Conical intersections in solution with polarizable embedding: Integral-exact direct reaction field

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Abstract

A common strategy to exploring the properties and reactivity of complex systems is to use quantum mechanics/molecular mechanics (QM/MM) embedding, wherein a QM region is defined and treated with electronic structure theory and the remainder of the system is treated with a force field. Important to the description of electronic excited states, especially those of charge-transfer character, is the treatment of the coupling between the QM and MM subsystems. The state-of-the-art is to use a polarizable force field for the MM region and mutually couple the QM wavefunction and MM induced dipoles, in addition to the usual electrostatic embedding, yielding a polarizable embedding (QM/MM-Pol) approach. However, we showed previously that current popular QM/MM-Pol approaches exhibit issues of root flipping and/or incorrect descriptions of electronic crossings in multistate calculations.[J. Chem. Theory Comput. 14, 2137 (2018)] Here we demonstrate a solution to these problems with an integralexact reformulation of the Direct Reaction Field approach of Thole and Van Duijnen (QM/MM-IEDRF). The resulting embedding potential includes one- and two-electron operators, and many-body dipole-induced dipole interactions, and thus includes a natural description of the screening of electron-electron interactions by the MM induced dipoles. Pauli repulsion from the environment is mimicked by effective core potentials on the MM atoms. Inherent to the DRF approach is the assumption that MM dipoles respond instantaneously to the positions of the QM electrons, therefore dispersion interactions are captured approximately. All electronic states are eigenfunctions of the same Hamiltonian while the polarization induced in the environment and the associated energetic stabilization are unique to each state. This allows for a consistent definition of transition properties and state crossings. We demonstrate QM/MM-IEDRF by exploring the influence of a (polarizable) inert xenon matrix environment on the conical intersection underlying the photoisomerization of ethylene.

1 Introduction

Electronic polarization¹ plays an important role in photo-induced charge-transfer (CT) reactions in the condensed phase. It is by no means a small effect and can influence CT-state energies by over one eV.² The efficiency of many photochemical processes such as charge separation in photosystem II³ and organic solar cells, or singlet fission⁴ depends crucially on the energetic position of CT states relative to the photoexcited valence states. Aside from long-range CT states between separated donors and acceptors, photochemical reactions often involve states of intramolecular CT character. For example, the prototypical cis-trans photoisomerization reaction of ethylene involves the crossing of a zwiterionic and valence state,⁵ giving rise to the phenomenon of *sudden polarization* in the first adiabatic excited state of ethylene at twisted geometries.^{6–8} In the condensed phase, polarization of the environment stabilizes states with CT character, thereby influencing their conical intersections that act as photochemical funnels. At the same time, charge-transfer states are difficult to measure and discern experimentally because of their low oscillator strength, so that theory can make important contributions in this regard.

Thanks to recent developments in local correlation methods,^{9–11} it is becoming possible to apply high-level electronic structure theory to compute vertical excitations of chromophores and a sufficiently large part of the surrounding environment. However, compared to energy calculations, analytical gradients of local correlation methods are much less developed. This hinders their application to geometry optimizations, conical intersection searches, and ab initio molecular dynamics simulations. Time-Dependent Density Functional Theory (TDDFT) is arguably the only ab initio excited-state method currently capable of performing critical point optimizations and dynamics simulations with large system sizes, but an accurate description of CT and valence states simultaneously is still a challenge for the method. Furthermore, the need for a full-system quantum mechanical description is questionable for many photochemical processes of interest, which involve excitations that are localized to one or more small chromophores, such as in photosynthetic reaction centers^{12,13} or the green fluorescent protein.^{14,15} Then, a high-level quantum-mechanical (QM) description of the chromophore(s) may be combined with a force field (or molecular mechanics - MM) description of the environment, as long as the coupling between the two regions accounts properly for steric, electrostatic, dispersion and polarization interactions. The earliest applications of multi-scale modeling by Warshel and Levitt already found that a microscopic model of the dielectric medium is very important for describing the stabilization of ionic groups.¹⁶

Nowadays, QM/MM simulations with electrostatic and polarizable embedding¹⁷ have become more or less routine for enzymatic reactions, but it is much more challenging to incorporate dielectric effects in photochemical reactions, since the induced polarization in the environment needs to be different for each electronic state. Much of the development of MM polarizable embedding methods has paralleled work in polarizable continuum models (PCM). In both PCM and polarizable QM/MM, the most common route to electronic excitation energies and properties follows a linear-response (LR) formalism,^{18–20} which is the natural choice for excited-state electronic structure theories that also invoke LR, such as TDDFT.²¹ In the standard formulation of LR polarization, the dynamic response of the environment arises from the QM region's oscillating electronic transition density, and therefore displays a different response for each excited state. However, within this formulation, the environment does not respond to changes in the QM region's charge distribution upon excitation, and therefore LR is not suitable to describe excitations involving significant electron redistribution, such as found in CT states.²² Furthermore, the use of LR electronic structure would lead to an incorrect description of the topology of electronic intersections with the reference state,²³ which is problematic for photochemical applications.

As an alternative to LR, in State-Specific Polarization (SS-Pol) models,²⁴ the reaction field of the solvent is optimized self-consistently together with the density of one specific electronic state. While solvatochromic shifts of vertical excitations and excited-state minima can be predicted accurately in this manner, problems are encountered close to state crossings.²⁵ As the reaction field is determined separately for each state, Born-Oppenheimer states for the same nuclear configuration belong to different Hamiltonians. Therefore electronic states are not orthogonal and transition properties are ill-defined. This, combined with root-flipping issues,²⁵ renders it impossible to optimize conical intersections in solution with SS-Pol, although the solvatochromic shifts of those photochemical funnels are of great interest when analyzing ultrafast pump-probe experiments in liquid microjets.^{26,27} Deriving the polarization from a state average (with fixed or dynamic weights) of the fields from multiple excited states^{25,28} ameliorates some of the problems of SS-Pol, at the cost of losing the ability to fully describe a different environment polarization for each electronic state.

The issues with LR and SS-Pol formulations discussed above have motivated a third way, which includes the environment's polarization to electronic excitations in a perturbative fashion,^{29–31} sometimes called corrected linear response.^{32,33} The idea, which appears to originate with Thompson and Schenter's seminal work,²⁹ starts with a fully self-consistent SS-Pol calculation for the ground state, followed by a first-order polarization energy correction for each excited state due to the difference in the QM region's field from the ground and excited states. As a result, the QM region's excited-state wavefunctions are polarized by the induced MM dipoles from the ground state, and all electronic states then arise from a single Hamiltonian. Similar ideas have been extended to PCM approaches.^{31,32} This scheme has been shown to describe vertical excitations in quantitative agreement with a fully state-specific approach, while avoiding root flipping issues;³⁰ however, to our knowledge, the description of state crossings has not been previously explored. Given that SS-Pol exhibits discontinuities even in the electronic ground state,²⁵ which is the starting point of the perturbative approach, we anticipate problems near electronic crossings. Beyond incorporating QM-MM polarization, recently, several approaches have emerged to also include Pauli repulsion and dispersion interactions at the Hamiltonian level.³⁴⁻³⁷

In this work, we reformulate the Direct Reaction Field (DRF) method, an early QM/MM polarizable embedding scheme that includes a polarization operator which captures manybody polarization and dispersion interactions.^{38–40} The polarization operator models the fast electronic response of the solvent to the solute charges, while the slow response comes from the (nuclear) reorganization of the MM region. In contrast to self-consistent reaction field models for non-equilibrium solvation,^{18,41} the polarization operator of DRF is not a functional of the solute wavefunction and therefore independent of any reference state, suggesting that DRF will correctly describe electronic state crossings, which we show explicitly for the first time in this work for the conical intersection of ethylene underlying its cis-trans photoisomerization reaction.

In addition to demonstrating DRF's utility for photochemical state crossing problems, we also solve three outstanding issues in the original method: (1) symmetry breaking due to the use of multipole approximations to integrals of the polarization operator. (2) Neglect of quantum mechanical Pauli repulsion in the QM/MM Hamiltonian that leads to severe electron spill-out problems when QM atoms approach polarizable centers. (3) Previous DRF implementations included the polarization operator only as a perturbative correction, which introduces artefacts at state crossings. These issues are solved by (1) an integral-exact reformulation (IEDRF). (2) Including effective core potentials (ECPs) on the MM atoms, to mimic Pauli repulsion. (3) Incorporating the polarization operator directly in the QM Hamiltonian. The resulting QM/MM-IEDRF method is in principle compatible with any electronic structure theory, and here we demonstrate its application to Hartree-Fock theory and multiconfigurational self-consistent field.

The remainder of the paper is as follows. As background, in sections 2.1 and 2.2, we provide a summary of the state-specific polarizable embedding QM/MM method and a perturbative version that is free of root-flipping issues. In section 2.3, we review the original DRF method before introducing our QM/MM-IEDRF version in section 2.4. Implementation details are presented in section 2.5. We verify our implementation for a simple diatomic system in section 3.1 and then in section 3.2 we test the performance of three different polarizable embedding schemes in describing potential energy surfaces near the electronic crossings of ethylene in an inert Xe matrix. Finally conclusions are drawn in section 4.

2 Theory

2.1 State-specific polarizable QM/MM

To provide the context for revisiting the DRF method, we first briefly describe state-specific polarizable embedding (QM/MM-SS-Pol), which is a popular approach to including the influence of a (polarizable) environment on a chromophore's electronic excitations.^{42,43}

Following standard QM/MM partitioning, the system is divided into an "active" region, where electrons are treated explicitly using quantum mechanics (QM), and the remainder of the system, which is treated with molecular mechanics (MM) force fields in which atoms are modeled by classical static charge distributions and induced dipoles.

The QM and MM regions are mutually coupled by the Coulomb interactions arising from the MM region's induced charge distributions. The molecular electronic Hamiltonian (following an additive scheme) is thus:

$$\hat{H}_{\text{SS-Pol}} = \hat{H}_0 + \hat{V}_{\text{SS-Pol}} + \hat{V}_{\text{Pauli}} + U_{\text{self}},\tag{1}$$

where \hat{H}_0 is the Hamiltonian of the QM region in isolation and $\hat{V}_{\text{SS-Pol}}$ is the Coulomb interaction between the QM system and the MM induced dipoles. \hat{V}_{Pauli} is a Pauli-repulsion operator that models the repulsion of QM electrons from the MM atoms, described below in more detail. This term is not always included in polarizable embedding, but has been shown to solve the electron spill-out problem.⁴⁴ The last term is the self-energy of the MM-Pol subsystem (the work needed to create the induced dipoles), $U_{\text{self}} = \frac{1}{2} \sum_{m}^{N} \boldsymbol{\mu}_{m}^{T} \boldsymbol{\alpha}_{m}^{-1} \boldsymbol{\mu}_{m}$, where $\boldsymbol{\mu}_{m} \in \mathbb{R}^{3}$ and $\boldsymbol{\alpha}_{m} \in \mathbb{R}^{3\times3}$ are respectively the induced dipole and polarizability of site m, of which there are N. Electrostatic and mechanical embedding terms, *i.e.* QM-MM Coulomb and Lennard-Jones interactions, are also typically added to Eq. 1, and their inclusion is straightforward. However, since our interest is in the differential solvation of electronic states of a solute by a frozen polarizable atomic environment, we do not consider additional embedding terms in this work.

 $\hat{V}_{\text{SS-Pol}}$ is the key addition to QM/MM-SS-Pol and arises from the interaction between the induced dipoles and the electrostatic field from the QM particles:

$$\hat{V}_{\text{SS-Pol}} = \sum_{i}^{N_{\text{elec}}} \sum_{m}^{N} \frac{\hat{\boldsymbol{r}}_{i} - \boldsymbol{R}_{m}}{|\hat{\boldsymbol{r}}_{i} - \boldsymbol{R}_{m}|^{3}} \cdot \boldsymbol{\mu}_{m} - \sum_{a}^{N_{\text{QM}}} \sum_{m}^{N} \frac{Z_{a}(\boldsymbol{R}_{a} - \boldsymbol{R}_{m})}{|\boldsymbol{R}_{a} - \boldsymbol{R}_{m}|^{3}} \cdot \boldsymbol{\mu}_{m}.$$
(2)

Eq. 2 thus modifies the one-electron Hamiltonian and couples the QM region to the induced dipoles: the dipoles respond to the wavefunction, and the wavefunction responds to the dipoles.

The induced dipoles are proportional to the total electric field at the MM site, which arises from the QM region, the MM point charges (not present in this work), and the other MM induced dipoles:

$$\boldsymbol{\mu}_{m} = \alpha_{m} \left[\boldsymbol{\mathcal{E}}_{m}^{0,\text{QM}} - \sum_{n \neq m}^{N} \boldsymbol{T}^{(mn)} \cdot \boldsymbol{\mu}_{n} \right].$$
(3)

Here $\mathbf{T}^{(mn)}$ is the dipole-dipole interaction tensor which, within the Thole damping scheme, has matrix elements of the form $T_{\alpha\beta}^{(mn)} = \lambda_3(r)\delta_{\alpha\beta}r^{-3} - \lambda_5(r)3r_{\alpha}r_{\beta}r^{-5}$ (α, β enumerate the Cartesian coordinates x, y and z) for the pairwise interaction of dipoles separated by $\mathbf{r} = \mathbf{R}_m - \mathbf{R}_n$.⁴⁵ To avoid the polarization catastrophe, the point dipoles are replaced by smearedout charge distributions giving rise to the damping functions $\lambda_3(r)$ and $\lambda_5(r)$.⁴⁵ The coupled nature of the induced dipoles means they must be solved self-consistently, either by iterating Eq. 3, or expressing it as a matrix equation and solving the linear equation directly by factorizing the matrix or iteratively e.g. with the conjugate gradient method.

 $\boldsymbol{\mathcal{E}}_{m}^{0,\mathrm{QM}}$ is the electric field from the QM region, which for a wavefunction variational in all parameters is:⁴⁶

$$\boldsymbol{\mathcal{E}}_{m}^{0,\text{QM}} = -\left\langle \Psi \left| \sum_{i}^{N_{\text{elec}}} \frac{\hat{\boldsymbol{r}}_{i} - \boldsymbol{R}_{m}}{|\hat{\boldsymbol{r}}_{i} - \boldsymbol{R}_{m}|^{3}} \right| \Psi \right\rangle + \sum_{a}^{N_{\text{QM}}} \frac{Z_{a}(\boldsymbol{R}_{a} - \boldsymbol{R}_{m})}{|\boldsymbol{R}_{a} - \boldsymbol{R}_{m}|^{3}}.$$
(4)

With a self-consistent solution to the induced dipoles (Eq. 3), the total polarization energy including QM/MM-Pol, $U_{\rm MMPol}$, and $U_{\rm self}$ contributions is shown to be:⁴²

$$E_{\rm pol} = \left\langle \Psi \left| \frac{1}{2} \hat{V}_{\rm SS-Pol} \right| \Psi \right\rangle, \tag{5}$$

where the factor of 1/2 arises from the dipoles being induced rather than permanent.

Eq. 4 makes clear where the "state-specific" nature of the polarization comes from: the MM dipoles are induced by the electric field from a particular QM state, and the induced dipoles should be found independently for each electronic state, one at a time. Furthermore, since the induced dipoles alter the one-electron Hamiltonian matrix elements via Eq. 2, the wavefunction and induced dipoles are coupled in a non-linear fashion, meaning they should be solved self-consistently. This can be achieved with dual-SCF cycles, which add

computational expense. Alternatively, the induced dipoles can be optimized simultaneously with the wavefunction, which to our knowledge has so far been implemented only for ground-state SCF.⁴⁷

QM/MM-SS-Pol has the advantage that the polarization response of the environment to each electronic state of the system is fully captured.²² Its variational nature also simplifies analytical gradients.⁴² The main limitation of QM/MM-SS-Pol is that the electronic Hamiltonian itself becomes state specific through Eqs. 2-4. As a result, transition properties between electronic states are ill defined. Root flipping issues are also common for close-lying electronic states.²⁵ And even if root-flipping can be avoided, the potential energy surface (PES), and other properties, exhibit discontinuities at electronic crossings.²⁵ These issues with QM/MM-SS-Pol are discussed in more detail below for the conical intersection of a prototypical cis-trans photoisomerization of ethylene in a polarizable inert xenon matrix.

2.2 State-specific perturbative polarizable QM/MM

Given the issues of ill-defined transition properties and root flipping in QM/MM-SS-Pol, as mentioned in the introduction, some excited-state polarizable embedding schemes instead treat the polarization response to an electronic excitation in a perturbative fashion. The usual approach starts with a fully self-consistent QM/MM-SS-Pol calculation for the ground state, followed by a 1st-order polarization energy correction for each excited state due to the difference in the QM region's fields from the ground and excited states. Since this treats the ground state and excited states differently, and is expected then to not describe their conical intersections correctly, an alternative perturbative approach (PTPol) we test here treats all states on equal footing. First, the ground- and excited-state QM wavefunctions are found from a non-polarizable QM/MM calculation with point-charge electrostatic embedding, defining the zeroth-order states, $|\Psi_I^{(0)}\rangle = |\Psi_I^{QM/MM}\rangle$, where I is the electronic state of interest. Then, for each state, the polarization energy is found from Eqs. 2-5, using the zeroth-order wavefunctions to find the QM electric fields (Eq. 4) and expectation energy (Eq. 5).

We show below that the PTPol approach avoids root flipping and PES discontinuities; however, it introduces a new issue of an incorrect description of the topology of a conical intersection: near the crossing, the lower and upper cones intersect each other. This problem could be anticipated from similar issues that arise in state-specific perturbation theory treatments of multireference electronic structure,⁴⁸ and is expected to afflict other previous perturbative approaches to excited-state polarizable embedding.

2.3 Direct Reaction Field

Given the issues with state-specific and perturbative treatments of polarizable embedding for electronic excited states, we now turn our attention to the DRF method of Thole and Van Duijnen.³⁸ The DRF polarization operator can be derived starting from the classical polarization energy for a set of polarizable sites according to Applequist's dipole interaction model⁴⁹ and replacing the electronic fields by their corresponding quantum mechanical operators. We briefly review the original formulation of DRF, before introducing our modifications as integral-exact DRF.

2.3.1 Dipole Interaction Model.

The distribution of free charges of the whole system consists of electrons and classical point charges, Q_c which comprise both the nuclei in the QM region and the partial charges of the MM atoms (zero in this work), of which there are $N_{\text{charge}} = N_{\text{QM}} + N_{\text{MM}}$:

$$\rho(\boldsymbol{r}) = -\sum_{i}^{N_{\text{elec}}} \delta(\boldsymbol{r} - \hat{\boldsymbol{r}}_{i}) + \sum_{c}^{N_{\text{charge}}} Q_{c} \delta(\boldsymbol{r} - \boldsymbol{R}_{c}).$$
(6)

As in the QM/MM-SS-Pol model, MM dipoles are induced by the electric fields due to the free charges (now indicated by the symbol f_m , to avoid confusion with Eq. 4, which have a slightly different form):

$$\boldsymbol{f}_{m}[\rho] = \int d^{3}r \ \rho(\boldsymbol{r}) \frac{\boldsymbol{R}_{m} - \boldsymbol{r}}{|\boldsymbol{R}_{m} - \boldsymbol{r}|^{3}} C(|\boldsymbol{R}_{m} - \boldsymbol{r}|), \tag{7}$$

as well as the field generated by the other induced dipoles. C(r) is a cutoff function that removes the singularity of the fields at $\mathbf{r} = \mathbf{R}_m$, which we will define below for IEDRF. In the original DRF model, C(r) = 1.

According to the dipole interaction model,^{45,49} the total polarization energy is given by

$$U_{\rm pol} = -\frac{1}{2} \boldsymbol{f}^T[\rho] \boldsymbol{A} \boldsymbol{f}[\rho], \qquad (8)$$

where the electric fields at the polarizable sites from Eq. 7 are stacked in the \mathbb{R}^{3n} supervector f, and

$$\boldsymbol{A} = \begin{pmatrix} \boldsymbol{\alpha}_{1}^{-1} & \boldsymbol{T}^{(12)} & \dots & \boldsymbol{T}^{(1N)} \\ \boldsymbol{T}^{(12)} & \boldsymbol{\alpha}_{2}^{-1} & \dots & \boldsymbol{T}^{(2N)} \\ \vdots & \vdots & \ddots & \vdots \\ \boldsymbol{T}^{(1N)} & \dots & \dots & \boldsymbol{\alpha}_{N}^{-1} \end{pmatrix}^{-1}$$
(9)

is the effective dipole polarizability supertensor of the MM region. A^{-1} consists of 3×3 blocks for each pair of polarizable sites (m, n). The diagonal contains the inverse of the isotropic atomic dipole polarizabilities $\alpha_m = \alpha_m \mathbb{1}_{3\times 3}$ and the off-diagonal blocks $T^{(mn)}$ are the dipole field tensors as defined above.⁴⁹ The inclusion of dipole-dipole interactions in Acaptures the many-body nature of polarization, while being defined purely in terms of the atomic polarizabilities and the geometry of the MM region. Eq. 9 is solved by brute-force inversion. Future work will explore iterative approaches.

2.3.2 DRF polarization operator

The charge density of Eq. 6 is inserted into the expression for the electric fields acting on the polarizable sites, Eq. 7, and the resulting fields are grouped into electronic (e) and nuclear

(or point charge, q) contributions:

$$\boldsymbol{f}_{m}[\rho] = \sum_{i}^{N_{\text{elec}}} \hat{\boldsymbol{f}}_{i,m}^{(e)} + \boldsymbol{f}_{m}^{(q)}, \tag{10}$$

where a little hat has been placed on the electronic fields to emphasize that these are oneelectron operators. The fields from all point charges and nuclei are combined into a single vector $\mathbf{f}_m^{(q)}$. Substituting this quantum-mechanical expression for the fields into Eq. 8 gives the additional polarization operator. Furthermore, since DRF assumes the MM dipoles respond instantaneously to the location of the QM electrons (indicated by the delta functions in Eq. 6), the method accounts for both polarization and dispersion interactions between the QM and MM regions. Since $U_{\rm pol}$ depends quadratically on the fields, the polarization operator contains both one- and two-electron contributions.

The DRF polarization operator thus has the general form:

$$\hat{V}_{\text{DRF}} = \frac{1}{2} \sum_{i,j \neq i} \hat{h}^{(2)}(i,j) + \sum_{i} \hat{h}^{(1)}(i) + h^{(0)}.$$
(11)

These terms account for the indirect electrostatic interactions between charged species, mediated by the polarizable sites. The two-electron operator contains the effective interaction between different electrons i and j, via their induced polarization of the MM system:

$$\hat{h}^{(2)}(i,j) = -\sum_{m,n}^{N} \hat{f}_{mi}^{(e)T} \boldsymbol{A}_{mn} \hat{f}_{nj}^{(e)} \quad \text{with } i \neq j,$$
(12)

while the one-electron operator accounts for the effective interaction of an electron i with the nuclei or point charges, as well as its self-interaction:

$$\hat{h}^{(1)}(i) = -\sum_{m,n}^{N} \boldsymbol{f}_{m}^{(q)T} \boldsymbol{A}_{mn} \hat{\boldsymbol{f}}_{ni}^{(e)} - \frac{1}{2} \sum_{m,n}^{N} \hat{\boldsymbol{f}}_{mi}^{(e)T} \boldsymbol{A}_{mn} \hat{\boldsymbol{f}}_{ni}^{(e)}.$$
(13)

Due to their opposite signs, the fields from the electrons screen the fields from the nuclei. The

polarization energy due to the classical point charges is a (geometry-dependent) constant,

$$h^{(0)} = -\frac{1}{2} \sum_{i,j}^{n} \boldsymbol{f}_{i}^{(n)T} \boldsymbol{A}_{ij} \boldsymbol{f}_{j}^{(n)}.$$
 (14)

This term therefore includes the classical polarization energy from the MMPol force field, as well as the polarization energy from the QM nuclei.

The polarization operator (Eq. 11) is added to the electronic Hamiltonian containing the kinetic energy, electron-nuclear attraction, electron repulsion, nuclear-nuclear repulsion and any Coulomb potential from MM point charges. Effectively this corresponds to a modification of the one- and two-electron integrals. Because of the polarizable environment, the Coulomb interaction in vacuum, $|\boldsymbol{r} - \boldsymbol{r}'|^{-1}$, has been replaced by a screened interaction,

$$\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} - \frac{1}{2} \sum_{m,n}^{N} \frac{\boldsymbol{r}_m}{r_m^3} C(r_m) \cdot \boldsymbol{A}_{mn} \cdot \frac{\boldsymbol{r}'_n}{r_n^{'3}} C(r'_n),$$
(15)

where $\mathbf{r}_m = \mathbf{R}_m - \mathbf{r}$ and $\mathbf{r}'_n = \mathbf{R}_n - \mathbf{r}'$ are the distance vectors from the electrons to the polarizable sites m and n. Since \mathbf{A} is positive-definite, the screened Coulomb interaction in the polarizable environment is weaker than in vacuum. This modifies the whole electronic structure inside the QM region and particularly stabilizes charge-transfer states.

The polarization operator is seen to factorize into products of one-electron terms. As a result, one-electron field integrals of the form $(\mu | \mathbf{f}_m | \nu)$ are needed. In the original DRF implementation, these integrals were approximated by a Taylor expansion of the polarization operator up to first order about arbitrary expansion points.⁴⁰ The advantage of such an approach is that the resulting field integrals are recast in terms of overlap and dipole matrix elements, which can be pre-calculated for a given nuclear configuration. Typically, the expansion points were chosen to be the QM atoms, but issues of symmetry breaking were noted.⁴⁰ Because of these issues, in addition to anticipated complications in a formulation of analytical gradients, we instead present an exact implementation of the integrals below.

A second issue, noted in the original DRF method,³⁸ is that the polarization operator

diverges to negative infinity at the location of each polarizable site. This divergence can lead to severe overpolarization as a QM atom approaches a polarizable site. The origin of the problem is both a break-down of the inherent dipole approximation at short distance (the MM atoms could more accurately be described by finite charge distributions) and the neglect of explicit Pauli repulsion between the MM atoms and QM electrons. The original DRF approach of approximating the field integrals by a local Taylor expansion avoids the divergence issue.³⁸ Since we will evaluate the field integrals exactly, we must address the overpolarization issue in another way, which we discuss below.

Finally, more recent implementations of DRF included the polarization operator in a perturbative fashion,⁴⁰ similar to the PTPol approach we described above. Furthermore, apart from the very first application,³⁸ the DRF operator was combined with the SS-Pol operator in a weighted fashion, in order to recover the QM/MM dispersion energy expected from a generalization of Alexander's upper bound to non-spherical systems.^{40,50} Since our interest is in a description of polarizable embedding for electronic state crossings, for which we show both SS-Pol and perturbative approaches exhibit artefacts, we will instead retain the original form of the DRF operator, and include it directly in the solution of the electronic structure problem. These developments are described below, which we name the integral-exact direct reaction field (IEDRF).

2.4 Integral-exact direct reaction field

2.4.1 Polarization Integrals.

Many of the integrals needed to express the polarization operator exactly in a basis of Cartesian Gaussian functions have appeared in the literature in the context of core-polarization potentials.⁵¹ For a single polarizable site, these are of the three-center type and have been solved by Schwerdtfeger and Silberbach.⁵²

The integrals of the field operators occurring in Eqs. 12 and 13 between basis functions

 $\mu(\mathbf{r})$ and $\nu(\mathbf{r})$, of which there are $N_{\rm AO}$, have the form:

$$F^{\alpha}_{\mu\nu}(\boldsymbol{R}) = (\mu | \frac{R_{\alpha} - r_{\alpha}}{|\boldsymbol{R} - \boldsymbol{r}|^3} C(|\boldsymbol{R} - \boldsymbol{r}|)|\nu), \qquad (16)$$

where the Cartesian component $\alpha = x, y, z$ of the field from an electron at position r is evaluated at a polarizable site at position \mathbf{R} . Here, r_{α} means the α Cartesian component of the electron' position. The cutoff function $C(r) = (1 - e^{-ar^2})^q$, with a cutoff exponent a > 0and an integer cutoff power q > 0, removes the divergence of the polarization operator and ensures the existence of the otherwise divergent integrals of the form $(\mu |r_{\alpha}r_{\beta}r^{-6}C(r)^2|\nu)$,⁵² that arise from same-site terms in Eq. 13. In this work, we use a = 0.0625 Bohr⁻² and q = 2to match the electron-xenon potential of Jonin (see below for more details);⁵³ however, excitation energies are insensitive to these parameters as long as a is large enough. The second term in Eq. 13 contains four-center integrals. We use the resolution of identity trick⁵⁴ to turn them into products of three-center integrals:

$$(\mu|\frac{r_{m\alpha}r_{n\beta}}{r_m^3r_n^3}C_mC_n|\nu) \approx \sum_{\rho,\sigma} (\mu|\frac{r_{m\alpha}}{r_m^3}C_m|\rho) \left(S^{-1}\right)_{\rho\sigma} (\sigma|\frac{r_{n\beta}}{r_n^3}C_n|\nu), \tag{17}$$

where $C_m = C(r_m)$, and $S_{\rho\sigma} = (\rho|\sigma)$ is the overlap matrix. In principle, the four-center integrals could be evaluated in a density-fitting-like approach using an auxiliary basis, but we found that the primary basis gave satisfactory accuracy. The same-site integrals (m = n)in the one-electron Hamiltonian, on the other hand, have the form:

$$I^{\alpha\beta}_{\mu\nu}(\boldsymbol{R}) = (\mu | \frac{(\boldsymbol{R} - \boldsymbol{r})_{\alpha} (\boldsymbol{R} - \boldsymbol{r})_{\beta}}{|\boldsymbol{R} - \boldsymbol{r}|^{6}} C(|\boldsymbol{R} - \boldsymbol{r}|)^{2} |\nu), \qquad (18)$$

and can be evaluated analytically.⁵² Complete details of our integral evaluation algorithm and its efficient implementation on CPUs and GPUs are provided elsewhere,⁵⁵ with opensource code available.⁵⁶

For notational convenience, we collect the field integrals of Eq. 16 into a supervector of

length 3N:

$$\boldsymbol{F}_{\mu\nu}^{(e)} = (\boldsymbol{F}_{\mu\nu}(\boldsymbol{R}_1), \dots, \boldsymbol{F}_{\mu\nu}(\boldsymbol{R}_m), \dots, \boldsymbol{F}_{\mu\nu}(\boldsymbol{R}_N))^T,$$
(19)

for each atomic orbital pair, $\mu\nu$. Similarly, the integrals of Eq. 18 are combined into a supertensor of length 9N:

$$\boldsymbol{I}_{\mu\nu} = (\boldsymbol{I}_{\mu\nu}(\boldsymbol{R}_1), \dots, \boldsymbol{I}_{\mu\nu}(\boldsymbol{R}_m), \dots, \boldsymbol{I}_{\mu\nu}(\boldsymbol{R}_N))^T.$$
(20)

The electric fields from the nuclei and point charges (if present),

$$\boldsymbol{F}(\boldsymbol{R}) = \sum_{c} Q_{c} \frac{\boldsymbol{R}_{c} - \boldsymbol{R}}{|\boldsymbol{R}_{c} - \boldsymbol{R}|^{3}} C(|\boldsymbol{R}_{c} - \boldsymbol{R}|)$$
(21)

are likewise collected into a supervector:

$$\boldsymbol{F}^{(n)} = (\boldsymbol{F}(\boldsymbol{R}_1), \dots, \boldsymbol{F}(\boldsymbol{R}_m), \dots, \boldsymbol{F}(\boldsymbol{R}_{N_{\text{pol}}}))^T.$$
(22)

Note: we use the same damping function, C(r) (defined above) for the electronic and nuclear fields, so that for a neutral molecule, the fields cancel appropriately at short and intermediate range.

For a given geometry, the vectors $\boldsymbol{F}_{\mu\nu}^{(e)}$, $\boldsymbol{F}^{(n)}$, and \boldsymbol{I} are calculated once and stored in memory. The memory requirements for this are $N_{AO}^2 \times 12 \times N + 3 \times N$. All matrix elements of the IEDRF polarization operator can be assembled from this information.

2.4.2 Pauli Repulsion

Since the magnitude of the polarization operator, $-\frac{1}{2}\alpha r^{-4}$, is larger than even the Coulomb potential near atomic centers, over-polarization and electron-spill-out problems, which can also afflict electrostatically embedded QM/MM calculations, become even more severe (see below). These issues can be traced to a neglect of explicit Pauli repulsion between the MM atoms and QM electrons and become most apparent when diffuse basis functions are used. To mimic the missing Pauli repulsion, repulsive one-electron pseudopotentials are placed on the MM atoms as described in Ref. 44. These prevent the leakage of electron density into the MM region and provide short-range repulsion between QM and MM atoms.

The total Pauli repulsion potential is taken to be a sum of effective core potentials (ECPs) on each MM atom, $\hat{V}_{\text{Pauli}} = \sum_{m}^{N_{\text{MM}}} \hat{V}_{m}^{\text{ECP}}$. To achieve this, we extended the efficient GPU implementation of ECPs in TeraChem⁵⁷ to allow ECP centers on MM atoms. ECP parameters for Xe were taken from the model of Jonin et al. which, when combined with a one-electron polarization potential of the form of Eq. 13, were fit to reproduce differential phase shifts from ab initio relativistic elastic electron scattering calculations.⁵³

2.4.3 Total Hamiltonian

We are now in a position to define the total QM Hamiltonian for the QM/MM-IEDRF method used in this work:

$$\hat{H}_{\rm IEDRF} = \hat{H}_0 + \hat{V}_{\rm DRF} + \hat{V}_{\rm Pauli},\tag{23}$$

where the individual terms have the same meaning as previously defined. In addition to the modified polarization operator, we note that compared to the SS-Pol Hamiltonian given in Eq. 1, the polarization self-energy, U_{self} , is absent, since it is included implicitly in the polarization energy expression of Eq. 8.

2.5 Implementation of IEDRF

We implemented QM/MM-IEDRF, as defined in Eq. 23, in a development version of TeraChem.⁵⁸ We take advantage of TeraChem's clever formulation of many electronic structure methods in terms of effective Coulomb and Exchange matrices, allowing IEDRF to be implemented by modifications to these matrices.

2.5.1 Core Hamiltonian

We start by considering the modifications to the core Hamiltonian. These arise from the one-electron terms of IEDRF (Eq. 13), which in the AO basis have the following matrix elements:

$$(\mu | \hat{h}^{(1)} | \nu) = -\mathbf{F}^{(n)} \mathbf{A} \mathbf{F}^{(e)}_{\mu\nu} - \frac{1}{2} \sum_{\rho,\sigma} (S^{-1})_{\rho,\sigma} \mathbf{F}^{(e)}_{\mu\rho} \mathbf{A} \mathbf{F}^{(e)}_{\sigma\nu} + \left(\frac{1}{2} \sum_{\rho,\sigma} (S^{-1})_{\rho\sigma} \mathbf{F}^{(e)}_{\mu\rho} \operatorname{diag}(\mathbf{A})_{3\times 3} \mathbf{F}^{(e)}_{\sigma\nu} - \frac{1}{2} \sum_{m=1}^{N} \sum_{\alpha,\beta=1}^{3} A^{\alpha\beta}_{mm} I^{\alpha\beta}_{\mu\nu} (\mathbf{R}_{m}) \right),$$
(24)

where we are using the supervector notation defined above. Subscripts μ, ν, ρ, σ represent AO indices, m and n index polarizable sites, and α, β run over Cartesian components x, y, z. In the second term of Eq. 24, the same-site contributions (m = n) are treated with the resolution-of-identity trick discussed above.⁵⁴ The last term in brackets removes these and replaces them by the exact integrals for m = n. diag(A)_{3×3} contains only the diagonal 3×3 blocks of A.

Thus, IEDRF's contributions to the core Hamiltonian are constructed entirely from the precalculated $\mathbf{F}^{(n)}$, $\mathbf{F}^{(e)}$, and \mathbf{I} vectors defined above. In addition, the Pauli repulsion potential, \hat{V}_{Pauli} , adds to the core Hamiltonian. To include Pauli contributions, we extended TeraChem's existing algorithm⁵⁹ to allow ECP centers on MM atoms.

2.5.2 Two-electron contributions

In addition to the one-electron contributions to the molecular electronic Hamiltonian described above, IEDRF has two-electron contributions, $(\mu\nu|\hat{h}^{(2)}|\gamma\delta)$, from the operator defined in Eq. 12. These can be evaluated efficiently by noting the operator factorizes as a tensor product of the same one-electron field operators that arise in Eq. 13. As a result, the full two-electron matrix does not need to be stored (which would introduce a storage cost that scales as $N_{\rm AO}^4$), but rather, the matrix elements of $\hat{h}^{(2)}$ can be formed on-the-fly from $\boldsymbol{F}^{(e)}$ in an integral-direct fashion. In particular, we take advantage of TeraChem's formulation of many electronic structure methods, including HF⁶⁰ and CASSCF,⁶¹ in terms of contractions of effective Coulomb- and exchange-like matrices with generalized density matrices.⁵⁸ Then, the two-electron contributions of IEDRF can be implemented as corrections to the effective Coulomb and exchange matrices:

$$\Delta J_{\mu\nu}(\boldsymbol{P}) = \sum_{\gamma\delta} (\mu\nu |\hat{h}^{(2)}|\gamma\delta) P_{\gamma\delta}$$

= $-\sum_{mn} \sum_{\gamma\delta} F_{m,\mu\nu} A_{mn} F_{n,\gamma\delta} P_{\gamma\delta}$ (25)

and

$$\Delta K_{\mu\nu}(\boldsymbol{P}) = \sum_{\gamma\delta} (\mu\gamma |\hat{h}^{(2)}|\nu\delta) P_{\gamma\delta}$$

= $-\sum_{mn} \sum_{\gamma\delta} F_{m,\mu\gamma} A_{mn} F_{n,\nu\delta} P_{\gamma\delta},$ (26)

where $P_{\gamma\delta}$ is an element of a generalized density matrix. The contractions in Eqs. 25 and 26 are evaluated as efficient matrix-matrix multiplications using GPU kernels.

3 Results

3.1 Sodium-xenon dimers

To verify our implementation of the IEDRF polarizable embedding schemes, we consider a simple dimer of a sodium atom (cation or neutral) interacting with a xenon atom, with the former treated at a QM level and the latter treated as a polarizable MM atom. This system was chosen for two reasons: (i) the Na⁺ - Xe potential at large internuclear separation should be dominated by charge-induced dipole interactions, which have a particularly simple $-0.5\alpha/r^4$ form. This molecule then serves as a test that the 0e, 1e, and 2e contributions in IEDRF sum correctly in Eq. 11. (ii) Na⁰ - Xe is a Van der Waals complex, so its potential should be dominated by $-C_6/r^6$ dispersion interactions at large internuclear separation. Furthermore, the equilibrium distance results from a balance of repulsion at short range and attraction at long range, and is therefore a sensitive test of IEDRF's description of Pauli repulsion, polarization damping, and dispersion interactions.

We computed ground-state potential energy curves of Na⁺ - Xe and Na⁰ - Xe at the restricted Hartree-Fock QM/MM-IEDRF level. We used the aug-cc-pV5Z basis⁶² with f, gand h functions removed since TeraChem does not yet support them and because we expect them to have a negligible contribution to the RHF wavefunction of this high-symmetry system. Given the very diffuse nature of the Na⁰ valence orbital, as we demonstrate in the supporting information we found it necessary to include basis functions on the Xe atom, even when it was treated at the MM level (*i.e.* contributing zero electrons). For this, we used Xe's aug-cc-pV5Z-PP basis⁶³ with f, g and h functions removed. The need to include basis functions on Xe with alkali-metal solutes was noted also by Salem.⁶⁴ The Xe polarizability was set to the experimental value of $\alpha_{Xe} = 4.048$ Å³.⁶⁵ QM/MM-IEDRF results were compared to those from restricted coupled-cluster with singles, doubles and perturbative triples,⁶⁶ abbreviated as CCSD(T)/aug-cc-pV5Z,Xe=aug-cc-pV5Z-PP, using Molpro 2015.1,⁶⁶⁻⁶⁸ with all angular momentum functions retained.

Figure 1 shows potential energy curves for a sodium cation interacting with a neutral xenon atom. Considering that none of the parameters in the QM/MM-IEDRF model (solid black curves) were adjusted to reproduce the full-system CCSD(T) results (dashed blue curves), we view the agreement as very good. The CCSD(T) dissociation energy is quantitatively reproduced by QM/MM-IEDRF, while the equilibrium distance is slightly too short, presumably as a result of an underestimate of short-range repulsion. Panel (b) shows that $-\alpha_{\rm Xe}/(2R^4)$ behavior, expected for a charge-induced-dipole interaction, is recovered at the large-distance asymptote. This gives us confidence that our QM/MM-IEDRF implementation is correct.

Next, we consider the potential energy curves of a neutral sodium atom interacting



Figure 1: (a) Potential energy curves of a sodium cation interacting with a xenon atom as a function of internuclear separation, R. The solid black curve shows QM/MM-IEDRF results, where the Na⁺ is treated as the QM region at the RHF level and Xe at the MM-IEDRF level (see inset molecular graphic). The dashed blue curve shows full-system CCSD(T) results. The zero of energy is taken to be the dissociation limit at the same level of theory. (b) As for panel (a), but showing the absolute value of the potential on a log-log plot. Green circles show the expected potential energy resulting from a point charge interacting with a polarizable atom.

with a neutral xenon atom, shown in Figure 2. Since the components of this system are absent of any permanent multipoles, any long-range attractive interaction arises solely from dispersion forces between the neutral atoms. We see from Fig. 2(a) that QM/MM-IEDRF (solid black curve) does indeed predict an attraction at long range, and thus the method captures dispersion interactions. Compared to CCSD(T) results (dashed blue curve), the minimum in the potential energy curve predicted by QM/MM-IEDRF appears at a distance that is somewhat too large (5.75 Å versus 5.10 Å), leading to a well that is too shallow. However, given the very weak interactions in this Van der Waals complex, the precise location of the potential well is very sensitive to the treatment of Pauli repulsion and short-range polarization, and we view the overall qualitative agreement between QM/MM-IEDRF and CCSD(T) as encouraging.



Figure 2: As in Fig. 1, but for a neutral sodium atom interacting with a xenon atom. The green circles in panel (b) show the expected potential energy resulting from the C_6 dispersion interaction.

The observation that dispersion interactions are captured by QM/MM-IEDRF is further supported by a log-log plot of the potentials in Figure 2(b), which shows the potential energy decays approximately as the expected $-C_6/R^6$ at large R (dotted green line), albeit with a C_6 coefficient that is about 25% larger than the value that results from a fit to the CCSD(T) potential. This slight overestimate of dispersion interactions is consistent with the findings of Ángyán and Jansen that DRF Hamiltonians provide an upper bound to dispersion interactions, and their accuracy will improve as the ionization energy of the QM region increases relative to the ionization energy of the MM region.⁶⁹

3.2 Ethylene in an inert Xe matrix

Having verified our implementation of QM/MM-IEDRF, we turn next to its ability to describe solvation effects on an electronic crossing. To that aim, we consider a minimal energy conical intersection (MECI) involved in the prototypical cis-trans photoisomerization of ethylene. The particular S_0 - S_1 MECI we consider has a twisted-pyramidalized structure (tw-pyr), shown in Figure 3. The tw-pyr distortions bring about an intersection between states of biradical (CH₂-CH₂) and zwitterionic (CH₂⁺-CH₂⁻) character,^{70,71} and are believed to dominate the non-radiative pathway taken by ethylene.^{72–74}

The charge separation in the zwitterionic state of ethylene should be energetically stabilized by a polarizable environment, while the biradical state should be largely unperturbed, resulting in a differential solvation of these states, and an influence on their conical intersections. Indeed, the effect of environment on ethylene's electronic states away from the conical intersection (CI) seam has been explored previously with the original DRF method.⁷⁵ For twisted geometries without pyramidalization, a polarizable environment can break the symmetry of the otherwise equivalent pair of zwitterionic states, leading to the phenomenon of *sudden polarization* of the first excited state.^{6–8} We extend this work to explore the influence of environment on the CI.

We consider a simple polarizable environment of an inert Xe matrix. This was chosen as it has an optical dielectric constant (resulting from electronic polarization) that is representative of most organic solids/liquids ($\epsilon_{\infty} \sim 2.2$),⁷⁶ while being absent of any permanent dipoles that would complicate our interpretations. While solvents such as chloroform and water might be expected to have a larger influence on the electronic states of ethylene, their interactions arise predominantly through the static charge distributions of the solvent molecules, which can already be described quite well with (non-polarizable) QM/MM. The focus of this paper is particularly on the treatment of *electronic* polarization of the environment and its influence on the description of CIs, which will be displayed even in a simple Xe matrix.

3.2.1 Computational details

We built a molecular model starting from the ground-state structure of gas-phase ethylene optimized at the 2-state-averaged complete active space self-consistent field level with a two-electron in two-orbital active space (π and π^* orbitals) using the 6-31G basis (SA-2-CASSCF(2,2)/6-31G). The molecule was then placed at the center of a 15-Å radius spherical droplet of 200 randomly placed Xe atoms using Packmol.⁷⁷ We quenched to a cluster representation of a solid matrix by optimizing the Xe positions at a full-system QM level with the PBE0 functional,^{78,79} D3-BJ dispersion corrections,⁸⁰ and the LANL2DZ basis and ECPs,⁸¹ while freezing the ethylene atoms. The resulting optimized ethylene/Xe₂₀₀ system represents the initial Franck-Condon (FC) geometry, and is shown in Fig. 3(a).

Next, we replaced the Xe atoms with an MM description, either with QM/MM (where QM and MM particles are coupled only via \hat{V}_{Pauli}), QM/MM-SS-Pol, QM/MM-PTPol, or QM/MM-IEDRF embedding. The Xe polarizability was set to the experimental value of 4.048 Å³,⁶⁵ and the ethylene solute was treated as the QM region at the SA-2-CASSCF(2,2) level. Except where otherwise noted, we included the Pauli repulsion operator, \hat{V}^{Pauli} , in all embedding calculations. The ECP parameters from Jonin et al.⁵³ were used to allow a direct comparison to QM/MM-IEDRF results.

To mimic an ultrafast photoisomerization reaction following vertical excitation to the $\pi\pi^*$ state of ethylene, we performed a S₀/S₁ MECI optimization at the QM/MM SA-2-CASSCF(2,2)/6-311[2+,2+]G(2d,2p) level (described below). The Xe atoms were frozen, which is justified by the ultrafast timescale of ethylene's non-adiabatic transition (< 45 fs⁷⁴) and the high mass of Xe. The resulting geometry is shown in Fig. 3(b) and is consistent with the gas-phase tw-pyr MECI of ethylene found previously.^{72–74} Since analytical gradients for



Figure 3: Critical-point molecular geometries of ethylene in an inert Xe matrix. Ethylene is represented as a licorice structure with turquoise carbon and white hydrogen atoms. Xe atoms (pink spheres) that obscure the view of ethylene have been removed for purposes of visualization. Molecular graphics were generated with VMD 1.9.4.⁸²

DRF are not yet available, the MECI was not refined further for the polarizable embedding calculations. Instead, the double-coned PES were plotted in the branching plane of the QM/MM MECI while freezing the Xe atoms. This allowed us to explore the qualitative impact of the polarizable environment on ethylene's CI.

3.2.2 Vertical excitation

We start by considering the convergence of the vertical excitation energy of ethylene with respect to basis set for the ground-state structure, i.e. the FC geometry. It is well known that the diffuseness of gas-phase ethylene's vertical S_1 state ($\pi\pi^*$) is sensitive to the choice of basis due to Rydberg-valence (RV) mixing.^{83–86} In addition to standard basis sets, we thus consider very diffuse basis sets, 6-311[n+,n+]G(2d,2p), which correspond to the 6-311++G(2d,2p) basis augmented with n-1 extra sets of diffuse functions following an eventempered progression by scaling the diffuse functions' exponents by 1/3.⁸⁷ Results for gasphase ethylene and ethylene in an inert Xe matrix computed with QM/MM and QM/MM-IEDRF embedding are presented in Fig. 4. Since gas-phase ethylene at its FC geometry has zero net dipole, polarization of the Xe environment is negligible and the QM/MM-SS-Pol and QM/MM-PT-Pol results (not shown) are indistinguishable from the QM/MM results.



Figure 4: Convergence of ethylene's vertical S_1 properties with basis set. Gas-phase results (black curves) are compared to ethylene in an inert Xe matrix, treated with different embedding approaches. Solid curves indicate the vertical excitation energy (left axis) and dashed curves represent the second moment of the excited electronic charge density in the direction perpendicular to the molecular plane (right axis).

Considering first the gas-phase vertical excitation energy (solid black curve), we find the

inclusion of diffuse basis functions causes the vertical excitation energy to drop significantly going from 6-311G^{**} to 6-311++G^{**}. Further augmentation with diffuse functions leads to an excitation energy of 7.36 eV with the 6-311[3+,3+]G(2d,2p) basis, which is lower than the gas-phase experimental value of 7.66 eV.⁸⁸ This is an artefact of RV mixing, which is sensitive to the treatment of electron correlation. CASSCF(2,2) largely neglects dynamic electron correlation and $\sigma\pi$ correlation, which are known to contract the $\pi\pi^*$ state of ethylene,^{86,89} and thus in the large-basis limit, CASSCF(2,2) predicts an S₁ state that is too diffuse. This is confirmed by considering the second moment of the excited-state charge distribution, $\langle x^2 \rangle$, where x is the direction perpendicular to the molecular plane, and the origin is taken to be the center of mass of ethylene. $\langle x^2 \rangle$ is plotted as the dashed curves in Fig. 4, where the gas-phase result (black dashed curve) is seen to progressively increase with the addition of diffuse basis functions, reaching a value of 35.9 Bohr² for the 6-311[3+,3+]G(2d,2p) basis, which is significantly larger than the theoretical best estimate of $\langle x^2 \rangle = 17 \pm 1$ Bohr².⁸⁶

Given the issue of excessive RV mixing in the large-basis limit of gas-phase ethylene treated with CASSCF(2,2), we will instead focus on the inert Xe matrix results. Considering the QM/MM calculations (blue curves in Fig. 4), in which the influence of the Xe atoms on ethylene is only via the Pauli repulsion operator, \hat{V}_{Pauli} , we see for basis sets without diffuse functions (*i.e.* 6-31G** and 6-311G**) that the results are indistinguishable from the gas-phase results. This indicates that ethylene resides in a solvent void in the Xe matrix that negligibly perturbs states of pure valence character without charge separation, as expected for an inert matrix environment. Upon extending the basis with diffuse functions, the QM/MM excitation energy is seen to lower in a gradual fashion, converging at 9.26 eV with the 6-311[2+,2+]G(2d,2p) basis. Clearly, Pauli repulsion from the Xe environment is correctly destabilizing ethylene's Rydberg states and preventing excessive RV mixing, as confirmed by $\langle x^2 \rangle$ (dashed blue curve) retaining a value consistent for valence states, even in the largebasis limit. It should be noted that due to the neglect of dynamic electron correlation in the CASSCF(2,2) electronic structure, the $\pi\pi^*$ excitation energy is considerably overestimated compared to experiment, even in the large-basis limit. Nevertheless, the structure and topography of ethylene's S_0 - S_1 MECI is similar to that found with high-level multireference perturbation theory.^{72–74} Furthermore, we expect the *relative* changes to the PES due to environment polarization to be captured correctly with our choice of electronic structure.

We next consider the performance of QM/MM-IEDRF on the vertical excited-state properties of ethylene (green curves in Fig. 4). For all basis sets, we find the inclusion of the IEDRF polarization operator consistently lowers the S₁ excitation energy by ~0.2 eV. Since neither QM/MM-SS-Pol nor QM/MM-PTPol display this stabilization, it must result from dispersion interactions between ethylene and Xe which, as discussed above, are approximately captured by DRF methods. In other words, the increased diffuseness and polarizability of ethylene's S₁ $\pi\pi^*$ state relative to its ground state leads to stronger dispersion interactions with the Xe matrix in its excited state, thus lowering the excitation energy.

To our knowledge, the strength of dispersion interactions between Xe and electronically excited ethylene has not been previously explored. Given the issues of RV mixing in the largebasis limit of gas-phase ethylene, we can only compare our DRF predictions to the QM/MM results. Pauli repulsion is likely overestimated in the latter, since the Jonin potential was fit to reproduce electron-Xe scattering in the presence of a DRF-like polarization potential,⁵³ which has considerable short-range attraction. We thus caution against interpreting the absolute magnitude of stabilization seen by QM/MM-IEDRF relative to QM/MM as representing the strength of dispersion interactions between ethylene and Xe, and a more detailed benchmarking of dispersion interactions is beyond the scope of this study. Nevertheless, it is interesting to note that the experimental absorption spectrum of ethylene in Ar and Kr matrices exhibits smaller, but similar order of magnitude, red shifts compared to the gas phase,⁹⁰ as would be expected due to the lower polarizabilities of these atoms compared to Xe. These differential dispersion-interaction effects are completely missed by QM/MM, QM/MM-SS-Pol, and QM/MM-PTPol embedding.

Finally, we demonstrate the importance of treating Pauli repulsion by removing \hat{V}_{Pauli}

from the QM/MM-IEDRF Hamiltonian (purple curves in Fig. 4). For compact basis sets (6-31G^{**} and 6-311G^{**}), the results match the full QM/MM-IEDRF results (green curves), but once diffuse basis functions are included, we find compared to even the gas-phase results, the excitation energy drops lower and $\langle x^2 \rangle$ grows larger. These findings are associated with an excessive attraction between ethylene and Xe due to the polarization operator alone that causes a variational collapse of the first excited state to that of a very diffuse 3s Rydberg-like state, even if the initial guess to the CASSCF active space comprises the valence π and π^* orbitals. Thus, if diffuse basis functions are used in a QM/MM-IEDRF calculation, it is imperative to include explicit QM-MM Pauli repulsion.

Since we found convergence of QM/MM and QM/MM-IEDRF excited-state properties with the 6-311[2+,2+]G(2d,2p) basis, we used this for the remainder of the study. We note however that qualitatively similar results are seen when the smaller $6-311G^{**}$ basis is used, consistent with ethylene's excited state having valence character when embedded in the inert Xe matrix environment.

3.2.3 S_0 - S_1 conical intersection

We turn now to the S₀-S₁ MECI of ethylene in an inert Xe matrix. Fig. 5(a) plots the S₀ and S₁ PES in the branching plane of the CI, computed at the QM/MM SA-2-CASSCF(2,2)/6-311[2+,2+]G(2d,2p) level. We find the features of the CI are in qualitative agreement with previous multireference theory.^{72,91} In particular, the MECI geometry has tw-pyr character and the gradient difference, g, and derivative coupling, h, vectors (shown at the top of the figure) are dominated by torsion and pyramidalization respectively. The energy of the MECI is 5.30 eV relative to the FC S₀ energy, which is somewhat higher than previous gas-phase multireference theoretical values that range from 4.42 to 4.71 eV,⁷²⁻⁷⁴ presumably due to the lack of dynamic electron correlation at the SA-2-CASSCF(2,2) level. Despite the overestimate in energy, the topography of the MECI has a peaked character, in agreement with previous theories that account for dynamic electron correlation,⁹² thus we expect the relative changes to the PES resulting from polarization of the environment will be qualitatively correct. To simplify a direct comparison between the different polarizable embedding schemes, we do not reoptimize the MECI for each scheme, but rather recompute the PES in the vicinity of the QM/MM-optimized MECI along its branching plane, *i.e.* using the same geometries.

Considering next the QM/MM-SS-Pol result in Fig. 5(b), we see that the inclusion of MM polarization alters the energies of S_0 and S_1 (blue and red surfaces respectively) relative to each other, such that the expected crossing point shifts to a geometry that is displaced largely in the +h direction. However, we observe two artefacts in the QM/MM-SS-Pol PES in the vicinity of the crossing that make a precise determination of the crossing point impossible, which will be deferred to the QM/MM-IEDRF calculations discussed below. Firstly, the variational QM/MM-SS-Pol procedure on S_1 fails to converge for several geometries in the neighborhood of the crossing, indicated by the white area on the upper surface. The convergence issues can be traced to the well-known root-flipping problem,²⁵ wherein the electronic character of the adiabatic S_1 state cycles between biradical and zitterionic character to the MM dipole updates. Secondly, the same root-flipping problem leads to a derivative discontinuity (kink) on the S_0 surface, even away from the true CI. For these reasons, QM/MM-SS-Pol can not be used to study electronic crossings.

It has been suggested that a perturbative treatment of MM polarization can be used to avoid the root-flipping issues seen with QM/MM-SS-Pol, since the influence of the induced MM dipoles back on the QM system is ignored. We explore this in Fig. 5(c), using the QM/MM-PTPol method described in Section 2.2. Away from the crossing point, we find that the PES agree quantitatively with the predictions of QM/MM-SS-Pol, justifying the neglect of re-polarization of the QM region by the MM induced dipoles. However, while avoiding root flipping, QM/MM-PTPol exhibits its own artefacts in the vicinity of the crossing point. In particular, the S₀ energy is observed to be *higher* than S₁ in the vicinity of the crossing! This issue is reminiscent of similar artefacts observed with state-specific mul-



Figure 5: Potential energy surfaces (red: S_1 , blue: S_0) of ethylene in an inert Xe matrix in the vicinity of its MECI, plotted in the branching plane formed from the derivative coupling, h, and gradient difference, g, vectors (shown as arrows overlaid on the MECI structures at the top of the figure and scaled to a root mean squared displacement of 1.5 Å. Xe atoms not shown). Each panel shows the PES computed with a different level of embedding theory but for the MECI geometry and branching plane of the QM/MM system. The white shaded areas of the S_1 surface in panel (b) indicate regions for which the QM/MM-SS-Pol calculations failed to converge.

tireference perturbation theory electronic structure in the vicinity of state crossings,⁴⁸ and can be traced to a breakdown of perturbation theory for degenerate reference states and the neglect of the perturbation's influence on electronic couplings between the reference states. This rules out the use of perturbative approaches to environment polarization (as currently formulated) for the study of electronic crossings. It is possible that a reformulation of PTPol in terms of quasi-degenerate perturbation theory could solve this issue, although this is not explored here.

Finally, we consider QM/MM-IEDRF's description of the PES, shown in Fig. 5(d). Here we see the shape of the PES is in qualitative agreement with QM/MM-SS-Pol, but encouragingly absent of any artefacts. Due to a differential solvation of the electronic states, their crossing point is displaced approximately to h = 0.005, g = -0.002 Å; however, since the CI was not reoptimized at the QM/MM-IEDRF level and instead evaluated for the QM/MM geometries, we observe a weakly-avoided crossing with a gap of 0.006 eV rather than a true conical intersection. In addition to a change in the relative energies of the S₀ and S₁ surfaces, we also observe an approximately uniform reduction of ~0.08 eV in the energies of both S₀ and S₁ states relative to the FC ground state at the QM/MM-IEDRF level compared to the QM/MM-SS-Pol level, and this presumably arises from dispersion interactions stabilizing the biradical and zwitterionic states by roughly the same amount.

We can understand the qualitative change to the PES and the displacement of the crossing point seen with inclusion of environment polarization by considering the charge distribution of the S₀ and S₁ states in the vicinity of the CI. This is explored in Fig. 6, which plots the dipole moment magnitude for S₀ (panel a) and S₁ (panel b), in the same branching plane considered in Fig. 5. We find that the S₀ dipole decreases significantly in the direction of increasing derivative coupling and to a lesser extent in the direction of decreasing gradient difference, consistent with a change in electronic character from zwitterionic to biradical on the ground state. The S₁ state then has a change in electronic character in the reverse of the ground state. That the derivative coupling direction dominates the change in electronic character is consistent with it corresponding largely to pyr motion, which strongly modulates the energy of the zwitterionic state relative to the biradical state. As a result, the influence of a polarizable environment is to differentially stabilize S₁ compared to S₀ in the direction of (+h, -g), and this explains why the electronic crossing is seen to displace in that direction. It should be noted that the influence of environmental electronic polarization on the features of the CI PES is rather modest, and this can be understood from the relatively small dipole of ethylene in its zwitterionic state (\sim 5 Debye), which arises from the charge separation occuring between two directly bonded carbon atoms. As a result, the differential stabilization of ethylene's electronic states due to environmental polarization is of a similar order of magnitude as differential dispersion interactions, suggesting that for small solutes, both interactions should be included. We expect a greater influence of environmental electronic polarization on molecules with longer ranged charge separation, such as in the purple bacteria reaction center.¹³



Figure 6: Variation in the state dipoles (shown as false color maps) of ethylene in an inert Xe matrix in the vicinity of its MECI, plotted in the branching plane formed from the derivative coupling and gradient difference vectors (see Fig. 5).

4 Conclusions

An integral-exact version of the DRF polarizable embedding method has been proposed and implemented in a development version of TeraChem.⁵⁸ It incorporates many-body polarization interactions between the QM and the MM regions and works for both ground and excited states simultaneously. The polarization Hamiltonian is derived by converting the classical polarization energy from the dipole interaction model into a quantum-mechanical operator. The exact evaluation of polarization integrals paves the way for analytical gradients and couplings,⁹³ which are needed for efficient geometry optimizations, conical intersection searches, and ab initio molecular dynamics.

Compared to other formulations of polarizable embedding, QM/MM-IEDRF has a number of attractive properties: (1) The same Hamiltonian is used for all electronic states, avoiding problems with state-specific or perturbative solvation models near crossings of electronic states. (2) Since the matrix elements of the core Hamiltonian and electron-electron repulsion integrals are modified with operators that depend only on the QM and MM nuclear positions (and not additional dipole degrees of freedom), the approach is compatible with any wavefunction-based electronic structure method such as Hartree-Fock, Configuration Interaction or Complete Active Space Self-Consistent Field, and furthermore avoids costly iterations between wavefunction and dipole updates. (3) As in the original DRF method, dispersion interactions with the environment are captured approximately.

We demonstrated QM/MM-IEDRF's ability to robustly describe potential energy surfaces in the vicinity of an electronic crossing for ethylene embedded in a inert Xe matrix. Treating Xe as a polarizable environment leads to a differential stabilization of ethylene's states of zwitterionic character compared to those of biradical character, leading to noticeable changes to the location of the electronic crossing point. We thus expect that the method will find broad use in the modelling of photochemistry in complex environments, for cases where a description of electronic polarization of the environment is necessary.

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Supporting Information Available

See the supplementary material for supporting figure S1, molecular coordinates of the critical points of ethylene in an inert Xe matrix, and its derivative coupling and gradient difference vectors.

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TOC Graphic

