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A multiconfigurational time-dependent Hartree-Fock method for excited electronic states. II. Coulomb interaction effects in single conjugated polymer chains

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Conjugated polymers have attracted considerable attention in the last few decades due to their potential for optoelectronic applications. A key step that needs optimisation is charge carrier separation following photoexcitation. To understand better the dynamics of the exciton prior to charge separation, we have performed simulations of the formation and dynamics of localised excitations in single conjugated polymer strands. We use a nonadiabatic molecular dynamics method which allows for the coupled evolution of the nuclear degrees of freedom and of multiconfigurational electronic wavefunctions. We show the relaxation of electron-hole pairs to form excitons and oppositely charged polaron pairs and discuss the modifications to the relaxation process predicted by the inclusion of the Coulomb interaction between the carriers. The issue of charge photogeneration in conjugated polymers in dilute solution is also addressed. © 2011 American Institute of Physics. [doi:10.1063/1.3600404]

I. INTRODUCTION

Conjugated polymers have attracted considerable attention in the last few decades because their unique properties make them suitable candidates for a wide range of applications in optoelectronics. The characteristic π -electron structure of conjugated compounds is such that they become conductive upon chemical doping, charge injection, or photoexcitation, and thus exhibit the electrical and optical properties of metals or semiconductors.^{1,2} They retain, however, the attractive mechanical properties and processing advantages of conventional insulating polymers. This class of materials exhibits strong electronic interactions, as well as a strong interconnection, and mutual influence, of the electronic and geometric structures. This is a most distinctive feature, which leads to the emergence of nonlinear excitations,^{1,2} such as polarons and (polaron-)excitons, whose properties are crucial to understanding the operation of organic optoelectronic devices. The luminescence that can follow the process of exciton formation through the combination of electron- and hole-polarons underlies the operation of organic light-emitting diodes.^{3–5} The reverse process of exciton dissociation into polaron pairs plays a central role in polymer-based solar cells,^{6–8} which stand out as one of the most promising sources of clean and renewable energy.

Despite many technological advances over the last couple of decades, the fundamental processes governing the photophysics of conjugated polymers are not yet completely un-

derstood. The nature of the species produced upon photoexcitation is a particularly controversial subject.^{9–16} It is unclear whether polaron pairs are primarily formed directly on ultrafast time scales, or the result of exciton dissociation over longer time scales. From the experimental viewpoint, this question appears to be settled, with considerable evidence^{10–15} suggesting that, in general, both excitons and polaron pairs are photogenerated directly on ultrafast time scales, but the branching ratio of such products depends critically on the strength of interchain interactions. In dense conjugated polymer films, for which the interchain coupling is typically strong, the charge carrier photogeneration yield can approach about 25%.^{10,13,14} In the case of conjugated polymers in dilute solution (and also of films depending on the preparation conditions^{11,13}), where the interchain interactions are weak, this efficiency is considerably lower^{12,13} ($\lesssim 1\%$), and the formation of polaron pairs must rely almost exclusively on exciton dissociation mechanisms. Much higher yields, in excess of 50%,^{14,15} can be obtained by blending the polymer with a suitable fullerene derivative, as a consequence of the efficient charge transfer that occurs at the polymer/fullerene interface. On the theory front, however, there is still some inconsistency, with predictions presumably valid only for isolated chains being used to explain results observed for dense conjugated polymer films.¹⁶

The theoretical treatment of the photophysics of conjugated polymers is challenging, since, as already mentioned, these systems exhibit both strong electron-electron and electron-nuclear interactions. Most photoexcitation dynamics calculations consider only the effect of

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electron-phonon coupling, on the basis of the widely used Su-Schrieffer-Heeger (SSH) model,^{17,18} which has contributed decisively to the current understanding of many dynamical processes inherent to conjugated polymer systems.^{1,16,19–22} On the other hand, electron correlation effects have been largely confined to static calculations, most notably within the framework of the Pariser-Parr-Pople (PPP) model,^{23–25} which has been successfully used to predict the reverse ordering of 2^1A_g and 1^1B_u excited states in linear polyenes,²⁶ thus explaining why not all conjugated polymers luminesce. Together, electronic interactions and electron-nuclear coupling are fundamentally important for the description of the behaviour of conjugated compounds, but dynamical calculations accounting for both types of interactions are scarce,^{27–30} and typically ignore the singlet character of the photoexcited state, by restricting the electronic wavefunction to the form of a single Slater determinant. The present work aims at bridging this gap and achieving a proper understanding of the photophysics of conjugated polymers in dilute solution.

In part I of this series,³¹ we have introduced a multiconfigurational time-dependent Hartree-Fock (MCTDHF) method for the approximate solution of the time-dependent Schrödinger equation for large systems of interacting electrons. In this second part, this approach is combined with a classical description of the nuclear degrees of freedom, through the Ehrenfest mean-field approximation.^{32,33} The resulting scheme is an efficient nonadiabatic molecular dynamics method, which provides a powerful tool to follow the evolution of the coupled electron-nuclear system. It is designed to take into account the appropriate spin symmetry of the electronic wavefunction, thus enabling the proper study of photoexcited states and allowing us to distinguish between singlet and triplet excited states, which exhibit quite different properties. The formalism is applied to semiempirical single-strand models of a prototypical conjugated polymer, both with and without Coulomb interactions, in order to investigate the importance of electron-electron interactions on the dynamics of low-lying excitations in conjugated polymers. The nature of the photoexcited states and the issue of charge photogeneration in conjugated polymers in dilute solution are also discussed.

The remainder of this paper is organised as follows. In Sec. II, the MCTDHF method for general open-shell states^{34–36} is briefly outlined and combined with Ehrenfest molecular dynamics. In Sec. III, the model Hamiltonians are defined and the equations of motion are derived in detail, while in Sec. IV we discuss the parameterisation appropriate to describe the properties of *cis*-polyacetylene. The method is applied to the dynamics of low-lying excitations in conjugated polymers in Sec. V, and, finally, Sec. VI is devoted to concluding remarks.

II. FORMALISM

Ehrenfest molecular dynamics^{32,33} provides an efficient approximation to the solution of the time-dependent Schrödinger equation for a system of interacting electrons and nuclei. Within this method, the nuclei are considered as classical particles, governed by Newton's laws, and move in an

effective potential due to the electrons:

$$M_n \ddot{\mathbf{R}}_n = -\nabla_n \langle \Psi | \hat{H} | \Psi \rangle. \quad (1)$$

The electrons, on the other hand, are treated quantum-mechanically and evolve according to the time-dependent wave equation

$$i\hbar |\dot{\Psi}\rangle = \hat{H} |\Psi\rangle. \quad (2)$$

In the above expressions, M_n and $\mathbf{R}_n$ denote the nuclear masses and coordinates, respectively, Ψ is the electronic wavefunction, and $\hat{H}$ gathers the electronic kinetic energy and all the potential energy terms.

Although the method of Ehrenfest molecular dynamics, as defined by the set of coupled Eqs. (1) and (2), is a mean-field approximation, transitions between different electronic states are possible in this formalism,^{32,33} which is therefore nonadiabatic. However, at this level of approximation, not all transitions are properly reproduced; the quantum electron correlation is partially missed, leading to an inadequate description of nonadiabatic processes governed by spontaneous phonon emission, such as Joule heating.³⁷ To obtain a more accurate description of the electron-nuclear interaction in conjugated polymers, other approaches can be used, including surface hopping³⁸ and quantum dynamical methods, such as correlated electron-ion dynamics^{39,40} and the hierarchical electron-phonon model of Tamura *et al.*⁴¹ Nevertheless, whenever the quantum nature of the nuclear motion can be safely neglected – as for the object of this paper – Ehrenfest molecular dynamics is the method of choice in condensed phase dynamics because of its efficiency, which enables the study of large systems over several hundreds (and even thousands) of femtoseconds.

If the electronic part of the Hamiltonian only contains one-body operators, the solution of Eq. (2) is trivial (the individual single-electron wavefunctions evolve independently according to the time-dependent Schrödinger equation). However, when two-body operators are present, as in the case of semiempirical models which include electron-electron interactions, further approximations are required. A suitable approach is a variant of the MCTDHF approximation, introduced in part I of this series.³¹ Within this method, the electronic wavefunction is written as a superposition of Slater determinants,

$$|\Psi\rangle = \sum_{\alpha} C_{\alpha} |\Phi_{\alpha}\rangle, \quad (3)$$

with fixed expansion coefficients, C_{α} . Note that many determinants are needed to capture the dynamic correlation; indeed, quite possibly this requires going beyond double excitations, as shown in early work for polyenes.^{42,43} However, in order to reach an acceptable compromise between efficiency and accuracy, we will retain only the smallest possible number of configurations that catches the essential features of the electronic wavefunction, notably its spin symmetry.

The spatial parts of the single-particle orbitals, ϕ_i , which are used to build each configuration in Eq. (3), are then optimised according to the Dirac-Frenkel time-dependent

variational principle,^{31,44,45}

$$\langle \delta \Psi | \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) \Psi \rangle + \langle \left(\hat{H} - i\hbar \frac{\partial}{\partial t} \right) \Psi | \delta \Psi \rangle = 0, \quad (4)$$

which must be satisfied for arbitrary variations, $\delta \Psi$, of the approximate many-body wavefunction, Ψ .

For general open-shell states,^{34–36} this procedure yields the set of optimal equations of motion³¹

$$i\hbar |\dot{\phi}_{i\mu}\rangle = \sum_{\substack{v,\lambda \\ (n^v \neq n^\lambda)}} \hat{P}^\lambda \frac{n^\lambda \hat{F}^\lambda - n^v \hat{F}^v}{n^\lambda - n^v} \hat{P}^v |\phi_{i\mu}\rangle, \quad (5)$$

where the shell μ gathers groups of orbitals with the same Fock operator,

$$\hat{F}^\mu = \hat{T} + \frac{1}{2} \sum_v \sum_{j_v} n^v (2a^{\mu v} \hat{J}_{j_v} - b^{\mu v} \hat{K}_{j_v}), \quad (6)$$

$\hat{P}^\mu$ is a projector onto the subspace spanned by shell μ ,

$$\hat{P}^\mu = \sum_{i_\mu} |\phi_{i\mu}\rangle \langle \phi_{i\mu}|, \quad (7)$$

and $n^\mu = 0, 1, 2$ its occupation number. In Eq. (6), the operator $\hat{T}$ collects all the one-electron interaction terms, $\hat{J}_{j_v}$ and $\hat{K}_{j_v}$ denote the usual Coulomb and exchange operators,^{44,45} and $a^{\mu v}$, $b^{\mu v}$ are numerical coefficients (or state parameters) specific to the particular form of the wavefunction.^{34–36}

For instance, in the case of an open-shell singlet (i.e., a photoexcited state), all the doubly occupied orbitals belong to the same shell (conventionally labelled by $\mu = 1$), whereas the singly occupied orbitals stand in separate shells (indexed by $\mu = 2, 3$). In this case, the state parameters are given by

$$\mathbf{a} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 2 & -2 \\ 1 & -2 & 2 \end{pmatrix}. \quad (8)$$

For high-spin multiplets, which include open-shell doublet (i.e., polaron) and triplet states, there are only two occupied shells ($\mu = 1$ gathers the doubly occupied orbitals, and $\mu = 2$ gathers the singly occupied ones), and the state parameters read

$$\mathbf{a} = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}. \quad (9)$$

Notice that we also consider the subspace of unoccupied orbitals as a proper shell (labelled by $\mu = 0$), even though its Fock operator is undefined (this is, however, irrelevant since it is always premultiplied by zero).

The devised scheme incurs a computational cost that is comparable to that of the widely used time-dependent Hartree-Fock approximation,⁴⁵ thus allowing for the study of large systems. This is in contrast to the case of an expansion with a large number of configurations and time-dependent coefficients, for which the computational cost quite rapidly becomes prohibitive as the number of degrees of freedom increases.³¹

Conceptually similar approaches have been previously used to study the dynamics of photoexcitations,^{16,19–22,27–30}

and to describe charge transport and mobility^{46,47} in conjugated polymers. As already mentioned in Sec. I, most of these studies consider only the effect of electron-phonon coupling,^{16,19–22,46,47} and the few that also include electron-electron interactions either use an adiabatic evolution method²⁷ or single-configurational wavefunctions.^{28–30} As we shall see in the following sections, the present method goes significantly beyond these approaches and provides a powerful analysis tool for ultrafast excited-state dynamics in conjugated polymers.

III. MODELS AND EQUATIONS OF MOTION

A. SSH + PPP model

We consider a linear chain with N sites and fixed ends, described by a model Hamiltonian with Coulomb interactions,

$$\hat{H}_{\text{SSH+PPP}} = \hat{H}_{\text{lattice}} + \hat{H}_{\text{coupling}} + \hat{H}_{\text{Coulomb}}, \quad (10)$$

which we refer to as the SSH + PPP model. The lattice is described by a simple harmonic Hamiltonian:^{1,2}

$$\hat{H}_{\text{lattice}} = \frac{1}{2M} \sum_i p_i^2 + \frac{K}{2} \sum_i (u_{i+1} - u_i)^2, \quad (11)$$

where M and p_i denote the nuclear mass and momenta, respectively, K is the elastic constant due to the σ -bonds, and u_i the displacement of site i from its equidistant position.

The second term in Eq. (10) represents a tight-binding interaction of the π -electrons and a linear coupling to the lattice displacements.^{1,2,16}

$$\hat{H}_{\text{coupling}} = - \sum_{i,\sigma} t_i (\hat{c}_{i\sigma}^\dagger \hat{c}_{i+1,\sigma} + \hat{c}_{i+1,\sigma}^\dagger \hat{c}_{i\sigma}), \quad (12)$$

where $\hat{c}_{i\sigma}^\dagger$ ($\hat{c}_{i\sigma}$) creates (annihilates) a π -electron with spin σ at site i (i.e., the basis functions are restricted to the set of orthonormalised p_z atomic orbitals, centred on different sites), and

$$t_i = t_0 - \alpha(u_{i+1} - u_i) + (-1)^{i+1} t_e \quad (13)$$

is the nearest-neighbour transfer integral, with t_0 denoting the hopping integral for the undistorted structure, α the electron-phonon coupling constant, and t_e the symmetry-breaking term, introduced to lift the ground state degeneracy.

The third contribution in Eq. (10) models long-range Coulomb interactions and can be written as²

$$\begin{aligned} \hat{H}_{\text{Coulomb}} = & U \sum_i \left(\hat{n}_{i\uparrow} - \frac{1}{2} \right) \left(\hat{n}_{i\downarrow} - \frac{1}{2} \right) \\ & + \frac{1}{2} \sum_{i,j \neq i} v_{ij} (\hat{n}_i - 1)(\hat{n}_j - 1). \end{aligned} \quad (14)$$

It is this term that gives rise to electron-electron correlations. In the above expression, U denotes the screened onsite Coulomb repulsion energy,

$$\hat{n}_i = \sum_\sigma \hat{n}_{i\sigma} = \sum_\sigma \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}, \quad (15)$$

and v_{ij} is a suitable semiempirical potential. In this work, we adopt the Ohno potential, defined as⁴⁸

$$v_{ij} = \frac{U}{\sqrt{1 + (\beta r_{ij}/r_0)^2}}, \quad (16)$$

where r_{ij} denotes the distance between sites i and j , r_0 is the average bond length, and β determines the ratio between the onsite and intersite repulsion energies. Note that the effect of screening of the π -system by the σ -electrons is included through the use of a screened U .^{29,49} Rather than simply taking the difference between the ionisation energy and electron affinity of an isolated sp^2 hybridised carbon atom, this model parameter is going to be fitted in order to reproduce known experimental data for *cis*-polyacetylene (see Sec. IV).

The force on atom k , $k = 2, \dots, N-1$ (we recall that atoms 1 and N are kept fixed), is a sum of nuclear and electronic contributions:

$$F_k \equiv F_k^{(n)} + F_k^{(e)} = -\frac{\partial}{\partial u_k} V_n - \frac{\partial}{\partial u_k} V_e, \quad (17)$$

where

$$V_n = \frac{K}{2} \sum_i (u_{i+1} - u_i)^2 + \frac{1}{2} \sum_{i,j \neq i} v_{ij}, \quad (18)$$

and V_e is the open-shell electronic energy, of the form^{34–36}

$$\begin{aligned} V_e &= \langle \Psi | \hat{H}_e | \Psi \rangle \\ &= \sum_{\mu} \sum_{i_{\mu}} n^{\mu} \langle \phi_{i_{\mu}} | \hat{T} | \phi_{i_{\mu}} \rangle + \frac{1}{4} \sum_{\mu, \nu} \sum_{i_{\mu}, j_{\nu}} n^{\mu} n^{\nu} \\ &\quad \times (2a^{\mu\nu} \langle \phi_{i_{\mu}} | \hat{J}_{j_{\nu}} | \phi_{i_{\mu}} \rangle - b^{\mu\nu} \langle \phi_{i_{\mu}} | \hat{K}_{j_{\nu}} | \phi_{i_{\mu}} \rangle). \end{aligned} \quad (19)$$

Notice that $\hat{H}_e$, the electronic part of the SSH + PPP Hamiltonian, is given by the sum of $\hat{H}_{\text{coupling}}$ and $\hat{H}_{\text{Coulomb}}$, subtracted by the constant term (with respect to the electronic degrees of freedom) $V = \frac{NU}{4} + \frac{1}{2} \sum_{i,j \neq i} v_{ij}$.

Taking the gradient of Eq. (18), we obtain for the nuclear contribution to the force:

$$F_k^{(n)} = K(u_{k+1} + u_{k-1} - 2u_k) - \sum_i d_{ik}, \quad (20)$$

with

$$d_{ik} = \frac{(\beta/r_0)^2 (r_i - r_k)}{1 + (\beta r_{ik}/r_0)^2} v_{ik} \quad (21)$$

and

$$r_i = (i-1)r_0 + u_i. \quad (22)$$

Let us now turn to the electronic contribution to the force. Writing the molecular orbitals, $\phi_{i_{\mu}}$, as a linear combination of atomic orbitals (LCAO), χ_j ,

$$|\phi_{i_{\mu}}\rangle = \sum_j C_{ji_{\mu}} |\chi_j\rangle, \quad (23)$$

we can recast the electronic energy for a general open-shell state as

$$\begin{aligned} V_e &= - \sum_{\mu} \sum_i n^{\mu} \left[P_{ii}^{\mu} \left(\frac{U}{2} + \sum_{j \neq i} v_{ij} \right) + P_{i+1,i}^{\mu} t_i + P_{i-1,i}^{\mu} t_{i-1} \right] \\ &\quad + \frac{1}{4} \sum_{\mu, \nu} \sum_{i,j} n^{\mu} n^{\nu} (2a^{\mu\nu} P_{ii}^{\mu} P_{jj}^{\nu} - b^{\mu\nu} P_{ji}^{\mu} P_{ij}^{\nu}) v_{ij}, \end{aligned} \quad (24)$$

where

$$P_{ij}^{\mu} = \sum_{k_{\mu}} C_{ik_{\mu}} C_{jk_{\mu}}^* \quad (25)$$

denotes an element of the projector onto shell μ , in the atomic orbitals basis set. In principle, the implicit dependence of the expansion coefficients on the lattice displacements should be taken into account when computing the gradient of Eq. (24). However, this may be safely disregarded, since for any real parameter, $x(t)$,

$$\left\langle \frac{\partial \Psi}{\partial x} \right| \hat{H} | \Psi \rangle + \langle \Psi | \hat{H} \left| \frac{\partial \Psi}{\partial x} \right\rangle = \frac{1}{x} (\langle \Psi | \hat{H} | \Psi \rangle + \langle \Psi | \hat{H} | \Psi \rangle) = 0, \quad (26)$$

as it follows from the Dirac-Frenkel time-dependent variational principle.³¹ Thus, we have

$$\nabla_n \langle \Psi | \hat{H}_e | \Psi \rangle = \langle \Psi | \nabla_n \hat{H}_e | \Psi \rangle, \quad (27)$$

which is analogous to the Hellmann-Feynman theorem.⁴⁵ Using the above expression, we find

$$\begin{aligned} F_k^{(e)} &= \sum_{\mu} n^{\mu} \left[\sum_i (P_{ii}^{\mu} + P_{kk}^{\mu}) d_{ik} + 2\alpha (\text{Re} P_{k,k+1}^{\mu} - \text{Re} P_{k,k-1}^{\mu}) \right] \\ &\quad - \frac{1}{2} \sum_{\mu, \nu} n^{\mu} n^{\nu} \sum_i [a^{\mu\nu} (P_{ii}^{\mu} P_{kk}^{\nu} + P_{kk}^{\mu} P_{ii}^{\nu}) - b^{\mu\nu} \text{Re} (P_{ki}^{\mu} P_{ik}^{\nu})] d_{ik}. \end{aligned} \quad (28)$$

Following Eq. (1), the lattice displacements obey the equations of motion

$$M \ddot{u}_k = F_k, \quad (29)$$

for $k = 2, \dots, N-1$, with the total force given by the sum of contributions (20) and (28). As discussed in Sec. II, the solution of Eq. (2) for the electronic degrees of freedom is provided by a variant of the MCTDHF approximation. Using Eq. (23), the optimal equations of motion (5) can be written in terms of the LCAO coefficients, $C_{ik_{\mu}}$:

$$i\hbar \dot{C}_{ik_{\mu}} = \sum_j R_{ij} C_{jk_{\mu}}, \quad (30)$$

with

$$R_{ij} = \sum_{\substack{\mu, \nu \\ (n^{\mu} \neq n^{\nu})}} \sum_{k,l} P_{ik}^{\nu} \frac{n^{\nu} F_{kl}^{\nu} - n^{\mu} F_{kl}^{\mu}}{n^{\nu} - n^{\mu}} P_{lj}^{\mu}. \quad (31)$$

The Fock matrix for shell μ is expressed in the atomic orbitals basis set as

$$F_{ij}^{\mu} = - \left[\frac{U}{2} + \sum_{k \neq i} v_{ik} \right] \delta_{ij} - t_i \delta_{i+1,j} - t_{i-1} \delta_{i-1,j} + \left[\sum_v \sum_k n^v a^{\mu v} P_{kk}^v v_{ik} \right] \delta_{ij} - \frac{1}{2} \sum_v n^v b^{\mu v} P_{ij}^v v_{ij}. \quad (32)$$

The set of differential equations that govern the evolution of the coupled electron-nuclear system [Eqs. (29) and (30)] can be efficiently integrated numerically using, e.g., an 8th order Runge-Kutta method with adaptive step-size control, due to Dormand and Prince.⁵⁰

B. SSH model

To investigate the effect of electron-electron interactions on the dynamics of conjugated polymers, results obtained using the SSH + PPP model will be compared to the predictions of the simpler SSH model,^{17,18}

$$\hat{H}_{\text{SSH}} = \frac{1}{2M} \sum_i p_i^2 + \frac{K}{2} \sum_i (u_{i+1} - u_i)^2 - \sum_{i,\sigma} t_i (\hat{c}_{i\sigma}^{\dagger} \hat{c}_{i+1,\sigma} + \hat{c}_{i+1,\sigma}^{\dagger} \hat{c}_{i\sigma}), \quad (33)$$

which includes only electron-phonon interactions. Notice that Eq. (33) is obtained from the SSH + PPP Hamiltonian by setting $U = 0$.

The evolution of the nuclear degrees of freedom is still governed by Eq. (29), but the total force [which can be obtained by setting $U = 0$ in the sum of contributions (20) and (28)] now reduces to

$$F_k = 2\alpha(\text{Re}\rho_{k,k+1} - \text{Re}\rho_{k,k-1}) + K(u_{k+1} + u_{k-1} - 2u_k), \quad (34)$$

where we have introduced the density matrix,

$$\rho_{ij} = \sum_{\mu} n^{\mu} P_{ij}^{\mu} = \sum_{\mu} \sum_{k_{\mu}} n^{\mu} C_{ik_{\mu}} C_{jk_{\mu}}^*. \quad (35)$$

In contrast to the SSH + PPP case, for the SSH model the time-dependent wave equation for the electronic degrees of freedom can be solved exactly, since the Hamiltonian only involves one-body operators. In this case, the equations of motion for the LCAO coefficients read¹⁶

$$i\hbar \dot{C}_{ij\mu} = -t_i C_{i+1,j\mu} - t_{i-1} C_{i-1,j\mu}. \quad (36)$$

The SSH model has been previously employed, within the framework of Ehrenfest molecular dynamics, to study the formation and dynamical properties of photoexcitations in conjugated polymers in the works of An *et al.*¹⁶ and Mele.²⁰ Generalisations to describe more accurately phenyl-based polymers and/or to include the effect of an external electric field have also been applied in the same context,^{22,29} as well as in the study of charge transport and mobility.^{46,47}

C. Models with applied electric field

It is also instructive to consider the presence of an external electric field, as in Refs. 22, 29, 46, and 47. In the dipole approximation, the applied field, $f(t)$, is assumed to be constant over the entire chain, thus coupling to the total dipole moment:²²

$$\hat{H}'(t) = \hat{H} + \hat{H}_{\text{ext}}(t), \quad (37)$$

with $\hat{H}$ being either the SSH or the SSH + PPP Hamiltonian,

$$\hat{H}_{\text{ext}}(t) = ef(t) \sum_i r_i (\hat{n}_i - 1), \quad (38)$$

and e denoting the electronic charge. From Eq. (38), it is straightforward to include the field contribution on the force on atom k :

$$F'_k = F_k + ef(t)(1 - \rho_{kk}). \quad (39)$$

Moreover, since $\hat{H}_{\text{ext}}(t)$ only contains one-body operators, the modifications to the equations of motion for the electronic degrees of freedom are also trivial. For the SSH + PPP model, the Fock matrices are simply augmented with a diagonal term,

$$F_{ij}^{\mu'} = F_{ij}^{\mu} + ef(t)r_i \delta_{ij}, \quad (40)$$

while, for the SSH model, Eq. (36) is replaced by

$$i\hbar \dot{C}_{ij\mu} = -t_i C_{i+1,j\mu} - t_{i-1} C_{i-1,j\mu} + ef(t)r_i C_{ij\mu}. \quad (41)$$

IV. MODEL PARAMETERISATION

The various parameters used in the calculations are chosen so as to model *cis*-polyacetylene. This is typically accomplished through a fitting procedure aimed at reproducing certain experimentally observed quantities, such as the optical gap, $E_g = 1.8$ eV, band width, $W = 10$ eV, and ground state dimerisation, $\delta = 0.05$ Å.^{1,2} For the special case of the SSH model, the best choice has been widely reported in the literature^{1,2,16} (see Table I). However, when Coulomb interactions are included, the choice is less consensual,^{2,51-53} which led us to perform our own parameterisation of the SSH + PPP model.

To this end, we first restricted the parameter space to the set $\{t_0, \alpha, U, \beta\}$, by keeping the remaining parameters fixed at their SSH values. The motivation behind this methodology is twofold. First, since the SSH and SSH + PPP models only

TABLE I. Model parameters appropriate for *cis*-polyacetylene.

Parameter	SSH model	SSH + PPP model
r_0 , Å	1.22	1.22
K , eV Å ⁻²	21	21
M , eV fs ² Å ⁻²	1349.14	1349.14
α , eV Å ⁻¹	4.1	3.2
t_0 , eV	2.5	2.1
t_e , eV	0.05	0.05
U , eV	...	4.1
β	...	3.4

FIG. 1. Schematic representation of the potential energy surfaces involved at each step of the iterative procedure developed for the parameterisation of the SSH + PPP model. The band width and dimerisation are computed at the ground state minimum, $E_{1^1A_g}(q')$, the optical gap is given by $E_g = E_{1^1B_u}(q') - E_{1^1A_g}(q')$, and the exciton singlet-triplet splitting is calculated as $\Delta = [E_{1^1B_u}(q'') - E_{1^1A_g}(q'')] - [E_{1^3B_u}(q''') - E_{1^1A_g}(q''')]$. Note that the coordinate sets q' , q'' , and q''' are found by geometry optimisation.

differ in their electronic parts, it is logical to take the same values for K and M in both cases. Second, we found that the effect of t_e on the investigated quantities is similar in both models, and thus it is reasonable to keep this parameter fixed. An initial guess for the varying parameters was then iteratively improved, using Powell's direction set method,⁵⁴ until a good agreement between the predictions of both models for the optical gap, band width, and ground state dimerisation (for a given chain length) was reached. To avoid falling in the SSH minimum (i.e., $U = 0$), we also fitted the experimentally observed value for the exciton singlet-triplet splitting, $\Delta = 0.7$ eV,⁵⁵ a quantity that is only nonzero when Coulomb interactions are included. As depicted in Fig. 1, each step of the iteration process requires the calculation of six points in some fairly complicated potential energy surfaces, which renders this approach computationally demanding. For this reason, we were only able to consider rather small chains, with $N = 40$ and 60 . We found that the parameters listed in Table I bring all the investigated quantities to within 10% of the expected values. Although the parameters used throughout the calculations only apply to *cis*-polyacetylene, the results of Sec. V should be qualitatively valid for other conjugated polymers with nondegenerate ground states.

V. RESULTS AND DISCUSSION

A. Dynamics of the 1^1B_u photoexcited state

We now specialise to the case of a 1^1B_u photoexcited state. Initially, the ionic momenta are set to zero, and the displacements are chosen so as to minimise the ground state potential energy. This is achieved using the Broyden-Fletcher-

Goldfarb-Shanno (BFGS) method.⁵⁴ Notice that the electronic subproblem requires a self-consistent field calculation to be performed at each iteration (for the SSH model, this is replaced by the diagonalisation of the Hamiltonian matrix). We found that a limited-memory variant of the BFGS strategy⁵⁶ with exact line searches, based on an exponential parameterisation of the wavefunction,³⁶ is appropriate for general open-shell states. A HOMO $\rightarrow$ LUMO excitation (or simply $1 \rightarrow 1$, in the notation in which the energy levels are counted downwards from the top of the valence band, and upwards from the bottom of the conduction band) is then set up, which requires an additional self-consistent field run in order to obtain the LCAO orbital coefficients at $t = 0$. In the special case of the SSH model, this only involves changing the orbital occupation numbers accordingly, since the single-particle wavefunctions take the same form as in the ground state. The initial conditions thus obtained are then propagated by numerical integration of the equations of motion, as discussed in Sec. III.

Figure 2 shows the time evolutions of the staggered bond order parameter, or dimerisation,^{1,16}

$$\delta_i = \frac{(-1)^{i+1}}{4}(u_{i+1} + u_{i-1} - 2u_i), \quad (42)$$

calculated for a 200-site *cis*-polyacetylene chain, considering both the SSH and SSH + PPP models. As can be seen, the results are qualitatively similar, with the lattice relaxing to form a single local deformation in both cases. There is an almost

FIG. 2. Time evolutions of the dimerisation pattern, obtained for a 1^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models.

FIG. 3. Snapshots of the dimerisation pattern at $t = 120$ fs (a valley region in Fig. 2), obtained for a 1^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models.

periodic behaviour, with alternating peaks and troughs, which corresponds to a continuous interchange of the positions of the single and double bonds at the middle of the chain (i.e., an oscillation between the so-called A and B phases²). This is most extreme in the SSH case, for which the dimerisation pattern in the valley regions exhibits two small split peaks rather than a single one. In contrast, by including Coulomb interactions this dynamical process is somewhat suppressed, particularly at later times. Indeed, as shown more clearly in Fig. 3, the single peak profile is preserved, and the dimerisation at the centre of the chain is not as low. It is also clear from Fig. 2 that the elapsed time between peaks is shorter for the SSH + PPP model, suggesting that Coulomb interactions have the effect of promoting the creation of the local deformation. Moreover, while the peaks are of comparable width (at half maximum) for both models, they are accompanied by “tails” which extend over many more lattice sites in the SSH case. Hence, adding Coulomb interactions results in the formation of a more localised region of lattice distortion.

In order to gain further insight into the nature of the 1^1B_u photoexcited state, it is instructive to investigate the time evolution of the energies and occupation numbers for the instantaneous adiabatic single-particle orbitals, φ_i . Notice that the occupation numbers can vary, in contrast to the time-evolving orbitals, $\phi_{i\mu}$. For the SSH model, this amounts to diagonalising the electronic part of the Hamiltonian at selected times, whereas, for the SSH + PPP model, it is necessary to minimise the electronic energy (24) through the self-consistent field procedure. In this case, we define the “orbital energies”

as the matrix elements

$$\varepsilon_i = \begin{cases} \langle \varphi_i | \frac{1}{2}(\hat{F}^{(2)} + \hat{F}^{(3)}) | \varphi_i \rangle, & \text{for the conduction band} \\ \langle \varphi_i | 2\hat{F}^{(1)} - \frac{1}{2}(\hat{F}^{(2)} + \hat{F}^{(3)}) | \varphi_i \rangle, & \text{for the valence band} \end{cases}, \quad (43)$$

which are conveniently distributed symmetrically about the midgap. Having found the instantaneous eigenstates, their occupation numbers can be calculated as²²

$$p_i = \sum_{\mu} \sum_{j_{\mu}} n^{\mu} |\langle \varphi_i | \phi_{j_{\mu}} \rangle|^2. \quad (44)$$

Figure 4 shows the time evolutions of the energies of the instantaneous eigenfunctions near the band edges, calculated for a 200-site *cis*-polyacetylene chain, both with and without Coulomb interactions. As for the dimerisation patterns, the results are qualitatively similar, exhibiting two states which oscillate back and forth, splitting from the bands and entering the gap, where they become localised. It is noteworthy that there is a direct correspondence between the time instants at which those two states are deep within the gap in Fig. 4, and the instants at which the peaks in the dimerisation patterns reach their maximum amplitude in Fig. 2. It is clear from Fig. 4 that the period between oscillations is much shorter in the SSH + PPP case, corroborating the important role of Coulomb interactions in promoting localisation. By using Eq. (44), we find that the occupancies of the gap states are

FIG. 4. Time evolutions of the energies of the instantaneous adiabatic orbitals (close to the band edges), obtained for a 1^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models. The energies of the gap states are shown in red.

always close to 1. All these results constitute a signature of an electron-hole pair, trapped in the region of lattice distortion. Therefore, within both the SSH and SSH + PPP models, the 1^1B_u photoexcited state corresponds to a polaron-exciton.

B. Dynamics of the 2^1B_u photoexcited state

Let us now consider the case of a 2^1B_u photoexcited state. The initial conditions are prepared as described in Sec. V A, with the difference that in this case a $\text{HOMO} - 1 \rightarrow \text{LUMO} + 1$ (or $2 \rightarrow 2$) excitation is created instead. The dimerisation patterns obtained for a 200-site *cis*-polyacetylene chain, through the numerical integration of the equations of motion for the SSH and SSH + PPP models, are shown in Fig. 5. As can be seen, in this case the lattice relaxes to form two separated local deformations rather than a single one. Similarly to what was observed for the 1^1B_u photoexcited state, there is a dynamical oscillation between the A and B phases at the centre of the regions of lattice distortion, leading to alternating peaks and troughs. Again, the “period” between peaks is shorter for the SSH + PPP model, which suggests that Coulomb interactions promote the creation of the local deformations in this case as well. Additionally, it is clear from the figure that the widths of the peaks are somewhat smaller in the SSH + PPP case, and thus adding Coulomb interactions results in the formation of more localised regions of distortion.

FIG. 5. Time evolutions of the dimerisation pattern, obtained for a 2^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models.

FIG. 6. Time evolutions of the energies of the instantaneous adiabatic orbitals (close to the band edges), obtained for a 2^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models. The energies of the gap states are shown in red (note that these constitute a set of two pairs of nearly-degenerate states).

To properly understand the nature of the 2^1B_u photoexcited state, we now proceed to investigate the instantaneous adiabatic single-particle orbitals, which are obtained as described in Sec. V A. Figure 6 shows the time evolutions of the energies of these orbitals near the band edges, calculated for the same 200-site chain, considering both the SSH and SSH + PPP models. In this case, there are two pairs of nearly-degenerate states oscillating back and forth between the bands and the gap. Similarly to what was observed for the 1^1B_u photoexcited state, there is a correspondence between the time instants at which those four states lie deepest in the gap, and the instants at which the peaks in the dimerisation patterns reach their maximum values. It is also clear from the figure that the period between oscillations is shorter in the SSH + PPP case, supporting the decisive role played by Coulomb interactions in promoting localisation.

Since the gap states, denoted by $\varphi_1^{(v)}$, $\varphi_2^{(v)}$ and $\varphi_1^{(c)}$, $\varphi_2^{(c)}$, form nearly-degenerate pairs, the symmetric and antisymmetric combinations

$$\begin{aligned} |\chi_{L,R}^{(v)}\rangle &= \frac{1}{\sqrt{2}}(|\varphi_1^{(v)}\rangle \pm |\varphi_2^{(v)}\rangle), \\ |\chi_{L,R}^{(c)}\rangle &= \frac{1}{\sqrt{2}}(|\varphi_1^{(c)}\rangle \pm |\varphi_2^{(c)}\rangle) \end{aligned} \quad (45)$$

are approximate eigenfunctions of the electronic part of the Hamiltonian (or, in the SSH + PPP case, they still bring the electronic energy to a minimum). As shown in Fig. 7, these

FIG. 7. Probability densities associated with the symmetric and antisymmetric combinations of the gap states, obtained for a 2^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH + PPP model (the SSH model yields similar results). Such linear superpositions lead to states localised on the left (a) or right (b) sides of the chain.

new orbitals are localised either on the left or on the right side of the chain. Moreover, if we calculate their occupation numbers using Eq. (44), we find that there is a total of 3 electrons in the states that split from the valence band, and only 1 in those which originated from the conduction band (the occupancies of $\chi_{L,R}^{(v)}$ are always around 1.5, while for $\chi_{L,R}^{(c)}$ they are close to 0.5). Thus, we may interpret the observed dimerisation patterns, with two separated local deformations, as corresponding to four possible configurations, depicted in Fig. 8. Depending on how the gap states are populated, species with different character emerge, namely, an exciton localised on one side of the chain, and two oppositely charged polarons localised on different sides (see Fig. 8). The probability of each case can be calculated by building an appropriate many-body wavefunction, Φ , using the valence band states $\phi_i^{(v)}$, $i = 3, \dots, N/2$, and the necessary orbitals from the set $\{\chi_L^{(v)}, \chi_R^{(v)}, \chi_L^{(c)}, \chi_R^{(c)}\}$, and projecting it onto the time-evolving many-body wavefunction, Ψ :

$$\begin{aligned} p(\text{Ex} + \text{Gr}) &= |\langle \Phi_{\text{Ex+Gr}} | \Psi \rangle|^2, \\ p(\text{Gr} + \text{Ex}) &= |\langle \Phi_{\text{Gr+Ex}} | \Psi \rangle|^2, \\ p(\text{P}^+ + \text{P}^-) &= |\langle \Phi_{\text{P}^+\text{P}^-} | \Psi \rangle|^2, \\ p(\text{P}^- + \text{P}^+) &= |\langle \Phi_{\text{P}^-\text{P}^+} | \Psi \rangle|^2. \end{aligned} \quad (46)$$

FIG. 8. Possible configurations corresponding to a dimerisation profile with two separated local deformations (Ref. 16), as obtained for a 2^1B_u photoexcited state.

Using the general relation for the inner product of two Slater determinants,⁵⁷

$$\langle \Phi | \Psi \rangle = \det \mathbf{M}, \quad (47)$$

where $\mathbf{M}$ denotes the matrix of elements $M_{ij} = \langle \phi_i | \psi_j \rangle$, the projections may be easily computed. We find that the probability of each configuration is about 25%. Therefore, within both the SSH and SSH + PPP models, the 2^1B_u photoexcited state corresponds to a superposition with equal weights of exciton and oppositely charged polarons, as previously suggested by An *et al.*¹⁶

C. The 2^1B_u photoexcited state under external field

In order to address the issue of charge photogeneration in conjugated polymers in dilute solution, it is instructive to investigate how the photoexcited states respond to an electric field. The case of a 2^1B_u state is particularly relevant, since, as we have shown, this state is partly polaronic in nature.

To set the stage, let us first examine what happens to free charges under an applied field. We consider a 200-site *cis*-polyacetylene chain with an added electron (i.e., with a total of 201 electrons) and depart from the minimum of the potential energy surface of this polaron state (which is found using the BFGS strategy, as in Secs. V A and V B). The initial conditions are completed by setting the ionic momenta and the external applied electric field to zero. The field then increases linearly with time, up to a strength of 5 mV/Å over a time window of 1 ps, as the system is propagated via numerical integration of the equations of motion. Figures 9 and 10 respectively show the time evolutions of the dimerisation and electronic charge distribution,

$$q_i = -e\rho_{ii}, \quad (48)$$

calculated both with and without Coulomb interactions. As can be seen, the added electron leads to a compact region of charge and lattice distortion, initially located at the centre of the chain. After a critical value of the field is reached, which is relatively low and not significantly different for both models, this polaron structure starts moving until it reaches the chain end, after which a series of oscillations take place. These correspond to the polaron being successively reflected at the boundary, and pushed back to the chain end by the field. It is clear from the figures that the polaron width is somewhat smaller for the SSH + PPP model, and thus, as already

FIG. 9. Time evolutions of the dimerisation pattern, obtained for a polaron state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models with applied field.

FIG. 11. Electronic charge distributions at $t = 0$, obtained for a polaron state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models.

FIG. 10. Time evolutions of the electronic charge distribution, obtained for a polaron state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models with applied field.

established for photoexcited states, adding Coulomb interactions gives rise to a more localised excitation. It is also noteworthy that the charge distributions exhibit oscillations in the region of distortion, a characteristic feature of soliton and polaron excitations.² As shown more clearly in Fig. 11, the charge oscillations are more pronounced when Coulomb interactions are included.

Let us now turn to the case of a 2^1B_u photoexcited state. We consider a 200-site chain and an external electric field applied at $t = 50$ fs, increasing linearly up to a strength of 5 mV/Å over a time window of 1 ps. The charge distributions obtained through the numerical integration of the equations of motion for the SSH and SSH + PPP models (with added field term), are shown in Fig. 12. The first thing to notice is that including Coulomb interactions leads to a substantially higher degree of charge confinement, which renders the picture obtained in the SSH + PPP case much more clear. In this case, it is seen that initially as the field increases there is a slight lattice polarisation, as one would expect for excitons [indeed, the whole dynamics is qualitatively similar to that of a 1^1B_u photoexcited state under the same external field (not shown)]. When the field strength reaches a value about 2–3 times higher than that required to trigger polaron motion, there are two regions of opposite charge which split at the centre of the chain, and start moving towards the chain ends. From this point on, the results may be interpreted as two oppositely charged polarons moving under an applied field. Although the picture obtained in the SSH case is less clear, since the charge is spread over many more lattice sites,

FIG. 12. Time evolutions of the electronic charge distribution, obtained for a 2^1B_u photoexcited state in a 200-site *cis*-polyacetylene chain, considering the SSH (a) and SSH + PPP (b) models with applied field.

there does not seem to be any evidence of polaron motion at the early stages, when the field strength is relatively low. These results suggest that, although the 2^1B_u photoexcited state corresponds to a superposition of exciton and oppositely charged polarons, the polarons do not behave as free charges, and the charge carriers are the result of the field-induced exciton dissociation.

D. Singlet vs. triplet excitons

We conclude this study with a comparison between the dynamics of the lowest singlet and triplet excited states, 1^1B_u and 1^3B_u . The lack of Coulomb interactions in the SSH model means that this model is “blind” to the spin symmetry of these two states, and thus unable to reproduce any difference between them. Indeed, in this case, the dynamics of the 1^3B_u state is exactly the same as for the 1^1B_u state, already studied in Sec. V A. In contrast, for the SSH + PPP model, within the MCTDHF formalism, the difference in the spin symmetries is captured by the different shell structures associated with each of those states, which may have important consequences for the dynamics. Hence, in the following we will only consider this latter model.

The initial conditions are prepared as described in Sec. V A, with the appropriate shell structures being set up. The time evolutions of the dimerisation obtained for the lowest singlet and triplet excited states in a 200-site *cis*-polyacetylene chain are shown in Fig. 13. As can be seen, in both cases the lattice relaxes to form a single local deformation, which corresponds to a polaron-exciton. There is a

FIG. 13. Time evolutions of the dimerisation pattern, obtained for 1^1B_u (a) and 1^3B_u (b) excited states in a 200-site *cis*-polyacetylene chain, considering the SSH + PPP model. Notice that the dimerisation pattern in panel (a) coincides with that shown in Fig. 2(b).

dynamical oscillation between the A and B phases at the centre of the chain, leading to alternating peaks and troughs, with a periodicity not significantly different in both cases. It is clear from the figure that the width of the peaks is much smaller for the 1^3B_u state. Additionally, the dimerisation in the region of distortion reaches values substantially higher in this case as well. Thus, triplet excitons are much more localised than singlet excitons, and they are accompanied by an enhanced lattice distortion. This is in agreement with other theoretical predictions and experimental observations.^{58–62}

VI. SUMMARY AND OUTLOOK

We have developed a nonadiabatic molecular dynamics method, which allows for the coupled evolution of classical ions and of multiconfigurational electronic wavefunctions. The proper spin symmetry is captured, thus providing a powerful tool to study the dynamics of photoexcited states and highlighting the differences between singlet and triplet excited states.

By applying the formalism to the dynamics of low-lying excitations in a prototypical conjugated polymer, described by simple semiempirical models, both with and without Coulomb interactions, a number of important differences were uncovered. Our findings suggest that adding Coulomb interactions promotes the localisation of photoexcitations, leading to the formation of more confined regions of

lattice distortion, which are created more rapidly. At the same time, it also suppresses certain dynamical processes, such as the continuous phase oscillation exhibited in the dynamics of photoexcitations. Polarons are also more localised when Coulomb interactions are included, and they show more pronounced charge oscillations in the region of distortion. Perhaps the most striking effect is the difference between the lowest singlet and triplet excited states, which can only be observed when Coulomb interactions are included. Our findings show that triplet excitons are much more localised than singlet excitons, and they are accompanied by an enhanced lattice distortion, in agreement with other theoretical predictions and experimental evidence.^{58–62}

The nature of the photoexcited states and the issue of charge photogeneration in conjugated polymers in dilute solution were also addressed. Our results show that the 1^1B_u photoexcited state corresponds to a polaron-exciton, while the 2^1B_u state is a superposition with equal weights of exciton and oppositely charged polarons. The conclusion is the same whether Coulomb interactions are included or not. This result, together with the similar energies and transition dipole moments of those excitations, has been used to argue that the charge carriers in conjugated polymers are photogenerated directly on ultrafast time scales, with a quantum yield of about 25%.¹⁶ However, as our calculations with an external electric field clearly indicate, the polarons of the 2^1B_u photoexcited state do not behave as free charges. In order to get a measurable photocurrent, the charge carriers must be produced on longer time scales through exciton dissociation mechanisms, such as the field-induced splitting.

In a forthcoming article in this series,⁶³ we will investigate the role of interchain interactions on the dynamics of conjugated polymers. The method will be applied to the study of interchain coupling effects on the dynamics of photoexcitations, as well as charge transfer dynamics at donor/acceptor interfaces, with the goal of assessing which conditions lead to the experimentally observed enhancement of the charge carrier photogeneration yield.^{13–15}

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