclassical Dynamics

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GPU-accelerated on-the-fly nonadiabatic semiclassical dynamics

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ABSTRACT

GPU-accelerated on-the-fly nonadiabatic dynamics is enabled by interfacing the linearized semiclassical dynamics approach with the Ter-aChem electronic structure program. We describe the computational workflow of the “PySCES” code interface, a Python code for semiclassical dynamics with on-the-fly electronic structure, including parallelization over multiple GPU nodes. We showcase the abilities of this code and present timings for two benchmark systems: fulvene solvated in acetonitrile and a charge transfer system in which a photoexcited zinc-phthalocyanine donor transfers charge to a fullerene acceptor through multiple electronic states on an ultrafast timescale. Our implementation paves the way for an efficient semiclassical approach to model the nonadiabatic excited state dynamics of complex molecules, materials, and condensed phase systems.

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I. INTRODUCTION

Nonadiabatic molecular dynamics (NAMD), where the motion of nuclei and electrons cannot be uncoupled and the dynamics occur beyond the Born–Oppenheimer regime, occur in many key chemical processes, such as photo-initiated molecular dissociation, photocatalytic reactions that use electronic excited states to drive chemical reactions, and photoinduced charge separation dynamics in photovoltaics.^{1–5} However, such dynamics are challenging to model with a fully quantum treatment of nuclei and electrons, especially for complex and condensed phase systems.

Widely considered the gold standard for NAMD simulations, the multiconfigurational time-dependent Hartree (MCTDH) approach is highly accurate but only computationally feasible for systems with a handful of nuclear degrees of freedom and generally requires pre-computed potential energy surfaces. Despite the recent development of multi-layer (ML) MCTDH methods⁶ that make possible applications of MCTDH to more complex systems, at present, on-the-fly dynamics for complex molecular systems with

many degrees of freedom.^{7,9} *Ab initio* multiple spawning (AIMS) is an approximate implementation of a formally exact spawning Gaussian wavepacket approach that can account for quantum effects. However, this method is expensive, requiring some remedies to the computational cost.^{3,7} Of the approximate methods available, the fewest switches surface hopping (FSSH) and Ehrenfest dynamics are, arguably, the most popular. Both employ classical nuclear trajectories and have been used in *ab initio* on-the-fly simulations. Unfortunately, neither approach accounts for nuclear quantum effects, and both suffer from strong coherence and slow decoherence, necessitating additional approximations.^{8–11}

Nonadiabatic semiclassical implementations for on-the-fly simulations are in their infancy, with the *ad hoc* symmetrical quasiclassical (SQC) method showing some promise.^{12,13} The linearized semiclassical (LSC) approach^{14,15} is a rigorous alternative to the SQC approximation that two of us recently demonstrated can be used for on-the-fly simulations of excited state dynamics.¹⁶ LSC offers two key advantages: (i) it directly approximates the quantum correlation function, allowing us to compute experimental observables;

and (ii) the implementation involves evolving independent classical trajectories from an initial quantum Wigner distribution and does not involve any parameters unlike FSSH (decoherence corrections) or AIMS (spawning thresholds). LSC is highly parallelizable with a computational expense that scales almost classically with system dimensions, making it a very promising candidate for on-the-fly simulations of excited state dynamics in condensed phase environments.

Beyond the method chosen for the dynamics, the main determination of computational cost for NAMD is the electronic structure calculations of the ground and excited state gradients as well as the nonadiabatic coupling (NAC) vectors. For many NAMD simulations of bond-breaking reactions, a multi-reference method such as state-averaged complete active space self-consistent field (SA-CASSCF) or CAS with configuration interaction (CAS-CI) is employed.^{17–19} In other nonadiabatic processes, more affordable single reference excited state methods such as linear response time-dependent density functional theory (TDDFT) are used.^{20–22} TDDFT, especially when employing a long-range corrected hybrid functional, can often provide accurate vertical excitation energies near the ground state minimum,^{23–26} but due to its single reference nature, it will generally poorly describe bond breaking, biradical intermediates, and crossings between ground and excited state potential energy surfaces.²⁷ TDDFT has recently been shown to be accurate in modeling conical intersections between excited states,²⁸ and variants of excited state single reference methods, e.g., with references with different spins, particle numbers, or excitation levels, have shown promise in capturing non-dynamic correlation^{29–33} but have not seen widespread use for NAMD simulations.

The TeraChem software package is built to take advantage of GPU parallelization^{34,35} and offers significant speed ups in quantum electronic structure calculations compared to CPU-based packages. A variety of excited state electronic structure methods have been implemented within TeraChem, including SA-CASSCF,³⁶ full-CI,³⁷ CASCI,³⁸ and TDDFT.^{39,40} These GPU-accelerated implementations have been used with both AIMS and surface hopping NAMD simulations.^{19,41–44} The recent extension of TeraChem to a protocol buffer client-server model has allowed for a straightforward interface between TeraChem's electronic structure capabilities and any external code for on-the-fly dynamics.⁴⁵

Motivated by the success of the recent on-the-fly nonadiabatic LSC simulations, here we introduce the PySCES code (Python code for Semiclassical Dynamics with on-the-fly Electronic Structure) that interfaces the LSC method with the TeraChem electronic structure code. We explain the interface between the LSC Python code and TeraChem, describing how NAMD can be run in parallel over multiple GPU nodes and how we account for the phase difference in wave function that leads to sign swapping of the NAC vector. We compare, for a single NAMD trajectory, the excited state occupations for ethylene using the GAMESS electronic structure code⁸⁰ and TeraChem, then showcase the performance of the code for two larger test systems: solvated fulvene and the charge transfer in a zinc phthalocyanine-C₆₀ donor-acceptor complex.

II. METHODS

Here, we provide a brief overview of the LSC method for non-adiabatic dynamics, introduce the relevant equations of motion,

and describe the distributions from which initial conditions are sampled.

A. Linearized semiclassical approximation to real-time correlation functions

We start with a general real-time quantum correlation function between two operators, $\hat{A}$ and $\hat{B}$,

$$C_{AB}(t) = \text{Tr} \left[\hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right], \quad (1)$$

where $\hat{H}$ is the Hamiltonian. The path integral formulation recasts a real-time quantum propagator into a sum over all possible paths in phase space, rendering Eq. (1) a double integral over forward and backward paths. The LSC approximation is obtained by linearizing the difference in action between the forward and backward paths to obtain^{15,46}

$$C_{AB}^{LSC}(t) = \frac{1}{(2\pi\hbar)^N} \iint d\mathcal{X}_0 d\mathcal{P}_0 A_W(\mathcal{X}_0, \mathcal{P}_0) B_W(\mathcal{X}_t, \mathcal{P}_t), \quad (2)$$

where A_W and B_W are the phase space functions resulting from the Wigner transforms⁴⁷ of $\hat{A}$ and $\hat{B}$, respectively. In Eq. (2), all the system degrees of freedom, electronic and nuclear, are represented by their corresponding phase space variables, $(\mathcal{X}, \mathcal{P})$. The LSC approximation to the quantum correlation function is obtained by sampling trajectory initial conditions from the function A_W at time $t = 0$, propagating trajectories under the classical analog Hamiltonian for a time t , and using the time-evolved phase space variables to evaluate function B_W .

We note that the LSC dynamics is entirely classical, and trajectories are independent of each other. Therefore, the parallelization of LSC dynamics is simple and intuitive, in contrast to more elaborate quantum dynamics methods such as MCTDH⁴⁸ and AIMS⁴⁹ and less approximate semiclassical methods with non-negligible interactions between trajectories.⁵⁰ However, the lack of trajectory interference in LSC dynamics means that the method fails to describe nuclear quantum coherence effects and deep tunneling, although coherences between electronic states are captured owing to the nature of the electronic mapping variables and the associated nonadiabatic equations of motion discussed in Sec. II B.^{51–53} Given that the present work is aimed at enabling simulations of high-dimensional systems where nuclear quantum coherences are not expected to play a significant role, we predict that the limitations of LSC dynamics will not significantly affect the resulting accuracy.

B. Mapping approach and nonadiabatic equations of motion

To express the quantum Hamiltonian in phase space and subsequently derive the associated equations of motion, we adopt the so-called mapping approach. Here, we limit our discussion to the Meyer Miller Stock Thoss (MMST) mapping,^{54–56} although several mapping protocols have been introduced recently that aim to better preserve the electronic phase space.^{57,58} For a comparative study of different types of mapping approaches in the context of on-the-fly LSC dynamics, we refer readers to an earlier study.¹⁶

In the MMST mapping, the occupation of electronic states is expressed using the ladder operators of a quantum harmonic oscillator,

$$\begin{aligned} |n\rangle &\mapsto \hat{a}_n^\dagger \\ |n\rangle\langle m| &\mapsto \hat{a}_n^\dagger \hat{a}_m, \end{aligned} \quad (3)$$

where $\hat{a}_n = (\hat{x}_n + i\hat{p}_n)/\sqrt{2}$ and $\hbar = 1$. The general Hamiltonian for F states is then

$$\hat{H} = \frac{1}{2} \mathbf{P}^\dagger \boldsymbol{\mu}^{-1} \mathbf{P} + \sum_{n,m}^F \varepsilon_{nm}(\mathbf{R}) |n\rangle\langle m|, \quad (4)$$

which can thus be reformulated in terms of nuclear and electronic phase space operators,

$$H = \frac{1}{2} \mathbf{P}^\dagger \boldsymbol{\mu}^{-1} \mathbf{P} + \sum_{n,m}^F \frac{1}{2} (x_n x_m + p_n p_m - \delta_{nm}) \varepsilon_{nm}(\mathbf{R}), \quad (5)$$

where $(\mathbf{R}, \mathbf{P})$ and $\boldsymbol{\mu}$ are the nuclear phase space operators and the associated mass vector, respectively, and $\varepsilon_{nm}(\mathbf{R})$ is the element of the diabatic potential energy matrix. In the adiabatic representation more suitable for interfacing with *ab initio* electronic structure programs, Eq. (5) becomes^{54,59}

$$\begin{aligned} H &= \frac{1}{2} \mathbf{P}_{\text{kin}}^\dagger \boldsymbol{\mu}^{-1} \mathbf{P}_{\text{kin}} + \sum_n^F \frac{1}{2} (x_n^2 + p_n^2 - 1) E_n(\mathbf{R}) \\ &= \frac{1}{2} \mathbf{P}_{\text{kin}}^\dagger \boldsymbol{\mu}^{-1} \mathbf{P}_{\text{kin}} + \frac{1}{F} \sum_n^F E_n(\mathbf{R}) \\ &\quad + \frac{1}{4F} \sum_{n,m}^F (x_n^2 + p_n^2 - x_m^2 - p_m^2) (E_n(\mathbf{R}) - E_m(\mathbf{R})), \end{aligned} \quad (6)$$

where $E_n(\mathbf{R})$ is the energy of the n th adiabatic state, and $\mathbf{P}_{\text{kin}}$ is the kinematic momentum,⁵⁹

$$\mathbf{P}_{\text{kin}} = \mathbf{P} + \sum_{n,m}^F x_n p_m \mathbf{d}_{nm}(\mathbf{R}), \quad (7)$$

and $\mathbf{d}_{nm}(\mathbf{R}) = \langle n | \frac{\partial}{\partial \mathbf{R}} | m \rangle$ is the NAC vector between adiabatic states $|n(\mathbf{R})\rangle$ and $|m(\mathbf{R})\rangle$. The second equality in Eq. (6) is the result of an exact transformation called symmetrization,^{12,59} which has been found to yield more accurate classical analog dynamics.

The equations of motion for the dynamical variables of the system are now derived from the classical analog of the Hamiltonian in Eq. (6). The complete forms of the equations of motion are presented in the Appendix. The force terms necessary to integrate the equations of motion require input from electronic structure $[E_n(\mathbf{R}), \mathbf{g}_n = \frac{\partial E_n(\mathbf{R})}{\partial \mathbf{R}}]$, and these are obtained from on-the-fly *ab initio* calculations. It bears reiterating that these equations of motion effectively describe nonadiabatic dynamics in multiple coupled electronic states, despite the fact that time evolution is entirely classical in both the electronic and nuclear degrees of freedom. The ability to describe electronic coherences and the efficiency resulting from using classical dynamics render LSC a compelling option for large-scale *ab initio* NAMD simulations.

C. Sampling of initial conditions

The initial conditions for an LSC simulation span $2(F+N)$ variables, two phase space variables for every F electronic states and N nuclear modes. Those variables are sampled from A_W , where $\hat{A} = e^{-\beta \hat{H}} / Z$ is the thermal density operator with $\beta = 1/k_B T$ and $Z = \text{Tr}[e^{-\beta \hat{H}}]$. We assume that initially the nuclear and electronic variables can be treated independently, which allows us to sample the nuclear variables from $[\hat{p}_n]_W(\mathbf{R}, \mathbf{P})$ and the electronic ones from $[\hat{p}_e]_W(\mathbf{x}, \mathbf{p})$, where $\hat{p}_n$ and $\hat{p}_e$ are the nuclear and electronic density operators, respectively (i.e., $\text{Tr}_e[\hat{p}_n] = \text{Tr}_e[\hat{p}_e] = 1$), and the notation $[\dots]_W$ indicates a Wigner transform. Making a harmonic approximation for the N nuclear vibrational normal modes yields an analytic expression for the nuclear Wigner distribution,

$$[\hat{p}_n]_W = \prod_i^N \frac{1}{2\pi} \exp \left[-\tanh \left(\frac{\beta \omega_i}{2} \right) \left(\frac{P_i^2}{\mu_i \omega_i} + \mu_i \omega_i R_i^2 \right) \right], \quad (8)$$

where ω_i and μ_i are the frequency and the reduced mass of the i th vibrational mode, respectively. For the purpose of excited state dynamics simulations following an impulsive photo-excitation and within the Franck–Condon approximation, nuclear modes are assumed to be in thermal equilibrium on the electronic ground state for which $\{\omega_i\}$ and $\{\mu_i\}$ are calculated.

Similarly, the initial electronic state population is assumed to be 1 in the initial photo-excited state i and zero for all other states,

$$|\alpha\rangle\langle\alpha| = \delta_{i\alpha}, \quad (9)$$

where $\delta_{i\alpha}$ is a Kronecker delta. The sampling functions for each state thus form the system of equations

$$\begin{aligned} [|\alpha\rangle\langle\alpha|]_W &= 2^{F+1} \left(x_\alpha^2 + p_\alpha^2 - \frac{1}{2} \right) \exp \left[-\sum_k^F (x_k^2 + p_k^2) \right] \\ &= \delta_{i\alpha}. \end{aligned} \quad (10)$$

Solving Eq. (10), we obtain equations describing circles in phase space with radii, r_i ,

$$\begin{aligned} x_i^2 + p_i^2 &= r_i^2, \\ x_\alpha^2 + p_\alpha^2 &= \frac{1}{2} \quad \text{for } \alpha \neq i, \end{aligned} \quad (11)$$

where the values of the radii vary with F . For some F values, there exist two possible roots for the value of r_i^2 from Eq. (10). Following previous work, we chose the larger one of the two for the numerical stability of subsequent trajectory propagation.⁶⁰

III. COMPUTATIONAL WORKFLOW AND IMPLEMENTATION

The computational expense of the LSC nonadiabatic dynamics stems from the computation of the electronic structure variables, $E_n(\mathbf{R})$, $\mathbf{g}_n$, and $\mathbf{d}_{nm}(\mathbf{R})$, for all electronic states under consideration at a given nuclear geometry, $\mathbf{R}$. Here, we describe how the workload of the TeraChem electronic structure calculations is distributed among the available GPU compute nodes used in a simulation and how they communicate with our LSC code to propagate nuclear motion. The PySCES code is available open-source on GitHub,

along with appropriate documentation and input files to test the code.⁶¹

Figure 1 depicts the workflow of running an LSC simulation with the PySCES code, starting with an optimized geometry. The user provides PySCES with the location of a TeraChem normal mode analysis of the optimized structure, for which initial nuclear and electronic conditions are assigned from the Wigner distributions in Eqs. (8) and (11), respectively. Starting from this new randomized geometry and for all subsequent geometries throughout the simulation, both the gradients $\mathbf{g}_i$ of each adiabatic energy surface and the NAC vectors $\mathbf{d}_{ij}$ between two surfaces need to be computed. The signs of the NACs are then checked and, if necessary, corrected for random sign-flips between time steps that occur due to a change in phase of the wave function (see Sec. III A below). We then obtain updated nuclear and electronic variables

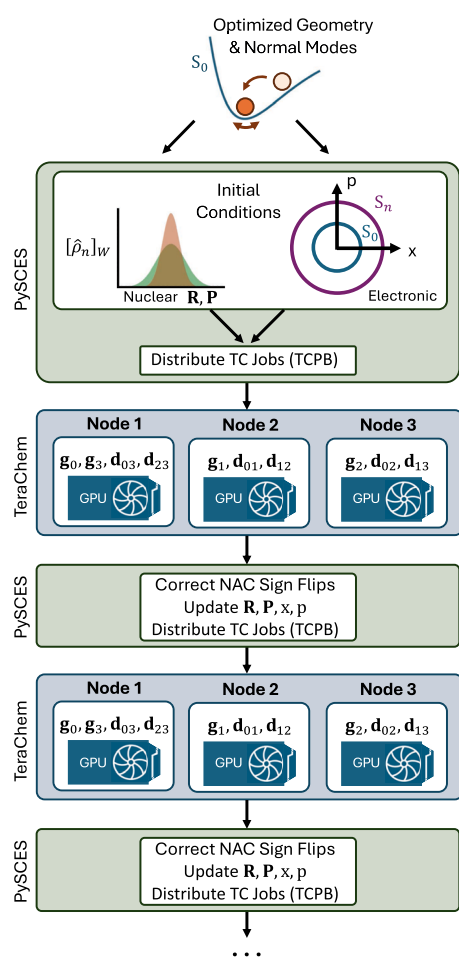


FIG. 1. Workflow of the PySCES code, an LSC-TeraChem interface. Initial nuclear positions and momenta of the normal modes are sampled from a Wigner distribution, and electronic mapping variables are initialized to populate the desired state as discussed in the text. The TeraChem gradient and NAC jobs are then distributed across GPUs. The NAC vectors are assessed, with a sign flip assigned as necessary, and then the nuclear and electronic positions and momenta are updated for the next step of the trajectory.

(position and momenta) via a Runge-Kutta fourth-order integrator as implemented in SciPy.^{62,63} The updated nuclear geometries are then used once again as inputs for electronic structure calculations, and the process continues. All relevant information, including the nuclear and electronic variables, gradients, NAC vectors, timings of the individual electronic structure calculations, and checkpoint files needed to restart the trajectory, is logged throughout the simulation as well.

Since the number of NAC vectors grows quadratically with the number of electronic states used in the simulation, the amount of electronic structure information needed for a single time step of a large molecular system can, very quickly, become prohibitively expensive to compute unless the work is parallelized across multiple computational nodes. Because each gradient and NAC computation can be performed independently from one another, we utilized the TeraChem Protocol Buffer (TCPB) library⁴⁵ to efficiently distribute the workload across all available GPUs within a computing network. As opposed to running TeraChem with multiple input files, TeraChem is instead executed in a server mode that receives and transmits “job” information as requested by PySCES via the TCPB library. A request to perform a particular job (gradient and NAC) is sent to the server along with the atomic coordinates, the basis set, the electronic structure method, and any setting otherwise used in a traditional TeraChem input file. Once all of the required gradients and NAC vectors are computed (energies E_i are also computed with each job), their results are summarized and used to update the molecular geometry.

One of the benefits of using TCPBs is that the electronic structure jobs can be efficiently parallelized in environments that have a limited or varying number of GPUs per compute node. For parallel jobs, multiple TeraChem servers can be run on a single or separate compute node, and each server can utilize any number of GPUs available on its respective node. PySCES will then distribute all computations to each of the servers on the same network. As the performance of TeraChem varies based on the hardware environment, such as the GPU model or the number of GPUs per compute node, it is left to the user to allocate TeraChem servers themselves and simply provide the IP addresses and port numbers to PySCES via the input file. PySCES will then distribute the gradient and NAC jobs in a round-robin manner across all specified servers, as depicted in each of the labeled “Node” blocks in Fig. 1.

Each job keeps track of the previously computed coefficients, both for the ground and excited states, and uses these files as inputs for the next job to speed up subsequent calculations. Completed jobs transmit minimal information from TeraChem through the network (only the energies, gradients, and NACs), and the remaining electronic structure properties of each job are copied from their local output files at every time step. Furthermore, because each computation is run as a separate job in TeraChem, GPUs only need to be initialized once with the server, a task that would otherwise introduce several seconds of inactive computation time at the start of every job.

For certain systems or geometries, electronic structure calculations of the ground or excited state can sometimes fail to converge, and then the NAMD simulation will need to be restarted. Additional TeraChem options, e.g., modified convergence or integral thresholds, can help limit or prevent these failures. We have implemented the ability to specify additional TeraChem runtime options for spe-

cific gradient/NAC jobs or for a specified number of initial time steps at the start of a simulation. These options can also request the calculation of additional electronic structure properties, such as ground and excited state point charges, throughout a simulation. We note that computing dynamical observables in the LSC method requires an ensemble of classical trajectories that can be evolved as independent simulations in parallel. The current implementation of PySCES does not parallelize this step.

A. Sign of the nonadiabatic coupling vector

We evaluate the NAC vectors using the states' adiabatic wave function representation as computed by TeraChem. Adiabatic wave functions are, however, defined only up to a phase factor, which can lead to phase inconsistencies between different time steps.⁶⁴ This phase inconsistency can also lead to a change in the sign of the calculated NACs, significantly affecting the resulting dynamics. In practice, TeraChem always uses real-valued state functions. Thus, during the propagation, the state functions (and the sign of the NAC vectors) can either keep their phase or change by a factor of -1 .

In order to preserve NAC sign consistency, we use two-level decision criteria during run time to estimate whether such a sign swap occurred for the NAC vectors between the current and previous time steps. The first level is to check if the NAC itself flipped the sign unexpectedly, while the second level is to check if the transition dipole moment (TDM), computed with the same adiabatic states, also flips the sign. We are able to combine both criteria by leveraging the property that if one of the adiabatic states flips a sign, then both the NAC and the TDM will contain the same sign flip.

Figure 2(a) illustrates the first level of the procedure in one dimension. In this scheme, we use the NAC from the two previous time steps to linearly extrapolate an estimation for the next time step. We then check whether the direction of the NAC from TeraChem matches our expectations by calculating the dot product of the TeraChem computed NAC vector with our extrapolated one. A positive dot product indicates that a sign-flip has not occurred between the current and previous time steps, and we continue the dynamics using the NAC from TeraChem. If instead, the direction of the NAC does not match our expectations (with a negative dot product), then we perform the second-level check by using the same extrapolation scheme to determine whether the TDM for the two corresponding states also flipped sign. If the transition dipole does not show a sign swap, we accept the sign swap of the computed NAC. However, if both the TDM and the NAC have negative dot products, then we correct the TeraChem computed NAC by a factor of -1 and continue the dynamics with the correction. We note that the extrapolated NAC is only used as a check for sign flips and is never used in the dynamics itself.

Figure 2(b) shows the first component of the NAC vector for photo-excited ethylene with and without the extrapolation correction scheme for a single (2, 2) SA-CASSCF trajectory with identical initial conditions. Without the correction, the NAC clearly undergoes discontinuous jumps due to the sign swaps, whereas the NAC with the correction smoothly evolves along the trajectory. Figures 2(c) and 2(d) show the corresponding S_2 and S_1 occupations along the trajectory, with substantial deviations observed after 10 fs.

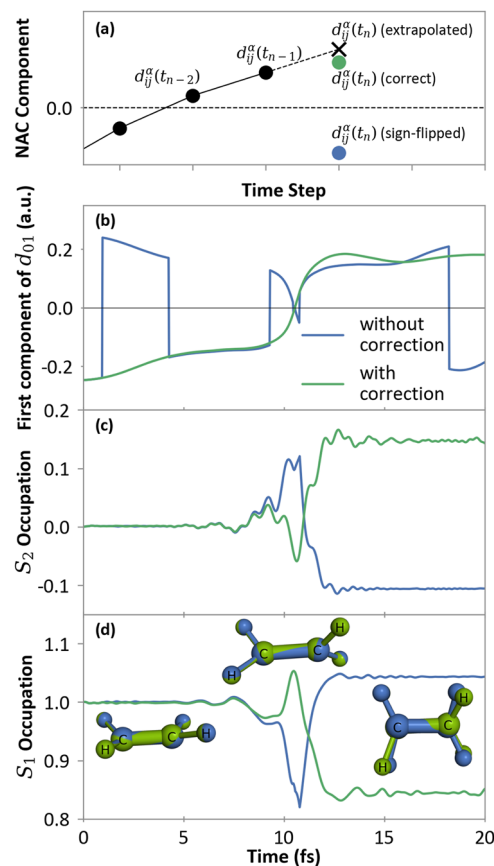


FIG. 2. (a) For a single trajectory, we show the linear extrapolation scheme implemented in PySCES to determine the sign of the NAC vector components, d_{ij} . (b) The value of the first component of the NAC vector between S_0 and S_1 for ethylene shown without correction (as computed) and with correction. (c) Corresponding populations of the S_2 and (d) S_1 states with and without the sign swap for the NAC vector.

IV. RESULTS AND DISCUSSION

We next show results for LSC trajectories generated using PySCES with the TeraChem TCPB interface. First, we validate our implementation through comparison to the GAMESS (version 2023 R1) results using identical initial conditions for a single ethylene trajectory. Next, we report timings for larger systems.

All TeraChem jobs in this paper were performed with version 1.9-2023.09-dev and ran as a docker image using Singularity 3.8.3. Computation nodes utilized a pair of NVIDIA A100 GPUs with 40 GB of VRAM in conjunction with dual 28 core Intel Xeon Gold 6330 CPUs. All TeraChem servers were initiated with both A100 GPUs on a single node.

A. Comparison of ethylene dynamics with GAMESS and TeraChem

To verify our implementation within PySCES with the TeraChem interface, we compared the dynamics of ethylene using (2, 2) SA-CASSCF with both GAMESS and TeraChem drivers. An

initial nuclear geometry was generated from a Wigner distribution over normal mode coordinates and frequencies determined from a ground state CAM-B3LYP/6-31G(d) computation. Electronic phase space variables were sampled from the circles in phase space defined in Eq. (11).⁶⁰ The S_0 , S_1 , and S_2 states were used in this assignment with an initial photoexcitation to S_1 , i.e., $F = 3$, and the radii, $r_{S_1} = 1.559$, $r_{S_2} = r_{S_0} = 0.707$. Both trajectories with GAMESS and TeraChem used the exact same initial conditions for each trajectory.

The resulting state energies and state populations from a single trajectory are shown in Fig. 3. The dynamics are in excellent agreement, both in energy and population, until 30 fs, when small numerical differences in the electronic structure output lead to visible differences in their trajectories. We verified that these differences remain even when employing full double precision and an integral threshold of 10^{-20} in TeraChem. Our testing revealed that, at least for ethylene, small differences in nuclear position can lead to large differences in NAC vectors. Take, for example, the avoided crossing that occurs around 46 fs when the S_1 and S_2 energies approach each other in Fig. 3. At this simulation frame, the minimum RMSD⁶⁵ between the geometry produced by the GAMESS and TeraChem driven trajectories is less than 0.03 Å, whereas the magnitude of their NAC vectors differed by over 30%, thus sending the TeraChem and GAMESS simulations on slightly different trajectories that eventually diverge from each other. However, we expect that, when averaged over multiple trajectories with varying initial conditions, the average rate of population change resulting from simulations utilizing both drivers should be very similar.

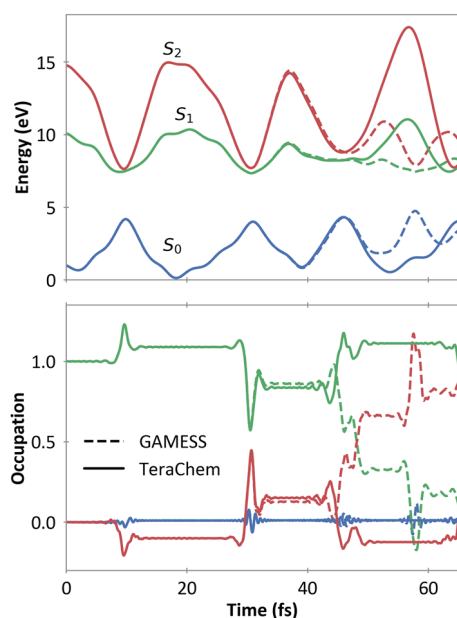


FIG. 3. Energy and occupations of the S_0 , S_1 , and S_2 states of ethylene for a single LSC trajectory with identical initial conditions generated by PySCES. The deviation between GAMESS and TeraChem due to a buildup of small numerical differences becomes apparent after 35 fs.

B. Computational timings

We next showcase the performance of PySCES for two larger systems using the TeraChem TCPB library. First, we compare timings for 1 and 2 nodes for solvated fulvene as we increase the size of the explicit solvent environment and demonstrate the scaling of our NAMD implementation as a function of system size. Next, we model the charge transfer in an excited zinc phthalocyanine- C_{60} donor-acceptor complex and provide insights into the computational effort needed to run NAMD LSC simulations for systems consisting of over 100 heavy atoms.

1. Fulvene in acetonitrile

The fulvene molecule, which is a well-studied benchmark system within the nonadiabatic dynamics community, possesses a sloped S_0/S_1 conical intersection along the methylene torsion coordinate that facilitates population transfer between the S_0 and S_1 surfaces after photo exciting to S_1 .^{43,66,67} In most studies of the conical intersections and nonadiabatic dynamics of fulvene, a multi-configurational approach with at least the π system is employed, i.e., a CASSCF(6, 6) wave function description. However, spin-flip TDDFT has also been employed to characterize the conical intersection,⁶⁸ as well as TDDFT within the Tamm-Dancoff approximation (TDA) to explore the region of potential around a conical intersection of fulvene as it rearranges to benzene.⁶⁹ Here, we do not perform a detailed study of the nonadiabatic dynamics of fulvene, and so we are not particularly concerned with the choice of electronic structure method and employ TD-CAM-B3LYP/6-31G(d) within the TDA to model the S_0 , S_1 , and S_2 states of fulvene in acetonitrile within the LSC approach.

The character of a conical intersection, as well as the nonadiabatic dynamics of chromophores through such intersections, will be affected by a solvent environment. However, such effects are rarely considered within NAMD simulations due to the computational expense of including explicit solvent molecules in on-the-fly dynamics. With the increased computational efficiency of TeraChem for large-scale electronic structure calculations, solvated chromophore NAMD, although still computationally formidable, becomes feasible within PySCES. We next show the performance of PySCES employing TeraChem as we increase the amount of explicit solvent included in the electronic structure calculations.

Individual fulvene and acetonitrile molecules were geometry optimized in isolation with TeraChem using CAM-B3LYP/6-31G(d). The PACKMOL⁷⁰ program was then used to generate a 20 Å³ solvated box of 200 acetonitrile molecules with the fulvene at the center, from which the closest 20 solvent molecules to the fulvene solute were selected to generate configurations for timings. Solvent molecules were then sorted by their distance from the fulvene center to generate configurations with fewer solvent molecules. A final ground state geometry optimization and normal-mode analysis were performed on each of the fulvene-solvent clusters, for which the geometries and normal mode properties of each cluster were used to generate initial conditions for the NAMD simulations according to Eq. (8). The smallest system, consisting of a single acetonitrile solvent molecule and fulvene, as well as the largest 20 solvent molecule-fulvene subsystem, are depicted as insets in Fig. 4(a).

In total, 15 chromophore-solvent subsystems were constructed and optimized, and the LSC NAMD was simulated for at least 1 fs

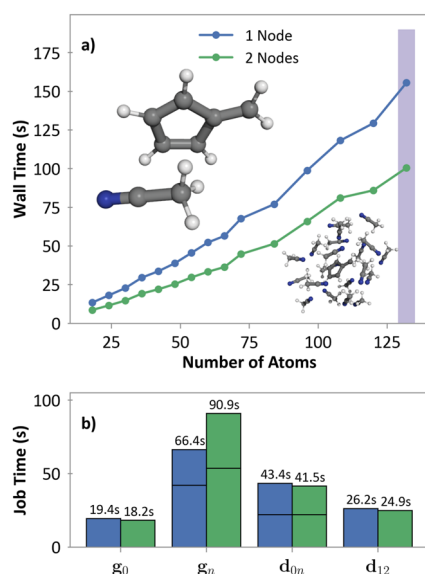


FIG. 4. (a) Average wall time for a single dynamics step for solvated fulvene using S_0 , S_1 , and S_2 states computed with CAM-B3LYP/6-31G(d). The increasing number of atoms is due to the increase in the number of acetonitrile solvent molecules included in the calculation. (b) Timings for the fully solvated system (136 atoms) broken down into the different gradient g_n and nonadiabatic coupling d_{mn} calculations over one (blue) and two (green) nodes. The total job time for a particular type of calculation is shown atop each set of bars.

with a 1 a.u. time step. CAM-B3LYP/6-31G(d) was also used for all simulations, and S_1 and S_2 excited states were computed with TDDFT within the TDA. The last 40 time steps of all simulations were used in our benchmarks, averaging the computational time needed to compute individual gradients and NAC vectors between the three states as well as the total wall time for a NAMD time step. Each time step within a simulation uses the ground state molecular orbitals and excited state guess coefficients of the previous geometry as the initial guess for the next TeraChem calculation. To ensure that our statistics are not influenced by time steps that do not have these initial guesses available, we eliminated the first few sets of timings of each simulation from our averaging. We compared the performance of using TCPBs to distribute work over multiple computers on the same network, running all 15 simulations on both a single and dual node setup.

The resulting wall clock timings for one and two compute nodes are shown in Fig. 4(a), where we show that as we increase the number of atoms in the solvent region, the computational time increases linearly, at least up to system sizes of 136 atoms in total. Figure 4(b) further decomposes the average time spent by TeraChem to compute each of the gradient and NAC vectors for the largest 20 solvent molecule-fulvene system, with the wall timings highlighted in purple in Fig. 4(a). When two nodes are used, all gradient and NAC “job times” do not sum to the “wall time” as indicated by the green line in Fig. 4(a); the wall time measures the real-world time as seen by the user while all of the TeraChem jobs are simultaneously running, whereas the job time is the cumulative time measured by the individual nodes themselves.

We find that for the job timings for solvated fulvene, shown in Fig. 4(b), excited state gradients take the longest time to compute, with gradients for the S_1 state taking the longest as subsequent calculations of higher lying states can use previous excited state vectors to reduce job time. As discussed in Sec. III, each gradient and NAC vector are computed as separate jobs within TeraChem, with the ground state orbital and excited state coefficients of the previous job used in subsequent calculations and saved to the server’s local storage. Therefore, each TeraChem job that is performed after the S_1 gradient job uses these guess orbitals and coefficients. The NAC jobs are not much more expensive than higher energy (S_2 or greater) excited state gradient jobs. In Fig. 4(b), we find that NAC vectors involving two excited states take longer time to compute than those involving the ground state, a trend also observed for the charge transfer system discussed later.

Figure 4(a) also shows that using two compute nodes can decrease the total wall time for a single simulation time step, although not perfectly with double the performance. To avoid having to save the ground and excited state coefficient files to a network shared storage system for every time step and every TeraChem excited state job, each server maintains its own local copy of the coefficient files. This strategy further ensures that future users of PySCES, who may wish to distribute their TeraChem jobs over dissimilar hardware, are not faced with the possibility that the (binary) coefficient files are incompatible between the different computing environments. As a result, each TeraChem server generates its own ground and excited state coefficient files.

For the dual node set up, the S_1 gradient (computed on node 2) will not have a ground state orbital file since it is the first job that is computed on this node. As evident in Fig. 4(b), the average S_1 gradient job time using two nodes is indeed larger than that of the equivalent S_1 gradient job using only one compute node. Similarly, the S_2 gradient (computed on node 1) does not have the excited state coefficient file since the previous gradient job on the same node was only for the S_0 state, also leading to a larger job time in Fig. 4(b) compared to the single node setup. Nevertheless, a performance gain of 153% was observed when using two compute nodes over just one. We expect that the relative performance gains using two nodes should get closer to the 200% limit when more than two excited states are involved, such as we describe below for the zinc-phthalocyanine and fullerene charge transfer systems.

2. Zinc-phthalocyanine and fullerene charge transfer

Another system that we applied the PySCES LSC-TeraChem interface to is the charge transfer at the interface of zinc phthalocyanine (ZnPc) and fullerene (C_{60}), a system of potential interest in organic photovoltaics.^{71–73} The ultrafast charge transfer dynamics of this system have previously been simulated employing TDDFT with the Ehrenfest and FSSH approaches.^{74,75} For the face-on configuration, Liu *et al.* found that charge transfer from a higher energy locally excited state on the ZnPc to lower energy charge transfer states with the electron transferred to the C_{60} acceptor is thermodynamically favorable, with exciton charge transfer completed within 100 fs.⁷⁵

For the face-on configuration of ZnPc- C_{60} , we optimized the geometry with CAM-B3LYP/6-31G and performed a normal mode analysis on the full 117 atom system. TDDFT calculations were performed with the same level of theory within the TDA. Our excited

state characterization showed the transition from the ground state to the S_4 state was the brightest and localized on ZnPc, in agreement with the analysis of Liu *et al.* We began the LSC NAMD trajectory with full occupation of the S_4 state at the optimized geometry, initiating the dynamics with only the momenta sampled from a Wigner distribution and including NACs between excited states S_0 through S_4 . In order to demonstrate the ability of LSC to simulate charge transfer between the two species and to measure the computational cost of performing the necessary electronic structure calculations, removing the Wigner sampling over nuclear positions allowed us to achieve these goals with fewer time steps. Initialization of electronic variables was performed to occupy the bright S_4 state only, and the trajectory was then propagated with a 1 a.u. step size.

For our single LSC trajectory depicted in Fig. 5, we found the charge transfer to occur from the S_4 state to the S_1 state within 25 fs. Figure 5(a) shows the excited state and ground state density difference plots at different times during the trajectory, where we weight the density difference according to the occupation of the excited

state, as shown in Fig. 5(b). For example, at $t = 1.5$ fs, where a crossing between the S_4 and S_3 surfaces occurred, the population was predominantly on the S_3 surface, so the density difference shown is primarily between S_3 and S_0 . Similarly, at the end of the trajectory, the population is mostly in the S_1 state, and the density difference shown is mostly that for S_1 and S_0 . At $t = 16$ fs shortly after the S_4 and S_3 avoided surface crossing, this state has mixed locally excited and charge transfer character, and the occupation is shared between S_4 and S_3 . Figure 5(b) shows the TDDFT energies of the four lowest lying excited states, colored according to the occupation during the trajectory. Surface crossings and avoided surface crossings occur throughout the trajectory, with state mixings often leading to population transfer between states, notably at $t \approx 14$ fs, $t \approx 17$ fs, and $t \approx 21$ fs. Note that these LSC NAMD dynamics are for a single trajectory, and an ensemble of LSC NAMD trajectories would be required to compute the LSC correlation function.

For the ZnPc- C_{60} donor-acceptor system, modeled with 661 basis functions and four excited states, we show the job time for electronic structure contributions averaged across the trajectory in Fig. 5(c). The calculation of the excited state gradient and the NAC vectors between excited states takes up the majority of the computation time. Because of the number of states used throughout the simulation, about 66% of the computational job time was spent computing the 10 NAC vectors. We note that for this trajectory, we see little participation from the S_0 state in the dynamics, suggesting that we may be able to eliminate this state from future simulations of the dynamics, thereby reducing the number of NAC vectors to be computed. The total job time for a single LSC step averaged across the trajectory was 784 s, but parallelization over two GPU nodes brought the average wall time per step to 399 s, a performance gain of 196%. Similarly, with the fulvene system in Fig. 4(b), which was also parallelized over two compute nodes, the first two excited state gradients, g_1 and g_2 , take the longest to compute as they are the first and only jobs that solve for the TDDFT excited state coefficients. However, because there are many more jobs after the S_1 and S_2 gradient calculations that use the excited state coefficients than in the fulvene system, the computational performance is nearly double that of a single node. We conclude with a reminder that the simulations reported here demonstrate the abilities of the PySCES code and document timings for a single trajectory; however, in an actual investigation of excited state dynamics, an ensemble of independent trajectories would be evolved to compute the corresponding LSC correlation function.

V. CONCLUSIONS

We introduce PySCES, an LSC-TeraChem Python interface code to enable GPU-accelerated NAMD simulations using classical dynamics trajectories within an extended phase space of nuclear and electronic variables. Our interface makes use of the TeraChem protocol buffer client-server model and can be parallelized over multiple GPU nodes, opening the door for semiclassical NAMD simulations of excited state dynamics in the condensed phase.

We detail our computational workflow and implementation, including a linear extrapolation scheme for determining the sign of the NAC vector. Computational timings are presented for two NAMD benchmark systems. The first system is fulvene solvated in acetonitrile, where we show a linear scaling in compute time as

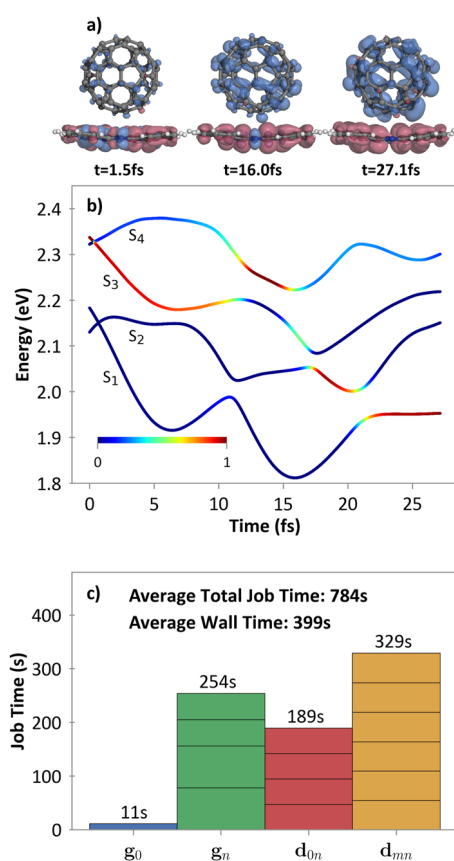


FIG. 5. (a) ZnPc- C_{60} excited state and ground state density differences at three different times in the LSC NAMD trajectory generated with PySCES. C_{60} accepts the charge after a local, bright photoexcitation of the zinc phthalocyanine to the higher lying S_4 state. (b) TD-CAM-B3LYP/6-31G excitation energies computed during the LSC trajectory with the corresponding occupation shown in the color bar. (c) Timings shown for electronic structure gradient g_n and nonadiabatic coupling d_{mn} calculations performed with CAM-B3LYP/6-31G averaged over all steps of LSC dynamics that included five electronic states: S_0 through S_4 .

we increase the amount of solvent included in the electronic structure calculations, and we show the performance of the code over one and two GPU nodes. The second benchmark system is a zinc-phthalocyanine donor face-on with a fullerene acceptor. We show the state occupations during the course of a single LSC NAMD trajectory, which shows population transfer from the locally excited bright state to lower energy dark charge transfer states over 25 fs. The corresponding timings show that the computation of the NAC vectors between excited states takes up a large portion of the total computation time.

Moving forward, we will continue to benchmark LSC NAMD against molecular systems studied using other on-the-fly nonadiabatic methods such as AIMS and surface hopping, with an emphasis on accuracy and numerical efficiency. We also plan to explore new and more efficient integrators and approaches to compute the NAC,⁷⁶ including its replacement with time-derivative coupling followed by its approximation by wavefunction interpolation, a commonly employed strategy in AIMS and surface hopping programs.^{77,78} Implementing these capabilities could further increase the efficiency of LSC NAMD simulations for complex excited state molecular phenomena in the condensed phase on an ultrafast timescale.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Christopher A. Myers: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal). **Ken Miyazaki:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Software (equal); Writing – original draft (equal); Writing – review & editing (equal). **Thomas Trepl:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (supporting); Software (equal); Writing – original draft (equal). **Christine M. Isborn:** Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Nandini Ananth:** Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request, along with files and software available on the GitHub repository for the PySCES code, <http://doi.org/10.5281/zenodo.11985696>.

APPENDIX: NONADIABATIC EQUATIONS OF MOTION

The equations of motion for the nuclear phase space variables, as well as the electronic mapping variables, are obtained from the classical analog mapping Hamiltonian in Eq. (6),

$$\dot{x}_n = \frac{p_n}{F} \sum_m^F (E_n(\mathbf{R}) - E_m(\mathbf{R})) + \sum_m^F x_m \mathbf{d}_{mn}(\mathbf{R}) \cdot \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (\text{A1})$$

$$\dot{p}_n = -\frac{x_n}{F} \sum_m^F (E_n(\mathbf{R}) - E_m(\mathbf{R})) + \sum_m^F p_m \mathbf{d}_{mn}(\mathbf{R}) \cdot \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (\text{A2})$$

$$\dot{\mathbf{R}} = \frac{\mathbf{P}_{\text{kin}}}{\mu}, \quad (\text{A3})$$

$$\begin{aligned} \dot{\mathbf{P}}_{\text{kin}} = & \sum_{n,m}^F (\dot{x}_n p_m + x_n \dot{p}_m) \mathbf{d}_{nm}(\mathbf{R}) \\ & - \frac{1}{4F} \sum_{n,m}^F (x_n^2 + p_n^2 - x_m^2 - p_m^2) (\mathbf{g}_n(\mathbf{R}) - \mathbf{g}_m(\mathbf{R})) - \frac{1}{F} \sum_n^F \mathbf{g}_n(\mathbf{R}), \end{aligned} \quad (\text{A4})$$

where $\mathbf{g}_n(\mathbf{R}) = \frac{\partial E_n(\mathbf{R})}{\partial \mathbf{R}}$ is the gradient of the adiabatic state $|n\rangle$. In deriving Eq. (15), the derivative of the nonadiabatic coupling vector $\mathbf{d}_{nm}(\mathbf{R})$ was tactically removed by utilizing the chain rule.³⁹ By recognizing $\Delta \mathbf{P} = \sum_{n,m}^F x_n p_m \mathbf{d}_{nm}(\mathbf{R}) \equiv f(\mathbf{x}, \mathbf{p}, \mathbf{R})$ and using V_{eff} to represent the electronic part of our Hamiltonian, we obtain

$$\begin{aligned} \dot{\mathbf{P}}_{\text{kin}} = & \dot{\mathbf{P}} + \frac{\partial \Delta \mathbf{P}}{\partial t} \\ = & -\frac{\mathbf{P}_{\text{kin}}}{\mu} \cdot \frac{\partial f}{\partial \mathbf{R}} - \frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} + \dot{\mathbf{x}} \cdot \frac{\partial f}{\partial \mathbf{x}} + \dot{\mathbf{p}} \cdot \frac{\partial f}{\partial \mathbf{p}} + \dot{\mathbf{R}} \frac{\partial f}{\partial \mathbf{R}} \\ = & -\frac{\partial V_{\text{eff}}}{\partial \mathbf{R}} + \sum_{n,m}^F (\dot{x}_n p_m + x_n \dot{p}_m) \mathbf{d}_{nm}(\mathbf{R}), \end{aligned} \quad (\text{A5})$$

which is in agreement with Eq. (15).

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