

Diabatic couplings for charge recombination via Boys localization and spin-flip configuration interaction singles

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We describe a straightforward technique for obtaining diabatic couplings applicable to charge transfer from or charge recombination to the electronic ground state. Our method is nearly black box, requiring minimal chemical intuition from the user, and merges two well-established approaches in electronic structure theory: first, smooth and balanced adiabatic states are generated using spin-flip-configuration interaction singles (SF-CIS) based on a triplet HF state; second, Boys localization is applied to rotate all adiabatic states into charge-localized diabatic states. The method is computationally inexpensive, scaling only with the cost of CIS, and does not require a choice of active space, which is usually required for such intrinsically multiconfigurational problems. Molecular LiF in vacuum and LiF solvated by a single water molecule are examined as model systems. We find nearly smooth diabatic potential energy surfaces and couplings and we find that the Condon approximation is obeyed approximately for this model problem. © 2011 American Institute of Physics. [doi:10.1063/1.3615493]

I. INTRODUCTION: MODELING CHARGE RECOMBINATION

Charge transfer (CT) processes come in several varieties. In charge separation (CS), the magnitude of the difference of local charge between donor and acceptor fragments is increased, typically involving electron transfer between initially neutral donor and acceptor fragments. In charge recombination (CR), the reverse occurs, usually resulting in the system returning to its ground electronic state. Charge shift (CSH) processes are those in which electron density is exchanged, but the magnitude of the difference difference of local charge is constant; for example, an electron may be transferred from a neutral (anionic) donor to a cationic (neutral) acceptor. Of particular interest to us is the case of dye-sensitized solar cells. Here, a certain fraction of sunlight is absorbed by organic molecules, provoking photoinduced CS which can be harnessed to drive a current which powers a load. Of course, one can lose a lot of power if the organic molecule returns to its ground electronic state before permanent charge separation, generating heat via CR. Understanding and predicting the rates of CS and CR in candidate dye molecules is therefore essential for determining the potential efficiency of such a device.

The very simplest means to calculate CT rates in a condensed environment is the Marcus equation in the limit of thermal activation,

$$k_{\text{ET}} = \frac{2\pi}{\hbar} |H_{AB}|^2 \frac{1}{\sqrt{4\pi\lambda k_b T}} \exp\left(-\frac{(\lambda + \Delta G^\circ)^2}{4\lambda k_b T}\right). \quad (1)$$

Here, λ is the reorganization energy, ΔG° is the change in Gibbs free energy for the reaction, and H_{AB} is the diabatic

coupling. Among λ , ΔG , and H_{AB} , the former two quantities can be obtained by geometric optimization of adiabatic state energies using traditional electronic structure packages, assuming weak coupling. As its signifier (H_{AB}) suggests, the diabatic coupling is the off-diagonal Hamiltonian matrix element between the initial and final electronic states of the system, which enters all perturbation or golden rule expressions. Moreover, H_{AB} is the key matrix element which drives all nonadiabatic electronic transitions and thus figures prominently both in Marcus theory and all higher order perturbation theories and complicated rate expressions. Because the electronic states produced by conventional wavefunction methods are approximations to the full CI adiabatic solutions of the Schrödinger equation, which by definition have no off-diagonal position-local Hamiltonian elements, non-standard techniques are required to compute these important quantities as described below.

With that in mind, suppose we now seek to model a CT event for a particular molecule or molecular environment, and we begin with standard electronic structure calculations. In general, the initial and final electronic states for ET processes of model systems will not be adiabatic eigenstates for one of the following reasons: (i) the effect of external perturbations including solvent, which are often ignored due to computational cost, (ii) the effect of intramolecular motion, which is ignored when we consider frozen nuclei, or (iii) the initial experimental preparation of states. In each case, H_{AB} represents the energetic coupling between wavefunctions that are non-stationary with regard to the *in vacuo* electronic Hamiltonian.

Several computational techniques for approximating the diabatic couplings have been proposed in the literature.¹⁻³⁷ For reviews on this topic, see Refs. 1 and 2. One approach for determining couplings is constrained density functional theory (CDFT), developed by Van Voorhis *et al.*³⁻⁶ This method

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computes diabatic states directly by minimizing the energy of a system using Kohn-Sham density functional theory with the constraint that either spin or electronic density must be localized on some set of atomic centers. On the one hand, CDFT has the advantages of being physically motivated and computationally inexpensive. On the other hand, because CDFT constraints are applied manually, different results can be obtained for different choices of how to localize charge. In particular, CDFT may be less trustworthy for intramolecular CT, including for donor-bridge-acceptor (DBA) molecules, and as such, CDFT is often not ideal. Another direct approach developed by Newton, and later Larsson and co-workers, involves symmetry-broken self-consistent field (SCF) calculations, in which a SCF calculation with relaxed symmetry constraints finds localized states as solutions.^{7–16} Biorthogonalization of these states produces diabatic states.

A separate approach for diabatization is to first construct adiabatic states and then rotate these states together to form diabatic states. Several techniques have been proposed for generating this so-called adiabatic-to-diabatic rotation matrix, \mathbf{U} . Some focus on minimizing the derivative couplings,^{17–21} other focus on keeping a constant electronic character over configuration space,^{22,23} such as those proposed by Ruedenberg and Atchity^{24,25} and Truhlar and Nakamura.^{26–28} We will use localized diabatization techniques, where \mathbf{U} is chosen to imitate the localizing effects of some external perturbation, such as solvent or nuclear motion. Whereas CDFT forces the electron density to localize around arbitrary atomic centers, localized diabatization techniques can generate a set of diabatic states without any parametrization.

Notwithstanding the advantage of being parameter-free, methods that generate diabatic states by transforming adiabatic states have a particular difficulty with the specific case of CT reactions involving the ground state. The reason has nothing to do with localized diabatization and everything to do with basic electronic structure theory. The CR reactions as well as certain CS and CSh reactions involve transitions to or from the ground electronic state. Unfortunately, the standard practice in quantum chemistry is to compute a ground state first and subsequently generate excited states using the same ground state as a reference. The above procedure is true for CIS, equation of motion coupled-cluster singles and doubles, or time-dependent DFT (TD-DFT). As such, most wavefunction methods do not form ground and excited states equivalently or in a balanced manner; any diabatization scheme that produces diabatic states from such an unbalanced combination of such ground and excited adiabatic states cannot be expected to be accurate or smooth. To that end, most calculations of such CT reactions require complete active space self-consistent field (CASSCF) calculations to produce the initial adiabatic eigenspace. (For some examples of such in the context of generalized Mulliken-Hush (GMH), see Refs. 38–42.) To reiterate, when modeling certain CT events, there is a basic electronic structure problem in computing stable and well-balanced adiabatic states.

With this background in mind, and a desire to compute diabatic states without too much user input, in this paper we construct diabatic states applicable to CR by merging (1) Boys localization and (2) spin-flip CIS (SF-CIS). Both of

these methods are black box and require no chemical intuition. In the first part of this paper, we describe in further detail each of these methods. We then present the results of the application of this method to a model system of molecular LiF and LiF solvated by a single water molecule. There follows a discussion of these results and future directions for this research.

II. THEORY AND METHODOLOGY

A. Localized diabatization techniques

As discussed above, there are many ways to define diabatic states^{17–19,22–30,43–47}; no single definition is appropriate for all situations. However, for the purposes of this paper, “diabatic states” will refer to electronic states generated by the Boys diabatization procedure as described below. These states can be thought of as approximating the “before” and “after” states of a CT reaction in which an external perturbation, such as solvent or nuclear motion, acts to localize the electronic states.

Boys localization³¹ is one example of a general class of localized diabatization techniques.^{43,48} Localization procedures similar to these were originally applied to single-electron orbitals; these diabatization methods can be thought of as the state-space analogs of the localized molecular orbital methods originally described by Boys and co-workers.^{49–53} For molecules with arbitrary molecular geometry, localized diabatization techniques create a set of diabatic states $\{|\Xi_I\rangle\}$ as linear combinations of adiabatic states $\{|\Phi_I\rangle\}$ through the action of a rotation matrix \mathbf{U} . Note that states are labeled by capital letters (I, J) and orbitals are labeled by lowercase letters (i, j, a, b). For N adiabatic states, we can write

$$|\Xi_I\rangle = \sum_{J=1}^N |\Phi_J\rangle U_{JI}. \quad (2)$$

The rotation matrix \mathbf{U} is chosen to maximize a given function, and it is in the specification of this function that the various diabatization techniques differ. In Boys localization, an extension of Cave and Newton’s GMH procedure^{29,30,54} to multiple charge centers, the diabatic states are maximally separated by optimizing the sum of the differences between the dipole moments of the states,

$$f_{\text{Boys}}(\mathbf{U}) = \sum_{I,J=1}^N |\langle \Xi_I | \vec{\mu} | \Xi_I \rangle - \langle \Xi_J | \vec{\mu} | \Xi_J \rangle|^2. \quad (3)$$

Although Boys localization is used exclusively in this paper, a separate method is the Edmiston-Ruedenberg (ER) procedure,⁴³ which generates localized states by maximizing the sum of electronic self-repulsion energies,

$$f_{\text{ER}}(\mathbf{U}) = \sum_{I=1}^N \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\langle \Xi_I | \hat{\rho}(\mathbf{r}_1) | \Xi_I \rangle \langle \Xi_I | \hat{\rho}(\mathbf{r}_2) | \Xi_I \rangle}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4)$$

where $\hat{\rho}(\mathbf{r})$ is the density operator, defined as

$$\hat{\rho}(\mathbf{r}) = \sum_j^{\text{all electrons}} \delta(\mathbf{r} - \mathbf{r}_j), \quad (5)$$

for \mathbf{r}_j the position of the j th electron. These methods have already been used to successfully predict the triplet–triplet energy transfer rate in DBA molecules.⁴⁸

B. Spin-flip

The spin-flip family of techniques, developed by Krylov and co-workers use a triplet ($M_s = 1$) electronic state as a reference from which other states may be constructed.^{55–61} The simplest model, SF-CIS, uses a Hartree-Fock-based reference triplet state and adds single spin-flipping excitations to generate both singlet and triplet $M_s = 0$ states. Formally, the SF-CIS wavefunction ansatz is

$$|\Phi_{\text{SF-CIS}}\rangle = \sum_{i,\bar{a}} t_i^{\bar{a}} |\Phi_i^{\bar{a}}\rangle, \quad (6)$$

where the i is an occupied alpha orbital, \bar{a} is a virtual beta orbital, $|\Phi_i^{\bar{a}}\rangle$ is the SF reference state after having undergone an $i \rightarrow \bar{a}$ excitation.

For our purposes, spin-flip CIS has several advantages over standard CIS. First and most importantly, SF-CIS generates the singlet ground state and all excited states equivalently. More precisely, the ground and excited singlet states are all generated as linear combinations of single excitations from the reference triplet state, and therefore have the same functional form. Consequently, the ground singlet state can be rotated into the diabatic basis on equal footing with the excited singlet states and as such we expect that localization routines based on SF-CIS will offer more balanced and meaningful diabatic states. By contrast, standard CIS excited states are generated directly from linear combinations of singly excited determinants of the ground state. Subsequently mixing the HF ground state and CIS excited states is not expected to yield either meaningful or smooth diabatic states.

Second, in cases of bond forming and breaking, and in cases of charge transfer where there are avoided crossings between the ground and excited states, SF-CIS has a better chance of success than standard CIS. Provided the triplet electronic ground state is well defined and well separated from triplet excited states, the reference state for SF-CIS will be smooth. All singlet states will then be automatically constructed with multireference character to allow for static correlation. Whereas standard CIS will certainly fail in these cases, the odds are reasonable that SF-CIS will solve the Schrödinger equation at least qualitatively correctly. Hsu and co-workers have previously taken advantage of these features by using SF-CIS to calculate diabatic coupling terms from energy splittings in the symmetric case.^{36,37}

C. Boys-localized SF-CIS states

A method for applying Boys localization to CIS excited states has been described previously.⁴⁸ In the present context, the application to SF-CIS requires nominal adjustments. Because Boys localization requires only the dipole moments between adiabatic states, we need only compute the dipole moments between SF-CIS states and then apply the standard Jacobi sweeps algorithm.⁵²

For SF-CIS states (Eq. (6)), we find

$$\langle \Phi_I | X | \Phi_J \rangle = \sum_i \delta_{IJ} X_{ii} - \sum_{ij\bar{a}} t_i^{\bar{a}} t_j^{\bar{a}} X_{ij} + \sum_{i\bar{a}\bar{b}} t_i^{\bar{a}} t_i^{\bar{b}} X_{\bar{a}\bar{b}}. \quad (7)$$

This quantity has nearly the same functional form as the equivalent quantity calculated for standard CIS states; the only difference is that we now include $\alpha \rightarrow \beta$ excitations in place of $\alpha \rightarrow \alpha$ and $\beta \rightarrow \beta$ excitations.

III. RESULTS

In order to test the method suggested above, we examine the potential energy surfaces of two model systems: molecular LiF and molecular LiF solvated with a single water molecule. To make a good comparison, values were obtained with standard CIS and SF-CIS with Boys diabatization. A modified version of the Q-CHEM software package⁶² was used with a 6-31G* basis for all calculations. Single-point calculations were performed along a reaction coordinate R representing the Li-F internuclear separation. For the solvated system, the nuclear geometries were optimized and then frozen in place with the exception of the fluorine atom. Finally, note that because independent calculations are needed for each point along the reaction coordinate, arbitrary phases are introduced that affect the sign of the diabatic coupling. Consequently, the sign of this quantity is chosen to maximize continuity.

A. Adiabatic states

Before considering diabatic representations of LiF, we first consider adiabatic energies. The most pronounced difference between quantities generated by the standard CIS and SF-CIS calculations is the lack of the closed-shell/open-shell discontinuity in the latter case (Fig. 1). This irregularity appears immediately in the adiabatic energies shown in Fig. 1(a). The UHF adiabatic energy has a large kink at $R = 3.4 \text{ \AA}$. This irregularity is propagated into other quantities as well, including the electric dipoles, the average of the squared total spin, and the diabatic couplings. By contrast, the SF adiabatic energies are smooth in Fig. 1(b) as are all other quantities obtained using a SF-CIS basis (Figs. 2, 5, and 7).

B. Diabatic states

We now turn to the diabatic state energies and couplings (Fig. 2). *Ab initio* calculations have been used to determine the diabatic coupling of LiF for several decades.^{63–67} As a comparison for the diabatic couplings obtained from the present work, we include results obtained by Werner and Meyer.⁶³ In their analysis of the system, the two lowest $^1\Sigma^+$ states were calculated using multiconfigurational SCF with the optimized valence configuration method and a hand-picked active space. They then produced diabatic states via rotation with the 2×2 unitary matrix that diagonalizes the dipole along the reaction coordinate. The present work is nearly black box and appears to overestimate the peak coupling value by ~ 0.005 hartree with respect to Werner and Meyer's results. However,

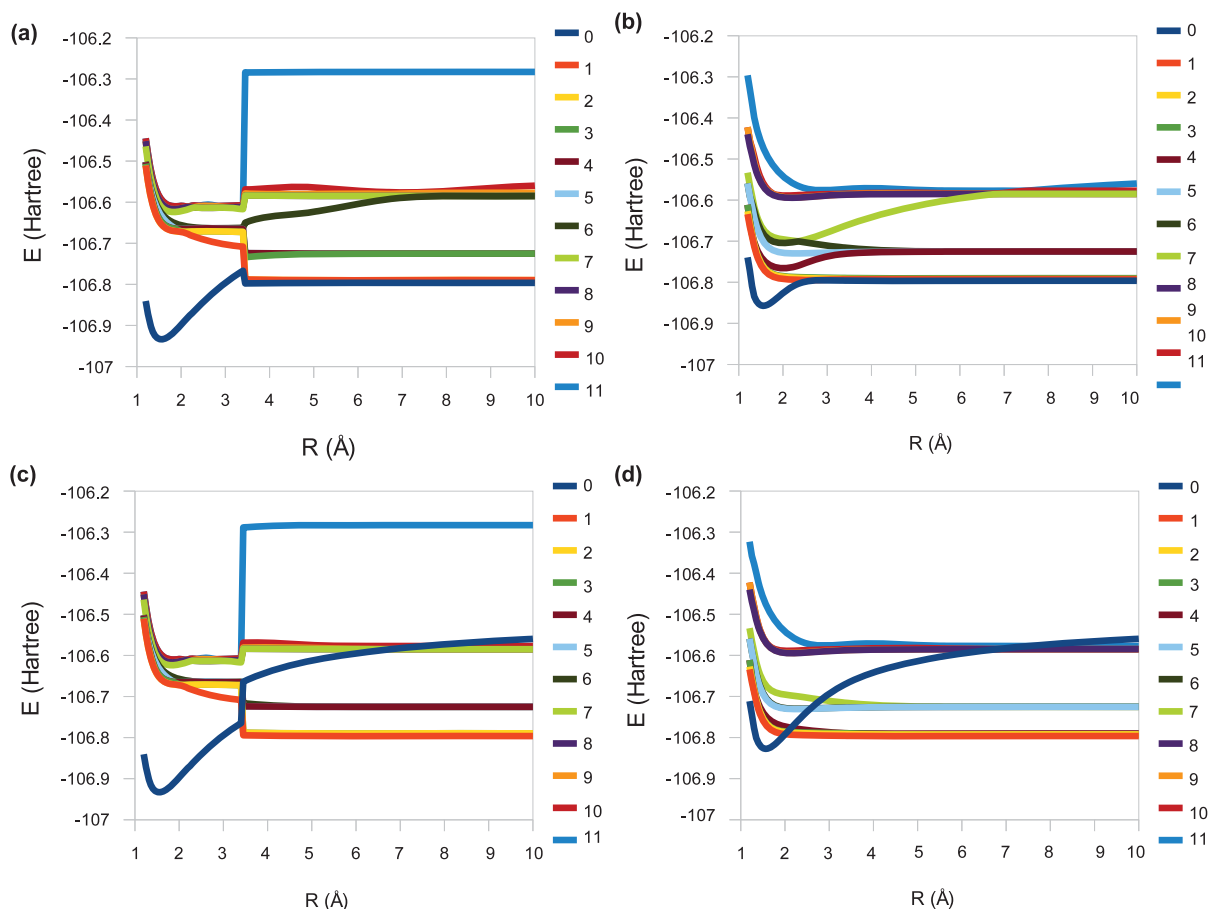


FIG. 1. Energies of the 12 lowest electronic states of molecular LiF in a vacuum as a function of internuclear separation R . (a) Standard CIS adiabatic states, (b) SF-CIS adiabatic states, (c) standard CIS diabatic states, and (d) SF-CIS diabatic states. States are ordered by energy in the adiabatic basis, and all states but the single CT state (state 0) are ordered by energy in the diabatic basis. All non-CT states have been block-diagonalized after diabatization. Values from the present work were constructed from an adiabatic space of the 12 lowest-energy eigenstates.

the peaks are located at the same internuclear separation and the behavior of our curves largely replicates that of Werner and Meyer.

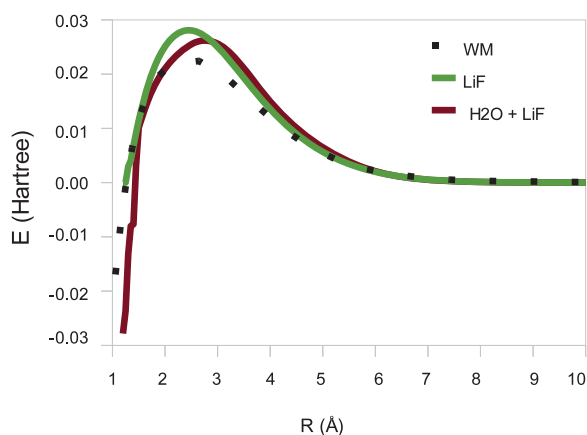


FIG. 2. Diabatic couplings to the CT state from lowest-energy covalent diabatic state as a function of Li and F internuclear separation R . Depicted are two quantities from the present work: LiF in a vacuum and LiF solvated by a single, frozen water molecule. Values from the present work were constructed from the 12 lowest states of the SF adiabatic eigenspace in the case of molecular LiF, and the 11 lowest states in the case of solvated LiF. The “WM” values are from Ref. 63, calculated for molecular LiF alone.

It should be noted that the diabatic states from the present work have been calculated using more than two adiabatic states. Instead, we use 12 adiabatic states, so U is 12×12 . For a discussion of subspace choice, see Sec. IV. We emphasize that all diabatic states have been block-diagonalized after the extraction of the CT state. This is in keeping with the constraints imposed by Cave and Newton for GMH.²⁹ Block diagonalization allows for the states associated with a particular charge center to be locally adiabatic while retaining diabatic coupling terms to electronic states localized elsewhere. LiF diabatic energies generated without the benefit of block diagonalization (Fig. 3) are notably less smooth; in particular, the diabatization procedure appears to create an unnatural discontinuity between states 1–3 in the region $R \cong 2.0$ – 2.6 Å. These apparent discontinuities are caused by the fact that there is no unique set of Boys localized states for this model problem – the Boys function appears to have a zero eigenvalue for the Hessian at the optimal point. This seems logical, because one can only localize down to the atom; when there are multiple states all with the same excitation character on the same atom center, further localization is not unique. As such, block localization would appear very important.

All 11 diabatic couplings from covalent states to the CT state of molecular LiF in the SF adiabatic basis can be seen in Fig. 4. In order to make this figure clear, in

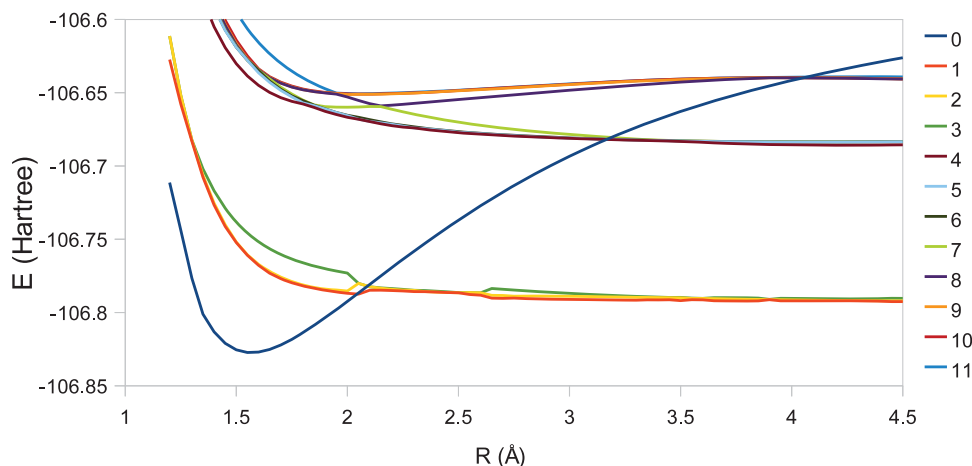


FIG. 3. Energy of 12 lowest electronic states for molecular LiF as a function of reaction coordinate R , which represents the separation between Li and F nuclei. All states but the single CT state (state 0) are ordered by energy. These are the energies of states that have not been block-diagonalized after undergoing diabaticization, and consequently demonstrate some irregularities and the empirical need for rediagonalization of non-CT states.

Figs. 2 and 6 we plot the diabatic coupling for a smaller subset of diabatic states: only the couplings from the lowest-energy covalent state with non-zero coupling to the CT state are shown. For $R \leq 3.4$ Å, these couplings are between the CT state and state 4, but for $R > 3.4$ Å, the identity of the appropriate coupling state abruptly changes to state 3. States 3 and 4 happen to be nearly degenerate in the SF adiabatic basis; this irregularity arises from an incidental switching of their identities at this point. Our SF calculations impose no symmetry constraints, and only one of these states has $^1\Sigma^+$ symmetry at each R value.

C. Solvation effects and Condon principle

Marcus theory assumes the “Condon approximation,” namely, that the diabatic coupling is independent of nuclear coordinates. When modeling CR in a condensed environment, we would like to compute the diabatic coupling in vacuum

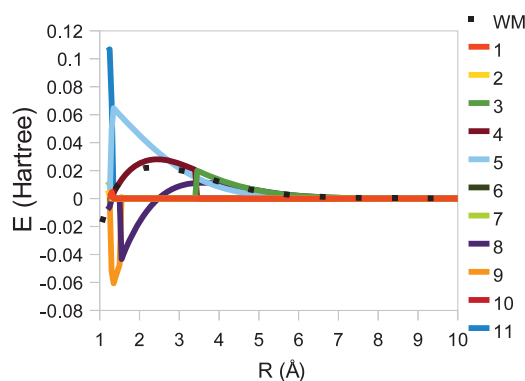


FIG. 4. Diabatic couplings to the CT state from the 11 lowest-energy covalent diabatic states as a function of internuclear separation R . Because each calculation is independent, the signs of these quantities have been chosen to maximize continuity. The “WM” values are from Ref. 63. See Fig. 2 for a more limited and clearer subset of these results.

and ignore CR to solvent for computational savings. As such, ideally the diabatic coupling between the covalent and ionic states of LiF should not depend on water position or orientation. When a solvent molecule is introduced to the system, modest changes in the diabatic coupling are apparent (Fig. 2). The peak of 0.028 hartree in the isolated case is reduced to 0.026 hartree with the introduction of the water molecule. Solvation also induces a peak shift, from 2.45 Å separation to 2.75 Å. This model suggests that coupling is weakened by solvation with one monomer, although only slightly. The ability of solvent-induced non-Condon effects to reduce diabatic coupling has been reported previously using dielectric continuum solvation.⁶⁸ In that case, the reduction was determined to be caused by an increase in the separation between centroids of the relevant donor and acceptor electronic states; a similar effect might be possible here. Finally, we see that in both the solvated and non-solvated cases, the diabatic coupling is sensitive to movement along the reaction coordinate. At large internuclear separations the expected exponential decay $H_{AB} \propto e^{-\frac{1}{2}\beta R}$ is observed. In the future, it might be interesting to explore the veracity of the Condon approximation in larger systems, e.g., by adding a larger solvation shell, although this introduces a new set of problems, including CT to solvent and long-range Coulomb interaction.

D. Electric dipole moment

In order to highlight the meaning of localized diabatic states, we now look at dipole moments. The changing character of the adiabatic basis is clear, if one examines the dipole moment as a function of internuclear separation, i.e., our choice of reaction coordinate (Fig. 5(a)). This picture makes clear how many avoided crossings there are in the adiabatic basis and why a diabatic basis is useful. The dramatic changes in the dipole moment of the adiabatic states are almost entirely resolved in the diabatic basis (Fig. 5(b)), suggesting that this procedure preserves the character of states across config-

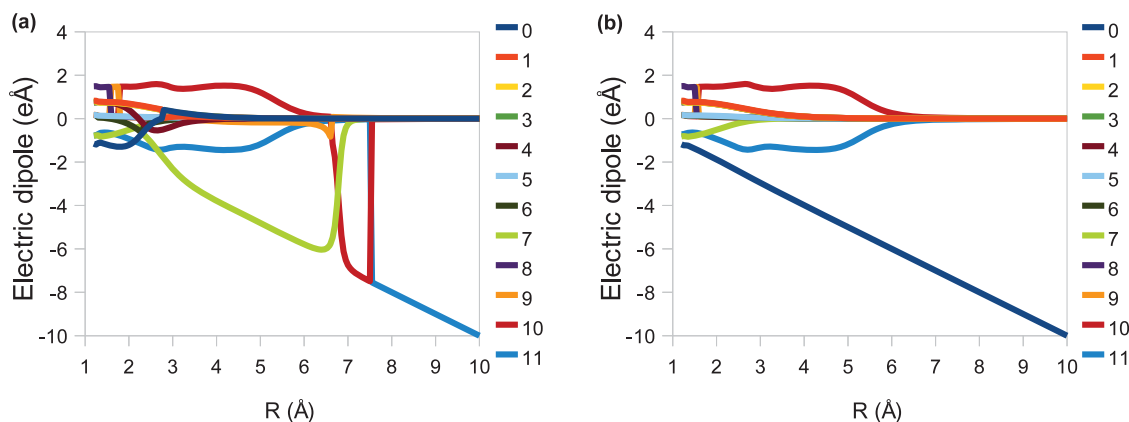


FIG. 5. Electric dipole along the internuclear axis of 12 lowest SF electronic states of molecular LiF as a function of internuclear separation R . Values obtained from (a) adiabatic states and (b) diabatic states are shown. States are ordered by energy in the adiabatic basis, and all states but the single CT state (state 0) are ordered by energy in the diabatic basis. Consider how much smoother the values are in the diabatic basis than in the adiabatic basis. These calculations highlight the changing electronic character of different adiabatic states at different nuclear geometries and the power of a diabatic representation.

uration space at least for those states with non-zero dipole moment. The CT state, in particular, has been isolated over the entire range of nuclear separations examined.

IV. DISCUSSION

We have shown that the Boys diabatization method successfully isolates the CT state using both standard CIS and SF-CIS adiabatic bases. For the standard CIS case, however, irregularities and discontinuities in the potential energy surface arise from the single-reference character of the reference HF state and are propagated into other quantities, including diabatic coupling values. By contrast, quantities generated from SF-CIS states contain none of these features: we have shown that Boys-localized SF-CIS diabatic states can have smooth energies, diabatic couplings, electric dipoles, and total spin squared angular momentum. This approach is nearly black box and does not require much user input or chemical intuition. It also applies to arbitrarily many adiabatic states, as demonstrated here with 12 electronic states. Thus localized diabatization of SF-CIS electronic states appears to be a promising, low-cost method of obtaining CT rates. That being said, we now address a few concerns and unexplored issues.

A. Choice of adiabatic subspace

Because the adiabatic states form a basis for the construction of the diabatic states, the choice of subspace is essential for localized diabatization. Errors associated with choosing too small of an adiabatic basis can be demonstrated in the current system (Fig. 6). Failure occurs in both the five- and eight-state calculations when the internuclear distance removes the ionic state from the adiabatic basis (at 2.6 Å and 6.9 Å, respectively). It is clear in the five-state calculation that the diabatic couplings have not converged with respect to adiabatic basis size even before this point. This alone may not be problematic, as recent work shows more states may not always be better for describing initial and final CT states.⁶⁹ Moreover, the block diagonalization criterion resolves some

problems caused by too large an adiabatic basis. In choosing a subspace, one criterion is certain, however. Because it can be shown that the degree of mixing between adiabatic states due to nuclear motion is inversely proportional to their difference in energy, typically all excited states below a certain energy cutoff are chosen as the basis. This cutoff must be selected to include a converged adiabatic basis, i.e., one which does not exclude any states that are close in energy to any state included in the basis and which therefore might contribute significantly to the diabatic states in a real system. Consequently, the basis is typically chosen to include states below some large energy gap in CIS spectrum. In the current work, a 12-state basis was chosen because the states included are separated from the next-lowest-energy state by ~ 0.3 hartree. However, there is no reason to think that such a gap will exist between a convenient set of adiabatic states in all systems. As this work progresses, a more general procedure for determining the state cutoff should be explored.

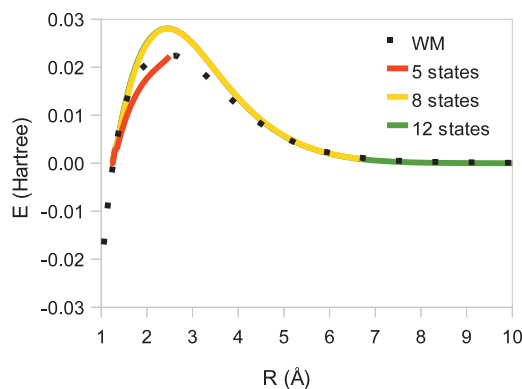


FIG. 6. Diabatic coupling to the CT state from the lowest-energy covalent diabatic state of molecular LiF as a function of reaction coordinate R , which represents nuclear separation between Li and F. Calculations were performed using a basis composed of the 5 lowest states, the 8 lowest states, and the 12 lowest states of the SF adiabatic eigenbasis. We see from the deviation of the five state calculations that this quantity is sensitive to the number of adiabatic states used as a basis for the diabaticization procedure. The “WM” values are from Ref. 63.

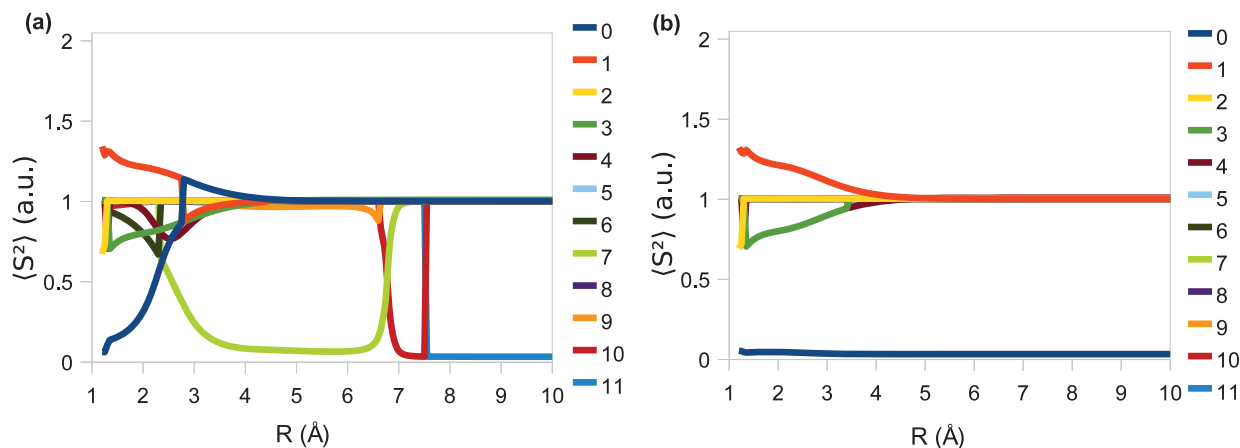


FIG. 7. $\langle S^2 \rangle$ for 12 lowest SF electronic states of molecular LiF as a function of internuclear separation R . The SF-CIS results in the (a) adiabatic and (b) diabatic basis are shown. States are ordered by energy in the adiabatic basis, and all states but the single CT state (state 0) are ordered by energy in the diabatic basis. All non-CT states been block diagonalized after diabaticization. These quantities demonstrate the high degree of spin purity of the CT state in the diabatic basis, and the high degree of spin contamination of all other states.

B. Black box block diagonalization

Block diagonalization after localization is important because one must relax electronic states with charge or excitation character on the same “fragment.” In the present work, it was known that only one CT state exists in the state space explored. Selecting the appropriate subspaces for block diagonalization was a simple matter of identifying the electronic state with the largest electric dipole along the internuclear axis. However, that approach requires user input to implement, and as such SF-CIS/Boys localization cannot yet be considered a wholly black box algorithm. Constructing an algorithm that can automatically relax diabatic states with charge or excitation character on the same fragment is a key objective in the future development of this method.

C. Spin contamination and energetic accuracy

Finally, both the standard and SF-CIS results presented here possess a high degree of spin contamination (Fig. 7). Ideally, we should find singlets ($S^2 = 0$) and triplets ($S^2 = 2$). In-

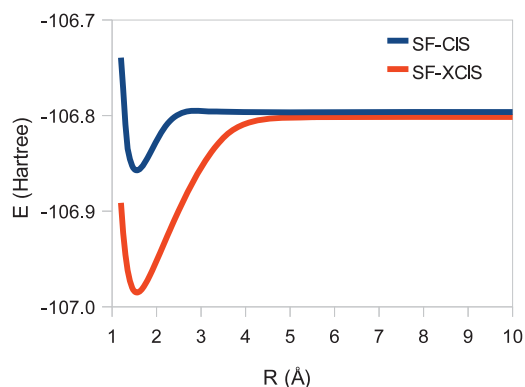


FIG. 8. The ground state adiabatic energy of molecular LiF as a function of internuclear separation R as calculated by both SF-CIS and SF-XCIS procedures. The spin-pure SF-XCIS energies show a marked improvement in variational accuracy. Future work will explore and compare localized diabaticization as applied to SF-XCIS adiabatic states.

stead, we find that most states have $\langle S^2 \rangle = 1$. That being said, the charge transfer state in both cases has been made nearly spin-pure by the diabaticization process, further suggesting that this method enforces a sort of uniformity of character across phase space in spite of the unrestricted nature of the adiabatic basis. However, this cannot be accomplished in general for every diabatic state in the SF-CIS basis. This problem can likely be addressed by use of the SF extended single excitation configuration interaction (SF-XCIS) method.^{59–61} SF-XCIS improves the SF-CIS description of states by including the use of singly- and certain doubly- and triply-excited states to produce less spin-contaminated adiabatic states. In principle, this should provide a more accurate depiction of the potential energy surface with a marginal increase in computational cost. As demonstrated previously by Casanova and Head-Gordon in the similar HF system, SF-XCIS also produces a much more accurate ground state energy for the dissociation of this type of molecule.⁵⁹ These results are born out in LiF as well, as shown in Fig. 8. Our next step is to apply localized diabaticization methods to the SF-XCIS algorithm and model the effects of the newly added double excitations on the resulting diabatic states. Following the work of Larsson and Braga,⁷⁰ we do not expect correlation effects to be large, but this will be checked explicitly.

V. CONCLUSIONS

In this paper, we have presented a general method for obtaining off-diagonal Hamiltonian coupling elements for intramolecular and intermolecular CT reactions. In contrast to other available techniques, this method is nearly black box and applicable to multiple charge centers. Using a model LiF system, it was shown that the diabaticization procedure is capable of producing a set of smoothly varying states that include an isolated CT state. Furthermore, diabatic couplings are calculated which (1) are only weakly impacted by the presence of solvent, confirming the Condon approximation and (2) are comparable to previously reported values calculated using MCSCF. The SF/Boys localization method relies

on a level of theory no higher than CIS and does not require a hand-picked active space. As such, we believe that this combination of algorithms offers a meaningful and computationally accessible approach for calculating diabatic couplings.

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