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The Requisite Electronic Structure Theory to Describe Photo-excited Nonadiabatic Dynamics: Nonadiabatic Derivative Couplings and Diabatic Electronic Couplings

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I. CONSPECTUS

Electronically photoexcited dynamics are complicated because there are so many different relaxation pathways: fluorescence, phosphorescence, radiationless decay, electon transfer, etc. In practice, to model photoexcited systems is a very difficult enterprise, requiring accurate and very efficient tools in both electronic structure theory and nonadiabatic chemical dynamics. Moreover, these theoretical tools are not traditional tools. On the one hand, the electronic structure tools involve couplings between electonic states (rather than typical single state energies and gradients). On the other hand, the dynamics tools involve propagating nuclei on multiple potential energy surfaces (rather than the usual ground state dynamics).

In this account, we review recent developments in electronic structure theory as directly applicable for modeling photo-excited systems. In particular, we focus on how one may evaluate the couplings between two different electronic states. These couplings come in two flavors. If we order states energetically, the resulting *adiabatic* states are coupled via *derivative couplings*. Derivative couplings capture how electronic wavefunctions change as a function of nuclear geometry and can usually be calculated with straightforward tools from analytic gradient theory. One nuance arises, however, in the context of TD-DFT: how do we evaluate derivative couplings between TD-DFT excited states (which are tricky, because no wavefunction is available)? This conundrum was recently solved, and we review the solution below. We also discuss the solution to a second, pesky problem of origin dependence, whereby the derivative couplings do not (strictly) satisfy translation variance which can lead to a lack of momentum conservation.

Apart from adiabatic states, if we order states according to their electronic character, the resulting *diabatic* states are coupled via *electronic* or *diabatic* couplings. The couplings between diabatic states $|\Xi_A\rangle$ and $|\Xi_B\rangle$ are just the simple matrix elements, $\langle\Xi_A|H|\Xi_B\rangle$. A difficulty arises, however, because constructing exactly diabatic states is formally impossible, and constructing quasi-diabatic states is not unique. To that end, we review recent advances in localized diabatization, which is one approach for generating adiabatic-to-diabatic (ATD) transformations. We also highlight outstanding questions in the arena of diabatization, especially how to generate multiple globally stable diabatic surfaces.

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II. INTRODUCTION: THE MATRIX ELEMENTS BEHIND ELECTRONIC RELAXATION

One of the central goals in modern physical chemistry is to elucidate and quantify pathways for electronic relaxation in photo-activated molecules. Innumerable experiments in time-resolved laser chemistry excite molecules or materials with photons and then probe the state of the system after a time delay. In a typical UV-Vis experiment, after a photon has been absorbed and the electronic state has been excited, one would like to know: do the excited electrons stay still or do they meander in real space, leading to electron transfer (ET)? Will there be electronic excitation transfer (EET) between excitons? Is there a relevant pathway for intersystem crossing to produce a triplet state, with the potential for triplet energy transfer (TT)? What is the lifetime of the excited electronic state and where does that energy go?

The questions above address the fundamental nature of energy conversion between systems of many nuclei and electrons. And from a practical point of view, often these questions cannot be answered completely using only spectroscopic data, without any theoretical guidance. Moreover, these questions lie directly at the intersection of two separate and largely isolated fields in theoretical chemistry– electronic structure theory and chemical dynamics. In this account, we will highlight recent progress towards understanding electronic relaxation from the perspective of electronic structure theory, including some results from our research group. In the applications section below, we will focus on photo-excited, intramolecular ET and TT, but the electronic structure methodology is quite general.

A. An Electronic Structure Theorist's Best Friend: The Born-Oppenheimer Approximation

From the perspective of an electronic structure theorist, when photo-excited electrons relax, they break the Born-Oppenheimer approximation. Mathematically, this Born-Oppenheimer breakdown is as follows: We begin with the total Hamiltonian as a function of nuclear (n) and electronic (e) coordinates, where V stands for potential energy and T stands for kinetic energy. Following standard nomenclature, $\vec{r}$ denotes electronic position and $\vec{R}$ denotes nuclear position (indexed by α):

$$H_{Tot}(\vec{r},\vec{R}) \;=\; T_n(\vec{R}) + V_{nn}(\vec{R}) + T_e(\vec{r}) + V_{ee}(\vec{r}) + V_{ne}(\vec{r},\vec{R})$$

At this point, the Hamiltonian is partitioned into the nuclear kinetic energy and everything else (the all inclusive electronic Hamiltonian, H_{el}).

$$H_{Tot}(\vec{r},\vec{R}) \;\equiv\; T_n(\vec{R}) + H_{el}(\vec{r},\vec{R}) \tag{1}$$

The electronic Hamiltonian is then diagonalized, yielding the many-body adiabatic electronic states $\Phi_I(\vec{r};\vec{R}) = \left\langle r \middle| \Phi_I(\vec{R}) \right\rangle$ (labeled by I, J):

$$H_{el}(\vec{R}) \left|\Phi_I(\vec{R})\right\rangle = E_I(\vec{R}) \left|\Phi_I(\vec{R})\right\rangle \tag{2}$$

Finally, the true nuclear-electronic wavefunction can be expanded in the basis of adiabatic electronic eigenstates $\{\Phi_I\}$, yielding:

$$\Psi_{Tot}(\vec{r},\vec{R}) = \sum_I \chi_I(\vec{R})\Phi_I(\vec{r};\vec{R}) \tag{3}$$

The set $\{\chi_I\}$ represent nuclear wavefunctions moving along electronic states $\{\Phi_I\}$ respectively. Plugging Eqn. 3 into the Schrodinger equation, $i\hbar\frac{\partial}{\partial t}\left|\Psi_{Tot}\right\rangle = H_{Tot}\left|\Psi_{Tot}\right\rangle$, it is straightforward to show that

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\chi_I(\vec{R}) &= \left(-\frac{\hbar^2}{2M}\nabla_R^2 + E_I(\vec{R})\right)\chi_I(\vec{R}) - \sum_{J\alpha}\frac{\hbar^2}{M^\alpha}d^\alpha_{IJ}(\vec{R})\frac{\partial\chi_J}{\partial R^\alpha} - \sum_{J\alpha}\frac{\hbar^2}{2M^\alpha}g^\alpha_{IJ}(\vec{R})\chi_J(\vec{R}) && (4) \\ d^\alpha_{IJ}(\vec{R}) &\equiv \int \Phi_I(\vec{r};\vec{R})\frac{\partial}{\partial R^\alpha}\Phi_J(\vec{r};\vec{R})\,d\vec{r} && (5) \\ g^\alpha_{IJ}(\vec{R}) &\equiv \int \Phi_I(\vec{r};\vec{R})\left(\frac{\partial}{\partial R^\alpha}\right)^2\Phi_J(\vec{r};\vec{R})\,d\vec{r} && (6) \end{aligned}$$

Intuitively, nuclear wavepackets on different Born-Oppenheimer surfaces are coupled together by the matrix elements $\vec{d}_{IJ}(\vec{R})$ (the derivative coupling) and $\vec{g}_{IJ}(\vec{R})$ (the second derivative coupling). To model electronic relaxation, these matrix elements are essential.

B. A Chemical Dynamicist's Best Friend: A Fixed Diabatic Basis

From the perspective of chemical dynamicists, the adiabatic electronic basis is awkward because it changes with nuclear position. From this perspective, a better ansatz is the simple one:

$$\Psi_{Tot}(\vec{r},\vec{R}) = \sum_I \tilde{\chi}_I(\vec{R})\Xi_I(\vec{r}) \tag{7}$$

where the diabatic states $\{\Xi_I\}$ are independent of nuclear position and form a static (complete) basis. Plugging Eqn. 7 into the Schrodinger equation, $i\hbar\frac{\partial}{\partial t}\left|\Psi_{Tot}\right\rangle = H_{Tot}\left|\Psi_{Tot}\right\rangle$, we now find:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\tilde{\chi}_I(\vec{R}) &= -\sum_\alpha\frac{\hbar^2}{2M^\alpha}\left(\frac{\partial}{\partial R^\alpha}\right)^2\tilde{\chi}_I(\vec{R}) - \sum_J W_{IJ}(\vec{R})\tilde{\chi}_J(\vec{R}) && (8) \\ W_{IJ}(\vec{R}) &\equiv \int \Xi_I(\vec{r})H_{el}(\vec{r};\vec{R})\Xi_J(\vec{r})d\vec{r} && (9) \end{aligned}$$

The matrix elements W_{IJ} $(I \neq J)$ are called diabatic or electronic couplings.

C. Outline

Both perspectives above are valid and there will be times when one or the other perspective is most useful (usually one wants small interstate couplings). An outline of this account is as follows. In section III, we will highlight recent work aimed at calculating derivative couplings, and in section IV, we will give an account of recent work to calculate diabatic couplings. We discuss open questions and future areas for exploration in section VI.

III. DERIVATIVE COUPLINGS

Derivative couplings have long been the "odd man" out in the global field of quantum chemistry. On the one hand, there is a long literature on computing derivative couplings going back to the early work of Lengsfield and Yarkony[1, 2]. Yarkony *et al* originally derived and implemented the necessary equations for computing derivative couplings in the context of multiconfigurational self-consistent field theory (MC-SCF)[2]. The resulting expressions for derivative coupling are quite tedious because of the nature of MC-SCF theory: both because the MCSCF wavefunctions are rather complicated and because MC-SCF theory is not invariant to the choice of which occupied (ijk) and which virtual (abc) orbitals are included in the active space. The earliest applications were towards understanding excited state-ground state crossings (which are essential for determining whether or not a photo-excited molecule fluoresces or not).

On the other hand, despite all of the history above, it is safe to say that derivative couplings have not been investigated as thoroughly in the literature as have energy gradients[3]. For quantum chemists interested in molecular structure (as opposed to interstate dynamics), the derivative couplings are clearly less important quantities than the gradient or hessian. Moreover, because running nonadiabatic dynamics *on the fly* was prohibitively expensive until recently[4–8], historically the main application of derivative couplings has been the search for conical intersections[9–11]. And while locating conical intersections yields intuition about nonradiative processes, extracting a rate for electronic relaxation is more complicated. For all of these reasons, the theory of derivative couplings between excited states is still evolving in the context of electronic structure theory.

A. Derivative Couplings Between Excited States from Response Theory

For wavefunction based electronic structure, derivative couplings can be calculated with standard analytic gradient theory. For example, configuration interaction singles (CIS) excited state wavefunctions[12] are just sums of excitations from occupied orbitals $\{i\}$ to virtual orbitals $\{a\}$: $\left|\Psi_I^{CIS}(R)\right\rangle = \sum_{ia} t_i^{Ia} \left|\Phi_i^a\right\rangle$. In this case, the derivative coupling is:

$$d_{IJ}^{CIS,\alpha} \equiv \left\langle \Psi_I^{CIS} \middle| \frac{\partial}{\partial R^\alpha} \Psi_J^{CIS} \right\rangle = \sum_{ia} t_i^{Ia} \frac{\partial}{\partial R^\alpha} t_i^{Ja} + \sum_{ijab} t_i^{Ia} \left\langle \Phi_i^a \middle| \frac{\partial}{\partial R^\alpha} \Phi_j^b \right\rangle t_j^{Jb} \tag{10}$$

Eqn. 10 can be easily evaluated with analytic gradient theory[13].

An interesting question now arises in the theory of derivative couplings as related to response theory. Nowadays, most excited state calculations are run with time-dependent density functional theory[14–16]. Until recently, only ground state-excited state couplings were easily available and reliable for TD-DFT[17–19]. However, for many applications, excited state-excited state couplings are needed to describe early time photodynamics. Furthermore, because TD-DFT will find the correct topology for a conical intersection between two excited states (rather than between one excited state and the ground state[20]), the former derivative couplings are especially valuable. That being said, computing excited state-excited state couplings is difficult for TD-DFT [21–27] because, as a formal response theory, TD-DFT never calculates an excited state wavefunction. Instead, according to TD-DFT, one computes only excited state energies by solving the TD-DFT response equations[15, 28]:

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} X^I \\ Y^I \end{pmatrix} = E_I \begin{pmatrix} X^I \\ Y^I \end{pmatrix} \tag{11}$$

Here, X_i^{Ia} and Y_i^{Ia} represent excitations and de-excitations from occupied i to virtual orbital a for excited state I, while $\mathbf{A}$ and $\mathbf{B}$ are excitation and de-excitation superoperators[28].

Now, very often, one invokes the Tamm-Dancoff (TDA) approximation, by setting $\mathbf{B} = \mathbf{0}$ and $Y^I = 0$. In such a case, one has access to the auxiliary TD-DFT/TDA wavefunction $\left|\Psi^I_{TDA}\right\rangle = \sum_{ia} X_i^{Ia} \left|\Phi_i^a\right\rangle$ and one can define a derivative couplings through Eqn. 10, just replacing t_i^{Ia} with X_i^{Ia} [25]. However, without the TDA, no such formula exists. For the full TD-DFT (RPA) problem (i.e. without TDA), we now understand that two approaches are possible:

1. Pseudowavefunctions

The first approach is a pseudowavefunction (PW) approach (which Li and Liu have called an equation of motion approach[23]). To motivate this first approach, one begins with an approximate TD-DFT ground-state wavefunction of the form,

$$\left|\Psi^{GS}_{RPA}\right\rangle = \left|\Psi_{DFT}\right\rangle + \sum_I X_i^{Ia} Y_j^{Ib} \left|\Phi_{ij}^{ab}\right\rangle \tag{12}$$

where $\left|\Phi_{ij}^{ab}\right\rangle$ represents a Slater determinant with two occupied orbitals ij excited to two virtual orbitals ab. The pseudowavefunction for excited state I is then given by exciting a combination of occupied orbitals k to virtual orbitals c, $\left|\Psi^I_{P/}\right\rangle \approx \sum_{kc} X_k^{Ic} a_c^\dagger a_k \left|\Psi^{GS}_{RPA}\right\rangle$. After a series of approximations[26, 27], one finds

$$\begin{aligned} d^{\alpha,PW}_{IJ} &= \left\langle \Psi^I_{PW} \middle| \frac{\partial}{\partial R^\alpha} \Psi^J_{PW} \right\rangle & (13) \\ &\approx \sum_{ia} \left(X_i^{Ia} \frac{\partial}{\partial R^\alpha} X_i^{Ja} - Y_i^{Ia} \frac{\partial}{\partial R^\alpha} Y_i^{Ja} \right) + \sum_{ijab} \left(X_i^{Ia} X_j^{Jb} + Y_i^{Ia} Y_j^{Jb} \right) \left\langle \Phi_i^a \middle| \frac{\partial}{\partial R^\alpha} \Phi_j^b \right\rangle & (14) \end{aligned}$$

Eqn. 14 recovers all of the correct symmetries around a conical intersection: (*i*) the derivative couplings lie in the branching plane and (in the correct units) are perpendicular to the diabatic state energy gradients; (*ii*) the derivative couplings yield the correct Berry phase when integrated around a circular loop enclosing the conical intersection. In the infinite basis limit, in the vicinity of a conical intersection, this equation is also consistent with the well-known Chernyak-Mukamel[29] hypervirial equality[26, 27].

2. *Matching Residues*

Besides the pseudowavefunction theory above, an alternative approach is to use response theory directly. Here, the idea is to use quadratic response theory applied to the exact many-body ground state and to express the resulting wavefunction as a sum over many-body states with residues. Then, by doing the same expansion for the Kohn-Sham DFT ground state and comparing residues, one can extract a meaningful formula for the derivative coupling. For adiabatic TD-DFT, this logic produces a slightly different response theory (RT) derivative coupling: $d_{IJ}^{\alpha,RT} = d_{IJ}^{\alpha,PW} + \zeta_{IJ}^{\alpha}$, where ζ_{IJ}^{α} is a new term arising specifically from response theory.

While direct response theory is the only fully rigorous approach towards solving TD-DFT problems, it turns out that in this case, response theory does not yield a meaningful answer. In particular, Li, Suo and Liu [30] and Ou, Bellchambers, Furche, and Subotnik [31] have independently shown that ζ_{IJ}^{α} diverges at those random geometries for which the two excited state energies differ by the energy of a third excited state $E_I - E_J \approx E_K$ (for some other TD-DFT energy E_K). See Fig. 1. As such, formal quadratic response theory fails[32] and we may conclude that the pseudowavefunction approach provides the most stable formula that can be applied for derivative couplings between adiabatic TD-DFT excited states.

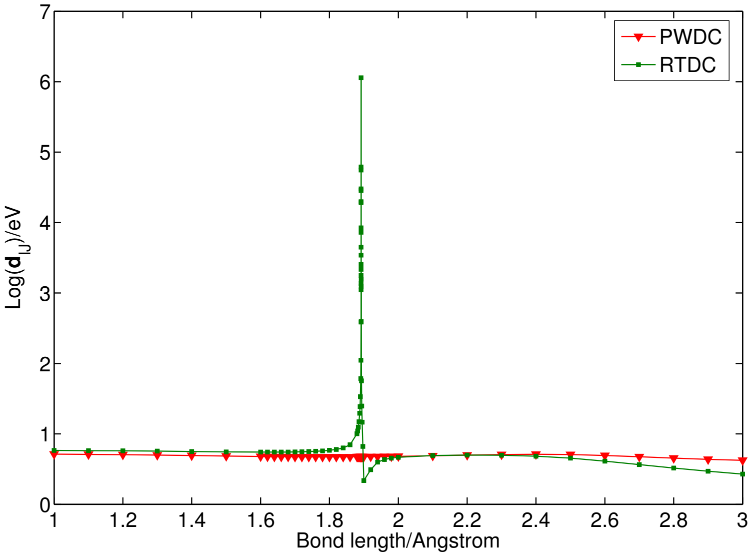


FIG. 1: The derivative couplings (DC's) between the first S_1 and fourth S_4 excited states of LiH as calculated by TDHF. Note that the pseudowavefunction (PW) and response theory (RT) formalisms mostly agree, but the RT matrix elements blows up around 1.9Å“by accident” when $E_4 - E_1 = E_1$. See Ref. [31]. For now, the PW approach is the only stable means to calculate derivative couplings between TD-DFT excited states.

Atom	Derivative Coupling
H	0.0479
Li	-0.1466

TABLE I: Derivative Couplings at the CIS/cc-pVDZ level of theory in units of inverse Bohr radius. The LiH distances ix 1.618436 Å. Formally, pushing the Li atom is not equivalent to pulling the H atom, but this translational distinction can be misleading.

B. Translational Variance and Electron Translation Factors

A second interesting feature that arises in the context of derivative couplings is translational variance, i.e. the fact that $\sum_{\alpha=1}^{N_{Atoms}} d^{\alpha}_{IJ} \neq 0$. For example, for the LiH molecule, the DC's between excited states 1 and 4 are given in Table I[13]. From this data, one might conclude that the overlap between S_4 and S_1 changes differently as a function of nuclear geometry, depending on whether one moves the Li atom or the H atom. In fact, using the raw values in Table I directly in Tully's surface-hopping (nonadiabatic) dynamics algorithm[33] would lead to unphysical trajectories, whereby electronic relaxation was exchanged for spurious jumps in total momentum for the LiH molecule. That being said, Yarkony and the experts of electronic structure have long recognized that derivative couplings do not obey translation invariance[34], and identities have long been known to estimate the size of these non-zero variations.

The conundrum above arises from the neglect of electronic momentum. Dynamicists have long recognized that, for a proper calculation of inelastic scattering, one cannot ignore electronic momentum, such as the Born-Oppenheimer picture would prescribe (given real electronic wavefunctions). Moreover, dynamicists have also long realized that, for single atom trajectories or atom-atom collisions, the translational invariance of derivative couplings and momentum conservation can be restored using electron translation factors[35]. For large molecules, however, electron translation factors can become awkward and method-dependent, and such translation factors have not been universally applied.

Recently, in the course of investigating the analytic form of derivative couplings, our research group made a very simple connection between these electronic structure and dynamics perspectives. According to standard analytic gradient theory, in an atomic orbital basis labeled by $\mu\nu$, the essential matrix elements are the nuclear derivatives of the one-electron Hamiltonian operator ($\frac{\partial}{\partial R^{\alpha}} h_{\mu\nu}$), the two-electron Coulomb operator($\frac{\partial}{\partial R^{\alpha}} \Pi_{\mu\nu\lambda\sigma}$), and the overlap operator ($\frac{\partial}{\partial R^{\alpha}} S_{\mu\nu}$). For derivative couplings, a fourth matrix enters, the antisymmetrized derivative of the overlap matrix: $S^{A[\alpha]}_{\mu\nu} = \frac{1}{2}\left(\left\langle \mu \middle| \frac{\partial \nu}{\partial R^{\alpha}} \right\rangle - \left\langle \frac{\partial \mu}{\partial R^{\alpha}} \middle| \nu \right\rangle\right)$. For all electronic structure methods we have studied (e.g., CIS, TDHF, TD-DFT), the $\mathbf{S}^{A}$ matrix elements always appear as $\sum_{\mu\nu} S^{A[\alpha]}_{\mu\nu} D^{IJ}_{\mu\nu}$, where $D^{IJ}_{\mu\nu}$ is the one electron transition density matrix between electronic states I and J.

In Refs. [13, 36], we observed that, by including electron translation factors and accounting for electronic momentum to zeroth order, all terms involving $S^{A[\alpha]}_{\mu\nu}$ vanish. Moreover, it is easy to show that ignoring all $S^{A[\alpha]}_{\mu\nu}$ terms restores translational invariance and allows for momentum conservation dynamically. Thus, we conclude that, *if the derivative couplings* d^{α}_{IJ} *are to be used dynamically in nonadiabatic trajectories, one can and must ignore all matrix elements involving the antisymmetrized derivative of the overlap matrix.*

IV. DIABATIC COUPLINGS AND ADIABATIC-TO-DIABATIC TRANSFORMATIONS

Like derivative couplings, diabatic couplings (also called electronic couplings) have a long history in the literature[37–50]. The most important result about diabatic states and diabatic couplings is the Mead and Truhlar[51] curl condition, showing one cannot diabatize a given subset of adiabatic states unless the adiabatic states obeyed the curl condition. Thus, imagine that one wants to model the dynamics of an electronic system subjected initially to a 5eV pulse of light. Whereas one would like to transform a given subspace of N_{states} adiabatic electronic states $\{\Phi_I\}$ into a set of diabatic electronic states $\{\Xi_A\}$,

$$|\Xi_A(R)\rangle = \sum_{J=1}^{N_{states}} |\Psi_J(R)\rangle\, U_{JA}(R) \qquad J = 1 \ldots N_{states} \tag{15}$$

it is usually impossible to construct an adiabatic-to-diabatic (ATD) transformation U_{JA} globally (as a function of nuclear position R).

Thus, we are left with the task of computing inexact ATD transformations, for which there has been ever increasing interest over the last 30 years or so. Several flavors of such diabatization exist. One flavor of ATD's goes under the title configurational uniformity and the fourfold way[37–41]. The basic premise here is to set up molecular orbitals and then, with such orbitals, construct many-body configurations that do not change over configuration space. Another flavor falls under the title "Block Diagonalization" [42, 43]. The basic premise here is to define a set of target diabatic states (using chemical intuition) and then construct such diabatic states by minimizing the distance to those target states.

A. Localized Diabatization

One of the most appealing ideas for diabatization is so-called "localized diabatization," whereby one constructs an ATD by localizing charge or excitation energy. Two basic frameworks exist for performing such a transformation. On the one hand, one can guess fragments and localize according to those fragment definitions. Examples include fragment charge diabatization[46] and fragment energy diabatization[48]. On the other hand, one can use some physical observable[52] to construct an ATD. The earliest and most important example of such a transformation was the Generalized Mulliken-Hush approach (GMH) of Cave and Newton[44, 45]. GMH prescribes that, for a two state electron transfer (ET) problem, one should build an ATD by diagonalizing the operator $\hat{\vec{\mu}} \cdot \vec{w}$. Here, $\hat{\vec{\mu}} = (\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z)$ is the dipole operator, and $\vec{w} = (w_x, w_y, w_z)$ is the dipole direction between adiabats 1 and 2, $\vec{w} = \vec{\mu}_{11} - \vec{\mu}_{22}$ [53]; the results of the GMH procedure have often been very good[54].

Our recent work in diabatization has focused on understanding the physical origins of the GMH transformation and extending GMH to the case of many charge or energy transfer centers. In practice, our approach has connected the notion of ATD's with standard 50-year old techniques from orbital localization[55–57], but now applying them to the many-body problem.

To extend GMH beyond the two-state problem, the natural generalization is Boys localization, whereby one constructs U_{Boys} by maximizing the distance between charge centers

~~by~~ according to:

$$f_{Boys}(U) = \sum_{A,B} \left| \langle \Xi_A | \vec{\mu} | \Xi_A \rangle - \langle \Xi_B | \vec{\mu} | \Xi_B \rangle \right|^2 \tag{16}$$

where $\vec{\mu}$ is the dipole moment. We have shown that Eqn. 16 can be physically motivated by assuming a fictitious, polar solvent degree of freedom that mixes together the nearly degenerate adiabatic electronic states of an isolated molecular system, thus producing charge localized diabatic states[58]. For the case of Boys localization, one assumes the solvent is polarized in one direction in real space.

For the case of CIS or TD-DFT excited states, Boys localization can be patched up to treat electronic excitation transfer (EET) or triplet spin transfer (TT) by separating the occ-occ and virt-virt parts of the dipole operator and summing these components separately:

$$\begin{aligned} f_{BoysOV}(U) = & \sum_{A,B} \left| \langle \Xi_A | \vec{\mu}_{occ} | \Xi_A \rangle - \langle \Xi_B | \vec{\mu}_{occ} | \Xi_B \rangle \right|^2 \\ & + \sum_{A,B} \left| \langle \Xi_A | \vec{\mu}_{virt} | \Xi_A \rangle - \langle \Xi_B | \vec{\mu}_{virt} | \Xi_B \rangle \right|^2 \end{aligned} \tag{17}$$

BoysOV localized diabatization proposes to separately localize both the particle and hole of an exciton. Though this BoysOV formalism has no simple physical motivation, we have found it does produce intuitively correct diabatic states with small derivative couplings (see below). Interestingly, recent work by Hoyer and Truhlar has also sought to extend Boys localization (which uses the dipole moment only) through the use of the quadrupole moment (but at the cost of breaking translational invariance) [59].

Beyond Boys localization, an even better approach for localized diabatization is the Edmiston-Ruedenberg[58] transformation. Again, in parallel with the ER orbital localization[57], ER localized diabatization maximizes the self-interaction energy of each diabatic state:

$$f_{ER}(U) = \sum_{A} R_{AAAA} \equiv \sum_{pqrsA} \langle \Xi_A | a_p^\dagger a_q | \Xi_A \rangle \langle \Xi_A | a_r^\dagger a_s | \Xi_A \rangle \left(\phi_p \phi_q | \phi_r \phi_s \right) \tag{18}$$

R_{AAAA} is defined by the right hand side of Eqn. 18, and $(\phi_p\phi_q|\phi_r\phi_s) = \int dr_1 \int dr_2 \phi_p(r_1)\phi_q(r_1)\frac{1}{|r_1-r_2|}\phi_r(r_2)\phi_s(r_2)$ is the two-electron integral between four molecular orbitals. ER localized diabatization can be physically motivated by assuming the existence of a fictitious solvent following linear response, so that one is merely maximizing the sum of the solvation energies for each diabatic state. As a general ATD approach, ER localization can be applied to all types of nonequilibrium transfer, including electron transfer (ET), triplet transfer (TT) and electronic excitation transfer (EET). ER is somewhat more expensive that Boys localization, however, in practice.

Lastly, let us mention a few words about the effect of real solvent (as opposed to fictitious solvent) on diabatic couplings. Cave and Newton have shown that solvent can alter the effective diabatic coupling between molecules[60], sometimes dramatically [61]. These findings remind us that, when modeling electron transfer in the condensed phase, especially intermolecular electron transfer, all diabatization must include nearby solvent (either explicitly[61] or, at least, through a polarized continuum model[60]). For a review, see Ref. [62].

B. “Small” Quasi-diabatic Derivative Couplings?

Since strictly diabatic states do not exist and derivative couplings can be a pain to construct, there has not been a long literature on evaluating the sizes of derivative couplings for quasi-diabatic states. Notably, however, recent work by the Yarkony group[63], has directly tackled the size of the derivative couplings for quasi-diabatic states for reasonably sized molecules.

In our research group, we have consistently sought quasi-diabatic states that capture the physical character of the stable or metastable states of electronic systems in condensed environments[58]. That being said, although such states need not necessarily have infinitesimal derivative couplings, their derivative couplings must be fairly small. Thus, one means to confirm the validity of localized diabatized states is to compute their derivative couplings. To that end, Ref. [64] examines how one can use analytic gradient theory to calculate derivative couplings between Boys-localized diabatic states and concludes definitively that the quasi-diabatic states have negligible coupling[64, 65] . This conclusion was predicted long ago by Yarkony who showed that most re-diagonalizations of adiabatic states should eliminate the divergence of derivative couplings around conical intersections[52]. Armed with the knowledge that localized diabatic states are primarily coupled through diabatic (and not derivative) couplings, one can safely use localized diabatic states in standard Marcus (perturbation) theory calculations[66, 67].

C. Constrained Density Functional Theory

Before finishing this section, we mention that there has been an interesting push in recent years to construct diabatic states directly with constrained DFT[68, 69] and thus bypass the impossibility of exact diabatization. This approach has had success treating electron transfer in mixed valence compounds[69, 70] and there has been some progress in treating spin transfer[71]. Recent research has focused on extending CDFT to excited states through the use of configuration interaction on top of CDFT ground-states[72]. Because, at bottom, CDFT requires predefined definitions of fragments and the resulting diabatic states will not be orthogonal, CDFT is most stable for treating intermolecular (rather than intramolecular) nonadiabatic processes. For a recent review of CDFT, see [73].

V. APPLICATIONS IN OUR RESEARCH GROUP

The discussion above has reviewed recent advances to the theory of derivative couplings and diabatic couplings in the context of nonadiabatic dynamics. We now highlight a few applications of these methods.

A. Benzaldehyde and Conical Intersections[74]

One application of the above theory has been to the molecule benzaldehyde [74], which exhibits strong phosphorescence experimentally. There are two low lying triplet excited states: T_1 is a $n \rightarrow \pi^*$ state and T_2 is a $\pi \rightarrow \pi^*$ state that are mixed together around a low-energy conical intersection (CI) [75]. Using Boys and ER diabatization, in combination with TD-DFT and Marcus theory, we were able to predict rates of intersystem crossing and phosphorescence that roughly matched experiment. See Fig. 2. Furthermore, and most importantly, we demonstrated that Boys and ER localization gives nearly exactly the correct mixing angle in the vicinity of the T_2/T_1 conical intersection (CI), as shown in Fig. 3. The dipole difference between these two states is reasonably large (3.22 Debye) so that T_2/T_1 transfer can almost be considered a weak example of photo-induced electron transfer (ET). To our knowledge, this was the first instance where *explicitly localized* diabatization has been examined for a CI involving a molecule with more than a few atoms (see Yarkony's earlier work on CH_2 using the dipole moment[76]). Our results suggest that black box, locally diabatic representations near conical intersections may play an important role in understanding nonadiabatic dynamics.

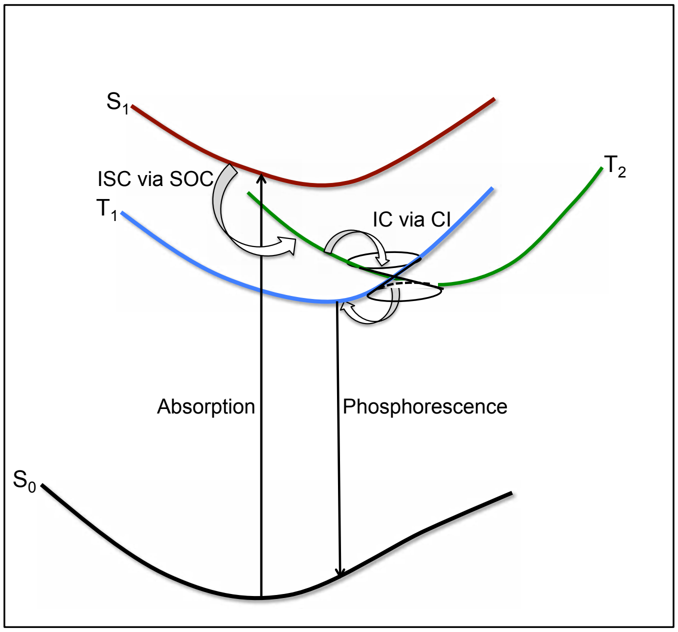


FIG. 2: Schematic of the the dynamics of photoexcited benzaldehyde (from Ref. [74]). After photoexcitation into the S_1 state, there is a quick intersystem crossing (ISC) into the $T_2, \pi \rightarrow \pi^*$ state, followed by internal conversion through a conical intersection to the $T_1, n \rightarrow \pi^*$ state, and finally phosphorescence to the ground state. Using Boys (Eqn. 16) or ER (Eqn. 18) localized diabatization, one can calculate accurate rates of ISC and phosphorescence.

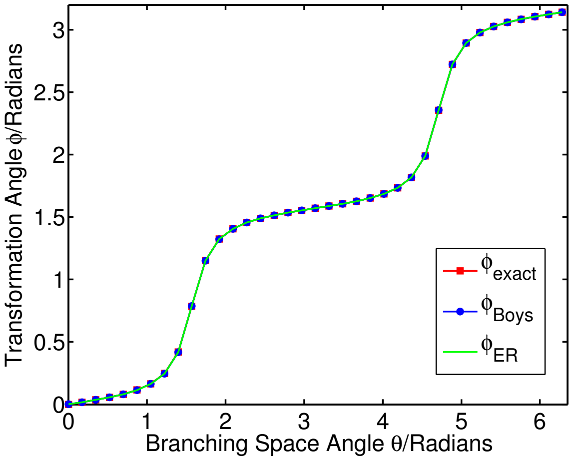
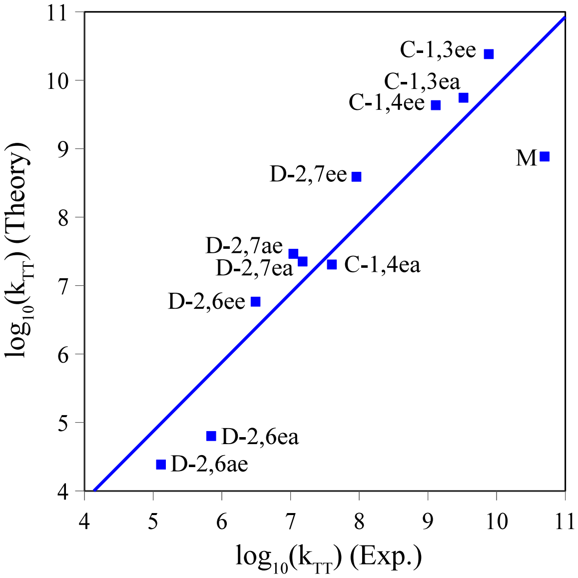


FIG. 3: Mixing angles around the $T_1 - T_2$ conical intersection in the $g - h$ plane for benzaldehyde (from Ref. [74]). Note that Boys (Eqn. 16) and ER (Eqn. 18) localized diabatization recover nearly the exact mixing angle (the latter obtained from fitting the local potential energy surface). This data strongly verifies the validity of localized diabatization approaches.

B. Energy Transfer and The Closs Systems

A second application of these methods has been to the Closs EET systems[77, 78], which have been studied extensively in our research group, both through diabatic couplings and derivative couplings. The Closs molecules are a set of donor-acceptor compounds that highlight many features of intramolecular triplet energy transfer (TT). See Fig. 4[79].

A complete analysis of the Closs compounds requires all of the tools listed above to construct both diabatic and derivative coupling matrix elements. On the one hand, most of the Closs molecules shown in Fig. 4 are rigid (except compound M) and can be studied in the framework of perturbation theory (Marcus theory). To that end, Fig. 4 shows the computed triplet transfer rates versus the experimentally observed rates. The theoretical rates were computed using Boys localization, a reorganization energy around 0.8 eV, and a driving force of roughly 0.6 eV. (See Ref. [80]). For the rigid molecules, Marcus theory works very well.



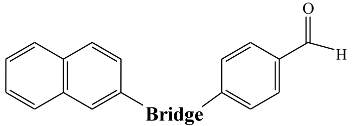
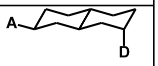
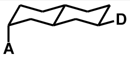
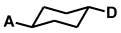
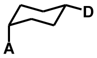
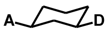
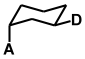
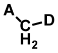
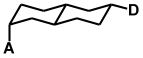
Donor/ acceptor			
D-2,6ee		D-2,7ae	
D-2,7ee		D-2,7ea	
C-1,4ee		C-1,4ea	
C-1,3ee		C-1,3ea	
D-2,6ae		M	
D-2,6ea			

FIG. 4: A plot of experimental versus theoretical energy transfer rates k_{TT} (as computed with Marcus theory and BoysOV localized diabatization [Eqn. 17]) for the Closs EET molecules. See Ref. [80] for more details.

On the other hand, the methyl-bridged species (compound M) in Fig. 4 is floppy and cannot be studied with Marcus theory. Fig. 5 shows the fluctuations in the diabatic coupling as a function of geometry interpolated between the donor and acceptor optimized geometries; we also show the initial and final geometries, which are highly displaced. Clearly, when an excitation transfers from the donor to the acceptor, the reorganization energy is concentrated in torsional motion (and the torsional motion also strongly modulates the diabatic coupling[81, 82]).

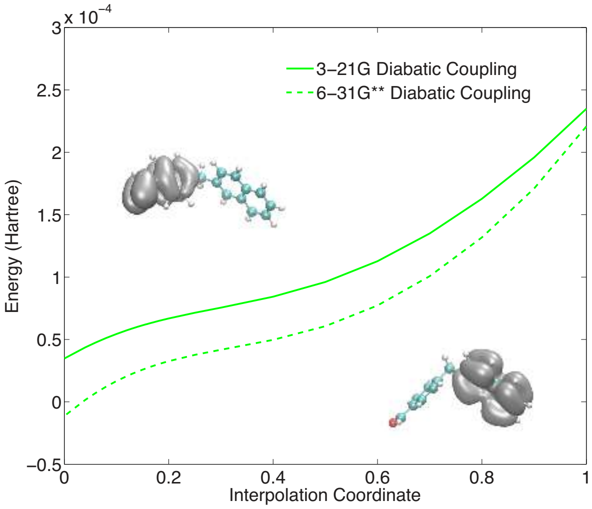


FIG. 5: A plot of donor-acceptor diabatic coupling interpolated as a function of nuclear geometry. Here, we interpolate between the donor and accepor geometries for the methyl-bridged Closs "M" molecule. The diabatic coupling is computed with BoysOV localized diabatization (Eqn. 17). See Ref. [8] for more details. We also plot the electronic excitation density at initial and final geometries. Note that the excitation has moved from donor to acceptor while the molecular geometry has twisted.

A careful study of the M molecule requires a fully nonadiabatic dynamics calculation. We have performed such a calculation with augmented fewest switches surface hopping[33, 83, 84], and have analyzed the resulting trajectories – both through a lens of adiabatic states and through a lens of diabatic states. First, through a lens of adiabatic states, Fig. 6 shows that, when the derivative couplings get large, they exhibit nonzero circulation–which proves the existence of a dynamically important conical intersection. Second, in Fig. 7, we plot the "g" and "h" vectors[85] around the conical intersection using BoysOV localized diabatization.

Perhaps surprisingly, these vectors are not torsional, showing that the local nonadiabatic dynamics near the crossing point can be very different from the overall classical (adiabatic) motion far away from the crossing point.

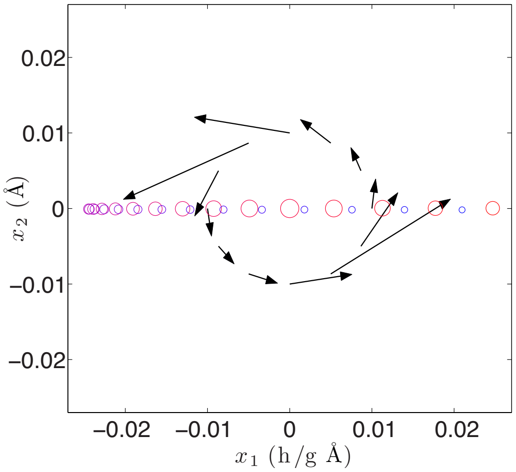


FIG. 6: Plot of the derivative couplings (in black) in the branching plane for the Closs M-molecule as studied by surface hopping dynamics. Each circle represents the projection of the nuclear coordinates (at different time steps in a surface hopping calculation) into the branching plane. The circle radius is inversely proportional to the distance from the branching plane, and the circle color represents increasing time from red to blue. For this trajectory, the molecule enters from the right and passes extremely close to the conical intersection before turning around and exiting back on the right. The nonzero curl proves definitively the existence of a conical intersection. See Ref. [8] for more details.

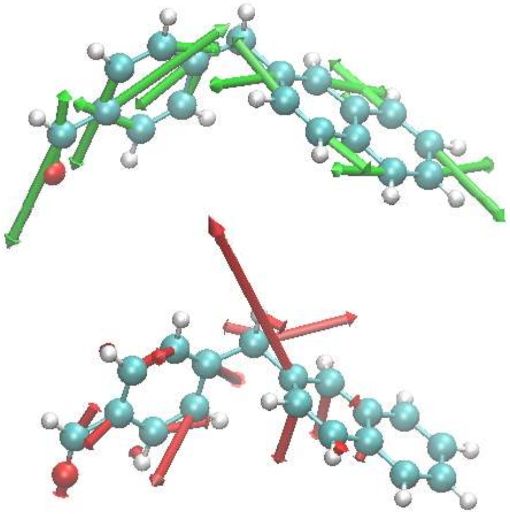


FIG. 7: The g (green) and h (red) vectors for the conical intersection in the Closs M molecule, as calculated by BoysOV localized diabatization (Eqn. 17). Note that the h vector field has been scaled up by a factor of 50. Most of the nuclear displacement in the dominant g direction is in the plane of the rings, suggesting that torsional motion – although important for reaching the conical intersection – is not the dominant motion at the conical intersection. See Ref. [8] for more details.

VI. DISCUSSION AND OPEN QUESTIONS

Before finishing this account, it seems natural that we should address the outstanding challenges remaining in electronic structure at the intersection of nonadiabatic dynamics (beyond the failure of adiabatic TD-DFT quadratic response theory, as mentioned in section III A 2).

A. A Dense Manifold of Diabatic States

While Boys and ER localized diabatization are convenient tools for solving many problems in condensed phase electronic dynamics, these methods are not universally applicable and cannot be applied in an entirely black box fashion. Recall that Boys and ER diabatization are based physically around the concept that nearly degenerate electronic states[58] can be mixed together by a fictitious, strong solvent degree of freedom. Unfortunately, in practice, one may not be able to easily isolate "nealy degenerate electronic states." Instead, one might find a manifold of many electronic states with large energy differences between some adiabats (perhaps, as large as 5 eV). In such a case, prescribing Boys and/or ER localization will often lead to overmixing and yield unphysically large diabatic couplings. Moreover, as nuclear geometries change, the character of the first N adiabatic electronic states can change and the solutions to Eqns. 16 or 18 can jump between minima (leading to discontinuous, unphysical diabatic potential energy surfaces). Ideally, if one diabatizes the first 10 electronic states, one would like to be confident that (almost everywhere) the first 5 diabatic states are smooth and accurate.

To improve upon these unfortunate limitations of ER/Boys localized diabatization, new methodologies and frameworks will be needed. We have offered one approach to solve this problem (entitled $ER-\epsilon$) that explicitly takes solvent character and temperature into account. The basic idea of $ER-\epsilon$ is to minimize the free energy of an electronic system plus its corresponding classical bath of solvent assuming both (a) linear response for the bath and (b) a slow solvent characterized by a single dielectric constant, ϵ. The precise functional form is as follows:

$$f_{ER-\epsilon}(U) = \sum_{A=1}^{N_{States}} \exp\left(-\beta\left(\langle \Xi_A | H_{el} | \Xi_A \rangle - \frac{C}{2} R_{AAAA}\right)\right) \tag{19}$$

where $\beta = 1/kT$, C is the Pekar factor, and R_{AAAA} is the self-interaction energy of the solute electrons (see Eqn. 18). Using Eqn. 19, one finds the correct limiting cases: strong mixing of the gas-phase adiabats in the case of high temperature and weak mixing in the case of small Pekar factor (i.e. weak solvent). Moreover, all indications are that the $ER-\epsilon$ algorithm should produce diabatic states where both the derivative *and* diabatic couplings are consistently small, in the spirit of an optimal diabatic basis considered by Michael Herman[86, 87] and Yeganeh and van Voorhis[88].

Nevertheless, the ER-ϵ approach is not a panacea. While ER-ϵ is certainly more robust than ER alone, the method does not eliminate all necessary over-mixing. The problem of overmixing ATD's remains is not fully solved.

B. Diabatic State Gradients On the Fly

One drawback from using localized diabatization is the difficulty in obtaining diabatic gradients–both in terms of computational cost and numerical stability. In principle, one must first compute adiabatic gradients and derivative couplings and then explicitly construct the gradient of the diabatization transformation. A simpler, approximate (but more stable) approach is to make a strictly diabatic assumption and assume that our localized diabatic states have no derivative couplings, $\left\langle \Xi_A \middle| \frac{\partial}{\partial R^\alpha} \Xi_B \right\rangle = 0$[65]. In such a case, one finds a much simplified (but still very accurate) expression [65] for the diabatic gradient. Future work will no doubt explore the general validity of this strictly diabatic ansatz. Assuming that the localized diabatization yields states for which the strictly diabatic approximation holds, one future challenge will be how to best use approximate gradients to perform diabatic dynamics. Obviously, because it will not be exact, a naive simulation of diabatic dynamics will not conserve energy. The interface of diabatization algorithms with dynamics may well be a fruitful area of study in the future.

VII. CONCLUSIONS

Electronic structure theory is still growing to meet the needs of nonadiabatic dynamics. This account has highlighted recent progress towards computing the necessary matrix elements that couple different electronic states: diabatic couplings between diabatic states and derivative couplings between adiabatic states. Several open questions remain. Looking forward, given the current interest in photo-excited dynamics and the plethora of practical challenges, we expect many future developments ahead at the intersection of electronic structure theory and chemical dynamics.

VIII. ACKNOWLEDGMENTS

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