The Second Order Ehrenfest Method

A Practical CASSCF Approach to Coupled Electron-Nuclear Dynamics

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Abstract This article describes the Ehrenfest method and our second-order implementation (with approximate gradient and Hessian) within a CASSCF formalism. We demonstrate that the second order implementation with the predictor-corrector integration method improves the accuracy of the simulation significantly in terms of energy conservation. Although the method is general and can be used to study any coupled electron-nuclear dynamics, we apply it to investigate charge migration upon ionization of small organic molecules, focusing on benzene cation. Using this approach, we can study the evolution of a non-stationary electronic wavefunction for fixed atomic nuclei, and where the nuclei are allowed to move, to investigate the interplay between them for the first time. Analysis methods for the interpretation of the electronic and nuclear dynamics are suggested: we monitor the electronic dynamics by calculating the spin density of the system as a function of time.

Keywords Ehrenfest method · CASSCF · Coupled electron-nuclear dynamics · Charge migration · Charge transfer

1 Introduction

Photo-ionization can create a coherent superposition of electronic states and therefore initiates electronic dynamics in atoms and molecules. Experiments on the latter are particularly difficult to interpret as change in the nuclear geometry is also expected. Indeed, the equilibrium geometry of the ionized and neutral species are unlikely to be the same. Therefore, the initial electron dynamics, that may last up to a few femtoseconds, is then followed by the onset of nuclear dynamics [1]. Theoretical methods are

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needed to help understand the effects seen in attosecond laser experiments (see for example the reviews of Kling [2] and Ivanov [3]).

Methods for non-adiabatic dynamics were the subject of a recent special issue of *J. Chem. Phys.*; in particular the lead article of Tully [4] provides a current summary of the state of the art. Quantum mechanical simulations are expensive computationally. Reducing the number of nuclear degrees of freedom of the system is sometimes done to make the calculation feasible but the validity of this approximation is limited [5–7]. Conventional molecular dynamics (MD) only allows one to simulate nuclear motion on a single potential energy surface and therefore does not describe non-adiabatic processes involving non-radiative electronic transitions. Mixed quantum-classical dynamics methods have been developed to address this issue. In the Ehrenfest method, one propagates quantum mechanically an electronic wavepacket consisting of a superposition of electronic eigenstates by solving the time-dependent Schrödinger equation; and one moves classically the nuclei integrating Newton’s equation of motion. The feedback between the quantum electronic and classical nuclear degrees of freedom is described in a mean-field manner. This simplification allows one to study the electronic and nuclear dynamics independently and discover whether the motions of the electrons and the nuclei are synchronous or asynchronous.

The Ehrenfest method is general and we have previously used it for photochemistry [8] and electron transfer [9]. In this article, we focus on the application of the Ehrenfest method to the simulation of electron dynamics (and the coupled nuclear dynamics) upon ionization in molecules. We have recently shown [10] how charge migration and charge transfer in benzene and 2-phenylethylamine cations can be studied using the Ehrenfest method within a CASSCF [11, 12]-like formulation. Charge migration is defined at a fixed nuclear geometry and corresponds to oscillations in the electronic density due to the non-stationarity of the electronic state. Charge transfer is a change in the electronic density due to a change in the nuclear geometry. In this work, after a review of the theory, we present our approximate second-order CASSCF implementation of the Ehrenfest method. We show that a second-order method augmented with a predictor-corrector integration method (devised by Schlegel [13] and implemented in the Gaussian program [14]), permits the use of larger step sizes while conserving the total energy.

We apply our second-order Ehrenfest method to a model system: benzene radical cation. Ionization of the neutral from the degenerate HOMO/HOMO-1 leads to the Jahn-Teller [15] effect in the cation. There is a peaked conical intersection between the two lowest-energy eigenstates D_0 and D_1 at geometries with D_{6h} symmetry. Figure 1 represents the surrounding “moat” of the conical intersection seen from above. It contains several valence bond (VB) resonance structures: three equivalent quinoid structures that are minima (Min) and three antiquinoid structures that are transition structures (TS). The degeneracy is lifted along two directions: the gradient difference X_1 and the interstate coupling X_2 . In this system, there is the possibility of charge migration / charge transfer around the ring.

Fig. 1 Benzene radical cation resonance structures. The directions X_1 and X_2 are the gradient difference and the gradient of the interstate coupling vector respectively. The gradient difference direction X_1 connects a pair of quinoid/antiquinoid forms by lowering the symmetry from D_{6h} to D_{2h} . The motion along the gradient of the interstate coupling vector X_2 preserves only C_{2h} and allows one to move from one quinoid (or antiquinoid) structure to a "60° rotated" antiquinoid (or quinoid) structure. Note that for each quinoid or anti-quinoid structure, there are actually two VB resonance structures with the unpaired electron and the positive charge exchanged (this is indicated by •/+ interchange in each case).

2 The Ehrenfest approach: General Theoretical development

The Ehrenfest method has been extensively discussed in the literature [16–26]. In this section, we review the Ehrenfest formalism following the elegant derivation of Tully [27]. Our aim is to explicitly state the approximations underlying the method and to discuss their implications.

2.1 Separation of nuclear and electronic variables

We shall start with the non-relativistic time-dependent Schrödinger equation, where r and R refer to the electronic (fast) and nuclear (slow) variables respectively:

$$i\hbar \frac{\partial}{\partial t} \Phi(r, R, t) = \mathcal{H} \Phi(r, R, t) \quad (1)$$

In order to derive mixed quantum-classical dynamics, the nuclear and electronic variables have to be separated. The simplest possible form is a product ansatz:

$$\Phi(r, R, t) = \Psi(r, t) \cdot \chi(R, t) \quad (2)$$

The first approximation made in the Ehrenfest method is thus the factorisation of the total wavefunction into a product of electronic and nuclear parts. One deficiency of the ansatz (2) is the fact that the electronic wavefunction does not have the possibility to decohere: the populated electronic states in $\Psi(r, t)$ share the same nuclear wavepacket $\chi(R, t)$ by definition of the total wavefunction. Decoherence here is defined as the tendency of the time-evolved electronic wavefunction to behave as a statistical ensemble of electronic states rather than a coherent superposition of them [26]. The neglect of electronic decoherence could lead to non-physical asymptotic behaviors in case of bifurcating paths. It is not expected to be a problem here as we are interested in relatively short timescale dynamics.

In order to simplify the appearance of the expressions at a later stage of the derivation, a phase factor is introduced for the total wavefunction and also some internal phase factors for the two individual wavefunctions. More details can be found here [27]. Inserting the ansatz (2) with the additional phase factors into equation (1), multiplying on the left by $\chi^*(R, t)$ and $\Psi^*(r, t)$ and integrating over R and r gives respectively:

$$i\hbar \frac{\partial \Psi(r, t)}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi(r, t) + \langle \chi(R, t) | \mathcal{V}_{n-e}(r, R) | \chi(R, t) \rangle_R \cdot \Psi(r, t) \quad (3)$$

$$i\hbar \frac{\partial \chi(R, t)}{\partial t} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi(R, t) + \langle \Psi(r, t) | \mathcal{H}_e(r, R) | \Psi(r, t) \rangle_r \cdot \chi(R, t) \quad (4)$$

The indices i and I refer respectively to the electrons and the nuclei; m_e is used to denote the mass of an electron and M_I is used to denote the mass of the nucleus I . $\mathcal{V}_{n-e}(r, R)$ includes all inter-particle interactions (electron-electron, nucleus-nucleus and electron-nucleus) and $\mathcal{H}_e(r, R)$ is the electronic Hamiltonian for the nuclei fixed at positions R .

To understand the consequence of using the ansatz (2), let us for instance look closer at the second term on the right hand side of equation (3). The interaction between electrons at points r in space and nuclei at points R is weighted by the probability that the nuclei are at these particular points R . This is the effective potential experienced by the electrons due to the nuclei. The corresponding remark can be made about the second term on the right hand side of equation (4). According to the set of coupled equations (3) and (4), the feedback between electronic and nuclear degrees of freedom is described in a mean-field manner, in both directions. In other words, both electrons and nuclei move in time-dependent effective potentials obtained from appropriate expectation values of the nuclear and electronic wavefunctions respectively.

2.2 Classical limit for nuclear motion

The Ehrenfest method is obtained by taking the classical limit of equations (3) and (4). To do that in equation (4), the nuclear wavefunction is (exactly) rewritten in a polar coordinate system in terms of an amplitude A and a phase S which are both considered to be real and positive:

$$\chi(R, t) = A(R, t) \cdot \exp\left(\frac{i}{\hbar} S(R, t)\right) \quad (5)$$

After inserting equation (5) in (4), the real parts on each side can be equal:

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + \langle \Psi(r, t) | \mathcal{H}_e(r; R) | \Psi(r, t) \rangle_r = \hbar^2 \sum_I \frac{1}{2M_I} \frac{\nabla_I^2 A}{A} \quad (6)$$

The classical limit is taken as $\hbar \rightarrow 0$:

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla_I S)^2 + \langle \Psi(r, t) | \mathcal{H}_e(r; R) | \Psi(r, t) \rangle_r = 0 \quad (7)$$

The resulting equation is isomorphic to the Hamilton-Jacobi equation and is thus equivalent to Newton's equation of motion, where $P_I = \nabla_I S$ is the classical momentum of nucleus I :

$$\frac{dP_I}{dt} = -\nabla_I \langle \Psi(r, t) | \mathcal{H}_e(r; R) | \Psi(r, t) \rangle_r \quad (8)$$

In equation (3), we can replace $\chi(R, t)$ by a delta function at the classical trajectory $R(t)$:

$$i\hbar \frac{\partial \Psi(r, t; R)}{\partial t} = \left(-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \mathcal{V}_{n-e}(r, R(t)) \right) \Psi(r, t; R) = \mathcal{H}_e(r; R(t)) \cdot \Psi(r, t; R) \quad (9)$$

Note that now the electronic wavefunction Ψ depends parametrically on $R(t)$ through $\mathcal{V}_{n-e}(r, R(t))$ and thus $\mathcal{H}_e(r; R(t))$. By treating the nuclear motion classically, we lose the spatial delocalisation of the nuclei and their motion is now described by a classical trajectory.

Equations (8) and (9) define the Ehrenfest method. It is important to keep in mind that it succeeds in describing nuclear motion if the potential energy surfaces of the various electronic states are similar in topology and energies [20]. However, in the case of weakly coupled electronic states, the nuclear motion will be dominated by the potential corresponding to the highly populated electronic state and regions of space accessible only on the sparsely populated electronic state may not be explored properly [28, 29]. One advantage of the Ehrenfest method is that its applications and results do not depend on the choice of basis functions (if complete) and can, in principle, be applied without choosing basis functions by numerical integration of equation (9).

2.3 Non-adiabatic couplings

Expanding the electronic wavefunction in a basis of orthonormal configurations $\{\phi_l\}$ or eigenstates $\{\tilde{\phi}_l\}$ gives:

$$\Psi(r, t; R) = \sum_l a_l(t) \phi_l(r; R) = \sum_l c_l(t) \tilde{\phi}_l(r; R) \quad (10)$$

In order to prove the presence of the non-adiabatic couplings, it is convenient to use the eigenstate expansion. Substituting expansion (10) into equation (9), multiplying on the left by $\tilde{\phi}_k^*(r; R)$ and integrating over r gives:

$$i\hbar \frac{\partial c_k(t)}{\partial t} = c_k(t) E_k(R) - i\hbar \sum_l c_l(t) \langle \tilde{\phi}_k | \frac{\partial}{\partial t} \tilde{\phi}_l \rangle = c_k(t) E_k(R) - i\hbar \sum_{l,j} c_l(t) d_{kl}^j(R) \cdot \dot{R}_j \quad (11)$$

with the non-adiabatic couplings $d_{kl}^j(R) = \int \tilde{\phi}_k^*(r; R) \nabla_{R_j} \tilde{\phi}_l(r; R) dr$ and the eigenvalues E_k . Thus, if the electronic wavefunction is expanded in the adiabatic basis, equation (11) gives the time-varying amplitudes along the classical trajectory. The latter depends on the non-adiabatic coupling terms. Note that the same equations define the time-dependence of the electronic basis amplitudes for the surface hopping method. Note that a similar expression can be derived for the diabatic basis [27].

3 Implementation within a CASSCF formalism

We now describe our CASSCF implementation of the Ehrenfest method which allows the electronic wavefunction to be made of multiple states. An approximate second-order method with a numerical fit procedure is used for the propagation of the nuclei.

3.1 Quantum propagation of a CASSCF electronic wavefunction

In practice, time is discretized and when integrating equation (9) assuming a constant Hamiltonian over the time step, we obtain:

$$\Psi(r, t_n; R(t_n)) = \exp\left(-\frac{i}{\hbar} \mathcal{H}_e(r; R(t_n)) \cdot (t_n - t_{n-1})\right) \Psi(r, t_{n-1}; R(t_{n-1})) \quad (12)$$

The time-dependent electronic wavefunction is expanded in the basis of configurations, here $\mathbf{A}(t_n)$ is the vector gathering the expansion coefficients at time t_n defined in equation (10). We use bold font to signify vectors and matrices.

$$\mathbf{A}(t) = \begin{pmatrix} a_1(t) \\ \vdots \\ a_k(t) \\ \vdots \end{pmatrix} \quad (13)$$

Using matrix notation, equation (12) reads as:

$$\mathbf{A}(t_n) = \exp\left(-\frac{i}{\hbar} \mathbf{H}_e(t_n) \cdot (t_n - t_{n-1})\right) \mathbf{A}(t_{n-1}) \quad (14)$$

$\mathbf{H}_e(t_n)$ is the matrix representation of the electronic Hamiltonian in the basis of configurations at time t_n . Using its spectral resolution, it becomes:

$$\mathbf{A}(t_n) = \mathbf{U}(t_n) \exp\left(-\frac{i}{\hbar} \mathbf{D}_e(t_n) \cdot (t_n - t_{n-1})\right) \mathbf{U}^\dagger(t_n) \cdot \mathbf{A}(t_{n-1}) \quad (15)$$

$\mathbf{U}$ is the matrix containing the eigenvectors arranged as columns. $\mathbf{D}_e$ is the matrix representation of the electronic Hamiltonian in the basis of eigenstates: it thus contains the eigenvalues $\{E_k\}$ on the diagonal and is zero elsewhere. Both $\mathbf{U}$ and $\mathbf{D}_e$ are assumed to be constant over a time step and their value at time t_n is used. If one expands $\mathbf{D}_e(t_n)$ as a Taylor series around its value at time t_{n-1} , one obtains to first order:

$$\mathbf{D}_e(t_n) = \mathbf{D}_e(t_{n-1}) + \frac{d\mathbf{D}_e(t_{n-1})}{dt} \cdot (t_n - t_{n-1}) \quad (16)$$

The electronic Hamiltonian is time-independent (no external electric field) but it changes with time if the nuclei are allowed to move. Hence, we have the following relation (if it obeys the Hellmann-Feynman theorem):

$$\frac{d\mathbf{D}_e}{dt} = \nabla_R \mathbf{D}_e \cdot \dot{R} = \langle \tilde{\phi}_k | \nabla_{R_l} (\mathcal{H}_e) | \tilde{\phi}_l \rangle \cdot \dot{R} \quad (17)$$

We can now identify the derivative coupling (see section 2.3):

$$\langle \tilde{\phi}_k | \nabla_{R_l} (\mathcal{H}_e) | \tilde{\phi}_l \rangle = \langle \tilde{\phi}_k | \nabla_{R_l} \tilde{\phi}_l \rangle \cdot (E_l - E_k) = d_{kl}^l(R) \cdot (E_l - E_k) \quad (18)$$

The non-adiabatic couplings are therefore included in our propagation of the electronic wavefunction by finite differentiation.

We thus obtain a sequence of vectors corresponding to the different steps:

$$\mathbf{A}(t_0) \rightarrow \mathbf{A}(t_1) \rightarrow \dots \rightarrow \mathbf{A}(t_n) \rightarrow \dots \quad (19)$$

The sequence of vectors may be obtained keeping the nuclei fixed, in which case the basis of configurations $\{\tilde{\phi}_l\}$ and also the basis of CASSCF eigenvectors do not change with time. The matrices $\mathbf{U}$ and $\mathbf{D}_e$ are time-independent.

Alternatively, the sequence of vectors $\{\mathbf{A}\}$ may be obtained in concert with nuclear motion. In the latter case, at each step t_n of the dynamics (or at each geometry of the classical trajectory), a state-averaged (SA) CASSCF calculation is done to update the electronic Hamiltonian matrix $\mathbf{H}_e$. One obtains a basis of CASSCF eigenvectors $\{\mathbf{U}_j(t_n)\}$ from its diagonalization and a set of SA optimised orbitals from the solution of the SA-MCSCF equations. Although we assume the configurations $\{\phi_l\}$ do not change for the propagation of the time-dependent wavefunction, the orbitals are in practice optimised at each step. This strategy is reasonable if the active space is large enough so that only small relaxations of the inactive orbitals occur.

The energy of the system is computed as the expectation value of the electronic Hamiltonian:

$$E(t_n) = \langle \Psi(r, t_n) | \mathcal{H}_e | \Psi(r, t_n) \rangle_r = \mathbf{A}^\dagger(t_n) \cdot \mathbf{H}_e(t_n) \cdot \mathbf{A}(t_n) \quad (20)$$

More conveniently, we can define a real time-dependent vector $\mathbf{M}$, by rotating the complex expansion coefficients into real coefficients. The rotation must be performed in the eigenstates basis for the energy to be preserved (see Appendix for details). The energy can then be computed without the need for complex algebra:

$$E(t_n) = \mathbf{M}^\dagger(t_n) \cdot \mathbf{H}_e(t_n) \cdot \mathbf{M}(t_n) \quad (21)$$

3.2 Classical nuclear trajectory

The nuclear geometry is updated at each time step, if wanted, by integrating the equation of motion (8). This is done using the Hessian-based predictor-corrector algorithm designed by Hase and Schlegel [13]. We use the first and second derivatives of the energy to make a local quadratic approximation of the energy:

$$E(R) = E^0 + \mathbf{G}^0 \cdot (R - R^0) + \frac{1}{2} (R - R^0)^\dagger \cdot \mathbf{H}^0 \cdot (R - R^0) \quad (22)$$

where E^0 , $\mathbf{G}^0$ and $\mathbf{H}^0$ are the energy, the gradient and the Hessian evaluated at R^0 , respectively. Newton's equation of motion on a quadratic surface is:

$$\frac{dP_I}{dt} = -\mathbf{G}_I^0 - \sum_J \mathbf{H}_{IJ}^0 (R_J - R_J^0) \quad (23)$$

Note that unlike the energy, the gradient and Hessian can not be calculated using a real TD vector: they depend intrinsically on the relative complex phase of the electronic eigenstates occupied (see Appendix for details on the gradient).

We now review the general approach to the gradient and Hessian computations using the methods of Almlöf and Taylor [30] and apply it specifically to the Ehrenfest wavefunction. We also explain the approximations used in computing the gradient and Hessian.

3.2.1 Gradient computation

The energy of a configuration interaction (CI)-like wavefunction depends on the large number of parameters that define the wavefunction. Among them, the optimized molecular orbital (MO) and CI coefficients depend on the nuclear geometry. One constraint is that the MO coefficients remain orthonormal under the change in geometry, which is possible using unitary transformations (a simpler alternative to Lagrange multipliers). We introduce the following notation: superscripts denote partial derivatives while subscripts denote total derivatives. The expression for the gradient

is obtained by applying the chain rule to the energy derivative with respect to a change in geometry [30, 10]:

$$E_{R_I} = E^{R_I} + \mathbf{E}^C \mathbf{C}_{R_I} + \mathbf{E}^X \mathbf{X}_{R_I} - \frac{1}{2} \mathbf{E}^Y \mathbf{S}_{R_I} \quad (24)$$

E^{R_I} is the Hellmann-Feynman term. It represents the intrinsic dependence of the energy with respect to a change in nuclear geometry. As the energy depends on parameters that depend themselves on the nuclear geometry, one obtains the non-Hellmann-Feynman terms: $\mathbf{C}_{R_I}$ and $\mathbf{X}_{R_I}$ are the CI vector and MO rotation derivatives and $\mathbf{E}^C$ and $\mathbf{E}^X$ are the corresponding energy derivatives. $\mathbf{S}_{R_I}$ is the atomic orbital overlap matrix and $\mathbf{Y}$ is the symmetric matrix arising from re-orthogonalization of the MO.

When the derivative is computed for an eigenvector $\mathbf{U}_i$, the $\mathbf{C}$ matrix corresponds to the rotation of the eigenvector $\mathbf{U}_i$ with the remaining orthogonal vectors $\mathbf{U}_{j \neq i}$. Here, the reference vector is chosen to be the TD vector of the previous step $\mathbf{A}(t_{n-1})$ and the matrix $\mathbf{C}$ expresses $\mathbf{A}(t_n)$ by a rotation between $\mathbf{A}(t_{n-1})$ and its orthogonal complements. As we propagate the time-dependent wavefunction assuming that the MO do not change, $\mathbf{X}_{R_I}$ is neglected and the gradient reads as:

$$E_{R_I} = E^{R_I} + \mathbf{E}^C \mathbf{C}_{R_I} - \frac{1}{2} \mathbf{E}^Y \mathbf{S}_{R_I} \quad (25)$$

By differentiating the Newton-Raphson equation with respect to nuclear motion, the derivative CI coefficients can be written as:

$$\mathbf{C}_{R_I} = -(\mathbf{E}^{CC})^{-1} \mathbf{E}_{R_I}^C = -(\mathbf{E}^{CC})^{-1} \left(\mathbf{E}^{R_I C} - \frac{1}{2} \mathbf{E}^{CY} \mathbf{S}_{R_I} \right) \quad (26)$$

Note that equation (26) assumes a quadratic expansion of the energy as a function of the CI parameters $\mathbf{E}(\mathbf{C})$ about a minimum. This approximation results in some error in the gradient. In practice, we also neglect the derivative due to the complex phase of the CI expansion coefficients, *i.e.* we calculate the matrix $\mathbf{C}$ by expressing the real vector $\mathbf{M}(t_n)$ by a rotation between $\mathbf{M}(t_{n-1})$ and its orthogonal complements. As we show in section 4.2, these errors are corrected via numerical fitting of the hypersurface along the trajectory.

3.2.2 Hessian computation

In the present work, at each step a CASSCF calculation is done with state-averaged orbitals over two states. The Hessian used in the integration of Newton's equation of motion is calculated for the highest of the two roots of the SA calculation.

$$\begin{aligned}
E_{R_I R_J} = & E^{R_I R_J} + \mathbf{E}^C \mathbf{C}_{R_I R_J} + \mathbf{E}^{C R_I} \mathbf{C}_{R_J} + \mathbf{E}^{C R_J} \mathbf{C}_{R_I} + \mathbf{E}^{C C} \mathbf{C}_{R_I} \mathbf{C}_{R_J} + \mathbf{E}^{C X} \mathbf{C}_{R_I} \mathbf{X}_{R_J} \\
& - \frac{1}{2} \mathbf{E}^{C Y} \mathbf{C}_{R_I} \mathbf{S}_{R_J} + \mathbf{E}^X \mathbf{X}_{R_I R_J} + \mathbf{E}^{X R_I} \mathbf{X}_{R_J} + \mathbf{E}^{X R_J} \mathbf{X}_{R_I} + \mathbf{E}^{X X} \mathbf{X}_{R_I} \mathbf{X}_{R_J} \\
& + \mathbf{E}^{X C} \mathbf{X}_{R_I} \mathbf{C}_{R_J} - \frac{1}{2} \mathbf{E}^{X Y} \mathbf{X}_{R_I} \mathbf{S}_{R_J} - \frac{1}{2} \mathbf{E}^{Y R_I} \mathbf{S}_{R_J} - \frac{1}{2} \mathbf{E}^{Y R_J} \mathbf{S}_{R_I} + \frac{1}{2} \mathbf{E}^Y \mathbf{S}_{R_I} \mathbf{S}_{R_J} \\
& - \frac{1}{2} \mathbf{E}^Y \mathbf{S}_{R_I R_J} + \frac{1}{4} \mathbf{E}^{Y Y} \mathbf{S}_{R_I} \mathbf{S}_{R_J} - \frac{1}{2} \mathbf{E}^{Y C} \mathbf{S}_{R_I} \mathbf{C}_{R_J} - \frac{1}{2} \mathbf{E}^{Y X} \mathbf{S}_{R_I} \mathbf{X}_{R_J} \quad (27)
\end{aligned}$$

For an optimised SA-CASSCF wavefunction, $\mathbf{E}^C = 0$ but only the weighted average of the anti-symmetric Lagrangians will vanish: $\sum_{i=1}^2 \omega_i \mathbf{E}^X(i) = 0$. In addition, we neglect the second derivative of the MO rotation matrix with respect to nuclear distortion $\mathbf{X}_{R_I R_J}$. With these few simplifications, the Hessian becomes:

$$\begin{aligned}
E_{R_I R_J}(i) = & E^{R_I R_J}(i) + \mathbf{E}^{C R_J}(i) \mathbf{C}_{R_I}(i) + \mathbf{E}^{C X}(i) \mathbf{C}_{R_I}(i) \mathbf{X}_{R_J} - \frac{1}{2} \mathbf{E}^{C Y}(i) \mathbf{C}_{R_I}(i) \mathbf{S}_{R_J} \\
& + \mathbf{E}^{X R_I}(i) \mathbf{X}_{R_J} + \mathbf{E}^{X R_J}(i) \mathbf{X}_{R_I} + \mathbf{E}^{X X}(i) \mathbf{X}_{R_I} \mathbf{X}_{R_J} - \frac{1}{2} \mathbf{E}^{X Y}(i) \mathbf{X}_{R_I} \mathbf{S}_{R_J} - \frac{1}{2} \mathbf{E}^{Y R_I}(i) \mathbf{S}_{R_J} \\
& - \frac{1}{2} \mathbf{E}^{Y R_J}(i) \mathbf{S}_{R_I} + \frac{1}{2} \mathbf{E}^Y(i) \mathbf{S}_{R_I} \mathbf{S}_{R_J} - \frac{1}{2} \mathbf{E}^Y(i) \mathbf{S}_{R_I R_J} + \frac{1}{4} \mathbf{E}^{Y Y}(i) \mathbf{S}_{R_I} \mathbf{S}_{R_J} - \frac{1}{2} \mathbf{E}^{Y X}(i) \mathbf{S}_{R_I} \mathbf{X}_{R_J} \quad (28)
\end{aligned}$$

The terms $\mathbf{C}_{R_I}(i)$ and $\mathbf{X}_{R_I}$ are obtained by solving the standard coupled-perturbed SA-MCSCF equations. These are obtained by differentiating Newton-Raphson equations with respect to a nuclear distortion:

$$\begin{aligned}
& \begin{pmatrix} \omega_1 \mathbf{E}^{X X}(1) + \omega_2 \mathbf{E}^{X X}(2) & \omega_1 \mathbf{E}^{X C}(1) & \omega_2 \mathbf{E}^{X C}(2) \\ \mathbf{E}^{C X}(1) & \mathbf{E}^{C C}(1) & 0 \\ \mathbf{E}^{C X}(2) & 0 & \mathbf{E}^{C C}(2) \end{pmatrix} \begin{pmatrix} \mathbf{X}_{R_I} \\ \mathbf{C}_{R_I}(1) \\ \mathbf{C}_{R_I}(2) \end{pmatrix} = \\
& - \begin{pmatrix} \omega_1 \{ \mathbf{E}^{R_I X}(1) - \frac{1}{2} \mathbf{E}^{X Y}(1) \mathbf{S}_{R_I} \} + \omega_2 \{ \mathbf{E}^{R_I X}(2) - \frac{1}{2} \mathbf{E}^{X Y}(2) \mathbf{S}_{R_I} \} \\ \mathbf{E}^{R_I C}(1) - \frac{1}{2} \mathbf{E}^{C Y}(1) \mathbf{S}_{R_I} \\ \mathbf{E}^{R_I C}(2) - \frac{1}{2} \mathbf{E}^{C Y}(2) \mathbf{S}_{R_I} \end{pmatrix} \quad (29)
\end{aligned}$$

Using an optimised SA-CASSCF wavefunction to calculate the Hessian for the time-dependent vector is a rough approximation; again, we show in section 4.2 that the numerical fitting of the hypersurface along the trajectory corrects most of the error.

3.2.3 Fifth order polynomial fit

The second-order method is used with the 5th order predictor-corrector integration scheme of Schlegel [13] in the Gaussian program [14]. In this method, the quadratic approximation (gradient, Hessian) at the current point R^0 is used in a predictor step to a predicted geometry R^p . Then the energies, gradients and Hessians at geometries R^0 and R^p are fitted by a 5th order polynomial. The equations of motion on this fitted surface are then integrated to give the corrector step to the geometry R^c .

4 Application to coupled electron-nuclear dynamics upon ionization

We apply our second-order Ehrenfest method to study the coupled electron-nuclear dynamics of benzene upon ionization. Because the nuclear geometry will be a non-stationary point on the cation potential energy surfaces and the electronic wavefunction will be a non-stationary state, we expect some electron and nuclear dynamics to occur after ionization. We use the Ehrenfest method to investigate the interplay between the electronic and nuclear dynamics.

The electronic structure is computed using the CASSCF method. Using the standard 6-31G* basis set, we choose the 6 π orbitals as active. The degenerate HOMO, HOMO-1 and matching degenerate LUMO, LUMO+1 are needed to recover the non-dynamic electron correlation. The remaining pair of benzene π orbitals contributes to dynamic correlation, and has to be included for stability (because of a large dynamic correlation effect).

4.1 Initial conditions

The initial conditions of the dynamics calculation (the nuclear geometry and the electronic wavefunction) depend on the state of the neutral species before ionization. The absorption of a photon leading to ionization is itself instantaneous so neither the electrons or the nuclei have time to relax. We assume that the system was in its nuclear and electronic ground state before ionization. In principle, to mimic the initial nuclear wavepacket distribution and obtain a realistic dynamics of the system, one must simulate many trajectories starting with sampled positions and momentum of the nuclei. Here, our aim is to illustrate the method using a single simulation with the initial nuclear geometry close to the equilibrium geometry of the neutral species, *i.e.* the minimum of its ground state, without initial kinetic energy. The initial electronic wavefunction will be a non-stationary state, *i.e.* a superposition of several cationic eigenstates. We neglect the interaction with the electric field and the interaction between the outgoing electron and the cation. These approximations are reasonable if a high-energy ultrashort pulse is used for the ionization so that the outgoing electron has a high kinetic energy and moves rapidly away from the cation. In other words, we assume the “sudden” removal of an electron.

In many studies [31–36] of the electronic dynamics upon ionization, the initial electronic wavefunction is created using the so-called “single-channel sudden approximation” [37–39]. This assumes the sudden removal of an electron *from a particular orbital*. The initial superposition of electronic eigenstates results therefore from electron correlation only (in this case, from the CI expansion used) [31]. This “single-channel sudden approximation” was used in our previous work [10]. However, one can investigate a particular ionization channel independently of the others only if they do not interfere: the valence ionization channels are not well separated in energy so they will interfere. We therefore choose to stay general: we assume the “sudden” removal of an electron but do not aim at studying electronic dynamics following a single-channel ionization. Relative weights and phases of the eigenstates in the initial superposition are parameters that can be investigated in numerical simulations. Ex-

perimentally, they depend on the photon energy but also on the field polarization for example.

We study the valence ionization of benzene. An instantaneous photoionization experiment would be carried out using a pulse of broad bandwidth which means that several electronic states may be populated. However, considering the energy gap between the first and second excited states (more than 2 eV), we can assume that the dynamics of the two lowest-energy electronic states will not interfere with the dynamics on the second excited state within the first few tens of femtoseconds. Our aim is to model the dynamics resulting from populating the lowest two eigenstates which would be part of any observed dynamics. We thus choose the initial electronic wavefunction to be an equal mixture of the two lowest eigenstates: $|\Psi(r, t = 0)\rangle = \frac{1}{\sqrt{2}}(|D_0\rangle + |D_1\rangle)$. As we observed in our first study [10], when the two eigenstates are exactly degenerate (which is the case at the equilibrium geometry of the neutral species), there is no charge migration. Indeed, at exact degeneracy, any combination of the two eigenstates is also an eigenstate and therefore, it is a stationary electronic wavefunction. An alternative explanation is the fact that the period of oscillation in charge migration is inversely proportional to the energy gap; thus, if the energy gap is zero, the period of oscillation is infinite, which means there is no charge migration. We suggested in our first study [10] to enhance charge migration by distorting the initial geometry away from the conical intersection in order to lift the degeneracy. We decide to start the ionization at a distorted geometry along the derivative coupling vector. The same test calculation is used throughout the rest of the article.

4.2 Conservation of energy

The accuracy in the integration of the equations of motion is monitored by the conservation of energy. To illustrate this, we run test calculations using two different integration algorithms involving: approximate gradient computation (section 3.2.1) only, or approximate gradient and approximate Hessian computations with the 5th order polynomial fit (sections 3.2.2 and 3.2.3). The results with approximate gradient and approximate Hessian are not shown here as we do not expect any improvement of the conservation of energy (the Hessian is calculated for the upper eigenstate of the SA-CASSCF calculation and not for the TD vector). In addition, the computational cost of the Hessian-based integrator using the polynomial fit is the same as without the polynomial fit. We use a mass-weighted step size of 0.03 amu^{1/2}bohr (about 0.3 fs). The trajectories are started with no kinetic energy.

Figure 2 shows the error in the total energy as a function of time for the different integration methods. We see oscillations that become bigger and bigger with time when using the approximate gradient only. Varying the step size does not improve the conservation of energy (not shown) which suggests that the error is more likely to come from the approximations in the analytical gradient rather than the integrator. The combination of approximate analytical gradient and Hessian with a numerical fit decreases the error significantly (below 2×10^{-4} kcal/mol for 50 fs). Indeed, the error in the conservation of energy due to the approximations made in the analytical expressions for gradient and Hessian is corrected by fitting numerically the poten-

Fig. 2 Error in conservation of energy. The error in the total energy is compared for two different integration algorithms involving the approximate gradient computation only, or the approximate gradient and approximate Hessian computations using the 5th order polynomial fit. The mass-weighted step size is 0.03 amu^{1/2}bohr (about 0.3 fs). This illustrates how the polynomial fit performs significantly better (error below 2×10^{-4} kcal/mol for 50 fs).

tial energy surface. The difference in cost between the two methods is essentially the computation of the Hessian at each step: this can partly be eliminated if a Hessian updating procedure is used (not explored here).

Figure 3 shows the total energy, the kinetic energy and the potential energy during the 50 fs trajectory using the 5th order polynomial fit (same simulation as in figure 2). The total and potential energies have been shifted by the initial potential energy so that they are plotted on the same vertical axis. The variations in kinetic and potential energies exactly cancel each other. Therefore, we can safely use step sizes as large as we use here (about 0.3 fs) using the 5th order polynomial fit and this is the integration algorithm we choose for applications.

4.3 Analysis tools

The number of degrees of freedom increases with the size of the system and it becomes difficult to extract qualitative trends from large amounts of data. Some efforts are necessary in analyzing results and getting a physical picture. Here, we suggest some ways to monitor electron and nuclear dynamics during such a simulated trajectory. We illustrate them with our model system, benzene radical cation, but they could in principle be applied to other systems where charge migration is initiated near

Fig. 3 Evolution of total, kinetic and potential energies during the trajectory. The 5th-order polynomial fit procedure is used with a mass-weighted step size of $0.03 \text{ amu}^{1/2}\text{bohr}$ (about 0.3 fs). The decrease of potential energy is compensated by a gain in kinetic energy so that the total energy is perfectly conserved for over 50 fs (error below $2 \times 10^{-4} \text{ kcal/mol}$ for 50 fs).

a conical intersection.

We suggest using figure 1 to represent both the electronic and the nuclear dynamics. Indeed, the structures can refer both to the nature of the electronic density and to the nuclear geometry. Figure 4 is a schematic cross-section of the conical intersection along the X_1 direction shown in figure 1. A set of optimised quinoid/antiquinoid structures is presented with their respective spin densities and important bond lengths. One can imagine the electronic character and the nuclear geometry evolving synchronously in equilibrium or asynchronously during the trajectory.

4.3.1 Monitoring changes in the electronic structure

Benzene radical cation can adopt different electronic characters during the simulation. The electronic wavefunction is, in theory, a superposition of several VB structures and we would like to monitor its time-dependence. One way to do it is to calculate its spin density as a function of time. The spin density is defined as the difference between the alpha density (density of electrons with spin up) and the beta density (density of electrons with spin down): $|\Psi^S(t)|^2 = |\Psi^\alpha(t)|^2 - |\Psi^\beta(t)|^2$. It allows one to locate the unpaired electron within the molecule. The spin density can be partitioned onto atomic sites using the standard Mulliken population analysis. Figure 4 gives the partitioned spin densities for the quinoid and antiquinoid VB structures: the

Fig. 4 Schematic representation of the benzene radical cation D_1/D_0 crossing. This is a cross-section through the conical intersection along X_1 shown in figure 1. The quinoid structure (on the right) is a minimum whereas the antiquinoid structure (on the left) is a transition structure in the moat of the conical intersection. Mulliken atomic spin densities are indicated in pink next to each carbon atom. Characteristic bond lengths are indicated in blue. Note that for the quinoid or antiquinoid structure, there are actually two resonance structures with the unpaired electron and the positive charge exchanged (this is indicated by $+/\bullet$).

unpaired electron is located on the top and bottom carbon atoms in the quinoid VB structure shown in the figure whereas it is delocalized onto the four carbons on the sides in the antiquinoid VB structure. One can thus assign a different spin density pattern to each VB structure.

To follow the evolution of the electronic wavefunction, its spin density is computed, partitioned onto the atoms and can be decomposed in the space of the VB structures of the moat at each step of the simulation. One can then plot the electron dynamics trajectory on the moat diagram (figure 1) where the structures represent exclusively the nature of the electronic wavefunction in this case. Because each structure in figure 1 is a superposition of two resonance structures where the unpaired electron and the positive charge are interchanged, following the unpaired electron is equivalent to following the positive charge. This is how we monitor the “hole” dynamics.

4.3.2 Monitoring changes in nuclear geometry

The question we would like to answer is whether nuclear geometry and electronic wavefunction evolve in equilibrium or not; how synchronous or asynchronous the electron and nuclear dynamics are. We are therefore interested in the nuclear motion in the branching space of the conical intersection. The nuclear trajectory can be plotted on the same moat diagram (figure 1) but here, the structures represent the nuclear geometry exclusively (*i.e.* the pattern of single bonds corresponding to longer bond lengths, versus double bonds corresponding to shorter bond lengths, etc.). By comparing the electronic dynamics with the nuclear motion when both are represented in terms of VB structures, we can study how they differ.

4.4 Simulations with fixed nuclei and nuclei moving

In the first calculation, we propagate only the electronic wavefunction without allowing the nuclei to move. This is to study first “pure” charge migration. In the second calculation, the nuclei are allowed to move along with the propagation of the electronic wavefunction. In figure 5, the spin densities partitioned onto the atoms are plotted as a function of time in each case. The bottom half aims to represent the corresponding evolution of both the electronic character (in pink) and the nuclear geometry (in blue) within the moat.

With fixed nuclei, we observe oscillation between a quinoid and an antiquinoid VB structures with a total period of about 10 fs. With nuclei moving, the electronic dynamics is the same as with fixed nuclei during the first 2 fs but after that, the effect of the nuclear motion is not negligible. Indeed, the pink arrow representing the electronic “trajectory” has the same initial direction but then, it deviates because of the nuclear motion. Now, let us look at the nuclear trajectory. The first blue arrow shows that the initial direction of the nuclear trajectory is “pulled” by the initial electronic character: the nuclear motion is driven by the effective electronic potential so they move in a way that minimizes the potential energy. In a classical picture, it means adopting the geometry that is in equilibrium with the electronic character. Then, the nuclear motion becomes more difficult to interpret because it is driven by the electronic potential but also by the kinetic energy built up. Note that the initial dynamics of the electronic wavefunction and the nuclei are asynchronous (the pink and blue arrows are not superimposed). At about 17 fs, both the electronic and nuclear trajectories are in the bottom left corner of the diagram and they both evolve towards the right. Their dynamics become more synchronous. Indeed, asynchronous dynamics of electrons and nuclei arise from the population of several electronic eigenstates. As the trajectory decays onto the ground state, the residual electronic dynamics will be charge transfer, where the electronic and nuclear dynamics are synchronous.

5 Conclusion

The Ehrenfest method allows one to study coupled electron-nuclear dynamics by treating the feedback between electronic and nuclear degrees of freedom in a mean-

Fig. 5 Results of two Ehrenfest simulations on benzene cation: with fixed nuclei (left side) and with nuclei moving (right side). The top figures plot the evolution of the Mulliken spin densities as the function of time. The electron and nuclear motions are represented on the bottom most diagrams (the nuclear geometry in blue and the electronic character in pink). With nuclei fixed, the electronic character of the system between a set of quinoid/antiquinoid structures. With moving nuclei, the oscillations in the electronic character seem damped until the nuclear geometry slowly “catches” the electronic character.

field manner. The nuclear state (expressed as a single classical trajectory) experiences an effective potential due to a time-dependent superposition of electronic eigenstates. Using this approach, we can study the evolution of a non-stationary electronic wavefunction for fixed atomic nuclei, and where the nuclei are allowed to move, to investigate the differences. So far we have used it to study both charge migration and charge transfer upon ionization of small organic molecules. Our CASSCF implementation with a second-order integration algorithm and an additional 5th order polynomial fit allows us step-sizes of the order of 0.3 fs (or 0.03 amu^{1/2}bohr) while keeping the error in energy conservation below 0.0002 kcal/mol for dynamics runs longer than 50 fs.

We choose benzene cation as a prototype because ionizing the neutral species leads to a Jahn-Teller degeneracy between ground and first excited states of the cation. Note that only illustrative simulations were presented here – one must sample the positions and momentum of nuclei to obtain a realistic dynamics of the system. Taking advantage of the approximation of the Ehrenfest method, we can analyze nuclear and electronic dynamics independently. We monitor the electronic dynamics by calculating the spin density of the system as a function of time. With nuclei fixed, there is

no electron dynamics in this case. However, if we distort the geometry [10] away from the exact degeneracy, we see “pure” charge migration: oscillations in the spin density that we can correlate with particular localized electronic structures, with a period depending on the gap between the states initially populated. Close to a conical intersection, the energy gap will be small and the resulting electron dynamics will be on a femtosecond timescale. Here, the oscillations in the spin density have a period of 10 fs (see figure 5), so we can use relatively big step sizes (0.3 fs). If we allow nuclear motion we see changes in the period of the electronic dynamics as the nuclei start to couple.

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6 Appendix. Computation of the energy and the gradient of a complex wavefunction

6.1 Energy computation

Let us consider the expansion of the TD wavefunction in the eigenstate basis set as defined in equation (10) with complex coefficients $\{c_k\}$. $\mathcal{H}_e$ is the electronic Hamiltonian operator and $\mathbf{H}$ its matrix representation in the eigenstate basis with elements $\mathbf{H}_{kl} = \langle \tilde{\phi}_k | \mathcal{H}_e | \tilde{\phi}_l \rangle$. The energy of the TD wavefunction is computed as the expectation value of this operator:

$$E = \langle \Psi | \mathcal{H}_e | \Psi \rangle = \sum_k \sum_l c_k^* c_l \mathbf{H}_{kl} \quad (30)$$

Note that in the eigenstate basis, $\mathbf{H}_{kl} = 0$ for $k \neq l$ so the double sum reduces to one. The energy expression then reads:

$$E = \sum_k |c_k|^2 E_k \quad (31)$$

Here, we see that the energy depends only on the weight of each eigenstate and not on their relative phase. From an implementation point of view, instead of repeating the operations for the real and imaginary components, we create a real wavefunction that has the same energy and using directly the machinery already programmed. For that, one needs to rotate all the complex coefficients in the TD vector expansion so that they are all real but conserving their magnitude. So the energy evaluated with the vector rotated to real is equal to the energy of the complex TD vector. Note this is only true because the rotation is done in the eigenstate basis. In general, we can compute the expectation value of an operator with the wavefunction rotated to real only if the operator is diagonal in the basis set we do the rotation in.

6.2 Gradient computation

The Hellman-Feynman term of the gradient is defined as the partial derivative of the energy with respect to a nuclear distortion R_I . To consider the intrinsic dependence of the energy, we assume an expansion in exact eigenstates. By applying the product rule, we obtain:

$$E^{R_I} = \sum_k \nabla_{R_I}(|c_k|^2) \cdot E_k + \sum_k |c_k|^2 \cdot \nabla_{R_I}(E_k) \quad (32)$$

The second term on the right hand side is the average of the gradient of each electronic eigenstate weighted by their occupation. It represents the change in potential energy staying on the same potential, *i.e.* keeping the same occupation on each electronic eigenstate. The first term however is the change in potential energy due to change in occupation of the electronic eigenstates because of non-adiabatic transitions. To calculate the derivative of $|c_k|^2$ with respect to a nuclear distortion, we can invoke the time derivative by applying the chain rule:

$$E^{R_I} = \sum_k \frac{\partial |c_k|^2}{\partial t} \frac{1}{\dot{R}_I} \cdot E_k + \sum_k |c_k|^2 \cdot \nabla_{R_I}(E_k) \quad (33)$$

The time derivative of the norm squared of the expansion coefficient $|c_k|^2$ with respect to time can be obtained using equation (11):

$$\frac{\partial |c_k(t)|^2}{\partial t} = - \sum_{l,J} (c_l(t)c_k^*(t) + c_l^*(t)c_k(t)) \cdot d_{kl}^J(R) \cdot \dot{R}_J \quad (34)$$

By inserting this in equation (33), it reads:

$$E^{R_I} = - \sum_{k \neq l} (c_l(t)c_k^*(t) + c_l^*(t)c_k(t)) \cdot d_{kl}^J(R) \cdot E_k + \sum_k |c_k|^2 \cdot \nabla_{R_I}(E_k) \quad (35)$$

We see that the non-adiabatic coupling $d_{kl}^J(R)$ is present in the term representing the change in energy due to electronic transitions. Using the relation $d_{kl}^J(R) = -d_{lk}^J(R)$ gives:

$$E^{R_I} = - \sum_{k \neq l} c_l^*(t)c_k(t) \cdot d_{kl}^J(R) \cdot (E_k - E_l) + \sum_k |c_k|^2 \cdot \nabla_{R_I}(E_k) \quad (36)$$

Using equation (18), it becomes:

$$E^{R_I} = \sum_{k \neq l} c_l^*(t)c_k(t) \cdot \langle \tilde{\phi}_l | \nabla_{R_I}(\mathcal{H}_e) | \tilde{\phi}_k \rangle + \sum_k |c_k|^2 \cdot \langle \tilde{\phi}_k | \nabla_{R_I}(\mathcal{H}_e) | \tilde{\phi}_k \rangle \quad (37)$$

The Hellmann-Feynman term of the gradient is the expectation value of the derivative of the Hamiltonian operator. On one hand, the diagonal terms represent the weighted average potential and they depend only on the norms of the expansion coefficients. On the other hand, the off-diagonal terms represent the change in energy due to non-adiabatic transitions and they do depend on the relative complex phase of the expansion coefficients. For this reason, one can not construct a real wavefunction whose gradient would be equal to the gradient of a complex wavefunction.