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Coupled electron-nuclear dynamics: Charge migration and charge transfer initiated near a conical intersection

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Coupled electron-nuclear dynamics, implemented using the Ehrenfest method, has been used to study charge migration with fixed nuclei, together with charge transfer when nuclei are allowed to move. Simulations were initiated at reference geometries of neutral benzene and 2-phenylethylamine (PEA), and at geometries close to potential energy surface crossings in the cations. Cationic eigenstates, and the so-called sudden approximation, involving removal of an electron from a correlated ground-state wavefunction for the neutral species, were used as initial conditions. Charge migration without coupled nuclear motion could be observed if the Ehrenfest simulation, using the sudden approximation, was started near a conical intersection where the states were both strongly coupled and quasi-degenerate. Further, the main features associated with charge migration were still recognizable when the nuclear motion was allowed to couple. In the benzene radical cation, starting from the reference neutral geometry with the sudden approximation, one could observe sub-femtosecond charge migration with a small amplitude, which results from weak interaction with higher electronic states. However, we were able to engineer large amplitude charge migration, with a period between 10 and 100 fs, corresponding to oscillation of the electronic structure between the quinoid and anti-quinoid cationic electronic configurations, by distorting the geometry along the derivative coupling vector from the D_{6h} Jahn-Teller crossing to lower symmetry where the states are not degenerate. When the nuclear motion becomes coupled, the period changes only slightly. In PEA, in an Ehrenfest trajectory starting from the D_2 eigenstate and reference geometry, a partial charge transfer occurs after about 12 fs near the first crossing between D_1 , D_2 (N^+ -Phenyl, N -Phenyl $^+$). If the Ehrenfest propagation is started near this point, using the sudden approximation without coupled nuclear motion, one observes an oscillation of the spin density – charge migration – between the N atom and the phenyl ring with a period of 4 fs. When the nuclear motion becomes coupled, this oscillation persists in a damped form, followed by an effective charge transfer after 30 fs. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4815914>]

I. INTRODUCTION

The recent development of attosecond laser technology (see, for example, the reviews of Kling¹ and Ivanov²) begins to provide the experimental technology for direct time domain measurements for the electronic motion in molecules. Laser ionization of a molecular system forms a coherent superposition of electronic states. This is predicted to be followed by a migration of electric charge within the molecule that may last up to few femtoseconds before the onset of nuclear dynamics.³

If an electron is “suddenly”⁴ removed from a molecule by ionization it will find itself in a superposition of electronic states, which will then evolve in time. However, the gradient with respect to the nuclear motion will not be zero, since the equilibrium geometry of the ionized state and the neutral state would be different. Thus, the geometry of the molecule must change and evolve in time as well. These two coupled processes can now be studied both experimentally and theoretically. In the limit where the electronic motion in the mixed state is not coupled to the nuclear motion, we have *charge migration*. In contrast, if the charge movement occurs as a consequence of the change in the electronic structure driving the

nuclear motion, we have *charge transfer*. We explore these definitions in more detail below; in this work, we will show that they overlap, and form a continuous spectrum.

Theoretical studies,^{5–15} where the nuclei are fixed and only the time evolution of the electronic wavepacket is allowed, have shown oscillatory charge migration. When the nuclear motion becomes coupled to this electronic motion, one may speculate that the electronic motion becomes damped, so that the end result is a net charge transfer. In this paper we discuss how theoretical simulations can be carried out in this regime using the Ehrenfest method, where one has an electronic wavepacket consisting of a superposition of electronic eigenstates, with coupled nuclear motion driven by the gradient of this electronic wavepacket.

The reason for using the Ehrenfest model in this work is that it provides a uniform methodology that can be used both with fixed nuclei and with coupled nuclear motion with no change to the basic formalism. The most commonly used method for non-adiabatic dynamics, where the nuclei are propagated classically, is the surface hopping approach (see recent reviews of Tully¹⁶ and Barbatti¹⁷ who have presented

FIG. 1. Benzene radical cation resonance structures. The directions X_1 and X_2 are the gradient difference and the gradient of the inter-state coupling vector, respectively. Note that for each quinoid or anti-quinoid structure, there are actually two resonance structures with the unpaired electron and the positive charge exchanged (this is indicated by $\bullet/+$ interchange in each case).

this subject exhaustively). However, this method has never been applied for fixed nuclei, when the electronic wavefunction is not an eigenstate. Thus, in the Ehrenfest approach, the method we use to propagate the wavefunction (i.e., as a solution of the time-dependent Schrödinger equation) is the same whether we couple the nuclear motion or not, and whether the time-dependent wavefunction is an eigenstate or not.

Our Ehrenfest approach is essentially a single configuration approximation to the multi-configuration formalism used by Shalashilin *et al.*¹⁸ (by configuration here we refer to the nuclei). We have previously used a “contracted basis function” assumption in our wavepacket dynamics.¹⁹ In our wavepacket dynamics work^{20,21} and in the multi-configuration Ehrenfest method of Shalashilin¹⁸ one is limited to pairs of electronic states but the nuclear wavepackets are fully interacting via the time-dependent Schrödinger equation. However, what distinguishes the approach used in this paper is that *all* electronic states (that are included in the CASSCF expansion) are fully coupled rather than just two. In this work, we have carried out only exploratory individual trajectories. To extend this, one would use the usual assumption made in trajectory computations: the trajectories are in-

dependent and the results of an ensemble of trajectories are averaged.

Our objective is to investigate the use of this method for two model systems: benzene and 2-phenyl-ethyl-amine (PEA) radical cations (see Figures 1 and 2). Benzene is chosen as a first example. Ionization of the neutral from the HOMO/HOMO-1 leads to the Jahn-Teller degenerate cation.^{22–25} In this case there is the possibility of charge migration/transfer around the ring. As we will see, we can engineer and control charge migration by distorting the benzene radical cation from the D_{6h} conical intersection along the derivative of the interstate coupling vector (derivative coupling).

We have chosen PEA as a simple model for phenylalanine that has been the subject of recent experiments²⁶ in which the N atom is ionized and charge transfer to the phenyl ring was observed in ~ 30 fs. Here, one has a subsequent charge migration/transfer process in which the acceptor is N^+ and the donor is phenyl. PEA is also a model for PENNA (2-phenyl-ethyl-*N,N*-dimethylamine) which has been studied for various fixed nuclear geometries by Cederbaum and co-workers.^{9,8} However, in PENNA the roles of the N lone pair/phenyl are interchanged in terms of ionization potential, and the phenyl has the higher ionization potential.

For both cationic systems (benzene Figure 1, and PEA Figure 2), several resonance (i.e., valence bond VB) structures are possible. We discuss benzene radical cation first. Benzene radical cation is a Jahn-Teller^{22–25} system (i.e., the D_{6h} geometry is a conical intersection^{27–30}). The degeneracy is lifted, to first order, along two directions X_1 and X_2 shown in Figure 1. The “moat” of the conical intersection contains the quinoid (Min) and in our computations anti-quinoid (TS) structures as shown. Notice that for each structure in Figure 1, there are actually two resonance structures with $(\bullet)$ and $(+)$ interchanged. The gradient difference direction X_1 connects quinoid/anti-quinoid forms, whereas the motion along the gradient of the interstate coupling vector X_2 moves from one quinoid (or anti-quinoid) structure to a “60° rotated” anti-quinoid (or quinoid) structure.

FIG. 2. Resonance structures for 2-phenylethylamine cation (PEA) $\phi^+ - C_2H_4NH_2$ (left hand side) resulting from charge displacement from initially ionized (right hand side) $\phi - C_2H_4N^+H_2$.

PEA, $\phi - \text{C}_2\text{H}_4 - \ddot{\text{N}}\text{H}_2$, is a substituted benzene whose cation has two forms (see Figure 2) $\phi - \text{C}_2\text{H}_4\text{N}^+\text{H}_2$ and $\phi^+ - \text{C}_2\text{H}_4\text{NH}_2$. The $\phi^+ - \text{C}_2\text{H}_4\text{NH}_2$ form has a similar set of resonance structures to the benzene radical cation (Figure 1). Each structure is distinguished by the position of the unpaired electron and the positive charge. Further, both anti-quinoid and quinoid forms are possible.

In our computations, we compute the spin density ($\rho_\alpha - \rho_\beta$) and partition it onto the atomic sites via the standard Mulliken Population analysis.³¹ Thus, by examining the spin density population at each atomic site as a function of time, we obtain the weights of the resonance structures in a fashion that is independent of the form of the wavefunction or the atomic orbital basis.

Now we must make a rather subtle point, that is a prerequisite for understanding subsequent discussion: the VB structures in Figures 1 and 2 can represent both the nature of the *wavefunction* (i.e., resonance structures or VB configurations) as just discussed, or they can give an indication of the *nuclear geometry* (i.e., the pattern of single bonds, corresponding to longer bond lengths, versus double bonds, corresponding to shorter bond lengths, etc.) in either Figure 1 or Figure 2. We will see both situations in our simulations. If the nuclei are not allowed to move, then the time-dependent wavefunction may explore the resonance structures as a function of time. In this case, the resonance structures in Figure 1 or Figure 2 would represent VB configurations in the wavefunction (that we can “observe” by looking at the spin density as a function of time). Cederbaum refers to the change in the configurations or resonance structures in the wavefunction as a function of time, with fixed nuclei, as *charge migration*. When the nuclei are allowed to move, a trajectory might actually pass through geometries indicated by the resonance structures. If molecular motion is constrained to the Born-Oppenheimer surface, then at a local minimum on the potential surface, a molecular structure (arrangement of bond lengths) may coincide with the resonance structure that dominates the wavefunction (or a combination of such structures). We will use the ideas of motion of charge or change in the VB configuration interchangeably.

The definitions of the terms charge migration and charge transfer are not universally accepted. In this paper we follow the convention of Cederbaum (see, for example, Refs. 9 and 8) in order that the reader can compare our results with his papers. In the end, it becomes difficult to distinguish these effects in coupled electron-nuclear dynamics and one must treat each case on its merits and try to understand the nature of the underlying physics.

According to Cederbaum,^{9,8} the term *charge migration* is used to refer to the motion of charge from one nuclear site to another (or equivalently, to the change in the VB configuration) when the nuclei are fixed. *Charge transfer*, on the other hand, only occurs when the nuclear motion is coupled. However, the clean separation of these two concepts is not always possible. As a reference, *charge transfer* can be defined when the Ehrenfest trajectory is initiated from an eigenstate (where charge migration is strictly null). When the trajectory is initiated from a superposition of eigenstates (e.g., the sudden approximation), without nuclear motion, then this is the

reference for *charge migration*. However, in actual examples, we can observe an oscillatory charge motion (previously identified as charge migration in a fixed nucleus computation) that persists even when the nuclear motion is coupled. We also observe, in examples where the wavefunction is a superposition, the case where a previously identified oscillatory charge migration (fixed nucleus) becomes damped and may collapse onto a single resonance form when the nuclear motion is coupled. This can be identified as charge transfer, however, because the electronic wavefunction is not an eigenstate (and charge migration only occurs on mixed state in the case of fixed nuclei).

II. THEORETICAL AND CONCEPTUAL DEVELOPMENT

A. Ehrenfest method

The Ehrenfest method provides a natural theoretical approach for the study of coupled electron-nuclear dynamics.^{32–38,40} We have used an implementation of the Ehrenfest method based on the CASSCF approach in applications to photochemistry⁴¹ and electron transfer.⁴² (For our purposes, CASSCF means CI with optimized orbitals. However, in subsequent discussion we will often use CI when we are referring to the features of the CI part alone.) For a discussion of a wide range of non-adiabatic dynamics methods the reader is referred to a recent special issue of J. Chem. Phys. where the lead article of Tully provides a useful summary of the state of the art.¹⁶

There have been two recent reviews, which include a comprehensive discourse on the Ehrenfest method,^{43,44} so we will be content with a few general statements. In the Ehrenfest approach, the nuclear motion is described by classical mechanics following a trajectory $Q(t)$, while the electronic motion is described quantum mechanically by a time-dependent wavefunction $\Psi(t)$, satisfying the time-dependent Schrödinger equation in atomic units

$$i \frac{\partial \Psi(t)}{\partial t} = \hat{H} \Psi(t). \quad (1)$$

The electronic wavefunction $\Psi(t)$ can be expanded in terms of a set of eigenstates $\phi_k(q; Q(t))$ of the electronic Hamiltonian with energies $E_k(Q(t))$ at fixed nuclear geometries $Q(t)$:

$$\Psi(q, t; Q(t)) = \sum_{k=1}^N z_k(t) \exp[-i E_k(Q(t))t] \phi_k(q; Q(t)), \quad (2)$$

where we use the intermediate representation as used by Gadea³⁵ and N is the number of terms in the CI expansion and q denotes the electronic co-ordinates. Equation (2) depends parametrically on $Q(t)$ at each time-step. The $z_k(t)$ are complex coefficients. Therefore, the electronic Hamiltonian is parameterized by $Q(t)$ and varies slowly. The solution of Eq. (1) is obtained by iteration, as we discuss below later in more detail. The wavefunction at time t_n ($t_n = t_{n-1} + \tau$) is propagated from the wavefunction at time t_{n-1} . After each electronic time-step, the nuclear positions can be updated following Newton's equation of motion, where the corresponding potential energy function for the classical nuclear degrees

of freedom is defined as the expectation value of the electronic Hamiltonian with the time-dependent electronic wavefunction.

B. Charge dynamics with the Ehrenfest method

We now give a simplified discussion of charge migration and charge transfer with a two-state model. From this point we will drop the explicit parametric dependence on $Q(t)$ in the formulae for simplicity, then we can write the time-dependent wavefunction, expanded in terms of the two eigenstates, using the intermediate representation,³⁵

$$\Psi(t) = z_1(t)e^{-iE_1(t)t}\phi_1(t) + z_2(t)e^{-iE_2(t)t}\phi_2(t), \quad (3)$$

where $\phi_1(t)$ and $\phi_2(t)$ are eigenstates with energies E_1 and E_2 . In Eq. (3) z_1 and z_2 are complex coefficients. If the nuclei do not move in time, the energies are constant and we have a coherent superposition of two states. We will distinguish two separate cases: (i) The Hamiltonian is not time-dependent (i.e., the nuclei are fixed) so that $\{z_1(t)\phi_1(t), z_2(t)\phi_2(t)\} = \{z_1(0)\phi_1(0), z_2(0)\phi_2(0)\}$ and the time dependence is in the exponential factors and (ii) the Hamiltonian is time-dependent and the nuclei are propagated in time.

The probability density $|\Psi(t)|^2$ can be written in a form derived from Eq. (3) as

$$|\Psi(t)|^2 = |z_1(t)|^2|\phi_1(t)|^2 + |z_2(t)|^2|\phi_2(t)|^2 + 2 \operatorname{Re}(z_1(t)^*z_2(t)e^{i(E_1(t)-E_2(t))t}\phi_1(t)^*\phi_2(t)). \quad (4)$$

If the nuclei are fixed, $z_1(t) = z_1(0)$ and $z_2(t) = z_2(0)$ (i.e., the eigenvalues $E_1(t)$ and $E_2(t)$ are time-independent and thus, one can talk about a coherent superposition), then the first two terms are time-independent, whereas the last term produces oscillations in the density due to the coherence of the system. The associated electronic motion is called charge migration. By looking at the last term, we can predict that oscillations in the density will be large in amplitude only if the two eigenstates are populated significantly. Also, the larger the energy difference is, the shorter the period of the oscillations will be. As we will see subsequently, we can engineer this situation by starting the trajectory adjacent to a conical intersection.

We can follow the evolution of the wavefunction (via the probability density $|\Psi(t)|^2$) by computing the spin density (which is related to the probability density). In practical terms, the alpha density is computed as

$$\rho_{ij}^\alpha = \sum_{K,L} \langle K | \eta_{i\alpha}^\dagger \eta_{j\alpha} | L \rangle a_K^* a_L. \quad (5)$$

The spin density is then $\rho_\alpha - \rho_\beta$. In Eq. (5), $|K\rangle$ and $|L\rangle$ are many-electron configuration state functions, i and j refer to AO basis functions, and we use general complex expansion coefficients a_K ($a_K = z_K e^{-iE_K t}$) where we use K, L, etc., to denote the configuration state function basis rather than the eigenvector basis (i.e., we will use lower case k, l, etc., to denote the eigenvector basis and upper case K, L, etc., to denote the configuration state function basis). The operator $\eta_{i\alpha}^\dagger \eta_{j\alpha}$ is a creator annihilator pair that annihilates orbital j with spin α (if it exists) and creates orbital i with spin α . If the result is other than K, then the matrix element is zero). Note that Eq. (4)

is the N-electron density (i.e., there are implicitly N creator-annihilator pairs), while Eq. (5) is the one-electron density that has to be transformed to the AO basis. The spin density can be subsequently partitioned onto atomic sites using the standard Mulliken Population analysis.³¹ Thus, the charge dynamics can be followed by computing the time-dependent Mulliken Population analysis of the spin density.

Let us now make two observations.

1. If we want to identify the charge migration component (no nuclear motion), starting from a sudden approximation Ehrenfest calculation, we need to fix the nuclei (i.e., $z_1(t) = z_1(0)$ and $z_2(t) = z_2(0)$, in Eq. (4)). We can use this strategy to compare with the computations of the Cederbaum group.¹⁰ However, as Cederbaum has discussed, the result is strongly dependent on the initial geometry.¹⁰
2. When the nuclei are propagated in concert with the electronic wavefunction (i.e., $z_1(t) \neq z_1(0)$ and $z_2(t) \neq z_2(0)$, in Eq. (4)), one cannot strictly separate the charge migration component. Nevertheless, we will see that the oscillation corresponding to charge migration persists in a damped form and with a variable period.

C. Ehrenfest implementation

We now outline our practical implementation of the Ehrenfest-CASSCF approach.⁴² At each step t_n of the dynamics, one obtains a basis of configuration-interaction eigenvectors $\mathbf{C}^k(t_n)$ (bold font is used to signify vectors and matrices) from diagonalization of the electronic Hamiltonian and a set of orbitals expressed by an orbital rotation matrix $\mathbf{X}(t_n)$. This can be illustrated by the following sequence:

$$\{\mathbf{C}^k(t_0)\}, \mathbf{X}(t_0) \xrightarrow{\tau} \{\mathbf{C}^k(t_1)\}, \mathbf{X}(t_1) \xrightarrow{\tau} \dots \xrightarrow{\tau} \{\mathbf{C}^k(t_n)\}, \mathbf{X}(t_n), \quad (6)$$

where $\{\mathbf{C}^k(t_n)\}, \mathbf{X}(t_n)$ refers to the adiabatic eigenstate k at time t_n and $\tau = t_n - t_{n-1}$.

We also propagate a sequence of vectors, $\mathbf{A}(t_n)$, which are solutions to the time-dependent Schrödinger equation:

$$\mathbf{A}(t_n) = \begin{pmatrix} a_1(t_n) \\ \vdots \\ a_k(t_n) \\ \vdots \end{pmatrix}. \quad (7)$$

(Note $a_k = z_k e^{-iE_k t}$ for comparison with Eq. (2).) The coefficient, $a_k(t_n)$, in the vector is a complex number whose magnitude gives the contribution of the eigenstate k to the time-dependent wave function:

$$\{\mathbf{A}(t_0)\} \xrightarrow{\tau} \{\mathbf{A}(t_1)\} \xrightarrow{\tau} \dots \xrightarrow{\tau} \{\mathbf{A}(t_n)\}. \quad (8)$$

The sequence of vectors defined in Eq. (8) may be obtained in concert with nuclear motion. Alternatively, the nuclei may be fixed, in which case the basis defined in Eq. (6) does not change with time.

From a practical point of view, the $\mathbf{A}(t_n)$ are obtained from the time-dependent Schrödinger equation via the integration sequence

$$\mathbf{A}(t_n) = \exp[-i\mathbf{H}(t_n)\tau]\mathbf{A}(t_{n-1}), \quad (9)$$

where $\mathbf{H}(t_n)$ is the matrix representation of the Hamiltonian, in the basis of the eigenstates $\{\mathbf{C}^k(t_{n-1})\}$ at time t_{n-1} , computed using the integrals evaluated at $t = t_n$ and $\mathbf{A}(t_n)$ is the new vector used to compute the gradient at $t = t_n$. The exponential term can be evaluated using the eigenstate representation of an operator, using the (real) eigenvalues $E(k)$ and eigenvectors $\mathbf{U}^k$ of $\mathbf{H}(t_n)$ as

$$\exp[-i\mathbf{H}\tau] = \sum_{k=1}^N \mathbf{U}^k \boldsymbol{\epsilon}_k \mathbf{U}^{k\dagger}. \quad (10)$$

In Eq. (10) $\mathbf{U}^{k\dagger}$ is the transpose of $\mathbf{U}^k$, $\boldsymbol{\epsilon}_k = \exp[-iE_k\tau]$, and the sum over k is over all the CI states, N . Park and Light⁴⁵ have a discussed practical scheme for the implementation of Eqs. (9) and (10).

Recently, Schlegel and co-workers³⁸ have used this type of integration sequence in the context of TD-HF. As discussed in that paper, the integration sequence of Eq. (9) is exact only for a constant $\mathbf{H}(t_n)$. Thus, the time step τ has to be small enough so that the step is accurate. However, the integrals used to construct the change in the CI Hamiltonian matrix in Eq. (9) vary little on this time scale and Schlegel suggests that they can be kept constant for several τ time steps. (However, we have not implemented this.)

An additional practical consideration in a CASSCF implementation arises from the orbitals. We also have to assume that the active space is large enough such that the change in the electronic structure is dominated by the changes in the wavefunction expansion rather than in the orbitals, which are assumed to remain almost constant.

To conclude this section, we emphasize that, in the method used in this paper, the electron and nuclear dynamics are treated on a different footing. The electrons are described quantum mechanically, while the nuclei are described classically. Clearly, the main limitations of this unbalanced treatment would be removed by treating the nuclei quantum mechanically. A very general strategy for treating the nuclei quantum mechanically has been discussed by Cederbaum.⁴⁶ Otherwise, the applicability of the method is limited mainly by the limitations of the CASSCF type approach and the choice of active orbital space such that a balanced treatment of the cationic states is possible.

D. Ehrenfest gradients

In the Ehrenfest method the energy is computed from

$$\hat{E}(t_n) = \mathbf{A}^\dagger(t_n)\mathbf{H}(t_n)\mathbf{A}(t_n), \quad (11)$$

where $\mathbf{A}^\dagger(t_n)$ is the complex conjugate transpose of $\mathbf{A}(t_n)$. $\mathbf{A}(t_n)$ is also used to compute the energy gradient $\partial\hat{E}/\partial\lambda$ that drives the nuclear propagation where λ denotes the set of internal co-ordinates of the molecule. Because the electronic wave function is a superposition of eigenstates $\mathbf{C}^k$ (and not a pure eigenstate), one cannot use the Hellmann-Feynman for-

mulation for the gradient of the energy with respect to nuclear motion. Thus, the resulting equations for the gradient must include the orbital rotation and CI derivatives.⁴⁷ (These corrections would not be needed if one used a non-local basis set.) The details are discussed in the supplementary material for our previous paper.⁴² The gradient $\hat{\mathbf{E}}_\lambda$, of Eq. (11), has the following form (where we use the formalism of Almlöf and Taylor⁴⁸):

$$\hat{\mathbf{E}}_\lambda = \hat{\mathbf{E}}^\lambda + \hat{\mathbf{E}}^A \mathbf{A}_\lambda + \hat{\mathbf{E}}^X \mathbf{X}_\lambda - \frac{1}{2} \hat{\mathbf{E}}^Y \mathbf{S}_\lambda. \quad (12)$$

$\hat{\mathbf{E}}^\lambda$ is the Hellmann-Feynman term $(\partial[\mathbf{A}^\dagger(t_n)\mathbf{H}(t_n)\mathbf{A}(t_n)]/\partial\lambda)$ and $\mathbf{A}_\lambda$, $\mathbf{X}_\lambda$ are the wavefunction and orbital rotation derivatives with the corresponding energy derivatives $\hat{\mathbf{E}}^A$, $\hat{\mathbf{E}}^X$, and $-\frac{1}{2}\hat{\mathbf{E}}^Y \mathbf{S}_\lambda$ is the term associated with the symmetric Lagrangian $\hat{\mathbf{E}}^Y$ that occurs in SCF theory.

The integration procedure for the nuclear dynamics in our Ehrenfest simulations can be chosen from the various possibilities within the Gaussian program;⁴⁹ our computations are carried out with the Velocity-Verlet method as implemented there.

E. Ehrenfest (mixed state) problem

Finally, we should comment on a possible difficulty with the Ehrenfest approach.¹⁶ It is often suggested that Ehrenfest trajectories may not decay from a mixed state to an unmixed state asymptotically. This situation can occur where the region of strong non-adiabatic coupling is very small along a trajectory. We have not encountered such anomalies in our previous computations,⁴¹ where in photochemistry decay at the conical intersection occurs cleanly.

Thus, the problem with unphysical mixed state propagation with the Ehrenfest does not seem to be an issue with our CASSCF calculations (Figure S2 in the supplementary material⁵³). It may be because we use all the possible eigenstates of the CASSCF problem (as opposed to just two states in other approaches). This is particularly important because when we start with a mixed state using the sudden approximation, we will not move on the Born-Oppenheimer surface. In the supplementary material,⁵³ we show that if we start an Ehrenfest trajectory near a Born-Oppenheimer surface with an artificially induced mixed state for benzene, it will collapse to the eigenstate. Similarly, in PEA we will see that the Ehrenfest trajectory passes many conical intersection crossings with a rapid relaxation to Born-Oppenheimer adiabatic states.

III. COMPUTATIONAL DETAILS

A. Active space

In our computations with the CASSCF method, the choice of active space needs to recover only the non-dynamic electron correlation (e.g., the $(\sigma)^2 - (\sigma^*)^2$ correlation in H_2 that allows for dissociation into two open-shell H atoms). We are not interested in the accuracy of the energy difference between neutral and cation states (where dynamic correlation is essential); rather, we are concerned with getting a balanced representation of the various cationic states themselves. In

CASSCF on closed shell systems, it is well established that a balanced active space is vital to success. One gets inconsistent results if one attempts to include only a part of the dynamic correlation.

In benzene, using the standard 6-31G* basis set, there are 6 active π orbitals: the 4 orbitals that would correspond to the degenerate HOMO/HOMO-1 and “matching” degenerate LUMO/LUMO+1, and the remaining pair of benzene π orbitals. The latter pair strictly contributes to dynamic correlation, but has to be included for stability (since the dynamic correlation is large). However, this does not make the active space unbalanced.

For PEA, three states will be studied, corresponding to ionization from a pair of quasi-degenerate HOMO orbitals and from the lone pair N orbital. We must treat the $Nlp(2p)$ orbital and the phenyl in a balanced way; thus, we need correlating orbitals corresponding to the “matching” two LUMO π^* orbitals and an $lp(3p)^*$. Since there is no $lp(3p)^*$ in a 6-31G* basis set (i.e., such a $3p$ orbital would be far too diffuse), we have augmented the 6-31G* basis set with a 3-1 contracted $3p$ orbital for the N atom. (This was constructed using phosphorus exponents taken from the standard 6-31G* basis.) This $3p$ orbital provides a “correlating orbital” for the N atom lone pair. The resulting correlating orbitals (two LUMO π^* orbitals and an $lp(3p)^*$) have one additional node relative to the closed shell occupied orbitals. This yields a 6-orbital 5-electron active space for PEA. We have demonstrated the efficacy of this strategy in previous work.⁵⁰

B. Initial conditions

Our purpose in this work is to investigate the efficacy of the Ehrenfest method, implemented within a CASSCF approach, for studying charge migration (nuclei fixed) versus charge transfer (nuclei moving). We have used the optimized neutral geometries for each molecule (with B3LYP for benzene and for PEA). We have distorted the C_s symmetry of PEA by an infinitesimal amount, while benzene has also been distorted from D_{6h} (also by a very small amount); the resulting symmetry is then C_s . We shall refer to these as the *reference geometries*. (This symmetry breaking was imposed to avoid artifacts arising from using the exact symmetry.)

Then we use various different starting conditions:

Case 1. Ehrenfest simulations starting from an eigenstate and the neutral reference geometry: Here, we start from the reference geometry of the neutral species. The initial wavefunction is either degenerate D_0/D_1 for the benzene cation, or D_2 (N^+ -phenyl) for PEA. We perform the simulation only with moving nuclei. The simulation is very similar to a classical trajectory (Born-Oppenheimer Molecular Dynamics BOMD) except at points where a surface crossing occurs.

Case 2. Ehrenfest simulations starting from the sudden approximation (not eigenstate) using the neutral reference geometry: For simulations that do not involve an eigenstate, we use the sudden approximation.⁴ For CASSCF, this means the sudden removal of an electron from a full CASSCF computation on the neutral. This is a non-stationary electronic state corresponding to a linear combination of cation configurations. These configurations are generated from the neutral

wavefunction by removing a single electron from the same orbital in each configuration while keeping the weights (i.e., coefficients) of the configurations fixed. We performed the simulation both with nuclear propagation and using fixed nuclei.

Case 3. Ehrenfest simulations with the sudden approximation (not eigenstate) at distorted geometries: As we will see, charge migration (oscillation of charge density without nuclear motion) is not significant when the initial wavefunction is constructed from the neutral ground state at the reference geometry. Cederbaum¹⁰ has also noticed strong dependence on the initial geometry. Thus, in case 3, we will use distorted geometries to demonstrate some conditions required for large charge migration. We will then investigate the effect of allowing nuclear motion.

C. Computation of the gradient

The full computation of the Ehrenfest gradient using the CP-MCSCF equations⁴² is very expensive so we have omitted the solution of the coupled perturbed equations (the terms $\hat{E}^A A_\lambda$ corresponding to the derivatives of the Ehrenfest vector and $\hat{E}^X X_\lambda$ corresponding to the orbital rotation derivatives in Eq. (12)). Fortunately, any error in the gradient in a trajectory computation shows itself up as an error in conservation of energy. The energy conservation error for all our calculations is given in Table S6 of the supplementary material.⁵³

To give an independent estimate of these errors we report the test S_1 trajectory for but-1-ene.⁵¹ The approximate gradient, neglecting the CI rotation and orbital rotation derivatives (green), only adds a minimal error (± 0.05 kcal mol⁻¹) after 5 fs. This information is given in Figure S1 of the supplementary material.⁵³

IV. RESULTS AND DISCUSSION

We now begin a discussion of Ehrenfest dynamics of the two model systems: the benzene radical cation and the PEA radical cation. We first discuss trajectories starting from the reference neutral geometry. Computations beginning with an eigenstate (case 1) are like classical (Born-Oppenheimer molecular dynamics, BOMD) trajectories except that they do not require a surface-hopping algorithm. They provide information about the various potential energy surfaces (corresponding to eigenstates) involved. The main focus of our results, however, is on trajectories that are initiated on mixed states (i.e., from the sudden approximation, which simulates ultrafast ionization and the subsequent dynamics, case 2). We will also discuss computations with fixed nuclei where only the electronic wavefunction is propagated in time. When the nuclear coupling is turned on, any charge migration is still present, but becomes damped and modified. Then we present results (case 3) where the geometry corresponds to a region of strong interaction between electronic states (charge migration without nuclear motion is possible).

A. Dynamics of the benzene radical cation

The main structures involved in the initial part of the simulation of benzene lie in the D_0 Jahn-Teller^{22–25,39} (conical

FIG. 3. Schematic representation of the benzene radical cation D_1/D_0 crossing. This is a cross section through the conical intersection along X_1 (Figure 1). The quinoid structure (on the left) is a minimum, whereas the anti-quinoid structure (on the right) is a transition state in the moat of the conical intersection. Mulliken atomic spin densities are indicated in red next to each carbon atom. Characteristic bond lengths are indicated in green. Note that for the quinoid or antiquinoid structure, there are actually two resonant structures with the unpaired electron and the positive charge exchanged (this is indicated by $\bullet/+$).

intersection) moat. The geometries and spin densities of the (optimized) critical points in the moat are shown in Figure 3.

We first turn our attention to the trajectory initiated on the D_0 eigenstate, at the reference geometry. (Our simulations start with a structure that is slightly distorted from D_{6h} and very close to the conical intersection.) The results are shown in Figure 4, where we have plotted the spin densities at the carbon atoms as a function of time. Comparing the values of the spin densities plotted in Figure 4 against the reference values given in Figure 3 enables one to determine the VB structures at different times in the simulation. For example, in Figure 4 at 36 fs, the $C_1 = C_4 = C_2 = C_5$ spin density can be read as 0.29, which corresponds to the value given for an anti-quinoid structure (right hand side of Figure 3, rotated 60° as shown in Figure 4). Further, the C_1-C_2 and C_4-C_5 bond lengths at 36 fs are 1.44 Å, in agreement with Figure 3. Therefore, at 36 fs both the VB structure and the geometry correspond to the anti-quinoid structure. The analysis is similar for the other points on the trajectory shown in Figure 4. To conclude, we essentially have a classical BOMD trajectory moving in the moat of the conical intersection.

We now turn to a discussion of simulations where the initial state is not an eigenstate. In Figure 5 we show an Ehrenfest trajectory for benzene, including nuclear motion, starting from a mixed state constructed using the sudden approximation (ionization from the HOMO) at the reference geometry. Since the electronic wavefunction is not an eigenstate, the trajectory does not lie on a Born-Oppenheimer surface. From the spin densities, one still see the succession of structures going around the moat (see Figure 1) adopting quinoid and anti-quinoid resonance forms successively. Notice, however, the new feature: there is a fast oscillation superimposed on the spin densities, which is not seen in Figure 4.

FIG. 4. Ehrenfest trajectory of the benzene radical cation starting from the D_0 electronic state at the reference geometry. The hexagon at the top left shows the numbering of the carbon atoms. The x-axis shows (a) Mulliken atomic spin densities at carbons 1,4 (red), carbons 2,5 (green) and carbons 3,6 (blue) and (b) bond lengths (Å) of the important structures explored during the trajectory. Note that in this trajectory, the nuclear motion is allowed.

When the nuclei are fixed, this rapid, very low amplitude, oscillation remains: it corresponds to charge migration. This is easily explained using Eq. (4). An expansion of the wavefunction in the eigenvector basis shows that only the first two eigenstates are populated significantly and they are degenerate. So the corresponding Bohr frequency is infinite. The other sparsely populated eigenstates are high in

FIG. 5. An Ehrenfest trajectory of the benzene radical cation starting from an electronic state constructed using the sudden approximation (ionization from the HOMO) at the reference D_{6h} geometry. The hexagon at the top left shows the numbering of the carbon atoms. The x-axis shows (a) Mulliken atomic spin densities at carbons 1,4 (red), carbons 2,5 (green) and carbons 3,6 (blue) and (b) bond lengths (Å) of the important structures explored during the trajectory. Note that in this trajectory, the nuclear motion is allowed.

energy, which causes very high frequency oscillation. In fact, after the first 0.2 fs, this trajectory almost collapses to the ground state (80% D_0 , 0% D_1 , and 1%–2% each for several very high excited states). So, we only have these small high-frequency oscillations on top of the charge transfer.

Comparing Figures 4 and 5 (both starting from the same geometries) we notice that the period of oscillation in Figure 5 is much slower and the bond-lengths are rather different in detail. Thus, the potential felt by the nuclei is quite different.

In our discussion so far, we started the Ehrenfest trajectory at a geometry very close to the conical intersection (or the Jahn-Teller degeneracy) of the benzene radical cation. At a conical intersection, there are two directions (X_1 and X_2) that lift the degeneracy (see Figure 1: the gradient difference and the gradient of the interstate coupling vector, which is related to the derivative coupling).

If a trajectory passes through the conical intersection strictly aligned along X_1 , then it passes through diabatically. Accordingly, the adiabatic state changes but the electronic configuration does not change. (Note: if one distorts the molecule along X_1 , then the sudden approximation will only populate one of the two lowest eigenstates so charge migration will not be seen, since in Eq. (4) only one eigenstate will be populated.) On the other hand, if a trajectory passes adjacent to the conical intersection, but with a significant component along X_2 , then it passes through a region where the states strongly interact: the crossing becomes avoided. In such a situation, the trajectory may progress adiabatically or non-adiabatically. In each case, we have a strong mixture of diabatic states. Thus, we can design a starting condition with very strongly coupled states that are nearly degenerate by displacing the geometry from the conical intersection along the direction X_2 . Since distorting the geometry along X_2 lifts the degeneracy, we can control the energy gap and thus the oscillation frequency.

In Figures 6 and 7 we show Ehrenfest trajectories beginning at two geometries displaced along the direction X_2 . In each case, we begin with a mixed state constructed using the sudden approximation (ionization from the HOMO). The behavior of the oscillation in charge or spin density is predicted from Eq. (4). If the states are close together in energy, the period of the charge density oscillations will be long (infinite if they are degenerate); but as the states become more widely separated in energy the oscillation period decreases.

We begin with a discussion of Figure 6, showing spin densities in the same manner as previously. The geometry distortion in this case is big and the D_0 – D_1 energy separation is ~ 0.4 eV. When the nuclei are fixed, we have oscillation in the spin density with a period of about 10 fs (see Figure 6(a)). It corresponds to an oscillation between the quinoid and anti-quinoid structures (see Figure 3). We emphasize that this corresponds to a change with time of the VB structure weights in the electronic wavefunction (quinoid to anti-quinoid); the nuclei are not moving. There are also sparsely populated higher-energy eigenstates, which give rise to the high-frequency oscillations superimposed.

In Figure 6(b), we show the result when nuclear motion becomes allowed. The evolution of the atomic spin densities

FIG. 6. Ehrenfest trajectory of the benzene radical cation starting from a mixed state constructed using the sudden approximation (ionization from the HOMO) at a first distorted geometry along X_2 : $C1-C2=C4-C5 = 1.36$ Å, $C2-C3=C5-C6 = 1.40$ Å, and $C3-C4=C6-C1 = 1.43$ Å. Mulliken atomic spin densities at carbons 1,4 (red), carbons 2,5 (green), and carbons 3,6 (blue). The hexagon at the top left shows the numbering of the carbon atoms. (a) Simulation with fixed nuclei. The spin density oscillates between the two electronic structures drawn below the plot with a period of about 10 fs – half a period, 5 fs, is necessary to go from one structure to the other. (b) Simulation with nuclear motion allowed.

is unchanged only up to 2 fs showing that the effect of nuclear motion cannot be neglected on a longer timescale. The main features associated with the quinoid/anti-quinoid charge migration are still present. However, the period changes from 10 fs to ~ 7 fs and the amplitudes are not constant any more. This is due to the fact that, as the nuclei move, the energy changes with time and the coherence is lost. In addition, the evolution is not symmetric anymore: the spin density on carbons 2,5 and 3,6 are predicted to be the same with fixed nuclei; whereas, they differ when the nuclei are allowed to move. This illustrates that the coupling with nuclear motion allows the electronic wavefunction to visit other resonance

FIG. 7. Ehrenfest trajectory of the benzene radical cation starting from a mixed state constructed using the sudden approximation (ionization from the HOMO) at a second distorted geometry along X_2 : $C1-C2=C4-C5 = 1.390$ Å, $C2-C3=C5-C6 = 1.395$ Å, and $C3-C4=C6-C1 = 1.400$ Å. Mulliken atomic spin densities at carbons 1,4 (red), carbons 2,5 (green), and carbons 3,6 (blue). The hexagon at the top left shows the numbering of the carbon atoms. (a) Simulation with fixed nuclei. The spin density oscillates between the two electronic structures drawn below the plot with a period of about 100 fs – half a period, 50 fs, is necessary to go from one structure to the other. (b) Simulation with nuclear motion allowed.

structures. However, it is not easy to interpret the details of the changes in the nuclear geometry.

In Figure 7(a), we present similar results to Figure 6(a), but with much smaller geometry displacement where the D_0 - D_1 energy separation is 0.04 eV. In this case, the period increases to about 100 fs. Again, other slightly populated eigenstates cause the additional small amplitude oscillations with high frequency. The 100 fs period is remarkable: charge migration is certainly not ultrafast in this case. When the coupling of the nuclei is turned on (Figure 7(b)), the result is very similar to that shown in Figure 5 (started near the reference geometry, computed with the sudden approximation): the charge transfer oscillations are superimposed on charge

FIG. 8. Expansion in the eigenstate basis of the electronic wavefunction constructed using the sudden approximation (ionization from the HOMO) at the first distorted geometry along X_2 : $C1-C2=C4-C5 = 1.36$ Å, $C2-C3=C5-C6 = 1.40$ Å, and $C3-C4=C6-C1 = 1.43$ Å. (cf. Eqs. (2) and (7), where $a_k = z_k(t)e^{-iE_k t}$).

migration; however, the charge migration oscillations have such a long period that we cannot see them anymore. This is due to the fact that because the nuclei move, the energy difference changes with time and the coherence is lost.

Of course benzene is a model system, in the sense that we can completely characterize the conical intersection. Consequently, we know that a distortion along the direction X_2 from the apex of the cone would generate a starting geometry with nearly degenerate but strongly coupled states. This idea is further illustrated in Figure 8 where we give the eigenstate populations after sudden ionization at the distorted geometry. From Figure 8, we have two nearly degenerate states with almost equal occupation numbers (associated with the avoided crossing along the derivative of the interstate coupling vector) along with a number of smaller peaks that correspond to the rapid oscillations associated with the couplings of these states. Whether or not one can design substituted benzenes that have such characteristics remains to be seen. We now move on to the PEA example, where we will see the same effect but which is much more difficult to engineer.

B. Dynamics of PEA radical cation

PEA has three very tightly coupled cationic configurations: N^+ -phenyl, $\phi - C_2H_4N^+H_2$, corresponding to a positive charge on the N atom, and two N :-phenyl $^+$ $\phi^+(1) - C_2H_4NH_2$ and $\phi^+(2) - C_2H_4NH_2$ configurations depending upon whether the single electron resides in the HOMO or HOMO-1. The two states with an ionized phenyl group are almost degenerate.

Ehrenfest dynamics starting from an eigenstate at the reference geometry provides our main insight into the nature of the potential energy surfaces in PEA. Such trajectories are very similar to classical (BOMD) trajectories, except in crossing regions. In Figure 9, we show such an Ehrenfest trajectory for the PEA radical cation, starting from the eigenstate D_2 , which is dominated by the $\phi - C_2H_4N^+H_2$ configuration.

FIG. 9. Ehrenfest trajectory (with coupled nuclear motion) of the PEA radical cation starting at the reference geometry of the neutral species. (a) The population of the three coupled eigenstates as a function of time: red D_0 , green D_1 , and blue D_2 . (b) Weights of the dominant configurations in the time-dependent wavefunction: blue (SD7, $\phi - C_2H_4N^+H_2$), green (SD3, $\phi^+(1) - C_2H_4\dot{N}H_2$), and red (SD1, $\phi^+(2) - C_2H_4\dot{N}H_2$).

Figure 9(a) shows the population of the three eigenstates (D_0 , D_1 , and D_2), while Figure 9(b) shows the composition of the time-dependent wavefunction with respect to the weights of the three main cationic configurations (SD7: $\phi - C_2H_4N^+H_2$, SD3: $\phi^+(1) - C_2H_4\dot{N}H_2$ and SD1: $\phi^+(2) - C_2H_4\dot{N}H_2$, where SD = Slater Determinant).

The data presented in Figure 9(a) show that the trajectory goes through several crossings of the adiabatic surfaces and one does not propagate on a mixed state for long periods (i.e., more than a few fs). The crossings seen in the eigenstates (Figure 9(a)) are not directly reflected by crossings of the configurations (Figure 9(b)). Indeed, the first crossing in Figure 9(a) at 6 fs is diabatic in nature: the electronic configuration does not change immediately. Instead, in Figure 9(b), one sees an avoided crossing (of configuration state functions), which is not reflected in the eigenstate populations in Figure 9(a), at 12 fs.

The behavior of the spin density on the nitrogen, and the spin density on the axial carbons of benzene is shown in Figure 10. The behavior of these spin densities reflects the behavior of the configurations in the time-dependent wavefunction shown in Figure 9(b). Thus, the BOMD-like Ehrenfest

FIG. 10. Ehrenfest trajectory (with coupled nuclear motion) of the PEA radical cation starting at the reference geometry of the neutral species. Mulliken atomic spin densities as a function of time at nitrogen atom (red); axial carbons C3 (green) and C6 (blue).

trajectory has many crossings and avoided crossings. As we have discussed previously, with an eigenstate trajectory, there can be no charge migration effect with fixed nuclei. Thus, the eigenstate trajectory provides a reference for charge dynamics where charge migration is excluded. Strong interactions occur at 10 and 30 fs, where there is partial charge transfer (seen in the spin densities in Figure 10) from the nitrogen to the phenyl ring. For phenylalanine,²⁶ charge transfer to the phenyl ring in ~ 30 fs has been observed.

We attempted to optimize a conical intersection (starting from a geometry corresponding to 8 fs in Figure 9(a) between $\phi - C_2H_4N^+H_2$ and $\phi^+(1) - C_2H_4\dot{N}H_2$, but this was unsuccessful because of the near degeneracy of $\phi^+(2) - C_2H_4\dot{N}H_2$, which means that we are close to a 3-state-intersection.⁵² In the Ehrenfest trajectory, all the eigenstates are included, so regions of more than two strongly coupled states do not cause any practical difficulties (indeed, this is one of the reasons for using such methods). However, it does mean that the main information about the potential surface has to be derived from such an Ehrenfest trajectory currently (i.e., one cannot optimize critical points conventionally because of multiple degeneracies).

From Figure 9, it can be seen that the onset of the strong interaction occurs in the region of 10 fs. The main geometry change for the first 10 fs (for the trajectory shown in Figure 9) is shown in Figure 11(b): the planarization of NH_2 . But notice that there is a faster oscillation in the spin density (Figure 10) that begins at around 16 fs. As we will discuss, this oscillation persists even when nuclear motion is turned off. In Figure 9, we do see the onset of strong interaction between 8 and 10 fs, both with a surface crossing in Figure 9(a), and, nearby, a few fs later an avoided crossing at 12 fs, as shown in Figure 9(b). As a result, as we will show subsequently, starting an Ehrenfest trajectory from the 10 fs geometry shown in Figure 11, with the sudden approximation, produces charge migration in a similar fashion as that which we engineered directly in the benzene radical cation.

FIG. 11. Approximate location of N^+ -phenyl/ N^- -phenyl $^+$ crossing at 10 fs (b) relative to geometry of neutral at 0 fs (a).

We now turn to a discussion of Ehrenfest trajectories for PEA, where the starting conditions are constructed using the sudden approximation, and are initiated at displaced geometries. Such simulations are more closely related to the way in which experiments may be carried out; namely, on a superposition of states that is not an eigenstate.

If one starts an Ehrenfest trajectory at a geometry near the reference geometry of neutral species using the sudden approximation (superposition of eigenstates), we obtain - as in benzene cation - a trajectory similar to the eigenstate trajectory, but with a more rapid and very low amplitude oscillation superimposed. However, it is clear from our simulations on benzene that the large oscillations associated with charge migration only begin to occur in regions of near degeneracy, where there is strong interaction between the states. Thus, we will focus our discussion on Ehrenfest trajectories initiated at displaced geometries instead.

In Figure 12, we show an Ehrenfest trajectory initiated using the sudden approximation at the 10 fs geometry given in Figure 11(b). The spin density on the nitrogen is shown together with the spin densities on the axial carbon atoms (C_3 and C_6). Figure 12(a) shows the spin density as a function of time, with no nuclear motion. It corresponds to charge migration: with a half-period of ~ 4 fs, we see the charge moving from the nitrogen to the carbon atoms of the phenyl ring then back. (Note: we have shown only the spin population on the two axial carbons for clarity; the remaining population resides on C_4 , C_5 , C_7 , and C_8 .) Remarkably, when the nuclear motion is allowed, in Figure 12(b), the oscillation is broadly similar except that one can see the amplitude corresponding to the nitrogen charge slowly decaying, corresponding to net transfer to the phenyl around 30 fs. The coupled nuclear motion in this case is mainly a symmetric $-NH_2$ stretch, coupled with skeletal deformation of the phenyl ring, associated with populations of the various VB structures shown in Figure 2.

Compare Figure 12(b) with Figure 10, where we can see, from 18 fs, an oscillation in the spin density that is heavily damped. In both figures, the period remains around 8 fs. Thus, in PEA we are able to simulate charge migration with fixed nuclei (Figure 12(a)) provided we start at a geometry where

FIG. 12. Ehrenfest trajectory of the PEA cation starting a mixed state constructed using the sudden approximation at the 10 fs geometry (Figures 10 and 11). Mulliken atomic spin densities as a function of time at N atom (red), axial carbons C_3 (green), and C_6 (blue). (a) Simulation with fixed nuclei. (b) Simulation with nuclear motion allowed.

there is a strong interaction at an avoided crossing (seen in Figure 9). This charge migration persists when the nuclear motion is coupled (Figure 12(b)). Indeed, one can also see this spin density oscillation even in Figure 10 beginning after 18 fs.

Thus, in PEA we are able to simulate charge migration with fixed nuclei (Figure 12(a)) provided we start at a geometry where there is a strong interaction at an avoided crossing (seen in Figure 9). This charge migration persists when the nuclear motion is coupled (Figure 12(b)). Indeed, one can also see this spin density oscillation even in Figure 10 beginning after 18 fs.

V. CONCLUSIONS

Coupled electron-nuclear dynamics, implemented using Ehrenfest trajectories, has been used to study charge migration with fixed nuclei, together with charge transfer when nuclei are allowed to move. Simulations were initiated at reference geometries of the benzene and PEA neutral species, and at geometries close to potential energy surface crossings

in their cations. Cation eigenstates, and the so-called sudden approximation, involving removal of an electron from a correlated ground state wavefunction for the neutral species, were used as initial conditions.

The central result of this paper is that charge migration, without coupled nuclear motion, can be observed with the Ehrenfest method, using the sudden approximation. For the two systems studied here, one has to displace the initial geometry away from the conical intersection to do this, so that the states are strongly coupled (to increase the amplitude) but not degenerate (so that the period is finite). Further, the main features associated with charge migration are still recognizable when nuclear motion is allowed to couple.

The fact that the onset of charge migration (without coupling to nuclear motion) is strongly dependent on nuclear geometry is already known.¹⁰ Our results make a contribution to understanding this problem since we have shown that we can “engineer” charge migration in benzene by choosing a region of strong interaction displaced along the direction of the derivative coupling from a conical intersection.

In a molecule like PEA, it is not easy to explore the potential surface by optimizing critical points such as conical intersections, and here, the eigenstate Ehrenfest trajectory provides much information. In particular, it suggests regions of strong interaction where charge migration can be initiated.

In both benzene and in PEA the rapid oscillation of the charge migration (as seen in the spin densities) seems to persist when the coupling with nuclear motion is included, although the period and amplitude change. This is due to the fact that as the nuclei move the energy changes with time and initial coherence is lost. However, when charge migration with fixed nuclei happens on a long timescale (Figure 7 for benzene), we do not seem to observe it any more when the nuclei are allowed to move: we see charge transfer instead.

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