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The initial and final states of electron and energy transfer processes: Diabatization as motivated by system-solvent interactions

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For a system which undergoes electron or energy transfer in a polar solvent, we define the diabatic states to be the initial and final states of the system, before and after the nonequilibrium transfer process. We consider two models for the system-solvent interactions: A solvent which is linearly polarized in space and a solvent which responds linearly to the system. From these models, we derive two new schemes for obtaining diabatic states from *ab initio* calculations of the isolated system in the absence of solvent. These algorithms resemble standard approaches for orbital localization, namely, the Boys and Edmiston–Ruedenberg (ER) formalisms. We show that Boys localization is appropriate for describing electron transfer [Subotnik *et al.*, J. Chem. Phys. **129**, 244101 (2008)] while ER describes both electron and energy transfer. Neither the Boys nor the ER methods require definitions of donor or acceptor fragments and both are computationally inexpensive. We investigate one chemical example, the case of oligomethylphenyl-3, and we provide attachment/detachment plots whereby the ER diabatic states are seen to have localized electron-hole pairs. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3148777]

I. INTRODUCTION TO DIABATIC STATES

There are many different definitions of diabatic states in the chemical literature.[1–3] Within the context of nonadiabatic quantum dynamics, one historical definition is that diabatic states are the many-electron states with zero (or minimal) nuclear derivative couplings.[4–7] Within the context of a system that can undergo electron or energy transfer in a condensed environment, another definition is that the diabatic states are the initial and final states of the system before or after the transfer process.[8,9] Many other definitions exist.[10–16] In this paper, we will adopt the second definition given above, appropriate for condensed environments, and we will present three new approaches for generating many-electron states relevant to nonequilibrium processes.

A. The historical motivation for diabatic states

Before discussing diabatic states relevant to condensed environments, we review the original, historical motivation for diabatic states. According to the standard dogma of quantum mechanics, the relevant stationary states of a physical system are the eigenstates of the Hamiltonian H. The standard route to these eigenstates is to invoke the Born–Oppenheimer approximation, whereby the full Hamiltonian is first partitioned into nuclear (R) and electronic (r) operators,

$$H(r,R) = H_{\text{nuc}}(R) + H_{\text{el}}(r;R). \tag{1}$$

According to the Born–Oppenheimer approximation, one should freeze the nuclei, diagonalize the electronic Hamiltonian H_{el}, and generate adiabatic states $\{|\Phi_j\rangle\}$,

$$H_{\text{el}}(r;R)|\Phi_j(r;R)\rangle = E_j(R)|\Phi_j(r;R)\rangle. \tag{2}$$

Next, one expands the full wave function in terms of the adiabatic electronic states and diagonalizes the full Schrodinger equation,

$$|\Psi_i(r,R)\rangle = \sum_j C_i^j |\Theta_j^i(R)\rangle \otimes |\Phi_j(r;R)\rangle, \tag{3}$$

$$H|\Psi_i(r,R)\rangle = E_i^{\text{tot}}|\Psi_i(r,R)\rangle. \tag{4}$$

Here $\{|\Psi_i(r,R)\rangle\}$ are the eigenfunctions of the total Hamiltonian H, and $\{|\Theta_j^i(R)\rangle\}$ are the nuclear wave functions that describe the vibrations and rotations associated with a given Born–Oppenheimer electronic state.

According to Eq. (4), it can be shown that the different adiabatic electronic states $\{|\Phi_j\rangle\}$ are coupled together by nuclear derivative couplings ($\langle\Phi_i(r;R)|\nabla_R|\Phi_j(r;R)\rangle_r$), where the subscript r indicates integration over electronic coordinates. The meaning of the derivative couplings is that because the electronic adiabatic states vary when the nuclear degrees of freedom are changed, any representation of nuclear motion in terms of adiabatic states must necessarily couple nuclear motion with electronic transitions. For this reason, diabatic states were historically defined[4–7] as rotations of adiabatic states with zero nuclear derivative couplings,

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$$|\Xi_i\rangle = \sum_{j=1}^{N_{\text{states}}} |\Phi_j\rangle U_{ji}, \quad i = 1, \ldots, N_{\text{states}}, \tag{5}$$

$$0 = \langle \Xi_i(r;R)|\nabla_R|\Xi_j(r;R)\rangle_r. \tag{6}$$

Although diabatic states satisfying Eqs. (5) and (6) exactly do not usually exist,[17] one can select diabatic states where the derivative couplings above are minimized.[6,7] With this definition, diabatic states are coupled together only very weakly through the nuclear derivative, but they can now be coupled together moderately through the electronic Hamiltonian $\langle \Xi_i(r;R)|H_{\text{el}}(r;R)|\Xi_j(r;R)\rangle$, resulting in the so-called diabatic couplings or H_{AB}'s that appear in nonadiabatic electron transfer theory.

B. The motivation for diabatic states in a condensed environment

When applying the Born–Oppenheimer treatment to a system capable of electron or energy transfer in a condensed environment, there is a separate motivation for constructing diabatic states. Namely, even if the system does not exchange electrons with its surroundings, one can find that the important quantum mechanical states of the system depend as much on the environment as on the system, in particular, when the environment is polarizable.[18] Thus, in many cases, the adiabatic states of the isolated system will not be the relevant stationary states of the solvated system, and they do not describe the system before or after an electron or energy transfer event.

For example, consider the standard example[19] of two solvated iron cations $(Fe(H_2O)_6)_2^{+5}$. If we ignore solvent and construct the Hamiltonian for the 107 electrons belonging to the two cation complexes in vacuum, we will find adiabatic states with exactly 53.5 electrons attached to each of the two iron centers (assuming the Fe–O distances are equal for both centers). In fact, because the electronic Hamiltonian is symmetric between the left and right, all eigenfunctions of $H_{\text{el}}(r)$ must also be eigenstates of the parity operator and therefore distribute charge equally between the two iron centers. The aforementioned electronic adiabatic states of $(Fe(H_2O)_6)_2^{+5}$ do not represent the important stationary states of iron in solution because, in a strongly polarizable environment, equal sharing of charge between the two cations is unphysical. In solution, the solvent will polarize around charge and the system-solvent interactions will drive an asymmetry, forcing the extra charge to be localized on one of the two iron centers. Indeed, if we relax the constraint of equal Fe–O distances even in the gas phase, the odd electron may well localize.[19]

With this motivation, *diabatic states for a system in a condensed environment can be defined as the projection onto the system of the stationary states of the system plus environment.* With this definition, when appropriate, the diabatic states of a system represent the initial and final states of the system before or after an electron or energy transfer event. There is a vast literature of research focused on computing these diabatic states when the surrounding solvent is modeled as a polarizable continuous medium[20–24] (PCM) designed to account for nuclear polarizability of the solvent.[24,25] For a comprehensive review, see Ref. 18.

C. The connection between the two definitions

Although *a priori* there is no reason to expect that diabatic states $\{|\Xi_i(r;R)\rangle\}$ representing the initial and final states of an electron transfer process should obey the historic definition of diabatic states (i.e., $\langle \Xi_i(r;R)|\nabla_R|\Xi_j(r;R)\rangle_r = 0$), as a practical matter the two definitions do usually agree. As pointed out by Atchity and Ruedenberg[10,11] and extended by Nakamura and Truhlar,[12–14] diabatic states with minimal derivative couplings should have "configurational uniformity" whereby the dominant configurations are unchanged over the entire potential energy surface. Pacher *et al.*[15,16] also independently published similar ideas of diabatization, proposing a "block diagonalization" algorithm that minimizes the distance (in wave function space) between the target diabatic states and a reference basis of states with fixed character (which were assumed always available). Because the initial and final states of an electron or energy transfer process should have a fixed character (e.g., covalent, ionic, etc.), we may expect that the historic definition of diabatic states will usually agree with the condensed environment definition.

D. Current algorithms for constructing diabatic states for electron and energy transfer

Unfortunately, including explicit solvent (beyond a continuum model) is computationally intractable for most calculations. There is an immense literature modeling the solvent as a continuum that polarizes the system self-consistently for use in electron transfer.[18,24,26] Two challenges with continuum models are sensitivity to cavity definition and the difficulty calculating a complete set of diabatic states when the nuclear geometry of the system is not close to the transition state and the effective solvent nuclear geometry needs to be very different for each of the diabatic states sought. For modern electron or energy transfer calculations, the standard approach to constructing diabatic states $\{|\Xi_i\rangle\}$ (and their diabatic couplings) is to rotate the adiabatic states of the system *in vacuum* $\{|\Phi_i\rangle\}$ [as in Eq. (5)] according to some physical criterion that should mimic the effect of solvent. Examples of such methods in the context of electron transfer include generalized Mulliken Hush (GMH),[8,9] Boys localization,[27] constrained density functional theory (CDFT),[28–31] fragment charge difference (FCD),[32] and in the context of energy transfer, fragment energy difference (FED).[33–35]

In some cases, the diabatic states are obvious. For instance, in the case of $(Fe(H_2O)_6)_2^{+5}$, our intuition is to rotate together the adiabatic ground state and the adiabatic first excited state so that the resulting two diabatic states would have charge localized either on the left or on the right cation. We make this choice of diabatic states for $(Fe(H_2O)_6)_2^{+5}$ because, according to electrostatic theory, the solvent should choose to localize the extra charge on one or the other iron center if the dielectric constant is sufficiently large and the metal-metal electronic coupling is not too strong. For a more general system, however, there can be no unique definition

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for constructing such diabatic states because the need for such diabatic states is based on the initial state preparation and our lack of information about solvent position and orientation. For this reason, many electron-transfer theorists have preferred to avoid calculating diabatic states altogether, choosing instead to extract the electronic couplings necessary for predicting electron transfer rates using indirect methods that do not make explicit reference to diabatic states.[36–43]

Nevertheless, because the physical meaning of diabatic states in condensed environments is paramount, it is worthwhile and useful to construct approximate system diabatic states even if these computed states are not unique. Ideally, a diabatization algorithm applicable to electron and energy transfer in condensed environments should

- treat the initial and final states of both electron and energy transfer equivalently;
- apply to both inter- and intramolecular electron or energy transfer;
- be computationally feasible for large molecules with arbitrarily many charge or energy excitation centers;
- apply to molecules with arbitrary amounts of electron-electron correlation;
- rely on as few parameters as possible (e.g., dielectric constants, cavity sizes, charge fragments, etc.);
- allow for the calculation of diabatic states at all nuclear geometries of the system with or without solvent [so that the Condon approximation (e.g., see Ref. 44) can be tested].

In Sec. II, we will present two new diabatization algorithms, namely, Boys and Edmiston–Ruedenberg (ER) diabatization. The Boys approach satisfies most of the above requirements (for electron transfer only) while the ER approach satisfies them all (for electron and energy transfer). A third approach, von Niessen–Edmiston–Ruedenberg (VNER) diabatization, will be discussed in Appendix B. Before introducing these new methods, we briefly review the four modern algorithms commonly used to construct diabatic states relevant to electron and energy transfer processes: GMH,[8,9] FCD,[32] FED,[33–35] and CDFT.[28–31]

1. Generalized Mulliken Hush

The GMH algorithm[8,9] is a simple approach that has proved very popular for the specific case of describing the initial and final states of an electron transfer process. The general idea behind GMH is to recognize that, when modeling electron transfer, the diabatic states should correspond to charge localized on different centers (donors and acceptors). The physical motivation underlying charge-localized diabatic states is that solvent localizes charge on a system by reorganizing around it.

When seeking charge-localized diabatic states, according to GMH theory, one constructs diabatic states as follows (for the two-state problem). First, one calculates all dipole matrix elements of the adiabatic states $|\Phi_1\rangle$ and $|\Phi_2\rangle$: $\vec{\mu}_{11}$, $\vec{\mu}_{22}$, and $\vec{\mu}_{12}$. Second, one recognizes that the important direction is the direction of the dipole moment of the initial adiabatic state minus the dipole moment of the final adiabatic state: $\vec{v}_0=(\vec{\mu}_{11}-\vec{\mu}_{22})/|\vec{\mu}_{11}-\vec{\mu}_{22}|$. Third, one projects all dipole matrix elements into the v_0 direction and diagonalizes the dipole matrix. The motivation here originally was proposed by Mulliken and Hush who reasoned that the transition dipole connecting localized diabatic states should be zero for charge transfer calculations due to the locality of the dipole moment operator and the exponential decay of the localized donor and acceptor states. The rotation matrix that diagonalizes the projected dipole matrix is taken as the GMH transformation matrix from adiabatic to diabatic states.

GMH theory has been used to model several experimental systems for two-state electron transfer. For systems with more than two states but only two charge centers, GMH makes the reasonable choice to diagonalize the Hamiltonian within the block of states for each charge center, thus generating unique, locally adiabatic diabatic states. For systems with more than two noncollinear charge systems, however, there is no unique charge transfer direction and GMH is unsatisfactory. GMH is also incapable of treating energy transfer.

2. Fragment charge difference

The FCD method[32] is based on GMH, with the advantage that FCD can account for multiple charge centers. The FCD approach works by associating each diabatic state $|\Xi_i\rangle$ with a given donor or acceptor fragment (indexed by i), and then maximizing the sum over all diabatic states of the charge density lying on the associated fragment. While this approach is general and can be applied to many charge centers, the price for this generality is that *a priori* one must define donor and acceptor fragments, rather than allowing the diabatization routine to distribute charge naturally. Thus, it is difficult to rigorously justify the FCD algorithm on physical grounds for intramolecular electron transfer. Moreover, the FCD algorithm does not treat energy transfer.

3. Fragment energy difference

The FED algorithm by Hsu and co-workers[33–35] extends the FCD approach to energy transfer by defining energy excitation density as the density of electron attachment plus the density of electron detachment, all relative to a molecular ground state. Similar to the FCD approach for electron transfer, FED makes diabatic states by first associating each diabatic state with one molecular fragment for energy excitation, and second maximizing the sum over all diabatic states $|\Xi_i\rangle$ of the energy excitation density associated with fragment i. Just like the FCD approach, the FED method can treat multiple energy excitation centers. However, as for FCD, the price for this flexibility is that the algorithm depends on *a priori* definitions of molecular fragments, which is difficult to justify on physical grounds for intramolecular energy transfer. Moreover, it is unclear if the FED algorithm can be directly applied to charge transfer.

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4. Constrained DFT

In the past decade, CDFT (Refs. 28–31) has evolved as an alternative approach to constructing diabatic states, entirely avoiding the adiabatic states normally produced by standard electronic structure methods. The idea behind CDFT is to define donor and acceptor fragments, and to constrain the Kohn–Sham wave function to have the correct charge on each fragment. While CDFT has the strong advantage of being computationally inexpensive, because of the necessary fragment definitions, the algorithm is more difficult to justify on physical grounds for intramolecular (rather than intermolecular) electron transfer. To our knowledge, CDFT-like methods have not yet been applied to energy transfer. Formally, CDFT diabatic states are not rotations of adiabatic states arising from standard *ab initio* quantum chemistry calculations.

E. A brief synopsis of orbital localization routines

In Sec. II, we will derive two new diabatization routines based on different models for the interaction of system with solvent (and a third model is given in Appendix B). These new techniques bear a striking resemblance to algorithms commonly used for molecular orbital localization, including the Boys,[45–47] ER,[48] and VNER (Refs. 48–50) localization routines. For completeness, we remind the reader how these different localized orbitals are defined.

For a closed molecular system, we denote the canonical molecular orbitals ϕ_i, $i=1,\ldots,N_{\text{orbitals}}$ which are almost always delocalized. One can construct localized orbitals η_i by applying a rotation matrix $\mathbf{U}$,

$$\eta_i = \sum_{j=1}^{N_{\text{orbitals}}} \phi_j U_{ji}, \quad i=1,\ldots,N_{\text{orbitals}}. \tag{7}$$

Because the (Slater) determinant is multiplicative, rotating occupied molecular orbitals together does not change the overall many-electron state of the system.

The rotation matrix $\mathbf{U}$ is usually defined by maximizing a localization function. For the three localization routines mentioned above, these localization functions are

$$f_{\text{Boys}}(\mathbf{U}) = f_{\text{Boys}}(\{\eta_i\}) = \sum_{i,j=1}^{N_{\text{states}}} |\langle \eta_i|\vec{\mathbf{r}}|\eta_i\rangle - \langle \eta_j|\vec{\mathbf{r}}|\eta_j\rangle|^2, \tag{8}$$

$$f_{\text{ER}}(\mathbf{U}) = f_{\text{ER}}(\{\eta_i\}) = \sum_{i=1}^{N_{\text{orbitals}}} (\eta_i\eta_i|\eta_i\eta_i) \tag{9}$$

$$= \sum_{i=1}^{N_{\text{orbitals}}} \int dr_1 \int dr_2 \frac{\eta_i(r_1)\eta_i(r_1)\eta_i(r_2)\eta_i(r_2)}{|r_1-r_2|}, \tag{10}$$

$$f_{\text{VNER}}(\mathbf{U}) = f_{\text{VNER}}(\{\eta_i\}) = \sum_{i=1}^{N_{\text{orbitals}}} \int dr_1\, \eta_i(r_1)\eta_i(r_1)\eta_i(r_1)\eta_i(r_1). \tag{11}$$

In Eq. (9), we use the chemists' notation for the two-electron Coulomb integral $(pq|rs)$.[51] Equations (8)–(11) should be compared to Eqs. (22), (28), and (B4) below. There would appear to be a remarkable connection between orbital localization techniques and many-electron state diabatization algorithms.

II. CONSTRUCTING DIABATIC STATES BASED ON SYSTEM-SOLVENT INTERACTIONS

We now present a new approach for constructing diabatic states relevant to electron and energy transfer, beginning with a standard model for a solvated system.

A. The difficulty modeling system-solvent interactions explicitly

As noted many times before (e.g., see Ref. 18), when treating electron and energy transfer in condensed environments, the need for diabatic states is motivated especially by the interactions between the system and the polar solvent. The full Hamiltonian for a quantum mechanical system interacting with solvent can always be written as[18]

$$H_{\text{full}} = H_{\text{sys}}(r,R_{\text{sys}}) + H_{\text{int}}(r,R_{\text{sys}},r_{\text{solv}},R_{\text{solv}}) + H_{\text{solvent}}(r_{\text{solv}},R_{\text{solv}}). \tag{12}$$

r,R denote electronic and nuclear degrees of freedom, respectively. We restrict ourselves to cases where electrons are not exchanged between system and solvent so that system electrons (denoted r) can be distinguished from solvent electrons (denoted r_{solv}).

We will also assume that for any nuclear configuration of the solvent (R_{solv}), the solvent electrons are in their ground state (independent of the system), which can be found by an electronic structure calculation on the solvent alone. This allows us to collectively represent solvent electrons and nuclei by the solvent nuclear coordinate (R_{solv}) alone,

$$H_{\text{full}} = H_{\text{sys}}(r,R_{\text{sys}}) + H_{\text{int}}(r,R_{\text{sys}},R_{\text{solv}}) + H_{\text{solvent}}(R_{\text{solv}}). \tag{13}$$

For future calculations, we seek an algorithm to compute meaningful diabatic electronic states that are applicable at any fixed nuclear configuration of the system (R_{sys}). Such states can be found by minimizing the ground state energy of the system as a function of all solvent nuclear coordinates,[18]

$$H_{\text{full}}^{\text{el}}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})|\Psi_0^{(m)}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})\rangle = E_0(R_{\text{sys}},R_{\text{solv}}^{(m)})|\Psi_0^{(m)}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})\rangle, \tag{14}$$

$$\frac{\partial}{\partial R_{\text{solv}}} E_0(R_{\text{sys}},R_{\text{solv}})|_{R_{\text{solv}}=R_{\text{solv}}^{(m)}} = 0. \tag{15}$$

In Eqs. (14) and (15), we have labeled one optimal choice of nuclear solvent coordinates by index m and index 0 denotes

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the fact that $|\Psi_0^{(m)}\rangle$ is the electronic ground state. The semicolons in Eq. (14) emphasize that nuclear and electronic motion are decoupled according to the Born–Oppenheimer approximation and, as stated above, solvent electrons are treated implicitly by assuming that they are in the solvent ground state.

Because there can be many optimal nuclear configurations satisfying Eqs. (14) and (15), in order for us to describe completely the stable states of the system, we must find all such optimal nuclear configurations for the system and solvent. The resulting electronic states $\{|\Psi_0^{(m)}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})\rangle\}$ are the important set of wave functions for the system electrons, and they depend parametrically on all nuclear coordinates (system and solvent). These wave functions are neither the adiabatic states of the system plus solvent (because we separate solvent electrons from system electrons) nor the adiabatic states of the system (because we have included the effect of solvent in our Hamiltonian). Instead, by our definitions above, the set $\{|\Psi_0^{(m)}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})\rangle\}$ are exactly the diabatic states for the system. Our goal is to compute these wave functions as easily as possible.

If one treats the solvent as a polarizable continuous medium (PCM), Eqs. (14) and (15) have been explored with great success over the past 30 years by Tomasi and co-workers.[20–23,52–54] The caveats in using PCM-like models for electron or energy transfer are (i) the dependence of the resulting diabatic states on cavity geometry and (ii) the difficulty computing a complete set of diabatic states for the system when the system nuclear geometry (R_{sys}) is biased toward one state and the effective solvent nuclear geometry needs to be very different for each of the diabatic states sought. In the future, when possible, it will be worthwhile to compare the diabatic states and diabatic coupling matrix elements (H_{AB}) produced with PCM with those produced by the algorithms presented below. In Sec. II B, we will derive an approximate description of the diabatic states in a polar solvent that requires neither modeling explicit solvent nor assuming a fixed cavity geometry.

B. Necessary approximations for system-solvent interactions

We follow the formal procedure given above for constructing diabatic states in a polar environment, attempting to satisfy Eqs. (14) and (15) approximately. In the process, we will eventually derive Boys and ER localizations, which require only calculations of the system *in vacuum*. To make any progress, we make several initial assumptions, which are discussed in detail in Sec. IV.

1. Nearly degenerate adiabatic system states

Our preliminary assumption is that, in the absence of solvent, the adiabatic eigenstates of the isolated system in vacuum will include some set of nearly degenerate levels which, in the presence of a solvent, are mixed together to form diabatic states. This assumption is clearly true in numerous physically relevant cases including, for instance, charge transfer systems between symmetric ions or energy transfer along a chain of chromophores.

Formally, we diagonalize the system Hamiltonian H_{sys} and generate a complete set of adiabatic states (denoted $\mathcal{A}$ and labeled by n) for the isolated system, $\mathcal{A}\equiv\{|\Phi_n(r;R_{\text{sys}})\rangle\}$, with no reference to a solvent coordinate,

$$H_{\text{sys}}(r;R_{\text{sys}})|\Phi_n(r;R_{\text{sys}})\rangle = E_n(R_{\text{sys}})|\Phi_n(r;R_{\text{sys}})\rangle. \tag{16}$$

Here, $n=0$ is the electronic ground state of the isolated system, $n=1$ is the first excited state, etc. We will assume that the important adiabatic states are nearly degenerate in energy, with the energy scale to be determined below.

2. The system-solvent interaction is neither too strong nor too weak

For systems that can undergo electron transfer, moving the solvent corresponds to an outer sphere reorganization, which should be small compared to the range of electronic energies for the adiabatic states of the system. The magnitude of a reorganization energy is usually between a few tenths of an eV and a couple of eV,[55] while quantum chemistry calculations routinely calculate molecular excited states with energies 10 eV above the ground state. Thus, we expect

$$|\Delta H_{\text{int}}| \ll \text{energy spread}(\mathcal{A}). \tag{17}$$

Given Eq. (17), when constructing diabatic states, it is reasonable to focus on a reduced subspace $\mathcal{W}\subset\mathcal{A}$ which includes all system states that are spread out over an energy range of no more than a 1–2 eV. $\mathcal{W}$ can include or exclude the ground state adiabatic wave function of the system, and we define the dimension of $\mathcal{W}$ to be N_{states}. We expect $\mathcal{W}$ should contain the nearly degenerate adiabatic system states predicated above. The possibility that other, dynamically unimportant system states are included in $\mathcal{W}$ is discussed in Sec. IV A. Now, suppose we are given an optimal set of solvent nuclear coordinates $R_{\text{solv}}^{(m)}$ satisfying Eq. (14). By assuming that ΔH_{int} should not be too large, the implication is that in order to compute the electronic ground state $|\Psi_0^{(m)}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})\rangle$, we need only minimize $H_{\text{sys}}(r;R_{\text{sys}})+H_{\text{int}}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})$ within the subspace $\mathcal{W}$.

Next, after assuming an upper bound for $|\Delta H_{\text{int}}|$ in Eq. (17), we assume that in a polar solvent, $|\Delta H_{\text{int}}|$ is not too small and is larger than the spread of system eigenvalues in $\mathcal{W}$,

$$\text{energy spread}(\mathcal{W}) < |\Delta H_{\text{int}}| \ll \text{energy spread}(\mathcal{A}). \tag{18}$$

Thus, the system-solvent interaction is assumed to be the dominant term in lifting the near degeneracy of the vacuum adiabatic states. The implication of this second and balancing assumption is that instead of diagonalizing $H_{\text{sys}}(r;R_{\text{sys}})+H_{\text{int}}(r;R_{\text{sys}},R_{\text{solv}}^{(m)})$ directly in the $\mathcal{W}$ subspace, a good approximation is to diagonalize ΔH_{int} alone (in the $\mathcal{W}$ subspace) and look for the lowest eigenvalue. If the adiabatic states in $\mathcal{W}$ were exactly degenerate, this would be equivalent to first-order degenerate perturbation theory.

3. The system-solvent interaction is electrostatic

Our last and biggest assumption is that the system-solvent interaction energy is based on electrostatics. With

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this in mind, we may write the electronic density at position $\underset{\sim}{\vec{r}}$ as a dynamic variable and the system-solvent interaction Hamiltonian as an integral over all space,

$$\hat{\rho}(\underset{\sim}{\vec{r}}) = \sum_j \delta(\underset{\sim}{\vec{r}} - \vec{r}^{(j)}), \tag{19}$$

$$H_{\text{int}}(r;R_{\text{sys}},R_{\text{solv}}^{(m)}) = \int d\underset{\sim}{\vec{r}}\,\phi_{\text{int}}(\underset{\sim}{\vec{r}};R_{\text{sys}},R_{\text{solv}}^{(m)})\hat{\rho}(\underset{\sim}{\vec{r}}). \tag{20}$$

Here, $\vec{r}^{(j)}$ represents the position of the jth electron and this expression is exact for arbitrary system-solvent interaction energies that are based on electrostatics. The hat on $\hat{\rho}$ denotes the fact that $\hat{\rho}$ is an operator, and ϕ_{int} is the electrostatic potential caused by the solvent acting on the system. We repeat that the index m stands for one configuration of solvent nuclei which is optimal for stabilizing the system.

C. Distinct models for the system-solvent interaction and the resulting diabatization algorithms

Thus far, we have outlined a general strategy for obtaining diabatic states based on assumptions about the strength of the system-solvent interaction potential H_{int} relative to other energy ranges of the system. The derivation of different diabatization methods now hinges on our specific treatment of the interaction potential H_{int}. As shown below, applying different models for H_{int} leads to distinct diabatization methodologies.

1. Multipole expansion: Boys diabatic states and electron transfer

For a system located near the origin, one simple approximation to the general expression in Eq. (20) is to represent the interaction energy as a multipole expansion of the electronic coordinate r of the system around zero,

$$\begin{aligned} H_{\text{int}}(r;R_{\text{sys}},R_{\text{solv}}^{(m)}) &= H_{\text{int}}^{(0,m)} + H_{\text{int}}^{(1,m)} + H_{\text{int}}^{(2,m)} + H_{\text{int}}^{(3,m)} + \cdots \\ &= Q^{(0)} + \sum_{i=x,y,z} Q_i^{(1)}(R_{\text{sys}},R_{\text{solv}}^{(m)})r_i \\ &\quad + \sum_{i,j=x,y,z} Q_{ij}^{(2)}(R_{\text{sys}},R_{\text{solv}}^{(m)})r_i r_j + \cdots . \end{aligned} \tag{21}$$

Here, r_i stands for a Cartesian component of the second-quantized electronic coordinate $\vec{r}$ (i.e., $r_i = x,y,z$). In the neighborhood of the system, we must assume that $|H_{\text{int}}^{(0,m)}| > |H_{\text{int}}^{(1,m)}| > |H_{\text{int}}^{(2,m)}| > \cdots$. This multipole expansion works best for small systems where the system-solvent interaction is dominated by the linear term.

Making all the assumptions in Sec. II B and approximating Eq. (21) by the linear term (as would be expected in the case of electron transfer), it follows that we can construct diabatic states by diagonalizing the operator $H_{\text{int}}^{(1,m)} = \Sigma_{i=x,y,z} Q_i^{(1)}(R_{\text{sys}},R_{\text{solv}}^{(m)})r_i$ in the subspace $\mathcal{W}$. The problem remains, however, that without actually constructing $R_{\text{solv}}^{(m)}$, which would be very costly, there is no straightforward way to minimize $H_{\text{int}}^{(1,m)}$ because the coefficients $Q_i^{(1)}(R_{\text{sys}},R_{\text{solv}}^{(m)})r_i$ depend on the solvent configuration. Thus, any diabatization algorithm would appear to require modeling the solvent, either explicitly as molecules or as a PCM.

Nevertheless, although computing $Q_x^{(1)}$, $Q_y^{(1)}$, and $Q_z^{(1)}$ formally requires $R_{\text{solv}}^{(m)}$, note that if all three component operators of $\mathbf{r}$, i.e., $\mathbf{x},\mathbf{y},\mathbf{z}$, were diagonalized simultaneously, then $H_{\text{int}}^{(1,m)}$ would automatically be diagonal and minimization would be trivial. Now, even though $\mathbf{x},\mathbf{y},\mathbf{z}$ cannot be simultaneously diagonalized in the subspace $\mathcal{W}$, an approximate diagonalization of all three operators in the subspace $\mathcal{W}$ can be achieved by rotating the basis states $\{|\Phi_n\rangle\}$ into new states $\{|\Xi_l\rangle\}$, where the variances of the $\mathbf{x},\mathbf{y},\mathbf{z}$ operators are minimal. It is important to note that, for any operator A and state η, if $\langle\eta|A^2|\eta\rangle - \langle\eta|A|\eta\rangle^2 = 0$, then η is an eigenvector of A.

Thus, we propose to rotate the adiabatic states into diabatic states as in Eq. (5) where we fix the rotation matrix U by minimizing the sum of the variances of each Cartesian component in each of the different rotated states,

$$\begin{aligned} f_{\text{Boys}}(\mathbf{U}) &= f_{\text{Boys}}(\{\Xi_i\}) \\ &= \sum_{l=1}^{N_{\text{states}}} \sum_{i=x,y,z} (\langle\Xi_l|r_i^2|\Xi_l\rangle - \langle\Xi_l|r_i|\Xi_l\rangle^2). \end{aligned} \tag{22}$$

Equation (22) is a reasonable minimization criterion because the linear expansion of a complex three-dimensional system-solvent interaction into three terms is a very compact representation, and minimizing the sum of the variances of all three dipole operators $(\mathbf{x},\mathbf{y},\mathbf{z})$ can be accomplished easily and effectively. As a bonus, minimization of Eq. (22) is invariant to translation of the origin or rotations of the coordinate axes [see Eq. (23)].

Now, minimizing Eq. (22) generates approximate eigenvectors of $H_{\text{int}}^{(1,m)}$ without any detailed knowledge of the solvent coordinate $R_{\text{solv}}^{(m)}$. Thus, for each solvent configuration $R_{\text{solv}}^{(m)}$, it would be pointless for us to find the exact $|\Xi_m\rangle$ that minimizes $\langle\Xi_m|H_{\text{int}}^{(1,m)}|\Xi_m\rangle$. Instead, we should assume that each basis function in the set $\{|\Xi_l\rangle\}$ corresponds to the optimal electronic state for a different solvent configuration, $R_{\text{solv}}^{(l)}$. This interpretation is particularly reasonable if each of the states in $\{|\Xi_l\rangle\}$ keeps excess charge localized on a different charge center. In that case, we will argue that the set $\{|\Xi_l(r;R_{\text{sys}})\rangle\}_{l=1}^{N_{\text{states}}}$ is a complete set of diabatic states for our system within the energy range defined by $\mathcal{W}$. At the same time, if two diabatic states have charge localized on the same center, the system Hamiltonian should be rediagonalized within this two-dimensional subspace to generate unique, locally adiabatic diabatic states. This completes our recipe for constructing the diabatic states of the electron transfer system.

Solving Eqs. (5) and (22) is exactly equivalent to the Boys algorithm, which was shown previously to give charge-localized diabatic states relevant to electron transfer.[27] This localization property of the Boys algorithm becomes most obvious if, using the fact that the trace of an operator is invariant to representation, we maximize Eq. (23) rather than minimize Eq. (22),

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$$f_{\text{Boys}}(\mathbf{U}) = f_{\text{Boys}}(\{\Xi_i\}) = \sum_{i,j=1}^{N_{\text{states}}} |\langle \Xi_i|\vec{\mu}|\Xi_i\rangle - \langle \Xi_j|\vec{\mu}|\Xi_j\rangle|^2. \tag{23}$$

Moreover, if we were to pick a charge transfer direction $\mathbf{v}_0$ and diagonalize the operator $\hat{\mathbf{r}}\cdot\mathbf{v}_0$ in the subspace $\mathcal{W}$, we would recover the GMH formalism. At this point, we have approximately justified the Boys and GMH algorithms on physical grounds, and we have motivated why it is important to rotate together only adiabatic states that are close in energy.

One final point must be made about Boys localization. The form of Eq. (23) should remind the reader that Boys localized diabatic states are applicable only for electron transfer and not for energy transfer.[56] The optimization function f_{Boys} in Eq. (23) seeks to separate the centers of charge between different diabatic states and if we focus on a subspace $\mathcal{W}$ of adiabatic states (within a certain energy range) that exhibits energy transfer and not electron transfer, we will find that the sum f_{Boys} is invariant to rotations in $\mathcal{W}$ and cannot be optimized. In such cases, the system-solvent interaction is not linear in space and cannot be described by the linear term in Eq. (21). Instead, we must work with a more general expression for the system-solvent interaction potential.

2. Linear response of the solvent: ER diabatic states and electron/energy transfer

Beyond the case of solvent fields which are linear in space, a more robust approximation to Eq. (20) is for us to assume that the response of the solvent is a linear function of the state of the system. With that in mind, we denote the electrostatic potential at a point $\underset{\sim}{\vec{\mathbf{r}}}_1$ in space *caused only by the system* as

$$\phi_{\text{sys}}(\underset{\sim}{\vec{\mathbf{r}}}_1) = \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \frac{\langle \hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_2)\rangle}{|\underset{\sim}{\vec{\mathbf{r}}}_1 - \underset{\sim}{\vec{\mathbf{r}}}_2|} + V_{\text{nuc}}(\underset{\sim}{\vec{\mathbf{r}}}_1). \tag{24}$$

Here, the bracket $\langle\ \rangle$ denotes that the density operator $\hat{\rho}$ must be evaluated in the state of the system.

We now assume that the solvent acts as a linear dielectric, with dielectric constant ϵ. Thus, the electrostatic potential from the solvent should be linearly proportional to the electrostatic potential from the system, with a constant $(1-\epsilon)/\epsilon$,

$$\phi_{\text{int}}(\underset{\sim}{\vec{\mathbf{r}}}_1) = \frac{1-\epsilon}{\epsilon}\phi_{\text{sys}}(\underset{\sim}{\vec{\mathbf{r}}}_1). \tag{25}$$

It follows that the total system-solvent interaction is nonlinear and can be written as

$$H_{\text{int}} = \frac{1-\epsilon}{\epsilon}\int d\underset{\sim}{\vec{\mathbf{r}}}_1 \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \frac{\langle \hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_2)\rangle \hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)}{|\underset{\sim}{\vec{\mathbf{r}}}_1 - \underset{\sim}{\vec{\mathbf{r}}}_2|} + \frac{1-\epsilon}{\epsilon}\int d\underset{\sim}{\vec{\mathbf{r}}}_1 V_{\text{nuc}}(\underset{\sim}{\vec{\mathbf{r}}}_1)\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1). \tag{26}$$

Equations (25) and (26) are commonly used in solid state physics when computing solvation energies and screening effects for a system immersed in a linear dielectric.[57] If we seek a diabatic state $|\Xi_i\rangle$ which minimizes the system-solvent interaction energy, we must minimize the energy,

$$E_{\text{int}}^{(i)} = \frac{1-\epsilon}{\epsilon}\left(\int d\underset{\sim}{\vec{\mathbf{r}}}_1 \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \frac{\langle \Xi_i|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_2)|\Xi_i\rangle\langle \Xi_i|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_i\rangle}{|\underset{\sim}{\vec{\mathbf{r}}}_1 - \underset{\sim}{\vec{\mathbf{r}}}_2|} + \int d\underset{\sim}{\vec{\mathbf{r}}}_1 \langle \Xi_i|V_{\text{nuc}}(\underset{\sim}{\vec{\mathbf{r}}}_1)\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_i\rangle\right). \tag{27}$$

Because we seek a complete set of orthogonal diabatic states, it would not be fruitful to search for the global minimum of Eq. (27). Instead, we will search for the rotation matrix $\mathbf{U}$ in Eq. (5) which minimizes the sum of the system-solvent interactions for each orthonormal diabatic state. The second term in Eq. (27) (arising from the system nuclear potential) is then a constant because the nuclei are fixed and the resulting trace is invariant to representation. Hence, because the dielectric constant of a condensed environment satisfies $\epsilon > 1$, we must maximize

$$f_{\text{ER}}(\mathbf{U}) = f_{\text{ER}}(\{\Xi_i\}) = \sum_{i=1}^{N_{\text{states}}} \int d\underset{\sim}{\vec{\mathbf{r}}}_1 \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \frac{\langle \Xi_i|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_2)|\Xi_i\rangle\langle \Xi_i|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_i\rangle}{|\underset{\sim}{\vec{\mathbf{r}}}_1 - \underset{\sim}{\vec{\mathbf{r}}}_2|}. \tag{28}$$

Because of its similarity to Eq. (9), Eq. (28) should be called the ER function for localizing diabatic states. In Appendix A, we show how to maximize the function f_{ER} in the context of configuration interaction singles (CIS) excited states.

In Sec. III, we give chemical examples showing that ER localization successfully generates diabatic states applicable both to electron transfer and energy transfer. In this sense, ER localization is much more powerful than Boys localization.

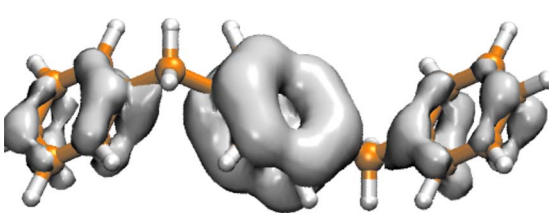

FIG. 1. (Color online) Detachment density plot for an adiabatic excited state in the trans conformer of OMP3. Note that the detached and attached densities are both delocalized over the molecule.

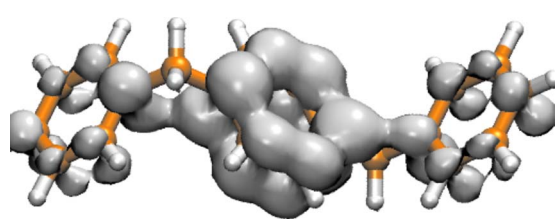

FIG. 2. (Color online) Attachment density plot for an adiabatic excited state in the *trans* conformer of OMP3.

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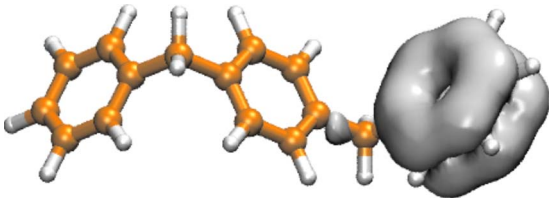

FIG. 3. (Color online) Detachment density plot for an ER localized diabatic excited state in the *trans* conformer of OMP3. Note that the detached density is localized on one and the same benzene monomer as the attached density. This state with a localized electron-hole pair could be called an exciton.

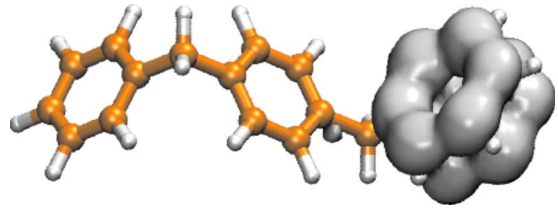

FIG. 4. (Color online) Attachment density plot for an ER localized diabatic excited state in the *trans* conformer of OMP3.

3. A delta function potential between free and induced charges: VNER diabatic states

For completeness, in Appendix B, we present a third algorithm for constructing diabatic states, the VNER formalism. The VNER approach can be derived by assuming that the solvent responds linearly to the system, but free charges in the system interact with induced charges in the solvent via a delta function in real space (rather than by Coulomb's law). VNER diabatic states satisfy a maximally different density criterion and have elements in common with both Boys and ER localized diabatic states.

III. A CHEMICAL EXAMPLE: OLIGOMETHYLPHENYL-3, ENERGY TRANSFER, AND THE CONDON APPROXIMATION

A previous article has already demonstrated that Boys localization leads to charge-localized diabatic states.[27] In order to verify that ER localization does the same, we have performed straightforward CIS calculations on linear $[\mathrm{Na-Be-Na}]^{2+}$ in a 6-31G* basis, where the Na–Be distance is 5 Å. All electronic structure calculations were performed using the Q-CHEM package.[58] In the ground state of the molecule, after a HF calculation, the Be atom is neutral and both Na atoms have charge +1. The first and second adiabatic excited states of the system, $|\Phi_1\rangle$ and $|\Phi_2\rangle$, are nondegenerate delocalized charge transfer states, wherein Be donates an electron into orbitals on *both* Na atoms. Performing either ER or Boys localization on the subspace $\mathcal{W}=|\Phi_1\rangle\oplus|\Phi_2\rangle$ produces two energetically degenerate diabatic states, $|\Xi_1\rangle$ and $|\Xi_2\rangle$, each with excess charge localized on a separate Na atom. The diabatic coupling elements between the two states are identical for the two algorithms. More details of this simple case are given in the online EPAPS depository,[59] including attachment/detachment plots. We conclude that, similar to Boys localization, ER localization can indeed describe diabatic states appropriate for charge transfer. The more challenging test, however, is whether ER can describe diabatic states appropriate for energy transfer. We demonstrate this now for one chemical example.

Consider the molecule shown in Figs. 1 and 2, where three benzene rings are attached together by two CH_2 single bonds. For notational ease, we will call this molecule oligomethylphenyl-3 (OMP3). CIS calculations for OMP3 in a 6-31G* basis in the HF optimized ground state geometry show that the six lowest-lying excited states have energies 6.137, 6.138, 6.267, 6.291, 6.427, and 6.553 eV relative to the ground state. The next lowest excited states begin at 7.652 eV and will be ignored. Figures 1 and 2 are attachment/detachment[60] plots for one of these six adiabatic states which shows that in the adiabatic picture, both the detached and attached electron density are delocalized over the whole molecule. According to Figs. 1 and 2, the effective detached electron comes from the π system and the attached electron goes into the π^* system.

Given that the six lowest excited states of OMP3 are so close in energy, we propose that these six states should be mixed together and diabatized according to the ER algorithm above, which should approximately represent solvent (or vibrational) effects. In order to check the Condon approximation, we have performed this diabatization procedure both for the *gauche* and *trans* conformers of OMP3, checking the sensitivity of the coupling element H_{AB} to nuclear geometry.

In contrast to the delocalized picture of electronic excitation in the adiabatic basis, the attachment/detachment plots in Figs. 3–6 show that the electronic excitation can be viewed as local in the basis of diabatic states. For each diabatic state, the attached and detached electron appears to be localized in the π and π^* orbitals of one specific monomer. Note that after the initial ER localization, we find two diabatic states with electron-hole pairs on each benzene monomer. In order to generate the locally adiabatic diabatic ER states shown in Figs. 3–6, we have rotated within each two-dimensional subspace so that the final Hamiltonian is diagonal between states with excitation energy on the same center. As described above, our intuition is that states with excitations (or charge) on the same center should be uncoupled, as the effect of solvent should be minimal between states so close together. We admit, however, that this approach is not general and cannot be rigorously justified. Nevertheless, it is comforting that the attachment/detachment plots of the ER diabatic states before and after this final diagonalization look very similar. Finally, we mention in passing that unlike ER diabatization, Boys localization (with the dipole operator) produces erratic and unphysical diabatic states with delocalized electron-hole pairs for this molecule.[56]

In Table I, we give the diabatic coupling elements ($H_{AB}=\langle\Xi_A|H_{\mathrm{el}}|\Xi_B\rangle$) between ER diabatic states. From the data, the six excited states can be separated into two sets of three, those with even state numbers and those with odd state numbers, and each set is nearly uncoupled from the other. Let us label the degenerate highest occupied molecular orbitals of benzene π_1 and π_2, and the degenerate lowest unoccupied molecular orbitals π_1^* and π_2^*. Because the diabatic states shown in Figs. 3–6 show no nodal plane perpendicular to the benzene plane, it is likely that the two diabatic states

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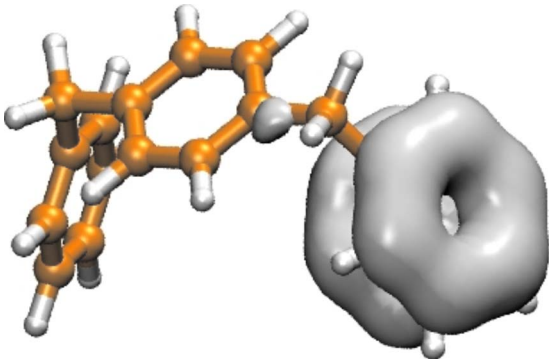

FIG. 5. (Color online) Detachment density plot for an ER localized diabatic excited state in the *gauche* conformer of OMP3. Note that the detached density is localized on one and the same benzene monomer as the attached density. This state with a localized electron-hole pair could be called an exciton.

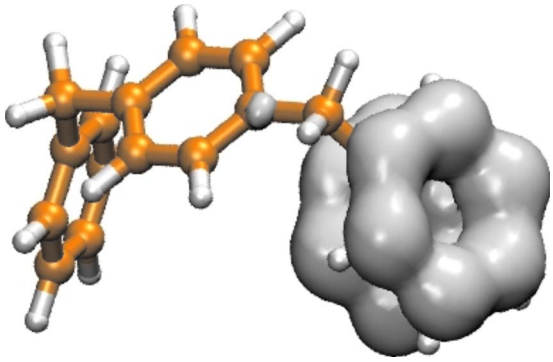

FIG. 6. (Color online) Attachment density plot for an ER localized diabatic excited state in the *gauche* conformer of OMP3.

on each benzene monomer are approximately $|\Xi_{1,2}\rangle = (1/\sqrt{2})((\pi_1^*)^\dagger \pi_1 \pm (\pi_2^*)^\dagger \pi_2)|\Psi_{\mathrm{HF}}\rangle$. In this second-quantized expression, we imagine replacing π_1 by π_1^* and π_2 by π_2^*, and adding or subtracting the two singly substituted Slater determinants. This rough picture of the diabatic states would fit the attachment/detachment density seen in Figs. 3–6, although this is not conclusive.

According to Table I for both groups of diabatic states, the nearest-neighbor diabatic couplings are very similar between the *trans* and *gauche* conformers, agreeing with the Condon principle that H_{AB} should be insensitive to nuclear geometry. Between diabatic states on opposite ends, however, the diabatic coupling is dramatically changed, in one case increasing by a factor of 3. This reflects the fact that the opposite benzene monomers become much closer when the molecule is rotated around the methylene group. Moreover, for the *gauche* conformation, the odd and the even groups of states are coupled more strongly than they are in the trans conformation. Nevertheless, the nearest-neighbor diabatic couplings within each group are still one to two orders of magnitude larger than all other couplings, and because these couplings vary only minimally from *trans* to *gauche*, the Condon approximation largely holds for the molecule.

Finally, note that we have calculated diabatic states and H_{AB} elements at the ground state geometry of the molecule, rather than at the formal transition state geometry, where the edge and middle states would be degenerate. While the latter geometry would be more common in typical Marcus theory electron or energy transfer applications, we point out that within each group, the energies of our diabatic states are within 0.15 eV. By contrast, for the adiabatic states, the spread in energies is approximately 0.41 eV. We also note that the on-diagonal energies of the diabatic states change only minimally (<0.01 eV) between the *trans* and *gauche* conformations. In the end, these ER diabatic states conform to our expectations of the initial and final states of an energy transfer process.

TABLE I. The diabatic coupling elements (H_{AB}) for the ER diabatic states of OMP3 in units of electron volts (eV). Here, we have included six adiabatic excited states in our subspace $\mathcal{W}$ and, because of symmetry, we find two groups of three states that are nearly uncoupled (i.e., the odd and even numbered states below). The six adiabatic excited states were computed with CIS in a 6-31G* basis. Because the nearest-neighbor couplings are very similar for both *trans* and *gauche* conformers, the ER diabatic states obey the Condon approximation.

State		1	2	3	4	5	6
	Monomer	Center	Center	Left	Left	Right	Right
				(a) *Trans* conformation			
1	Center	6.1615	0	−0.0394	1×10^{-5}	0.0396	−0.0001
2	Center		6.2759	0.0002	0.1384	−0.0003	0.1383
3	Left			6.2673	0	4×10^{-5}	0.0007
4	Left				6.4213	−0.0007	−0.0061
5	Right					6.2671	0
6	Right						6.4212
				(b) *Gauche* conformation			
1	Center	6.1609	0	−0.0395	0.0011	0.0391	−0.0011
2	Center		6.2736	−0.0010	−0.1391	−0.0011	−0.1388
3	Left			6.2670	0	0.0001	−0.0011
4	Left				6.4204	−0.0009	−0.0068
5	Right					6.2669	0
6	Right						6.4203

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IV. DISCUSSION AND SUMMARY

Rather than seeking diabatic states with zero derivative couplings, in this paper, we have examined diabatic states which describe a system interacting with a polar solvent before or after an electron or energy transfer process. In practical terms, we have proposed constructing such diabatic states by (i) calculating the adiabatic states of the system without solvent; (ii) grouping together those adiabatic states that fall within an energy window approximately equal to the reorganization energy of the solvated system; (iii) performing either Boys or ER localization on this relevant subspace of adiabatic states. Both the Boys and ER diabatization schemes have very physical foundations, and we believe both will be successful in describing nonequilibrium transport phenomena. Boys localization is based upon a system-solvent potential that is linear in space and is applicable to electron transfer. ER localization is based upon linear response of the solvent to the system and is applicable to both electron and energy transfer. Overall, the ER method satisfies all six of the desirable criteria for diabatization algorithms listed in Sec. I D, and the Boys method satisfies five. We emphasize that neither algorithm requires definitions of charge fragments (unless multiple diabatic states have charge or excitation energy on the same atom center or monomer and we choose to rediagonalize the Hamiltonian within this subblock). For the OMP3 problem, the compatibility of the ER approach with the Condon approximation is encouraging and the attachment-detachment plots in Figs. 3–6 agree with our intuition for the shape of excitons in this system.

Although we have tried to be as rigorous as possible in deriving the Boys and ER diabatization algorithm above from system-solvent interactions, we would now like to analyze the approximations made in modeling the effect of solvent and make explicit the limitations of our approach.

A. Assumption of nearly degenerate, well-separated system states in a polar solvent environment

Our methods of diabatization assume that the relevant adiabatic system states are nearly degenerate and can be grouped together in a subspace $\mathcal{W}$. Furthermore, we assume that changes in the system-solvent interaction ΔH_{int} are on the order of the reorganization energy, which is small compared to the full energy spectrum of the system but large compared to the energy width of the nearly degenerate states. It follows that diabatic states can be constructed by minimizing H_{int} in the subspace $\mathcal{W}$. These two assumptions have clear limitations, however.

First, for a general molecule or system, there is no guarantee that the adiabatic states of interest will be close in energy but well separated from other states. Such a case would appear to be the exception rather than the rule. Moreover, in practice, when doing electronic structure calculations with active space models (e.g., CASSCF/CASPT2), unwanted "intruder" states can appear that are not physical or dynamically important.[61] Thus, for real *ab initio* calculations, there is not always a black-box algorithm for picking adiabatic states to mix together in order to form meaningful diabatic states, and some physical intuition may be necessary, using properties other than just energy. For difficult cases, when choosing the appropriate adiabatic states to mix together, investigating the sizes of derivative couplings may be helpful as a last resort.

Second, when diagonalizing H_{int} instead of $H_{\text{int}}+H_{\text{sys}}$ in this subspace, we assume that solvent effects are strong and, thus, the algorithm here can work only with a polar solvent strongly coupled to the system. For less extreme conditions, besides applying PCM for the solvent, one approach to balance the quantum mechanical system energetics (H_{sys}) with the electrostatic system-solvent interaction (H_{int}) would be to introduce an empirical parameter α, such that the diabatic states are the minimal solution to either

$$f_{\text{ER}}^{\text{comp}} = \alpha \sum_{l=1}^{N_{\text{states}}} (\langle \Xi_l | H_{\text{sys}}^2 | \Xi_l \rangle - \langle \Xi_l | H_{\text{sys}} | \Xi_l \rangle^2) + (1-\alpha) \int d\vec{\mathbf{r}}_1 \int d\vec{\mathbf{r}}_2 \frac{\langle \Xi_l | \rho(\vec{\mathbf{r}}_1) | \Xi_l \rangle \langle \Xi_l | \rho(\vec{\mathbf{r}}_2) | \Xi_l \rangle}{|\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2|}, \tag{29}$$

$$f_{\text{Boys}}^{\text{comp}} = \alpha \sum_{l=1}^{N_{\text{states}}} (\langle \Xi_l | H_{\text{sys}}^2 | \Xi_l \rangle - \langle \Xi_l | H_{\text{sys}} | \Xi_l \rangle^2) + (1-\alpha) \sum_{l=1}^{N_{\text{states}}} \sum_{i=x,y,z} (\langle \Xi_l | r_i^2 | \Xi_l \rangle - \langle \Xi_l | r_i | \Xi_l \rangle^2). \tag{30}$$

When $\alpha=0$, we recover either the Boys or the ER diabatic states. When $\alpha=1$, we recover the adiabatic states. The computational cost of solving Eq. (29) is identical to solving Eq. (28), and the cost of solving Eq. (30) is identical to Eq. (22). For weak system-solvent interactions, it may be beneficial to see whether choosing $0<\alpha<1$ best matches experiment. Similar attempts to mix energetic effects with locality effects within the context of molecular orbital theory have had moderate success.[62] A good choice for α would necessarily depend on the dielectric constant of the solvent and diabatic states computed with Eqs. (29) and (30) should be compared to models using PCM for the solvent.

B. Electrostatic assumption

Both the Boys and ER diabatization schemes have assumed that H_{int} arises only from electrostatics. This allowed us to use one-electron operators [either $\hat{\mathbf{r}}$ or $\rho(\vec{\mathbf{r}})$] to approximate the effect of solvent on the system, which makes diabatization practical and fast. It is worthwhile, however, to consider under what circumstances the system-solvent interactions can be safely modeled by a one-electron electrostatic operator.

Interactions with solvent may induce strong effects between different system electrons, and these are not included in our Hamiltonian [Eq. (21)], especially given that we diagonalize H_{int} instead of $H_{\text{int}}+H_{\text{sys}}$. We are also ignoring charge transfer between system and solvent and induced dipole-dipole effects, which could both be important. In particular, for the problem of energy transfer, we have assumed that local electronic excitations will lead to different charge dis-

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tributions, and that the solvent response to these electrostatic changes is enough to stabilize excitons, which may not always be true. Many different physical effects may force the system-solvent interaction to be neither electrostatic nor a one-electron operator, and for comparison future research should explore diabatization using alternative *ansätze* for the interaction. In particular, for a higher computational cost, it may be possible to construct better diabatic states using both one-electron and two-electron operators to account more accurately for both external and internal interactions.

Beyond electrostatics, we remind the reader that Boys localization makes the additional assumption that the system-solvent interaction potential has a valid multipole expansion near the system which is dominated by the linear term. In the future, it will be very interesting to compare ER results with Boys localization computations on charge transfer systems, and assess the relative accuracy of each method. If our experience with orbitals is relevant, different localization schemes usually agree qualitatively, except in cases of symmetry (π versus σ, etc.). For the trivial example of $[\mathrm{Na-Be-Na}]^{2+}$ in Sec. III, the ER and Boys localized diabatic states were identical.

C. Derivative couplings and potential energy surfaces

Beyond the limitations expressed above, there remains the question of how Boys or ER localized diabatic states compare to more standard diabatization algorithms. To connect our diabatization scheme with other approaches, the size of the derivative couplings[63] must be small. Second, near a conical intersection where analytical forms exist for exact diabatic states, the behavior of diabatic couplings and derivative couplings produced with Boys localized states must match standard solutions. These computational benchmarks will yield important information toward understanding and validating Boys localization and the ER approach. We are currently implementing the necessary code to perform such calculations, and we will report our results in a later communication.

A separate concern is to whether the potential energy surfaces and off-diagonal coupling terms are smooth in the basis of Boys or ER diabatic surfaces. In this article, we have performed diabatization at one geometry alone, which was chosen to resemble the nonadiabatic transition state. We have not checked for smoothness of the global potential energy surface, which will likely be problematic because, as the molecular geometry changes, different adiabatic states will necessarily enter and leave the energetic window defined by the $\mathcal{W}$ subspace. Moreover, we have not examined the shape of the potential energy curves in the vicinity of a crossing point. We presume that one can compute the analytical gradients (with respect to nuclear displacements) of the energies of these diabatic states, although we have not yet done so. For these reasons, use of the Boys or ER diabatic states as a complete basis for chemical dynamics requires more benchmarking and may be challenging.

Ultimately, however, the usefulness of any diabatization algorithm for electron and energy transfer can be measured only by how well it matches experiment. In the near future, we hope to use Boys localization and ER to generate diabatic states for *ab initio* models of electron or energy transfer for comparison with experimental data.

D. Computational cost

Before finishing this discussion, we want to emphasize that if optimally implemented, both algorithms discussed here are computationally inexpensive and will never be rate-limiting compared to the necessary electronic structure calculations. Like GMH, Boys localization requires as input only the dipole matrices in the basis of adiabatic states, and because these are one-electron operators, they can usually be computed with effectively zero cost. Likewise, the ER approach also requires matrix elements of one-electron operators $a_r^\dagger a_s$ in the basis of adiabatic states, which have effectively zero cost. See Appendix A for details on how the ER algorithm is applied in the context of CIS excited states.

Although neither Boys localization nor ER have a transportable formula for predicting the H_{AB} coupling elements such as GMH, the standard algorithm for optimizing quartic functions of rotation matrices converges rapidly using so-called Jacobi sweeps.[47,48,64] Because Boys localization requires the storage of only a quadratic number of variables, the algorithm runs almost instantaneously compared to any prerequisite electronic structure method no matter how big the system size. The ER algorithm scales worse than the Boys localization because one must work with the two-electron matrix elements of $1/r_{12}$, i.e., $(\mu\nu|\lambda\sigma)$ (see Appendix A). Nevertheless, if one uses the sparsity of the atomic orbital basis and one works in a subspace $\mathcal{W}$ with fewer than twenty adiabatic states (as would be expected usually), an optimal implementation of the ER algorithm should be fast, with only a marginal increase in computational cost after the necessary electronic structure calculations. Recent advances with resolution of the identity (RI) methods have made ER localization for orbitals relatively inexpensive,[64,65] and the same should be true for ER localization of diabatic states. See Appendix A for more details.

Ultimately, both Boys localization and ER can be applied to large chemical systems, where they can model either electron transfer or energy transfer (in the case of ER). This applicability to large systems is not true for other diabatization approaches involving analytical derivative couplings, which are very computationally expensive to calculate.

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APPENDIX A: IMPLEMENTATION OF ER DIABATIZATION AS APPLIED TO CIS EXCITED STATES

For concreteness, we derive the principal equations necessary for implementing ER localization of CIS excited states. Many of the equations below can be found also in the work of Hsu and co-workers.[33–35] For the remainder of this subsection, many-electron states are indexed with capital letters $\{I,J,K,L,M\}$ and molecular spin orbitals are indexed by lower-case letters: $\{i,j\}$ identify occupied orbitals, $\{a,b\}$ identify virtual orbitals, and $\{p,q,r,s\}$ identify either occupied or virtual orbitals. States are labeled by capital Greek letters (adiabatic states Φ, diabatic states Ξ) and orbitals are labeled by lower-case Greek letters (ϕ).

ER localization for a group of adiabatic excited states $\{|\Phi_I\rangle\}$ is defined by the rotation $\mathbf{U}$ satisfying

$$|\Xi_I\rangle = \sum_J |\Phi_J\rangle U_{JI}, \tag{A1}$$

$$f_{\mathrm{ER}}(\mathbf{U}) = \max_{\{\Xi_I\}} \sum_{I=1}^{N_{\mathrm{states}}} \int d\underset{\sim}{\vec{\mathbf{r}}}_1 \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \frac{\langle \Xi_I|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_2)|\Xi_I\rangle\langle \Xi_I|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_I\rangle}{|\underset{\sim}{\vec{\mathbf{r}}}_1 - \underset{\sim}{\vec{\mathbf{r}}}_2|}. \tag{A2}$$

The one-electron density of diabatic state I at position $\underset{\sim}{\vec{\mathbf{r}}}$ can be expressed using second-quantized operators in the basis of molecular orbitals as

$$\langle \Xi_I|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}})|\Xi_I\rangle = \sum_{rs} \langle \Xi_I|c_r^\dagger c_s|\Xi_I\rangle \phi_r(\underset{\sim}{\vec{\mathbf{r}}})\phi_s(\underset{\sim}{\vec{\mathbf{r}}}) \tag{A3}$$

$$= \sum_{JK} U_{JI}U_{KI} \sum_{rs} \langle \Phi_J|c_r^\dagger c_s|\Phi_K\rangle \phi_r(\underset{\sim}{\vec{\mathbf{r}}})\phi_s(\underset{\sim}{\vec{\mathbf{r}}}) \tag{A4}$$

For CIS excited states, the ansatz of the adiabatic wave function is

$$|\Phi_J\rangle = \sum_{ia} t_i^{Ja} c_a^\dagger c_i |\Phi_{\mathrm{HF}}\rangle. \tag{A5}$$

According to Wick's theorem, it follows that the density matrix D is

$$D_{rs}^{JK} = \langle \Phi_J|c_r^\dagger c_s|\Phi_K\rangle, \tag{A6}$$

$$= \begin{cases} \sum_i t_i^{Jr} t_i^{Ks}, & r,s = \text{virtual} \\ -\sum_a t_r^{Ja} t_s^{Ka} + \delta_{rs}\delta_{JK}, & r,s = \text{occupied}. \end{cases} \tag{A7}$$

Finally, using the chemists' notation for the two-electron Coulomb integral $(rs|pq)$,[51] f_{ER} can be expressed as

$$f_{\mathrm{ER}}(\mathbf{U}) = \sum_{IJKLM} U_{JI}U_{KI}U_{LI}U_{MI} \sum_{rspq} D_{rs}^{JK} D_{pq}^{LM} \int d\underset{\sim}{\vec{\mathbf{r}}}_1 \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \times \frac{\phi_r(\underset{\sim}{\vec{\mathbf{r}}}_1)\phi_s(\underset{\sim}{\vec{\mathbf{r}}}_1)\phi_p(\underset{\sim}{\vec{\mathbf{r}}}_2)\phi_q(\underset{\sim}{\vec{\mathbf{r}}}_2)}{|\underset{\sim}{\vec{\mathbf{r}}}_1 - \underset{\sim}{\vec{\mathbf{r}}}_2|}, \tag{A8}$$

$$= \sum_{IJKLM} U_{JI}U_{KI}U_{LI}U_{MI} R_{JKLM}, \tag{A9}$$

$$R_{JKLM} = \sum_{rspq} D_{rs}^{JK}(rs|pq) D_{pq}^{LM} \tag{A10}$$

Equation (A9) shows that ER localization of diabatic states is identical to ER localization of orbitals. All standard localization algorithms are quartic functions of the unitary matrix $\mathbf{U}$ and can be solved with standard "Jacobi sweeps"[48] or with other iterative approaches.[64,65] Because we do not anticipate having too many states to localize (usually, under 20) and computing an element of the tensor R_{JKLM} will be expensive, Jacobi sweeps should be the most attractive approach for ER localization of states. In order to have a fast implementation of ER diabatization, the key bottleneck to overcome will be computing the tensor R_{JKLM} in Eq. (A10) quickly. Research is currently ongoing to develop an algorithm to make this contraction as fast as possible. In calculations for this paper, we have computed R_{JKLM} using the RI-approximation[69] with an auxiliary basis $(\tilde{y},\tilde{z})$,

$$R_{JKLM} = \sum_{rspq} \sum_{\tilde{y}\tilde{z}} D_{rs}^{JK}(rs|\tilde{y})(\tilde{y}|\tilde{z})^{-1}(\tilde{z}|pq) D_{pq}^{LM}. \tag{A11}$$

In the future, we expect that this contraction can be made much faster.

Finally, we note that the form of Eqs. (A8)–(A10) is completely general and can be applied to arbitrary excited states, not just CIS states. The largest obstacle will be computing the tensor $D_{rs}^{JK} = \langle \Phi_J|c_r^\dagger c_s|\Phi_K\rangle$ when $|\Phi_J\rangle$ and $|\Phi_K\rangle$ are not CIS excited states. For CIS, Eq. (A7) is simple to derive and the three terms are the density of attached electrons, detached electrons, and the ground state. The ground state density is just a constant and does not affect Boys or ER localization, suggesting a connection with the FED approach—FED only uses electron attachment/detachment densities.

APPENDIX B: THE MAXIMUM DENSITY DIFFERENCE CRITERION: VON NIESSEN–EDMISTON–RUEDENBERG DIABATIC STATES

In Secs. II C 1 and II C 2 above, we derived Boys and ER diabatization on the basis of system-solvent interactions. Boys localization was based upon a linear expression for the interaction potential in terms of the $\mathbf{x},\mathbf{y},\mathbf{z}$ operators, and ER was based upon a linear response of the solvent to system. We now derive a third diabatization scheme, which shares similarities with both standard algorithms and may also prove useful. Because of the similarity to VNER localization [see Eq. (11)], these diabatic states should be called VNER diabatic states.

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Recall that in our derivation of Boys localization, although we wanted to minimize H_{int} in Eq. (21) directly, instead our approach was to minimize the sum of the variances of the three dipole operators, $\mathbf{x},\mathbf{y},\mathbf{z}$. This was a reasonable proposition because we did not know the coefficients in front of the different dipole operators, but the linear expansion of a complex three-dimensional system-solvent interaction into three terms is a very compact representation, and minimizing the sum of the variances of each operator was effective. As a bonus, the resulting Boys localization algorithm was invariant to translation of the origin or rotations of the coordinate axes.

Now, according to Eqs. (19) and (20), even when the system-solvent potential is not linear in space, the interaction can always be expanded over an infinite number of operators indexed by $\underset{\sim}{\vec{\mathbf{r}}}$, namely, $\{\rho(\underset{\sim}{\vec{\mathbf{r}}})\}$, where $\underset{\sim}{\vec{\mathbf{r}}}$ can be any position in real, three-dimensional space. Moreover, this expansion is actually a compact description of the system-solvent interaction because electrostatic potential energies are diagonal only in position space (and not in momentum space). Thus, just like for Boys localization, we can attempt to diagonlize H_{int} in Eq. (19) by minimizing the integral of the variances of all of the $\{\rho(\underset{\sim}{\vec{\mathbf{r}}})\}$ operators,

$$f_{\text{VNER}}(\mathbf{U}) = f_{\text{VNER}}(\{\Xi_i\}) = \sum_{l=1}^{N_{\text{states}}} \int d\underset{\sim}{\vec{\mathbf{r}}}(\langle\Xi_l|\rho^2(\underset{\sim}{\vec{\mathbf{r}}})|\Xi_l\rangle - \langle\Xi_l|\rho(\underset{\sim}{\vec{\mathbf{r}}})|\Xi_l\rangle^2). \tag{B1}$$

Because the trace of an operator is invariant to representation, minimizing f_{VNER} is equivalent to maximizing

$$f_{\text{VNER}}(\mathbf{U}) = f_{\text{VNER}}(\{\Xi_i\}) = \sum_{k,l=1}^{N_{\text{states}}} \int d\underset{\sim}{\vec{\mathbf{r}}}(\langle\Xi_k|\rho(\underset{\sim}{\vec{\mathbf{r}}})|\Xi_k\rangle - \langle\Xi_l|\rho(\underset{\sim}{\vec{\mathbf{r}}})|\Xi_l\rangle)^2. \tag{B2}$$

Optimizing f_{VNER} breaks the near energetic degeneracy in $\mathcal{W}$ by rotating the adiabatic states so that their diabatic densities are maximally different. Thus, this approach has the flavor of the FCD approach[32] and the FED approach,[33–35] only without defining any fragments. Moreover, from the form of the function f_{VNER} in Eq. (B2), it is clear that similar to the Boys algorithm, VNER diabatization is invariant to translations and rotations of the origin.

Looking back at Eqs. (26)–(28), we see that the VNER approach can also be derived by assuming that the response of the solvent is linearly dependent on the system, but that the induced charges in the solvent interact via a delta function $\delta(\underset{\sim}{\vec{\mathbf{r}}}_1-\underset{\sim}{\vec{\mathbf{r}}}_2)$ with free charges in the system (instead of the Coulomb operator $1/|\underset{\sim}{\vec{\mathbf{r}}}_1-\underset{\sim}{\vec{\mathbf{r}}}_2|$),

$$f_{\text{VNER}}(\mathbf{U}) = \sum_{l=1}^{N_{\text{states}}} \int d\underset{\sim}{\vec{\mathbf{r}}}_1 \int d\underset{\sim}{\vec{\mathbf{r}}}_2 \langle\Xi_l|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_2)|\Xi_l\rangle \times \langle\Xi_l|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_l\rangle\delta(\underset{\sim}{\vec{\mathbf{r}}}_1-\underset{\sim}{\vec{\mathbf{r}}}_2), \tag{B3}$$

$$= \sum_{l=1}^{N_{\text{states}}} \int d\underset{\sim}{\vec{\mathbf{r}}}_1 \langle\Xi_l|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_l\rangle\langle\Xi_l|\hat{\rho}(\underset{\sim}{\vec{\mathbf{r}}}_1)|\Xi_l\rangle. \tag{B4}$$

Given the similarities between VNER and ER localization, VNER diabatic states should be applicable to both electron transfer and energy transfer, but this must be checked explicitly. One potential advantage of the VNER approach will be computational speed. Whereas ER localization requires the contraction of the two-electron Coulomb integral $(pq|rs)$ in Eq. (A10), the VNER approach requires only the one-electron overlap of four orbitals,

$$S_{pqrs} = \int d\underset{\sim}{\vec{\mathbf{r}}}\phi_p(\underset{\sim}{\vec{\mathbf{r}}})\phi_q(\underset{\sim}{\vec{\mathbf{r}}})\phi_r(\underset{\sim}{\vec{\mathbf{r}}})\phi_s(\underset{\sim}{\vec{\mathbf{r}}}). \tag{B5}$$

In an atomic orbital basis, $S_{\mu\nu\lambda\sigma}$ is much more sparse than $(\mu\nu|\lambda\sigma)$, and the VNER approach will be faster than ER localization, although still slower than Boys localization. In general, we expect the VNER approach to be a compromise between Boys and ER localization and it may also find use in future diabatization calculations.

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