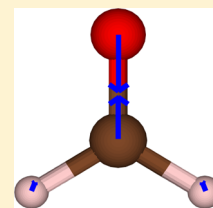


Calculating Derivative Couplings between Time-Dependent Hartree–Fock Excited States with Pseudo-Wavefunctions

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ABSTRACT: A pseudo-wavefunction description of time-dependent Hartree–Fock (TDHF) states is proposed and used to develop an analytic expression for derivative couplings between TDHF excited states based on the Hellmann–Feynman theorem. The resulting expression includes Pulay terms associated with using an atom-centered basis as well as a correction to ensure translational invariance. We demonstrate that our formalism recovers the well-known Chernyak–Mukamel expression near a crossing and in the limit of a complete basis, and thus our approach is consistent with time-dependent response theory. In a companion paper (DOI 10.1021/jp5057682), we investigate these derivative couplings near conical intersections and show that they behave correctly.



I. INTRODUCTION

Derivative couplings, or DCs, describe the coupling between electronic states induced by nuclear motion

$$d_{ij}^{[Q]} = \langle \Psi_i | \nabla_Q | \Psi_j \rangle \quad (1)$$

where Q indexes a nuclear degree of freedom. Given an orthonormal basis of electronic states $\{|\Psi_j\rangle\}$, we expect this quantity to be largest when a small change in the nuclear configuration results in a large change in the electronic states. In many cases, adiabatic electronic states change little as the molecular nuclear arrangement is perturbed, and therefore $d_{ij}^{[Q]}$ can be safely ignored. Neglect of such terms forms the basis of the Born–Oppenheimer or adiabatic approximation, which posits the separability of the nuclear and electronic parts of the molecular wavefunction. However, there are numerous examples for which the adiabatic approximation breaks down; even for diatomic systems, there are nuclear configurations for which the probability of a nonradiative transition is high.^{1,2} Such configurations become more pervasive for systems with more nuclear degrees of freedom.

A great deal of effort has been spent calculating DCs within the multireference configuration interaction (MRCI) formalism by Lengsfeld, Saxe, Yarkony, Lischka, Shepard, and co-workers.^{3–6} Going forward, many researchers are keen to explore excited state dynamics for even larger systems. As such, there is growing demand for analytic DCs by means of a less expensive formalism, such as configuration interaction singles (CIS),⁷ and time-dependent Hartree–Fock (TDHF), or equivalently time-dependent density functional theory under the Tamm–Dancoff approximation (TDDFT-TDA),^{8–10} and full time-dependent density functional theory.^{11–22}

In this manuscript, our goal is to calculate a reasonable expression for derivative couplings between excited states within the TDHF formalism. Rather than use time-dependent response theory, we will construct DCs via a wavefunction-based Hellmann–Feynman expression with a projector-modified Hamiltonian. This approach is analogous to that described in ref 7 for CIS. Our approach also matches exactly the DCs as recently suggested by Li

and Liu from a time-dependent equation of motion (which was published while the present article was under review).²³ It is worth mentioning that our final answer does not match the result from the Tavernelli group,⁸ who proposed DCs based on Casida's assignment of TDHF states.²⁴ As in the work of Send and Furche,²¹ our approach includes Pulay terms that account for a finite, atom-centered basis.²⁵ In addition, we note that, while the expression in the current work contains terms that violate translational invariance, the use of electron translation factors (ETFs)^{7,26} allows us to recover translationally invariant DCs without any additional computational cost. To justify our approach, we will show that near an excited state crossing we recover the Chernyak–Mukamel formula, in which the DC is described as a function of the transition density (as calculated by response theory).^{11,12,27}

The structure of this manuscript is as follows: In section I.A, we briefly introduce the TDHF formalism. After establishing notational conventions in section II, we propose a Hellmann–Feynman approach for TDHF DCs in section III. In section IV, we compare our results to those obtained from a finite difference approximation. In section V, we show that our proposed expression for DCs matches the exact Chernyak–Mukamel formalism and is thus completely consistent with time-dependent response theory near an excited state crossing. In an accompanying paper,²⁸ we extend the approach here to include TDDFT and show that the theory explored in this paper produces DCs with the correct behavior around a conical intersection.

A. Time-Dependent Hartree–Fock. While the first appearance of TDHF^{29–33} (also known as the random phase approximation, or RPA) predates configuration interaction singles,³⁴ TDHF can be considered (loosely) an extension to CIS. The CIS formalism is defined by a wavefunction

Special Issue: John R. Miller and Marshall D. Newton Festschrift

Received: June 10, 2014

Revised: August 2, 2014

$$|\Phi_I^{\text{CIS}}\rangle = \sum_{ia} t_i^{Ia} |\Phi_i^a\rangle \quad (2)$$

and the set of eigenvalue equations

$$\mathbf{A}\mathbf{t}^I = \sum_{jb} A_{ajib} t_j^{Ib} = E_I^{\text{CIS}} \mathbf{t}^I \quad (3)$$

Here, \mathbf{t}^I is a set of amplitudes for state I , E_I is the corresponding excitation energy, and \mathbf{A} is the single excitation subspace of the Hamiltonian

$$A_{ajib} = \langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle - \delta_{ij} \delta_{ab} E_{\text{HF}} = \delta_{ab} \delta_{ij} (\varepsilon_a - \varepsilon_i) + \langle ib || aj \rangle \quad (4)$$

In eq 4, E_{HF} is the Hartree–Fock energy, ε_p is the Fock energy of orbital p and $\langle pq || rs \rangle$ is the antisymmetrized two-electron integral in physicists' notation.

While TDHF does not correspond to a static wavefunction ansatz, the TDHF formalism is governed by an eigenvalue equation which is similar to eq 3

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^I \\ \mathbf{Y}^I \end{pmatrix} = E_I \begin{pmatrix} \mathbf{X}^I \\ \mathbf{Y}^I \end{pmatrix} \quad (5)$$

Here, we assume real orbitals and amplitudes, and \mathbf{B} is the subspace of the Hamiltonian associated with coupling between the Hartree–Fock ground state and doubly excited states

$$B_{ajib} = \langle \Phi_i^{ab} | \hat{H} | \Phi_{\text{HF}} \rangle = \langle ab || ij \rangle \quad (6)$$

\mathbf{X}^I is a set of amplitudes indexed by X_i^{Ia} that are analogous to \mathbf{t}^I , and \mathbf{Y}^I is a set of amplitudes that is associated with the energy contribution from \mathbf{B} and captures electronic correlation in the ground state. TDHF amplitudes associated with different electronic states have an orthonormality relationship given as

$$(\mathbf{X}^{I\dagger} - \mathbf{Y}^{I\dagger}) \begin{pmatrix} \mathbf{X}^J \\ \mathbf{Y}^J \end{pmatrix} = \mathbf{X}^{I\dagger} \mathbf{X}^J - \mathbf{Y}^{I\dagger} \mathbf{Y}^J = \delta_{IJ} \quad (7)$$

Compared to CIS, TDHF produces slightly improved excited state energies. It also obeys the Thomas–Reiche–Kuhn sum rule for oscillator strengths, and as such usually produces more accurate transition moments.^{33,35}

It is well-known that, in order for TDHF to be accurate, the \mathbf{Y} amplitudes must have small magnitude.^{35,36} Consequently, our goal in this manuscript is to determine DCs up to $O(\mathbf{Y}^2)$. For these purposes, note that eq 7 can be rewritten

$$\mathbf{X}^{I\dagger} \mathbf{X}^J = \delta_{IJ} + O(\mathbf{Y}^2) \quad (8)$$

The relative magnitude of the \mathbf{X} and \mathbf{Y} amplitudes should reflect the fact that TDHF must offer only a small correction to CIS; if we let $\mathbf{B} \rightarrow 0$ in eq 5, then we recover the CIS energies and amplitudes.

II. NOTATION AND PRELIMINARY CONSIDERATIONS

The uppercase letters $\{I, J\}$ index adiabatic electronic states. The lowercase letters $\{i, j, k, l, m, n\}$ index occupied molecular orbitals (MOs), while $\{a, b, c, d, e, f\}$ index virtual MOs, $\{p, q, r, s\}$ index general MOs, and Greek letters $\{\alpha, \beta, \mu, \nu, \lambda, \sigma\}$ index atomic orbitals (AOs). MO coefficients are denoted $C_{\mu p}$. Following the convention established in ref 7, nuclear degrees of freedom in the Cartesian basis are indexed by the letter Q , and gradients with respect to such degrees of freedom are denoted by a superscript Q enclosed in square brackets, such as

$f^{[Q]}$. The Hartree–Fock ground state is denoted $|\Phi_{\text{HF}}\rangle$, and derivative couplings are denoted $d_{ij}^{[Q]}$.

Configuration interaction projection operators are denoted \mathcal{P}_n , where n indicates the level of excitation to which the projection operator corresponds; for example,

$$\mathcal{P}_0 \equiv |\Phi_{\text{HF}}\rangle \langle \Phi_{\text{HF}}| \quad (9)$$

$$\mathcal{P}_1 \equiv \sum_{ia} |\Phi_i^a\rangle \langle \Phi_i^a| \quad (10)$$

$$\mathcal{P}_2 \equiv \frac{1}{4} \sum_{ijab} |\Phi_{ij}^{ab}\rangle \langle \Phi_{ij}^{ab}| \quad (11)$$

and so forth, so that the full configuration interaction resolution of the identity is given by

$$\mathbf{1} = \mathcal{P}_0 + \mathcal{P}_1 + \mathcal{P}_2 + \mathcal{P}_3 + \dots \quad (12)$$

We define the Hartree–Fock density matrix

$$P_{\mu\nu} \equiv \sum_i C_{\mu i} C_{\nu i} \quad (13)$$

and a related quantity

$$\tilde{P}_{\mu\nu} \equiv \sum_p C_{\mu p} C_{\nu p} = P_{\mu\nu} + \sum_a C_{\mu a} C_{\nu a} \quad (14)$$

TDHF transition density matrices from the ground to an excited state are given by

$$R_{\mu\nu}^{XI} \equiv \sum_{ia} C_{\mu a} X_i^{Ia} C_{\nu i} \quad (15)$$

and

$$R_{\mu\nu}^{YI} \equiv \sum_{ia} C_{\mu a} Y_i^{Ia} C_{\nu i} \quad (16)$$

where X_i^{Ia} and Y_i^{Ia} are the TDHF amplitudes associated with state I . Generalized difference density matrices between excited states are given by

$$D_{\mu\nu}^{IJ} \equiv \sum_{iab} C_{\mu a} (X_i^{Ia} X_i^{Jb} + Y_i^{Ja} Y_i^{Ib}) C_{\nu b} - \sum_{ija} C_{\mu i} (X_i^{Ja} X_j^{Ia} + Y_i^{Ia} Y_j^{Ja}) C_{\nu j} \quad (17)$$

We define the “right” molecular orbital overlap gradient

$$O_{pq}^{R[Q]} \equiv \langle p | q^{[Q]} \rangle = \sum_{\alpha\beta} C_{\mu p} S_{\alpha\beta}^{A[Q]} C_{\nu q} - \Theta_{pq}^{[Q]} \quad (18)$$

where the second equality is derived in ref 7. Here, $\Theta_{pq}^{[Q]}$ is the orbital response term describing the mixing between MOs p and q . (Any quantity that is traced against $\Theta_{pq}^{[Q]}$ contributes to the orbital response Lagrangian, and is ultimately resolved using standard coupled-perturbed Hartree–Fock theory.^{37,38} The contributions to the DC arising from orbital response will end up “relaxing” the generalized difference density matrices $D_{\mu\nu}^{IJ}$ that appear in the final expression in exactly the same manner as in the corresponding density matrices from the CIS DCs described in ref 7. In what follows, we will neglect intra-subspace (or “redundant”) orbital response terms, as all such terms ultimately vanish from the final expression, just as they do for CIS derivative couplings.⁷) $S_{\mu\nu}^{A[Q]}$ is the antisymmetrized atomic orbital overlap gradient

$$S_{\mu\nu}^{A[Q]} \equiv \frac{1}{2} (\langle \mu | \nu^{[Q]} \rangle - \langle \mu^{[Q]} | \nu \rangle) \quad (19)$$

Similarly, the symmetric AO overlap gradient is written

$$S_{\mu\nu}^{[Q]} \equiv \frac{1}{2} (\langle \mu | \nu^{[Q]} \rangle + \langle \mu^{[Q]} | \nu \rangle) \quad (20)$$

Terms containing $S^{A[Q]}$ arise from the inability of real-valued basis functions to account for translational momentum of the electrons as they follow the perturbed nuclei. Ultimately, this contribution to the derivative coupling can lead to a lack of translational invariance; i.e., systems can acquire some overall translational motion from electronic relaxation that violates conservation of momentum. These nonphysical terms are small, and can be neglected to first order if we include atomic electronic translational factors.⁷ Finally, terms containing $S^{[Q]}$ are the so-called Pulay terms that account for the effect of an atom-centered basis on nuclear gradients.

Throughout the text, we will make use of orbital creation (\hat{a}_p^\dagger) and annihilation (\hat{a}_p) operators; e.g., for the Hamiltonian, we write

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{4} \sum_{pqrs} \Pi_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \quad (21)$$

where h_{pq} is the single electron Hamiltonian matrix element and Π_{pqrs} is an antisymmetrized two-electron integral, explicitly given by $\Pi_{pqrs} = \int \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) r_{12}^{-1} \chi_r(\mathbf{x}_1) \chi_s(\mathbf{x}_2) - \int \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) r_{12}^{-1} \chi_s(\mathbf{x}_1) \chi_r(\mathbf{x}_2)$, where χ is a molecular spin orbital, and r_{12} is the distance between electrons 1 and 2. In physicists' notation, this integral is denoted by

$$\Pi_{pqrs} = \langle pq || rs \rangle \quad (22)$$

III. THEORY

A. Hellmann–Feynman Derivative Coupling Expression. Let $|\Psi_I^{\text{Ex}}\rangle$ and E_I^{Ex} be exact eigenstates and eigenvalues of the electronic Hamiltonian \hat{H} . The Hellmann–Feynman expression for derivative couplings is

$$d_{IJ}^{\text{Ex}[Q]} = \langle \Psi_I^{\text{Ex}} | \nabla_Q | \Psi_J^{\text{Ex}} \rangle = \frac{\langle \Psi_I^{\text{Ex}} | \hat{H}^{[Q]} | \Psi_J^{\text{Ex}} \rangle}{E_J^{\text{Ex}} - E_I^{\text{Ex}}} \quad (23)$$

where $I \neq J$.

As we have shown,⁷ one can obtain an analogous expression for the derivative couplings between CIS states ($|\Phi_I^{\text{CIS}}\rangle$). Noting that these states have the properties

$$\begin{aligned} \mathcal{P}_I \hat{H} \mathcal{P}_I |\Phi_I^{\text{CIS}}\rangle &= \sum_{ia} A_{aibj} t_i^{Ia} |\Phi_j^b\rangle \\ &= E_I^{\text{CIS}} \sum_{jb} t_j^{Ib} |\Phi_j^b\rangle \\ &= E_I^{\text{CIS}} |\Phi_I^{\text{CIS}}\rangle \end{aligned} \quad (24)$$

and

$$\langle \Phi_I^{\text{CIS}} | \mathcal{P}_I \hat{H} \mathcal{P}_I |\Phi_J^{\text{CIS}}\rangle = \sum_{ijab} t_i^{Ia} t_j^{Jb} A_{aibj} = \delta_{IJ} E_I^{\text{CIS}} \quad (25)$$

(cf. eqs 2 and 3), we can obtain an exact Hellmann–Feynman expression for CIS DCs by replacing the Hamiltonian \hat{H} in eq 23 with a modified operator

$$\tilde{A} = \mathcal{P}_I \hat{H} \mathcal{P}_I \quad (26)$$

Here, \mathcal{P}_I is a projection operator onto singly excited states (eq 10). In this case,

$$\begin{aligned} d_{IJ}^{\text{CIS}[Q]} &= \langle \Phi_I^{\text{CIS}} | \nabla_Q | \Phi_J^{\text{CIS}} \rangle = \frac{\langle \Phi_I^{\text{CIS}} | \tilde{A}^{[Q]} | \Phi_J^{\text{CIS}} \rangle}{E_J^{\text{CIS}} - E_I^{\text{CIS}}} \\ &= \frac{1}{E_J^{\text{CIS}} - E_I^{\text{CIS}}} \sum_{ijab} t_i^{Ia} t_j^{Jb} \langle \Phi_I^a | \tilde{A}^{[Q]} | \Phi_j^b \rangle \end{aligned} \quad (27)$$

Equation 27 can be resolved into a gradient of the Hamiltonian, which represents the naïve Hellmann–Feynman result, plus the gradient of the projection operators. This second term contributes to the orbital response, reflecting the fact that the CIS wavefunctions are restricted to sums of singly excited determinants.

In this paper, we would like to find an analogous approach to derive DCs for the TDHF formalism. However, because the Hellmann–Feynman method clearly depends on the existence of wavefunctions, we must define a “wavefunction” that corresponds to the TDHF states.

B. TDHF Pseudo-Wavefunctions. Unlike CIS, the TDHF formalism is derived as a response theory without a static wavefunction ansatz. That being said, for a pair of TDHF solutions, we can write TDHF pseudo-wavefunctions that exhibit certain desired behaviors upon the inner product. For a pair of states I and J , these pseudo-wavefunctions are given by

$$|\Psi_I\rangle \equiv (\hat{X}^I + \hat{X}^I \hat{X}^J \hat{Y}^J) |\Phi_{\text{HF}}\rangle \quad (28)$$

and

$$|\Psi_J\rangle \equiv (\hat{X}^J + \hat{X}^J \hat{X}^I \hat{Y}^I) |\Phi_{\text{HF}}\rangle \quad (29)$$

Here we define the TDHF excitation operators

$$\hat{X}^I \equiv \sum_{ia} X_i^{Ia} \hat{a}_a^\dagger \hat{a}_i \quad (30)$$

and

$$\hat{Y}^I \equiv \sum_{ia} Y_i^{Ia} \hat{a}_a^\dagger \hat{a}_i \quad (31)$$

Notice that these wavefunctions are not entirely independent; the wavefunction for state I depends on state J , and vice versa.

Assuming the HF energy is zero ($E_{\text{HF}} = 0$), the Hamiltonian matrix element between two of these pseudo-wavefunctions can be written as

$$\langle \Psi_I | \hat{H} | \Psi_J \rangle = \langle \Phi_{\text{HF}} | (\hat{X}^{I\dagger} + \hat{Y}^{J\dagger} \hat{X}^{J\dagger} \hat{X}^{I\dagger}) \hat{H} (\hat{X}^J + \hat{X}^J \hat{X}^I \hat{Y}^I) | \Phi_{\text{HF}} \rangle \quad (32)$$

The TDHF eigenvalue equation (eq 5) can be approximately derived from eq 32 by discarding all terms but a single disconnected component. To arrive at this result, we employ the following reasoning: given that TDHF X amplitudes are nearly orthonormal (eq 8), any term containing $\mathbf{X}^{I\dagger} \mathbf{X}^I$ will dominate the following expressions. Using Wick's theorem, we can write

$$\begin{aligned} &\langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} \hat{X}^{J\dagger} \hat{X}^{I\dagger} \hat{H} \hat{X}^J | \Phi_{\text{HF}} \rangle \\ &= \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} \hat{X}^{J\dagger} \hat{H} | \Phi_{\text{HF}} \rangle \mathbf{X}^{I\dagger} \mathbf{X}^I + \dots \\ &\approx \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} \hat{X}^{J\dagger} \hat{H} | \Phi_{\text{HF}} \rangle \\ &= \mathbf{X}^{I\dagger} \mathbf{B} \mathbf{Y}^J \end{aligned} \quad (33)$$

and

$$\begin{aligned} \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} \hat{X}^{J\dagger} \hat{X}^{J\dagger} \hat{I} | \hat{H} | \hat{X}^J \hat{X}^J \hat{Y}^J | \Phi_{\text{HF}} \rangle \\ = \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} | \hat{H} | \hat{Y}^J | \Phi_{\text{HF}} \rangle (\mathbf{X}^{J\dagger} \mathbf{X}^J) (\mathbf{X}^{J\dagger} \mathbf{X}^J) + \dots \\ \approx \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} | \hat{H} | \hat{Y}^J | \Phi_{\text{HF}} \rangle \\ = \mathbf{Y}^{J\dagger} \mathbf{A} \mathbf{Y}^J \end{aligned} \quad (34)$$

so that we obtain

$$\begin{aligned} \langle \Psi_I | \hat{H} | \Psi_I \rangle &\approx \mathbf{X}^{I\dagger} \mathbf{A} \mathbf{X}^I + \mathbf{X}^{I\dagger} \mathbf{B} \mathbf{Y}^I + \mathbf{Y}^{I\dagger} \mathbf{B} \mathbf{X}^I + \mathbf{Y}^{I\dagger} \mathbf{A} \mathbf{Y}^I \\ &= (\mathbf{X}^{I\dagger} - \mathbf{Y}^{I\dagger}) \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^I \\ \mathbf{Y}^I \end{pmatrix} \\ &= \delta_{IJ} E_I \end{aligned} \quad (35)$$

Equation 35 shows that the TDHF pseudo-wavefunctions sandwiched around the Hamiltonian approximately reproduce the TDHF eigenvalue equation (eq 5). From the same perspective, the overlap between TDHF pseudo-wavefunctions

$$\begin{aligned} \langle \Psi_I | \Psi_J \rangle &\approx \langle \Phi_{\text{HF}} | \hat{X}^{I\dagger} \hat{X}^J | \Phi_{\text{HF}} \rangle + \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} \hat{Y}^I | \Phi_{\text{HF}} \rangle \\ &= \mathbf{X}^{I\dagger} \mathbf{X}^J + \mathbf{Y}^{I\dagger} \mathbf{Y}^J \\ &\approx \mathbf{X}^{I\dagger} \mathbf{X}^J \approx \delta_{IJ} \end{aligned} \quad (36)$$

approximately recovers eq 8.

Now, our heuristic derivation of TDHF requires that the X amplitudes be nearly orthonormal and, equivalently, that Y amplitudes remain below a certain magnitude. In particular, we would like to ignore all terms on the order of $O(\mathbf{Y}^2)$ if possible. In this case, we require that if $\mathbf{Y}^{J\dagger} \mathbf{Y}^I \approx 0$,

$$\begin{aligned} \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} | (\hat{Y}^J | \Phi_{\text{HF}} \rangle)^{[Q]} \\ \approx -\langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} | \rangle^{[Q]} | \hat{Y}^J | \Phi_{\text{HF}} \rangle \\ = -\langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} | (\hat{Y}^J | \Phi_{\text{HF}} \rangle)^{[Q]} \end{aligned} \quad (37)$$

In eq 37, we note that even though Y is small, the gradients of Y amplitudes need not be small: $\hat{Y}^{[Q]}$ terms cannot be neglected in a gradient expression.

We are finally prepared to examine the derivative couplings between TDHF pseudo-wavefunctions. By evaluating the overlap between pseudo-wavefunction $|\Psi_I\rangle$ and the nuclear gradient of pseudo-wavefunction $|\Psi_J\rangle$, we find

$$\begin{aligned} \langle \Psi_I | \nabla_Q | \Psi_J \rangle &\approx \langle \Phi_{\text{HF}} | \hat{X}^{I\dagger} | (\hat{X}^J | \Phi_{\text{HF}} \rangle)^{[Q]} \\ &\quad + \langle \Phi_{\text{HF}} | \hat{Y}^{J\dagger} | (\hat{Y}^I | \Phi_{\text{HF}} \rangle)^{[Q]} \\ &\approx \langle \Phi_{\text{HF}} | \hat{X}^{I\dagger} | (\hat{X}^J | \Phi_{\text{HF}} \rangle)^{[Q]} \\ &\quad - \langle \Phi_{\text{HF}} | \hat{Y}^{I\dagger} | (\hat{Y}^J | \Phi_{\text{HF}} \rangle)^{[Q]} \\ &= \sum_{ijab} (X_i^{Ia} X_j^{Jb} - Y_i^{Ia} Y_j^{Jb}) \langle \Phi_i^a | \Phi_j^b \rangle^{[Q]} \\ &\quad + \sum_{ia} (X_i^{Ia} X_i^{Ja} \rangle^{[Q]} - Y_i^{Ia} Y_i^{Ja} \rangle^{[Q]} \end{aligned} \quad (38)$$

where we have used eq 37 to obtain the second approximate equality. Equation 38 for DCs will be explored in ref 28.

In this manuscript, we note that eq 38 can be transformed into an effective Hellmann–Feynman expression for TDHF DCs analogous to eq 27

$$\begin{aligned} d_{IJ}^{\text{TDHF}[Q]} &= \frac{1}{E_J - E_I} \sum_{ijab} [(X_i^{Ia} X_j^{Jb} + Y_i^{Ia} Y_j^{Jb}) \langle \Phi_i^a | \tilde{\mathbf{A}}^{[Q]} | \Phi_j^b \rangle \\ &\quad + (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb}) \langle \Phi_{ij}^{ab} | \tilde{\mathbf{B}}^{[Q]} | \Phi_{\text{HF}} \rangle] \end{aligned} \quad (39)$$

where $\tilde{\mathbf{A}}$ is defined in eq 26, and

$$\tilde{\mathbf{B}} = \mathcal{P}_2 \hat{H} \mathcal{P}_0 \quad (40)$$

To better see the correspondence between the CIS and TDHF Hellmann–Feynman DC equations, compare the relationship between eqs 25 and 27 to that of eqs 35 and 39. We will now show how to evaluate eq 39 in practice, and in Appendix A, we will show that our final result matches the result obtained working directly from eq 38.

C. Evaluating the Hellmann–Feynman Derivative Coupling. The first step in evaluating the Hellmann–Feynman DC is to expand eq 39 and apply the product rule. To simplify the resulting expression, we partition it into four terms:

$$d_{IJ}^{\text{TDHF}[Q]} = \frac{1}{E_J - E_I} (W_1 + W_2 + W_3 + W_4) \quad (41)$$

where

$$\begin{aligned} W_1 &= \sum_{ijab} (X_i^{Ia} X_j^{Jb} + Y_i^{Ia} Y_j^{Jb}) \langle \Phi_i^a | [H^{[Q]} + (\sum_{kc} |\Phi_k^c\rangle \langle \Phi_k^c|)] H \\ &\quad + H (\sum_{kc} |\Phi_k^c\rangle \langle \Phi_k^c|) + (\sum_{kc} |\Phi_k^c\rangle \langle \Phi_k^c|) H \\ &\quad + H (\sum_{kc} |\Phi_k^c\rangle \langle \Phi_k^c|) | \Phi_j^b \rangle \end{aligned} \quad (42)$$

$$W_2 = \sum_{ijab} (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb}) \langle \Phi_{ij}^{ab} | H^{[Q]} | \Phi_{\text{HF}} \rangle \quad (43)$$

$$W_3 = \sum_{ijab} (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb}) \langle \Phi_{ij}^{ab} | H | \Phi_{\text{HF}} \rangle^{[Q]} \quad (44)$$

and

$$\begin{aligned} W_4 &= \frac{1}{4} \sum_{ijab} (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb}) \langle \Phi_{ij}^{ab} | [\hat{H} (|\Phi_{\text{HF}}\rangle \langle \Phi_{\text{HF}}|^{[Q]}) \\ &\quad + (\sum_{klcd} |\Phi_{kl}^{cd}\rangle \langle \Phi_{kl}^{cd}|) \hat{H} + (\sum_{klcd} |\Phi_{kl}^{cd}\rangle \langle \Phi_{kl}^{cd}|) \hat{H}] | \Phi_{\text{HF}} \rangle \end{aligned} \quad (45)$$

Beginning with W_4 , we see that the first term in square brackets in eq 45 involves the derivative coupling between the HF state and itself, $\langle \Phi_{\text{HF}}^{[Q]} | \Phi_{\text{HF}} \rangle$, which is easily shown to be zero. The second term involves the Hartree–Fock ground state coupled via a Hamiltonian to the gradient of a doubly excited state, $\langle \Phi_{kl}^{cd}\rangle | \hat{H} | \Phi_{\text{HF}} \rangle$. In order to evaluate this term, we insert the configuration interaction resolution of the identity (eq 12) between the Hamiltonian and the gradient term. Because the Hamiltonian is a two-electron operator, it can only couple the Hartree–Fock state on the left-hand side of the term to another Hartree–Fock state, a singly excited state, or a doubly excited state. By Brillouin’s theorem, however, the Hamiltonian cannot couple the Hartree–Fock state to a singly excited state. This leaves only

$$\langle \Phi_{kl}^{cd[Q]} | \left(|\Phi_{HF}\rangle \langle \Phi_{HF}| + \frac{1}{4} \sum_{mnef} |\Phi_{mn}^{ef}\rangle \langle \Phi_{mn}^{ef}| \right) \hat{H} | \Phi_{HF}\rangle \quad (46)$$

When the gradient operator ($^{[Q]}$) acts on states, it behaves like a single electron operator. As such, it cannot couple doubly excited states to the Hartree–Fock state. Finally, the only remaining terms include expressions of the form $\langle \Phi_{kl}^{cd[Q]} | \Phi_{mn}^{ef}\rangle$. Applying the gradient and resolving the second quantization operators, we find

$$\begin{aligned} \sum_{mnef} \langle \Phi_{kl}^{cd[Q]} | \Phi_{mn}^{ef}\rangle &= \sum_{mnef} [(\delta_{mk}\delta_{nl} - \delta_{ml}\delta_{nk}) \\ &(\delta_{fd}O_{ce}^{R[Q]} - \delta_{ed}O_{cf}^{R[Q]} + \delta_{ec}O_{df}^{R[Q]} \\ &- \delta_{fc}O_{de}^{R[Q]})(\delta_{ec}\delta_{fd} - \delta_{ed}\delta_{fc}) \\ &(\delta_{mk}O_{ln}^{R[Q]} - \delta_{nk}O_{lm}^{R[Q]} + \delta_{nl}O_{km}^{R[Q]} \\ &- \delta_{ml}O_{kn}^{R[Q]})] \quad (47) \end{aligned}$$

It is trivial to show by relabeling the indices that eq 47 is equal to zero. Thus, both remaining terms in W_4 evaluate to zero, and no part of W_4 contributes to the final DC expression: $W_4 = 0$.

Turning our attention to W_1 (eq 42), inspection reveals that it is nearly identical to the CIS derivative coupling expression (cf. eq 17 of ref 7), with the CIS amplitudes $t_i^{a\mu}t_j^{b\nu}$ replaced by TDHF amplitudes $X_i^{Ia}X_j^{Jb} + Y_i^{Ia}Y_j^{Jb}$. The derivation for CIS derivative couplings can be followed to obtain an expression for W_1 that is very similar to the final expression for CIS derivative couplings (ref 7, eqs 81–83) once the amplitude substitution is made. In the AO basis, W_1 becomes

$$\begin{aligned} W_1 &= \sum_{\mu\nu} h_{\mu\nu}^{[Q]} D_{\mu\nu}^{IJ} + \sum_{\mu\nu\lambda\sigma} \Pi_{\mu\nu\lambda\sigma}^{[Q]} (R_{\mu\nu}^{XI}R_{\sigma\lambda}^{XJ} + R_{\mu\nu}^{YI}R_{\sigma\lambda}^{YJ} + D_{\mu\nu}^{IJ}P_{\sigma\lambda}) \\ &- \frac{1}{2} \sum_{\mu\nu\alpha\beta} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (D_{\beta\nu}^{IJ} + D_{\nu\beta}^{IJ}) E_{\alpha\beta} \\ &- \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} P_{\nu\beta} (D_{\sigma\lambda}^{IJ} + D_{\lambda\sigma}^{IJ}) \Pi_{\alpha\lambda\beta\sigma} \\ &- \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\nu\beta}^{XI}R_{\sigma\lambda}^{XJ} + R_{\sigma\lambda}^{XI}R_{\nu\beta}^{XJ} + R_{\beta\nu}^{XI}R_{\lambda\sigma}^{XJ} \\ &+ R_{\lambda\sigma}^{XI}R_{\beta\nu}^{XJ}) \Pi_{\alpha\lambda\beta\sigma} \\ &- \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\nu\beta}^{YI}R_{\sigma\lambda}^{YJ} + R_{\sigma\lambda}^{YI}R_{\nu\beta}^{YJ} + R_{\beta\nu}^{YI}R_{\lambda\sigma}^{YJ} \\ &+ R_{\lambda\sigma}^{YI}R_{\beta\nu}^{YJ}) \Pi_{\alpha\lambda\beta\sigma} - \sum_{ck} L_{ck}^{A,IJ} \Theta_{ck}^{[Q]} + (E_J - E_I) \\ &\sum_{\mu\nu} S_{\mu\nu}^{A[Q]} G_{\mu\nu}^A \quad (48) \end{aligned}$$

L^A is the W_1 contribution to the orbital response Lagrangian, given by

$$\begin{aligned} L_{ck}^{A,IJ} &= \sum_{\mu\nu\lambda\sigma} C_{\lambda c} C_{\sigma k} (D_{\mu\nu}^{IJ} + D_{\nu\mu}^{IJ}) \Pi_{\mu\nu\lambda\sigma} \\ &+ \sum_{\alpha\mu\nu\lambda\sigma} C_{\lambda c} C_{\sigma\alpha} (R_{\mu\nu}^{XI}X_k^{Ja} + X_k^{Ia}R_{\mu\nu}^{XJ} + R_{\mu\nu}^{YI}Y_k^{Ja} \\ &+ Y_k^{Ia}R_{\mu\nu}^{YJ}) \Pi_{\mu\nu\lambda\sigma} - \sum_{i\mu\nu\lambda\sigma} C_{\lambda i} C_{\sigma k} (R_{\mu\nu}^{XI}X_i^{Jc} + X_i^{Ic}R_{\mu\nu}^{XJ} \\ &+ R_{\mu\nu}^{YI}Y_i^{Jc} + Y_i^{Ic}R_{\mu\nu}^{YJ}) \Pi_{\mu\nu\lambda\sigma} \quad (49) \end{aligned}$$

and $G^{A,IJ}$ contains the translationally variant contributions from W_1 (eq 50).

$$\begin{aligned} G_{\mu\nu}^{A,IJ} &= \frac{1}{E_J - E_I} [\sum_{ijabc} C_{\mu c} C_{\nu a} \Pi_{ibaj} (X_i^{Ic}X_j^{Jb} + X_j^{Ib}X_i^{Jc} + Y_i^{Ic}Y_j^{Jb} + Y_j^{Ib}Y_i^{Jc}) \\ &- \sum_{ijkab} C_{\mu i} C_{\nu k} \Pi_{ibaj} (X_k^{Ia}X_j^{Jb} + X_j^{Ib}X_k^{Ja} + Y_k^{Ia}Y_j^{Jb} + Y_j^{Ib}Y_k^{Ja}) \\ &+ \sum_{iac} C_{\mu c} C_{\nu a} \varepsilon_i (X_i^{Ia}X_i^{Jc} + X_i^{Ic}X_i^{Ja} + Y_i^{Ia}Y_i^{Jc} + Y_i^{Ic}Y_i^{Ja}) \\ &+ \sum_{ika} C_{\mu i} C_{\nu k} \varepsilon_i (X_i^{Ia}X_k^{Ja} + X_k^{Ia}X_i^{Ja} + Y_i^{Ia}Y_k^{Ja} + Y_k^{Ia}Y_i^{Ja})] \quad (50) \end{aligned}$$

D. Evaluating the TDHF Cross-Terms. We now turn our attention to a contribution that is unique to TDHF, W_2 (eq 43). The second-quantization expression for the Hamiltonian is given in eq 21, so that its gradient is

$$\begin{aligned} \hat{H}^{[Q]} &= \sum_{pq} (h_{pq}^{[Q]} \hat{a}_p^\dagger \hat{a}_q + h_{pq} \hat{a}_p^\dagger [Q] \hat{a}_q + h_{pq} \hat{a}_p^\dagger \hat{a}_q^{[Q]}) \\ &+ \frac{1}{4} \sum_{pqrs} (\Pi_{pqrs}^{[Q]} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r + \Pi_{pqrs} \hat{a}_p^\dagger [Q] \hat{a}_q^\dagger \hat{a}_s \hat{a}_r \\ &+ \Pi_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger [Q] \hat{a}_s \hat{a}_r + \Pi_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s^{[Q]} \hat{a}_r \\ &+ \Pi_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r^{[Q]}) \quad (51) \end{aligned}$$

As demonstrated in ref 7 (eq 28), the gradient of creation/annihilation operators is given by

$$\hat{a}_p^{[Q]} = - \sum_q O_{pq}^{R[Q]} \hat{a}_q \quad (52)$$

for the “right” molecular orbital overlap gradient $O_{pq}^{R[Q]}$ (eq 18). This expression makes it clear that the one-electron operator component of the Hamiltonian remains a one-electron operator after the application of the gradient. As such, all one-electron terms cannot couple the Hartree–Fock state to a doubly excited state and can be discarded. The remaining contributions, from the two-electron integral, yield

$$\begin{aligned} \langle \Phi_{HF} | \hat{H}^{[Q]} | \Phi_{ij}^{ab} \rangle &= \Pi_{abij}^{[Q]} - \sum_p (O_{pa}^{R[Q]} \Pi_{pbij} + O_{pb}^{R[Q]} \Pi_{apij} \\ &+ O_{pi}^{R[Q]} \Pi_{abpj} + O_{pj}^{R[Q]} \Pi_{abip}) \quad (53) \end{aligned}$$

After reassigning some indices and utilizing the symmetry properties of the two-electron integral ($\Pi_{pqrs} = -\Pi_{qprs} = \Pi_{rspq}$) and the molecular overlap gradient ($O_{pq}^{R[Q]} = -O_{qp}^{R[Q]}$), we obtain the expression

$$\begin{aligned}
 W_2 = & \sum_{ijab} \Pi_{abij}^{[Q]} (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb}) \\
 & - \sum_{acijk} O_{pk}^{R[Q]} (X_i^{Ia} Y_k^{Jb} + Y_i^{Ia} X_k^{Jb} + X_k^{Ib} Y_i^{Ja} + Y_k^{Ib} X_i^{Ja}) \Pi_{bapi} \\
 & + \sum_{abck} O_{cp}^{R[Q]} (X_i^{Ia} Y_j^{Jc} + Y_i^{Ia} X_j^{Jc} + X_j^{Ic} Y_i^{Ja} + Y_j^{Ic} X_i^{Ja}) \Pi_{paji}
 \end{aligned} \quad (54)$$

The MO overlap gradient $O_{pq}^{R[Q]}$ can be further decomposed according to eq 18, and the two-electron integral can be expanded in terms of MO coefficients

$$\Pi_{abij} = \sum_{\mu\nu\lambda\sigma} \Pi_{\mu\nu\lambda\sigma} C_{\mu a} C_{\lambda b} C_{\nu i} C_{\sigma j} \quad (55)$$

so that

$$\begin{aligned}
 \Pi_{abij}^{[Q]} = & \sum_{\mu\nu\lambda\sigma} (\Pi_{\mu\nu\lambda\sigma}^{[Q]} C_{\mu a} C_{\lambda b} C_{\nu i} C_{\sigma j} + \Pi_{\mu\nu\lambda\sigma} C_{\mu a}^{[Q]} C_{\lambda b} C_{\nu i} C_{\sigma j} \\
 & + \Pi_{\mu\nu\lambda\sigma} C_{\mu a} C_{\lambda b}^{[Q]} C_{\nu i} C_{\sigma j} + \Pi_{\mu\nu\lambda\sigma} C_{\mu a} C_{\lambda b} C_{\nu i}^{[Q]} C_{\sigma j} \\
 & + \Pi_{\mu\nu\lambda\sigma} C_{\mu a} C_{\lambda b} C_{\nu i} C_{\sigma j}^{[Q]})
 \end{aligned} \quad (56)$$

As a function of AO overlap (S) and orbital rotation (Θ), the MO coefficient gradient is given by eq 63 of ref 7.

$$\begin{aligned}
 C_{\mu p}^{[Q]} = & \sum_{\alpha\beta} \frac{\partial C_{\mu p}}{\partial S_{\alpha\beta}} S_{\alpha\beta}^{[Q]} + \sum_{ck} \frac{\partial C_{\mu p}}{\partial \Theta_{ck}} \Theta_{ck}^{[Q]} \\
 = & -\frac{1}{2} \sum_{\alpha\beta} \tilde{P}_{\mu\alpha} C_{\beta p} S_{\alpha\beta}^{[Q]} + \sum_{ck} (C_{\mu k} \Theta_{cp}^{[Q]} - C_{\mu c} \Theta_{pk}^{[Q]})
 \end{aligned} \quad (57)$$

After substituting these expressions into eq 54 and rearranging the indices, the response terms cancel entirely and the expression becomes

$$\begin{aligned}
 W_2 = & \sum_{ijbcp\alpha\beta} S_{\alpha\beta}^{A[Q]} C_{ac} C_{\beta p} (X_i^{Ic} Y_j^{Jb} + X_j^{Ib} Y_i^{Jc} + Y_i^{Ic} X_j^{Jb} + Y_j^{Ib} X_i^{Jc}) \Pi_{pbij} \\
 & - \sum_{jkabp\alpha\beta} S_{\alpha\beta}^{A[Q]} C_{ap} C_{\beta k} (X_k^{Ia} Y_j^{Jb} + X_j^{Ib} Y_k^{Ja} + Y_k^{Ia} X_j^{Jb} + Y_j^{Ib} X_k^{Ja}) \Pi_{abpj} \\
 & - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\beta\nu}^{XI} R_{\sigma\lambda}^{YJ} + R_{\sigma\lambda}^{XI} R_{\beta\nu}^{YJ} + R_{\nu\beta}^{XI} R_{\lambda\sigma}^{YJ} + R_{\lambda\sigma}^{XI} R_{\nu\beta}^{YJ}) \Pi_{\alpha\lambda\beta\sigma} \\
 & - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\beta\nu}^{YI} R_{\sigma\lambda}^{XJ} + R_{\sigma\lambda}^{YI} R_{\beta\nu}^{XJ} + R_{\nu\beta}^{YI} R_{\lambda\sigma}^{XJ} + R_{\lambda\sigma}^{YI} R_{\nu\beta}^{XJ}) \Pi_{\alpha\lambda\beta\sigma} \\
 & + \sum_{\mu\nu\lambda\sigma} \Pi_{\mu\nu\lambda\sigma}^{[Q]} C_{\mu a} C_{\lambda b} C_{\nu i} C_{\sigma j} (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb})
 \end{aligned} \quad (58)$$

Finally, we turn to W_3 , eq 44. The gradient operating on the Hartree–Fock state couples the Hartree–Fock ground state to singly excited states, so that

$$\begin{aligned}
 \langle \Phi_{\text{HF}}^{[Q]} | \hat{H} | \Phi_{ij}^{ab} \rangle = & \langle \Phi_{\text{HF}}^{[Q]} | (\mathcal{P}_0 + \mathcal{P}_1 + \mathcal{P}_2 + \dots) | \hat{H} | \Phi_{ij}^{ab} \rangle \\
 = & \langle \Phi_{\text{HF}}^{[Q]} | (\sum_{kc} |\Phi_k^c\rangle \langle \Phi_k^c|) | \hat{H} | \Phi_{ij}^{ab} \rangle \\
 = & \sum_{kc} O_{ck}^{R[Q]} \langle \Phi_k^c | \hat{H} | \Phi_{ij}^{ab} \rangle
 \end{aligned} \quad (59)$$

where we have taken $\langle \Phi_{\text{HF}}^{[Q]} | \Phi_k^c \rangle = O_{ck}^{R[Q]}$ due to the orthogonality of the molecular orbital basis. Furthermore, if we expand the Hamiltonian matrix element and make use of the orthogonality of the Fock matrix

$$h_{pq} + \sum_m \Pi_{pmqm} = F_{pq} = \delta_{pq} \varepsilon_p \quad (60)$$

we obtain, after the rearrangement of the indices and the use of eq 18,

$$\begin{aligned}
 W_3 = & - \sum_{ijk\alpha\beta} S_{\alpha\beta}^{A[Q]} C_{ac} C_{\beta k} (X_i^{Ic} Y_j^{Jb} + X_j^{Ib} Y_i^{Jc} + Y_i^{Ic} X_j^{Jb} + Y_j^{Ib} X_i^{Jc}) \Pi_{kbij} \\
 & + \sum_{jkab\alpha\beta} S_{\alpha\beta}^{A[Q]} C_{ac} C_{\beta k} (X_k^{Ia} Y_j^{Jb} + X_j^{Ib} Y_k^{Ja} + Y_k^{Ia} X_j^{Jb} + Y_j^{Ib} X_k^{Ja}) \Pi_{abkj} \\
 & + \sum_{ijkbc} \Theta_{ck}^{[Q]} (X_i^{Ic} Y_j^{Jb} + X_j^{Ib} Y_i^{Jc} + Y_i^{Ic} X_j^{Jb} + Y_j^{Ib} X_i^{Jc}) \Pi_{kbij} \\
 & - \sum_{jkabc} \Theta_{ck}^{[Q]} (X_k^{Ia} Y_j^{Jb} + X_j^{Ib} Y_k^{Ja} + Y_k^{Ia} X_j^{Jb} + Y_j^{Ib} X_k^{Ja}) \Pi_{abkj}
 \end{aligned} \quad (61)$$

By inspection, it is clear that, when p indexes an occupied orbital, the first term of W_2 (eq 58) is the additive inverse of the first term of W_3 (eq 61), thus negating these contributions to the final derivative coupling expression. The same is true for the respective second terms of eqs 58 and 61 in the case that p indexes a virtual orbital. Noting this, we obtain the sum $W_{2+3} = W_2 + W_3$

$$\begin{aligned}
 W_{2+3} = & -\frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\beta\nu}^{XI} R_{\sigma\lambda}^{YJ} + R_{\sigma\lambda}^{XI} R_{\beta\nu}^{YJ} + R_{\nu\beta}^{XI} R_{\lambda\sigma}^{YJ} + R_{\lambda\sigma}^{XI} R_{\nu\beta}^{YJ}) \Pi_{\alpha\lambda\beta\sigma} \\
 & - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\beta\nu}^{YI} R_{\sigma\lambda}^{XJ} + R_{\sigma\lambda}^{YI} R_{\beta\nu}^{XJ} + R_{\nu\beta}^{YI} R_{\lambda\sigma}^{XJ} + R_{\lambda\sigma}^{YI} R_{\nu\beta}^{XJ}) \Pi_{\alpha\lambda\beta\sigma} \\
 & + \sum_{ijab\mu\nu\lambda\sigma} \Pi_{\mu\nu\lambda\sigma}^{[Q]} C_{\mu a} C_{\lambda b} C_{\nu i} C_{\sigma j} (X_i^{Ia} Y_j^{Jb} + Y_i^{Ia} X_j^{Jb}) - \sum_{kc} \Theta_{ck}^{[Q]} L_{ck}^{B,IJ} \\
 & + (E_j - E_i) \sum_{\mu\nu} S_{\mu\nu}^{A[Q]} G_{\mu\nu}^{B,IJ}
 \end{aligned} \quad (62)$$

where the CPHF Lagrangian $L^{B,IJ}$ is

$$\begin{aligned}
 L_{ck}^{B,IJ} = & \sum_{jab} \Pi_{abkj} (X_k^{Ia} Y_j^{Jb} + X_j^{Ib} Y_k^{Ja} + Y_k^{Ia} X_j^{Jb} + Y_j^{Ib} X_k^{Ja}) \\
 & - \sum_{ijb} \Pi_{kbij} (X_i^{Ic} Y_j^{Jb} + X_j^{Ib} Y_i^{Jc} + Y_i^{Ic} X_j^{Jb} + Y_j^{Ib} X_i^{Jc})
 \end{aligned} \quad (63)$$

and $G^{B,IJ}$ is given by

$$\begin{aligned}
 G_{\mu\nu}^{B,IJ} = & \frac{1}{E_j - E_i} \left[\sum_{ijabc} C_{\mu c} C_{\nu a} \Pi_{abij} (X_i^{Ic} Y_j^{Jb} + X_j^{Ib} Y_i^{Jc} + Y_i^{Ic} X_j^{Jb} \right. \\
 & + Y_j^{Ib} X_i^{Jc}) - \sum_{ijkab} C_{\mu i} C_{\nu k} \Pi_{abij} (X_k^{Ia} Y_j^{Jb} + X_j^{Ib} Y_k^{Ja} \\
 & \left. + Y_k^{Ia} X_j^{Jb} + Y_j^{Ib} X_k^{Ja}) \right]
 \end{aligned} \quad (64)$$

If W_1 corresponds to CIS-like contributions to the DC, W_{2+3} constitutes the non-CIS-like contributions. Just as for the CIS DCs in ref 7, the non-translationally invariant term (here, $G^{IJ} = G^{A,IJ} + G^{B,IJ}$) can be simplified into an expression that has no explicit dependence on the energy difference between states. This is described in detail in Appendix A. Combining eqs 48 and 62 while fully converting the latter to the AO representation, we arrive at our final expression

$$\begin{aligned}
d_{IJ}^{\text{TDHF}[Q]} = & \frac{1}{E_J - E_I} \left[\sum_{\mu\nu} t_{\mu\nu}^{[Q]} D_{\mu\nu}^{IJ} \right. \\
& + \sum_{\mu\nu\lambda\sigma} \Pi_{\mu\nu\lambda\sigma}^{[Q]} (R_{\mu\nu}^{XI} R_{\sigma\lambda}^{XJ} + R_{\mu\nu}^{YI} R_{\sigma\lambda}^{YJ} + R_{\mu\nu}^{XI} R_{\lambda\sigma}^{YJ} + R_{\mu\nu}^{YI} R_{\lambda\sigma}^{XJ}) \\
& + D_{\mu\nu}^{IJ} P_{\sigma\lambda}) - \frac{1}{2} \sum_{\mu\nu\alpha\beta} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (D_{\beta\nu}^{IJ} + D_{\nu\beta}^{IJ}) F_{\alpha\beta} \\
& - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} P_{\nu\beta} (D_{\sigma\lambda}^{IJ} + D_{\lambda\sigma}^{IJ}) \Pi_{\alpha\lambda\beta\sigma} \\
& - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\nu\beta}^{XI} R_{\sigma\lambda}^{XJ} + R_{\sigma\lambda}^{XI} R_{\nu\beta}^{XJ} + R_{\beta\nu}^{XI} R_{\lambda\sigma}^{XJ} \\
& + R_{\lambda\sigma}^{XI} R_{\beta\nu}^{XJ}) \Pi_{\alpha\lambda\beta\sigma} - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\nu\beta}^{YI} R_{\sigma\lambda}^{YJ} + R_{\sigma\lambda}^{YI} R_{\nu\beta}^{YJ} \\
& + R_{\beta\nu}^{YI} R_{\lambda\sigma}^{YJ} + R_{\lambda\sigma}^{YI} R_{\beta\nu}^{YJ}) \Pi_{\alpha\lambda\beta\sigma} - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} \\
& (R_{\beta\nu}^{XI} R_{\sigma\lambda}^{YJ} + R_{\sigma\lambda}^{XI} R_{\beta\nu}^{YJ} + R_{\nu\beta}^{XI} R_{\lambda\sigma}^{YJ} + R_{\lambda\sigma}^{XI} R_{\nu\beta}^{YJ}) \Pi_{\alpha\lambda\beta\sigma} \\
& - \frac{1}{2} \sum_{\mu\nu\alpha\beta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} (R_{\beta\nu}^{YI} R_{\sigma\lambda}^{XJ} + R_{\sigma\lambda}^{YI} R_{\beta\nu}^{XJ} + R_{\nu\beta}^{YI} R_{\lambda\sigma}^{XJ} \\
& + R_{\lambda\sigma}^{YI} R_{\nu\beta}^{XJ}) \Pi_{\alpha\lambda\beta\sigma} \left. \right] - \frac{1}{E_J - E_I} \sum_{ck} L_{ck}^{IJ} \Theta_{ck}^{[Q]} \\
& + \sum_{\mu\nu} S_{\mu\nu}^{A[Q]} G_{\mu\nu}^{IJ} \quad (65)
\end{aligned}$$

where L^{IJ} is the full orbital response Lagrangian, composed of the contributions from $L^{A,IJ}$ (eq 49) and $L^{B,IJ}$ (eq 63). In the basis of atomic orbitals, this term is

$$\begin{aligned}
L_{ck}^{IJ} = & \sum_{\mu\nu\lambda\sigma} C_{\lambda c} C_{\sigma k} (D_{\mu\nu}^{IJ} + D_{\nu\mu}^{IJ}) \Pi_{\mu\nu\lambda\sigma} \\
& + \sum_{\mu\nu\lambda\sigma} C_{\lambda c} C_{\sigma a} (R_{\mu\nu}^{XI} X_k^{Ja} + X_k^{Ia} R_{\mu\nu}^{XJ} + R_{\mu\nu}^{YI} Y_k^{Ja} + Y_k^{Ia} R_{\mu\nu}^{YJ}) \Pi_{\mu\nu\lambda\sigma} \\
& - \sum_{\mu\nu\lambda\sigma} C_{\lambda i} C_{\sigma k} (R_{\mu\nu}^{XI} X_i^{Jc} + X_i^{Ic} R_{\mu\nu}^{XJ} + R_{\mu\nu}^{YI} Y_i^{Jc} + Y_i^{Ic} R_{\mu\nu}^{YJ}) \Pi_{\mu\nu\lambda\sigma} \\
& + \sum_{\mu\nu\lambda\sigma} C_{\lambda c} C_{\sigma a} (R_{\nu\mu}^{XI} X_k^{Ja} + X_k^{Ia} R_{\nu\mu}^{XJ} + R_{\nu\mu}^{YI} Y_k^{Ja} + Y_k^{Ia} R_{\nu\mu}^{YJ}) \Pi_{\mu\nu\lambda\sigma} \\
& - \sum_{\mu\nu\lambda\sigma} C_{\lambda i} C_{\sigma k} (R_{\nu\mu}^{XI} X_i^{Jc} + X_i^{Ic} R_{\nu\mu}^{XJ} + R_{\nu\mu}^{YI} Y_i^{Jc} + Y_i^{Ic} R_{\nu\mu}^{YJ}) \Pi_{\mu\nu\lambda\sigma} \quad (66)
\end{aligned}$$

Equations 65 and 66 represent our final expression for the DC. With the exception of the $S^{A[Q]}$ term, this expression is identical to that obtained from direct differentiation, as shown in eq 50 of ref 28. Note that the terms containing the antisymmetrized AO overlap gradients ($S^{A[Q]}$) are responsible for a lack of translational invariance in eq 65. As ref 7 shows, by including electron translation factors to account for the momentum experienced by electrons as they follow moving nuclei, we find that $S^{A[Q]}$ terms are entirely eliminated, restoring translational invariance. However, the antisymmetrized overlap gradients are present in finite difference approximations to the derivative coupling, and thus must be included for purposes of debugging (though they may be neglected otherwise). For details on how the $S^{A[Q]}$ term in the present work is reconciled with the direct differentiation result, see Appendix A.

IV. RESULTS

Equations 65, 66, and A83 were implemented in a development version of the Q-CHEM software package.^{39,40} To evaluate the analytic solution, the direct coupling expression (eq 38) was approximated via finite difference (eq 67).

$$\begin{aligned}
d_{IJ}^{\text{TDHF}[Q]} \approx & \langle \Phi_{\text{HF}} | \hat{X}^{I\dagger} | (\hat{X}^J \Phi_{\text{HF}})^{[Q]} \rangle - \langle \Phi_{\text{HF}} | \hat{Y}^{I\dagger} | (\hat{Y}^J \Phi_{\text{HF}})^{[Q]} \rangle \\
\approx & \frac{\langle \mathcal{X}^I(\mathbf{x}) | \mathcal{X}^J(\mathbf{x} + \mathbf{h}) \rangle - \langle \mathcal{X}^I(\mathbf{x}) | \mathcal{X}^J(\mathbf{x} - \mathbf{h}) \rangle}{2|\mathbf{h}|} \\
& - \frac{\langle \mathcal{Y}^I(\mathbf{x}) | \mathcal{Y}^J(\mathbf{x} + \mathbf{h}) \rangle - \langle \mathcal{Y}^I(\mathbf{x}) | \mathcal{Y}^J(\mathbf{x} - \mathbf{h}) \rangle}{2|\mathbf{h}|} \quad (67)
\end{aligned}$$

Here, \mathbf{x} is the reference nuclear configuration and \mathbf{h} is a small perturbation with respect to the degree of freedom Q . We have defined $|\mathcal{X}^I\rangle \equiv |\hat{X}^I \Phi_{\text{HF}}\rangle$ and $|\mathcal{Y}^I\rangle \equiv |\hat{Y}^I \Phi_{\text{HF}}\rangle$ for simplicity.

For our test case, we calculated the derivative couplings between TDHF states S_1 , S_4 , and S_5 of formaldehyde. Results were generated using the 6-31G* basis set and the HF minimum-energy geometry. Both analytic and finite difference results are summarized in Table 1. The analytic results agree with the finite difference values to within $\sim 10^{-4} a_0^{-1}$, which is the expected precision of the finite difference approximation. It is clear by inspection that these derivative coupling components lack translational invariance. The nontranslationally invariant term ($S^{A[Q]} G^{IJ}$, eqs 65 and A83) was included in this calculation to match the finite-difference result.

V. DISCUSSION AND CONCLUSIONS

By defining pseudo-wavefunctions that approximately correspond to TDHF states, we have been able to develop an analytic expression for derivative couplings between TDHF states in the form of a Hellmann–Feynman expression. Our final expression is similar in form to the corresponding CIS derivative couplings,⁷ though there are important differences. In particular, XY coupling appears in the orbital response Lagrangian (eq 66) that has no CIS counterpart. The derivative couplings calculated according to eqs 65, 66, and A83 agree exactly with a direct differentiation expression (eq 38), and numerical results match finite difference results to a high degree of precision in practice.

A. Comparison with Chernyak–Mukamel and Time-Dependent Response Theory. To further justify our approach to DCs, we would like to compare our expression (eq 65) with the exact Chernyak–Mukamel formula (eq 73),¹¹ which expresses DCs as a function of the transition density matrix in the limit of exact wavefunctions. In such a limit, the basis set is complete, so we may naturally dispense with the Pulay terms ($S^{[Q]}$) and the antisymmetrized AO overlap gradients ($S^{A[Q]}$). Additionally, as noted by Send and Furche,^{21,41} the only component of the Hamiltonian that depends on nuclear position (and therefore a finite atom-centered basis) is the nuclear-electronic potential, v ; the electron kinetic energy and two-electron operators can therefore also be eliminated. Consequently, in the MO basis, we can write our complete basis DC expression

$$d_{IJ}^{\text{CB}[Q]} = \frac{1}{E_J - E_I} \sum_{pq} v_{pq}^{[Q]} D_{pq}^{IJ} - \frac{1}{E_J - E_I} \sum_{ck} \Theta_{ck}^{[Q]} L_{ck}^{IJ} \quad (68)$$

where the MO-basis difference density matrix is

Table 1. Derivative Coupling between the TDHF Excited States S_1 , S_4 , and S_5 of Formaldehyde Using the 6-31G* Basis Set^a

Q	S_1-S_4		S_1-S_5		S_4-S_5	
	FD	analytic	FD	analytic	FD	analytic
C_x	0.00000	0.00000	0.00000	0.00000	-0.00005	0.00000
C_y	0.00000	0.00000	-0.76790	-0.76790	0.00000	0.00000
C_z	-0.15739	-0.15741	0.00001	0.00000	1.99752	1.99721
H_{1x}	0.00002	0.00000	0.04297	0.04299	0.00023	0.00000
H_{1y}	0.00001	0.00000	0.08164	0.08162	0.00008	0.00000
H_{1z}	0.07660	0.07660	-0.00001	0.00000	-0.66402	-0.66410
H_{2x}	0.00000	0.00000	-0.04297	-0.04299	-0.00001	0.00000
H_{2y}	0.00000	0.00000	0.08164	0.08162	-0.00003	0.00000
H_{2z}	0.07659	0.07660	0.00000	0.00000	-0.66407	-0.66410
O_x	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
O_y	0.00000	0.00000	0.35603	0.35599	0.00000	0.00000
O_z	0.02519	0.02514	0.00009	0.00000	-0.65012	-0.65073

^aResults presented for both the finite difference approximation ("FD", eq 67) and our analytic method (eq 65). All results are presented in a_0^{-1} . To match finite difference results, the non-translationally invariant term ($S^{A[Q]}G^{IJ}$, eqs 65 and A83) was included. For the finite difference calculation, a step size of $h = 1.89 \times 10^{-4} a_0$ was used. For all degrees of freedom (Q), the analytic result agrees with the finite difference approximation at least to the expected level of accuracy for finite difference, $\sim 10^{-4} a_0^{-1}$.

$$D_{pq}^{IJ} = \begin{cases} -\sum_a (X_p^{Ja} X_q^{Ia} + Y_p^{Ia} Y_q^{Ja}) & \text{for } p, q \in \text{Occ} \\ \sum_i (X_i^{Ip} X_i^{Jq} + Y_i^{Jp} Y_i^{Iq}) & \text{for } p, q \in \text{Virt} \\ 0 & \text{otherwise} \end{cases} \quad (69)$$

Note that this matrix can be recovered using the pseudo-wavefunctions described in Section III.B acting on a single-electron density operator, $D_{pq}^{IJ} \approx \langle \Psi_I | \hat{a}_p^\dagger \hat{a}_q | \Psi_J \rangle$. The MO-basis orbital response Lagrangian is

$$\begin{aligned} L_{ck}^{IJ} = & \sum_{pq} \Pi_{pcqk} (D_{pq}^{IJ} + D_{qp}^{IJ}) \\ & + \sum_{jab} [\Pi_{bcja} (X_k^{Ia} X_j^{Jb} + X_j^{Ib} X_k^{Ja} + Y_k^{Ia} Y_j^{Jb} + Y_j^{Ib} Y_k^{Ja}) \\ & + \Pi_{bajc} (X_k^{Ia} Y_j^{Jb} + X_j^{Ib} Y_k^{Ja} + Y_k^{Ia} X_j^{Jb} + Y_j^{Ib} X_k^{Ja})] \\ & - \sum_{ijb} [\Pi_{bijk} (X_i^{Ic} X_j^{Jb} + X_j^{Ib} X_i^{Jc} + Y_i^{Ic} Y_j^{Jb} + Y_j^{Ib} Y_i^{Jc}) \\ & + \Pi_{bkji} (X_i^{Ic} Y_j^{Jb} + X_j^{Ib} Y_i^{Jc} + Y_i^{Ic} X_j^{Jb} + Y_j^{Ib} X_i^{Jc})] \end{aligned} \quad (70)$$

Equivalently, we can write

$$d_{IJ}^{CB[Q]} = \frac{1}{E_J - E_I} \sum_{pq} u_{pq}^{[Q]} \Gamma_{pq}^{IJ} \quad (71)$$

for a matrix Γ^{IJ} given by

$$\Gamma_{pq}^{IJ} = \begin{cases} D_{pq}^{IJ} & \text{for } p, q \in \text{Occ or} \\ & p, q \in \text{Virt} \\ -\frac{1}{2} \sum_{ai} (A + B)_{pqa}^{-1} L_{ai} & \text{for } p \in \text{Virt}, q \in \text{Occ} \\ -\frac{1}{2} \sum_{ai} (A + B)_{qpa}^{-1} L_{ai} & \text{for } p \in \text{Occ}, q \in \text{Virt} \end{cases} \quad (72)$$

If we now compare our complete basis DC expression to the Chernyak–Mukamel formula,

$$d_{IJ}^{CM[Q]} = \frac{1}{E_J - E_I} \sum_{pq} u_{pq}^{[Q]} \gamma_{pq}^{IJ} \quad (73)$$

it is clear that, if our pseudo-wavefunction approach is meaningful, Γ^{IJ} from eq 72 should correspond to γ^{IJ} , the exact transition density matrix. According to response theory,^{42,43} the exact transition density matrix between states I and J is

$$\gamma_{pq}^{IJ} = \begin{cases} D_{pq}^{IJ} & \text{for } p, q \in \text{Occ or } p, q \in \text{Virt} \\ \gamma_{pq}^{(1),IJ} & \text{for } p \in \text{Virt}, q \in \text{Occ} \\ \gamma_{pq}^{(2),IJ} & \text{for } p \in \text{Occ}, q \in \text{Virt} \end{cases} \quad (74)$$

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

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} + (E_J - E_I) \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & -\mathbf{I} \end{pmatrix} \right] \begin{pmatrix} \gamma^{(1),IJ} \\ \gamma^{(2),IJ} \end{pmatrix} = - \begin{pmatrix} \mathbf{L}^{(1),IJ} \\ \mathbf{L}^{(2),IJ} \end{pmatrix} \quad (75)$$

where \mathbf{I} is the identity matrix

$$\begin{aligned} L_{ck}^{(1),IJ} = & \sum_{pq} \Pi_{pcqk} D_{pq}^{IJ} + \sum_{jab} [\Pi_{bcja} (X_k^{Ia} X_j^{Jb} + Y_j^{Ib} Y_k^{Ja}) \\ & + \Pi_{bajc} (X_j^{Ib} Y_k^{Ja} + X_k^{Ia} Y_j^{Jb})] \\ & - \sum_{ijb} [\Pi_{bijk} (X_i^{Ic} X_j^{Jb} + Y_j^{Ib} Y_i^{Jc}) \\ & + \Pi_{bkji} (X_j^{Ib} Y_i^{Jc} + X_i^{Ic} Y_j^{Jb})] \end{aligned} \quad (76)$$

and

$$\begin{aligned} L_{ck}^{(2),IJ} = & \sum_{pq} \Pi_{pcqk} D_{qp}^{IJ} + \sum_{jab} [\Pi_{bcja} (X_j^{Ib} X_k^{Ja} + Y_k^{Ia} Y_j^{Jb}) \\ & + \Pi_{bajc} (Y_j^{Ib} X_k^{Ja} + Y_k^{Ia} X_j^{Jb})] \\ & - \sum_{ijb} [\Pi_{bijk} (X_j^{Ib} X_i^{Jc} + Y_i^{Ic} Y_j^{Jb}) \\ & + \Pi_{bkji} (Y_j^{Ib} X_i^{Jc} + Y_i^{Ic} X_j^{Jb})] \end{aligned} \quad (77)$$

The key point to notice is that $L_{ck}^{IJ} = L_{ck}^{(1),IJ} + L_{ck}^{(2),IJ}$. Furthermore, in the limit of an excited state crossing, where $(E_j - E_i) \rightarrow 0$, it follows that

$$(\gamma_{ai}^{(1),IJ} + \gamma_{ia}^{(2),IJ}) = - \sum_{jb} (A + B)_{ajib}^{-1} L_{jb}^{IJ} \quad (78)$$

Thus, in the end, we may conclude that whenever the state energy difference is $(E_j - E_i) \ll E_1$, where E_1 is the lowest TDHF/TDDFT excitation energy, we recover the Chernyak–Mukamel formula, $d_{IJ}^{CB[Q]} = d_{IJ}^{CM[Q]}$. Therefore, our DCs agree with response theory in the limit of an excited state crossing. Altogether, this analysis provides further evidence of the reliability of the approximations made in the present work.

B. Future Work. Although our approach is able to recover the Chernyak–Mukamel formula for TDHF DCs, the reader may still ask him- or herself whether our intuitive pseudo-wavefunctions can be entirely trusted in practice. After all, we have made several approximations along the way, most notably the assumption of small Y amplitudes. To convince the reader of the reliability of eqs 65 and 66, in a companion paper,²⁸ we will show that our derivative coupling expression displays the correct behavior near conical intersections. In particular, the DCs in eqs 65 and 66 recover the correct branching plane and Berry's phase behavior, which provide yet another crucial piece of empirical evidence that our approach captures the correct physics underlying the derivative couplings between TDHF or, equivalently, TDDFT states. In the future, it will be interesting to compare our derivative couplings with derivative couplings derived entirely from response theory. Li and Liu²³ have recently made such a comparison in the abstract, but no practical or numerical examples have been published yet. Looking forward, there are many possible applications for our model of pseudo-wavefunctions, including the construction of locally diabatic states^{44–48} and nonadiabatic dynamics.

■ APPENDIX A

The Equivalence of the Hellmann–Feynman and Direct Differentiation DCs

The derivative coupling expression in the current work is derived from a modified Hellmann–Feynman approach (starting from eq 39, we obtain eqs 65 and 66). In a companion paper,²⁸ we start with eq 38 to obtain the final result. By inspection, these two expressions agree—with the exception of the antisymmetric AO overlap gradient terms. Thus, to explicitly show that these two DC expressions are fully equivalent, we must reconcile only the apparent differences between the $S^{A[Q]}$ terms given in the current work by $G^{IJ} = G^{A,IJ} + G^{B,IJ}$, the sum of eqs 50 and 64, and in eq 50 in the companion paper (ref 28).

To show that these expressions are equivalent, we will transform our results into those of ref 28. We first note that several non-translationally invariant terms which arise in this derivation are symmetric under exchange of μ and ν . The trace of these contributions with the antisymmetric $S^{A[Q]}$ must therefore be zero and so these terms have been discarded. Second, we note that, following directly from the TDHF eigenvalue equations (eq 5), we must have

$$\sum_{jb} (\Pi_{ibaj} X_j^{Ib} + \Pi_{abij} Y_j^{Ib}) = (E_I + \varepsilon_i - \varepsilon_a) X_i^{Ia} \quad (A79)$$

and

$$\sum_{jb} (\Pi_{ibaj} Y_j^{Ib} + \Pi_{abij} X_j^{Ib}) = (-E_I + \varepsilon_i - \varepsilon_a) Y_i^{Ia} \quad (A80)$$

Making use of these expressions in the context of the remaining terms of G , we arrive at

$$\begin{aligned} G_{\mu\nu} = & \frac{1}{E_j - E_i} \left[\sum_{ijabc} C_{\mu c} C_{\nu a} [(E_I + \varepsilon_i) X_i^{Ia} X_i^{Ic} + (E_j + \varepsilon_i) X_i^{Ic} X_i^{Ia}] \right. \\ & - \sum_{ijkab} C_{\mu i} C_{\nu k} [(E_I - \varepsilon_a) X_i^{Ia} X_k^{Ia} + (E_j - \varepsilon_a) X_k^{Ia} X_i^{Ia}] \\ & + \sum_{ijabc} C_{\mu c} C_{\nu a} [(-E_I + \varepsilon_i) Y_i^{Ia} Y_i^{Ic} + (-E_j + \varepsilon_i) Y_i^{Ic} Y_i^{Ia}] \\ & \left. - \sum_{ijkab} C_{\mu i} C_{\nu k} [(-E_I - \varepsilon_a) Y_i^{Ia} Y_k^{Ia} + (-E_j - \varepsilon_a) Y_k^{Ia} Y_i^{Ia}] \right] \quad (A81) \end{aligned}$$

By writing

$$C_{\mu c} C_{\nu a} = \frac{1}{2} (C_{\mu c} C_{\nu a} + C_{\nu c} C_{\mu a}) + \frac{1}{2} (C_{\mu c} C_{\nu a} - C_{\nu c} C_{\mu a}) \quad (A82)$$

we can partition the first term of eq A81 into two components: one that is symmetric under exchange of μ and ν and one that is antisymmetric under such an exchange. By using this transformation to selectively eliminate symmetric (non-contributing) terms and rearrange the MO indices on the amplitudes, we obtain our final expression

$$\begin{aligned} G_{\mu\nu} = & - \sum_{iab} C_{\mu b} C_{\nu a} (X_i^{Ia} X_i^{Ib} - Y_i^{Ia} Y_i^{Ib}) \\ & - \sum_{ija} C_{\mu j} C_{\nu i} (X_i^{Ia} X_j^{Ia} - Y_i^{Ia} Y_j^{Ia}) \quad (A83) \end{aligned}$$

in which the energy difference denominator is eliminated in a manner similar to that achieved for the analogous term in the CIS derivative coupling expression (cf. eq A25 of ref 7). Thus, we have explicitly shown that eq A83 is equivalent to the $S^{A[Q]}$ term derived in eq 50 of ref 28.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by NSF CAREER Grant CHE-1150851. J.E.S. acknowledges an Alfred P. Sloan Research Fellowship and a David & Lucile Packard Fellowship. J.E.S. thanks Filipp Furche for very stimulating conversations and his suggestion to compare our results with the Chernyak–Mukamel formalism.

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