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Δ SCF with Subsystem Density Embedding for Efficient Nonadiabatic Molecular Dynamics in Condensed Phase Systems

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Abstract

An approach combining subsystem density embedding with the variational delta self-consistent field is presented, which extends current capabilities for excited electronic state calculations. It was applied on a full-atomic nonadiabatic dynamics of a solvated diimide system, demonstrating that comparable accuracy can be achieved for this system for the investigated configuration space and with a shorter simulation time than the computationally more expensive conventional Kohn-Sham density functional theory-based method. This opens a new pragmatic technique for efficient simulation of nonadiabatic processes in the condensed phase, in particular liquids.

1 Introduction

Nonadiabatic (NA) processes in the condensed phase represent a formidable challenge for accurate simulations. Even though a semiclassical approach, where the nuclei are treated classically and electrons modeled via some quantum chemistry method, is often sufficient

to describe the underlying mechanisms taking place after photoexcitation, the sheer size of the system hinders the methodology from routine application. The bottleneck lies in the electronic structure description of the condensed phase, usually periodic systems, where currently Kohn-Sham (KS) density functional theory (DFT) based methods are the most efficient means to tackle such systems. Strategies combining DFT with semiclassical description of atomic nuclei for modeling NA processes can be roughly categorized in two domains, the Ehrenfest dynamics and trajectory surface hopping (TSH). For an overview of these methods see, for example, Refs.¹⁻³. While the former can be combined with (real-time) time-dependent (TD) DFT propagation schemes to obtain the effective gradient along which the atomic nuclei are evolved,⁴⁻⁶ the missing details due to averaging makes the method unpractical for unraveling new photochemical mechanisms and investigating kinetic detail between possible reaction channels.⁷ These details can be accounted for with TSH by including several electronic states into the description. Delta self-consistent field (Δ SCF) represents an efficient method for obtaining excited electronic states at the cost of a ground state energy calculation.⁸⁻¹⁵ Despite being a variational method that treats electronic states independently, accuracy similar to TD-DFT over a wide range of configuration space can be achieved,^{14,16-19} while the easily accessible gradients make it suitable for studying NA processes at an all-atom DFT level in the condensed phase.¹⁹⁻²¹ In principle, any arbitrary number of excited electronic states can be reproduced with Δ SCF, provided that SCF converges to the targeted excited electronic state density. A number of procedures have been designed to aid in convergence,^{11,13-15,19,22,23} where the maximum overlap method devised by Gill and coworkers is particularly suitable for converging single excited state reference densities and preventing them from variational collapse back to the ground electronic state.²⁴⁻²⁶ An electronic density constructed with fractional occupations and mixed pairs of KS orbitals can describe more exactly the multireference character of electronic states, especially at critical configuration space regions such as conical intersections (CI) or at bond dissociation limits.^{11,14}

Quantum density embedding methods enable simulations of complex condensed phase systems by efficiently computing their electronic structure without strongly compromising the accuracy compared to the conventional methods.^{27,28} Systems composed of millions of atoms were computed at such levels of theory.²⁹ This success relies on the ability to partition the full system into parts that mutually interact via an effective potential in the DFT formulation. Typically the subdivision is made between weakly interacting system parts, i.e., covalent bonds are preserved and the full system is segmented into mutually interacting molecules.³⁰ The quality of the intermolecular potential determines, among others, the accuracy of the method. This is particularly important when modeling excited electronic states as their properties highly depend on the precision of description of the environmental effects.³¹

With the frozen density embedding approach,³² the part of the system of interest is modeled completely at a KS DFT level, while the surrounding subsystem electronic densities are constrained to their isolated values, and in some variants of the procedures they are allowed to relax in a gradual step-wise manner, for example in the freeze-and-thaw method,³³ but not in a fully self-consistent way among all system parts.²⁷ Nonetheless, with more accurate electrostatic, exchange-correlation, spin polarization, and short-range Pauli repulsion interactions^{27,34} these methods capture far more details than the quantum mechanics/molecular mechanics (QM/MM) approach³⁵. But the sudden change of excited electronic state character requires that the polarization effects are instantaneous, for which polarizable QM/MM methods were specifically developed.³⁶⁻³⁸ Arising complications when using such approximations are avoided when treating all of the system parts on an equal self-consistent footing while keeping the total density partitioned and influenced only via the external intermolecular potential that is also updated simultaneously with systems subdensities.³⁹ Subsystem DFT methods are available as an extension of the FDE methods where each of the system's part electronic densities is optimized until all subsystems reach SCF convergence.⁴⁰

Density embedding schemes were generalized to excited electronic states by linear-response as well as real-time TD-DFT⁴¹⁻⁴⁶ and applied for calculations of a number of spectroscopic

properties, including for some impressively large systems with multiple chromophores.^{47–52} But unlike these static calculations, to the best of our knowledge, there is only one report of using density embedding methods for simulating NA processes in a dynamic manner using Ehrenfest NA molecular dynamics (MD) with real-time TD-DFT.²⁹ In this work, we combine the power of the subsystem DFT with the practicality of the Δ SCF method to obtain excited electronic states. Since our focus has been on condensed phase systems, we applied it to liquid calculations using periodic boundary conditions. More specifically, we extend our previous NA-MD implementation of the TSH method with the CP2K program package, which we have developed to examine nonradiative deactivation mechanisms in condensed systems,¹⁹ with the Δ SCF method utilizing periodic subsystem density embedding. As a best comparison between the NA-MD conducted with and without embedding, we chose the same diimide molecule solvated in water on which an extensive Δ SCF analysis was conducted recently.¹⁹

The paper is structured as follows: Section 2 deals with the theoretical and computational details of the subsystem DFT with Δ SCF; Section 3 shows and discusses the comparison of the embedding with nonembedding results, and the final conclusions are given in Section 4. In the following text we termed the conventional DFT method as nonembedding (NE) to easily distinguished it from the subsystem density embedding (SDE) method.

2 Theory and Computational Details

Subsystem DFT relies on partitioning of the system’s total electronic density $\rho_{tot}(\vec{r})$ into subsystem electronic densities. For a system divided into N_s subsystems, $\rho_{tot}^i(\vec{r})$ of the i -th electronic state is partitioned into a sum,

$$\rho_{tot}^i(\vec{r}) = \sum_s^{N_s} \rho_s^i(\vec{r}), \tag{1}$$

of individual subsystem densities $\rho_s^i(\vec{r})$. $\vec{r}$ is a three-dimensional position vector in an arbitrary coordinate system. Each subsystem density is expanded into contributions of KS molecular orbitals according to

$$\rho_s^i(\vec{r}) = \sum_j^{N_{e_s}} n_{sj}^i |\phi_{sj}^i(\vec{r})|^2, \quad (2)$$

where n_{sj}^i is the occupation number of each j KS spin orbital $\phi_{sj}^i(\vec{r})$ constrained to subsystem s . The occupation numbers for each subsystem add to the total number of electrons N_{e_s} within the subsystem. The total energy of the system's electronic state i is given by the Hohenberg-Kohn (HK) functional

$$E_{tot}^i[\rho_{tot}^i] = E_{HK}[\rho_{tot}^i] + \sum_s^{N_s} (E_{KS}[\rho_s^i] - E_{HK}[\rho_s^i]), \quad (3)$$

which is corrected with the contributions from the difference between the KS and HK energies for each subsystem.⁵³ For simplicity reasons the explicit dependence on the $\vec{r}$ is left out. Written into contributions of each HK and KS energy functional terms, namely their external energy (E_{ext}), Coulomb energy (E_{Coul}), and exchange-correlation functional (E_{xc}) and corresponding kinetic energy terms,

$$E_{HK}[\rho] = E_{ext}[\rho] + E_{Coul}[\rho] + E_{xc}[\rho] + E_{kin}[\rho], \quad (4)$$

$$E_{KS}[\rho] = E_{ext}[\rho] + E_{Coul}[\rho] + E_{xc}[\rho] + T[\{\phi\}], \quad (5)$$

the total energy relation (3) is

$$\begin{aligned} E_{tot}^i[\rho_{tot}^i] &= E_{ext}[\rho_{tot}^i] + E_{Coul}[\rho_{tot}^i] + E_{xc}[\rho_{tot}^i] + \\ &E_{kin}[\rho_{tot}^i] + \sum_s^{N_s} (T[\{\phi_s^i\}] - E_{kin}[\rho_s^i]), \end{aligned} \quad (6)$$

where the E_{kin} is the HK kinetic energy functional term, dependent only on the electronic density, while $T[\{\phi\}]$ is the KS kinetic energy term, which explicitly depends on the KS orbitals as $T[\{\phi\}] = -1/2 \sum_j n_j \langle \phi_j(\vec{r}) | \nabla^2 | \phi_j(\vec{r}) \rangle$. Extension of the above expression to hybrid exchange-correlation functionals can be found in Ref.⁵⁴. The Δ SCF method finds the local minimum of the total energy expression (6) by optimizing the occupation numbers and KS molecular orbital in a SCF procedure, so that the final electronic state density resembles that of an excited electronic state. In the subsystem DFT embedding (SDE) approach used, all the subsystem KS orbitals are optimized simultaneously by solving the coupled KS eigensystem equations of expression (5),^{53,54}

$$\left\{ -\frac{1}{2} \nabla^2 + V_{KS}[\rho_{tot}^i](\vec{r}) + V_{emb}[\rho_{tot}^i, \rho_s^i](\vec{r}) \right\} \phi_{sj}^i(\vec{r}) = \epsilon_{sj}^i \phi_{sj}^i(\vec{r}), \quad (7)$$

with the KS potential $V_{KS}[\rho]$ and embedding potential

$$V_{emb}[\rho_{tot}^i, \rho_s^i] = \left. \frac{\delta E_{kin}[\rho]}{\delta \rho} \right|_{\rho_{tot}^i} - \left. \frac{\delta E_{kin}[\rho]}{\delta \rho} \right|_{\rho_s^i}. \quad (8)$$

From the enforcement of splitting the total electronic density into subsystem electronic densities (1) by appropriately choosing basis set functions which are constrained to individual subsystems, the coupled KS equation (7) partitions into a block diagonal form, which also makes the KS orbitals associated to individual subsystem.^{53,54} This simultaneous optimization of all KS orbitals enables the direct use of any Δ SCF procedure to also include the optimization of occupation numbers.^{14,23,55,56} Note that Δ SCF requires a priori information on the target excited electronic state which can be obtained e.g. from linear-response TD-DFT or some wave function based method. The SCF procedure (6) and (7) scales approximately linearly with the number of subsystems,⁵³ for any electronic state.

In our case, the only imposed orbital constrain is that KS orbitals belonging to the same subsystem are orthogonal, from which the eigenrelation (7) originates, and even though KS orbitals between different subsystems are not formally orthogonal, because of the absence of

basis function overlaps between different subsystems, the KS orbitals satisfy the following orthogonality relation

$$\langle \phi_{sj}^i | \phi_{s'j'}^{i'} \rangle = \begin{cases} \delta_{ss'} \delta_{jj'}; & i = i' \\ \delta_{ss'} \delta_{jj'} S_{ii'}; & i \neq i' \end{cases}. \quad (9)$$

The overlap element $S_{ii'} := \langle \phi_{sj}^i | \phi_{sj}^{i'} \rangle$ appears because each electronic state is optimized independently, and introduces additional terms into the nonadiabatic coupling elements obtained via the Tully–Hammes-Schiffer approximation⁵⁷

$$D_{ij}(t + \Delta t/2) = \frac{1}{2\Delta t} \{ \langle \psi_i(t) | \psi_j(t + \Delta t) \rangle - \langle \psi_i(t + \Delta t) | \psi_j(t) \rangle \} + \frac{1}{2\Delta t} \{ \langle \psi_i(t + \Delta t) | \psi_j(t + \Delta t) \rangle - \langle \psi_i(t) | \psi_j(t) \rangle \}, \quad (10)$$

where the $|\psi_i\rangle$ and $|\psi_j\rangle$ are the spin-adapted Slater determinants for the i and j electronic states, respectively, determined at every Δt time step of the nuclear trajectory. Substituting the overlaps $S_{ii'}$ between wave functions at same nuclear time steps with $\delta_{ii'}$ the second right hand side term in (10) vanishes, and simplifies the Tully’s SH implementation within Δ SCF.¹⁹

Details of our NA-MD with the CP2K program can be found in our previous paper.¹⁹ We remind the reader that we use the restricted KS formalism within the Δ SCF procedure as well as rounding of the occupation numbers to integers of 0, 1, and 2. The former assures that the electronic densities for both spin channels are equal and mimic that of the singlet electronic state, while the latter enables us to assign a single Slater determinant with a single occupied (o) to virtual (v) KS orbital substitution ($\phi_o \rightarrow \phi_v$). Such a single-excited spin-adapted Slater determinant represents the electronic state wave function whose square is the total electronic state density (1). A drawback of using just one determinant is the loss of multireference character while the restricted KS formalism potentially introduces a fraction of double electron excitation character into the excited electronic states.⁵⁸ However, for the diimide system the first excited electronic state is dominantly single reference and one single

Slater determinant is mostly sufficient to describe the entire relevant part of the configuration space of the first excited electronic state potential energy surface. Only for the CI seam region between the ground and first singlet excited states the multireference character dominates in the ground electronic state. A more accurate description remains inaccessible with single reference KS DFT, but the local potential energy surface topology is still adequately described.¹⁹ Whenever Δ SCF encounters convergence issues, occupation numbers are allowed to relax and the new ones are obtained with the TD-DFT method,¹⁹ which is conducted only on the diimide subsystem. TD-DFT on the whole system is conducted just once in the initial NA-MD step to obtain the initial occupation guesses for target excited electronic states (here the first singlet excited electronic state). To model the nonradiative deactivation from the diimide first excited electronic state it is sufficient to conduct the NA-MD in the manifold of its ground and first excited electronic states,¹⁹ as was previously reported for the methylated diimide analogue.^{59–61}

All calculations were conducted with the CP2K code.⁶² It utilizes Gaussian and plane-wave basis set functions, and while the former are easily associated to certain atoms and enable straightforward partitioning into individual subsystems, the latter directly introduce periodic properties into the electronic density necessary for periodic condensed phase calculations. Nonlocal contributions of the pseudopotentials are restricted to subsystems,⁵³ as are the exact Hartree exchange terms of hybrid functionals.⁵⁴

The SDE implementation in CP2K was used where all subsystem densities are optimized simultaneously.^{53,54} All calculations were made with the PBE0 exchange-correlation functional,⁶³ while the PBE⁶⁴ was employed for the kinetic energy density functional. The auxiliary density matrix method with the cFIT3 auxiliary basis set⁶⁵ was employed together with the empirical D3 type dispersion corrections by Grimme et al.⁶⁶ as described in Ref.⁵⁴ for the SDE with hybrid exchange–correlation functionals. To compare with the previous calculations TZVP-GTH basis set⁶⁷ with Goedecker-Teter-Hutter pseudopotentials⁶⁸ was used. The plane wave cutoff was 500 Ry. Periodic boundary conditions were applied for all

calculations.

SH was done separately with the adiabatic formulation of the Landau–Zener (LZ)⁶⁹ and with Tully’s fewest-switches (FS)⁷⁰ algorithms implemented in the Zagreb SH code.^{71–73} The same initial conditions were used for the *cis*-diimide system as in the NE case, which were originally sampled from a NVT ab initio MD trajectory equilibrated at 300 K. NA-MD trajectories were propagated independently in a NVE manner with a nuclear time step Δt of 0.5 fs up to 500 steps to match the NE results.¹⁹ With Tully’s FS-SH NA-MD, for every nuclear time step electronic state coefficients were propagated in 10^4 steps with a time step of $5 \cdot 10^{-5}$ fs, and within each the hopping probability was calculated. The correction by Granucci et al.⁷⁴ with a $C = 0.1$ Hartree parameter⁷⁵ was applied to electronic coefficients to account for the missing decoherence. The NA coupling terms between electronic states were computed using only the antihermitian first right-hand-side term of expression (10). Velocities were rescaled along the direction of the gradient difference vector between the two state after a NA hop in order to preserve the total energy.⁷⁶ 150 and 160 NA-MD trajectories were propagated employing LZ and Tully’s FS SH algorithms, respectively. Further details on any of the aforementioned points can be found in our previous publication.¹⁹

3 Results and Discussion

SDE was applied on the solvated diimide in water. The *cis* conformer was selected since most of the previous calculations were conducted on it.¹⁹ The periodic cubic box simulation with cell length of 8.98654 Å contains one *cis*-diimide and 27 water molecules. While the *cis*-diimide was always selected as a separate subsystem, the remaining water molecules were partitioned in a number of ways to examine the influence of different partitionings on the embedding calculations. The water molecules were partitioned into subsystems with each containing the common divisor of the total number of water molecules, namely into 3 subsystems with 9 water molecules, 9 subsystems with 3 water molecules, and 27 where each

water molecule constitutes a subsystem. These systems will be further indicated with abbreviations P3, P9, and P27, respectively. Selection of water molecules for each subsystem was done randomly, and a number of random selections were examined for potential discrepancies. The change of the energy gap between the first and ground electronic states for various random selections of the water molecules constituting the same subsystem was of the order of 1 meV, or less for the examined MD snapshots. The case where all water molecules constitute one subsystem proved difficult to converge with the current SDE, exceeding reasonable computational limits, so this partitioning is not considered further. Lastly, water molecules, whose oxygen atom is within a 4 Å radius from the diimide’s center of mass were selected as one subsystem, representing the first solvation shell, while the remaining water molecules constitute another subsystem. This threshold value roughly coincides with the first minimum after the first peak of the radial distribution function for the water oxygen – diimide’s center of mass distance.¹⁹ Within this partitioning, the inner solvation shell contains 8 water molecules in direct contact with the *cis*-diimide, while the outer 19. No exchange of water molecules between the two solvation shells was observed during the NA-MD simulation. Selection with a value of 4.5 Å was also examined, as it partitions the solvent into two subsystems of similar size, with 13 and 14 water molecules for the inner and outer shells, respectively. These two system partitionings are indicated with P8/19 and P13/14 in the text. Affiliations of each water molecule to the initially designated subsystem are kept along the NA-MD trajectory despite whatever relative repositioning they might undergo during the dynamics.

Figure 1: Examined partitionings of the *cis*-diimide (gray) in a periodic box with 27 water molecules. Diimide was always a separate subsystem, while the water molecules were partitioned randomly into three (P3), nine (P9), and twenty seven (P27) subsystems, each with an equal number of water molecules. P8/19 and P13/14 show two different partitions of water into inner and outer solvation shells. The inner solvation shell for the first (second) partitioning contains 8 (13), while outer 19 (14) water molecules.

Δ SCF SDE reproduces properly the $n\pi^*$ character electronic density for diimide’s first singlet excited electronic state, as seen by comparing the SDE and NE electronic density differences between the first excited and ground electronic states. Figure 2a compares the ground and the first excited (dashed) electronic state energies along a NA-MD trajectory originally obtained without the SDE for which the electronic energies were recomputed for comparison at the NE geometries using the SDE with different partitioning schemes. The energy difference between the SDE and NE values for each excited state indicates that the energies obtained with SDE tend to shift above the reference values in an oscillating manner with a period of about 100 fs. However, the energy difference between the first excited and the ground electronic states obtained with SDE shows less variation compared to the NE value (Fig. 2b). Variations due to different solvent partitioning schemes are minor, and all display the same behaviour along the trajectory, due to which they all overlay in Fig. 2b. The inset of Fig. 2a is an enlargement of a gray shaded portion of NA-MD trajectory in a vicinity of a CI. Note that with the used Δ SCF methods the two electronic state energies are about 1 eV apart at the CI structure. This is due to the enforced symmetry between α and β KS orbitals to construct the singlet excited electronic state. Fig. 2 displays that the SDE with the solvent partitioned into three subsystems deviates more from the

other solvent partitions. Cases with solvent partitioned into inner and outer solvation shell resemble more the values corresponding to the solvent randomly partitioned into a larger number of individual subsystems (P9 and P27). The ground state energy also shows a sudden discontinuity at the 14 fs time mark due to the missing multireference contributions in DFT,⁷⁷ with virtually indistinguishable difference between partitioning schemes.

Figure 2: a) Energies of the ground (solid lines) and first excited (dashed lines) electronic states of a solvated diimide system along a selected NA-MD trajectory which displays no hop from the excited to the ground state in the represented simulation time. The trajectory was propagated without the embedding while the SDE energies were recalculated along the original trajectory. The inset shows the expanded energy profile for the region shaded in gray. b) Energy differences between the first and ground electronic states displayed in figure a. The inset shows the expanded energy differences for the region shaded in gray. c) Nonadiabatic coupling element between the ground and the first excited electronic states. Black color indicates the NE reference values, while blue, red, orange, cyan and purple stand for the P3, P9, P27, P8/19 and P13/14 SDE systems, respectively.

The same observation holds for the electronic state energy gradients with respect to

nuclear coordinates. Gradient vectors for each atom between SDE and NE (reference) values are compared by similarities between gradient norms and gradient directions separately. Corresponding SDE gradients are evaluated at the NE geometries for every trajectory point in Fig. 2, with the exception of the P3 system for which SCF convergence could not be achieved after the 107 fs time mark. Fig. 3a displays the distribution of the gradient norms for selected atoms, obtained with different partitioning schemes, as a ratio to the corresponding NE reference gradient norm determined at every ab initio MD step in Fig. 2, while Fig. 3b the distribution of the gradient directions, which is determined as the scalar product between the SDE and NE normalized gradient directions. Errors increase inversely with the gradient norm (see Figs. S1–S4 of the Supporting Information), but the majority of SDE gradients shows close similarity with the counterpart NE values. Deviations of SDE gradient norms from the corresponding NE values also follow the discrepancy between the SDE and NE energies (Fig. 2a). In average, the diimide gradient norms in the ground electronic state are the largest and show most similarity with the reference values (58% have a norm discrepancy smaller than $\pm 10\%$ of the reference value, and 91% have directions parallel to the reference directions), with the slight exception of the P3 system. The diimide first excited electronic state, as well as the water molecules in both electronic states, have wider distributions around the corresponding reference values but without compromising the averaged gradient trend (see Figs. S5 and S6 of the Supporting Information).

The larger gradient deviations are reflected as larger fluctuations of the total system’s energy (see Fig. S7 in the Supporting Information). The total energy displays an immediate drop in value at the beginning of each trajectory because initial conditions from the NE system were used, but afterward remains conserved during the entire NA-MD, regardless of partitioning scheme.

Figure 3: Comparison of gradients between SDE values to counterpart NE values for all trajectory points in Fig. 2a. a) Distribution of ratios between SDE gradient norms ($|\vec{\nabla}_i E^{\text{SDE}}|$) for different partitionings of the solvent relative to NE gradient norms ($|\vec{\nabla}_i E^{\text{NE}}|$) for all diimide molecule atoms (upper set of figures), and all water molecule atoms (lower set of figures). b) Distribution of scalar products between normalized gradient directions for SDE ($\vec{\nabla}_i E^{\text{SDE}}/|\vec{\nabla}_i E^{\text{SDE}}|$) and NE normalized gradient directions ($\vec{\nabla}_i E^{\text{NE}}/|\vec{\nabla}_i E^{\text{NE}}|$) for all diimide molecule atoms (upper set of figures), and all water molecule atoms (lower set of figures). Gray (red) color indicates ground (first excited) electronic state values.

Figure 2c compares the NA coupling elements between the ground and the first excited electronic state along the selected trajectories between the NE and SDE with different solvent partitionings. NA coupling peaks of SDE values are positioned as those of the NE calculations, and those with negative values tend to be slightly smaller in magnitude compared to the NE reference. SDE NA coupling values also diminish much quicker to zero when leaving configuration regions of smaller energy gap, making the curve more flat compared to the NE terms. NA couplings calculated by taking only the diimide subsystem KS orbitals give values equal to full SDE NA values.

While in principle the SDE scales linearly with the number of subsystems,^{29,53,54} details in implementation and used computational infrastructure play a crucial role on the overall method efficiency. We observed a reduction of computational cost of the P9 systems by between three and two times compared to that of the NE. It is expected that the efficiency

further increases with system size.

NA-MD trajectories were obtained with the P9 system since its SCF convergence proved stable when compared to other partitionings. Trajectories were launched from the same set of initial conditions as the NE trajectories, and the SH between electronic states was examined with the LZ-SH and Tully’s FS-SH algorithms, respectively. Fig. 4 compares the population evolution of the first excited electronic state for all examined cases. Effects of the SDE, at least in the case of system P9, appears to be small compared to NE values, and most of the differences arise from the choice of the SH algorithm. For the LZ-SH, the population decay is biexponential, with the shorter lifetime of 36 fs, and the longer of 251 fs. The shorter accounts for 67% of decays and matches the corresponding NE lifetime (37 fs), while the longer lifetime is only by 10% larger than the NE value (226 fs). The NA-MD of the *cis*-diimide molecule in system P9 is analogue to the NE system (see full trajectories in Figs. S8 and S9 in the Supporting Information). In the initial phase of the NA-MD (first 50 fs) the two cases are almost indistinguishable, and only towards the end of the simulation time small deviations appear, most notable that with SDE the final *cis* to *trans* distribution ratio is about 1:1, while in NE is 2:1. The other is in the slight change of the hydrogen bond interactions between the diimide and water molecules (for details see the Supporting Information).

Figure 4: Averaged population of *cis*-diimide’s first singlet excited electronic state for the corresponding ensembles. The black solid and black dashed lines stand for the NE system evolved with the LZ-SH and Tully’s FS-SH algorithms, respectively, while the red counterpart lines for the P9 system. The cyan solid line is the fitted biexponential decay function (formula in inset), while the cyan dashed line shows the monoexponential decay function (bold terms of the inset formula).

With the application of the Tully’s FS-SH algorithm, the excited state population decay becomes monoexponential. While it was shown empirically that on several different systems the LZ-SH and Tully’s FS-SH results match very well when convergence of trajectory sampling over the initial conditions is satisfied,^{78,79} the origin of discrepancy between the two algorithms can be traced back to the Δ SCF potential energy surfaces of diimide. Since the energy gap between the two electronic states is about 1 eV at the diimide CI geometry, the hopping probability is mostly influenced by the underlined denominator in the exponential part of the LZ i to j state hopping probability expression, $\mathcal{P}_{i \rightarrow j} = \exp[-\pi/(2\hbar)(Z_{ij}^3/(d^2 Z_{ij}/dt^2))^{1/2}]$, where $Z_{ij} = |E_i - E_j|$, as it depends on the local topology at the CI points. Single-reference electronic structure methods, including DFT, cannot adequately describe these regions of configuration space, and the hopping probability is influenced by the sudden changes of the ground electronic state energy. By shifting the energy of the excited electronic state to reduce the gap between the two states, the decay becomes monoexponential (see our previous paper¹⁹). On the other hand, through the use of

approximated wave function overlaps, Eq. (10), Tully’s FS-SH algorithm is more indifferent to the artificial energy shift of the first excited Δ SCF singlet state energy, and follows the correct intrinsic adiabatic change of states at the CI point. Though there are instances along the trajectories where the continuity of the nonadiabatic coupling elements is disrupted at the CI points, despite the proper wave function sign readjustments, such events are still seldom compared to the frequency of the inadequate DFT topology at these configuration space points. This explains why the Tully’s FS-SH algorithm is largely unaffected by the discrepancies in the potential energy surfaces and gives a monoexponential excited state population decay.

4 Conclusions

We have presented a methodology for nonadiabatic (NA) molecular dynamics (MD) where the Δ SCF procedure was coupled with subsystem density embedding (SDE). To our knowledge, this is the first use of SDE with Δ SCF for trajectory surface hopping NA-MD. The Landau–Zener and the Tully’s fewest-switches surface hopping algorithms were employed, respectively. A NA-MD of the first singlet excited electronic state of solvated *cis*-diimide in water was reinvestigated for detailed comparison with previously published nonembedding (NE) results. Our observations shown that, i) the potential energy surface properties of the ground and excited electronic states match well over the entire investigated configuration space between the SDE and NE calculations used; which ii) remain invariant to different partitioning into subsystems; and iii) consequentially the NA-MD remains comparable between SDE and NE. The choice of system partitioning in this case is therefore guided mainly by the increase in speedup of SDE calculations. The linear scaling of SDE with the number of subsystems makes this approach appealing for simulation and unraveling NA processes of larger systems in the condensed phase, particularly in solutions, but might be less applicable to simulations of solids, or surfaces, where the subsystems interact more strongly which the

embedding potential can less accurately describe. It remains to be investigated how different kinetic energy potentials affect the excited states and influence the NA-MD, as well as extending the methodology towards more complex embedding procedures, for example, the density functional embedding theory,^{80–82} and apply it to more complex systems. By combining Δ SCF with SDE we have presented an efficient tool for describing NA process in condensed phase systems at a DFT level of accuracy.

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Supporting Information Available

This information is available free of charge via the Internet at <http://pubs.acs.org>. Detail comparison of gradients; NA-MD Total Energy Comparison; Full NA-MD trajectories of the solvated *cis*-diimide P9 system; Radial distribution functions of the *cis*-diimide P9 system.

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Graphical TOC Entry