AIP | The Journal of Chemical Physics

Derivative couplings between TDDFT excited states obtained by direct differentiation in the Tamm-Dancoff approximation

Qi Ou, Shervin Fatehi, Ethan Alguire, Yihan Shao, and Joseph E. Subotnik

Citation: The Journal of Chemical Physics **141**, 024114 (2014); doi: 10.1063/1.4887256
View online: http://dx.doi.org/10.1063/1.4887256
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/141/2?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Two-component hybrid time-dependent density functional theory within the Tamm-Dancoff approximation
J. Chem. Phys. **142**, 034116 (2015); 10.1063/1.4905829

Publisher's Note: "Derivative couplings between TDDFT excited states obtained by direct differentiation in the Tamm-Dancoff approximation" [J. Chem. Phys.141, 024114 (2014)]
J. Chem. Phys. **141**, 069903 (2014); 10.1063/1.4891539

Valence excitation energies of alkenes, carbonyl compounds, and azabenzenes by time-dependent density functional theory: Linear response of the ground state compared to collinear and noncollinear spin-flip TDDFT with the Tamm-Dancoff approximation
J. Chem. Phys. **138**, 134111 (2013); 10.1063/1.4798402

Analytical Hessian of electronic excited states in time-dependent density functional theory with Tamm-Dancoff approximation
J. Chem. Phys. **135**, 014113 (2011); 10.1063/1.3605504

Nonadiabatic coupling vectors for excited states within time-dependent density functional theory in the Tamm–Dancoff approximation and beyond
J. Chem. Phys. **133**, 194104 (2010); 10.1063/1.3503765



Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

Derivative couplings between TDDFT excited states obtained by direct differentiation in the Tamm-Dancoff approximation

Qi Ou,[1] Shervin Fatehi,[1,a)] Ethan Alguire,[1] Yihan Shao,[2] and Joseph E. Subotnik[1,b)]
[1]*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*
[2]*Q-Chem, Inc., 6601 Owens Drive, Suite 105, Pleasanton, California 94588, USA*

(Received 17 February 2014; accepted 25 June 2014; published online 14 July 2014; publisher error corrected 25 July 2014)

Working within the Tamm-Dancoff approximation, we calculate the derivative couplings between time-dependent density-functional theory excited states by assuming that the Kohn-Sham superposition of singly excited determinants represents a true electronic wavefunction. All Pulay terms are included in our derivative coupling expression. The reasonability of our approach can be established by noting that, for closely separated electronic states in the infinite basis limit, our final expression agrees exactly with the Chernyak-Mukamel expression (with transition densities from response theory). Finally, we also validate our approach empirically by analyzing the behavior of the derivative couplings around the T_1/T_2 conical intersection of benzaldehyde. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4887256]

I. INTRODUCTION

A. Derivative couplings: Essential matrix elements for modeling nonadiabatic processes

Within the Born-Oppenheimer (BO) approximation,[1,2] one attempts to separate electronic and nuclear motion by diagonalizing the electronic Hamiltonian and generating adiabatic electronic states which are (hopefully) minimally coupled. Nevertheless, the BO approximation often breaks down,[3–5] and nonadiabatic dynamical transitions between different electronic states—including charge transfer, electronic quenching, and spin-forbidden reactions[6]—are ubiquitous in chemistry.[3,4] When the BO approximation fails, the adiabatic electronic states are coupled together (to first order) by the so-called derivative couplings $\langle\Psi_I|\nabla_Q|\Psi_J\rangle$, which promote electronic transitions as mediated by the motion of a given nucleus Q.[7,8] Applying the logic of the Hellmann-Feynman theorem, one can always express the derivative coupling as[9]

$$\mathbf{d}_{IJ}(\mathbf{R}) = \frac{\langle\Psi_I|\nabla_{\mathbf{R}}H|\Psi_J\rangle}{E_J - E_I}. \tag{1}$$

Calculating derivative couplings is absolutely essential for modeling nonadiabatic processes.

B. Previous computational studies and motivation

Theoretical studies of derivative couplings date back to the early work of Lengsfield and Yarkony.[10–12] Originally, these authors focused on multi-reference configuration-interaction (MR-CI) wavefunction theory and developed the necessary computational formalism.[8,13,14] MR-CI is an especially attractive theory because it generates ground and excited states in a balanced framework, which cannot be obtained by single-reference methods[15,16] (though see Ref. 17). Thus, one can study electronic relaxation from an excited state to the ground state via MR-CI. Today, analytic gradients and derivative couplings are readily available for MR-CI calculations,[18–23] and many MR-CI applications have been conducted.[14,24–28] However, the large computational cost is one of the unavoidable downsides of using MR-CI, and as a result, calculations are limited to relatively small systems (or at least to systems with small active spaces).[29–31]

Because of the large cost of MR-CI, many modern studies have focused on single-reference approaches which can evaluate excited states and derivative couplings in a more affordable way,[32–39] although almost certainly with less accuracy. In particular, several decades after the formulation of the Runge-Gross theorem,[40] time-dependent density functional theory (TDDFT) appears to be the current method of choice for modeling electronic relaxation in photoexcited organics.[41–43] (DFT orbitals have been shown to resemble Dyson orbitals.[44]) Unfortunately, calculating derivative couplings is complicated for TDDFT because the Kohn-Sham wavefunction is not a true wavefunction. To circumvent this obstacle, the Chernyak-Mukamel approach is to notice that, for an exactly stationary state, the derivative coupling can be expressed as a function of the transition density (γ^{IJ}) between two states and their relative energy gap[32,45,46] (with detailed discussion given in Appendix C),

$$\mathbf{d}_{IJ}^{\mathrm{CM}} = \frac{1}{E_J - E_I}\sum_{pq} v_{pq}^{[x]}\gamma_{pq}^{IJ}. \tag{2}$$

Furthermore, a meaningful transition density can be computed from linear response TDDFT,[47] and Send and Furche[48,49] have already used this fact to calculate exact TDDFT derivative couplings from ground to excited state.

Recently, Tavernelli et al.[33–36] have derived expressions for the derivative couplings between TDDFT excited states

a)Current address: Department of Chemistry and Henry Eyring Center for Theoretical Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84103, USA.
b)Electronic mail: subotnik@sas.upenn.edu

 © 2014 AIP Publishing LLC

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

that partially reduce to the Chernyak-Mukamel expression in the limit of excited state wavefunctions that exactly solve the Schrödinger equation, as have Hu et al.[37–39] (Ref. 38 including the Pulay terms[50]). Derivative couplings between TDDFT excited states are likely more meaningful than those between ground state and excited state because, in the former case, one recovers the correct dimensionality of a conical intersection branching plane, whereas this is not always true in the latter case.[15,16] Nevertheless, for the Tamm-Dancoff approximation (TDA) states, the Tavernelli formalism constructs a derivative coupling by differentiating only the Kohn-Sham Fock matrix and omits the full coupling that is induced by the second derivative of the exchange-correlation (*xc*) functionals. Thus, for example, whereas the third derivative of the *xc* functional appears in TDA analytic gradient theory,[51] it is not presented in the Tavernelli formalism for the derivative coupling. As such, the Tavernelli formalism cannot exactly agree with the Chernyak-Mukamel expression.[84]

Following up on our earlier work on CIS derivative couplings,[52] the goal of this article is to reexamine the derivative couplings between TDDFT excited states (including all Pulay and response terms) by using the simplest possible approach: direct differentiation. More specifically, we will treat the TDDFT/TDA Kohn-Sham wavefunction as if it were a true electronic wavefunction and, through direct differentiation, we will derive an analytical expression for the derivative couplings between two Tamm-Dancoff TDDFT states. Our rationality is as follows: even though the Kohn-Sham linear-response wavefunction is not rigorously meaningful, the true derivative couplings between TDA excited states must obey certain conditions around a conical intersection. For instance, (i) the derivative coupling should be orthogonal to the difference gradient in properly scaled coordinates; (ii) it should diverge at a conical intersection; (iii) its integral should be π for a loop encircling the conical intersection. For all of these reasons, it is not unreasonable to consider a derivative coupling $\mathbf{d}_{IJ}$ from direct differentiation where the behavior around a conical intersection is guaranteed to be correct (and the formal expression can be easily transformed to the energy gradient when $I = J$). Moreover, we will show in Appendix C that, near a conical intersection, our computed derivative couplings match the exact derivative coupling expression in Eq. (2) with the transition density calculated according to response theory (in the limit of an infinite basis).

C. Outline

An outline of this article is as follows: all of our theory will be presented in Sec. II. Our analytical expressions will be a little messy because, as is common for molecular systems, we will work in a basis of atomic orbitals (AOs) – and by including all Pulay terms, we will quantitatively investigate the effect of the basis set on the final answer. In Sec. III, we show that our results match finite-difference data for lithium hydride using three different *xc* functionals (B3LYP, ωB97, and ωB97X). In Sec. IV, we will apply our new formalism to the T_1/T_2 conical intersection of benzaldehyde, which shows the substantial effects of Pulay terms, response terms, and second derivative of the *xc* functionals. In Sec. V, we conclude. In Appendix C, a comparison of our approach with the Chernyak-Mukamel formula is given.

D. Notation

Here, we summarize the notation in this work as follows: spin molecular orbitals (MO) are denoted by lowercase latin letters (a, b, c, d for virtual orbitals, i, j, k, l, m for occupied orbitals, p, q, r, s, w for arbitrary orbitals). AOs are denoted by Greek letters (α, β, γ, δ, λ, σ, μ, ν). The TDA excited states are denoted by Ψ (with uppercase latin indices I, J).

II. ANALYTIC DERIVATION FOR TDDFT/TDA DERIVATIVE COUPLINGS

A. Single-reference excited states within the Tamm-Dancoff approximation

The derivation of TDDFT/TDA derivative couplings presented here will parallel the derivation given in Ref. 52 for CIS derivative couplings. TDDFT/TDA Kohn-Sham eigenstates have the form

$$|\Psi_I\rangle = \sum_{ia} t_i^{Ia} \left|\Phi_i^a\right\rangle \tag{3}$$

$$= \sum_{ia} t_i^{Ia} a_a^\dagger a_i |\Phi_{\mathrm{DFT}}\rangle. \tag{4}$$

TDDFT/TDA states are linear combinations of singly excited determinants $\{|\Phi_i^a\rangle\}$, which differ from the DFT ground state determinant $|\Phi_{\mathrm{DFT}}\rangle$ by the replacement of a spin orbital from the occupied subspace (of size O) with a spin orbital from the virtual subspace (of size V). The procedure for determining the TDDFT/TDA amplitudes (t_i^a) requires diagonalizing the Kohn-Sham linear-response tensor $\mathbf{A}$,

$$A_{iajb} = \left\langle \Phi_i^a \middle| \mathcal{O}_{\mathrm{KS}} \middle| \Phi_j^b \right\rangle, \tag{5}$$

that appears in the eigenvalue equation

$$\mathbf{AT} = \mathbf{E}_{\mathrm{TDA}}\mathbf{T}, \tag{6}$$

where $\mathbf{T}$ is the tensor of amplitudes for all states. The resulting TDDFT/TDA energy is given by $\sum_{ijab} t_i^{Ia} A_{iajb} t_j^{Jb} = E_I \delta_{IJ}$.

The Kohn-Sham operator $\mathcal{O}_{\mathrm{KS}}$ can be written in second-quantized and antisymmetrized form (with physicists notation for the two-electron-integrals[53])

$$\mathcal{O}_{\mathrm{KS}} = \sum_{pq} F_{pq} a_p^\dagger a_q + \sum_{cdkl} [\Omega_{clkd} a_c^\dagger a_k a_l^\dagger a_d + \Omega_{cdkl}(a_c^\dagger a_d^\dagger a_l a_k + a_l^\dagger a_k^\dagger a_c a_d)], \tag{7}$$

where F_{pq} is the Fock matrix, and Ω_{pqsr} is the two-electron effective operator in DFT,

$$F_{pq} = h_{pq} + \sum_m \Pi_{pmqm}, \tag{8}$$

$$\Omega_{pqsr} = \Pi_{pqsr} + \omega_{pqsr}. \tag{9}$$

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

The diagonal entries of the Fock matrix $F_{pp} \equiv \varepsilon_p$ are the usual Kohn-Sham orbital energies, if we define h^0_{pq} as the matrix element of the kinetic energy plus the external potential (Eq. (10)) and g_{pq} is the first derivative of the *xc* functional f_{xc} (Eq. (11)),[54] then the sum of h^0_{pq} and g_{pq} gives the one-electron effective operator h_{pq} (Eq. (12)),

$$h^0_{pq} \equiv \langle p|h^0|q\rangle, \tag{10}$$

$$g_{pq} \equiv \sum_{pq} \int d\mathbf{r}\phi_p(\mathbf{r}) \frac{\partial f_{xc}}{\partial \rho(\mathbf{r})} \phi_q(\mathbf{r}), \tag{11}$$

$$h_{pq} \equiv h^0_{pq} + g_{pq}. \tag{12}$$

Π_{pqsr} is the Coulomb term plus whatever fraction of Hartree-Fock exchange is included in the DFT functional (c_{HF} in Eq. (13)), and ω_{pqsr} is the second derivative of the *xc* functional (Eq. (14)). The sum of Π_{pqsr} and ω_{pqsr} gives Ω_{pqsr} (Eq. (9)),

$$\Pi_{pqsr} \equiv \langle pq|sr\rangle - c_{\mathrm{HF}}\langle pq|rs\rangle, \tag{13}$$

$$\begin{aligned}\omega_{pqsr} &\equiv \langle pq|f''_{xc}|sr\rangle \\ &= \sum_{pqsr} \int d\mathbf{r}\phi_p(\mathbf{r})\phi_q(\mathbf{r}) \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} \phi_r(\mathbf{r})\phi_s(\mathbf{r}).\end{aligned} \tag{14}$$

With the definitions above, $\mathcal{O}_{\mathrm{KS}}$ can be rewritten as

$$\begin{aligned}\mathcal{O}_{\mathrm{KS}} = &\sum_{pq} \left(h^0_{pq} + g_{pq} + \sum_m \Pi_{pmqm} \right) a^\dagger_p a_q \\ &+ \sum_{cdkl} [(\Pi_{clkd} + \omega_{clkd}) a^\dagger_c a_k a^\dagger_l a_d \\ &+ (\Pi_{cdkl} + \omega_{cdkl})(a^\dagger_c a^\dagger_d a_l a_k + a^\dagger_l a^\dagger_k a_c a_d)].\end{aligned} \tag{15}$$

Note that the Ω_{cdkl} term in $\mathcal{O}_{\mathrm{KS}}$ will not contribute to the single-single coupling as stated in TDA. Inserting these expressions into Eq. (5), one has

$$A_{iajb} = \Omega_{ajib} + \delta_{ij} F_{ab} - \delta_{ab} F_{ij} + \delta_{ij}\delta_{ab} E_{\mathrm{DFT}}. \tag{16}$$

B. The "brute force" expression

Before we start this section, it is helpful to define several density matrices for future use. These definitions are consistent with those in Ref. 52.

1. The general density matrices

$$P_{\mu\nu} = \sum_m C_{\mu m} C_{\nu m}, \tag{17}$$

$$\tilde{P}_{\mu\nu} = \sum_p C_{\mu p} C_{\nu p} = P_{\mu\nu} + \sum_a C_{\mu a} C_{\nu a}. \tag{18}$$

Here, **C** is the matrix of MO coefficients. Note that we may express the real-space density as $\rho(\mathbf{r}) = P_{\mu\nu}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})$.

2. The TDA excitation-amplitude matrix, also called the transition density matrix

$$R^I_{\mu\nu} = \sum_{ia} C_{\mu a} t^{Ia}_i C_{\nu i}. \tag{19}$$

3. The generalized difference-density matrix[55]

$$D^{IJ}_{\mu\nu} = \sum_{iab} C_{\mu a} t^{Ia}_i t^{Jb}_i C_{\nu b} - \sum_{ija} C_{\mu i} t^{Ja}_i t^{Ia}_j C_{\nu j}. \tag{20}$$

We will now construct derivative couplings by a "brute force" approach. For the Hellmann-Feynman analogue, see Appendix B. The "brute force" expression for the derivative coupling can be obtained by direct differentiation (with a superscript $[x]$ denoting a gradient in the x direction),

$$\langle \Psi_I | \Psi^{[x]}_J \rangle = \sum_{ijab} t^{Ia}_i \langle \Phi^a_i | \left(t^{Jb}_j | \Phi^b_j \rangle \right)^{[x]} \tag{21}$$

$$= \sum_{ijab} t^{Ia}_i t^{Jb[x]}_j \langle \Phi^a_i | \Phi^b_j \rangle + \sum_{ijab} t^{Ia}_i t^{Jb}_j \langle \Phi^a_i | \Phi^{b[x]}_j \rangle \tag{22}$$

$$= \sum_{ia} t^{Ia}_i t^{Ja[x]}_i + \sum_{ijab} t^{Ia}_i t^{Jb}_j \langle \Phi^a_i | \Phi^{b[x]}_j \rangle \tag{23}$$

$$\begin{aligned}= &\frac{1}{E_J - E_I} \sum_{ijab} t^{Ia}_i A^{[x]}_{iajb} t^{Jb}_j - \sum_{iab} t^{Ia}_i t^{Jb}_i O^{\mathrm{R}[x]}_{ba} \\ &- \sum_{ija} t^{Ia}_i t^{Ja}_j O^{\mathrm{R}[x]}_{ji},\end{aligned} \tag{24}$$

where we define the "right" spin-orbital derivative overlap,

$$O^{\mathrm{R}[x]}_{pq} \equiv \langle p|q^{[x]}\rangle. \tag{25}$$

In the MO representation,

$$O^{\mathrm{R}[x]}_{bi} = \langle b|i^{[x]}\rangle \tag{26}$$

$$= \left(\sum_\mu C_{\mu b} \langle \mu | \right) \left(\sum_\nu |\nu\rangle C^{[x]}_{\nu i} + \sum_\nu |\nu^{[x]}\rangle C_{\nu i} \right) \tag{27}$$

$$= \sum_{\mu\nu} C_{\mu b} S_{\mu\nu} C^{[x]}_{\nu i} + \sum_{\mu\nu} C_{\mu b} S^{\mathrm{R}[x]}_{\mu\nu} C_{\nu i}, \tag{28}$$

where the atomic orbital overlap is

$$S_{\mu\nu} \equiv \langle \mu|\nu\rangle. \tag{29}$$

Analogous to the $O^{\mathrm{R}[x]}_{bi}$, we define the right derivative of the overlap as follows:

$$S^{[x]}_{\mu\nu} \equiv \langle \mu^{[x]}|\nu\rangle + \langle \mu|\nu^{[x]}\rangle \tag{30}$$

$$\equiv S^{\mathrm{L}[x]}_{\mu\nu} + S^{\mathrm{R}[x]}_{\mu\nu}. \tag{31}$$

At this point, we need to calculate the tensor **A** and its derivatives. Formally, from Eq. (16),

$$A^{[x]}_{iajb} = \Omega^{[x]}_{ajib} + \delta_{ij} F^{[x]}_{ab} - \delta_{ab} F^{[x]}_{ij} + \delta_{ij}\delta_{ab} E^{[x]}_{\mathrm{DFT}}. \tag{32}$$

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

Here, all derivative terms are important except for $E^{[x]}_{\mathrm{DFT}}$, which cannot contribute to the final expression by orthogonality of TDDFT/TDA excited states. The following expression is then obtained by plugging Eq. (32) into Eq. (24):

$$\begin{aligned}\left\langle \Psi_I \middle| \Psi^{[x]}_J \right\rangle = &\frac{1}{E_J - E_I} \sum_{ijab} t^{Ia}_i t^{Jb}_j \Omega^{[x]}_{ajib} \\ &+ \sum_{iab} t^{Ia}_i t^{Jb}_i \left(\frac{1}{E_J - E_I} F^{[x]}_{ab} - O^{\mathrm{R}[x]}_{ba} \right) \\ &- \sum_{ija} t^{Ia}_i t^{Ja}_j \left(\frac{1}{E_J - E_I} F^{[x]}_{ij} + O^{\mathrm{R}[x]}_{ji} \right). \end{aligned} \quad (33)$$

Finally, we now use the formal derivations in Ref. 52 to acquire the expressions for $\mathbf{F}^{[x]}$, $\mathbf{\Omega}^{[x]}$, and $\mathbf{O}^{R[x]}$. Expanding these terms in our expression for $A^{[x]}_{iajb}$, we find a long and complicated coupling expression,

$$\begin{aligned}\left\langle \Psi_I \middle| \Psi^{[x]}_J \right\rangle = &\frac{1}{E_J - E_I} \sum_{ijab} t^{Ia}_i t^{Jb}_j \left\{ \sum_{\mu\nu\lambda\sigma} C_{\mu a} C_{\nu j} \Omega^{[x]}_{\mu\nu\lambda\sigma} C_{\lambda i} C_{\sigma b} \right. \\ &- \frac{1}{2} \sum_{\alpha\beta w} C_{\alpha w} S^{[x]}_{\alpha\beta} \begin{bmatrix} C_{\beta a} \Omega_{wjib} \\ + C_{\beta j} \Omega_{awib} \\ + C_{\beta i} \Omega_{ajwb} \\ + C_{\beta b} \Omega_{ajiw} \end{bmatrix} \\ &+ \sum_k \Omega_{kjib} \Theta^{[x]}_{ak} + \sum_c \Omega_{acib} \Theta^{[x]}_{jc} \\ &\left. + \sum_c \Omega_{ajcb} \Theta^{[x]}_{ic} + \sum_k \Omega_{ajik} \Theta^{[x]}_{bk} \right\} \\ &+ \sum_{iab} t^{Ia}_i t^{Jb}_i \left\{ \frac{1}{E_J - E_I} \left[\sum_{\mu\nu} C_{\mu a} h^{[x]}_{\mu\nu} C_{\nu b} \right. \right. \\ &+ \sum_{\mu\nu\lambda\sigma m} C_{\mu a} C_{\nu m} \Pi^{[x]}_{\mu\nu\lambda\sigma} C_{\lambda b} C_{\sigma m} \\ &- \frac{1}{2} \left(\varepsilon_a \sum_{\alpha\beta} C_{\alpha a} S^{[x]}_{\alpha\beta} C_{\beta b} + \varepsilon_b \sum_{\alpha\beta} C_{\alpha b} S^{[x]}_{\alpha\beta} C_{\beta a} \right) \\ &- \frac{1}{2} \sum_{\alpha\beta m w} C_{\alpha w} S^{[x]}_{\alpha\beta} C_{\beta m} \left(\Pi_{awbm} + \Pi_{ambw} \right) \\ &\left. - \sum_{mc} \Theta^{[x]}_{cm} (\Pi_{acbm} + \Pi_{ambc}) \right] - \sum_{\mu\nu} C_{\mu b} C_{\nu a} S^{\mathrm{A}[x]}_{\mu\nu} \Big\} \\ &- \sum_{ija} t^{Ia}_i t^{Ja}_j \left\{ \frac{1}{E_J - E_I} \left[\sum_{\mu\nu} C_{\mu i} h^{[x]}_{\mu\nu} C_{\nu j} \right. \right. \\ &+ \sum_{\mu\nu\lambda\sigma m} C_{\mu i} C_{\nu m} \Pi^{[x]}_{\mu\nu\lambda\sigma} C_{\lambda j} C_{\sigma m} \\ &- \frac{1}{2} \left(\varepsilon_i \sum_{\alpha\beta} C_{\alpha i} S^{[x]}_{\alpha\beta} C_{\beta j} + \varepsilon_j \sum_{\alpha\beta} C_{\alpha j} S^{[x]}_{\alpha\beta} C_{\beta i} \right) \\ &- \frac{1}{2} \sum_{\alpha\beta m w} C_{\alpha w} S^{[x]}_{\alpha\beta} C_{\beta m} (\Pi_{iwjm} + \Pi_{imjw}) \\ &\left. \left. - \sum_{mc} \Theta^{[x]}_{cm} (\Pi_{icjm} + \Pi_{imjc}) \right] + \sum_{\mu\nu} C_{\mu j} C_{\nu i} S^{\mathrm{A}[x]}_{\mu\nu} \right\}, \end{aligned} \quad (34)$$

where $S^{\mathrm{A}[x]}_{\mu\nu}$ is defined as $S^{\mathrm{R}[x]}_{\mu\nu} - \frac{1}{2} S^{[x]}_{\mu\nu}$. Henceforward, all terms in Eq. (34) with a factor of $\mathbf{S}^{[x]}$ will be called "Pulay" terms.[50] Note that the orbital rotations between occupied and virtual subspaces (Θ_{ab} and Θ_{ij}) disappear and are absent in Eq. (34) (just as for CIS).[52] Compared with the corresponding CIS expression (Eq. (A21) in Ref. 52), Eq. (34) differs by including the gradient of the first derivative of the *xc* functional in the derivative of the Fock matrix $\mathbf{F}^{[x]}$ ($\mathbf{g}^{[x]}$), an extra term in $\mathbf{\Omega}^{[x]}$ which is the gradient of the second derivative of the *xc* functional ($\boldsymbol{\omega}^{[x]}$), and the fraction of Hartree-Fock exchange term (c_{HF}) present in the DFT functional ($\mathbf{\Pi}^{[x]}$).

C. Exact TDDFT/TDA derivative couplings: The non-response component

Equation (34) is quite lengthy and, for the most part, the right hand side is almost identical with the corresponding CIS derivative couplings (Eq. (A21) in Ref. 52). Thus, at this juncture, let us focus only on those terms which are unique to the TDDFT expressions. To begin, we need several new definitions. First, note that the gradient of the first derivative of the *xc* functional $\mathbf{g}^{[x]}$ can be decomposed in the AO representation as

$$g^{[x]}_{\mu\nu} \equiv \tilde{g}^{[x]}_{\mu\nu} + g^{\mathrm{Y}[x]}_{\mu\nu}, \quad (35)$$

where[54]

$$\begin{aligned}\tilde{g}^{[x]}_{\mu\nu} \equiv &\int^{[x]} d\mathbf{r} \phi_\mu(\mathbf{r}) \frac{\partial f_{xc}}{\partial \rho(\mathbf{r})} \phi_\nu(\mathbf{r}) \\ &+ \int d\mathbf{r} \frac{\partial f_{xc}}{\partial \rho(\mathbf{r})} (\phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}))^{[x]} \\ &+ \sum_{\lambda\sigma} \int d\mathbf{r} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} P_{\lambda\sigma} (\phi_\lambda(\mathbf{r}) \phi_\sigma(\mathbf{r}))^{[x]}, \end{aligned} \quad (36)$$

$$g^{\mathrm{Y}[x]}_{\mu\nu} \equiv \sum_{\lambda\sigma} P^{[x]}_{\lambda\sigma} \omega_{\mu\nu\lambda\sigma}. \quad (37)$$

The integral $\int^{[x]}$ shown in the first term of Eq. (36) represents differentiation with respect to the Becke weights in the quadrature for the exchange-correlation functional. Note that $g^{[x]}_{\mu\nu}$ enters in $h^{[x]}_{\mu\nu}$, and the total one-electron-integral

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

derivative for TDDFT can be written as

$$\begin{aligned} h_{\mu\nu}^{[x]} &= h_{\mu\nu}^{0[x]} + g_{\mu\nu}^{[x]} \\ &= h_{\mu\nu}^{0[x]} + \tilde{g}_{\mu\nu}^{[x]} + g_{\mu\nu}^{\mathrm{Y}[x]} \\ &\equiv \tilde{h}_{\mu\nu}^{[x]} + g_{\mu\nu}^{\mathrm{Y}[x]}. \end{aligned} \tag{38}$$

Recall that $h_{\mu\nu}^{0[x]}$ is the derivative of the kinetic energy plus the external potential, which is exactly the same as in the CIS expression. We label the sum of $h_{\mu\nu}^{0[x]}$ and $\tilde{g}_{\mu\nu}^{[x]}$ as $\tilde{h}_{\mu\nu}^{[x]}$ to denote the non-response part of the one-electron-integral derivative.

Second, analogous definitions can be made for the two-electron-integral derivatives $\omega^{[x]}$,

$$\omega_{\mu\nu\lambda\sigma}^{[x]} = \tilde{\omega}_{\mu\nu\lambda\sigma}^{[x]} + \omega_{\mu\nu\lambda\sigma}^{\mathrm{Y}[x]}, \tag{39}$$

where

$$\begin{aligned} \tilde{\omega}_{\mu\nu\lambda\sigma}^{[x]} \equiv & \int^{[x]} d\mathbf{r}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\frac{\partial^2 f_{xc}}{\partial\rho(\mathbf{r})^2}\phi_\lambda(\mathbf{r})\phi_\sigma(\mathbf{r}) \\ & + \int d\mathbf{r}(\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}))^{[x]}\frac{\partial^2 f_{xc}}{\partial\rho(\mathbf{r})^2}\phi_\lambda(\mathbf{r})\phi_\sigma(\mathbf{r}) \\ & + \int d\mathbf{r}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\frac{\partial^2 f_{xc}}{\partial\rho(\mathbf{r})^2}(\phi_\lambda(\mathbf{r})\phi_\sigma(\mathbf{r}))^{[x]} \\ & + \sum_{\gamma\delta}\int d\mathbf{r}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\frac{\partial^3 f_{xc}}{\partial\rho(\mathbf{r})^3}\phi_\lambda(\mathbf{r})\phi_\sigma(\mathbf{r}) \\ & \times P_{\gamma\delta}(\phi_\gamma(\mathbf{r})\phi_\delta(\mathbf{r}))^{[x]}, \end{aligned} \tag{40}$$

$$\omega_{\mu\nu\lambda\sigma}^{\mathrm{Y}[x]} \equiv \sum_{\gamma\delta} P_{\gamma\delta}^{[x]}\Xi_{\mu\nu\lambda\sigma\gamma\delta}, \tag{41}$$

and $\Xi_{\mu\nu\lambda\sigma\gamma\delta}$ is the *xc* functional third derivative,

$$\Xi_{\mu\nu\lambda\sigma\gamma\delta} \equiv \int d\mathbf{r}\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\frac{\partial^3 f_{xc}}{\partial\rho(\mathbf{r})^3}\phi_\lambda(\mathbf{r})\phi_\sigma(\mathbf{r})\phi_\gamma(\mathbf{r})\phi_\delta(\mathbf{r}). \tag{42}$$

Thus, the total two-electron-integral derivatives for TDDFT can be written as

$$\begin{aligned} \Omega_{\mu\nu\lambda\sigma}^{[x]} &= \Pi_{\mu\nu\lambda\sigma}^{[x]} + \omega_{\mu\nu\lambda\sigma}^{[x]} \\ &= \Pi_{\mu\nu\lambda\sigma}^{[x]} + \tilde{\omega}_{\mu\nu\lambda\sigma}^{[x]} + \omega_{\mu\nu\lambda\sigma}^{\mathrm{Y}[x]} \\ &\equiv \tilde{\Omega}_{\mu\nu\lambda\sigma}^{[x]} + \omega_{\mu\nu\lambda\sigma}^{\mathrm{Y}[x]}. \end{aligned} \tag{43}$$

With the definitions made in Sec. II B and the expressions above, Eq. (34) can be rewritten as

$$\begin{aligned} &\langle\Psi_I|\Psi_J^{[x]}\rangle \\ &= \frac{1}{E_J - E_I}\Bigg\{\sum_{\mu\nu} D_{\mu\nu}^{IJ}\left(\tilde{h}_{\mu\nu}^{[x]} + g_{\mu\nu}^{\mathrm{Y}[x]}\right) \\ &\quad + \sum_{\mu\nu\lambda\sigma}\left(R_{\mu\lambda}^I R_{\sigma\nu}^J\left(\tilde{\Omega}_{\mu\nu\lambda\sigma}^{[x]} + \omega_{\mu\nu\lambda\sigma}^{\mathrm{Y}[x]}\right) + D_{\mu\lambda}^{IJ}P_{\sigma\nu}\Pi_{\mu\nu\lambda\sigma}^{[x]}\right) \\ &\quad - \frac{1}{2}\sum_{\alpha\beta\mu\nu} S_{\mu\nu}^{[x]}\tilde{P}_{\mu\alpha}\left(D_{\beta\nu}^{IJ} + D_{\nu\beta}^{IJ}\right)F_{\alpha\beta} \\ &\quad - \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[x]}\tilde{P}_{\mu\alpha}\left(R_{\nu\gamma}^I R_{\delta\beta}^J + R_{\delta\beta}^I R_{\nu\gamma}^J\right)\Omega_{\alpha\beta\gamma\delta} \\ &\quad - \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[x]}\tilde{P}_{\mu\alpha}\left(R_{\gamma\nu}^I R_{\beta\delta}^J + R_{\beta\delta}^I R_{\gamma\nu}^J\right)\Omega_{\alpha\beta\gamma\delta} \\ &\quad + \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[x]}\tilde{P}_{\mu\alpha}P_{\nu\delta}\left(D_{\gamma\beta}^{IJ} + D_{\beta\gamma}^{IJ}\right)\Pi_{\alpha\beta\gamma\delta} \\ &\quad - \sum_{bi}\tilde{Y}_{bi}\Theta_{bi}^{[x]}\Bigg\} \\ &\quad - \sum_{\mu viab} C_{\nu a}t_i^{Ia}t_i^{Jb}C_{\mu b}S_{\mu\nu}^{\mathrm{A}[x]} - \sum_{\mu vija} C_{\nu i}t_i^{Ia}t_j^{Ja}C_{\mu j}S_{\mu\nu}^{\mathrm{A}[x]}, \end{aligned} \tag{44}$$

where

$$\begin{aligned} \tilde{Y}_{bi} = & \sum_{\mu\nu\lambda\sigma d} C_{\mu b}C_{\lambda d}\left(R_{\nu\sigma}^I t_i^{Jd} + t_i^{Id}R_{\nu\sigma}^J\right)\Omega_{\mu\nu\lambda\sigma} \\ & + \sum_{\mu\nu\lambda\sigma} C_{\nu b}C_{\sigma i}\left(D_{\mu\lambda}^{IJ} + D_{\lambda\mu}^{IJ}\right)\Pi_{\mu\nu\lambda\sigma} \\ & + \sum_{\mu\nu\lambda\sigma\ell} C_{\mu\ell}C_{\sigma i}\left(R_{\nu\lambda}^I t_\ell^{Jb} + t_\ell^{Ib}R_{\nu\lambda}^J\right)\Omega_{\mu\nu\lambda\sigma}. \end{aligned} \tag{45}$$

D. Response terms in TDDFT/TDA derivative couplings

Finally, all that remains to do is to treat the so-called "response" terms, $\mathbf{g}^{\mathrm{Y}[x]}$ and $\boldsymbol{\omega}^{\mathrm{Y}[x]}$ in Eq. (44). Combining $\mathbf{g}^{\mathrm{Y}[x]}$ and $\boldsymbol{\omega}^{\mathrm{Y}[x]}$ with their multiplying coefficients in Eq. (45), one has

$$\sum_{\mu\nu} D_{\mu\nu}^{IJ}g_{\mu\nu}^{\mathrm{Y}[x]} = \sum_{\mu\nu\lambda\sigma} D_{\mu\nu}^{IJ}P_{\lambda\sigma}^{[x]}\omega_{\mu\nu\lambda\sigma}, \tag{46}$$

$$\sum_{\mu\nu\lambda\sigma} R_{\mu\lambda}^I R_{\sigma\nu}^J\omega_{\mu\nu\lambda\sigma}^{\mathrm{Y}[x]} = \sum_{\mu\nu\gamma\delta\lambda\sigma} R_{\mu\lambda}^I R_{\sigma\nu}^J P_{\gamma\delta}^{[x]}\Xi_{\mu\nu\lambda\sigma\gamma\delta}. \tag{47}$$

Now, using standard analytic gradient theory summarized in Ref. 52, one can always write (a derivation is provided in Appendix A),

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

$$P^{[x]}_{\nu\sigma} = -\frac{1}{2}\sum_{\alpha\beta}(\tilde{P}_{\nu\alpha}P_{\sigma\beta} + \tilde{P}_{\sigma\alpha}P_{\nu\beta})S^{[x]}_{\alpha\beta} - \sum_{ib}(C_{\nu b}C_{\sigma i} + C_{\nu i}C_{\sigma b})\Theta^{[x]}_{bi}. \tag{48}$$

Combining Eqs. (46)–(48), one finds

$$\sum_{\mu\nu} D^{IJ}_{\mu\nu} g^{\mathrm{Y}[x]}_{\mu\nu} = -\sum_{\mu\nu\lambda\sigma} D^{IJ}_{\mu\nu}\left[\begin{array}{l}\frac{1}{2}\sum_{\alpha\beta}(\tilde{P}_{\lambda\alpha}P_{\sigma\beta} + \tilde{P}_{\sigma\alpha}P_{\lambda\beta})S^{[x]}_{\alpha\beta} \\ +\sum_{bi}(C_{\lambda b}C_{\sigma i} + C_{\lambda i}C_{\sigma b})\Theta^{[x]}_{bi}\end{array}\right]\omega_{\mu\nu\lambda\sigma}, \tag{49}$$

$$\sum_{\mu\nu\lambda\sigma} R^{I}_{\mu\lambda}R^{J}_{\sigma\nu}\omega^{\mathrm{Y}[x]}_{\mu\nu\lambda\sigma} = -\sum_{\mu\nu\gamma\delta\lambda\sigma} R^{I}_{\mu\lambda}R^{J}_{\sigma\nu}\left[\begin{array}{l}\frac{1}{2}\sum_{\alpha\beta}(\tilde{P}_{\gamma\alpha}P_{\delta\beta} + \tilde{P}_{\delta\alpha}P_{\gamma\beta})S^{[x]}_{\alpha\beta} \\ +\sum_{bi}(C_{\nu b}C_{\sigma i} + C_{\nu i}C_{\sigma b})\Theta^{[x]}_{bi}\end{array}\right]\Xi_{\mu\nu\lambda\sigma\gamma\delta}, \tag{50}$$

and after relabeling the indices, Eqs. (49) and (50) become

$$\begin{aligned}\sum_{\mu\nu} D^{IJ}_{\mu\nu} g^{\mathrm{Y}[x]}_{\mu\nu} = &\frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S^{[x]}_{\alpha\beta}\tilde{P}_{\alpha\mu}P_{\beta\sigma}\left(D^{IJ}_{\lambda\nu} + D^{IJ}_{\nu\lambda}\right)\omega_{\mu\nu\lambda\sigma} \\ &- \sum_{\mu\nu\lambda\sigma bi} C_{\nu b}C_{\sigma i}\left(D^{IJ}_{\mu\lambda} + D^{IJ}_{\lambda\mu}\right)\omega_{\mu\nu\lambda\sigma}\Theta^{[x]}_{bi},\end{aligned} \tag{51}$$

$$\begin{aligned}\sum_{\mu\nu\lambda\sigma} R^{I}_{\mu\lambda}R^{J}_{\sigma\nu}\omega^{\mathrm{Y}[x]}_{\mu\nu\lambda\sigma} = &-\frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta\lambda\sigma} S^{[x]}_{\alpha\beta}\tilde{P}_{\alpha\gamma}P_{\beta\delta}\left(R^{I}_{\mu\lambda}R^{J}_{\sigma\nu} + R^{I}_{\sigma\nu}R^{J}_{\mu\lambda}\right)\Xi_{\mu\nu\lambda\sigma\gamma\delta} \\ &- \sum_{\mu\nu\lambda\sigma\gamma\delta bi} C_{\gamma b}C_{\delta i}\left(R^{I}_{\mu\lambda}R^{J}_{\sigma\nu} + R^{I}_{\sigma\nu}R^{J}_{\mu\lambda}\right)\Xi_{\mu\nu\lambda\sigma\gamma\delta}\Theta^{[x]}_{bi}.\end{aligned} \tag{52}$$

Finally, after a bit of tedious algebra and simplification, one arrives at the final expression,

$$\begin{aligned}&\left\langle\Psi_I\middle|\Psi^{[x]}_J\right\rangle \\ &= \frac{1}{E_J - E_I}\left\{\sum_{\mu\nu} D^{IJ}_{\mu\nu}\tilde{h}^{[x]}_{\mu\nu}\right. \\ &\quad + \sum_{\mu\nu\lambda\sigma}\left(R^{I}_{\mu\lambda}R^{J}_{\sigma\nu}\tilde{\Omega}^{[x]}_{\mu\nu\lambda\sigma} + D^{IJ}_{\mu\lambda}P_{\sigma\nu}\Pi^{[x]}_{\mu\nu\lambda\sigma}\right) \\ &\quad -\frac{1}{2}\sum_{\alpha\beta\mu\nu} S^{[x]}_{\mu\nu}\tilde{P}_{\mu\alpha}\left(D^{IJ}_{\beta\nu} + D^{IJ}_{\nu\beta}\right)F_{\alpha\beta} \\ &\quad -\frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S^{[x]}_{\mu\nu}\tilde{P}_{\mu\alpha}\left(R^{I}_{\nu\gamma}R^{J}_{\delta\beta} + R^{I}_{\delta\beta}R^{J}_{\nu\gamma}\right)\Omega_{\alpha\beta\gamma\delta} \\ &\quad -\frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S^{[x]}_{\mu\nu}\tilde{P}_{\mu\alpha}\left(R^{I}_{\gamma\nu}R^{J}_{\beta\delta} + R^{I}_{\beta\delta}R^{J}_{\gamma\nu}\right)\Omega_{\alpha\beta\gamma\delta} \\ &\quad -\frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta\lambda\sigma} S^{[x]}_{\mu\nu}\tilde{P}_{\mu\lambda}P_{\nu\sigma}\left(R^{I}_{\alpha\gamma}R^{J}_{\delta\beta} + R^{I}_{\delta\beta}R^{J}_{\alpha\gamma}\right)\Xi_{\alpha\beta\gamma\delta\lambda\sigma} \\ &\quad +\frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta} S^{[x]}_{\mu\nu}\tilde{P}_{\mu\alpha}P_{\nu\delta}\left(D^{IJ}_{\gamma\beta} + D^{IJ}_{\beta\gamma}\right)\Omega_{\alpha\beta\gamma\delta} \\ &\quad \left.-\sum_{bi} Y_{bi}\Theta^{[x]}_{bi}\right\} \\ &\quad - \sum_{\mu\nu iab} C_{\nu a}t^{Ia}_{i}t^{Jb}_{i}C_{\mu b}S^{\mathrm{A}[x]}_{\mu\nu} - \sum_{\mu\nu ija} C_{\nu i}t^{Ia}_{i}t^{Ja}_{j}C_{\mu j}S^{\mathrm{A}[x]}_{\mu\nu},\end{aligned} \tag{53}$$

where

$$\begin{aligned}Y_{bi} = &\sum_{\mu\nu\lambda\sigma d} C_{\mu b}C_{\lambda d}\left(R^{I}_{\nu\sigma}t^{Jd}_{i} + t^{Id}_{i}R^{J}_{\nu\sigma}\right)\Omega_{\mu\nu\lambda\sigma} \\ &+ \sum_{\mu\nu\lambda\sigma} C_{\nu b}C_{\sigma i}\left(D^{IJ}_{\mu\lambda} + D^{IJ}_{\lambda\mu}\right)\Omega_{\mu\nu\lambda\sigma} \\ &+ \sum_{\mu\nu\lambda\sigma\ell} C_{\mu\ell}C_{\sigma i}\left(R^{I}_{\nu\lambda}t^{Jb}_{\ell} + t^{Ib}_{\ell}R^{J}_{\nu\lambda}\right)\Omega_{\mu\nu\lambda\sigma} \\ &+ \sum_{\mu\nu\lambda\sigma\gamma\delta} C_{\gamma b}C_{\delta i}\left(R^{I}_{\mu\lambda}R^{J}_{\sigma\nu} + R^{I}_{\sigma\nu}R^{J}_{\mu\lambda}\right)\Xi_{\mu\nu\lambda\sigma\gamma\delta}.\end{aligned} \tag{54}$$

Note that the complete orbital-response Lagrangian **Y** in the TDDFT expression (Eq. (54)) differs from that in CIS (Eq. (60b) in Ref. 52) in three ways. First, there is only a fraction of Hartree-Fock exchange (c_{HF}) in the two-electron integral. Second, the second derivative of the *xc* functional appears, i.e., there is a $\boldsymbol{\omega}$ term in $\boldsymbol{\Omega}$ (compared with $\boldsymbol{\Pi}$ for CIS). Third, the third derivative of the *xc* functional $\boldsymbol{\Xi}$ also appears (which has no CIS counterpart).[56]

E. Coupled-perturbed Hartree-Fock equation (CPHF)

As a practical matter, in order to compute the $\boldsymbol{\Theta}$ derivative in Eq. (53), one needs to solve the CPHF equation,[57,58]

$$\Theta^{[x]}_{bi} = -\sum_{ja}\left(\frac{\partial^2 E}{\partial\Theta_{aj}\partial\Theta_{bi}}\right)^{-1} M^{[x]}_{aj}, \tag{55}$$

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

where $\mathbf{M}^{[x]}$ is the matrix that contains all the mixed derivatives,

$$M_{aj}^{[x]} = \sum_{\alpha\beta} \frac{\partial^2 E}{\partial \Theta_{aj} \partial S_{\alpha\beta}} S_{\alpha\beta}^{[x]} + \sum_{\alpha\beta} \frac{\partial^2 E}{\partial \Theta_{aj} \partial h_{\alpha\beta}} h_{\alpha\beta}^{[x]} + \sum_{\alpha\beta\gamma\delta} \frac{\partial^2 E}{\partial \Theta_{aj} \partial \Pi_{\alpha\beta\gamma\delta}} \Pi_{\alpha\beta\gamma\delta}^{[x]}. \quad (56)$$

As is standard in analytic gradient methods, we use the "**z**-vector" method developed by Handy and Schaefer,[59] and we iteratively construct

$$z_{aj} = \sum_{ib} Y_{bi} \left(\frac{\partial^2 E}{\partial \Theta_{aj} \partial \Theta_{bi}} \right)^{-1}. \quad (57)$$

With this **z**-vector saved to disk, we compute $M_{aj}^{[x]}$ for each coordinate x so that $\sum_{bi} Y_{bi} \Theta_{bi}^{[x]}$ can be obtained. Thus, Eqs. (53) and (54) become

$$\begin{aligned}
\left\langle \Psi_I \middle| \Psi_J^{[x]} \right\rangle &= \frac{1}{E_J - E_I} \Bigg\{ \sum_{\mu\nu} \bar{D}_{\mu\nu}^{IJ} \tilde{h}_{\mu\nu}^{[x]} \\
&+ \sum_{\mu\nu\lambda\sigma} \left(R_{\mu\lambda}^I R_{\sigma\nu}^J \tilde{\Omega}_{\mu\nu\lambda\sigma}^{[x]} + \bar{D}_{\mu\lambda}^{IJ} P_{\sigma\nu} \Pi_{\mu\nu\lambda\sigma}^{[x]} \right) \\
&- \frac{1}{2} \sum_{\alpha\beta\mu\nu} S_{\mu\nu}^{[x]} \tilde{P}_{\mu\alpha} \left(\bar{D}_{\beta\nu}^{IJ} + \bar{D}_{\nu\beta}^{IJ} \right) F_{\alpha\beta} \\
&- \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[x]} \tilde{P}_{\mu\alpha} \left(R_{\nu\gamma}^I R_{\delta\beta}^J + R_{\delta\beta}^I R_{\nu\gamma}^J \right) \Omega_{\alpha\beta\gamma\delta} \\
&- \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[x]} \tilde{P}_{\mu\alpha} \left(R_{\gamma\nu}^I R_{\beta\delta}^J + R_{\beta\delta}^I R_{\gamma\nu}^J \right) \Omega_{\alpha\beta\gamma\delta} \\
&- \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta\lambda\sigma} S_{\mu\nu}^{[x]} \tilde{P}_{\mu\lambda} P_{\nu\sigma} \left(R_{\alpha\gamma}^I R_{\delta\beta}^J + R_{\delta\beta}^I R_{\alpha\gamma}^J \right) \Xi_{\alpha\beta\gamma\delta\lambda\sigma} \\
&+ \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[x]} \tilde{P}_{\mu\alpha} P_{\nu\delta} \left(\bar{D}_{\gamma\beta}^{IJ} + \bar{D}_{\beta\gamma}^{IJ} \right) \Omega_{\alpha\beta\gamma\delta} \Bigg\} \\
&- \left(\sum_{\mu\nu iab} C_{\nu a} t_i^{Ia} t_i^{Jb} C_{\mu b} + \sum_{\mu\nu ija} C_{\nu i} t_i^{Ia} t_j^{Ja} C_{\mu j} \right) S_{\mu\nu}^{\mathrm{A}[x]},
\end{aligned} \quad (58)$$

where $\bar{D}^{IJ}$ represents the relaxed difference density matrix,

$$\begin{aligned}
\bar{D}_{\mu\nu}^{IJ} &\equiv D_{\mu\nu}^{IJ} - \sum_{aj} z_{aj} (C_{\mu a} C_{\nu j} + C_{\mu j} C_{\nu a}) \\
&= D_{\mu\nu}^{IJ} - (z_{\mu\nu} + z_{\nu\mu}).
\end{aligned} \quad (59)$$

Equations (54), (57)–(59) are a complete recipe for derivative couplings that is easy to evaluate. In summary, the differences between TDDFT and CIS expressions are the presences of (i) different one-electron-integral derivative for TDDFT $\tilde{\mathbf{h}}^{[x]}$ (compared with $\mathbf{h}^{0[x]}$ in CIS), (ii) $\tilde{\mathbf{\Omega}}^{[x]}$ and $\mathbf{\Omega}$ (compared with $\mathbf{\Pi}^{[x]}$ and $\mathbf{\Pi}$ in CIS), which include the second *xc* functional derivative and specific fraction of Hartree-Fock exchange term involved in TDDFT functionals, and (iii) $\mathbf{\Xi}$, the third *xc* functional derivative (which has no CIS counterpart).

III. COMPARISON WITH FINITE-DIFFERENCE

In order to verify the equations above and also check our numerical implementations of TDDFT/TDA derivative couplings, we calculated the magnitude of the derivative couplings between the S_1 and S_4 states of lithium hydride (LiH), and compared the results with finite-difference method. The standard central-difference formula yields an expression for the derivative coupling as

$$\left\langle \Psi_I \middle| \Psi_J^{[x]} \right\rangle \approx \frac{\langle \Psi_I(x) | \Psi_J(x + \Delta x) \rangle - \langle \Psi_I(x) | \Psi_J(x - \Delta x) \rangle}{2\Delta x}. \quad (60)$$

The *ab initio* quantum chemistry package Q-Chem[60,61] was employed for the calculations. Three different functionals (B3LYP,[62,63] ωB97, and ωB97X[64]) were tested using 6-31G* basis set (CIS results are also listed for comparison). As shown in Table I, our analytical approach matches the finite-difference data with an error $\sim 10^{-4}\ a_0^{-1}$. When Pulay terms ($\mathbf{S}^{[x]}$) are neglected, the resulting derivative couplings change significantly.

IV. APPLICATION TO BENZALDEHYDE

As a prototypical aromatic carbonyl compound, benzaldehyde has drawn significant attention in both experimental and theoretical studies because of its unique spectroscopic properties.[65–74] A great deal of theory and experiment has focused on the two lowest triplet states of benzaldehyde in order to explain the mechanism of the molecule's highly phosphorescent radiation.[65,66,71,73–77] The interstate mixing between the T_1(n-π^*) and T_2(π-π^*) states of benzaldehyde was estimated as long ago as the 1970s.[68,78,79] Since the derivative coupling is essential for understanding nonadiabatic dynamics and radiationless transitions in general, we will also

TABLE I. Derivative couplings between the S_1 and S_4 states of LiH as computed by finite difference (FD), analytical theory (full-DC), and DC without Pulay terms (NP).

		$\langle \Psi_1 \vert \Psi_4^{[Q]} \rangle (a_0^{-1})$		
xc functional	Atom moved (Q)	FD	Full-DC	NP
B3LYP	H	−0.00564	−0.00570	−0.12611
	Li	0.15804	0.15810	0.12611
ωB97	H	−0.04049	−0.04053	−0.06985
	Li	0.15150	0.15154	0.06985
ωB97X	H	−0.05952	−0.05955	−0.07422
	Li	0.16457	0.16460	0.07422
CIS	H	−0.05765	−0.05766	−0.04389
	Li	0.17475	0.17476	0.04389

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

investigate here the T_1/T_2 derivative coupling of benzaldehyde with our analytic gradient method.

In a previous paper,[80] we showed that a conical intersection point can be located between the first and the second triplet states of benzaldehyde according to the TDDFT/ωB97X functional. Now, with a working code for calculating derivative couplings, we revisit geometries around the conical intersection point on the branching plane and calculate the derivative coupling with and without Pulay terms for each geometry. Consistent with the previous work, the ωB97X functional and 6-31G** basis set are used for all calculations.

In Ref. 80, we defined raw **g** and **h** vectors and located the branching plane for benzaldehyde as follows:

i. Find a CI point, $\vec{R}_{CI}$.
ii. Displace each of the 3N Cartesian coordinates in positive and negative directions, and at every displaced point perform (6N) gradient calculations for the adiabatic energies

$$\vec{D}_i^{\pm} = \frac{1}{2}\big(\nabla E_2^{ad}(\vec{R}_{CI} \pm \Delta R \cdot \vec{e}_i) - \nabla E_1^{ad}(\vec{R}_{CI} \pm \Delta R \cdot \vec{e}_i)\big), \quad i = 1, \ldots, 3N. \quad (61)$$

iii. Notice that all 3N gradients actually lie in a single 2D plane – the $\mathbf{g} - \mathbf{h}$ branching plane. At this point, we must make a non-unique choice of **g** and **h** that corresponds to a unique diabatic basis.
iv. In our calculations, we check the energy difference gradient $\vec{D}$ along a circle that is centered at $\vec{R}_{CI}$ in the $\mathbf{g} - \mathbf{h}$ plane. If θ is the angle of rotation around $\vec{R}_{CI}$, we have already computed $\vec{D}(\theta)$ in step ii. We define **g** as $\vec{D}(\theta_{max})$ when θ_{max} is chosen as the angle that maximizes $\|\vec{D}(\theta)\|$.
v. Finally, we check for the angle that minimizes $\|\vec{D}(\theta)\|$. By construction, $\vec{D}(\theta_{min})$ must be perpendicular to **g** and can be defined as **h**.

In this article, we rescale **g** and **h** vectors so that the norm of the gradient difference is identical at every point on the loop,

$$\mathbf{x} = \frac{1}{\|\mathbf{g}\|}\mathbf{g}, \quad (62)$$

$$\mathbf{y} = \frac{\|\mathbf{g}\|}{\|\mathbf{h}\|^2}\mathbf{h}. \quad (63)$$

Note that **x** and **y** are perpendicular (just like **g** and **h**). In what follows, we will investigate the derivative couplings in a loop around the CI point, chosen as $\mathbf{x}\cos\theta + \mathbf{y}\sin\theta$ for $\theta = 0°, 10°, 20°, \ldots, 350°$ at the distance $r = 0.001$ Å. Thus, with normalized coordinates **x** and **y**, we construct a loop defined by the Cartesian coordinates

$$\mathbf{R}(\theta) = \mathbf{R}_{\mathrm{CI}} + 0.001(\mathbf{x}\cos\theta + \mathbf{y}\sin\theta). \quad (64)$$

Note that 0.001 is in units of Angstroms. Five different types of derivative couplings below are calculated:

i. Full-DC: complete derivative couplings given by Eq. (58).
ii. ETF-DC: corrected derivative couplings given by Eq. (58) when setting $\mathbf{S}^{A[x]} = 0$ or $\mathbf{S}^{R[x]} = \frac{1}{2}\mathbf{S}^{[x]}$. As was illustrated in Refs. 52 and 81, this replacement is equivalent to including perturbative electron-translation factors (ETF) in the derivative coupling and restores translational invariance.
iii. NP: derivative couplings without all Pulay terms in Eq. (58), i.e., $\mathbf{S}^{R[x]}, \mathbf{S}^{[x]} \to 0$.
iv. Rel-DH: derivative couplings given by using a Hellmann-Feynman expression with the Fock operator in place of the Hamiltonian. In other words, we collect all terms that contain $\bar{\mathbf{D}}^{IJ}$ in Eq. (58) (including orbital response terms).
v. DH: derivative couplings given by using a Hellmann-Feynman expression with the Fock operator in place of the Hamiltonian. In other words, we collect all terms that contain $\mathbf{D}^{IJ}$ in Eq. (53) (no orbital response terms).

A. Results

For a physical picture of the nondiabatic motion in benzaldehyde, the full-DC, NP, rel-DH, and DH vectors are visualized by the quiver plots shown in Fig. 1. Note the ETF-DC

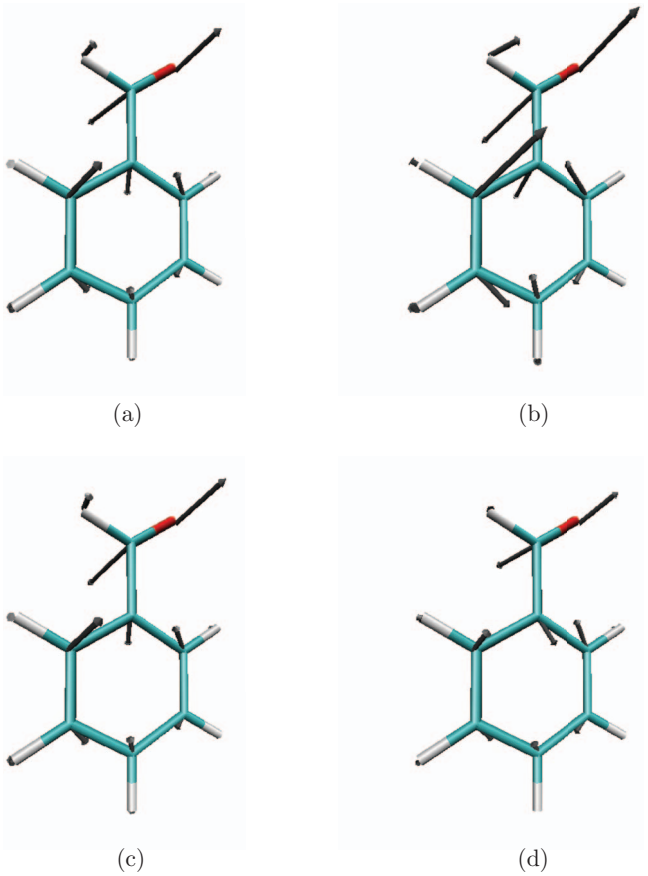


FIG. 1. Derivative coupling vectors for benzaldehyde at $\theta = 30°$ (a) using full analytic gradient theory (full-DC, Eq. (58)), (b) neglecting all Pulay terms (NP), (c) using only the terms that contain $\bar{\mathbf{D}}^{IJ}$ in Eq. (58) (rel-DH), (d) using the terms that contain $\mathbf{D}^{IJ}$ in Eq. (53) (DH).

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

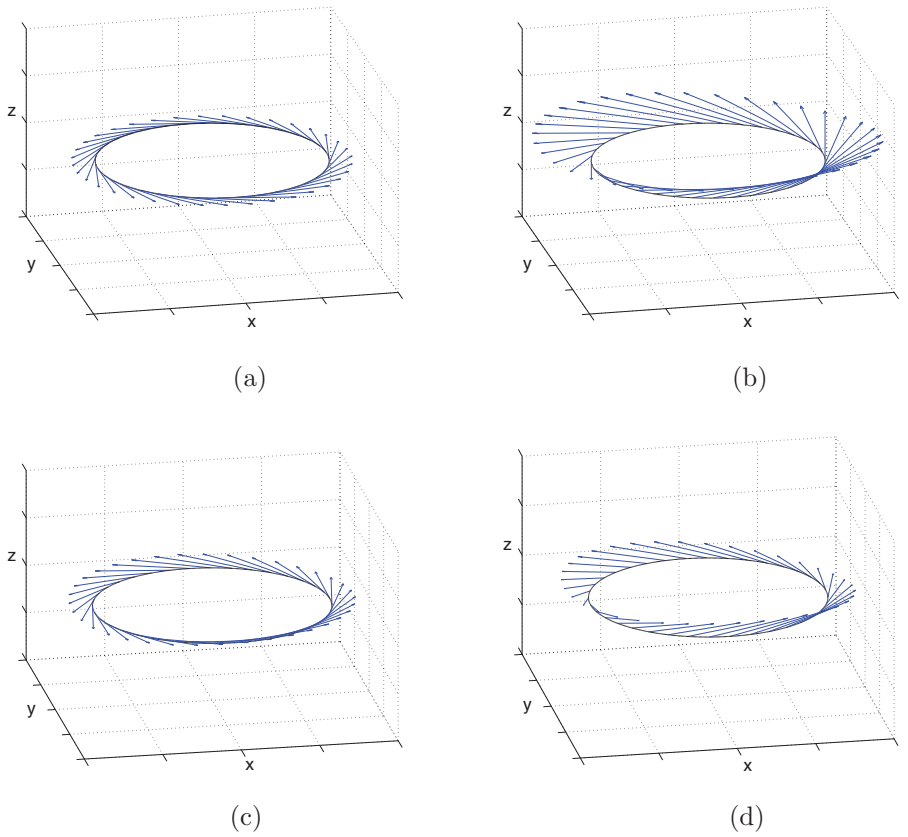


FIG. 2. Full-DC, NP, rel-DH, and DH derivative coupling vectors on the circular loop ($r = 0.001$ Å) in the branching plane. 36 single-point calculations were performed. (a) full-DC, (b) NP, (c) rel-DH, (d) DH.

plot is omitted (since it looks almost exactly the same as full-DC). In Fig. 2, we plot the derivative couplings on the loop around the conical intersection. As Fig. 2 shows, only the full-DC and ETF-DC vectors (which are roughly identical) lie rigorously on the same physically correct branching plane. The other vectors, NP, rel-DH, and DH, are somewhat out of the plane. The out-of-plane angle varies from 2° to 10° for rel-DH vectors and from 15° to 20° for DH and NP vectors. In Table II, we list the out-of-plane angles for the rel-DH, DH, and NP vectors at $\theta = 30°$. To further assess the behavior around the conical intersection, we project these derivative coupling vectors on the branching plane in order to make a meaningful evaluation of their performances around the conical intersection. The full-DC and ETF-DC vectors as well as the rel-DH projections on the branching plane are tangent to the loop, i.e., perpendicular to the gradient difference. By contrast, even after projection, the other methods (NP and DH projection) do not yield that correct orientation for the derivative couplings around the conical intersection point. To prove this point, for $\theta = 30°$, in Table III, we list the exact magnitudes of the derivative couplings and their angles relative to the gradient difference.

Another means to check the reasonability of our derivative coupling is to calculate the phase factor around the conical intersection. It is well-known that Berry's phase will not disappear for a closed path surrounding a conical intersection. Mathematically, for a loop C in the branching plane, the

TABLE II. Out-of-plane angles for the rel-DH, DH, and NP vectors at $\theta = 30°$.

Terms	Out-of-plane angles (deg)
rel-DH	5.642
DH	16.831
NP	15.898

TABLE III. Magnitudes of derivative coupling vectors between T_1 and T_2 states of benzaldehyde and their angles relative to the gradient difference at $\theta = 30°$. Full-DC: The complete derivative couplings given by Eq. (58). ETF-DC: Corrected derivative couplings given by Eq. (58) when setting $\mathbf{S}^{R[x]} = \frac{1}{2}\mathbf{S}^{[x]}$. rel-DH: All terms that contain $\tilde{\mathbf{D}}^{IJ}$ in Eq. (58). DH: All terms that contain $\mathbf{D}^{IJ}$ in Eq. (53). NP: Derivative couplings without all Pulay terms. Note that only the full-DC, ETF-DC, and projected rel-DH vectors are effectively orthogonal to the energy gradient difference in properly scaled coordinates.

Terms	Magnitudes (a_0^{-1})	Angles (deg)
full-DC	261.05361	90.234
ETF-DC	260.45083	90.228
rel-DH (unprojected)	263.67060	90.034
rel-DH (projected)	262.39583	90.034
DH (projected)	180.52366	74.510
NP (projected)	362.58573	96.113

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

TABLE IV. Circulations of derivative couplings vectors around the T_1/T_2 conical intersection point of benzaldehyde. Note that only the full-DC, ETF-DC, and the projected rel-DH vectors recover the correct Berry's phase.

Terms	Magnitudes (in units of π)
full-DC	0.99939
ETF-DC	0.99938
rel-DH (projected)	1.00137
DH (projected)	0.77513
NP (projected)	1.46068

circulation of the derivative coupling must be π,

$$\phi = \oint_C \mathbf{d}_{IJ}(\mathbf{R}) \cdot d\mathbf{R} = \int_0^{2\pi} r\mathbf{d}_{IJ}(\boldsymbol{\theta}) \cdot d\boldsymbol{\theta} = \pi, \quad (65)$$

where $\mathbf{d}_{IJ}$ refers to the derivative coupling between the corresponding states. With a finite number of points (i.e., 36) taken on the loop as shown in Fig. 2, we calculated the sum of the derivative coupling vectors dotted into the direction of each $\delta\theta$, i.e., the tangential direction,

$$\phi \approx \sum_{i=1}^{36} r\mathbf{d}_{IJ}(\boldsymbol{\theta}_i) \cdot \delta\boldsymbol{\theta}_i. \quad (66)$$

Results for different variations of derivative coupling vectors are shown in Table IV. The result for the full-DC (or ETF-DC), which is very close to π, perfectly reproduces the geometric phase factor and further justifies our analytical theory for the derivative coupling. Interestingly, note that the projected rel-DH vectors also recover the exact Berry's phase. Given the fact that the out-of-plane angles for rel-DH vectors are relatively small (less than 10°), it may be true that the rel-DH is a decent approximation to the exact derivative coupling around a conical intersection point. Further investigation is needed. Finally, we observe that NP and DH approximations do not come close to satisfying $\oint_C \mathbf{d}_{IJ}(\mathbf{R})d\mathbf{R} = \pi$. In particular, referring to Table III, one can see that the magnitude of the projected NP vector is twice as large as the one of the full-DC vector, and the magnitude of the projected DH vector is significantly smaller; this explains the incorrect behavior of the NP and DH circulations in Table IV. Overall, our calculation highlights the facts that, (i) in a finite atomic-orbital basis, Pulay terms are non-negligible for the correct derivative coupling in the vicinity of a conical intersection; (ii) the orbital responses also need to be taken into account in order to yield the exact properties of the derivative coupling; (iii) only the full-DC recovers both the correct branching plane and Berry's phase behavior around a conical intersection.

V. CONCLUSION

In this work, we calculated derivative couplings between TDDFT/TDA states via analytic gradient theory by assuming that we can treat the Kohn-Sham excited state wavefunction as if it were a true wavefunction, and then we implemented the resulting equations numerically. With all Pulay terms included, our theory has been numerically validated against the finite-difference data for lithium hydride, with an error less than $10^{-4}\ a_0^{-1}$ for three types of *xc* functionals (B3LYP, ωB97, and ωB97X).

As an application, we investigated benzaldehyde and we studied the T_1/T_2 conical intersection point located in Ref. 80. The considerable differences between the NP, DH, and rel-DH derivative couplings and the full-DC result emphasizes the qualitative significance of Pulay terms as well as the orbital responses. Only the full-DC and ETF-DC vectors lie in the branching plane and are perpendicular to the energy gradient difference. Furthermore, the full-DC and ETF-DC vectors for benzaldehyde computed by our analytical method also satisfy the expected Berry's phase behavior for a loop around the conical intersection point. Finally, in Appendix C, we show that our derivative couplings agree with the exact derivative couplings according to the Chernyak-Mukamel expression in Eq. (2) (with the transition density matrix calculated according to response theory). Altogether, these results strongly suggest that our TDDFT/TDA derivative coupling are quite reasonable. Given the current popularity of TDDFT and the modern interest in photochemistry and photoexcited nonadiabatic dynamics, we believe this computational formalism will be very useful in the future.

ACKNOWLEDGMENTS

We thank Filipp Furche for extremely helpful conversations and his suggestion to include Appendix C. This work was supported by National Science Foundation (NSF) CAREER Grant No. CHE-1150851. J.E.S. also acknowledges an Alfred P. Sloan Research Fellowship and a David and Lucile Packard Fellowship.

APPENDIX A: DERIVATION OF THE DENSITY MATRIX DERIVATIVE $P^{[x]}$

To justify Eq. (48) above, note that besides one- and two-electron-integrals, the only independent variables in quantum chemistry are $\mathbf{S}$ (the overlap) and $\boldsymbol{\Theta}$ (the orbital rotations).[52,82] Therefore, for any matrix $\mathbf{P}$,

$$P_{\mu\nu}^{[x]} = \sum_{\alpha\beta} \frac{\partial P_{\mu\nu}}{\partial S_{\alpha\beta}} S_{\alpha\beta}^{[x]} + \sum_{aj} \frac{\partial P_{\mu\nu}}{\partial \Theta_{aj}} \Theta_{aj}^{[x]}. \quad (A1)$$

Now, the definition of the one-electron ground state density matrix is

$$P_{\mu\nu} = \sum_m C_{\mu m} C_{\nu m}. \quad (A2)$$

To find these partial derivatives, one simply differentiates $\mathbf{P}$ with respect to $\mathbf{S}$ and $\boldsymbol{\Theta}$ to find

$$\frac{\partial P_{\mu\nu}}{\partial \Theta_{aj}} = \sum_m \frac{\partial C_{\mu m}}{\partial \Theta_{aj}} C_{\nu m} + \sum_m C_{\mu m} \frac{\partial C_{\nu m}}{\partial \Theta_{aj}}, \quad (A3)$$

$$\frac{\partial P_{\mu\nu}}{\partial S_{\alpha\beta}} = \sum_m \frac{\partial C_{\mu m}}{\partial S_{\alpha\beta}} C_{\nu m} + \sum_m C_{\mu m} \frac{\partial C_{\nu m}}{\partial S_{\alpha\beta}}. \quad (A4)$$

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

Combining Eqs. (A1)–(A4) and Eq. (63) in Ref. 52 into the above expressions, one gets the final expression for $\mathbf{P}^{[x]}$,

$$P_{\mu\nu}^{[x]} = -\frac{1}{2}\sum_{\alpha\beta}(\tilde{P}_{\mu\alpha}P_{\nu\beta} + \tilde{P}_{\nu\alpha}P_{\mu\beta})S_{\alpha\beta}^{[x]} - \sum_{aj}(C_{\mu a}C_{\nu j} + C_{\mu j}C_{\nu a})\Theta_{aj}^{[x]}. \tag{A5}$$

APPENDIX B: HELLMANN-FEYNMAN DERIVATIVE COUPLINGS

In the text above, we formed derivative couplings from a "brute force" expression whereby we differentiate the ket directly. We will now show that such an approach has a clear Hellmann-Feynman analogue. By applying the logic of the Hellmann-Feynman theorem, the TDDFT/TDA derivative coupling should be equivalent to

$$\mathbf{d}_{IJ}(\mathbf{R}) = \frac{\langle\Psi_I|\nabla_{\mathbf{R}}\mathcal{H}_{KS}|\Psi_J\rangle}{E_J - E_I} \tag{B1}$$

$$= \sum_{ijab} t_i^{Ia}t_j^{Jb}\frac{\langle\Phi_i^a|\mathcal{H}_{KS}^{[x]}|\Phi_j^b\rangle}{E_J - E_I}, \tag{B2}$$

where $\mathcal{H}_{KS} = Q\mathcal{O}_{KS}Q$. Here, $\mathcal{O}_{KS}$ is defined in Eq. (7) and Q is the projector onto the singles manifold. Recall that the matrix element of the Kohn-Sham linear-response tensor $\mathbf{A}$ is given by Eq. (5), so that

$$\mathcal{H}_{KS} = \sum_{ijab}|\Phi_i^a\rangle A_{iajb}\langle\Phi_j^b|. \tag{B3}$$

Inserting Eq. (B3) to Eq. (B2), one has

$$\mathbf{d}_{IJ}(\mathbf{R}) = \frac{1}{E_J - E_I}\sum_{ijab}\{t_i^{Ia}t_j^{Jb}A_{iajb}^{[x]} + \langle\Psi_I|\Phi_i^{a[x]}\rangle A_{iajb}t_i^{Jb} + t_i^{Ia}A_{iajb}\langle\Phi_j^{b[x]}|\Psi_J\rangle\} \tag{B4}$$

$$= \frac{1}{E_J - E_I}\left\{\sum_{ijab}t_i^{Ia}t_j^{Jb}A_{iajb}^{[x]} + E_J\sum_{jkbc}t_k^{Ic}t_j^{Jb}\langle\Phi_k^c|\Phi_j^{b[x]}\rangle - E_I\sum_{ilad}t_i^{Ia}t_l^{Jd}\langle\Phi_l^d|\Phi_i^{a[x]}\rangle\right\}. \tag{B5}$$

By relabeling the indices, one can combine the like terms and reach the following equation:

$$\mathbf{d}_{IJ}(\mathbf{R}) = \sum_{ijab}t_i^{Ia}t_j^{Jb}\left[\frac{1}{E_J - E_I}A_{iajb}^{[x]} + \langle\Phi_i^a|\Phi_j^{b[x]}\rangle\right] \tag{B6}$$

which is exactly the same expression as Eq. (24). Therefore, our direct differentiation method for derivative couplings has an obvious Hellmann-Feynman analogue.

APPENDIX C: THE CHERNYAK-MUKAMEL EXPRESSION AND THE TRANSITION DENSITY MATRIX ACCORDING TO RESPONSE THEORY

In the limit of two exact eigenstates of the Hamiltonian, $|\Psi_I\rangle$ and $|\Psi_J\rangle$, the derivative coupling takes a very simple form known as the Chernyak-Mukamel formula (Eq. (C1)),

$$\mathbf{d}_{IJ}^{\mathrm{CM}} = \frac{1}{E_J - E_I}\sum_{pq}v_{pq}^{[x]}\gamma_{pq}^{IJ}, \tag{C1}$$

where γ_{pq}^{IJ} is the one-electron transition density matrix. Here, $v_{pq}^{[x]} = \sum_{\mu\nu}C_{\mu p}v_{\mu\nu}^{[x]}c_{\nu q}$, where $v_{\mu\nu}^{[x]}$ is the derivative of the nuclear-electronic potential in the AO basis. Equation (C1) can be derived easily from the exact Hellmann-Feynman expression,

$$\mathbf{d}_{IJ}^{\mathrm{exact}} = \frac{\langle\Psi_I^{\mathrm{exact}}|\nabla_{\mathbf{R}}H^{\mathrm{exact}}|\Psi_J^{\mathrm{exact}}\rangle}{E_J - E_I} \tag{C2}$$

using the fact that only $v_{\mu\nu}$ in the Hamiltonian depends on nuclear coordinates in the limit of an infinite basis. According to time-dependent response theory,[49,83] γ_{pq}^{IJ} is given by

$$\gamma_{pq}^{IJ} = \begin{cases} -\sum_a t_p^{Ja}t_q^{Ia} & \text{for } p,q \in \text{occupied orbitals,} \\ \sum_i t_i^{Ip}t_i^{Jq} & \text{for } p,q \in \text{virtual orbitals,} \\ \gamma_{pq}^{(1),IJ} & \text{for } p \in \text{virtual orbitals, } q \in \text{occupied orbitals,} \\ \gamma_{pq}^{(2),IJ} & \text{for } q \in \text{virtual orbitals, } p \in \text{occupied orbitals.} \end{cases} \tag{C3}$$

The occupied-virtual components of γ^{IJ} are obtained by solving

$$\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} + \Delta E\begin{pmatrix}\mathbf{I} & 0\\ 0 & -\mathbf{I}\end{pmatrix}\right]\begin{pmatrix}\gamma^{(1),IJ}\\ \gamma^{(2),IJ}\end{pmatrix} = -\begin{pmatrix}\mathbf{Y}^{(1)}\\ \mathbf{Y}^{(2)}\end{pmatrix}, \tag{C4}$$

where $\Delta E = E_J - E_I$,

$$B_{iajb} = \langle\Phi_{ij}^{ab}|\mathcal{O}_{\mathrm{KS}}|\Phi_{\mathrm{DFT}}\rangle \tag{C5}$$

$$= \Omega_{abij}, \tag{C6}$$

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

$$Y_{bi}^{(1)} = \sum_{pq} \Omega_{pbqi} D_{pq}^{IJ} + \sum_{jcd} t_j^{Ic} t_i^{Jd} \Omega_{bcdj} + \sum_{jlc} t_j^{Ic} t_l^{Jb} \Omega_{lcji} + \sum_{jlcd} t_j^{Ic} t_l^{Jd} \Xi_{cljdbi}, \tag{C7}$$

$$Y_{bi}^{(2)} = \sum_{pq} \Omega_{pbqi} D_{qp}^{IJ} + \sum_{jcd} t_i^{Id} t_j^{Jc} \Omega_{bcdj} + \sum_{jlc} t_l^{Ib} t_j^{Jc} \Omega_{lcji} + \sum_{jlcd} t_l^{Id} t_j^{Jc} \Xi_{cljdbi}. \tag{C8}$$

We now want to compare our derivative couplings with Eq. (C1). We will assume a complete basis and ignore Pulay terms ($\mathbf{S}^{[x]}$) and the antisymmetrized AO overlap derivatives ($\mathbf{S}^{A[x]}$). Hence, our derivative coupling expression in a complete basis limit ($\mathbf{d}_{IJ}^{\mathrm{CB}}$) becomes

$$\mathbf{d}_{IJ}^{\mathrm{CB}} = \frac{1}{E_J - E_I} \sum_{pq} v_{pq}^{[x]} D_{pq}^{IJ} - \frac{1}{E_J - E_I} \sum_{bi} Y_{bi} \Theta_{bi}^{[x]}, \tag{C9}$$

where the difference density matrix D_{pq}^{IJ} and the Lagrangian Y_{bi} in the MO basis can be represented as

$$D_{pq}^{IJ} = \begin{cases} -\sum_a t_p^{Ja} t_q^{Ia} & \text{for } p, q \in \text{occupied orbitals}, \\ \sum_i t_i^{Ip} t_i^{Jq} & \text{for } p, q \in \text{virtual orbitals}, \\ 0 & \text{otherwise}, \end{cases} \tag{C10}$$

$$Y_{bi} = \sum_{pq} \Omega_{pbqi} \left(D_{pq}^{IJ} + D_{qp}^{IJ} \right) + \sum_{jcd} \left(t_j^{Ic} t_i^{Jd} + t_i^{Id} t_j^{Jc} \right) \Omega_{bcdj} + \sum_{jlc} \left(t_j^{Ic} t_l^{Jb} + t_l^{Ib} t_j^{Jc} \right) \Omega_{lcji} + \sum_{jlcd} \left(t_j^{Ic} t_l^{Jd} + t_l^{Id} t_j^{Jc} \right) \Xi_{cljdbi}. \tag{C11}$$

As illustrated in Sec. II E, $\sum_{bi} Y_{bi} \Theta_{bi}^{[x]}$ is obtained according to the "**z**-vector" method

$$\sum_{bi} Y_{bi} \Theta_{bi}^{[x]} = \sum_{ja} z_{aj} M_{aj}^{[x]} \tag{C12}$$

$$= -\sum_{jaib} \left(\frac{\partial^2 E}{\partial \Theta_{aj} \partial \Theta_{bi}} \right)^{-1} Y_{bi} M_{aj}^{[x]}. \tag{C13}$$

With an infinite basis, the only term in $\mathbf{M}^{[x]}$ that contributes to the final result is the $v^{[x]}$ term. Hence,

$$\sum_{bi} Y_{bi} \Theta_{bi}^{[x]} = -\sum_{jaib} \left(\frac{\partial^2 E}{\partial \Theta_{aj} \partial \Theta_{bi}} \right)^{-1} Y_{bi} (v_{aj}^{[x]} + v_{ja}^{[x]}) \tag{C14}$$

$$= \sum_{jaib} (A+B)_{jaib}^{-1} Y_{bi} v_{aj}^{[x]}. \tag{C15}$$

Thus, our derivative coupling can be rewritten as

$$\mathbf{d}_{IJ}^{\mathrm{CB}} = \frac{1}{E_J - E_I} \sum_{pq} v_{pq}^{[x]} \Gamma_{pq}^{IJ}, \tag{C16}$$

where Γ_{pq}^{IJ} is given by

$$\Gamma_{pq}^{IJ} = \begin{cases} D_{pq}^{IJ} & \text{for } p, q \in \text{occupied orbitals or } p, q \in \text{virtual orbitals}, \\ -\frac{1}{2} \sum_{bi} (A+B)_{qpib}^{-1} Y_{bi} & \text{for } p \in \text{virtual orbitals}, q \in \text{occupied orbitals}, \\ -\frac{1}{2} \sum_{bi} (A+B)_{pqib}^{-1} Y_{bi} & \text{for } q \in \text{virtual orbitals}, p \in \text{occupied orbitals}. \end{cases} \tag{C17}$$

Finally, if we compare our derivative coupling expression (Eq. (C16)) to the Chernyak-Mukamel formula (Eq. (C1)), it is clear that the two expressions will agree if $\Gamma_{pq}^{IJ} = \gamma_{pq}^{IJ}$. To that end, note that $Y_{bi} = Y_{bi}^{(1)} + Y_{bi}^{(2)}$ if we compare Eqs. (C7)–(C8) and Eq. (C11). Furthermore, in the limit that $\Delta E \to 0$, one finds that from Eq. (C4),

$$\gamma_{aj}^{(1),IJ} + \gamma_{ja}^{(2),IJ} = -\sum_{bi} (A+B)_{jaib}^{-1} Y_{bi} = \Gamma_{aj}^{IJ} + \Gamma_{ja}^{IJ}. \tag{C18}$$

Therefore, we may now conclude that near a crossing or a conical intersection ($\Delta E \to 0$), our derivative couplings in a complete basis ($\mathbf{d}_{IJ}^{\mathrm{CB}}$) agree with the Chernyak-Mukamel formula ($\mathbf{d}_{IJ}^{\mathrm{CM}}$), provided that the transition density matrix (γ^{IJ}) is computed with time-dependent response theory.

[1] M. Born and R. Oppenheimer, Ann. Phys. **389**, 457 (1927).
[2] M. Born and K. Huang, *The Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, Amen House, London, 1954).
[3] D. R. Yarkony, Rev. Mod. Phys. **68**, 985 (1996).
[4] D. R. Yarkony, J. Phys. Chem. A **105**, 6277 (2001).
[5] S. Matsika and P. Krause, Annu. Rev. Phys. Chem. **62**, 621 (2011).
[6] C. Ng, M. Baer, I. Prigogine, and S. A. Rice, "State-selected and state-to-state ion-molecule reaction dynamics, Part 1. Experiment," *Advances in Chemical Physics* (John Wiley and Sons, Inc., 1992), Vol. 82.
[7] J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[8] B. H. Lengsfield III and D. R. Yarkony, Adv. Chem. Phys. **82**(part 2), 1 (1992).
[9] P. Habitz and C. Votava, J. Chem. Phys. **72**, 5532 (1980).
[10] B. H. Lengsfield III, P. Saxe, and D. R. Yarkony, J. Chem. Phys. **81**, 4549 (1984).
[11] P. Saxe, B. H. Lengsfield III, and D. R. Yarkony, Chem. Phys. Lett. **113**, 159 (1985).
[12] B. H. Lengsfield III and D. R. Yarkony, J. Chem. Phys. **84**, 348 (1986).
[13] W. Domcke, D. R. Yarkony, and H. Köppel, *Conical Intersections: Electron Structure Dynamics and Spectroscopy* (World Scientific Publishing Co. Pte. Ltd., Singapore, 2004).

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24

[14]H. Lischka, M. Dallos, P. G. Szalay, D. R. Yarkony, and R. Shepard, J. Chem. Phys. **120**, 7322 (2004).
[15]B. G. Levine, C. Ko, J. Quenneville, and T. J. Martínez, Mol. Phys. **104**, 1039 (2006).
[16]B. G. Levine, J. D. Coe, and T. J. Martínez, J. Phys. Chem. B **112**, 405 (2008).
[17]S. L. Li, A. V. Marenich, X. Xu, and D. G. Truhlar, J. Phys. Chem. Lett. **5**, 322 (2014).
[18]P. Jørgensen and J. Simons, J. Chem. Phys. **79**, 334 (1983).
[19]T. U. Helgaker and J. Almlöf, Int. J. Quantum Chem. **26**, 275 (1984).
[20]M. Page, P. Saxe, G. F. Adams, and B. H. Lengsfield III, J. Chem. Phys. **81**, 434 (1984).
[21]R. Shepard, Int. J. Quantum Chem. **31**, 33 (1987).
[22]R. Shepard, H. Lischka, P. G. Szalay, T. Kovar, and M. Ernzerhof, J. Chem. Phys. **96**, 2085 (1992).
[23]H. Lischka, M. Dallos, and R. Shepard, Mol. Phys. **100**, 1647 (2002).
[24]D. R. Yarkony, J. Chem. Phys. **90**, 1657 (1989).
[25]D. R. Yarkony, J. Chem. Phys. **105**, 10456 (1996).
[26]D. R. Yarkony, J. Phys. Chem. A **101**, 4263 (1997).
[27]S. Matsika and D. R. Yarkony, J. Chem. Phys. **116**, 2825 (2002).
[28]M. Dallos, H. Lischka, R. Shepard, D. R. Yarkony, and P. G. Szalay, J. Chem. Phys. **120**, 7330 (2004).
[29]R. A. Young, Jr. and D. R. Yarkony, J. Chem. Phys. **125**, 234301 (2006).
[30]W. C. Chung, Z. Lan, Y. Ohtsuki, N. Shimakura, W. Domcke, and Y. Fujimura, Phys. Chem. Chem. Phys. **9**, 2075 (2007).
[31]S. Mukherjee, S. Bandyopadhyay, A. K. Paul, and S. Adhikari, J. Phys. Chem. A **117**, 3475 (2013).
[32]V. Chernyak and S. Mukamel, J. Chem. Phys. **112**, 3572 (2000).
[33]E. Tapavicza, I. Tavernelli, and U. Rothlisberger, Phys. Rev. Lett. **98**, 023001 (2007).
[34]I. Tavernelli, B. F. E. Curchod, and U. Rothlisberger, J. Chem. Phys. **131**, 196101 (2009).
[35]I. Tavernelli, E. Tapavicza, and U. Rothlisberger, J. Chem. Phys. **130**, 124107 (2009).
[36]I. Tavernelli, B. F. E. Curchod, A. Laktionov, and U. Rothlisberger, J. Chem. Phys. **133**, 194104 (2010).
[37]C. Hu, H. Hirai, and O. Sugino, J. Chem. Phys. **127**, 064103 (2007).
[38]C. Hu, O. Sugino, and Y. Tateyama, J. Chem. Phys. **131**, 114101 (2009).
[39]C. Hu, O. Sugino, H. Hirai, and Y. Tateyama, Phys. Rev. A **82**, 062508 (2010).
[40]E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[41]M. Barbatti, A. J. A. Aquino, H. Lischka, C. Schriever, S. Lochbrunner, and E. Riedle, Phys. Chem. Chem. Phys. **11**, 1406 (2009).
[42]T. Fuji, Y.-I. Suzuki, T. Horio, T. Suzuki, R. Mitri, U. Werner, and V. Bonai-Koutecký, J. Chem. Phys. **133**, 234303 (2010).
[43]M. Barbatti, Z. Lan, R. Crespo-Otero, J. J. Szymczak, H. Lischka, and W. Thiel, J. Chem. Phys. **137**, 22A503 (2012).
[44]P. R. Koren, F. Chen, and E. R. Davidson, Mol. Phys. **99**, 1329 (2001).
[45]M. Tommasini, V. Chernyak, and S. Mukamel, Int. J. Quantum Chem. **85**, 225 (2001).
[46]S. Tretiak and S. Mukamel, Chem. Rev. **102**, 3171 (2002).
[47]M. Casida, in *Recent Advances in Density Functional Methods*, edited by D. P. Chong (World Scientific, 1995), Vol. 1, pp. 155–192.
[48]R. Send and F. Furche, J. Chem. Phys. **132**, 044107 (2010).
[49]F. Furche, J. Chem. Phys. **114**, 5982 (2001).
[50]P. Pulay, Mol. Phys. **17**, 197 (1969).
[51]F. Liu, Z. Gan, Y. Shao, C.-P. Hsu, A. Dreuw, M. Head-Gordon, B. T. Miller, B. R. Brooks, J.-G. Yu, T. R. Furlani, and J. Kong, Mol. Phys. **108**, 2791 (2010).
[52]S. Fatehi, E. Alguire, Y. Shao, and J. E. Subotnik, J. Chem. Phys. **135**, 234105 (2011).
[53]In physicists' notation, Π_{pqsr} is given by Eq. (13) where $\langle pq|sr\rangle = \iint d\mathbf{r_1} d\mathbf{r_2} \frac{\phi_p^*(\mathbf{r_1})\phi_q^*(\mathbf{r_2})\phi_s(\mathbf{r_1})\phi_r(\mathbf{r_2})}{|\mathbf{r_1}-\mathbf{r_2}|}$.
[54]In this article, for simplicity, we will treat f_{xc} as if it is a strictly local functional $f[\rho(\mathbf{r})]$. Extending to Generalized Gradient Approximation (GGA) functionals $f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]$ and meta GGA's is straightforward.
[55]Note that the difference-density matrix is slightly different from that in Ref. 52 in so far as I and J are switched in the second term. This modification will not influence our final result since $\mathbf{D}^{IJ}$ is always dotted into some symmetric matrices; it does however allow an easier comparison with response theory in Appendix C.
[56]Note that Tavernelli *et al.* (in Ref. 36) use only the Fock operator in Eq. (15) and therefore include only the attach-detach pieces in Eqs. (53) and (54), i.e., terms that contain $\mathbf{B}^{IJ}$ matrix.
[57]J. Gerratt and I. M. Mills, J. Chem. Phys. **49**, 1719 (1968).
[58]J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. **16**, 225 (1979).
[59]N. C. Handy and H. F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984).
[60]J. Kong, M. S. Lee, A. M. Lee, S. R. Gwaltney, T. R. Adams, C. Ochsenfeld, A. T. B. Gilbert, G. S. Kedziora, V. A. Rassolov, D. R. Maurice, N. Nair, Y. Shao, N. A. Besley, P. E. Maslen, J. P. Dombroski, H. Daschel, W. Zhang, P. P. Korambath, J. Baker, E. F. C. Byrd, T. V. Voorhis, M. Oumi, S. Hirata, C.-P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B. G. Johnson, P. M. W. Gill, M. Head-Gordon, and J. A. Pople, J. Comput. Chem. **21**, 1532 (2000).
[61]Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. Distasio, R. C. Lochan, T. Wang, G. J. O. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. V. Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simmonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, A. K. Chakraborty, D. M. Chipman, F. J. Keil, A. Warshel, W. J. Hehre, H. F. Schaefer, J. Kong, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon, Phys. Chem. Chem. Phys. **8**, 3172 (2006).
[62]C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[63]A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[64]J. D. Chai and M. Head-Gordon, J. Chem. Phys. **128**, 084106 (2008).
[65]M. Berger, I. L. Goldblatt, and C. Steele, J. Am. Chem. Soc. **95**, 1717 (1973).
[66]N. Ohmori, T. Suzuki, and M. Ito, J. Chem. Phys. **92**, 1086 (1988).
[67]C. R. Silva and J. P. Reilly, J. Phys. Chem. **100**, 17111 (1996).
[68]J. Smolarek, R. Zwarich, and L. Goodman, J. Mol. Spectrosc. **43**, 416 (1972).
[69]Y. Hirata and E. C. Lim, J. Chem. Phys. **72**, 5505 (1980).
[70]A. Bagchi, Y. Huang, Z. Xu, P. Raghunath, Y. Lee, C. Ni, M. Lin, and Y. Lee, Chem. Asian. J. **6**, 2961 (2011).
[71]J. Metcalfe, R. G. Brown, and D. Phillips, J. Chem. Soc. Faraday Trans. II **71**, 409 (1975).
[72]V. Molina and M. Merchan, J. Phys. Chem. A **105**, 3745 (2001).
[73]G. Cui, Y. Lu, and W. Thiel, Chem. Phys. Lett. **537**, 21 (2012).
[74]W. Fang, Acc. Chem. Res. **41**, 452 (2008).
[75]M. Biron and P. Longin, Chem. Phys. Lett. **116**, 250 (1985).
[76]O. Sneh and O. Cheshnovsky, J. Phys. Chem. **95**, 7154 (1991).
[77]W. Fang and D. L. Phillips, Chem. Phys. Chem. **3**, 889 (2002).
[78]R. J. Zwarich and L. Goodman, Chem. Phys. Lett. **7**, 609 (1970).
[79]L. Goodman and I. Özkan, Chem. Phys. Lett. **61**, 216 (1979).
[80]Q. Ou and J. E. Subotnik, J. Phys. Chem. C **117**, 19839 (2013).
[81]S. Fatehi and J. E. Subotnik, J. Phys. Chem. Lett. **3**, 2039 (2012).
[82]D. Maurice, *Single Electron Theories of Excited States* (University of California, Berkeley, 1998).
[83]F. Furche and R. Ahlrichs, J. Chem. Phys. **117**, 7433 (2002).
[84]Z. Li and W. Liu, J. Chem. Phys. **141**, 014110 (2014) (this article appeared online too late to be considered here).

Reuse of AIP Publishing content is subject to the terms: https://publishing.aip.org/authors/rights-and-permissions. Downloaded to IP: 130.91.66.124 On: Tue, 26 Apr 2016 16:51:24