

Optimal diabatic states based on solvation parameters

Ethan Alguire and Joseph E. Subotnik

Citation: *J. Chem. Phys.* **137**, 194108 (2012); doi: 10.1063/1.4766463

View online: <http://dx.doi.org/10.1063/1.4766463>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v137/i19>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



**ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.**

[LEARN MORE](#)

Optimal diabatic states based on solvation parameters

Ethan Alguire^{a)} and Joseph E. Subotnik^{b)}

Department of Chemistry, 231 S. 34th Street, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA

(Received 12 June 2012; accepted 24 October 2012; published online 21 November 2012)

A new method for obtaining diabatic electronic states of a molecular system in a condensed environment is proposed and evaluated. This technique, which we denote as Edmiston-Ruedenberg (ER)- ϵ diabaticization, forms diabatic states as a linear combination of adiabatic states by minimizing an approximation to the total coupling between states in a medium with temperature T and with a characteristic Pekar factor C . ER- ϵ diabaticization represents an improvement upon previous localized diabaticization methods for two reasons: first, it is sensitive to the energy separation between adiabatic states, thus accounting for fluctuations in energy and effectively preventing over-mixing. Second, it responds to the strength of system-solvent interactions via parameters for the dielectric constant and temperature of the medium, which is physically reasonable. Here, we apply the ER- ϵ technique to both intramolecular and intermolecular excitation energy transfer systems. We find that ER- ϵ diabatic states satisfy three important properties: (1) they have small derivative couplings everywhere; (2) they have small diabatic couplings at avoided crossings, and (3) they have negligible diabatic couplings everywhere else. As such, ER- ϵ states are good candidates for so-called “optimal diabatic states.” © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4766463>]

I. INTRODUCTION

Conventional electronic structure calculations generate orthonormal adiabatic states, where the electronic charge and excitation is usually delocalized at an avoided crossing. Within the construct of time-dependent quantum mechanics, however, a more interesting question is: what are the initial and final electronic states of a physical system undergoing electron transfer (ET) or excitation energy transfer (EET)? These electronic states are usually denoted diabatic states (in contrast with the “historical” definition of diabatic states as those with minimal derivative couplings¹⁻³), and for these states, electronic charge or excitation is necessarily localized, even at an avoided crossing. In principle, diabatic states should be stationary with respect to perturbations from nuclear motion (Born-Oppenheimer coupling) or, as we have argued,^{4,5} to fluctuations in solvent structure. Methods that construct such diabatic states do so by (i) imposing constraints on wavefunctions⁶⁻¹⁷ or density,¹⁸ such as constrained density functional theory,¹⁹⁻²³ or (ii) rotating a basis of adiabatic states, either to diagonalize an observable,²⁴⁻²⁸ a technique most notably used in the generalized Mulliken-Hush method developed by Cave and Newton,^{29,30} or more generally, to optimize some diabaticization function.^{4,5,31,32}

Now, supposing we can generate a set of reasonable diabatic states, we can imagine two different uses for such an electronic basis. First, one might use such states in the context of Marcus theory to model ET^{4,6-10,12-14,18-24,29-34} or EET^{4,5,25-28,35,36} according to the golden rule perturbation theory. This scenario only makes sense if (i) the electronic coupling is small; (ii) the electronic coupling does not de-

pend on nuclear constraints (in accordance with the Condon approximation), which effectively restricts the usefulness of such couplings to rigid molecules (for example, see Ref. 5); (iii) the derivative couplings between such diabatic states must be mostly negligible. In this context and the activated crossing limit, diabatic potential energy surfaces (PESs) are unnecessary; one needs only an approximate value for the electronic coupling (H_{IF}) for the Marcus rate of ET,^{35,36}

$$k_{IF} = \frac{2\pi}{\hbar} |H_{IF}|^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} e^{-(\Delta G^\circ + \lambda)^2 / 4\lambda k_B T}, \quad (1)$$

in which the indices I and F refer to the initial and final electronic states of the system, λ is the solvent reorganization energy, and ΔG° is the change in free energy between the fully relaxed initial and final states.

Of course, there is a second scenario wherein one needs diabatic potential energy surfaces in addition to the diabatic and derivative couplings, all as a function of nuclear coordinates ζ . Namely, if one of the three conditions above is not satisfied, and thus one cannot simply apply Marcus theory. In this case, one must run some version of nonadiabatic dynamics for a more comprehensive picture of ET/EET.³⁷ To do so, a good first step is to develop optimal smooth diabatic PESs, which should have small diabatic *and* derivative couplings, along the lines of Michael Herman’s suggestion.^{38,39}

To that end, in this paper we propose to generate such diabatic states using an implicit solvent (with Pekar factor C) to model environmental effects that are absent in our electronic structure calculations. Certainly solvent can play a role in understanding diabatic states.⁴⁰ In fact, a strong motivation for this paper is the recent work of Yeganeh and Van Voorhis,⁴¹ who incorporated temperature and system-solvent

^{a)}Electronic mail: alguire@sas.upenn.edu.

^{b)}Electronic mail: subotnik@sas.upenn.edu.

coupling parameters into a new method for evaluating diabatic states for a model spin-boson Hamiltonian. In this paper, we report a new localized diabaticization method that is both sensitive to environmental conditions and which produces diabatic states for arbitrary systems, in a sense extending the approach used in Ref. 41. All of this is done within the framework of conventional electronic structure calculations. Armed with such a new tool, we will explore whether one should expect diabatic states with localized electronic charge, excitation, or couplings, and the subsequent consequences for predicted ET/EET rates.

II. NOTATION

The uppercase letters $\{I, J, K, L\}$ index adiabatic electronic states, while A will be used to index diabatic electronic states. The lowercase letters $\{i, a, p, q, r, s\}$ index molecular orbitals, with i and a indexing occupied and virtual orbitals, respectively. An uppercase italic E denotes a diagonal element of the Hamiltonian H . Electronic states are denoted Φ , and diabatic states in particular are denoted Ξ . All other terms are explained as they arise.

III. THEORY AND METHODOLOGY

In order to generate our optimal diabatic states, we use some variation of localized diabaticization: a basis of N adiabatic electronic states is mixed together via an adiabatic-to-diabatic rotation matrix \mathbf{U} , such that

$$\Xi_A = \sum_{I=1}^N \Phi_I U_{IA}. \quad (2)$$

This rotation matrix is chosen by optimizing some diabaticization function $f(\mathbf{U})$. Because N is generally small, the computational cost of any such procedure is minimal compared to that of the electronic structure technique used to generate the adiabatic basis. Previously, our research group has explored Edmiston-Ruedenberg (ER) diabaticization⁴ as a means to create localized electronic states for golden rule ET/EET rates. In principle, ER diabatic states are derived by including electrostatic interactions from a homogeneous linear dielectric solvent. The relevant diabaticization function, f_{ER} (Eq. (3)), accounts for system-solvent interactions by summing the solvation energies of the diabatic states (up to a constant).

$$f_{\text{ER}}(\mathbf{U}) = \sum_{A=1}^N \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\langle \Xi_A | \hat{\rho}(\mathbf{r}_1) | \Xi_A \rangle \langle \Xi_A | \hat{\rho}(\mathbf{r}_2) | \Xi_A \rangle}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (3)$$

$$\equiv \sum_{A=1}^N R_{AAAA}. \quad (4)$$

In f_{ER} , the diabatic self-interaction term R_{AAAA} can be obtained from the adiabatic self-interaction tensor via the transformation

$$R_{AAAA} = \sum_{I,J,K,L=1}^N U_{IA} U_{JA} U_{KA} U_{LA} R_{IJKL}, \quad (5)$$

and the density operator $\hat{\rho}$ is defined

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{\text{all electrons}} \delta(\mathbf{r} - \mathbf{r}_i), \quad (6)$$

where \mathbf{r}_i is the position operator for the i th electron.

Although ER localization has many advantages, there are two drawbacks to the procedure: (i) ER diabaticization does not take the energy difference between states into account, and will therefore mix states together even when such states are separated by a large energy gap, provided there is enough gain in solvation energy. In other words, ER diabaticization “overmixes” adiabatic states because it ignores the off-diagonal fluctuations in the electronic Hamiltonian. Consequently, diabatic states constructed by maximizing f_{ER} can strongly depend on the choice of adiabatic basis (in particular, the number of adiabatic states), which is not optimal. (ii) The localization function f_{ER} is independent of temperature or any kind of solvent parameter, and therefore is insensitive to environmental conditions, which is not always realistic. The original justification for ER⁴ was based on a strong polar solvent, which limits the generality of the algorithm.

To correct these deficiencies and ideally generate optimal PESs for surface hopping, we propose a new localization function, $f_{\text{ER}-\varepsilon}$ (Eq. (7)). This function uses the same approximation of a linear dielectric solvent as f_{ER} , but now mediates its effect on the system through the inclusion of diabatic state energies in addition to the temperature and polarity of the medium. We define $f_{\text{ER}-\varepsilon}$ as

$$f_{\text{ER}-\varepsilon}(\mathbf{U}) = \sum_{A=1}^N \exp\left(-\beta \left(E_A - \frac{C}{2} R_{AAAA}\right)\right), \quad (7)$$

where the diabatic state energies can be obtained from the adiabatic Hamiltonian via the transformation

$$E_A = \sum_{I,J=1}^N U_{IA} U_{JA} H_{IJ} = \sum_{I=1}^N U_{IA}^2 E_I, \quad (8)$$

where $\beta = \frac{1}{k_B T}$ (see also the Appendix), and where C is the Pekar factor,

$$C = \frac{1}{\varepsilon_e} - \frac{1}{\varepsilon_s}, \quad (9)$$

with ε_e and ε_s the high-frequency and static dielectric permittivities of the environment, respectively. The Pekar factor was chosen as a coefficient to this term so that only the permanent dipole contributions are taken into account when calculating the system-bath interaction energy. Although the electronic contributions from the solvent are important, these cannot be adequately accounted for without treating the solvent at a much higher level of theory.⁴² Consequently, this method assumes that the solvent is only able to reorient slowly with respect to the system, allowing nuclei to be treated classically. Both this system-solvent interaction term and the electronic state energy are incorporated into the ER- ε function (Eq. (7)) in such a way that maximizing $f_{\text{ER}-\varepsilon}$ is approximately analogous to minimizing the Helmholtz free energy A (Eq. (10)) for an electronic Hamiltonian perturbed by solvent interactions,

with $H = H_{\text{el}} + H_{\text{system-bath}}$.

$$A = -\beta^{-1} \ln \text{Tr}(e^{-\beta H}) = -\beta^{-1} \ln \left(\sum_I e^{-\beta E_I} \right). \quad (10)$$

The new ER- ε function addresses the shortcomings of ER diabatization in two ways. First, by including state energies in the expression for $f_{\text{ER-}\varepsilon}$, this method discourages mixing between states that have different energies, i.e., where the energy difference between adiabatic states is larger than any possible gain in solvation energy. Second, this function introduces parameters for temperature and solvent polarity, which can account for the different degrees of localization resulting from changing the solvent environment.

Furthermore, $f_{\text{ER-}\varepsilon}$ behaves appropriately in the required limiting cases. For example, in the high temperature limit, the function becomes

$$\lim_{\beta \rightarrow 0} f_{\text{ER-}\varepsilon}(\mathbf{U}) \approx 1 - \beta \text{Tr}(H) + \beta \frac{C}{2} \sum_{A=1}^N R_{AAAA}. \quad (11)$$

Because the trace of the Hamiltonian is invariant under unitary transformation, maximizing $f_{\text{ER-}\varepsilon}$ becomes equivalent to maximizing f_{ER} . Thus, $f_{\text{ER-}\varepsilon}$ recovers the expected behavior in the high temperature limit, i.e., the localization of charge or excitation density in response to rapid nuclear motion, and subsequent electronic decoherence (in the localized basis).^{43–45} Conversely, at lower temperatures nuclei become effectively frozen, therefore allowing electronic tunneling to dominate, resulting in delocalized excitations^{44,45} and coherent oscillations between diabatic electronic states.⁴³ As a result, there is a well-known transition between band and hopping descriptions of electron transfer as a function of increasing temperature.^{44,45}

Similarly, in the case of a very small Pekar factor (which is equivalent to removing the solvent), the ER- ε function becomes

$$\lim_{C \rightarrow 0} f_{\text{ER-}\varepsilon}(\mathbf{U}) = \sum_{A=1}^N \exp(-\beta E_A). \quad (12)$$

Maximizing this expression is equivalent to diagonalizing the Hamiltonian, therefore recovering adiabatic states in a vacuum. By increasing C , the system-solvent interaction term can be “turned on,” thus continuously increasing the amount of state localization. The strength of the ER- ε approach is that by altering these parameters, we can walk between maximally localized and delocalized electronic states as a function of solvent polarity (C) and temperature (T).

IV. RESULTS

We have modified the Q-CHEM 3.2 package⁴⁶ to implement ER- ε diabatization, and tested the procedure on both intramolecular and intermolecular model systems. All excited state calculations were performed using standard configuration interaction singles (CIS) with a 6-31G* basis. ER- ε states are computed assuming benzene solvent ($C = 0.5$ ^{47–49}) at room temperature ($T = 298$ K) unless otherwise specified.



FIG. 1. DBA molecule in which the 4-benzaldehyde donor and the 2-naphthyl acceptor groups are joined at 1,4-equatorial positions on a cyclohexane bridge, henceforth known as C-1,4ee. Here, C-1,4ee is shown in the geometry optimized for the A*D configuration of the T_1 excited state.

All visualizations were generated using Visual Molecular Dynamics (VMD).⁵⁰

A. Multi-state mixing and total coupling minimization

As discussed in Sec. III, according to many modern diabatization algorithms, diabatic states are constructed without reference to the energy differences between adiabatic states, thereby generating over-mixed diabatic states, which must be remedied by the block diagonalization of charge centers after mixing.^{29,30,32} The ER- ε diabatization function was designed in part to remedy such unphysical behavior. In order to evaluate the new function’s tendency to over-mix, we will compare ER- ε with ER diabatic states along an EET reaction coordinate using a large ($N = 7$) adiabatic basis, including states separated by both large and small energy gaps. In particular, we have modeled the lowest-energy triplet states of the system identified as C-1,4ee by Closs *et al.* in Ref. 51: a donor-bridge-acceptor (DBA) molecule in which the donor and acceptor are joined to a cyclohexane bridge at 1,4 equatorial positions (Fig. 1). In Ref. 51, the donor is a 4-benzophenonyl group, and the acceptor is a 2-naphthyl group, but in the current work we substitute 4-benzaldehyde as the donor for simplicity (as in Ref. 5). The surfaces and diabatic couplings are calculated over a set of nuclear geometries interpolated linearly between optimized A*D and AD* minimum-energy configurations of the T_1 state.

The diabatic state energies for the DBA system are presented in Fig. 2. Although ER has been shown to perform well on this system with a smaller ($N = 2$) adiabatic basis,⁵ it clearly fails if a larger basis is employed. Of particular concern is the over-mixing of T_1 and T_2 with higher-energy states, as these states are energetically well-separated from the remainder of the basis set. Admittedly, this over-mixing is not entirely unexpected, as the ER diabatization function does not take state energies into account, as discussed in Sec. III. Nevertheless, the ER- ε states do not appear to be over-mixed (Fig. 2(c)). Although there is mixing among the closely-spaced, high-energy states (T_4 - T_7), the energies of T_1 and T_2 are virtually identical to that of their adiabatic counterparts, indicating minimal mixing between these states and higher-energy states. However, it is clear that mixing does occur between states T_1 and T_2 in this basis, as evidenced by the diabatic couplings shown in Fig. 3. This result suggests that given enough adiabatic states (with high enough energy), one can construct meaningful diabatic

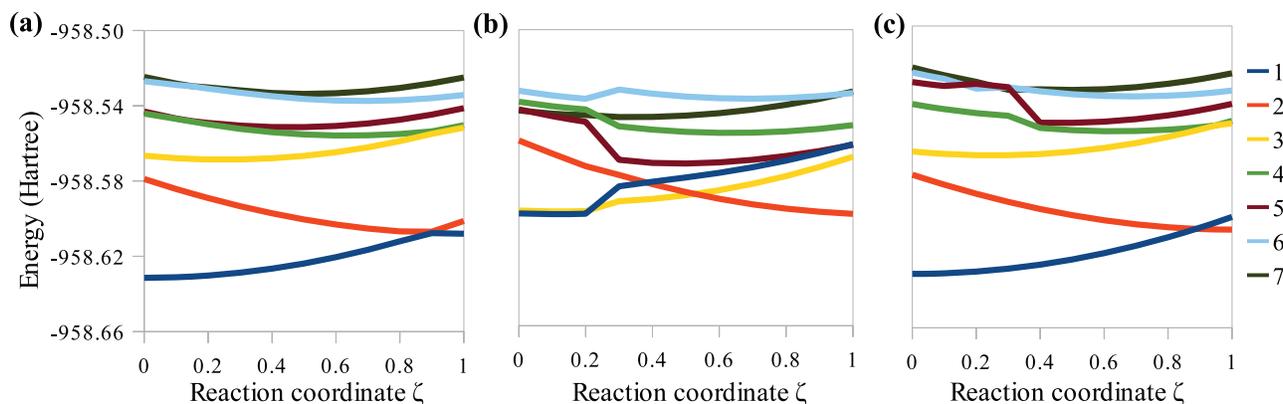


FIG. 2. PES of the seven lowest-energy triplet states of C-1,4ee in three bases: (a) the adiabatic basis, (b) the ER diabatic basis, and (c) the ER- ϵ diabatic basis. The reaction coordinate ζ denotes a linear interpolation between two geometries: $\zeta = 0$ corresponds to the optimized A*D geometry, and $\zeta = 1$ corresponds to the optimized AD* geometry. While the two lowest-energy ER diabatic states are clearly over-mixed with higher-energy states, this is not a problem for ER- ϵ diabatic states.

states without having to cherry-pick an adiabatic subspace or manually block-diagonalize after diabaticization.³²

Another way to determine the effect of basis set size on diabatic states is to calculate the diabatic coupling between states, as shown in in Fig. 3. The first thing to note is that whether we include two or seven states in the adiabatic basis, ER- ϵ yields nearly the same diabatic couplings between states T_1 and T_2 , providing further corroboration that this method is resistant to over-mixing. The second salient feature of Fig. 3 is the ζ -dependence of the diabatic couplings. On the one hand, the ER diabatic coupling is essentially constant with respect to the reaction coordinate, suggesting the Condon approximation should hold, and ER diabatic states can be used in the context of Marcus theory.^{35,36} On the other hand, the ER- ϵ diabatic coupling is maximized close to the avoided crossing and is small elsewhere. While the latter behavior does not take full advantage of the Condon approximation, these data suggest a reason why diabatic states from ER- ϵ may be useful for

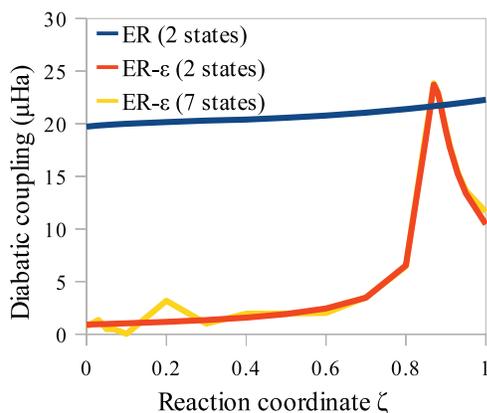


FIG. 3. Diabatic coupling between the two lowest-energy triplet states of C-1,4ee: the reaction coordinate ζ denotes a linear interpolation between two geometries; $\zeta = 0$ corresponds to the optimized A*D geometry, and $\zeta = 1$ corresponds to the optimized AD* geometry. The diabatic coupling calculated by ER localization is nearly constant over the reaction coordinate, while that produced by ER- ϵ peaks at $\zeta = 0.85$, close to the avoided crossing at $\zeta = 0.887$. Notice also that the two ER- ϵ couplings are very similar, despite having been generated from adiabatic bases of different size, indicating that ER- ϵ localization is not prone to over-mixing.

semiclassical dynamics: both the derivative and the diabatic couplings for the ER- ϵ diabatic states should be negligible outside a small volume of configuration space, thus simplifying and localizing certain kinds of dynamics calculations. For example, such states were originally suggested^{38,39} to be optimal for surface-hopping⁵² calculations. We wonder if these “optimal diabatic states” might also be helpful in the context of multiple spawning.^{53–56}

Although an analytical method for calculating the derivative coupling between localized diabatic CIS states is not yet available, an estimate of this quantity may be obtained via finite difference approximation,

$$\left\langle \Phi_I \left| \frac{d}{d\zeta} \Phi_J \right. \right\rangle \approx \frac{\langle \Phi_I(\zeta) | \Phi_J(\zeta + h) \rangle - \langle \Phi_I(\zeta) | \Phi_J(\zeta - h) \rangle}{2h}, \quad (13)$$

where $|\Phi_I\rangle$ and $|\Phi_J\rangle$ are CIS states that are functions of an arbitrary reaction coordinate ζ . In the present work, changes in molecular orbitals are neglected in calculating cross-state overlap, so that CIS states can be expressed

$$|\Phi_I\rangle \approx \sum_{i,a} t_i^{I,a}(\zeta) |\Phi_i^a\rangle. \quad (14)$$

In this approximation, overlaps are determined solely by CIS amplitudes t , so that

$$\langle \Phi_I(\zeta) | \Phi_J(\zeta + h) \rangle = \sum_{i,a} t_i^{I,a}(\zeta) t_i^{J,a}(\zeta + h). \quad (15)$$

The approximate magnitudes of the derivative couplings with respect to movement along the triplet-triplet energy transfer reaction coordinate are shown in Figs. 4 and 5. While the adiabatic derivative coupling becomes large near the avoided crossing ($\zeta = 0.887$), the derivative couplings in both diabatic bases remain small across all geometries explored. In the ER basis, derivative couplings are reliably small, peaking at $0.05 a_0^{-1}$. While the derivative coupling in the ER- ϵ is often larger than that in the ER basis, it does not suffer from the enormous couplings present near the avoided crossing in the adiabatic basis. This behavior results from the penalties incurred in $f_{\text{ER-}\epsilon}$ when adiabatic state energies differ by too great an amount: mixing is discouraged everywhere,

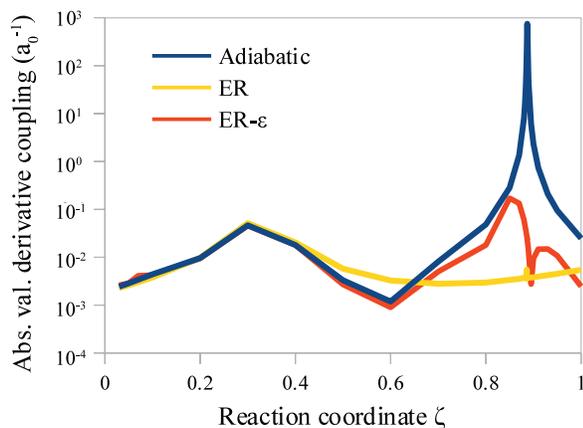


FIG. 4. Magnitude of the approximate derivative coupling between the two lowest-energy triplet states of C-1,4ee: the reaction coordinate ζ denotes a linear interpolation between two geometries; $\zeta = 0$ corresponds to the optimized A*D geometry, and $\zeta = 1$ corresponds to the optimized AD* geometry. Derivative couplings in three bases are represented: the adiabatic basis, the ER diabatic basis, and the ER- ϵ diabatic basis. In the adiabatic basis, the derivative coupling becomes large close to the avoided crossing at $\zeta = 0.887$, as expected, reaching values as large as 750 a_0^{-1} . In the ER basis, the derivative couplings are consistently small, peaking at 0.05 a_0^{-1} . In the ER- ϵ basis, derivative couplings match adiabatic values for many nuclear geometries, and become as large as 0.17 a_0^{-1} . Close to the avoided crossing, however, this is not the case, and the enormous couplings present in the adiabatic basis are eliminated. The apparent “kink” in the ER- ϵ derivative coupling is in fact a sign change (see Fig. 5).

but near the avoided crossing. Although this property of $f_{\text{ER-}\epsilon}$ results in generally larger derivative couplings than in the ER basis, the very large derivative couplings in the adiabatic basis are nonetheless avoided, and this is achieved without accumulating a consistently large diabatic coupling (see Fig. 3). As our goal is to minimize the total couplings between states (both diabatic and derivative), this is a promising initial result.

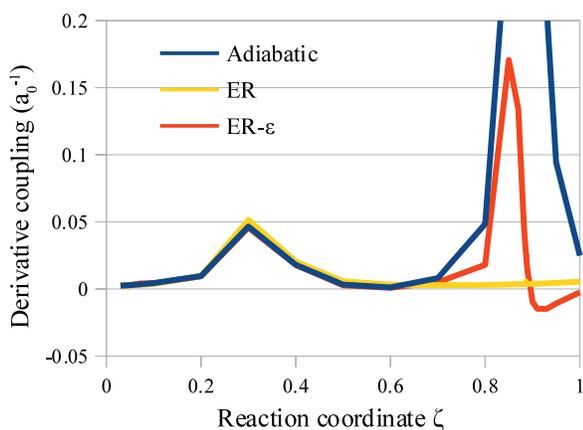


FIG. 5. Approximate derivative coupling between the two lowest-energy triplet states of C-1,4ee: the reaction coordinate ζ denotes a linear interpolation between two geometries; $\zeta = 0$ corresponds to the optimized A*D geometry, and $\zeta = 1$ corresponds to the optimized AD* geometry. Derivative couplings in three bases are represented: the adiabatic basis, the ER diabatic basis, and the ER- ϵ diabatic basis. The derivative coupling values presented here are identical to those presented in Fig. 4, with the exception that sign information has been included in this figure. The “kink” in the ER- ϵ derivative coupling near the avoided crossing in Fig. 4 is in fact a change of sign, as shown here.

B. Localization phase diagrams

Because ER- ϵ includes measurable solvation parameters, it is essential that the behavior of the function responds to these parameters in a realistic way. In order to investigate the influence of these parameters on ER- ϵ diabatic states, we have calculated the magnitude of mixing as a function of T and C . For simplicity, a two state adiabatic basis was used, and therefore the mixing information from the rotation matrix

$$\mathbf{U} = \begin{pmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix} \quad (16)$$

can be condensed into a single mixing angle θ . In our model system, as must be true, the electronic excitation density is completely delocalized in the adiabatic basis at the crossing point, so any subsequent mixing between these states can only serve to localize the excitation density.

To evaluate the effects of external environment and solvation parameters on state localization, we chose as our model system the two lowest-energy excited singlet states of two adjacent benzene molecules. For our calculations, the two rings are oriented in a clamshell configuration, rotated $\frac{7\pi}{16}$ radians with respect to one another, and are separated at their closest point by 2.54 \AA . Our results are summarized in Fig. 6. We see a dramatic shift from fully delocalized ($\theta = 0$) to fully localized ($\theta = \frac{\pi}{4}$) as C and T are increased beyond a certain threshold. To illustrate this effect, we have included attachment/detachment densities of the bimolecular system at three points on the phase diagram (Fig. 7). These results correspond nicely with our intuitive understanding of electronic behavior in a condensed environment: higher temperatures reflect rapid solvent motion, which encourages the electronic states to localize.^{44,45} As discussed previously, $f_{\text{ER-}\epsilon}$ enforces maximal localization in the high-temperature limit (Eq. (11)). However, no localization was observed in this system for small Pekar factor ($C \lesssim 0.4$) below 400 K.

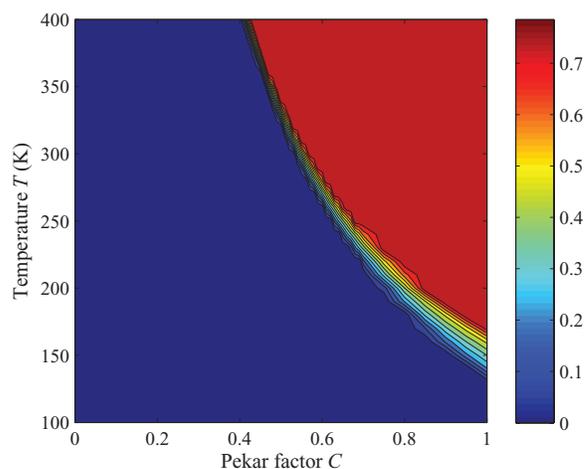


FIG. 6. Localization phase diagram of S_1 and S_2 states of dibenzene: the degree of mixing between states S_1 and S_2 of the molecular system is presented via mixing angle θ as a function of Pekar factor C and temperature T . A mixing angle of $\theta = 0$ represents total delocalization (unchanged from adiabatic states), and $\theta = \frac{\pi}{4}$ represents total localization. The model predicts complete localization of these electronic states at room temperature for a sufficiently polar ($C \gtrsim 0.6$) solvent.

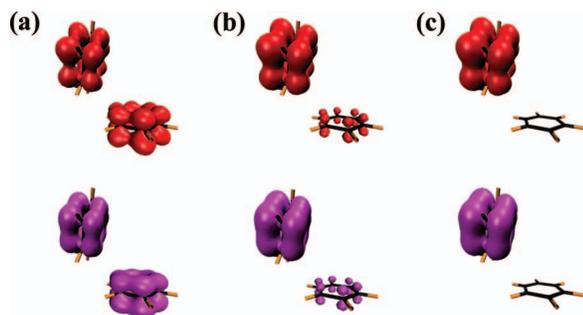


FIG. 7. Attachment/detachment densities of the lowest-energy singlet excited state of the dibenzene system in the ER- ε basis with three different sets of solvation parameters: (a) $C = 0.4$ and $T = 200$ K, (b) $C = 0.8$ and $T = 200$ K, and (c) $C = 0.8$ and $T = 300$ K. In each case, top figure is the attachment density, and the bottom figure is the detachment density. As solvent perturbations are applied, the delocalized excitation in the adiabatic basis begins to localize onto one ring. Increasing the polarity and temperature of the environment results in more rapid solvent fluctuations, which further trap electron density.

It is clear that the localization effects of temperature can be strongly mediated by the polarity of the solvent.

As shown above, the degree of localization determined by $f_{\text{ER-}\varepsilon}$ responds in an appropriate way to changes in T and C , and our method allows a very rough qualitative prediction of electronic properties of bichromophores in solution. To test our predictions, it would be interesting to see an experimental evaluation of state localization as a function of solvent and temperature, perhaps via time-dependent fluorescence anisotropy measurements. Choosing an appropriate model system would be a key to the success of such an endeavor; in our model of localized diabaticization, we account for nuclear motion only through a dielectric parameter, never explicitly, so systems with strong intramolecular vibronic coupling likely cannot be represented accurately by the electronic structure at only one nuclear geometry (the crossing point); instead, some nuclear dynamics calculations are probably necessary.

V. CONCLUSIONS AND FUTURE DIRECTIONS

We have introduced the ER- ε localization function as a simple, low-cost method for obtaining diabatic states of molecules in a condensed environment. Not only is this method more realistically independent of adiabatic basis than previous methods (Sec. IV A), but it also makes qualitative predictions about state localization as a function of the dielectric constant and solvent temperature (Sec. IV B).

As previously mentioned, a principle application of this method is to generate potential energy surfaces for semiclassical surface hopping calculations. Our preliminary results strongly support the proposition that ER- ε diabatic states offer a decent approximation to the optimal diabatic basis in which total coupling (diabatic and derivative) between electronic surfaces is minimized. However, we have only determined the couplings along a single reaction coordinate; a more thorough exploration of configuration space is needed to confirm that the couplings between surfaces in the ER- ε basis are consistently small over the all accessible geometries.

In order to efficiently accomplish this goal, an analytic evaluation of the derivative couplings of ER- ε states is necessary. As such, we will soon derive and implement such an algorithm. In the end, if the ER- ε basis succeeds in minimizing interstate coupling, it may prove to be a valuable tool in performing tractable surface-hopping calculations and pushing the limits of nonadiabatic dynamics simulations. As a side note, ER- ε orbitals could be interesting as well, in the context of local correlation theory, as such valence orbitals may have sparse electron-electron correlations.

ACKNOWLEDGMENTS

The authors would like to thank David Reichman and Robin Hochstrasser for helpful discussions. This work was supported by the NSF CAREER grant (Grant No. CHE-1150851). J.E.S. also acknowledges an Alfred P. Sloan Research Fellowship.

APPENDIX: CALCULATION OF THE SELF-INTERACTION TERM

In this paper, for ER- ε diabaticization, we have slightly modified the definition of the R_{AAAA} tensor as compared with Ref. 5. Previously, we had defined

$$R_{IJKL} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\langle \Phi_I | \hat{\rho}(\mathbf{r}_1) | \Phi_J \rangle \langle \Phi_K | \hat{\rho}(\mathbf{r}_2) | \Phi_L \rangle}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (\text{A1})$$

$$= \sum_{pqrs} D_{pq}^{IJ} (pq|rs) D_{rs}^{KL}, \quad (\text{A2})$$

where $(pq|rs)$ is the two-electron Coulomb integral

$$(pq|rs) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \phi_p^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \phi_r^*(\mathbf{r}_2) \phi_s(\mathbf{r}_2), \quad (\text{A3})$$

for molecular orbitals ϕ , and the density matrix D for CIS states is

$$D_{pq}^{IJ} = \langle \Phi_I | c_p^\dagger c_q | \Phi_J \rangle \quad (\text{A4})$$

$$= \begin{cases} \sum_i t_i^{I,p} t_i^{J,q}, & \text{if } p, q \text{ are virtual} \\ -\sum_a t_q^{I,a} t_p^{J,a} + \delta_{pq} \delta_{IJ}, & \text{if } p, q \text{ are occupied,} \end{cases} \quad (\text{A5})$$

where c^\dagger and c are creation and annihilation operators, respectively, and t is a CIS amplitude. In this paper, when calculating R_{IJKL} in the context of ER- ε diabaticization, we neglect the term $\delta_{pq} \delta_{IJ}$. Our rationale for doing so is that this term corresponds to the stationary unexcited (negatively charged) electrons, whose electric field is largely canceled by the background of (positively charged) nuclei. Of course, the same assumption could be made in the calculation of ER diabatic states, but doing so would not affect the ER algorithm at all. Because the trace of a matrix is invariant unitary transformation, it is easy to show that the resultant ER diabatic states are entirely independent of the $\delta_{pq} \delta_{IJ}$ term.

- ¹M. Baer, *Chem. Phys. Lett.* **35**, 112 (1975).
- ²Z. H. Top and M. Baer, *J. Chem. Phys.* **66**, 1363 (1977).
- ³G. J. Halász, A. Vibók, S. Suhai, and M. Baer, *J. Chem. Phys.* **127**, 244101 (2007).
- ⁴J. E. Subotnik, R. J. Cave, R. P. Steele, and N. Shenvi, *J. Chem. Phys.* **130**, 234102 (2009).
- ⁵J. E. Subotnik, J. Vura-Weis, A. J. Sodt, and M. A. Ratner, *J. Phys. Chem. A* **114**, 8665 (2010).
- ⁶M. D. Newton, *Int. J. Quantum Chem. Symp.* **14**, 363 (1980).
- ⁷J. Logan and M. D. Newton, *J. Chem. Phys.* **78**, 4086 (1983).
- ⁸M. D. Newton, *J. Phys. Chem.* **90**, 3734 (1986).
- ⁹M. D. Newton, *J. Phys. Chem.* **92**, 3049 (1988).
- ¹⁰R. J. Cave, D. V. Baxter, W. A. Goddard, and J. D. Baldeschwieler, *J. Chem. Phys.* **87**, 926 (1987).
- ¹¹T. Pacher, L. S. Cederbaum, and H. Köppel, *J. Chem. Phys.* **89**, 7367 (1988).
- ¹²A. Farazdel, M. Dupuis, E. Clementi, and A. Aviram, *J. Am. Chem. Soc.* **112**, 4206 (1990).
- ¹³M. Braga, A. Broo, and S. Larsson, *Chem. Phys.* **156**, 1 (1991).
- ¹⁴K. M. Rosso, D. M. A. Smith, and M. Dupuis, *J. Phys. Chem. A* **108**, 5242 (2004).
- ¹⁵H. Nakamura and D. G. Truhlar, *J. Chem. Phys.* **115**, 10353 (2001).
- ¹⁶H. Nakamura and D. G. Truhlar, *J. Chem. Phys.* **117**, 5576 (2002).
- ¹⁷H. Nakamura and D. G. Truhlar, *J. Chem. Phys.* **118**, 6816 (2003).
- ¹⁸A. Cembran, L. Song, Y. Mo, and J. Gao, *J. Chem. Theory Comput.* **5**, 2702 (2009).
- ¹⁹O. V. Prezhdo, J. T. Kindt, and J. C. Tully, *J. Chem. Phys.* **111**, 7818 (1999).
- ²⁰Q. Wu and T. Van Voorhis, *Phys. Rev. A* **72**, 024502 (2005).
- ²¹Q. Wu and T. Van Voorhis, *J. Phys. Chem. A* **110**, 9212 (2006).
- ²²Q. Wu and T. V. Voorhis, *J. Chem. Phys.* **125**, 164105 (2006).
- ²³Q. Wu and T. Van Voorhis, *J. Chem. Theory Comput.* **2**, 765 (2006).
- ²⁴A. A. Voityuk and N. Rösch, *J. Chem. Phys.* **117**, 5607 (2002).
- ²⁵C.-P. Hsu, Z.-Q. You, and H.-C. Chen, *J. Phys. Chem. C* **112**, 1204 (2008).
- ²⁶H.-C. Chen, Z.-Q. You, and C.-P. Hsu, *J. Chem. Phys.* **129**, 084708 (2008).
- ²⁷C.-P. Hsu, *Acc. Chem. Res.* **42**, 509 (2009).
- ²⁸Z.-Q. You and C.-P. Hsu, *J. Chem. Phys.* **133**, 074105 (2010).
- ²⁹R. J. Cave and M. D. Newton, *Chem. Phys. Lett.* **249**, 15 (1996).
- ³⁰R. J. Cave and M. D. Newton, *J. Chem. Phys.* **106**, 9213 (1997).
- ³¹J. E. Subotnik, S. Yeganeh, R. J. Cave, and M. A. Ratner, *J. Chem. Phys.* **129**, 244101 (2008).
- ³²E. Alguire and J. E. Subotnik, *J. Chem. Phys.* **135**, 044114 (2011).
- ³³M. D. Newton, *Chem. Rev.* **91**, 767 (1991).
- ³⁴T. Van Voorhis *et al.*, *Annu. Rev. Phys. Chem.* **61**, 149 (2010).
- ³⁵M. Ratner and G. Schatz, *Quantum Mechanics in Chemistry* (Dover, Mineola, NY, 2002).
- ³⁶A. Nitzan, *Chemical Dynamics in Condensed Phases* (Oxford University Press, New York, 2006).
- ³⁷A. W. Jasper, S. Nangia, C. Zhu, and D. G. Truhlar, *Acc. Chem. Res.* **39**, 101 (2006).
- ³⁸M. F. Herman, *J. Chem. Phys.* **110**, 4141 (1999).
- ³⁹M. F. Herman, *J. Chem. Phys.* **111**, 10427 (1999).
- ⁴⁰T. M. Henderson and R. J. Cave, *J. Chem. Phys.* **109**, 7414 (1998).
- ⁴¹S. Yeganeh and T. V. Voorhis, *J. Chem. Phys.* **135**, 104114 (2011).
- ⁴²J. N. Gehlen, D. Chandler, H. J. Kim, and J. T. Hynes, *J. Phys. Chem.* **96**, 1748 (1992).
- ⁴³H. Wang, M. Thoss, and W. H. Miller, *J. Chem. Phys.* **115**, 2979 (2001).
- ⁴⁴T. Holstein, *Ann. Phys.* **8**, 325 (1959).
- ⁴⁵T. Holstein, *Ann. Phys.* **8**, 343 (1959).
- ⁴⁶Y. Shao *et al.*, *Phys. Chem. Chem. Phys.* **8**, 3172 (2006).
- ⁴⁷J. R. Hammond, K. Kowalski, and W. A. deJong, *J. Chem. Phys.* **127**, 144105 (2007).
- ⁴⁸A. Rizzo *et al.*, *J. Chem. Phys.* **121**, 8814 (2004).
- ⁴⁹G. L. Ritchie and J. N. Watson, *Chem. Phys. Lett.* **322**, 143 (2000).
- ⁵⁰W. Humphrey, A. Dalke, and K. Schulten, *J. Mol. Graphics Modell.* **14**, 33 (1996).
- ⁵¹G. L. Closs, P. Piotrowiak, J. M. MacInnis, and G. R. Fleming, *J. Am. Chem. Soc.* **110**, 2652 (1988).
- ⁵²J. C. Tully, *J. Chem. Phys.* **93**, 1061 (1990).
- ⁵³M. Ben-Nun and T. J. Martinez, *J. Chem. Phys.* **108**, 7244 (1998).
- ⁵⁴M. Ben-Nun, J. Quenneville, and T. J. Martinez, *J. Phys. Chem. A* **104**, 5161 (2000).
- ⁵⁵M. Ben-Nun and T. J. Martinez, *Ab Initio Quantum Molecular Dynamics* (Wiley, 2002).
- ⁵⁶C. Evenhuis and T. J. Martinez, *J. Chem. Phys.* **135**, 224110 (2011).