How Long Do Energy and Charge Transfer Take in a Model Buckminsterfullerene/Pentacene Heterojunction? Assessment of Fewest Switches Time-Dependent Density-Functional Tight-Binding with and without Long-Range Correction

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Tully-type mixed time-dependent long-range corrected density-functional tight-binding/classical surface-hopping photodynamics is used to investigate the nature of and time scales for energy and charge transfer in the simplest model of an organic photovoltaic heterojunction, namely a single molecule of buckminsterfullerene ($C_{60}$) together with a single molecule of pentacene. The distinction between energy and charge transfer is more difficult to make in practical calculations than might at first seem to be the case, but several criteria are used to make a clear distinction between these two phenomena. It is found that the excitation fluctuates from one molecule to the other, with the first change within about 20 fs. However it is only after 188±28 fs that real charge transfer occurs. This is commensurate with what is known from experiment and very different from the severe underestimate obtained when the same calculation is repeated without a long-range correction. The long-range charge separation is not feasible to simulate in this model due to lack off appropriate charge collection sinks. We believe that these encouraging results obtained with time-dependent long-range corrected density-functional tight-binding/classical surface-hopping photodynamics opens the way, because of their intrinsic computational efficiency compared with time-dependent long-range corrected density-functional theory/classical surface-hopping photodynamics, to investigating a larger variety of increasingly realistic model organic photovoltaic heterojunctions.

I. INTRODUCTION

So far, solar cell technology is dominated by silicon-based solar cells as these provide excellent energy output for the amount of energy obtained per amount of money spent. Part of the reason for this is, of course, the result of many years devoted to understanding and engineering silicon-based electronics [5]. However organic electronics is a rapidly developing technology based upon similar, but different, principles [6]. It is increasingly able to compete with traditional silicon-based technologies for niche applications, especially where ease of fabrication (including the possibility to print circuits with only minor modification of existant printing technology), lightness, and flexibility are concerned. And one of the very interesting niche applications of organic electronics is organic solar cells [also known as organic photovoltaics (OPV)] [4, 7–11]. According to the American National Renewable Energy Lab’s best energy efficiencies [12], crystalline silicon solar cell technology achieves between 25% and 30% efficiency, approaching the theoretical Shockley-Queisser efficiency of 33.16% [13]. In contrast, organic solar cells are currently limited to 10% to 12% efficiency at best. It is a challenge to know if this is close to some intrinsic limit of organic materials or whether significant increases in organic solar cell efficiency are still possible. Theoretical investigation of the fundamental mechanism of organic solar cell operation is likely to be helpful here. The accepted model of power conversion in the popular bulk heterojunction configuration is summarized in Table I. These steps highlight the importance of the heterojunction between an electron acceptor and an electron donor phase. Experimental evidence indicates that step (iii) occurs on a time scale on the order of about 100 fs (e.g., 200 fs for APFO3/PCBM [14], 70-100 fs for pentacene/C_{60} [15], ≤ 100 fs for MDMO-PPV/PC70BM and for PCPDTBT/PC_{70}BM [16], and 82 fs for p-DTS(FBTTh2)$_2$/PC_{71}BM [17]). This short time scale has sometimes been used by certain researchers (particularly those coming from a solid-state physics background) to neglect nuclear displacements during the CT process. However key photochemical events involving nuclear motion often occur on time scales of this same order of magnitude. This has led us to model the bulk heterojunction excitation dissociation event using techniques from the photochemical modeler’s toolbox, in particular mixed Tully-type quantum chemical/classical surface hopping photodynamics. Our specific objective is to obtain a better understanding of the types of photochemical phenomena that are occurring, and how quickly they are occurring, on the scale of a few hundred fs.

Charge separation in organic solar cells has been intensively studied and several review articles may be found in the literature [4, 7, 11, 18, 19]. The previously-mentioned six step model focusing on events at, or in the vicinity of, the heterojunction gradually emerged after Ching Tang’s key demonstration in the 1980s that the excitations which ultimately lead to charge separation originate on average at no more than 10 nm from the heterojunction [20]. Central questions inspired by this model concern the time scales and efficiencies of different steps. Step (v) is often mentioned as particularly puzzling. In-

### TABLE I: The generally accepted model for organic heterojunction solar cells [4].

| Step | Description |
|------|-------------|
| i)   | Exciton formation via photon absorption |
| ii)  | Exciton diffusion to the heterojunction |
| iii) | Exciton dissociation into closely-bound charge-transfer (CT) states at the heterojunction |
| iv)  | Dissociation of these CT states into charge-separated states composed of free mobile charges |
| v)   | Charge transport away from the heterojunction |
| vi)  | Charge collection at the electrodes |

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Indeed a back-of-the-envelope calculation based upon the idea of the formation of a dipole layer at the heterointerface suggests that the charges should be bound to the interface by on the order of 0.1-0.5 eV which may be compared to the amount of available thermal energy which is on the order of 0.025 eV \cite{19}, leading to the question of how organic heterojunction solar cells can work at all? Experimental techniques have provided some illumination, but are usually time-scale specific. Thus ultrafast spectroscopic methods can probe excited-state dynamics on subpicosecond time scales \cite{16, 21–24}, pump-probe electron field-induced second harmonic (EFISH) generation experiments \cite{25} can probe excited-state dynamics on ps to ns time scales, and electrical methods can probe free carrier motion on ns to ms time scales. As it stands, step (iii) of the model is known experimentally to take place on a time scale of the order of 100 fs, while step (iv) is known experimentally to take place on a ps time scale. The exact mechanism of step (iv) might be explained by “simple” diffusion in a hopping model \cite{25} but several other factors are likely to contribute or may provide better explanations \cite{19}. As we shall see, our simulations of a model heterojunction are designed, not to address the motion of well-separated charge carriers, but rather to gain insight into the initial charge separation event (iii).

Several considerations were taken into account in choosing a model heterojunction. Rather than focusing on components of the most efficient solar cells, we chose to focus on two well-studied components, namely pentacene (Pent) and buckminsterfullerene (C_{60}) as well as devices made with them as components. Pentacene belongs to the family of acenes which has been reviewed in Ref. \cite{26}. It is the largest conveniently synthesized member of the family and is a good choice as electron donor (D). Buckminsterfullerene is an excellent electron acceptor (A) and its derivatives are frequently found in organic solar cells \cite{27}. These molecules have been extensively studied both experimentally and theoretically. They have also been combined to make interesting A/D devices, including field-effect transistors \cite{28} and solar cells \cite{29, 30}. C_{60}/Pent devices have also been investigated in the context of singlet fission \cite{15, 30}. How pentacene molecules align themselves on a surface should depend both upon the type of surface and perhaps also upon sample preparation. There is experimental evidence that pentacene aligns in a head-on configuration with silicon oxide corresponding to a (001) cut of the pentacene crystal \cite{31} but aligns itself in a flat-side configuration on graphene corresponding to a (010) cut of the pentacene crystal \cite{32}. This is consistent with the general chemistry concept of “like-likes-like” that is often used to explain solubility and phase separation. The stability of different cuts of a pentacene crystal interfaced with crystalline C_{60} has been investigated theoretically with the conclusion that the head-on configuration formed by a (001) cut of the pentacene crystal is likely to be more stable than the flat-side configuration formed by a (010) cut of the pentacene crystal \cite{33}. This might suggest that we should orient Pent in a head-on configuration with C_{60} in our model as has been done in several previous articles focusing on excitation energies without dynamical modeling \cite{34–36}. However other studies have chosen to focus on both the head-on and flat-side configurations \cite{37, 38}. Indeed we find it interesting that the flat-side configuration is known to undergo an electrocyclic addition reaction \cite{39} (though no indication of such a reaction was found in our photochemical simulations.) After investigating the energetics of a single buckminsterfullerene acceptor molecule together with a single pentacene donor molecule in several different orientations, we chose a low energy model consisting of a single buckminsterfullerene molecule together with a single pentacene molecule with the carbons 6 and 13 centered over the C_{60} bond formed by two fused 6-membered rings as shown in Fig. 1. This is close to the ideal configuration for the above mentioned electrocyclic addition reaction. There is no exact correspondence with any of the C_{60}/Pent models in reported in the literature but most closely resembles Models 1 and 2 of Ref. \cite{38} as they differ primarily by rotation of the C_{60} “sphere.”

We have chosen to study the photodynamics of our system using mixed Tully-type quantum chemical/classical surface hopping photodynamics \cite{40, 42}. This is versatile enough to describe nonadiabatic surface hopping processes where the system can change from electronic states of different character (e.g., charge localized to charge transfer type) and, if enough trajectories are run, can
give an idea of branching ratios for different photochemical processes. The difficulty with this method is that the choice of quantum chemical method must be efficient enough to do many trajectories and many time steps for each trajectory. One approach is to use time-dependent (TD) density-functional theory (DFT). Mixed Tully-type TD-DFT/classical surface hopping photodynamics was first introduced by Tapavicza, Tavernelli, and Roethlisberger in 2007 [44] (Refs. [45, 46] provide reviews). As the model system studied here is getting to be too large for mixed TD-DFT/classical surface hopping calculations, further approximations are necessary. We have chosen to replace DFT with density-functional tight-binding (DFTB) [47–49] which is a semiphenomenological approximation to DFT. TD-DFTB was introduced by Niehaus et al. [50, 51] and is now well established. Naturally we have to expect some loss of accuracy, but DFTB is now sufficiently tested that we know that it is reasonably accurate for, for example, obtaining trends in the ionization potentials and electron affinities of molecules important for organic electronics [54] and that TD-DFTB is able to effectively mimic excitonic effects in TD-DFT calculations of molecular aggregates [55]. Mitrič and coworkers were apparently the first to develop mixed Tully-type TD-DFTB/classical surface hopping photodynamics [56] and this is what we use here in the recent program DFT-BABY [59]. We note that this includes both Grimme’s empirical van der Waals correction [60] which is important for describing intermolecular forces between organic molecules and the (TD)-DFTB version of a long-range corrected (also known as a range-separated hybrid) [(TD-)]lc-DFTB [61] which is needed for a correct description of CT excitations. Indeed previous work indicates that TD-lc-DFTB gives similar results to those obtained in TD-CAM-B3LYP calculations [55].

A complete description of exciton energy transfer (EET) and of charge transfer (CT) requires taking into account not only the molecule(s) of interest but also their environment [62]. Our model neglects environmental effects and has 96 atoms. It is large enough to demand significant computational resources for the relatively long photodynamics calculations reported here, but it is small enough that we must expect recurrences. At the beginning of the calculation, the overlap with the initial state is expected to diminish in a process known as dephasing (p. 81, Ref. [62]). However rephasing — or the process of returning to the initial state — is also expected in finite quantum mechanical systems (p. 81, Ref. [62]). This quantum mechanical effect is reminiscent of Poincaré’s recurrence theorem in classical mechanics which says that we should expect to see any finite size dynamical system return arbitrary close to its stating point after some time interval. The result is that we should expect to see energy and charge sloshing (most likely) nonperiodically back and forth between C60 and Pent. In the case of EET, additional mechanisms such as Foerster or Dexter energy transfer could be invoked to describe how the process occurs. However we shall not be concerned with this level of detail here, only with the fact that EET does indeed occur. Our interest is focused on discovering typical times for EET in this system. We will also see CT but, because of rephasing, it will not be a permanent separation of charges as that would require adding an environment capable of carrying away the charges. Nevertheless, our calculations should provide a lower estimate of how long charge separation should take at a bulk heterojunction. As our A/D system is C60/Pent, we expect electrons to be transferred from Pent to C60.

This article is organized as follows: The next section provides a brief review of the basic theory used in this paper. Section [11] provides computational details and our results are presented in Sec. IV. Section V contains our concluding discussion.

II. THEORETICAL METHODS

This is a review section whose intent is to keep this article reasonably self-contained. As photochemical modeling techniques have been reviewed in several places [45, 46, 63], we will focus only on the specific techniques needed to understand this article.

Following Tully [43], we use a mixed quantum mechanical/classical trajectory surface hopping model where the nuclear dynamics is assumed to be classical while the electron dynamics is described by quantum mechanics. Thus, the $k$th nucleus with mass $M_k$ and position $\vec{R}_k(t)$ follows Newton’s equation,

$$M_k \frac{d^2 \vec{R}_k(t)}{dt^2} = -\nabla_k V_I(\vec{R}(t)), \quad (2.1)$$

where $\vec{R} = [\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M]$ is the matrix of nuclear position (column) vectors and $V_I$ is the adiabatic potential energy function for the $I$th electronic state. In contrast, electron dynamics is governed by the time-dependent field due to the classical nuclei,

$$\hat{H}_e(\vec{r}; \vec{R}(t)) \Psi(x, t) = i \frac{d}{dt} \Psi(x, t), \quad (2.2)$$

where $\hat{H}_e$ is the usual electronic Hamiltonian, $\vec{r} = [\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N]$, $\vec{x} = (\vec{r}, \sigma)$ includes both space and spin, and $\vec{x} = [\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N]$. Such a model cannot be derived from first principles, but is physically appealing even if quantum effects of nuclear motion are lost. The probability that a classical particle, following a classical trajectory on the potential energy hypersurface of the $I$th electronic state hops to the hypersurface for the $J$th electronic state is governed by the quantum mechanical evolution of the electronic state. Tully [40, 43] proposed an efficient way to calculate the hopping probability known as fewest switches surface hopping (FSSH).
A. FSSH

To determine the probability that a classical trajectory describing nuclear motion hops to a new trajectory on another potential energy surface, we expand

$$\Psi(x, t) = \sum_I \Psi_I(x; R(t))C_I(t),$$

(2.3)
in solutions of the time-independent electronic Schrödinger equation,

$$\hat{H}_e \Psi_I(x; R(t)) = E_I(R(t))\Psi_I(x; R(t)).$$

(2.4)
The probability of finding the system on potential energy surface $m$ is then given by

$$P_I(t) = |C_I(t)|^2.$$  (2.5)

The coefficients $C_I(t)$ are found by integrating the first-order differential equation,

$$\frac{dC_I(t)}{dt} = -iE_I(t) - \sum_J d_{I,J}C_J(t),$$

(2.6)

where the nonadiabatic coupling element,

$$d_{I,J}(t) = \langle \Psi_I(R(t))|\frac{d\Psi_J(R(t))}{dt}\rangle = \frac{d\hat{R}_I(t)}{dt} \cdot \hat{F}_{I,J}(R(t)),$$

(2.7)
is related to the derivative coupling matrix,

$$\hat{F}_{I,J}(R(t)) = \langle \Psi_I(R(t))|\nabla_{R(t)}|\Psi_J(R(t))\rangle.$$  (2.8)

Note that this last quantity is both a function of the nuclear coordinates, a vector with respect to the nuclear coordinates, and a matrix with respect to the electronic degrees of freedom. (\langle \cdot \cdot \cdot \rangle refers only to integration over the electronic degrees of freedom.) We have arrived at this point at a very nice physical picture of swarms of trajectories of particles hopping between multiple potential energy surfaces with the relative number of trajectories on each potential energy surface giving the probability of finding the system in that electronic state at any given time.

We have to go a bit further in order to make our model well-defined and to overcome some technical problems. For one thing, we must be careful to conserve energy during the calculation. This is accomplished by rescaling the classical velocities after a hop from one surface to another so that the potential plus kinetic energies of the classical particle always remains constant. The element $d_{m,n}(R(t))$ may at first seem hard to calculate, but in fact may be calculated numerically as,

$$d_{I,J}(R(t + \Delta t/2) = \frac{1}{2\Delta} \left[ \langle \Psi_I(R(t))|\Psi_J(R(t + \Delta)\rangle - \langle \Psi_I(R(t + \Delta)|\Psi_J(R(t))\rangle \right].$$

(2.9)

A more difficult problem becomes evident when the derivative coupling matrix is rewritten as,

$$\hat{F}_{I,J}(R) = \frac{\langle \Psi_I|\nabla_{R}H_e(R)|\Psi_J\rangle - \delta_{I,J}\nabla E_I(R)}{E_J(R) - E_I(R)}.$$  (2.10)

which shows that numerical difficulties can appear near conical intersections when $E_J(R) \approx E_I(R)$. This difficulty is usually solved by switching from adiabatic to diabatic surfaces and following diabatic dynamics [34]. However the major problem with this sort of model is that surface hopping at every time step rapidly becomes unmanageable.

Tully [40, 43] solved this problem by coming up with an especially efficient Monte Carlo procedure to carry out the above calculation, namely the FSSH procedure. The hopping probability from the $I$th to the $J$th potential energy surface during a time interval of duration $\Delta t$ is given by,

$$g_{I,J}(t, \Delta t) = \frac{(dP_{I,J}(t)/dt)\Delta t}{P_I(t)}.$$  (2.11)

where,

$$P_{I,J}(t) = C_I(t)C_J^*(t).$$  (2.12)

A random number $\xi$ is generated with uniform probability over the interval $(0,1)$. The transition $m \rightarrow n$ only occurs if

$$P_J^{(\xi)} < \xi < P_J^{(I)},$$  (2.13)

where

$$P_J^{(I)} = \sum_{K=1,J} P_{J,K}$$  (2.14)

is the sum of the transition probabilities for the first $m$ states.

B. TD-DFT FSSH

The calculations in the present model are based upon the ground state density-functional tight binding (DFTB) method and upon time-dependent (TD) DFT. As these are semi-empirical versions of density functional theory (DFT) and of TD-DFT, we must first give a brief description of DFT and of TD-DFT as well as of TD-DFT FSSH.

DFT [65, 66] is now so well known that little needs to be said except to introduce notation. (Refs. [67, 69] provide an introduction to DFT.) The basic idea of the Kohn-Sham formulation is to replace the real system of $N$ interacting electrons in an external potential $v_{ext}$, with a fictitious system of noninteracting electrons moving in a new potential,

$$v_s = v_{ext} + v_H + v_{xc}.$$  (2.15)
Here
\[ v_H(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{r_{1,2}} d\vec{r}_2 \]  
(2.16)
is the Hartree (also known as the classical coulomb) potential,
\[ \rho(\vec{r}) = \sum_i n_i |\psi_i(\vec{r})|^2 \]  
(2.17)
is the charge density, and
\[ v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \]  
(2.18)
is the exchange-correlation (xc) potential. (Hartree atomic units \( m_e = e = \hbar = 1 \) are used throughout unless otherwise indicated.) The Kohn-Sham molecular orbitals (MOs) \( \psi_i \) with associated occupation number \( n_i \) satisfy the orbital Schrödinger equation,
\[ \left( -\frac{1}{2} \nabla^2 + v_s \right) \psi_i = \epsilon_i \psi_i, \]  
(2.19)
and the exact ground-state electronic energy for the real system may be written as,
\[ E_0 = \sum_i n_i \epsilon_i + G \]
\[ G = -\frac{1}{2} \int \int \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{1,2}} d\vec{r}_1 d\vec{r}_2 + E_{xc} - \int v_{xc}(\vec{r}) \rho(\vec{r}) d\vec{r}, \]  
(2.20)
where \( E_{xc} \) is the xc energy.

Thus far the theory is exact but impractical. To make it practical, we must introduce density functional approximations (DFAs) for the xc energy. We are not very concerned in the present article about the details of different DFAs with the exception of DFAs which introduce some orbital-dependent Hartree-Fock exchange. The first such DFA was a “global hybrid,” introduced by Becke in order to achieve near thermochemical accuracy \[70\]. This was clearly no longer pure Kohn-Sham theory \[71\] and has been properly rebaptized as a generalized Kohn-Sham theory \[72\]. In particular, molecular orbital energies in generalized Kohn-Sham theory will behave differently from those in traditional Kohn-Sham theory. In recent years, global hybrids are being replaced with “range-separated hybrids” \[72\] where the electron repulsion is separated into a short-range (sr) part and a long range (lr) part,
\[ \frac{1}{r_{1,2}} = \left( \frac{1}{r_{1,2}} \right)_{sr} + \left( \frac{1}{r_{1,2}} \right)_{lr} \]
\[ \left( \frac{1}{r_{1,2}} \right)_{sr} = \text{erfc}(\mu r_{1,2}) \]
\[ \left( \frac{1}{r_{1,2}} \right)_{lr} = \frac{\text{erf}(\mu r_{1,2})}{r_{1,2}}, \]  
(2.21)
where erf is the error function and erfc is the complementary error function. These become especially important for a correct description of charge-transfer corrections in TD-DFT.

TD-DFT is generally said to be based upon the Runge-Gross theorem \[73\]. It has been extensively reviewed in two recent proceedings \[74\] \[75\] and in one single author book \[76\] as well as in several recent review articles \[77\] \[78\]. The most common application of TD-DFT is to solve for excitation energies and oscillator strengths for UV-Vis spectra (usually) using Casida’s linear-response formalism \[79\].

The energy of the \( I \)th electronic excited state is then,
\[ E_I = E_0 + \omega_I. \]  
(2.27)
As it is now known how to take gradients of both the ground-state energy \( E_0 \) and of the excitation energy \( \omega_I \) \cite{ref1, ref2, ref3}, dynamics becomes possible on the potential energy hypersurface for the \( n \)th excited state, opening up the way for the TD-DFT FSSH method.

The first implementation of TD-DFT FSSH was due to Tapavicza, Tavbernelli, and R"othlisberger in 2007 \cite{ref4} in a development version of the CPMD code. They proposed that the nonadiabatic coupling be calculated using Casida’s Ansatz which was originally intended as an aid for assigning TD-DFT excited states \cite{ref5}. Specifically, an excited-state wave function

\[
\Psi_I = \sum_{i,a,\sigma} \Phi_{i\sigma}^{a\sigma} C_{i\sigma}^a, \tag{2.28}
\]

made up of singly excited determinants \( \Phi_{i\sigma}^{a\sigma} \) (corresponding to the \( i\sigma \rightarrow a\sigma \) excitation) is postulated and it is argued that

\[
C_{i\sigma}^a = \sqrt{\frac{\epsilon_{a\sigma} - \epsilon_{i\sigma}}{\omega_I}} F_{i\sigma}^a, \tag{2.29}
\]

where

\[
\vec{F}_I \propto (\mathbf{A} - \mathbf{B})^{-1/2} \left( \vec{X}_I + \vec{Y}_I \right), \tag{2.30}
\]

is renormalized so that

\[
\vec{F}_I^\dagger \vec{F}_I = 1. \tag{2.31}
\]

This was followed by an application to the photochemical ring opening of oxirane \cite{ref6} which showed that the nonexistence of a proper conical intersection in conventional TD-DFT \cite{ref7} was not a serious practical problem of TD-DFT FSSH. TD-DFT FSSH has also been implemented in a version of TURBOMOl capable of calculating nonadiabatic coupling elements analytically \cite{ref8} and this has been applied to study the photochemistry of vitamin-D \cite{ref9}.

C. TD-DFTB FSSH

As TD-DFT FSSH requires many repeated electronic structure calculations, it rapidly becomes computationally resource intensive. For example, we did try to use NEWTON-X \cite{ref10} to carry out TD-DFT FSSH calculations for the Pent/C\(_{60}\) system, but we found such calculations to be too resource intensive to be practical for the long run times reported in this paper. Instead we make use of a semi-empirical version of TD-DFT, known as TD-DFTB. (Other related TD-DFTB and DFTB methods for photochemical dynamics have also been developed \cite{ref11, ref12} but are not of direct importance for the present work.) DFTB is reviewed in Refs. \cite{ref13, ref14}. Like other semi-empirical quantum chemistry theories, DFTB uses an atom-centered minimal basis set which treats only the valence electrons. The core electrons are included as an ionic potential within \( v_{\text{ext}} \). Approximations are made so that no more than two-center integrals need be evaluated. For invariance reasons, the two-center integrals are generally restricted to integrals over \( s \)-type functions, albeit different \( s \)-type functions for different values of the angular momentum quantum number \( l \). In recent years, the theory has been extended to TD-DFTB \cite{ref15, ref16, ref17, ref18}, to lc-DFTB \cite{ref19, ref20, ref21}, to TD-lc-DFTB, and most recently to TD-lc-DFTB FSSH \cite{ref22}. The basic theory is only very briefly reviewed here, so the reader is referred to the original literature for additional information.

The original form of DFTB \cite{ref23} was noniterative. We will denote the \( \mu \)th basis function on atom \( I \) by,

\[
\chi_{\mu I} = \chi_{\mu \in I}, \tag{2.32}
\]

where the left-hand side is just a shorter form of the right-hand side. The density is the superposition of atomic densities,

\[
\rho_0 = \sum_I \rho_I^0, \tag{2.33}
\]

and the H\(xc\) part of the Kohn-Sham potential is assumed separable,

\[
v_{\text{H}\text{xc}}[\rho] = \sum_I v_{\text{H}\text{xc}}[\rho_I]. \tag{2.34}
\]

The matrix elements of the Kohn-Sham hamiltonian \( \hat{f} \) are calculated as,

\[
f_{\mu I, \nu J} = \begin{cases} 
\delta_{\mu \nu} \langle \chi_{\mu I} | \hat{t} + v_\text{s}[\rho_I] | \chi_{\nu J} \rangle & : I = J \\
\langle \chi_{\mu I} | \hat{t} + v_\text{s}[\rho_I] + v_{\text{H}\text{xc}}[\rho_I] | \chi_{\nu J} \rangle & : I \neq J 
\end{cases}, \tag{2.35}
\]

where \( \hat{t} \) is the kinetic energy operator. Frequently \( v_{\text{H}\text{xc}}[\rho_I] + v_{\text{H}\text{xc}}[\rho_J] \) is replaced with \( v_{\text{H}\text{xc}}[\rho_I + \rho_J] \) in modern implementations of DFTB. It then suffices to solve the matrix form of the Kohn-Sham equation,

\[
\hat{f} \rho_I^0 = \epsilon_I^0 s \rho_I^0, \tag{2.36}
\]

to be able to find the “band structure” (BS) part of the DFTB total energy,

\[
E_{\text{BS}} = \sum_I n_I \epsilon_I^0. \tag{2.37}
\]

Here

\[
s_{\mu I, \nu J} = \langle \chi_{\mu I} | \chi_{\nu J} \rangle \tag{2.38}
\]

is the usual overlap matrix and the superscript \( 0 \) is a reminder that these quantities are evaluated in a one-shot procedure with unperturbed atomic densities.

An examination of the expression for the DFT total energy \cite{ref24} shows that the BS part of the energy is only the first term. This term must be corrected by the \( G \) term plus the repulsion between the core potentials. This is the so-called “repulsive potential” which, in DFTB, is
assumed to be expandable as a set of pairwise potentials between different types of atom types,

$$E_{\text{rep}} = \sum_{I<J} V_{I,J}(R_{I,J}).$$  \hfill (2.39)

Probably the most difficult part of DFTB is developing and tabulating these pairwise potentials. The theory presented thus far is not yet suitable for response theory calculations as we must still be able to take into account the effect of distortions of atomic densities due to external potentials such as those due to other atoms in a molecule. The extension of the theory may be through second- \[121\] or third-order \[122\], but only the second-order theory will be described here. In particular the DFTB total energy is completed with a self-consistent charge (SCC) coulomb (coul) correction

$$E = E_{\text{BS}} + E_{\text{rep}} + E_{\text{coul}},$$  \hfill (2.40)

where, in principle,

$$E_{\text{coul}} = \frac{1}{2} \int \int \delta \rho(\vec{r}_1)(f_H(\vec{r}_1, \vec{r}_2) + f_{xc}(\vec{r}_1, \vec{r}_2)) \delta \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2.$$  \hfill (2.41)

However this expression is replaced by a new semi-empirical expression by making two approximations. The first is Mulliken’s approximation, developed for use in approximating electron repulsion integrals \[123\]. This gives,

$$\psi^*_r(\vec{r}) \psi_s(\vec{r}) = \sum_{\mu,I} q_{\mu,I}^r \chi_{\mu,I}^*(\vec{r}) \chi_{\mu,I}(\vec{r}),$$  \hfill (2.42)

after a bit of algebra, where

$$q_{\mu,I}^r = \frac{1}{2} (c_{\mu,I,r} s_{\mu,I,s} + c_{\mu,I,s} s_{\mu,I,r} c_{\mu,I,r}^\sigma)$$  \hfill (2.43)

is a Mulliken transition charge and the $c_{\mu,I,r}$ are the coefficients obtained from expanding the MOs in terms of atomic orbitals. The second approximation is an approximate expansion in terms of $s$-type functions $g_I$,

$$\chi_{\mu,I}^*(\vec{r}) \chi_{\mu,I}(\vec{r}) = g_I(\vec{r}).$$  \hfill (2.44)

It leads to the monopole expansion,

$$\psi^*_r(\vec{r}) \psi_s(\vec{r}) = \sum_{\mu,I} q_{\mu,I}^r \chi_{\mu,I}^*(\vec{r})$$  \hfill (2.45)

Equation (2.44) might be called the “gamma approximation” because it allows us to define the integrals,

$$\gamma_{I,J} = \int g_I(\vec{r}) (f_H(\vec{r}_1, \vec{r}_2) + f_{xc}(\vec{r}_1, \vec{r}_2)) g_J(\vec{r}) d\vec{r}_1 d\vec{r}_2.$$  \hfill (2.46)

As the Mulliken charge on atom $I$,

$$q_I = \sum_i q_{I,i}^s n_i,$$  \hfill (2.47)

then the coulomb energy [Eq. (2.41)] becomes

$$E_{\text{coul}} = \frac{1}{2} \sum_{I,J} \Delta q_I \gamma_{I,J} \Delta q_J$$  \hfill (2.48)

in these approximations, because

$$\delta \rho(\vec{r}) = \sum_I \Delta q_I g_I(\vec{r})$$  \hfill (2.49)

in terms of the Mulliken charge fluctuations on each atom. In practice, in this work, we will add one more term to to the DFTB energy, namely Grimme’s D3 correction for van der Waals interactions \[60\].

Comparing Eqs. (2.25) and (2.46) makes it fairly clear that Casida’s equation may be solved in DFTB. In particular, we need only replace the TD-DFT expression for the coupling matrix with the new expression,

$$K_{i\sigma,j\tau} = \sum_{I,J} \gamma_{I,J}^{\sigma,\tau} q_{I,J}^{\mu,i\sigma,jb}.$$  \hfill (2.50)

where the transition charges are

$$q_{I,J}^{\mu,i} = \sum_{\mu} q_{\mu,J}^{\mu,i}.$$  \hfill (2.51)

and $\gamma_{I,J}^{\sigma,\tau}$ takes on the spin indices $\sigma$ and $\tau$ because we now include a spin dependence in

$$f_{xc}^{\sigma,\tau}(\vec{r}_1, \vec{r}_2) = \frac{\delta E_{xc}}{\delta \rho_{\mu}(\vec{r}_1) \delta \rho_{\tau}(\vec{r}_2)}.$$  \hfill (2.52)

Note that Grimme’s D3 correction for van der Waals interactions does not enter into either TD-DFT or TD-DFTB calculations except indirectly through an initial ground-state geometry optimization.

As (TD-)DFTB is a semi-empirical approximation to (TD-)DFT, we can expect (TD-)DFTB to inherit the problems of (TD-)DFT—notably the underestimation of CT excitation energies. Unfortunately the $\Lambda$ criterion [Eq. (2.26)] is difficult to evaluate directly within (TD-)DFTB. Instead, use is made of the monopole expansion [Eq. (2.45)] to approximate

$$O_{ia} = \sum_{I,J} \gamma_{I,J}^{\sigma,\tau} \int g_I(\vec{r}) g_J(\vec{r}) d\vec{r} q_{I,J}^{\mu,s}.$$  \hfill (2.53)

Additional details may be found in Ref. \[61\].

Of course, the better approach would be to develop the (TD-)lc-DFTB method. The obvious difficulty here is that the introduction of the semi-empirical equivalent of Hartree-Fock exchange means a return to traditional semi-empirical quantum chemistry techniques \[124\] whose somewhat less rigorous approximations have so far been avoided in DFTB. It also highlights a fundamental difficulty with DFTB, namely the need for extensive reparameterization each time a new DFA is used. This is avoided in the method of Humeniuk and Mitrić.
III. COMPUTATIONAL DETAILS

Three different programs were used to carry out the calculations reported in this paper: GAUSSIAN09 [127] was used to construct start geometries and to carry out some single-point spectra calculations. DFTB+ [128] was used to prepare an initial ensemble of trajectories. DFTBABY [59] was used to carry out Tully-type TD-ncDFTB/classical trajectory surface hopping calculations.

a. GAUSSIAN09 was used to generate start geometries and for some single-point spectra calculations. Start geometries for the individual Pent and C_{60} molecules were obtained by gas-phase optimization of initial crystal geometries taken from theCrystallography Open Database (COD) [129–131] and then optimized at the B3LYP/6-31G(d,p) level — that is, with the B3LYP functional (i.e., Becke’s B3P functional [70] with Perdew’s correlation generalized gradient approximation (GGA) replaced with the Lee-Yang-Parr GGA [132] without further optimization [133] [70,134] using the 6-31G(d,p) basis set [135,136].

The start geometry of the Pent/C_{60} van der Waals complex as obtained from the minimum of the potential energy curve for the unrelaxed molecules as a function of the intermolecular distance using the orientation shown in the upper left-hand corner of Fig. [1]. These curves were calculated at the CAM-B3LYP-D3/6-31G(d,p) level — that is, the range-separated CAM-B3LYP [137] was supplemented with Grimme’s semi-empirical van der Waals correction [69].

A few single point time-dependent (TD) DFT calculations [83,138,139] where carried out at the TD-CAMD3LYP/6-31G(d,p) level for the individual Pent and C_{60} molecules.

b. DFTB+ was used to take the start geometries and to generate a thermal distribution of 30 start configurations for our FSSH calculations. It is not entirely clear whether it is best to use a thermal distribution or one which approximates a quantum distribution of vibrational states or, perhaps, something taking into account both thermal and quantum effects. We believe that the choice of thermal distribution used here is best for the Pent-C_{60} intermolecular coordinate, but may lead to overly narrow distributions for the intramolecular coordinates of the monomers [140]. Calculations were performed at the DFTB2/mio-0-1 level [121] using a Lennard-Jones dispersion correction [111] and equilibrated at T = 300 K using the Nosé-Hoover thermostat and a time step of 0.5 fs. The system was judged to be equilibrated after 1000 fs (Fig. [2] and geometrical coordinates for the start geometries began to be collected after 1050 fs.

c. DFTBABY was used to carry out mixed TD-ncDFTB/classical trajectory surface hopping using the FSSH algorithm. Each molecule from the 300K ensemble was excited to the excited state having the highest oscillator strength. This corresponds very roughly to broad band absorption in a solar cell. A different method of

(used in the present article) where a long-range correction for exchange is added with

\[ \gamma_{f,j}^{R}(R_{f,j}) = \text{erf}(\mu R_{f,j}) \gamma_{f,j}(R_{f,j}) \] (2.54)

and no reparameterizations. Furthermore Humeniuk and Mitrić neglect the lr contribution to the BS energy on the grounds that the zero-order system “already accounts for all interactions between electrons in the neutral atoms” [59]. In practice, the resultant (TD-)nc-DFTB method appears to behave very much like the (TD-)CAM-B3LYP method [55].

As TD-DFTB is very closely analogous to TD-DFT, it should not be too surprising that the advent of TD-DFTB FSSH quickly followed the advent of TD-DFT FSSH [56–58,125]. The main difficulties to be overcome involved the development of analytic derivatives and the calculation of the nonadiabatic coupling matrix element \( d_{I,J}(R(t)) \). In the implementation used in this article, the calculation of \( d_{I,J}(R(t)) \) is accomplished by Casida’s wave function Ansatz [Eqs. (2.28) and (2.29)] combined with Eq. (2.29). This leads to a linear combination of overlap terms between two Slater determinants at different times which is evaluated using the observation [126] that

\[ \langle \Phi_{a}^{\alpha}(R(t)) \rangle \Phi_{b}^{\beta}(R(t + \Delta)) = \text{det}(AB) = (\text{det}A)(\text{det}B), \] (2.55)

for a system of \( N = 2n \) electrons where

\[ A = \begin{bmatrix}
   \langle \psi_{1} | \psi_{1}' \rangle & \cdots & \langle \psi_{1} | \psi_{n}' \rangle \\
   \vdots & \ddots & \vdots \\
   \langle \psi_{n} | \psi_{1}' \rangle & \cdots & \langle \psi_{n} | \psi_{n}' \rangle
\end{bmatrix} \] (2.56)

is the determinant of overlaps of spin \( \alpha \) orbitals and

\[ B = \begin{bmatrix}
   \langle \psi_{1} | \psi_{1}' \rangle & \cdots & \langle \psi_{1} | \psi_{n}' \rangle \\
   \vdots & \ddots & \vdots \\
   \langle \psi_{n} | \psi_{1}' \rangle & \cdots & \langle \psi_{n} | \psi_{n}' \rangle
\end{bmatrix} \] (2.57)

is the determinant of overlaps of spin \( \beta \) orbitals. Unprimed and primed orbitals are evaluated at times \( t \) and \( t + \Delta \) respectively. The merger of TD-nc-DFTB with TD-DFTB FSSH has only been achieved very recently and is used in this work [59]. The interested reader who is further interested in the technical details of this method should see that reference.
sample preparation (not used here), appropriate for excitation in a laser experiment, would be to use an excitation energy window.

The use of a range-separated hybrid has been previously investigated and shown to be important when calculating TD-DFT spectra of Pent/C$_{60}$ systems [34–38] in order to correct the well-known underestimation of charge-transfer excitations (for reviews of difficulties encountered with traditional TD-DFT and suggestions for correcting them see Refs. 77–79). We used the TD-lc-DFTB as formulated by Humeniuk and Mitrič [61] and used in their mixed TD-lc-DFTB/classical trajectory surface hopping program DFTBaby [59].

Calculations were carried out with a nuclear time step of 0.5 fs for trajectories as long as 500 fs. At least ten excited states, in addition to the ground state, have been followed during each trajectory calculation. Excited state gradients were calculated analytically (Appendix B of Ref. [59]). Adiabatic energies and scalar non-adiabatic couplings were interpolated linearly when integrating the electronic Schrödinger equation between nuclear time steps. Although decoherence effects can be important [142], no decoherence correction was used in the present calculations. Hops from a lower to a higher state were rejected if the kinetic energy was less than the energy gap between the states so as not to violate the principle of conservation of energy. Velocities were uniformly scaled after an allowed hop so that the total (kinetic plus potential) energy was conserved. It is known that artifacts can occur when integrating the electronic Schrödinger equation in an adiabatic basis near a photochemical funnel. This problem was avoided using a locally diabatic basis [64] which avoids numerical instabilities due to “trivial crossings.” Unlike some previous implementations of DFTB which may not have been suitable for some dynamics calculations because they were not parameterized for all interatomic distances, DFT-Baby is well adapted for dynamics calculations as it is parameterized for every interatomic distances from zero to infinity.

IV. RESULTS

Photodynamics calculations were run with and without the long-range correction. The results without the long-range correction showed a CT excitation much too quickly (as will be briefly discussed at the end of this section) compared to the expectation of roughly 100 fs based upon experimental results. For this reason, we concentrate on the results with long-range correction. These results are divided into four subsections. The first subsection describes the assignment of absorption spectra obtained from a single ground-state optimized geometry. The next subsection explains how the initial excited states were prepared in our photodynamics simulation and classifies the resultant states. This is followed by a discussion of exciton energy transfer (EET) which is seen on a relatively short time scale and then by a subsection discussing CT which is seen on a longer time scale, comparable to what is expected based upon experimental results. A final subsection comments on the CT times that we see when the same simulation is done without any long-range correction.

A. Assignment of Absorption Spectra

Replacing a first-principles method such as TD-DFT with a semi-empirical approximation implies a trade-off between accuracy and computational efficiency. We look at calculated absorption spectra in this section in order to obtain a better understanding of the implications of this trade-off.

The initial model geometry has been used to calculate the absorption spectrum of thirty excited states by using both the TD-lc-DFTB the TD-CAM-B3LYP/6-31G(d,p) methods. The resultant spectra are shown in Fig. 3. At first glance, the TD-lc-DFTB and TD-CAM-B3LYP/6-31G(d,p) spectra may seem very different. However the peaks do lie between 2.2 and 4.1 eV in both cases, both have significant absorption between 3.3 and 4.2 eV and two intense peaks between 2.1 and 3.3 eV.

Figure 4 shows the MO analysis of the 4 most intense peaks in the TD-CAM-B3LYP absorption spectra. Note the remarkable qualitative similarity of the lc-DFTB and CAM-B3LYP hole and particle MOs. The exception is the second major peak in the TD-CAM-B3LYP spectrum at 2.66 eV with oscillator strength $f = 0.0495$. Here we could not find a corresponding TD-lc-DFT peak based upon the MO analysis. Instead we compared against the energetically closest TD-lc-DFT peak which lies at 3.03 eV and has a very small oscillator strength of $f = 0.0000001$. The 2.66 eV TD-CAM-B3LYP is a
Pent $\rightarrow$ C$_{60}$ CT excitation, while the 3.03 eV TD-lc-DFT peak is a local excitation on Pent. Other than this peak mismatch, the two spectra are in good qualitative agreement. Note that the replacement of quantitative agreement with a more qualitative picture is, of course, the “price” we pay for using a semi-empirical method. However, it should be emphasized that the type of dynamics calculations reported here for molecules of this size and on this time scale are extremely difficult to do without making approximations.

As our model is similar to Models 1 and 2 in Ref. 38, we have compared our excitation energies with those reported in that article. It is interesting that the excitation energies of Models 1 and 2 may differ by as much as about 0.2 eV with the same functional, indicating the importance of small rotations of the C$_{60}$ “sphere.” Our model corresponds to yet a different rotation of the C$_{60}$ “sphere.” Our results appear to us to be in good agree-

![FIG. 3: Calculated absorption spectra using lc methods. Note that the “oscillator strength” has been renormalized so that the largest peak has unit height.](image)

![FIG. 4: Dominant particle $\rightarrow$ hole contributions and excitation energies showing the correspondence between the most intense TD-CAM-B3LYP/6-31G(d,p) absorption peak and the corresponding TD-lc-DFTB absorption peak.](image)

| Excitation Energies (eV) |
|-------------------------|
| Method                  | Pent | CT     |
|-------------------------|
| TD-CAM-B3LYP            | 2.29/3.7 | 2.66/4.1 |
| TD-lc-DFTB              | 2.21/3.03/3.16 | 3.9 |
| Ref. 38 (Model 1/Model 2) |     |
| TD-LC-BLYP              | 2.55/2.49 | 3.33/3.30 |
| TD-LC-\omegaPBE         | 2.52/2.46 | 3.16/3.17 |
| TD-\omegaB97X           | 2.44/2.37 | 3.01/3.02 |
| TD-\omegaB97XD          | 2.31/2.20 | 2.48/2.45 |
| TD-OPT-LC-BLYP          | 2.22/2.09 | 2.33/2.09 |
| TD-OPT-\omegaPBE        | 2.23/2.06 | 2.25/2.06 |
| TD-OPT-\omegaB97X       | 2.23/2.08 | 2.30/2.08 |
| TD-OPT-\omegaB97XD      | 2.24/2.09 | 2.31/2.09 |

TABLE II: Comparison of the excitation energies of the present work with those of Models 1 and 2 given in Table 3 of Ref. 38.
FIG. 5: Assignment of the physical character of the initial excitation of several trajectories based upon the two most important MO contributions to the singlet excitation: Traj 1, DL-type; Traj 2, P-type; Traj 18, P-type; Traj 6, P-type.

B. Initial Excited States

Having discussed the (static vertical) absorption spectrum, we now proceed to describe our photodynamics calculation and what results it gave. We ran thirty TD-lc-DFTB FSSH trajectories (numbered Traj 1, Traj 2, ..., Traj 30) whose initial states were obtained by exciting from a ensemble of molecules with different geometries equilibrated at 300 K to the singlet excited state with the highest oscillator strength at that geometry. This led to an initial ensemble of states which will be described in this subsection.

The energetic gap between the first several singlet excited states is much smaller than that between the ground state ($S_0$) and the first excited singlet state ($S_1$). For this reason, it is perhaps not surprising that only 36.7% of the Trajs began from $S_1$. Moreover only an additional 16.7% of the initial states are accounted for by the next four states ($S_2 - S_5$), leaving 46.6% of the initial states in still higher states. Note however that the ordering of these energetically dense states is sensitive to the geometry of the molecules which is different for the initial states of different trajectories.

Some programs, such as Newton-X [111, 143] have special routines (e.g., CALCDEN in the case of Newton-X) or are interfaced with special programs (e.g., TheoDORE [144]) which allow the automatic assignment of state character [145–148]. DFTBABY is less advanced in this respect, but is more advanced in its implementation of the lc-DFTB needed for the present study. In the present case, the physical nature of the initial states was determined by direct visualisation of the MOs involved in each excitation. An example of this analysis is shown in Fig. 5. Two types of excited states were found. Excitations localized on Pent are designated as P-type while those excited states which are delocalized over both Pent and $C_{60}$ are designated as DL. Of course, there is an element of subjectivity in this analysis. However no amount of automation seems likely to be able to totally eliminate the fuzzy boundary between what is a localized and what is a delocalized excitation. In practice, we found it fairly clear how to label the states. For example, although Traj 18 is partly of P → DL character, it is clear that the dominant contribution is of P-type (i.e., P → P character.)

In total, there were 16 initial excited states of P-type and 14 initial excited states of DL-type. To some extent, these two types of excitations are associated with particular orbitals. For example, all but three of the P-type initial states are dominated by the $^1(H, L)$ transition. The exceptions are Traj 18 which is still about 33% $^1(H, L)$ and Trajs 4 and 6 which are predominantly $^1(H, L + 1)$. However caution should be taken when basing assignments on orbital ordering as this can change when the molecules are deformed from one geometry to another. All of the 14 DL-type initial states are dominated by the $^1(H, L + 3)$ transition.

C. Exciton Energy Transfer Dynamics

The 30 initial excited states were propagated for 500 fs. To do this, it is necessary to specify for how may other excited states surface hopping will be allowed. In general this number was varied from 10 (if the initial state was low in energy) to 17 (if the initial state was higher in energy.) It is also necessary to use multiple criteria when analysing the character of the electronic states during the photodynamics simulations. We have mainly followed three properties of the active state over time, namely (i) the transition dipole moment (TDM), (ii) the oscillator strength $f$, and (iii) the degree of spatial overlap between occupied and virtual orbitals as measured by $\Lambda$. Note that two of these properties are closely related (but not proportional) because the oscillator strength $f_I$ for a transition with excitation energy $\omega_I$ is related to the TDM

$$\mu_{I\rightarrow 0} = |\langle \Psi_I | \vec{r} | \Psi_0 \rangle|,$$ (4.1)

by

$$f_I = \frac{2}{3} \omega_I \mu_{I\rightarrow 0}^2.$$

(4.2)
In addition this was accompanied by looking at (iv) the molecular orbital contributions to the active excited state and (v) visualization of the particle-hole charge distribution or (vi) particle-hole charge density difference. As noted above, the MO contributions can be misleading because the ordering of the MOs may change during the simulation. However this was only one of several criteria examined.

We found that exciton energy transfer (EET) happens very quickly. So our discussion of EET focuses on what happens on the a short-time scale, on the order of 50 fs or less. As shown in Fig. 6, $S_1$ and $S_4$ dominate during the first 50 fs, but other excited states are present. This is because the manifold of singlet excited states is quite dense compared to their energetic separation from the ground state.

MO analysis of the 30 trajectories (Supplementary Information) shows that all but one of the P-type initial-state trajectories follow the pathway $P \rightarrow P \rightarrow C_{60}$. (The exception follows the pathway $P \rightarrow DL \rightarrow C_{60}$.) All but one of the DL-type initial state trajectories follows the $DL \rightarrow C_{60} \rightarrow P$ pathway. (The exception follows the pathway $DL \rightarrow P \rightarrow C_{60}$.)

The results are shown for some initial P-type trajectories in Fig. 7. It is immediately obvious that something dramatic is happening at around 20 fs because there is a dramatic fall in oscillator strength and in the related quantity, the TDM. The effect is somewhat less dramatic for $\Lambda$ but is also present. The hole-particle charge analysis (Supplementary Information) shows that the excitation is moving from a P-type excitation to become a $C_{60}$-type excitation. The results are shown for some initial DL-type trajectories in Fig. 8. The situation is less dramatic here, but something is clearly happening 10-20 fs into each run as all three properties move up to a maximum. The particle-hole analysis (Supplementary Information) show that a localization procedure is taking place followed by movement of the localized excitation from one molecule to another. While these results may at first seem puzzling, they are in fact consistent with the well-known process of energy transfer. The natural direction is from the donor ($D$) to the (A) acceptor,

$$D^* + A \rightarrow D + A^*. \quad (4.3)$$

Such an energy transfer has been explained via electron exchange (i.e., Dexter’s mechanism) or via a coulombic mechanism [i.e., Förster resonance energy transfer (FRET) [149]]. But, because the system is finite, recurrences will occur, so we also see the excitation being passed back again,

$$D + A^* \rightarrow D^* + A. \quad (4.4)$$

Let us try to summarize the main conclusion of this subsection: We are seeing excitonic energy transfer on a very short time scale: $17 \pm 11$ fs for P-type initial-state Trajs and $13 \pm 5$ fs for DL-type initial-state Trajs. Such a time is too short for the nuclei to move very much. Nevertheless, the period of a C=C vibration in a conjugated

![Figure 6: Variation of state populations during the first 50 fs of the simulation.](image)
FIG. 7: Temporal variation of properties for the active state of five initially P-type trajectories (trajectory numbers 4, 6, 17, 28, and 30): (a) Λ, (b) oscillator strength, and (c) transition dipole moment.

system is about 20-25 fs. Since these vibrations are excited together with the electronic excitations, it is not unreasonable to see the first excitonic energy transfer on a similar time scale. Also some more global change in molecular geometry is apparent as the pentacene forms a crescent shape around C$_{60}$ (Supplementary Information.) Such a shape enhances the van der Waals bonding between the two fragments, thereby making exciton energy transfer easier than it might otherwise have been.

D. Charge Transfer Dynamics

At the heart of the modern OPVs is charge separation at the heterointerface. This is something we see in six out of 30 of trajectories at 188±28 fs. Of these trajectories, two had P-type initially-excited states and the other four had DL-type initially-excited states. As we shall illustrate by taking an in-depth look at two typical trajectories, it is only by carefully examining images of particle-hole charge distributions that we were able to establish what value of Λ is low enough to indicate CT. We have chosen to discuss the charge separation process in detail by focusing on Traj 6 which is an initially P-type excited state and on Traj 27 which is an initially DL-type excited state.

1. Traj 6: Example of a P-type initial state

Figure 8 shows the evolution of the active state in time for Traj 6 as it hops from one state to another. It is clear that the excited states form a close-packed manifold well-separated from the ground state. This leads to a high probability of surface hopping as is confirmed in Fig. 9.

Now let us follow in detail what is happening for the active state along its trajectory. Figure 10 shows the
FIG. 9: Traj 6: Ground and excited state energies as a function of time: (a) first 500 fs, (b) zoom to 150-250 fs. The active state is marked by red bullets.

FIG. 10: Traj 6: Surface hopping during the first 250 fs of the trajectory.

At 17.5 fs, there is a sudden change in properties (Fig. 13). The active state has become $S_8$, which is a $C_{60}$-type state [(2) in Fig. 12]. The MO analysis of the active state shows a major (86.3%) $H \rightarrow L+1$ and a minor (13.7%) $H-1 \rightarrow L+1$. All the particle and hole MOs of these transitions are located mainly on the pentacene.

The particle and hole MOs involved in the excited state and Fig. 12 shows the particle-hole charge density difference for several snapshots of the active state. The initial state is $S_4$, a P-type state, consisting mainly of $H \rightarrow L+1$ (96.5%) with a little bit of $H-7 \rightarrow L+8$ (3.5%). At the time of this hopping from the $S_1$ state, the active state becomes a linear combination of two transitions (86.3% $H \rightarrow L+1$ and 13.7% $H-1 \rightarrow L+1$). All the particle and hole MOs of these transitions are located mainly on the pentacene.

| Major Component | Minor Component |
|-----------------|-----------------|
| 1) 0 fs, $S_4$  | 96.5% $H \rightarrow L+1$ |
| 2) 17.5 fs, $S_8$ | 3.5% $H-7 \rightarrow L+8$ |
| 3) 20 fs, $S_8$ | 88.7% $H-1 \rightarrow L+2$ |
| 4) 22 fs, $S_{10}$ | 11.3% $H-2 \rightarrow L+3$ |
| 5) 56 fs, $S_2$ | 58.4% $H-1 \rightarrow L+4$ |
| 6) 60 fs, $S_1$ | 41.6% $H-4 \rightarrow L+1$ |
| 7) 157 fs, $S_5$ | 96.7% $H \rightarrow L$ |
| 8) 157.5 fs, $S_6$ | 3.3% $H-8 \rightarrow L+8$ |
| 9) 158.5 fs, $S_6$ | 73.2% $H-1 \rightarrow L+1$ |
| 10) 166.5 fs, $S_{10}$ | 26.8% $H-2 \rightarrow L+2$ |
| 11) 210 fs, $S_2$ | 73.5% $H-6 \rightarrow L$ |
| 12) 221 fs, $S_{10}$ | 26.5% $H-3 \rightarrow L$ |
| 13) 222 fs, $S_8$ | 62.9% $H-1 \rightarrow L+3$ |
| 14) 222 fs, $S_8$ | 37.1% $H-3 \rightarrow L+3$ |

FIG. 11: Traj 6: Snapshots of the principle particle and hole MOs characterizing the active state.
FIG. 12: Traj 6: Snapshots of the particle-hole charge density difference for the active state.

FIG. 13: Evolution of some properties of the Traj 6 active state: (a) $\Lambda$, (b) oscillator strength, and (c) transition dipole moment.
a minor (11.3%) H-2 \rightarrow L+3 component. All these MOs are localized on C_{60}. Hence the 17.5 fs transition is the first exciton energy transfer. Values of \Lambda, TDM, and Osc are high for P-type excitations. For C-60-type excitations, \Lambda falls considerably and values of both the TDM and Osc fall nearly to zero. These values (Fig. [13]) are initially high, drop at 17.5 fs, and then rise again at 20 fs. They subsequently drop at 22 fs and remain low until 56 fs before they rise up again. They remain high for another 13 fs, and then drop again at 69 fs, indicating that the active state has changed its nature. These oscillations are very tricky to analyze as they occur for both exciton energy transfer and for charge transfer. However the MO analysis (Fig. [11]) and particle-hole charge density difference (Fig. [12]) indicates that the active state changes its nature at 20 fs from local on C_{60} to local on pentacene and then, 2 fs later, local on C_{60}. At 56 fs, the active state is once again a local excitation on pentacene. This exciton energy transfer continues up to 69 fs and beyond — up to 157 fs.

At 157.5 fs, there is a dramatic change in the nature of the excited state from a C_{60}-type state to a charge transfer state with a hole on the C_{60} and an extra electron on pentacene [(8) in Fig. [11] and (8) in Fig. [12]]. This qualitatively different change is not visible in the \lambda or in the TDM graphs, and it is only visible in the \Lambda graph as a particularly low value of \Lambda (i.e., \leq 0.5). The MO analysis shows a major H-6 \rightarrow L component (67.4%) with a minor H-3 \rightarrow L component (32.6%). Both the major and minor components show particles and holes located on different fragments, thus confirming the charge-transfer nature of the 157.5 fs active state. Interestingly the charge transfer is happening from C_{60} to pentacene, which is not the intuitively expected direction. However there is sufficient energy for this to happen in our finite system and the charge separation only lasts about 1.5 fs before becoming localized once again on C_{60} [(10) of Fig. [11] and (10) of Fig. [12]].

At 210 fs, the hole and particle become delocalized over both molecules and this leads to another charge-transfer state at 221 fs, this time with the hole on the pentacene and an extra electron on C_{60}. This is confirmed by examination of the MOs involved in the H \rightarrow L+1 (57.9%) excitation and in the particle-hole charge density difference for the active S_{10} state. Once again, this charge transfer state is transitory and after only 1 fs it has become a local excitation on C_{60}. There is no particular reason for charge transfer to be permanent in such a small system.

2. **Traj 27: Example of a DL-type initial state**

We carry out a similar analysis to that for the initially P-type Traj 6, but this time for the initially DL-type Traj 27. Figures [14] and [15] show the evolution of the active state. It generally stays among the lower energy singlet excited states—especially S_1 and S_2—but does not remain exclusively in these states.

Now let us follow in detail what is happening for the active state along its trajectory. Figures [16] and [17] show the particle and hole molecular orbitals (MOs) and the particle-hole charge density difference for several snapshots of the active state. The initial state is S_{13}, a DL-type state which passes to S_{12} after 3 fs, returns to S_{11} for 1.5 fs more, then hops to S_9 for 1 fs before hopping to S_8 for 5.5 fs, and then passes through S_3 and S_4, staying on each for about 0.5 fs, until finally relaxing to the lowest excited state S_1 after 15 fs.

Figure [18] shows the same sort of oscillations that we have seen in the case of Traj 6. Indeed the MO analysis of the active state shown in Fig. [16] indicates that we are once more seeing excitonic energy sloshing back and forth between pentacene and C_{60}, with the first exciton energy transfer happening at 16 fs. This process continues without the development of significant charge transfer until 127.5 fs, when the \Lambda value falls below 0.5, which appears to us to be a critical value for intermolecular charge transfer. This is an important point: Higher values of \Lambda such as \Lambda = 0.6 generally also indicate charge transfer but only intramolecular charge transfer within one or the
other molecule. To have intermolecular charge transfer, \( \Lambda \) must fall lower still and the value that we have found to correlate with intermolecular transfer is \( \Lambda \leq 0.5 \). Figures [16] and [17] indicate that true intermolecular charge transfer is indeed happening at 127.5 fs. Once again, this intermolecular charge transfer is only short lived but is expected to recur were we to run the simulation for long enough.

### 3. Summary of all six CT times

Figure [19] provides a summary in terms of charge density difference maps of what CT looks like for the six trajectories where it was observed. We note that the CT may take place either from Pent to C\(_{60}\) or from C\(_{60}\) to Pent, but that, whichever the direction of CT, the opposite CT will take place in the opposite direction for this finite system. Fig. [19] shows that precisely this phenomenon has been observed in our calculations for both Trajs 6 and 14. An especially important point is that our observation of a CT time of 188±28 fs is commensurate with experimental observations of CT times at heterojunctions in OPV devices (i.e., 200 fs for APFO3/PCBM [14], 70-100 fs for pentacene/C\(_{60}\) [15], ≤ 100 fs for MDMO-PPV/PC\(_{70}\)BM and for PCPDTBT/PC\(_{70}\)BM [16], and 82 fs for p-DTS(FBTTh\(_2\))\(_2\)/PC\(_{71}\)BM [17].)

### E. Charge Transfer Dynamics without Long-Range Correction

As we had also done the same type of TD-DFTB FSSH calculations with DFTBaby *without any long-range correction*, we can see the importance of the lc. Details are reported in the Supplementary Information. All 30 Trajs show at least one CT and we have found two CTs in most

| Major Component | Minor Component |
|-----------------|-----------------|
| 1) 0 fs, \(S_{13}\) | 97.9\% H→L+3, 2.1\% H-6→L+7 |
| 2) 0.5 fs, \(S_{13}\) | 56.2\% H-4→L+5, 43.8\% H-1→L+6 |
| 3) 16 fs, \(S_1\) | 89.4\% H→L, 10.6\% H-1→L+1 |
| 4) 41.5 fs, \(S_5\) | 84.2\% H-3→L+1, 15.8\% H-4→L+1 |
| 5) 89.5 fs, \(S_1\) | 96.3\% H→L, 3.7\% H-6→L+8 |
| 6) 105 fs, \(S_1\) | 92\% H-1→L+1, 8\% H-2→L+1 |
| 7) 118 fs, \(S_5\) | 63.8\% H→L+1, 36.2\% H→L+1 |
| 8) 122 fs, \(S_{11}\) | 74.2\% H-4→L+3, 28.8\% H-5→L+2 |
| 9) 127.5 fs, \(S_{11}\) | 67.2\% H→L+1, 32.8\% H-4→L+3 |
| 10) 133 fs, \(S_2\) | 90.7\% H→L, 9.3\% H→L+1 |

FIG. 16: Traj 27: Snapshots of the principle particle and hole MOs characterizing the active state.

FIG. 15: Traj 27: Surface hopping during the first 250 fs of the trajectory.
FIG. 17: Traj 27: Snapshots of the particle-hole charge density difference for the active state.

1) 0 fs, State: \( S_{13} \)  
2) 0.5 fs, State: \( S_{13} \)  
3) 16 fs, State: \( S_1 \)  
4) 41.5 fs, State: \( S_5 \)  
5) 89.5 fs, State: \( S_1 \)  
6) 105 fs, State: \( S_1 \)  
7) 118 fs, State: \( S_5 \)  
8) 122 fs, State: \( S_{11} \)  
9) 127.5 fs, State: \( S_{11} \)  
10) 133 fs, State: \( S_2 \) 

FIG. 18: Evolution of some properties of the Traj 27 active state: (a) \( \Lambda \), (b) oscillator strength, and (c) transition dipole moment.

V. CONCLUSION

We have carried out Tully-type mixed time-dependent long-range-corrected density-functional tight binding/classical trajectory surface hopping calculations on a van der Waals complex consisting of a single buckminsterfullerene (C\(_{60}\)) molecule together with a single pentacene (C\(_{22}H_{14}\)) molecule. Calculations for an ensemble of 30 trajectories were run for 500 fs for this 96 atom system and were carefully analyzed to see what processes were happening on different time scales. Although several approximations have been made — including taking only two molecules into account in our dynamics, the use of the semi-empirical TD-\( \text{lc-DFTB} \) ap-
FIG. 19: Charge density difference maps and CT times for the six trajectories where CT was observed.

proach, and the use of Tully’s semi-classical approximation — there is a certain satisfaction that is obtained from being able to follow the photodynamical process in such detail. Excitations were made, not from a single geometry, but from a thermally-equilibrated ensemble of ground state geometries. The initial excited state lay anywhere within a bundle of closely-spaced states lying well above the ground state. Both nuclei and electrons were free to move, though the nuclei did not move very far in 500 fs. Nevertheless, pentacene was found to twist and to wrap itself around C\textsubscript{60}, offering ample symmetry reduction to mix different excited states. Generally speaking, the molecules soon relaxed to the lowest excited state, but they did not generally remain in the lowest excited state. Nor was there time for the system to go all the way to the ground state and, indeed, the ground state was not our hoped-for objective anyway. Instead we expected to see charge separation and the production of some sort of precursor to a conducting state as befits a model for the heterojunction of an organic solar cell.

What we actually observed on a short time scale of about the period of a C=C vibration in a conjugated system was a localized excited state on one molecule transforming into a localized excited state on another molecule and then going back again, with the first energy transfer occurring within less than about 20 fs. This is a known phenomenon though we have found that it is rarely mentioned in the organic solar cell literature. As the system is finite, recurrences are inevitable, so that the energy continues to go back and forth. However Fourier transforming various properties showed no particular periodicity in the sloshing back and forth of energy. The literature does talk about excimer trapping at the interface, which would prevent the exciton from departing very quickly from the interface. Our model van der Waals complex consisting of only one pentacene and one C\textsubscript{60} is too small to conclude regarding the formation of an excimer, but the rapidity of the movement of energy from one molecule to the next raises the question of whether the geometry at the interface can relax fast enough to catch the exciton before it diffuses away from the interface or whether the energy is simply sloshing back and forth within an excimer potential energy well?

A sudden change in oscillator strength was found to be a good indication of EET. The best criterion that we found for CT was when $\Lambda$ fell below about 0.5. Assuming the energy remains trapped at the interface, our calculations show that charge separation takes place after 188±28 fs. This is quite encouraging in so far as this is the order of magnitude of the time-scale reported in the literature for charge separation at organic solar cell bulk heterojunction interfaces based upon experimental results. We also carried out calculations without the long-range correction and found significantly shorter CT times which are in no way consistent with experiment. This emphasizes the importance of using a long-range corrected theory not just for calculating spectra but also in photodynamics simulations. As our system is finite, CT also recurs. That is, the charges recombine so that they can separate again at some later time. Recombination could be prevented if the system were large enough to allow charge to diffuse away from the interface.

Shortly before submitting this article, we became aware of a recently published paper by Joseph, Ravva, and Bredas \[150\] reporting results of TD-ωB97XD FSSH calculations a similar but not identical system. Their model also consists of a single pentacene molecule face on with a single C\textsubscript{60} molecule with a the central hexagon of pentacene roughly over a hexagonal face of C\textsubscript{60} as in Model 2 of Ref. 38. In the model used in the present work, the C\textsubscript{60} sphere has been rotated to a position known to be favorable for an electrocyclic reaction (though none was observed in the present work). Despite the different orientations, we might hope that Joseph \textit{et al.} would have found similar CT times in their simulation with a long-range corrected functional as we did in our simulation using TD-le-DFTB and this is indeed the case to some extent. There is order of magnitude agreement, but
they reported a 25 fs CT time based upon an apparently very careful analysis. Interestingly this which seems more like the EET times coming out of our own careful analysis, rather than the longer (100-200 fs) CT times that we observed. As we have shown, it can be difficult to distinguish between EET and CT times and, although this may be one explanation of the discrepancy between the results of Ref. [150] and the present results, we must point out that the two calculations differ significantly in the details of the simulation, including both the orientation of C$_{60}$ and the preparation of the initial ensemble of excited states. Also neither the study of Ref. [150] nor the present study involved enough trajectories to determine a reliable CT rate and hence the CT time has not been accurately determined over a macroscopic ensemble.

All of these points to the need for simulations on model systems composed of larger numbers of molecules and, eventually, varying the types of molecules. We believe that such future studies will be aided by the present study in so far as we have done the pioneering work applying state-of-the-art TD-IC-DFTB FSSH to fs CT dynamics. As TD-IC-DFTB FSSH has a better scaling than TD-ωB97XD FSSH, we may hope to be able to treat still larger systems in the future. At the same time, we are also fully aware of the need to explore other methods for preparing the ensemble of initial excited states and of the limitations of the analytic tools that we have used to characterize CT. While we believe our results to be improvable, we believe that they have already shown beyond any serious doubt the importance of including long-range corrections in studies of CT at OPV heterojunctions.

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Author Contributions

This project began when Bhaarathi Natarajan, a former Ph.D. student of Mark E. Casida, left Grenoble to do postdoctoral work with Haibin Su in Singapore using software from Roland Mitrić’s lab. The project was continued from that small, but important, beginning first by Xi Zhu with Haibin Su in Singapore and then as part of the Ph.D. project of Ala Aldin M. H. M. Darghouth under the direction of Mark E. Casida in Grenoble. Major coding was done by Alexander Humeniuk and by Roland Mitrić in their TD-DFTB program. The bulk of the manuscript writing was done by Mark E. Casida and Ala Aldin M. H. M. Darghouth.

Conflicts of Interest

The authors declare no conflict of interest.

Supplemental

The supplemental information for this paper contains the following:

- Short-time analysis for the 16 states initially localized on pentacene.
- Short-time analysis for the 14 states initially delocalized over pentacene and buckminsterfullerene.
- CT analysis of TD-DFTB FSSH calculations.

Abbreviations

For the reader’s convenience, we have collected together the abbreviations used in this chapter:

- A Degree of spatial overlap between occupied and virtual orbitals
- A Acceptor.
- BS Band structure.
- C$_{60}$ Buckminsterfullerene.
- coul Coulomb.
- CT Charge transfer.
D Donor.
DFA Density-functional approximation.
DFT Density-functional theory.
DFTB Density-functional tight binding.
DL Delocalized.
$D_{KI}$ Nonadiabatic coupling.
E Energy.
EFISH Electric field-induced second harmonic.
erf Error function.
erfc Complementary error function.
ET Energy transfer.
ETT Exciton energy transfer.
FRET Förster resonance energy transfer.
FSSH Fewest switches surface hopping.
fs Femtoseconds.
f Oscillator strength.
GGA Generalized gradient approximation.
H Highest-occupied molecular orbital.
H-n $n$th level below the HOMO.
HOMO Highest-occupied molecular orbital.
HF Hartree-Fock.
L Lowest-unoccupied molecular orbital.
L+n $n$th level above the LUMO.
LUMO Lowest-unoccupied molecular orbital.
HOMO Highest-occupied molecular orbital.
L Lowest-unoccupied molecular orbital.
L+n $n$th level above the LUMO.
lc Long-range corrected.
lc-DFTB long-range corrected Density-functional tight binding.
lr Long range.
LUMO Lowest-unoccupied molecular orbital.
MO Molecular orbital.
ms Milliseconds.
ns Nanoseconds.
NTO Natural transition orbital.
OPV Organic photovoltaics.
P Pentacene.
Pent Pentacene.
ps Picoseconds.
rep Repulsion.
S Singlet.
SCC Self-consistent charge.
sr Short range.
TD Time-dependent
TD-DFT Time-dependent density-functional theory.
TD-DFTB Time-dependent density-functional tight binding.
TD-lc-DFTB long-range corrected time dependent Density-functional tight binding.
TDM Transition dipole moment.
Traj Trajectory.
UV-Vis Ultraviolet-visible.
xc Exchange-correlation.

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