Optimizing Conical Intersections of Solvated Molecules: The Combined Spin-Flip Density Functional Theory/Effective Fragment Potential Method

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Abstract
Solvent effects on a potential energy surface crossing are investigated by optimizing a conical intersection (CI) in solution. To this end, the analytic energy gradient has been derived and implemented for the collinear spin-flip density functional theory (SFDFT) combined with the effective fragment potential (EFP) solvent model. The new method is applied to the azomethane-water cluster and the chromophore of green fluorescent protein in aqueous solution. These applications illustrate not only dramatic changes in the CI geometries but also strong stabilization of the CI in a polar solvent. Furthermore, the CI geometries obtained by the hybrid SFDFT/EFP scheme reproduce those by the full SFDFT, indicating that the SFDFT/EFP method is an efficient and promising approach for understanding nonadiabatic processes in solution.

Keywords
Solvents, Polarization, Density functional theory, Ground states, Optimization

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Optimizing conical intersections of solvated molecules: The combined spin-flip density functional theory/effective fragment potential method

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Conical intersections (CIs) play an important role in photochemistry and photobiology.1–3 CI points provide a funnel that connects multiple potential energy surfaces (PESs) and enables an ultrafast radiationless decay. Since the location of a CI can control reaction mechanisms, it is not surprising that an excited-state lifetime can change significantly in the presence of a solvent.4,5 Squillacote et al.6 have explored the excited-state PES of substituted hexadiene and suggested that the solvent polarity can control the relaxation pathways via two different CI points. Xu et al.7 have discussed the photochemistry of merocyanine and showed that applying an electric field or varying the solvent polarity changes the relative energies of the CI points; these authors considered the possibility of electrostatic control in photochemical reactions. In a subsequent paper, Kahan et al.8 confirmed experimentally that the solvent polarity controls the fluorescence lifetime of merocyanine due to the tuning of CI properties. As clearly seen in these studies, taking account of environmental effects can be critical if one is to obtain an adequate understanding of excited-state nonadiabatic dynamics in solution.9

Several studies have been reported in which CI points including environmental effects have been located.10–27 Burghardt et al.10,11 have evaluated solvent effects on a CI point within the dielectric continuum model and applied the nonequilibrium free energy formulation to a model protonated Schiff base. Using the reference interaction site model self-consistent field (RISM-SCF) method, Yamazaki and Kato12,13 determined the CI points of ethylene, CH2NH2+, and 9H-adenine in polar solvents. Mori et al.14 have combined the RISM-SCF method with the multistate formulation of second-order multireference perturbation theory (MS-CASPT2) and located the CI point of a protonated Schiff base in methanol solution. The hybrid quantum mechanics/molecular mechanics (QM/MM) approach has been also employed to optimize CI points in solution. Toniolo et al.15 have combined a semiempirical configuration-interaction approach with the TIP3P water model and optimized the CI points of several molecules in aqueous solution. Losa et al. have determined a CI in solution using the averaged solvent electrostatic potential scheme16 and applied the method to examine the solvent effects on the internal conversion and intersystem crossing of aqueous acrolein.17 Bearpark et al.18 have successfully located the CI point of the hexatriene chromophore in previtamin D using our own N-layered integrated molecular orbital and molecular mechanics (ONIOM) method. Very recently, Cui and Yang19 have developed a CI search algorithm using sequential QM CI optimizations and MM minimizations or samplings.

A correct description of CI points by density functional theory (DFT) is an important step to achieve efficient large-scale nonadiabatic dynamics simulations in solution. Recently, Kaduk and Voorhis28 have successfully located a CI using configuration-interaction based on constrained DFT,29 although the constraint is not trivial for the CI optimization. Linear-response time-dependent density functional theory (LR-TDDFT) (Refs. 30–38) is a promising approach to describe electronically excited states, and the method has been extensively employed to calculate absorption and fluorescence energies with a reasonable computational cost. In spite of the successful description of these spectroscopic quantities, LR-TDDFT has difficulty in predicting the location of a CI. In ethylene, for example, LR-TDDFT fails to locate the twisted-pyramidalized CI geometry.39 This is because LR-TDDFT lacks the doubly excited configuration that stabilizes the ionic state along the pyramidalization coordinate. Levine et al.39 suggested the possibility of employing a spin-flip TDDFT (SF-DFT) (Refs. 40–50) approach to locate a CI, because SF-DFT employs a triplet reference state that has two unpaired alpha electrons, and the doubly excited configuration is naturally taken into account. Due to its two-electron in two-orbital nature, the SF-DFT method is problematic when more than two orbitals are important.

I. INTRODUCTION

Solvent effects on a potential energy surface crossing are investigated by optimizing a conical intersection (CI) in solution. To this end, the analytic energy gradient has been derived and implemented for the collinear spin-flip density functional theory (SFDFT) combined with the effective fragment potential (EFP) solvent model. The new method is applied to the azomethane-water cluster and the chromophore of green fluorescent protein in aqueous solution. These applications illustrate not only dramatic changes in the CI geometries but also strong stabilization of the CI in a polar solvent. Furthermore, the CI geometries obtained by the hybrid SF-DFT/EFP scheme reproduce those by the full SF-DFT, indicating that the SF-DFT/EFP method is an efficient and promising approach for understanding nonadiabatic processes in solution. © 2012 American Institute of Physics.
Huix-Rotllant et al.\textsuperscript{45} examined the photochemical ring-opening of oxirane and found that SFDFT is only partially successful for the CI point involving three nearly degenerate orbitals. Another example is the $A_g$ states of polyene. Rinkevicius et al.\textsuperscript{47} have reported that these electronic states are heavily spin-contaminated due to some non-spin-adapted configurations that are beyond the two-electron in two-orbital model. The excitation from this $2 \times 2$ active space to the virtual space, for example, cannot be described by the SFDFT method (see Fig. 2 in Ref. 50). Although the spin-contamination problem potentially limits the applicability of the SFDFT method, several promising methods have recently been proposed to avoid the problem. Sears et al.\textsuperscript{51} have examined a spin-complete version for the SF-CIS method and found that the method significantly improves the quality of the SF-CIS results. Casanova and Head-Gordon\textsuperscript{52} have developed the formulation of the SFDFT/EFP1 energy and gradient,\textsuperscript{58,62,63} in order to examine solvent effects on the CI points. Special attention is paid to the solvent-induced changes in the CI location and properties, because a polar solvent can stabilize the ionic state that is often involved in surface crossings.

In addition to the hybrid SFDFT/EFP1 method, a new algorithm is implemented to afford an efficient CI optimization. Maeda et al.\textsuperscript{65} have shown that the branching-plane (BP) updating method is an efficient algorithm to locate CI points, because the method does not require the nonadiabatic coupling matrix elements (NACMEs) that are missing or computationally demanding for some correlated electronic structure methods. Although the penalty-constrained optimization\textsuperscript{59,66} was adopted in the previous studies,\textsuperscript{56,57} a comparative study at the semiempirical configuration-interaction level has shown that the penalty-constrained method needs many more optimization steps.\textsuperscript{67}

The organization of this paper is as follows. Section II describes the formulation of the SFDFT/EFP1 energy and gradient. The BP updating method is also introduced. In Sec. III, the new method is applied to the $S_0/\pi^*$ CI point of an azomethane-water cluster and the $S_0/\pi^*$ CI point of 4'-hydroxybenzylideneimidazolinone (HBI), the chromophore of green fluorescent protein (GFP), illustrated in Fig. 1. Concluding remarks are summarized in Sec. IV.

\section{II. THEORETICAL APPROACH}

\subsection{A. SFDFT/EFP1 method}

In the present work, the reference triplet state is described by the restricted open shell method, and the DFT version of EFP\textsuperscript{61} is used throughout. Each molecular orbital (MO) is assigned to the doubly occupied (DOC), singly occupied (SOCC), or virtual (VIRT) space. The Fock matrix is constructed as a linear combination of alpha and beta Fock matrices

\[
\begin{pmatrix}
\text{DOC} & \text{SOCC} & \text{VIRT} \\
\frac{(F_\alpha + F_\beta)}{2} & F_\alpha & \frac{(F_\alpha + F_\beta)}{2} \\
F_\beta & \frac{(F_\alpha + F_\beta)}{2} & F_\beta \\
\frac{(F_\alpha + F_\beta)}{2} & F_\beta & \frac{(F_\alpha + F_\beta)}{2}
\end{pmatrix}
\]

\begin{align}
F & = \\
& \begin{pmatrix}
\frac{(F_\alpha + F_\beta)}{2} & F_\alpha & \frac{(F_\alpha + F_\beta)}{2} \\
F_\beta & \frac{(F_\alpha + F_\beta)}{2} & F_\beta \\
\frac{(F_\alpha + F_\beta)}{2} & F_\beta & \frac{(F_\alpha + F_\beta)}{2}
\end{pmatrix}
\end{align}

by that model. Therefore, incorporating solvent effects into the SFDFT method is a viable approach to examine the location and properties of a CI in solution.

The effective fragment potential (EFP) method\textsuperscript{58-63} provides a polarizable \textit{ab initio} based solvent model to describe solute-solvent intermolecular interactions. The EFP method has been applied successfully to QM/MM studies of molecules in clusters and in solution. The interface of TDDFT with the EFP water model\textsuperscript{58,62,63} or other polarizable water models\textsuperscript{64} has recently been developed for describing electronically excited states of solvated molecules and applied to excited-state molecular dynamics simulations. In the present work, the analytic energy gradient for the combined SFDFT/EFP method is derived and implemented, in a manner that is similar to the conventional LR TDDFT/EFP1 gradient,\textsuperscript{58} in order to examine solvent effects on the CI points. Special attention is paid to the solvent-induced changes in the CI location and properties, because a polar solvent can stabilize the ionic state that is often involved in surface crossings.

In addition to the hybrid SFDFT/EFP1 method, a new algorithm is implemented to afford an efficient CI optimization. Maeda et al.\textsuperscript{65} have shown that the branching-plane (BP) updating method is an efficient algorithm to locate CI points, because the method does not require the nonadiabatic coupling matrix elements (NACMEs) that are missing or computationally demanding for some correlated electronic structure methods. Although the penalty-constrained optimization\textsuperscript{59,66} was adopted in the previous studies,\textsuperscript{56,57} a comparative study at the semiempirical configuration-interaction level has shown that the penalty-constrained method needs many more optimization steps.\textsuperscript{67}

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In Eq. (1), the canonicalization by Guest and Saunders, which assumes a 1:1 average of the $\alpha$ and $\beta$ Fock matrices for the diagonal blocks, is adopted. The off-diagonal blocks represent the variational conditions, i.e., rotations between DOC-SOCC, DOC-VIRT, and SOCC-VIRT orbitals go to zero. When each unpaired electron has $\alpha$ spin, the Fock matrix is given by

$$F_{pq\alpha} = h_{pq\alpha} + V^{xc}_{pq\alpha} + V^{es}_{pq\alpha} + V^{pol}_{pq\alpha} + V^{rep}_{pq\alpha} + \sum_i (2pq|ii\rangle - c_s(p|i\rangle q\rangle) + \sum_x [(pq|xx\rangle - c_s(p|x\rangle q\rangle)]$$

$$+ \sum_i (2(pq|ii\rangle - c_s(p|i\rangle q\rangle)) + \sum_x (pq|xx\rangle), \quad (2)$$

where the Mulliken notation is adopted for the two-electron integrals. Indices $i, j, \ldots$ label DOC, $x, y, \ldots$ SOCC, $a, b, \ldots$ VIRT, and $p, q, \ldots$ general MOs, and orbitals are assumed to be real throughout the paper. Greek letters $\sigma$ and $\tau$ denote the spin variable, and $c_s$ is the mixing weight of Hartree-Fock exchange. In Eq. (2), $h_{pq\alpha}$ is a one-electron Hamiltonian matrix element that is the sum of the kinetic energy and the electron-nucleus attraction terms. $V^{xc}_{pq\alpha}$ is the exchange-correlation potential obtained by taking the first functional derivative of the exchange-correlation energy functional. The three remaining terms, $V^{es}_{pq\alpha}$, $V^{pol}_{pq\alpha}$, and $V^{rep}_{pq\alpha}$, describe the electrostatic (Coulomb), polarization (induction), and repulsive potential of the QM-EFP1 interaction, respectively. In the EFPI model, the repulsive potential includes effectively the exchange repulsion and charge-transfer interactions as well as short-range electron correlation effects and is determined empirically by fitting to a large number of points on the DFT/B3LYP water dimer PES. Care must be taken when evaluating the polarization term, because the EFPI induced dipoles depend on the QM electron density.

In the collinear SFDFT formulation, the excitation energy $\Omega$ and transition amplitude $X$ are given by solving the Hermitean matrix equation

$$AX = \Omega X. \quad (3)$$

The coupling matrix $A$ is given by

$$A_{pa\bar{q}b,\bar{r}a\bar{s}b} = \left(F_{pq\alpha} \delta_{pr} - F_{pra\delta_{\bar{q}s}}\right) - c_s(p|r\rangle q\rangle + f^{xc}_{pq\bar{q}b,\bar{r}a\bar{s}b} + f^{pol}_{pq\bar{q}b,\bar{r}a\bar{s}b}, \quad p, r \in \text{d.s.}, \quad q, s \in \text{s.v.}, \quad (4)$$

where d.s. (s.v.) extends over the DOC and SOCC (SOCC and VIRT) spaces. $f^{xc}$ is the exchange-correlation kernel given by the second functional derivative of the exchange correlation energy, and the collinear approximation assumes $f^{xc} = 0$ for the spin-flip excitation. The last term, $f^{pol}$, is the EFP polarization kernel given by

$$f^{pol}_{pq\bar{q}b,\bar{r}a\bar{s}b} = \int dr dr' \psi_{pa}(r) \psi_{\bar{q}b}(r) f^{pol}(r, r') \psi_{ra}(r') \psi_{s\tau}(r')$$

$$= -\frac{1}{2} \left(E^{pol}_{pq\bar{q}b}\right)^{T} [\mathbf{M}^{-1} + (\mathbf{M}^{T})^{-1}] E^{pol}_{ra\bar{s}b}. \quad (5)$$

The matrix $\mathbf{M}$ contains information on the fragment-fragment distances and orientations and the dipole polarization tensors. $E^{pol}_{pq\bar{q}b}$ is a matrix element of the electric field operator and is also a column vector whose dimension is three times the number of polarizable points. The superscript $T$ denotes the transpose. Since the electric field is independent of spin variables, the EFP polarization kernel is exactly zero due to the spin orthogonality in the spin-flip excitation. Consequently, there is no EFP polarization contribution to the coupling matrix $A$. Note that $f^{pol} = 0$ is valid whether or not the collinear approximation is assumed.

The spin-flip excitations are affected only indirectly by the EFPI solvent molecules, since the reference-state density depends on the EFPI solvent. In the present study, induced dipoles are treated in a static manner; these dipoles are optimized at the reference triplet state DFT/EFPI level although some correction terms enter into the force calculation (see discussion below). In particular, these dipoles are assumed to be in equilibrium with the triplet QM electron density. Within the linear-response approximation, the induced dipoles do not feel the QM electron density for the target state, and thus the induced dipoles are not optimal for the singlet states in the SFDFT method. A fully self-consistent calculation requires a state-specific formulation. A recent QM/MM study by Sneskov et al. has considered a fully self-consistent treatment of polarization for the linear-response QM methods. However, recent EFPI papers on excited states have demonstrated that the self-consistent polarization is not important (see Refs. 71–73).

Furche and Ahlrichs have derived the TDDFT analytic energy gradient using the Lagrangian formulation. The corresponding Lagrangian for the SFDFT/EFPI method is

$$L[X, \Omega, C, \vec{Z}, \vec{W}] = G[X, \Omega] + 2 \sum_i \sum_a Z_{ia} \vec{F}_{ia} + \sum_i \sum_x Z_{ix} \vec{F}_{ix}$$

$$+ \sum_s \sum_a Z_{sa} \vec{F}_{sa} - 2 \sum_{s \leq q} \vec{W}_{pq}(S_{pq} - \delta_{pq}). \quad (6)$$

Here,

$$G[X, \Omega] = \sum_{p, r, q, s} A_{pa\bar{q}b,\bar{r}a\bar{s}b} X_{pa\bar{q}b} X_{ra\bar{s}b} \quad (7)$$

is dependent on the transition amplitude matrix $X$ and excitation energy $\Omega$. The vector $C$ consists of MO coefficients $C_{\mu\nu}$ ( $\mu$ indexes atomic basis functions), and $S_{pq}$ is an overlap integral between the MOs $p$ and $q$. The vector $\vec{Z}$ enforces the condition that the DOC-SOCC, DOC-VIRT, and SOCC-VIRT blocks of the Fock matrix $\vec{F}$ [see Eq. (1)] are zero. The Lagrange multipliers $\vec{Z}$ and $\vec{W}$ are determined from the stationary condition of the Lagrangian, $\delta L / \delta \bar{C}_{\mu\nu} = 0$ (see the Appendix). As shown in the following discussion, the matrix $\vec{W}$ is the energy-weighted difference density matrix.

To obtain the SFDFT/EFPI gradient, one needs to solve the $Z$-vector equation

$$\sum_{r, s} \sum_{p, q, r} \vec{J}_{rq, rs} = -\vec{R}_{pq} \quad p \in \text{d.s.}, \quad q \in \text{s.v.}. \quad (8)$$
where the orbital Hessian $\tilde{J}$ is defined as follows:

$$\tilde{J}_{ix,jy} = (ix|jy) - \frac{c_i}{2}[(iy|jx) + (ij|xy)] + f_{x,b,y}^{bc} + \frac{1}{2} F_{ijb} \delta_{xy} + \frac{1}{2} F_{i,jb} \delta_{ij},$$

$$\tilde{J}_{ia,jy} = 2(ia|jy) - \frac{c_i}{2}[(iy|ja) + (ij|ya)] + f_{ia,jy}^{bc} + \frac{1}{2} F_{ia,jy} \delta_{ij},$$

$$\tilde{J}_{xa,y} = (xa|y) + f_{xa,y}^{bc} - \frac{1}{2} F_{xa,y} \delta_{xy},$$

$$\tilde{J}_{ia,jb} = 4(ia|jb) - c_i[(ib|ja) + (ij|ab)] + f_{ia,jb}^{bc} + \frac{1}{2} F_{ia,jb} \delta_{ij},$$

$$\tilde{J}_{xa,yb} = (xa|yb) - \frac{c_i}{2}[(xb|ya) + (xy|ab)] + f_{xa,yb}^{bc} + \frac{1}{2} F_{xa,yb} \delta_{ab},$$

and the linear transformation operators are introduced for the arbitrary vector $V$,

$$H_{p,q}^\dagger(V) = \sum_{rst} [2(pq|rs) + 2f_{x,b,y}^{bc} + 2f_{p,q,r}^{pol} - c_i \delta_{rt} [(pq|rs) + (pr|qs)] \ V_{rst},$$

and for the transition amplitude $X$,

$$H_{p,q}^0[X] = \sum_{r} \sum_{s} [f_{q,s}^{bc} - F_{pra} \delta_{qs} - c_i \delta_{rs} X_{ra} s].$$

After solving the $Z$-vector equation, the relaxed difference density matrix $P$ is obtained as

$$P_{pq} = T_{pq} + Z_{pq} \ p, q \in d.s.v.,$$

where the spin-dependent $Z$ matrix (without the bar symbol) is introduced

$$Z_{iaa} = Z_{iaa} = Z_{aia} = Z_{aia} \ p, q \in d.s.v.,$$

Finally, the energy-weighted density matrix $\tilde{W}$ is determined: the intra-block elements are

$$\tilde{W}_{ij}(1 + \delta_{ij}) = \frac{1}{2} \left( H_{ij}^+[P] + H_{ij}^+[P] \right)$$

$$\tilde{W}_{xy}(1 + \delta_{xy}) = \frac{1}{2} H_{xy}^0[P] + \sum_{p,r} (\Omega \delta_{pr} - F_{pra}) X_{pa} x Y_{ri} y,$$

and the inter-block elements are

$$\tilde{W}_{ia} = \frac{1}{2} (H_{ix}^+ + H_{ix}^+)[P]$$

$$\tilde{W}_{ia} = \sum_{q} F_{x,y} Z_{i,a} + \sum_{p} H_{pa}^{0} X_{pa} a b,$$

$$\tilde{W}_{ia} = \epsilon_i Z_{ia} + \sum_{q} F_{x,a} Z_{iq} + \sum_{p} H_{pa}^{0} X_{pa} a b,$$

The matrix $T$ is the unrelaxed difference density matrix defined by

$$T_{p,q} = \sum_{d.s.} X_{p,a} q X_{r,a} q,$$

$$T_{q} = \sum_{p} X_{p,a} q X_{pa} a b,$$

$$T_{p,r} = \sum_{q} X_{p,a} q X_{pa} a b.$$
In Eqs. (16) and (17), the bold terms in square brackets (e.g., \(P\) and \(X\)) indicate arguments of the respective functions. The spin-dependent energy-weighted density matrix \(W\) (without the bar symbol) is \(W_{pq} = W_{qp} = \bar{W}_{pq}\).

One can obtain the analytic gradient of the SF DFT excitation energy with respect to a QM nuclear coordinate \(\xi\), expressed in the atomic orbital (AO) basis as

\[
\Omega(\xi) = \sum_{\mu \nu \sigma} (h^{\mu \nu}_{\sigma} + V_{\mu \nu}^{\mathrm{exc}, \xi} + V_{\mu \nu}^{\mathrm{rep}, \xi}) P_{\mu \nu \sigma} - \sum_{\mu \nu \sigma} S_{\mu \nu \sigma} W_{\mu \nu \sigma} + \sum_{\mu \nu \sigma, \kappa \lambda \tau} (\mu \nu | \kappa \lambda \xi \sigma) \Gamma_{\mu \nu \sigma, \kappa \lambda \tau} + \Omega^{\mathrm{xc}, \xi} + \Omega^{\mathrm{pol}, \xi} .
\]  
\(\text{(18)}\)

The matrix element \(P_{\mu \nu \sigma}\) is calculated from the corresponding quantity in the MO basis using \(P_{\mu \nu \sigma} = \sum_{pq} C_{\mu \mu'} C_{\nu \nu'} C_{\sigma \sigma'}\), and a similar transformation is applied to obtain \(X_{\mu \nu \sigma}\) and \(W_{\mu \nu \sigma}\). \(\Gamma_{\mu \nu \sigma, \kappa \lambda \tau}\) is an element of the effective two-particle difference density matrix \(\Gamma_{\mu \nu \sigma, \kappa \lambda \tau} = \left[ 2P_{\mu \nu \sigma} D_{\kappa \lambda \tau} - c_{\xi} \delta_{\kappa \sigma}(P_{\mu \kappa \sigma} D_{\lambda \tau} + P_{\mu \lambda \sigma} D_{\kappa \tau}) - c_{\xi} \delta_{\lambda \tau}(P_{\mu \kappa \sigma} D_{\lambda \tau} + P_{\mu \lambda \sigma} D_{\kappa \tau}) - c_{\xi} \delta_{\sigma \tau}(P_{\mu \kappa \sigma} D_{\lambda \tau} + P_{\mu \lambda \sigma} D_{\kappa \tau}) \right] \].

Also in Eq. (18) \(h^{\mu \nu}_{\sigma}, S^{\mu \nu}_{\sigma}\), and \((\mu \nu | \kappa \lambda \xi \sigma)\) are the derivatives of the one-electron gas-phase Hamiltonian, the overlap, and the two-electron integrals, respectively. The matrix \(D\) is the reference-state density matrix. In the present work \(\xi\) can also represent an EFP translation or an EFP rotation. Equation (18) includes the gradients of the EFP1 electrostatic and repulsive terms as well as those of the polarization interaction.

The gradient of the exchange-correlation part is given by

\[
\Omega^{\mathrm{xc}, \xi} = \sum_{\mu \nu \sigma} V_{\mu \nu \sigma}^{\mathrm{xc}, \xi} P_{\mu \nu \sigma} .
\]  
\(\text{(20)}\)

Here the collinear approximation, \(f^{\mathrm{xc}} = 0\), is assumed. The extension to the noncollinear formulation is straightforward. The superscript in parentheses, \((\xi)\), on the right-hand side indicates that the derivatives are evaluated with respect to \(\xi\) but keeping the MO coefficients constant at the reference-state values. The details of the evaluation of Eq. (20) are presented in Ref. 75.

The gradient of the EFP polarization term is

\[
\Omega^{\mathrm{pol}, \xi} = \sum_{\mu \nu \sigma} V_{\mu \nu \sigma}^{\mathrm{pol}, \xi} P_{\mu \nu \sigma} = -\frac{1}{2} (\mu + \bar{\mu})^T E^{\mathrm{pol}, \xi} + \frac{1}{2} (\mu + \bar{\mu})^T \frac{\partial M}{\partial \xi} \mu + \frac{1}{2} (\mu + \bar{\mu})^T \frac{\partial M}{\partial \xi} \mu^\Delta .
\]  
\(\text{(21)}\)

This term accounts for the contribution from the change in the one-particle density matrix. Here, \(\mu\) and \(\bar{\mu}\) are the EFP induced dipoles determined for the reference triplet state. \(E^\Delta = T(-PE^\Delta)\) is the solute electric field due to the relaxed difference density matrix, \(P\), and \(\mu^\Delta = M^\Delta E^\Delta\) is the resultant change in induced dipoles. Note that there is no contribution from the transition amplitude due to \(f^{\mathrm{pol}} = 0\) in the coupling matrix element [Eq. (4)]. Therefore, the implementation of the SF DFT/EFP1 analytic energy gradient is much simpler than that of the conventional TDDFT/EFP1 gradient.

Finally, the gradient of the excitation energy obtained above is added to that of the ground-state energy

\[
E^{\xi} = \sum_{\mu \nu \sigma} \left( h_{\mu \nu \sigma}^{\xi} + V_{\mu \nu \sigma}^{\mathrm{exc}, \xi} + V_{\mu \nu \sigma}^{\mathrm{rep}, \xi} \right) D_{\mu \nu \sigma} - \sum_{\mu \nu \sigma} S_{\mu \nu \sigma} W_{\mu \nu \sigma} + \sum_{\mu \nu \sigma, \kappa \lambda \tau} (\mu \nu | \kappa \lambda \xi \sigma) \Gamma_{\mu \nu \sigma, \kappa \lambda \tau} + E^{\mathrm{xc}, \xi} + E^{\mathrm{pol}, \xi} ,
\]  
\(\text{(22)}\)

where \(D_{\mu \nu \sigma}\) is a ground-state density matrix element and \(\Gamma_{\mu \nu \sigma, \kappa \lambda \tau}\) is the DFT two-particle density matrix

\[
\Gamma_{\mu \nu \sigma, \kappa \lambda \tau} = \frac{1}{2} (D_{\mu \nu \sigma} D_{\kappa \lambda \tau} - c_{\xi} \delta_{\kappa \sigma} D_{\mu \lambda \sigma} D_{\nu \kappa \tau} ) .
\]  
\(\text{(23)}\)

Note that the superscript in parentheses, \((\xi)\), appears in the last two terms of Eq. (22), and the MO coefficients are held constant in the gradient calculation. It is not necessary to compute the derivatives of MO coefficients because these terms are absorbed in the energy-weighted density matrix (the second term). The last term in Eq. (22), the gradient of the ground-state polarization energy, is easily derived

\[
E^{\mathrm{pol}, \xi} = -\frac{1}{2} (\mu + \bar{\mu})^T [E^{\mathrm{nuc}, \xi} + E^{\mathrm{el}, \xi} + E^{\mathrm{pol}, \xi} ] + \frac{1}{2} (\mu + \bar{\mu})^T \frac{\partial M}{\partial \xi} .
\]  
\(\text{(24)}\)

In summary, the SF DFT/EFP1 gradient can be computed easily by modifying the ground-state DFT/EFP1 gradient as follows: (a) the electrostatic interaction between QM electrons and EFP permanent multipoles

\[
\text{Tr}[DV^{\mathrm{exc}, \xi}] \rightarrow \text{Tr}[(D + P)V^{\mathrm{exc}, \xi}] .
\]  
\(\text{(25a)}\)

(b) the repulsive interaction between QM electrons and EFP molecules

\[
\text{Tr}[DV^{\mathrm{rep}, \xi}] \rightarrow \text{Tr}[(D + P)V^{\mathrm{rep}, \xi}] ,
\]  
\(\text{(25b)}\)

and the polarization contribution due to (c) QM nuclei-EFP induced dipoles

\[
-\frac{1}{2} (\mu + \bar{\mu})^T E^{\mathrm{nuc}, \xi} \rightarrow -\frac{1}{2} (\mu + \bar{\mu})^T [E^{\mathrm{el}, \xi} + E^{\Delta}] .
\]  
\(\text{(25c)}\)

d) the QM-EFP induced dipoles

\[
-\frac{1}{2} (\mu + \bar{\mu})^T E^{\mathrm{pol}, \xi} \rightarrow -\frac{1}{2} (\mu + \bar{\mu})^T [E^{\mathrm{el}, \xi} + E^{\Delta}] .
\]  
\(\text{(25d)}\)

e) the EFP permanent multipoles-EFP induced dipoles

\[
-\frac{1}{2} (\mu + \bar{\mu})^T E^{\mathrm{pol}, \xi} \rightarrow -\frac{1}{2} (\mu + \bar{\mu})^T [E^{\mathrm{pol}, \xi} ] .
\]  
\(\text{(25e)}\)

and (f) the EFP induced dipoles-EFP induced dipoles

\[
\frac{1}{2} (\mu + \bar{\mu})^T \frac{\partial M}{\partial \xi} \rightarrow \frac{1}{2} (\mu + \bar{\mu})^T [\mu + \mu^\Delta] \frac{\partial M}{\partial \xi} \mu^\Delta .
\]  
\(\text{(25f)}\)
All of these terms can be computed with the existing code by modifying the arguments for the density matrix and the induced dipoles as in the TDDFT/EFP1 gradient.

B. Branching-space updating method

In the gradient projection method,76 the CI optimization requires the difference gradient vector (DGV) and the coupling derivative vector (CDV). The DGV $f$ is the derivative of the potential energy difference between electronic states $I$ and $J$, \[
 f \equiv \nabla_\xi (E_I - E_J),
\]
and the CDV $g$ is the interstate coupling vector defined as \[
 g \equiv \langle \Psi_I | \nabla_\xi | \Psi_J \rangle.
\]

Again, the coordinate $\xi$ can also represent an EFP translation or rotation, and the dimension of these vectors is equal to three times the number of QM atoms plus six times the number of EFP fragments.

The gradient vector employed in the CI optimization is expressed as \[
 2(E_I - E_J)f(R) + \hat{P}\nabla_\xi E_J.
\]
The first term is the derivative of squared energy difference, $\nabla_\xi (E_I - E_J)^2$. The projection operator $\hat{P}$ in the second term is \[
 \hat{P} = 1 - \hat{f}^T \hat{f} - \hat{g}_\perp \hat{g}_\perp^T,
\]
where $\hat{f} = f/f$, $g_\perp = (1 - \hat{f}^T)f$, and $g_{\perp\perp} = g_\perp/g_\perp$. Note that it is not the CDV itself, but rather the modified CDV, $\hat{g}_\perp$, that appears in Eq. (29). The CDV is orthogonalized with respect to $\hat{f}$ and then normalized to unity.

The BP updating method65 allows the CI optimization without the need to compute NACMEs. Let $\hat{f}$ and $\hat{g}_\perp$ at the $m$th optimization step be $\hat{f}_m$ and $\hat{g}_m$. These two vectors are orthonormal (see the definition of $\hat{g}_\perp$). At the $(m+1)$-th step, the CDV is not computed by Eq. (27). Instead, the CDV is constructed as a linear combination of $\hat{f}_m$ and $\hat{y}_m$ obtained in the previous step \[
 \hat{y}_{m+1} = u\hat{f}_m + v\hat{y}_m, \quad u^2 + v^2 = 1.
\]
The coefficients $u$ and $v$ are determined by the orthonormality condition at the $(m+1)$-th step, $\hat{f}_{m+1} \cdot \hat{y}_{m+1} = 0$, and the resultant vector $\hat{y}_{m+1}$ is given as follows: \[
 \hat{y}_{m+1} = \frac{(\hat{f}_{m+1} \cdot \hat{y}_m)\hat{f}_m - (\hat{f}_{m+1} \cdot \hat{f}_m)\hat{y}_m}{\sqrt{(\hat{f}_{m+1} \cdot \hat{f}_m)^2 + (\hat{f}_{m+1} \cdot \hat{y}_m)^2}}.
\]
At the initial step, $\hat{y}_0$ cannot be obtained by Eq. (30) and is set to be a unit vector parallel to the mean gradient vector, $\nabla_\xi (E_I + E_J)/2$.

C. Computational details

The SFDFT/EFP1 energy and analytic gradient were implemented in the electronic structure code general atomic and molecular electronic structure system (GAMESS).77,78 In the present study, the BHLYP (50% Hartree-Fock plus 50% Becke exchange79 with Lee-Yang-Parr correlation80) hybrid functional was adopted. The basis set employed was of double-zeta plus polarization (DZP) (Ref. 81) quality.

Three CI search algorithms have been implemented in GAMESS: the gradient projection method using the NACME,76 the BP updating method,65 and the penalty-constrained optimization.39,66 As described in Sec. II B, the BP updating method was adopted in this work since the NACME for SFDFT is not available in the current version of GAMESS. The SFDFT NACME will be reported in a forthcoming paper.

The SFDFT/EFP1 method was applied to azomethane and the neutral HBI molecule. In the azomethane calculations, two water molecules were randomly generated around the azomethane molecule optimized in the gas phase by using the particle randomization routine in the global minimum energy optimization module of GAMESS, and the geometry optimizations were performed using several configurations. For computing aqueous HBI, a QM water molecule was attached to the phenol OH, because some optimizations without the QM water failed due to the strong interaction between the OH group and an EFP water. The HBI-water 1:1 complex was immersed in 50 EFP water molecules. Three important points were considered: the $S_0$ trans isomer, the $\pi\pi^*$ twisted minimum, and the $S_0/\pi\pi^*$ CI. In the geometry optimization, the gradient convergence tolerance was increased to be $3 \times 10^{-4}$ hartree/bohr for the 50 EFP1 cluster system, because the calculations were not converged in spite of a large number of steps (>200). To prepare initial configurations, 1 ns classical molecular dynamics (MD) simulations were performed for the three points (the $S_0$ trans isomer, $\pi\pi^*$ twisted minimum, and the $S_0/\pi\pi^*$ CI) using 1024 TIP4P water82 molecules. The HBI geometries at the three points were optimized in the gas phase and fixed during the simulation. The electrostatic interaction in the classical MD was evaluated by a pairwise Coulomb potential. The partial charges of HBI were determined by a least-square-fitting procedure to reproduce the SFDFT electrostatic potential. To prepare the initial configurations for the CI optimization, the partial charges were averaged over two relevant electronic states. The exchange repulsion and dispersion interaction in the pure classical MD were modeled by an empirical 12-6 Lennard-Jones potential, and the potential parameters were taken from AMBER force field.83 Five snapshots were chosen from the classical MD simulation, and the SFDFT/EFP1 calculations were performed. The minimum energy structures of the five SFDFT/EFP1 calculations were considered for each point: the $S_0$ trans isomer, $\pi\pi^*$ twisted minimum, and the $S_0/\pi\pi^*$ CI. Although the results obtained by a few configurations are far from statistically converged, solvent-induced changes could be captured by these calculations.

III. CONICAL INTERSECTIONS IN SOLUTION

A. Azomethane-water cluster

Azoxalkanes have been extensively studied to examine the photochemistry and thermal decomposition process that occurs after photoexcitation. These molecules undergo cis-trans
isomerization in the solution phase, while the dissociation into alkyl radicals and molecular nitrogen is a major reaction channel in the gas phase. Since azomethane is the simplest molecule in theazo family, both experiments and theoretical calculations have been reported.84–90

Before describing the CI points of hydrated azomethane, consider the accuracy of the present implementation of SFDFTEFP analytic energy gradients. The analytic gradient was calculated for the azomethane·2(H2O) cluster. For comparison, numerical gradient calculations were also carried out using a five-point numerical differentiation formula. A QM atom was displaced along a Cartesian coordinate, while the molecular translation and rotation was considered for the EFP1 water due to the frozen internal geometry of an EFP. The numerical gradients were evaluated with a translational step size of 0.001 bohr and a rotational step size of 0.001 radian. Good agreement is observed for all of the trial configurations; the difference between the analytic and numeric gradients is ∼10−5 a.u. for the EFP translation and rotation coordinates and ∼10−5 a.u. for the QM atomic coordinates. These values are small enough to perform the geometry optimization in light of the default convergence tolerance, 1 × 10−4 hartree/bohr. Quantitative agreement between the analytic and numerical gradients indicates that the present implementation of analytic energy gradients is correct.

Further test calculations were performed on a trans-azomethane·2(H2O) cluster (Fig. 2(a)). The geometries were optimized for the ground state at the SF-BHHLYP/DZP level of theory. In the cluster, the two water molecules are treated as QM or EFP1. Table I summarizes the ground-state geometric parameters and vibrational frequencies of azomethane and the azomethane·2(H2O) cluster. The vibrational frequency analysis was performed by the numerical differentiation of the analytic energy gradients, and no imaginary frequency was observed. The SFDFTEFP1 results are in good agreement with those obtained by the full SFDFT: the difference in geometry is ∼0.001 Å and 0.5°. Therefore, the present implementation of SFDFTEFP analytic energy gradients is correct for both geometry optimizations and force constant matrix calculations.

### Table I. Selected geometric parameters and vibrational frequencies of trans-azomethane and trans-azomethane·2H2O cluster.

<table>
<thead>
<tr>
<th>Geometry parameters</th>
<th>Azomethane</th>
<th>Azomethane+2 water</th>
<th>Azomethane+2 EFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(N1N2)</td>
<td>1.233</td>
<td>1.231</td>
<td>1.232</td>
</tr>
<tr>
<td>r(N1C3)</td>
<td>1.454</td>
<td>1.456</td>
<td>1.456</td>
</tr>
<tr>
<td>r(N2C4)</td>
<td>1.454</td>
<td>1.454</td>
<td>1.453</td>
</tr>
<tr>
<td>ζ(N1N2C3)</td>
<td>113.0</td>
<td>113.6</td>
<td>113.4</td>
</tr>
<tr>
<td>ζ(N2N1C3)</td>
<td>113.0</td>
<td>114.5</td>
<td>114.0</td>
</tr>
<tr>
<td>ζ(C3N1N2C4)</td>
<td>180.0</td>
<td>179.4</td>
<td>179.6</td>
</tr>
<tr>
<td>Vibrational frequencies</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1N2 stretch</td>
<td>1792</td>
<td>1806</td>
<td>1806</td>
</tr>
<tr>
<td>HCN sym. bend</td>
<td>1270</td>
<td>1279</td>
<td>1277</td>
</tr>
</tbody>
</table>

Table II summarizes the relative energies at the equilibrium and CI points. The SFDFTEFP1 (full SFDFT) calculation on trans-azomethane provides an n→π* absorption energy of 3.81 (3.80) eV, which is slightly blueshifted with respect to that of the isolated azomethane, 3.71 eV. The present results are in line with the previous theoretical studies: ∼3.8 eV by the multireference configuration-interaction (MRCI) method,87,88 ∼3.7 eV by the state-averaged complete active space SCF (SACAS) method,90 and 3.49 eV by the TDB3LYP/6-311++G(d,p) method.90 Experimentally, the absorption maximum is estimated to be ∼3.6 eV.90 Quantitative agreement between the SFDFTEFP and full SFDFT is also observed for the absorption energy of cis-azomethane, 3.61 (3.61) eV.

Figure 2(b) shows the S0/π* CI geometry of the azomethane·2(H2O) cluster, and Table III summarizes selected geometric parameters. For comparison, the CI geometry obtained by the MRCI method is also included.88 The CNNC torsion angle is nearly 90°, and the two NCH3 groups are decoupled. One of the CN bonds is stretched by 0.02 Å, and the other is shortened by 0.02 Å. At the same time, one of the NNC bonds increases by 20°. The solvent-induced changes at the CI point are minimal; the energy decreases only by 0.03 eV, and the geometric differences are ∼0.01 Å and ∼0.5°. These small changes may be attributed to similar solute-solvent interactions for the two electronic states. At the gas-phase twisted minimum geometry, the dipole moment is calculated to be 1.54 and 1.52 D for the S0 and S1 states, respectively. The SFDFTEFP1 method reproduces quantitatively the full SFDFT in which all water molecules are treated.

### Table II. SFDFT relative energies (in eV) at the equilibrium and CI points of azomethane.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>State</th>
<th>Gas</th>
<th>+2 water</th>
<th>+2 EFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S0)trans</td>
<td>S0+</td>
<td>0.00 (0.00)</td>
<td>0.00 (0.01)</td>
<td>0.00 (0.01)</td>
</tr>
<tr>
<td>nπ*</td>
<td>3.71 (0.01)</td>
<td>3.80 (0.01)</td>
<td>3.81 (0.01)</td>
<td></td>
</tr>
<tr>
<td>(S0)cis</td>
<td>S0+</td>
<td>0.43 (0.01)</td>
<td>0.34 (0.01)</td>
<td>0.35 (0.01)</td>
</tr>
<tr>
<td>nπ*</td>
<td>3.95 (0.01)</td>
<td>3.95 (0.02)</td>
<td>3.96 (0.01)</td>
<td></td>
</tr>
<tr>
<td>(nπ*)min</td>
<td>S0+</td>
<td>2.16 (0.01)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>nπ*</td>
<td>3.01 (0.05)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>(S0/nπ*)c3</td>
<td>2.898 (0.02)</td>
<td>2.873 (0.03)</td>
<td>2.874 (0.04)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.898 (0.05)</td>
<td>2.873 (0.05)</td>
<td>2.874 (0.04)</td>
<td></td>
</tr>
</tbody>
</table>

*Values in parentheses are spin expectation values (δΩ).

### Table III. Selected geometric parameters at the CI points of azomethane.

<table>
<thead>
<tr>
<th>Geometry parameters</th>
<th>Gas</th>
<th>+2 water</th>
<th>+2 EFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(N1N2)</td>
<td>1.252</td>
<td>1.281</td>
<td>1.252</td>
</tr>
<tr>
<td>r(N1C3)</td>
<td>1.434</td>
<td>1.449</td>
<td>1.444</td>
</tr>
<tr>
<td>r(N2C4)</td>
<td>1.471</td>
<td>1.482</td>
<td>1.470</td>
</tr>
<tr>
<td>ζ(N1N2C3)</td>
<td>116.5</td>
<td>115.0</td>
<td>116.9</td>
</tr>
<tr>
<td>ζ(N2N1C3)</td>
<td>132.2</td>
<td>131.7</td>
<td>132.4</td>
</tr>
<tr>
<td>ζ(C3N1N2C4)</td>
<td>94.5</td>
<td>91.6</td>
<td>94.8</td>
</tr>
</tbody>
</table>

*Multireference configuration-interaction method, Ref. 1.
quantum mechanically; both methods compute the relative energy of the CI point to be 2.87 eV, and the geometric differences are ~0.002 Å and ~0.4°. Therefore, the EFP solvent model is able to represent the solute-solvent complex effectively at both the equilibrium and CI points.

The azomethane-water cluster calculations illustrate the importance of local solute-solvent interactions to determine the PES profiles in spite of the minimal changes in geometric parameters. The addition of just two water molecules affects the nπ* minimum. While gas-phase azomethane has the nπ* minimum at a CNNC twisting angle of 113.7°, the corresponding minimum energy point disappears in the hydrated cluster. Therefore, the minimum energy CI point may become the absolute minimum in aqueous solution.

Finally, the energy gap obtained by the BP updating method is very small (~0.001 eV), while a typical value observed for the penalty-constrained optimization is 0.02 eV. Further benchmark studies are needed to confirm the robustness and reliability of the method.

B. GFP chromophore in water

The GFP has been extensively employed in biology, physiology, and medicine as a useful biomarker, and numerous experimental and theoretical studies have been reported.91–105 The protein environment plays a crucial role in the fluorescence of the chromophore (HBI). It has been argued that the surrounding residues prevent the chromophore from twisting around the phenoxy (“P-bond”: τP) or imidazolinone (“I-bond”): τI) bonds of the bridge (see Fig. 1). In aqueous solution, however, a strong fluorescence is quenched because the nπ* minimum at a CNNC twisting angle of 113.7°, the corresponding minimum energy point disappears in the hydrated cluster. Therefore, the minimum energy CI point may become the absolute minimum in aqueous solution.

Next, consider the solvent effects on the geometries and PES profiles. Marginal solvent effects are observed for the absorption energy of HBI. The addition of a single water molecule decreases the vertical excitation energy by 0.09 eV. In the bulk solution, however, the absorption energies taken from the five snapshots lie in the range of 3.88–4.03 eV, and the former value shown in Table IV is obtained at the minimum energy geometry of the five trial calculations. Extensive sampling is essential to examine the broadening of the absorption spectrum of aqueous HBI.

Large solvent-induced changes are expected for the CI of aqueous HBI, because the two relevant electronic states differ significantly in their electronic distributions. At the gas-phase twisted minimum geometry, the dipole moment is calculated to be 3.59 and 10.05 D for the S0 and nπ* states, respectively. The nπ* state clearly shows a charge migration from the phenol ring to imidazolinone group. The solute-solvent interaction stabilizes the polar nπ* state more strongly than the S0 state, and this distinct stabilization induces a large displacement of the CI as discussed below.

Table V shows selected geometric parameters for the CI points of HBI, and those at the twisted minimum energy point are also included for comparison. Noticeable changes are observed for the pyramidalization angle ω and the twisting angle around C8-C9 bond (τI). While a sizable pyramidalization
is observed in the gas phase (~30°), the corresponding angle reduces to 14° in the cluster. Notably, HBI becomes planar around the C9 atom in aqueous solution. The twisting angle τ1 decreases monotonically from 104° in the gas phase to 91° in solution, implying that the CI point approaches the ππ* twisted minimum due to the stabilization of the ππ* state by the polar solvent. These structural changes are closely related to the charge separation that occurs in the ππ* state. Figure 3 shows the hydration structure at the CI. Several hydrogen bonds are formed at the CI geometry: carbonyl oxygen and water hydrogen, imidazole NH, and water oxygen. Clearly, these hydrogen bonds enhance the charge migration.

The polar solvent alters the PES of HBI. The energy difference between the twisted minimum and the CI point is 0.13 eV for the isolated HBI, and the addition of a single water molecule reduces the difference to 0.03 eV. In the bulk solution, the CI point becomes the absolute minimum; the five trial optimizations started at the gas-phase twisted minimum geometry with different solvation structures all lead to the CI. The CI point is close to the twisted minimum, and the strong solute-solvent interaction stabilizes the ππ* PES. The CI is found at 2.13 eV above the ground-state minimum in water, while the corresponding energy in the gas phase is estimated to be 3.02 eV. The energy difference between the Franck-Condon (FC) and CI points increases monotonically from the gas phase (0.92 eV) to the 1:1 cluster (1.11 eV) to the bulk solution (1.75 eV). A direct approach to the CI point is also observed using the ground-state geometry as the initial guess. Therefore, aqueous HBI would reach the CI point easily from the FC region.

Finally, the BP updating method works well for the HBI cluster consisting of a large number of EFP solvent molecules, even though the method was initially applied to the optimization of isolated molecules.65 The energy gap between the two electronic states is less than 0.001 eV.

IV. CONCLUDING REMARKS

In the present paper, solvent effects on the CI points are examined using the combined SFDFTEFP1 method. Special attention is paid to the solvent-induced changes in geometric parameters and the solvent-induced shift of the CI point. To achieve an efficient CI optimization, the BP updating method has been implemented. The new method has been applied to the S0/ππ* CI point of azomethane-water cluster and the S0/ππ* CI of HBI. Large solvent-induced changes are observed for the latter system due to the ionic character of the ππ* state. The stabilization of charge-transfer state by polar solvents is essential at the CI. The torsion and pyramidalization angles at the CI geometry are decreased in solution, and the CI point becomes the absolute minimum in solution. Qualitative changes in the PES profile would alter the mechanisms of the relaxation process in solution.

The CI energies and geometries obtained by the hybrid SFDFTEFP scheme reproduce those obtained using the full SFDFTEFP, indicating that the SFDFTEFP approach is an efficient and promising method for understanding surface crossing problems in solution. The present method offers important possibilities in several directions. First, the present method enables a large-scale solution-phase nonadiabatic QM/MM MD simulation for electronically excited states, although the development of NACME within the SFDFTEFP is required. Several authors have applied the TDDFT method combined with the trajectory surface-hopping approach to investigate the relaxation pathways of photoexcited molecules,106–114 and the TDDFT/MM nonadiabatic simulation has recently been reported.115, 116 The SFDFTEFP1 nonadiabatic simulation is useful to understand dynamical aspects of solvent effects on such surface crossing problems. Further work is in progress along these lines.

ACKNOWLEDGMENTS

This work was supported by a National Science Foundation Petascale Applications grant.

APPENDIX: COUPLED-PERTURBED EQUATION FOR THE SFDFTEFP WITH RESTRICTED-OPEN REFERENCE

In this Appendix, the Z-vector equation is derived using the stationary condition of the Lagrangian. Multiplying both
sides of $\partial L/\partial C_{\mu p} = 0$ by $C_{\mu q}$ and summing over $\mu$,
\[
\sum_{r \leq s} \tilde{W}_{rs} \sum_{\mu} A_{\chi p} \frac{\partial S_{\mu p}}{\partial C_{\mu p}} C_{\mu q} = \tilde{Q}_{pq} + 2 \sum_{i} \sum_{\mu} A_{\chi p} \frac{\partial F_{i \chi a}}{\partial C_{\mu p}} C_{\mu q} \\
+ \sum_{i} \sum_{\mu} \tilde{Z}_{ia} \sum_{\mu} A_{\chi p} \frac{\partial F_{i \chi a}}{\partial C_{\mu p}} C_{\mu q} \\
+ \sum_{a} \sum_{\mu} \tilde{Z}_{ia} \sum_{\mu} A_{\chi p} \frac{\partial F_{i \chi a}}{\partial C_{\mu p}} C_{\mu q}, \tag{A1}
\]
where
\[
\tilde{Q}_{pq} = \sum_{\mu} A_{\chi p} \frac{\partial G[X, \Omega]}{\partial C_{\mu p}} C_{\mu q}. \tag{A2}
\]
If $p = i \leq j = q$ both belong to DOC, Eq. (A1) transforms to
\[
\tilde{Q}_{ij} + \frac{1}{2}(H_{ij a}^{+}(Z) + H_{ij b}^{+}(Z)) = \tilde{W}_{ij}(1 + \delta_{ij}), \tag{A3}
\]
where
\[
\tilde{Q}_{ij} = \frac{1}{2}(H_{ij a}^{+}(T) + H_{ij b}^{+}(T)) \\
+ \sum_{q,s} (\Omega \delta_{qs} - F_{qst}) X_{ia qst} X_{ja st}, \tag{A4}
\]
Note that the argument of the second term in Eq. (A3) is $Z$, not $\tilde{Z}$ (see the relation defined in Eq. (17)). Similarly, other blocks are obtained as follows: the SOCC-SOCC block ($x \leq y$),
\[
\tilde{Q}_{xy} + \frac{1}{2} H_{xy a}^{+}(Z) = \tilde{W}_{xy}(1 + \delta_{xy}), \tag{A5}
\]
\[
\tilde{Q}_{xy} = \frac{1}{2} H_{xy a}^{+}(T) + \sum_{p,r} (\Omega \delta_{pr} + F_{pra}) X_{pa xrb} X_{ra yb} \\
+ \sum_{q,s} (\Omega \delta_{qs} - F_{qst}) X_{xa qst} X_{ya st}, \tag{A6}
\]
the VAL-VAL block ($a \leq b$),
\[
\tilde{Q}_{ab} = \tilde{W}_{ab}(1 + \delta_{ab}), \tag{A7}
\]
\[
\tilde{Q}_{ab} = \sum_{p,r} (\Omega \delta_{pr} + F_{pra}) X_{pa xrb} X_{ra yb}, \tag{A8}
\]
the DOC-SOCC block,
\[
\tilde{Q}_{ix} + \frac{1}{2}(H_{ix a}^{+}(Z) + H_{ix b}^{+}(Z)) + \frac{1}{2} \sum_{y} F_{xy b} \tilde{Z}_{iy} \\
+ \frac{1}{2} \sum_{a} F_{xab} \tilde{Z}_{ia} = \tilde{W}_{ix}, \tag{A9}
\]
\[
\tilde{Q}_{ix} = \frac{1}{2}(H_{ix a}^{+}(T) + H_{ix b}^{+}(T)) + \sum_{q} H_{ia q}^{0}(X) \cdot X_{ia qst} \\
- \sum_{q,s} X_{ia qst} F_{qst} X_{xa st}, \tag{A10}
\]
the SOCC-DOC block,
\[
\tilde{Q}_{ix} + \frac{1}{2} H_{ix a}^{+}(Z) + \frac{1}{2} \sum_{j} F_{ij b} \tilde{Z}_{ix} + \frac{1}{2} \sum_{a} F_{iab} \tilde{Z}_{ia} = \tilde{W}_{ix}, \tag{A11}
\]
\[
\tilde{Q}_{ix} = \frac{1}{2} H_{ix a}^{+}(T) + \sum_{p} H_{ipa}^{0}(X) \cdot X_{pa xst} \\
+ \sum_{q,s} H_{ia q}^{0}(X) \cdot X_{xa qst} - \sum_{q,s} X_{ia qst} F_{qst} X_{xa st}, \tag{A12}
\]
the DOC-VAL block,
\[
\tilde{Q}_{ia} + \epsilon_{i} \tilde{Z}_{ia} + \frac{1}{2} \sum_{x} F_{ixa} \tilde{Z}_{ia} = \tilde{W}_{ia}, \tag{A13}
\]
\[
\tilde{Q}_{ia} = \sum_{p} H_{iba}^{0}(X) \cdot X_{pa xst}, \tag{A14}
\]
the VAL-DOC block,
\[
\tilde{Q}_{ai} + \epsilon_{i} \tilde{Z}_{ia} + \frac{1}{2} \sum_{x} F_{ixa} \tilde{Z}_{ia} = \tilde{W}_{ia}, \tag{A15}
\]
\[
\tilde{Q}_{ai} = \sum_{p} H_{pa i}^{0}(X) \cdot X_{pa xst}, \tag{A16}
\]
the SOCC-VAL block,
\[
\tilde{Q}_{xa} + \frac{1}{2} H_{xa a}^{+}(Z) - \frac{1}{2} \sum_{i} F_{iab} \tilde{Z}_{ia} + \frac{1}{2} \sum_{b} F_{aba} \tilde{Z}_{ab} = \tilde{W}_{xa}, \tag{A17}
\]
\[
\tilde{Q}_{xa} = \frac{1}{2} H_{xa a}^{+}(T) + \sum_{p} H_{pa a}^{0}(X) \cdot X_{pa xst} \\
+ \sum_{q,s} H_{da q}^{0}(X) \cdot X_{xa qst} + \sum_{p,s} X_{pa xst} F_{pra} X_{ra a st}, \tag{A18}
\]
and the VAL-SOCC block,
\[
\tilde{Q}_{ax} + \frac{1}{2} \sum_{y} F_{xy a} \tilde{Z}_{ya} + \frac{1}{2} \sum_{i} F_{ixa} \tilde{Z}_{ia} = \tilde{W}_{xa}, \tag{A19}
\]
\[
\tilde{Q}_{ax} = \frac{1}{2} H_{xa a}^{+}(T) + \sum_{p} H_{pa a}^{0}(X) \cdot X_{pa a st} \\
+ \sum_{q,s} X_{pa xst} F_{pra} X_{ra a st}. \tag{A20}
\]
Subtracting Eq. (A11) from Eq. (A9), the Z-vector equation for the DOC-SOCC block is obtained as
\[
\frac{1}{2} H_{ijp}^+ [Z] - \frac{1}{2} \sum_j F_{ijb} \bar{Z}_{jx} + \frac{1}{2} \sum_y F_{xyb} \bar{Z}_{iy} + \frac{1}{2} \sum_a (F_{iaa} \bar{Z}_{ia} - F_{iaa} \bar{Z}_{xa}) = - (\bar{Q}_{ix} - \bar{Q}_{xi}) \quad (A21)
\]
Similarly, the Z-vector equation for the DOC-VAL block is
\[
(\epsilon_i - \epsilon_j) \bar{Z}_{ia} + \frac{1}{2} (H_{iaa}^+ [Z] + H_{iaa}^+ [Z]) + \frac{1}{2} \sum_b (F_{iaa} \bar{Z}_{ix} - F_{iaa} \bar{Z}_{xa}) = - (\bar{Q}_{ia} - \bar{Q}_{ai}) \quad (A22)
\]
and that for the SOCC-VAL block is
\[
\frac{1}{2} H_{xa}^+ [Z] - \frac{1}{2} \sum_i (F_{iia} \bar{Z}_{ix} + F_{iia} \bar{Z}_{ia}) - \frac{1}{2} \sum_y F_{xya} \bar{Z}_{ya} + \frac{1}{2} \sum_b F_{aba} \bar{Z}_{xb} = - (\bar{Q}_{ax} - \bar{Q}_{xa}) \quad (A23)
\]
The terms on the left-hand side of Eqs. (A21)–(A23) correspond to the orbital Hessian in Eq. (9), and those on the right-hand side correspond to the vector \( \bar{R} \) in Eq. (10). After solving the Z-vector equation, the energy-weighted density matrix \( \bar{W} \) is determined using Eqs. (A3), (A5), (A7), (A9), (A15) and (A19): the intra-block elements are
\[
\bar{W}_{ij}(1 + \delta_{ij}) = \bar{Q}_{ij} + \frac{1}{2} (H_{ijx}^+ [Z] + H_{ijy}^+ [Z])
\]
\[
\bar{W}_{xy}(1 + \delta_{xy}) = \bar{Q}_{xy} + \frac{1}{2} H_{xya}^+ [Z]
\]
\[
\bar{W}_{ab}(1 + \delta_{ab}) = \bar{Q}_{ab}
\]
and the inter-block elements are
\[
\bar{W}_{ix} = \bar{Q}_{ix} + \frac{1}{2} H_{ixa}^+ [Z] + \frac{1}{2} \sum_j F_{ijb} \bar{Z}_{jx} + \frac{1}{2} \sum_a F_{iaa} \bar{Z}_{xa}
\]
\[
\bar{W}_{ia} = \bar{Q}_{ia} + \epsilon_i \bar{Z}_{ia} + \frac{1}{2} \sum_x F_{ixa} \bar{Z}_{xa}
\]
\[
\bar{W}_{xa} = \bar{Q}_{ax} + \frac{1}{2} \sum_y F_{xya} \bar{Z}_{ya} + \frac{1}{2} \sum_i F_{ixa} \bar{Z}_{ia}.
\]
This is identical to the definition of \( \bar{W} \) as given in Eqs. (16) and (17).