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Cite as: J. Chem. Phys. 153, 184106 (2020); https://doi.org/10.1063/5.0018441
Submitted: 15 June 2020 . Accepted: 28 September 2020 . Published Online: 11 November 2020

Hung-Hsuan Teh, and Joseph E. Subotnik

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Analytic gradients and derivative couplings for configuration interaction with all single excitations and one double excitation—En route to nonadiabatic dynamics

Hung-Hsuan Teh\textsuperscript{a)} and Joseph E. Subotnik\textsuperscript{b)}

AFFILIATIONS
University of Pennsylvania, Philadelphia, Pennsylvania 19104–6323, USA

\textsuperscript{a)}Author to whom correspondence should be addressed: teh@sas.upenn.edu
\textsuperscript{b)}subotnik@sas.upenn.edu

ABSTRACT
We present analytic gradients and derivative couplings for the simplest possible multireference configuration interaction method, CIS-1D, an electronic structure Ansatz that includes all single excitations and one lone double excitation on top of a Hartree–Fock reference state. We show that the resulting equations are numerically stable and require the evaluation of a similar number of integrals as compared to standard CIS theory; one can easily differentiate the required frontier orbitals (h and l) with minimal cost. The resulting algorithm has been implemented within the Q-Chem electronic structure package and should be immediately useful for understanding photochemistry with $S_0$–$S_1$ crossings.

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I. INTRODUCTION
Nonadiabatic couplings are key quantities of interest that cannot be ignored when discussing nuclear motion concurrently with multiple electronic degrees of freedom. When solving the exact Schrödinger equation for the nuclear wave functions attached to one electronic basis, the nonadiabatic couplings appear naturally and mix together different electronic potential energy surfaces (PESs). At the same time, if we consider mixed quantum–classical dynamics—e.g., surface-hopping algorithms,\textsuperscript{1} the generalized Langevin equation,\textsuperscript{2} or the mixed quantum–classical Liouville formalism—the derivative couplings inevitably appear and incorporate the coupling between nuclear motion on different PESs through electronic state transitions. No matter what level of theory one applies, nonadiabatic couplings cannot be ignored, especially so when a nuclear wave function approaches a small energy gap region in the configuration space, or most dramatically a region with a degenerate set of electronic states (so-called conical intersections\textsuperscript{3}), where the Born–Oppenheimer approximation completely breaks down.

In practice, accurate nonadiabatic couplings are necessary in order to model many chemical and material processes, e.g., to predict the lifetimes of chemical reaction intermediates,\textsuperscript{4} to estimate electron transfer rates in singlet fission processes,\textsuperscript{5} to quantify energy dissipation in gas–metal interfaces,\textsuperscript{6} to simulate charge recombination in mixed perovskites,\textsuperscript{7} and to model photo-induced charge transfer in graphene layers.\textsuperscript{8} In order to treat the phenomena above, a host of simulation methods have been proposed and their performance can range from very successful to minimally successful. Despite enormous progress in the area of chemical dynamics and nonadiabatic electronic structure,\textsuperscript{9} calculating accurate electronic structure and simulating chemical dynamics for large complex systems with $S_n \rightarrow S_0$ transitions remain a direct challenge to modern theory;\textsuperscript{10,11} in particular, there still remains today the need for accurate and inexpensive $S_1 \rightarrow S_0$ nonadiabatic couplings.\textsuperscript{12}

To that end, within the context of modern electronic structure theory, a combination of density functional theory (DFT) and time-dependent density functional theory (TDDFT) remains the most
likely possible candidate to produce the needed electronic structure matrix elements, with a reasonable balance between accuracy and computational cost. This statement remains true, even though, as is well known, standard DFT/TDDFT [just like configuration interaction singles (CIS)] does not predict the correct dimensionality of the S_0–S_1 conical intersection manifold seam due to the lack of including any interaction between the "DFT ground state configuration" and singly excited configuration states. With this fact in mind, there is a strong impetus to invoke complete active space methods when running photochemical simulations, ideally with a balanced reference set of orbitals. Other researchers have focused on using spin–flip DFT methods as a means of calculating S_0–S_1 crossings with the correct topology and derivative couplings.

Very recently, we have proposed an alternative means of merging DFT with configuration interaction to address the S_0–S_1 failure of DFT, following the previous ideas of Maitra et al. Our Ansatz is to build a configuration interaction framework that includes not just the ground state configuration and all of the singly excited state configuration but also one extra doubly excited configuration state. Within the context of a restricted Hartree–Fock (HF) state, this special lone doubly excited configuration \( \Phi^{(1)} \) is chosen through a self-consistent field (SCF) procedure for minimizing the energy \( E^{(1)} = \int H \Phi^{(1)} \Phi^{(1)*} \). Here, \( h \) is the optimized HOMO (to be determined), \( l \) is the optimized LUMO (also to be determined), and \( H \) is an effective Hamiltonian. In principle, if we make the Tamm–Dancoff approximation, this concept of including one double (1D) can be combined not just with canonical Hartree–Fock theory (and HF orbitals) but also with DFT (and Kohn–Sham orbitals), yielding CIS-1D and TDDFT-1D Ansätze. Thus, within the panoply of electronic structure methods, this selected conical intersection approach would seem to fall somewhere in between a complete active space (CAS) and multi-reference configuration interaction (MRCI) methods.

As far as how the method performs, in practice, in Ref. 26, we have already demonstrated the following features: (i) both CIS-1D and TDDFT-1D predict the correct topology for the S_0–S_1 conical intersection manifold seam; (ii) both methods predict relatively small changes for the excitation energies far away from conical intersections/avoided crossings; (iii) the correct geometric phase dressing the electronic wave functions is preserved. Besides these already proven features, there is every reason to presume that (iv) the computational costs of CIS-1D and TDDFT-1D should be nearly the same as the CIS and TDDFT calculations, respectively (although we have not yet produced a production, fully polished code); and (v) the 1D framework is simple enough so that both the analytic gradients and derivative couplings should be possible. Note that gradients are essential for all quantum dynamics approaches and the calculation of time-correlation functions; also, a combination of gradients and derivative couplings is usually required to locate conical intersections.

In this paper, our focus will be on point (v). We will present a detailed derivation of the necessary equations for CIS-1D derivative couplings and gradients. We have implemented the relevant equations within a developmental version of the Q-Chem electronic structure package, and we report a few preliminary results to convince the reader that the implemented code does indeed match finite difference. For this initial manuscript, we will work exclusively in the CIS-1D framework; the extension to TDDFT-1D derivative couplings/analytic gradients will be shown in a separate manuscript to be submitted soon. The algorithm presented here should be immediately relevant for chemical researchers investigating photochemical reactions.

This article is organized as follows: In Sec. II, the CIS-1D Hamiltonian will be introduced. In Sec. III, we review the necessary orbital response theory and the coupled perturbed Hartree–Fock equations, which will allow us to describe how orbitals change as we move the nuclei in the configuration space. Note that unlike the case of conventional post-HF methods (where only inter-subspace response appears), intra-subspace response becomes important for CIS-1D (just as for a CAS calculation) and we must carefully differentiate two special frontier orbitals, the optimized HOMO (\( h \)) and the optimized LUMO (\( l \)); note that these orbitals are not the canonical HOMO and LUMO. The determination of the optimized orbitals as well as the derivation of the intra-subspace orbital response equations will be described in Sec. IV. In Sec. V, we will present the complete, final equations for the analytic derivative coupling, and many helpful details of the calculation can be found in Appendix B. For the sake of completeness, in Sec. VI, we write down the final equations for the analytic gradient. Finally, in Sec. VII, we present the results and compare our analytic findings with the finite difference results. We discuss our results and conclude in Sec. IX.

Notation: Throughout this article, \( \{a, b, c, d\} \) denote the atomic orbitals (AOs), \( \{i, j, k, m\} \) represent the occupied molecular orbitals (MOs), \( \{a, b, c, d\} \) serve as the virtual MOs, and \( \{p, q, r, s, t, u\} \) are used for the general MOs (can be occupied or virtual).

II. CIS-1D HAMILTONIAN

Within a CIS-1D framework, our basic Ansatz is to apply variational theory for wave functions that span a vector space composed of the ground HF state \( |\Phi_0\rangle \), all the singly excited configurations \( \{|\Phi^1\rangle\} \) and one doubly excited configuration from the frontier HOMO orbital \( h \) to the frontier LUMO orbital \( l \): \( |\Phi^{(2)}\rangle \). We consider only singlet systems here so that we can focus on spin-allowed \( S_1 \rightarrow S_0 \) crossings; the case of triplets will be addressed in a forthcoming paper. The set \( \{|\Phi_0\rangle, |S^0\rangle \equiv (|\Phi^1_0\rangle + |\Phi^1_l\rangle)/\sqrt{2}, |\Phi^{(2)}\rangle\} \) includes all of the configurations that we must treat. The CIS-1D wave function can be written down as

\[
|\Psi\rangle = X_0|\Phi_0\rangle + \sum_{ia} X_i^a |S^a_i\rangle + X_d^l |\Phi^{(2)}_d\rangle,
\]

where \( X_0, X_i^a, X_d^l \) are variational parameters.

A general two-body interaction Hamiltonian (without any spin operators considered) can be written in the CIS-1D basis as follows:

\[
\mathbf{H} = E_0 + \begin{pmatrix}
|\Phi_0\rangle & |S^0_1\rangle & |\Phi^{(2)}_d\rangle \\
0 & \pi_{hh11} & \sqrt{2}(\delta_{a1}\pi_{hl1} + \delta_{bl}\pi_{ha1}) \\
0 & \sqrt{2}(\delta_{a1}\pi_{hl1} + \delta_{bl}\pi_{ha1}) & -2\pi_{hl1} + 2\pi_{1l1} + \pi_{hl1} + \pi_{ha1}
\end{pmatrix}
\begin{pmatrix}
|\Phi_0\rangle \\
|S^0_1\rangle \\
|\Phi^{(2)}_d\rangle
\end{pmatrix}
\]

(1)
Here, $f_{pq} = h_{pq} + \sum \pi_{pq}$ is a Fock matrix element and \( \pi_{pq} \equiv 2 \langle pr | qs \rangle - | ps | qr \rangle \). We use chemist notation (\( pq/rs \) = \( \int dx_1 dx_2 \phi_l^* (x_2) \phi_l^* (x_1) (\phi_k (x_1) \phi_k (x_2)) \phi_l (x_2) \phi_l (x_1) \)) so that \( (pr | qs \rangle \) and \( | ps | qr \rangle \) are the Coulomb and exchange two-electron integrals, respectively. Note that we have integrated out all the spin degrees of freedom in Eq. (1), so all the orbital subscripts are indices for spatial orbitals. \( H \) is a \( (N_o N_v + 2) \times (N_o N_v + 2) \) matrix, where \( N_o \) and \( N_v \) are the numbers of occupied and virtual orbitals, respectively.

In order to construct CIS-1D derivative couplings and gradients, our path is straightforward: we will need to take the derivative of all of the quantities inside of the \( H \) matrix in Eq. (1). Note, however, that this will require taking the derivative of the CIS-1D optimized orbitals, in particular, the \( h \) space in Eq. (1), so all the orbital subscripts are indices for unique means of rigorously parameterizing \( C \) in terms of \( C_0 \) as is follows:\textsuperscript{25,31}

\[
C = C_0 (C_0^\dagger SC_0)^{-1/2} e^{-\Theta},
\]

where \( S \) is the atomic orbital (AO) overlap matrix (that depends on the nuclear coordinate \( x \)) and \( \Theta \) is the rotation angle matrix. The factor \( (C_0^\dagger SC_0)^{-1/2} \) enters into Eq. (2) as a way of enforcing the normalization condition: \( C_0^\dagger SC_0 = 1 \). The exponential describes how the MO coefficient \( C \) is rotated away from the reference \( C_0 \), and the exponent \( \Theta \) must be antisymmetric. The antisymmetric nature of the rotation matrix can lead to a few notational complexities, and it will be helpful for us to be as explicit as possible. Henceforward, we will write

\[
\Theta = \begin{pmatrix}
0 & -\Theta_{21} & \ldots \\
\Theta_{21} & 0 & \ldots \\
\vdots & \vdots & \ddots
\end{pmatrix}
\]

In other words, consider a system with an orbital basis of dimension \( N \). Although the response theory in this section is standard and can be worked out the relevant derivative couplings, we must extensively review both (i) standard orbital response (i.e., the response of canonization so that we can derive the non-standard response theory (as beyond) standard coupled-perturbed HF theory. For the reader who will be helpful to review standard analytic response theory, which dictates how one can calculate the change in molecular orbitals as a function of nuclear geometry. Although the response theory in this section is standard and can be found in many references (e.g., Refs. 35–39), we include this information so that we can derive the non-standard response theory (as relevant to CIS-1D) in Sec. IV.

### A. Derivative of the MO coefficient

In all that follows, we will assume real MO coefficients. Let \( C_0 \) be the MO coefficient at a reference nuclear position \( x_0 \), and let \( C \) represent the MO coefficient after moving slightly away from \( x_0 \) in a nuclear position space. We need to find the derivative of the MO coefficient at \( x_0 \); let us denote this derivative as \( C_0^{[x]} \) (the superscript \( [x] \) representing the total derivative). One (non-unique) means of rigorously parameterizing \( C \) in terms of \( C_0 \) is as follows:\textsuperscript{30,31}

\[
\frac{\partial C_{\mu\nu}}{\partial S_{ab}} \bigg|_{S_0, \Theta = 0} = \frac{1}{2} \sum_{q} C_{0,\mu q} C_{0,\nu q} C_{0,\delta p}.
\]

Henceforward, for notational ease, we will discard the subscript 0 from the derivative of the MO coefficient \( C \) we will implicitly assume that all derivatives are taken at \( \Theta = 0 \) relative to an updated set of MO coefficients.

### B. \( a_{\mu}^{[x]} \) and \( \tilde{a}_{\mu}^{[x]} \)

In Sec. V, we will require the derivatives of many creation/annihilation operators, e.g., \( a_{\mu}^{[x]} \). In order to calculate these derivatives, we begin by proving the following identity:

\[
a_{\mu}^{[x]} = -\sum_{p} \tilde{a}_{p}^{[x]} a_{p},
\]
where \( O^{[s]}_{rs} \equiv \langle r \mid \sigma \rangle \) and \( r \) and \( p \) label spin orbitals. To prove this identity, consider the identity \( \langle r \mid L \rangle = \delta_{rs} \), where \( L \) is an arbitrary set of spin orbitals. Without loss of generality, let us assume that \( L \) does not contain either \( r \) or \( s \). If we take the derivative of both sides, we obtain

\[
(\langle L | a_r | s \rangle) + (\langle L | a_s | r \rangle) + (\langle L | a_r | s \rangle) + (\langle L | a_s | r \rangle) = 0,
\]

which implies that

\[
\langle L | a_r | s \rangle = -\langle L | a_s | r \rangle = -O^{[s]}_{rs}.
\]

Since \( L \) is arbitrary, we have proven Eq. (7), and by taking the adjoint of Eq. (7), we can also show that

\[
a_i^{[s]} = \sum_p O^{[s]}_{ip} a_p.
\]

Having expressed the derivatives of creation/annihilation operators in terms of \( O^{[s]}_{rs} \), the only problematic item is to compute \( O^{[s]}_{rs} \) explicitly. If the orbitals \( r \) and \( s \) have different spins, \( O^{[s]}_{rs} \) will vanish as we are working with a spin-free Hamiltonian (and all molecular orbitals will have good spin numbers). Hence, we only need to consider the same spin case, where \( r \) and \( s \) are considered as spatial orbitals. We find

\[
O^{[s]}_{rs} = \left( \sum_{\mu} C_{\mu r} \right) \left( \sum_{\nu} C_{\nu s}^{\dagger} \right) + \sum_{\mu \nu} \sum_{\sigma \lambda} C_{\mu r} C_{\nu s} S^{[s]}_{\sigma \lambda} = \sum_{\mu \nu} \sum_{\sigma \lambda} C_{\nu s} S^{[s]}_{\sigma \lambda} + \Theta_{rs},
\]

where \( S^{[s]}_{\sigma \lambda} \equiv \langle \sigma \beta \rangle \). Here, we have utilized Eqs. (4)–(6).

### C. Inter-subspace response \( \Theta^{[s]}_{ik} \)

The central item of standard response theory is the calculation of \( \Theta^{[s]}_{ik} \), which we will now briefly review. Note that in this paper, we will work exclusively with systems having an even number of electrons and our calculations will always be with a restricted closed shell HF calculation (so that all alpha and beta orbitals are identical). The HF ground state energy written in a spatial orbital basis is

\[
E_0 = 2 \sum_j \left( i \delta_{ij} \right) + \sum_{ij} \pi_{ij} = 2 \sum_j \sum_{\mu} \mu_i C_{\mu j} C_{\sigma j} + \sum_{ij} \sum_{\mu \nu \sigma \lambda} \pi_{ijkl} C_{\mu i} C_{\nu j} C_{\sigma k} C_{\lambda l}.
\]

By utilizing Eqs. (6) and (8), we can discern how the ground state energy changes as we change \( \Theta \). We imagine differentiating by \( \partial / \partial \Theta_{rs} \),

\[
\frac{\partial E_0}{\partial \Theta_{rs}} = -2 \sum_{\mu \nu} \mu_i C_{\mu i} C_{\nu j} + C_{\mu i} C_{\nu j} \delta_{rs} - \sum_{\mu \nu \sigma \lambda} \pi_{ijkl} C_{\mu i} C_{\nu j} C_{\sigma k} C_{\lambda l} + C_{\mu i} C_{\nu j} \delta_{rs} - \sum_{\mu \nu \sigma \lambda} \pi_{ijkl} C_{\mu i} C_{\nu j} C_{\sigma k} C_{\lambda l} + C_{\mu i} C_{\nu j} \delta_{rs} - \sum_{\mu \nu \sigma \lambda} \pi_{ijkl} C_{\mu i} C_{\nu j} C_{\sigma k} C_{\lambda l} + C_{\mu i} C_{\nu j} \delta_{rs}.
\]

Recall that the value of \( \partial E_0 / \partial \Theta_{rs} \) will depend strongly on the nature of the orbitals \( s \) and \( t \). For instance, if \( t \) in \( \Theta_{st} \) is an occupied orbital, say \( k \), then

\[
\frac{\partial E_0}{\partial \Theta_{rk}} = -2 (f_k + f_k).
\]

In contrast, if \( t \) is a virtual orbital, say \( c \),

\[
\frac{\partial E_0}{\partial \Theta_{ck}} = 0.
\]

For a coupled perturbed calculation (see below), we will require taking the second derivative of \( E_0 \) with respect to the rotations of the molecular orbitals. In particular, we will require the inverse of the matrix \( \partial^2 E_0 / \partial \Theta_{pq} \partial \Theta_{jk} \). Note that inverting a singular matrix is always unstable, and so it will be necessary to work with the independent variables \( \Theta_{pq} \) rather than the dependent variables \( \Theta_{pq} \). To calculate the relevant matrix \( \partial^2 E_0 / \partial \Theta_{pq} \partial \Theta_{jk} \), which will be symmetric), we can simply use the derivatives above plus the chain rule,

\[
\frac{\partial E_0}{\partial \Theta_{pq}} \left[ \frac{\partial E_0}{\partial \Theta_{jk}} + \frac{\partial E_0}{\partial \Theta_{jk}} \right]_{\Theta_{rs} = -\Theta_{js}} = -2 (f_j + f_j) - 2 (f_j + f_j) (-1) = 0.
\]

Similarly,

\[
\frac{\partial E_0}{\partial \Theta_{pq}} = 0,
\]

\[
\frac{\partial E_0}{\partial \Theta_{ai}} = -2 (f_i + f_i).
\]

In all that follows, we will work with the independent variables \( \Theta_{pq} \) rather than the constrained variables \( \Theta_{pq} \).

Note that the derivatives in Eqs. (9) and (10) are always 0, but \( \partial E_0 / \partial \Theta_{ai} \) in Eq. (11) vanishes only when the Fock matrix satisfies \( f_{ai} = 0 \), i.e., for HF or DFT theory, where one rotates the orbitals until one minimizes the ground state energy. For our purposes, we must emphasize the well-known fact that once one has converged a DFT or HF calculation, \( E_0 \) is invariant to any rotation between occupied and virtual orbitals (or of course virtual and virtual orbitals).

Thus, the right-hand side of Eq. (11) will always be equal to 0 so long as one does not mix the occupied and virtual subspaces; this fact will be extremely relevant for the CIS-1D formalism presented below.

Standard response theory computes the inter-subspace response \( \Theta^{[s]}_{ik} \) by differentiating Eq. (11),
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(\frac{\partial E_0}{\partial \theta_{ai}})^{[x]} = -4f^{[x]}_i

= \sum_{ck} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \theta_{ck}} \phi_{\theta_{ck}}^{[x]} + \sum_{af} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial S_{af}} S_{af}^{[x]} + \sum_{\mu \nu} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial h_{\mu \nu}} h_{\mu \nu}^{[x]} + \sum_{\mu \nu \alpha \beta} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \pi_{\mu \nu \alpha \beta}} \pi_{\mu \nu \alpha \beta}^{[x]}

= 0. \quad (12)

Note that (i) The terms \(\sum_{ck} (\partial^2 E_0 / \partial \theta_{ai} \partial \theta_{ck}) \phi_{\theta_{ck}}^{[x]}\) and \(\sum_{af} (\partial^2 E_0 / \partial \theta_{ai} \partial S_{af}) S_{af}^{[x]}\) do not appear, since Eqs. (9) and (10). (ii) The term \(\sum_{\mu \nu \alpha \beta} (\partial^2 E_0 / \partial \theta_{ai} \partial \theta_{\mu \nu \alpha \beta}) \pi_{\mu \nu \alpha \beta}^{[x]}\) also does not appear, since \(\Theta\) is antisymmetric.

All the second order partial derivatives in Eq. (12) can be computed by taking derivatives over Eq. (11) [and using Eq. (4)],

\[ \frac{\partial^2 E_0}{\partial \theta_{ai} \partial S_{af}} = 2 \sum_{\mu \nu} h_{\mu \nu}^P \left( C_{iu} \phi_{\mu} + C_{a\mu} \phi_{\nu} \right) \]

\[ + 2 \sum_{\mu \nu} \pi_{\mu \nu \alpha \beta} \left( C_{iu} P_{\alpha \beta} + C_{a\mu} P_{\alpha \beta} \right), \quad (13) \]

\[ \frac{\partial^2 E_0}{\partial \theta_{ai} \partial h_{\mu \nu}} = -2 \left( C_{a\mu} C_{\nu \alpha} + C_{\mu \nu} C_{a\alpha} \right), \quad (14) \]

\[ \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \pi_{\mu \nu \alpha \beta}} = -2P_{\mu \nu} \left( C_{a \mu} C_{\nu \alpha} + C_{\mu \nu} C_{a \alpha} \right). \quad (15) \]

Here, we have defined,

\[ P_{\mu \nu} \equiv \sum_k C_{ak} C_{dk}, \quad (16) \]

\[ P_{\mu \nu} \equiv \sum_k C_{ak} C_{ck}. \quad (17) \]

With regard to the second order derivative \(\frac{\partial^2 E_0}{\partial \theta_{ai} \partial \theta_{\mu \nu}}\), we can differentiate the Fock matrix with respect to \(\Theta\) (not \(\Theta\)). Following the same procedure as in Eqs. (9)–(11), we obtain

\[ \frac{\partial f_{ai}}{\partial \theta_{\mu \nu}} = -f_{ai} \delta_{\mu \nu} - f_{ci} \delta_{\mu \nu} + f_{ck} \delta_{\mu \nu} + \pi_{a \mu \nu \alpha} - \pi_{a \nu \mu \alpha}, \]

and therefore,

\[ \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \theta_{\mu \nu}} = 4 \left( f_{ci} \delta_{\mu \nu} - f_{ck} \delta_{\mu \nu} + \pi_{a \mu \nu \alpha} - \pi_{a \nu \mu \alpha} \right). \]

Note that \(\pi_{a \nu \mu \alpha} = \pi_{a \mu \nu \alpha} = \pi_{a \nu \mu \alpha} = \pi_{a \mu \nu \alpha}\) as we consider real MOs. Moreover, \(\partial^2 E_0 / \partial \theta_{ai} \partial \theta_{\mu \nu}\) is symmetric so that one can invert the matrix in a straightforward fashion.

Finally, armed with all the second order derivatives in Eq. (12), we can calculate \(\Theta_{\theta_{ck}}^{[x]}\),

\[ \Theta_{\theta_{ck}}^{[x]} = -\sum_a \left( \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \theta_{ck}} \right)^{-1} \xi_{ai}, \quad (18) \]

where

\[ \xi_{ai} \equiv \sum_{af} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial S_{af}} S_{af}^{[x]} - \sum_{\mu \nu} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial h_{\mu \nu}} h_{\mu \nu}^{[x]} - \sum_{\mu \nu \alpha \beta} \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \pi_{\mu \nu \alpha \beta}} \pi_{\mu \nu \alpha \beta}^{[x]}. \]

In principle, according to Eq. (18), one should calculate the inverse of the response matrix \(3N^2\) times (since the matrix element \(\xi_{ai}\) depends on the direction of a nuclear displacement). Such a calculation would be impractical for large complex systems. However, as is well known in the response theory, the usual target (see details below) actually has the form \(\sum_{\mu \nu} \Theta_{\mu \nu}^{[x]} Y_{\mu \nu}\). Below, we will use the standard Z-vector trick of Handy and Schaefer,

\[ \sum_{\mu \nu} \Theta_{\mu \nu}^{[x]} Y_{\mu \nu} = \sum_{\mu \nu} \left( \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \theta_{\mu \nu}} \right)^{-1} \xi_{ai} Y_{\mu \nu} = \sum_{a i} \xi_{ai} Y_{ai}. \quad (19) \]

where \(\sum_{a i} \xi_{ai} Y_{ai} = \sum_{\mu \nu} \sum_{a i} \left( \frac{\partial^2 E_0}{\partial \theta_{ai} \partial \theta_{\mu \nu}} \right)^{-1} \xi_{ai} Y_{\mu \nu} = \sum_{a i} \xi_{ai} Y_{ai}\).

IV. REVIEW OF ORBITAL RESPONSE THEORY AS SPECIFIC TO THE CIS-1D FRAMEWORK

Above, we have recapitulated standard orbital response theory. For the CIS-1D Hamiltonian, however, one constructs optimized orbitals that are distinct from the usual, canonical HF orbitals, and so the standard theory above will need a little reworking. In Subsection IV B, we will demonstrate how the relevant optimized orbitals can be differentiated. Before doing so, however, let us first review the definition of CIS-1D optimized orbitals.

A. Optimized orbitals

We allow for a complex set of coefficients only for the derivation of the necessary equations of motion in this subsection alone; however, in the end, all MO coefficients will be real. The first step of a CIS-1D calculation is to perform a standard HF calculation. Thereafter, one allows for mixing of the occupied orbitals to generate a not necessarily canonical set of occupied orbitals; one also allows for mixing of the virtual orbitals to generate a not necessarily canonical set of virtual orbitals. Within these sets of orbitals, let \(c\) be our target frontier orbital within the occupied set and \(b\) be our target frontier orbital within the virtual set.
The energy of the doubly excited configuration $|\Phi_{ab}^{\uparrow\downarrow}\rangle$ (in which a pair of electrons is excited from HOMO 0 to LUMO 1) is

$$E_d = E_0 - 2h_{ab} + 2h_{1\uparrow} - 2\sum_i \pi_{aib},$$

$$+ 2\sum_i \pi_{aib} + \pi_{abab} + \pi_{1111} - 2\pi_{11ab},$$

$$= E_0 + E_d.$$ \hspace{1cm} (20)

Here, $h_{ab}$ is the one-electron integral. The indices $i$ in the two summations on the right-hand side of Eq. (20) can index any complete basis of occupied HF orbitals; $E_0$ is the original HF energy. According to CIS-1D, we minimize $E_d$ as a function of the two distinct unitary transformations that rotate the occupied and virtual orbital spaces separately; note that $E_0$ is invariant under such a transformation.

In order to generate concrete equations of motion for finding the optimized, frontier orbitals that minimize $E_d$, we express $|\Phi\rangle$ and $|1\rangle$ in terms of the canonical HF occupied orbitals $|\{l_i\}\rangle$ and canonical virtual orbitals $|\{a_0\}\rangle$, respectively,

$$|\Phi\rangle = \sum_i c_i |l_i\rangle,$$

$$|1\rangle = \sum_a \tilde{c}_a |a_0\rangle,$$

where $c_i$ and $\tilde{c}_a$ are linear combination coefficients. The subscript 0 denotes the original (canonical) HF orbitals. Note that we can also define non-frontier optimized orbitals as well in the same fashion so that we can equate the canonical subspace of occupied orbitals spanned by $|\{l_i\}\rangle$ with a subspace of optimized orbitals spanned by vectors labeled $|\{1\}, [2], \ldots, [i], \ldots, [h-1], [h]\rangle$); similarly, the canonical subspace of virtual orbitals $|\{a_0\}\rangle$ is equivalent to a subspace of optimized orbitals spanned by the vector labeled $|\{1\}, [1+1], \ldots, [a], \ldots, [N-1], [N]\rangle$.

Using the invariance of the occupied space under any occupied–occupied unitary transformation, one can easily show that $\sum_{\alpha} \pi_{\alpha\alpha} = \sum_{\alpha\beta} \pi_{\alpha\beta}$, so that all HF orbitals in $E_d'$ can be expanded in the canonical basis,

$$E_d' = -2\sum_{ab} h_{ab} c^*_a c_b + 2\sum_{ijkl} \pi_{ijkl} c^*_i c^*_j c_k c_l - 2\sum_{ijkl} \pi_{ijkl} c^*_i c^*_j c_k c_l$$

$$+ 2\sum_{ijkl} \pi_{ijkl} c^*_i c^*_j c_k c_l + \sum_{ijkl} \pi_{ijkl} c^*_i c^*_j c_k c_l - 2\sum_{ijkl} \pi_{ijkl} c^*_i c^*_j c_k c_l,$$

Since we require that both $|\Phi\rangle$ and $|1\rangle$ be normalized ($\langle\Phi|\Phi\rangle = 0$ is already guaranteed), the Lagrangian function is

$$L = E_d' - 2\varepsilon_h \left( \sum_i c^*_i c_i - 1 \right) - 2\varepsilon_1 \left( \sum_a c^*_a c_a - 1 \right).$$

where $\varepsilon_h$ and $\varepsilon_1$ are Lagrange multipliers. By setting the derivatives of $L$ with respect to $c^*_a$ and $c^*_i$ to 0, we obtain

$$\langle m_0 | f' | h \rangle = \langle m_0 | e_h | h \rangle,$$

$$\langle e_0 | f' | 1 \rangle = \langle e_0 | e_1 | 1 \rangle,$$ \hspace{1cm} (21)

$$\langle 0 | f' | 1 \rangle = \langle 0 | e_1 | 1 \rangle,$$ \hspace{1cm} (22)

where $f'$ is

$$f' = f - \pi_h + \pi_l,$$

$$\Rightarrow f_{\nu\rho} = \nu_{\rho\nu} + \sum_{r=1,2,..} \pi_{\rho\nu} = \nu_{\rho\nu} + \sum_{a} \pi_{a\nu} P'_{\rho a},$$

with the definition $[\pi_{\alpha\beta}] = \pi_{\alpha\beta}h\nu$.

Note that whereas $f$ denotes the Fock operator constructed from the canonical HF orbital space, $f'$ denotes the Fock operator constructed from the optimized CIS-1D orbital space (with where 1 has replaced h in the occupied space). The new density matrix satisfies

$$P' = \sum_{r=1,2,..} C_{\nu \rho} C_{\rho \nu},$$ \hspace{1cm} (24)

In order to solve Eqs. (21) and (22), we must again use the fact that the CIS-1D optimized orbitals do not mix the canonical virtual and occupied orbitals. Working with the optimized orbitals, we can rewrite Eqs. (21) and (22) exclusively in the optimized orbital basis,

$$\langle m | f' | h \rangle = \langle m | e_h | h \rangle,$$

$$\langle e | f' | 1 \rangle = \langle e | e_1 | 1 \rangle,$$

which can be further decomposed into the atomic orbital basis,

$$\sum_{i \rho \nu} C_{\nu \rho} f'_{\rho i} C_{\rho i} = e_h c_h,$$

$$\sum_{\alpha \rho \nu} C_{\nu \rho} f'_{\rho i} C_{\rho i} = e_1 c_1,$$

$$\Rightarrow \left[ C_{\nu \rho} f'_{\rho i} C_{\rho i} \right] = e_h c_h,$$

Here, we have redefined $c_i = \langle i | h \rangle$ and $\tilde{c}_a = \langle a | 1 \rangle$.

Although the math above might at first look a bit overwhelming, at bottom the matrix $f'$ is the same as the normal Fock matrix $f$ after exchanging the HOMO column and the LUMO column in the MO coefficient $C$; in other words, the new and canonical Fock matrices are of the same form, just with different density matrices $[f = f(P) and \ f' = f'(P')]$, where $P$ and $P'$ are defined in Eqs. (16) and (24), respectively. Thus, we can easily find the new set of optimized orbitals through the following SCF steps (which clearly resemble the elements of Gill’s maximum overlap method[15-24]), and Morokuma and Iwata’s Extended HF approach[45].

1. Perform a standard HF calculation and generate the canonical MO coefficient $C = \left[ C_{\alpha \beta} \right]$; order the columns of $C$ according to energy (with $C_{1\uparrow}$ having the lowest energy, $C_{2\uparrow}$ having the next lowest energy, etc.) For our initial guess, we will let $h$ be approximated by column h of C, $C_{h\uparrow}$; we will let $[1]$ be approximated by column 1 of $C_{1\uparrow}$.

2. Build the density matrix $P'$ by choosing to occupy the $(1, 2, \ldots, h - 1, 1)$-th columns in $C$, i.e., skip of over column h. Then, construct $f'$ according to Eq. (23).

3. Calculate $C_{\alpha \beta} f'_{\beta \alpha}$ and $C_{\alpha \beta} f'_{\alpha \beta}$, and diagonalize each matrix separately (ordering by energy). Let $U_{\alpha \alpha}$ and $U_{\beta \beta}$ be the respective eigenvector matrices (of dimension $N_\alpha \times N_\alpha$ and $N_\beta \times N_\beta$, respectively). The last column of $U_{\alpha \alpha}$ will represent the
frontier orbital $h$ with the highest eigenvalue $\epsilon_h$ in the occupied subspace ($c$); the first column of $U_\text{vir}$ will represent the frontier orbital $1$ with the lowest eigenvalue $\epsilon_1$ in the virtual subspace ($\bar{c}$).

4. Construct by matrix multiplication: $C_\text{occ}^{\text{new}} = C_\text{occ} U_\text{occ}$ and $C_\text{vir}^{\text{new}} = C_\text{vir} U_\text{vir}$. The updated MO coefficient is then

$$C_\text{occ}^{\text{new}} = [C_\text{occ}^{\text{new}}, C_\text{vir}^{\text{new}}].$$

5. Check whether $|C_\text{occ}^{\text{new}} - C|$ is below a threshold for convergence. If not, set $C = C_\text{occ}^{\text{new}}$ and return to step 2.

In all that follows, we will use the converged, optimized orbitals described above. Although it may appear unnatural, we will necessarily need to express both the new and the old canonical Fock matrix in the basis of the new optimized orbitals. Because we have mixed together occupied with occupied orbitals (and virtual with virtual orbitals), $f_{ij} \neq \delta_{ij}$ and $f_{ab} \neq \delta_{ab}$, however, $f_{ia} = 0$ remains zero.

### B. Intra-subspace responses $\Theta_{ih}^{[x]}$ and $\Theta_{1j}^{[x]}$

Having constructed the well-defined optimized orbitals, we are now in a position to take their derivatives. Following Eqs. (9)–(11) where we differentiated $E$, a similar set of equations must hold for $E_\text{d}$; after all, $E$ and $E_\text{d}$ have the same functional form—just with different orbitals. By utilizing Eqs. (20) and (6) and the chain rule, we can obtain

$$\frac{\partial E_\text{d}}{\partial \Theta_{ij}} = 2\delta_{ij}(f_{ij}^* + f_{ij}^0) - 2\delta_{ij}(f_{ij}^0 + f_{ij}^*),$$

$$\frac{\partial E_\text{d}}{\partial \Theta_{ab}} = -2\delta_{ab}(f_{ab}^* + f_{ab}^0) + 2\delta_{ab}(f_{ab}^0 + f_{ab}^*),$$

$$\frac{\partial E_\text{d}}{\partial \Theta_{ai}} = -2(f_{ai}^* + f_{ai}^0 - \delta_{ai}(f_{ai}^0 + f_{ai}^*).$$

As in Eq. (11), the partial derivatives above are not automatically zero, but do vanish when the optimized orbitals are substituted in. For the purposes of a CIS-1D calculation, we will need to calculate only $\Theta_{ih}^{[x]}$ and $\Theta_{1j}^{[x]}$. To that end, we set $i = h (i \neq h)$ and $j = 1 (a \neq 1)$ in Eqs. (25) and (26), respectively.

$$\frac{\partial E_\text{d}}{\partial \Theta_{ih}} = 2(f_{ih}^* + f_{ih}^0),$$

$$\frac{\partial E_\text{d}}{\partial \Theta_{1j}} = -2(f_{1j}^* + f_{1j}^0).$$

We recover expressions similar to Eq. (12) by taking the total derivative of $\partial E_\text{d}/\partial \Theta_{ih}$ and $\partial E_\text{d}/\partial \Theta_{1j}$ with respect to $x$,

$$\left(\frac{\partial E_\text{d}}{\partial \Theta_{ih}}\right)^{[x]} = \sum_{a} \frac{\partial^2 E_\text{d}}{\partial \Theta_{ih} \partial \Theta_{a}} \Theta_{ah}^{[x]} + \sum_{a} \frac{\partial^2 E_\text{d}}{\partial \Theta_{ih} \partial \Theta_{a}} \Theta_{a}^{[x]},$$

$$+ \sum_{a} \frac{\partial^2 E_\text{d}}{\partial \Theta_{ih} \partial \Theta_{a}} \Theta_{ah}^{[x]} + \zeta_i = 0,$$
\[ A_{hk} = 4\left(f_{ik} \delta_{ik} - f_{ik} \delta_{ih} + \pi_{ikl} + \pi_{ikl}ight), \]
\[ B_{hk} = 4\left[-f_{ik} \delta_{ik} + f_{ik} \delta_{ih} - \pi_{iik} + \pi_{ikl} + \delta_{ih}(\pi_{iik} + \pi_{ikl}) + \delta_{ih}(\pi_{iik} + \pi_{ikl})\right], \]
\[ C_{hk} = 4\left[-f_{ik} \delta_{ik} - f_{ik} \delta_{ih} - \pi_{ikl} + \pi_{iik} + \delta_{ih}(\pi_{iik} + \pi_{ikl}) - \delta_{ih}(\pi_{iik} + \pi_{ikl})\right], \]
\[ D_{ih} = 4\left(-f_{ih} + f_{ih} \delta_{ih} + \pi_{ihm} + \pi_{ihm}\right), \]
\[ E_{id} = 4\left(-\pi_{hidl} - \pi_{hidl}\right), \]
\[ F_{ad} = 4\left(f_{ad} + f_{ad} \delta_{ad} + \pi_{adl1} + \pi_{adl1}\right). \]

The second and third terms on the right-hand side of Eq. (33) are 0 either by inspection utilizing Wick’s theorem—the creation and annihilation operators cannot match up. The full contraction of the first term is 0 since \( \langle \Phi_0 | \phi^{[x]}_{hk} \rangle = 0 \). For the singly contracted terms, note that \( a_i^\dagger \) and \( a_i \) are annihilation operators with our definition of the ground state, and so we must contract them for any nonzero term to emerge after normal ordering (again using Wick’s theorem); however, \( a_i^\dagger a_i = 0 \) and all singly contracted terms are zero. Finally, let us use the notation \( Q \) to refer to the normal ordered version of \( Q \). Because the spins have to match, there is only one doubly contracted term that does not vanish,

\[-\langle \phi_0^{[x]} | : a_i^\dagger a_i a_i^\dagger a_i a_i^\dagger a_i^\dagger a_i : | \Phi_0 \rangle = -\delta_{i \alpha} \delta_{i \alpha} \langle \phi_0^{[x]} | a_i^\dagger a_i a_i^\dagger a_i | \Phi_0 \rangle \]
\[= 0, \]

The other term \( \langle \Phi_0^{[x]} | \phi^{[x]}_{hk} \rangle \) will give the same contribution. Thus, the derivative coupling between the singlet configurations \( | S_i \rangle \) and the lone doubly excited configuration in Eq. (32) is

\[ \langle S_i | \phi^{[x]}_{hk} \rangle = \sqrt{2} \delta_{ih} \delta_{ik} \langle S_i | \phi^{[x]}_{hk} \rangle = -\langle S_i | \phi^{[x]}_{hk} \rangle. \]

Similarly, we can calculate the derivative couplings between all other configurations,

\[ \langle \Phi_0^{[x]} | \phi^{[x]}_{ia} \rangle = \sqrt{2} \delta_{i} \delta_{a} \delta_{i} \delta_{a} \langle \Phi_0^{[x]} | \phi^{[x]}_{ia} \rangle = -\langle \Phi_0^{[x]} | \phi^{[x]}_{ia} \rangle, \]
\[ \langle S_i | \phi^{[x]}_{ia} \rangle = \delta_{i} \delta_{a} \delta_{i} \delta_{a} \langle S_i | \phi^{[x]}_{ia} \rangle = -\langle S_i | \phi^{[x]}_{ia} \rangle. \]

These are the only nonzero derivative couplings. In the end, we find that the second term in Eq. (32) reads

\[ \sum_{kk'} X_{k} X_{k'} \langle \Phi_{kk'} | \phi^{[x]}_{kk'} \rangle = \sqrt{2} \sum_{ia} \left[X_{a} X_{a} - X_{a} X_{a}'\right] \sum_{ij} C_{ij} C_{ji} \left(S_{ii}^{[x]} - \frac{1}{2} S_{ii}^{[x]} - \Theta_{ij}^{[x]} \right) + \sum_{ia} \left[X_{a} X_{a} - X_{a} X_{a}'\right] \sum_{ij} C_{ij} C_{ji} \left(S_{ii}^{[x]} - \frac{1}{2} S_{ii}^{[x]} - \Theta_{ij}^{[x]} \right) + \sqrt{2} \left[X_{a} X_{a} - X_{a} X_{a}'\right] \sum_{ia} C_{ia} C_{ia} \left(S_{ii}^{[x]} - \frac{1}{2} S_{ii}^{[x]} - \Theta_{ia}^{[x]} \right). \]
where again \( S_{\alpha \beta}^{[x]} \equiv \langle a | b | x \rangle \).

Next, let us focus on the first term of Eq. (32). For \( I \neq J \) and assuming \( E^J \neq E^I \) (no degeneracy),

\[
\sum_k X^*_k X^I_k = \frac{1}{E^J - E^I} \sum_k X^*_k H^{[x]}_{kk} X^I_k.
\]

To move forward, we must evaluate the derivatives of all of the Hamiltonian matrix elements, where the Hamiltonian is given in Eq. (1). Note that the ground state energy \( E_0 \) will not contribute to the final derivative coupling, since \( \sum_K X^*_K X^I_K \delta_{KK} = F_{0} = \sum_K X^*_K X^I_K = 0 \). Thus, we will need to differentiate only \( p_{\tau i j u} \) and \( f_{\tau} \). By utilizing Eqs. (4)–(6),

\[
\sum_{\mu \nu \sigma \lambda} \mu \nu \sigma \lambda
\]

Next, let us focus on the first term of Eq. (32). For \( I \)

\[
\sum_{\mu \nu \sigma \lambda} \mu \nu \sigma \lambda
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\]

Next, let us focus on the first term of Eq. (32). For \( I \)

\[
\sum_{\mu \nu \sigma \lambda} \mu \nu \sigma \lambda
\]
Here, we have also defined,

$$M_{lk} = \sum_{\mu\nu\lambda\kappa} \pi_{\nu\mu\lambda\kappa} \left[ -2\left( X_{\mu\lambda} X_{\nu\kappa} + X_{\nu\kappa} X_{\mu\lambda} \right) C_{\mu\lambda} C_{\nu\kappa} \right] + \sqrt{2} \left( F - G \right)_{\mu\lambda} C_{\mu\lambda} C_{\nu\kappa} - 2 \left( X_{\mu\lambda} X_{\nu\kappa} \right) \left( \rho_{\mu\lambda} - p^{11} \right)_{\mu\lambda} C_{\nu\kappa} C_{\mu\lambda} \right]$$

and

$$N_{lk} = \sum_{\mu\nu\lambda\kappa} \pi_{\nu\mu\lambda\kappa} \left[ 2\left( X_{\mu\lambda} X_{\nu\kappa} + X_{\nu\kappa} X_{\mu\lambda} \right) C_{\mu\lambda} C_{\nu\kappa} \right] + \sqrt{2} \left( F - G \right)_{\mu\lambda} C_{\mu\lambda} C_{\nu\kappa} - 2 \left( X_{\mu\lambda} X_{\nu\kappa} \right) \left( \rho_{\mu\lambda} - p^{11} \right)_{\mu\lambda} C_{\nu\kappa} C_{\mu\lambda} \right]$$

Finally, for the intra-subspace response terms,

$$Z_{lk} = \sum_{\mu\nu\lambda\kappa} \pi_{\nu\mu\lambda\kappa} \left[ 2\left( X_{\mu\lambda} X_{\nu\kappa} + X_{\nu\kappa} X_{\mu\lambda} \right) C_{\mu\lambda} C_{\nu\kappa} \right] - \sqrt{2} \left( F - G \right)_{\mu\lambda} C_{\mu\lambda} C_{\nu\kappa}$$

and

$$W_{lk} = \sum_{\mu\nu\lambda\kappa} \pi_{\nu\mu\lambda\kappa} \left[ 2\left( X_{\mu\lambda} X_{\nu\kappa} + X_{\nu\kappa} X_{\mu\lambda} \right) C_{\mu\lambda} C_{\nu\kappa} \right] - \sqrt{2} \left( F - G \right)_{\mu\lambda} C_{\mu\lambda} C_{\nu\kappa}$$

Note that in Eq. (34), we found the response terms between arbitrary occupied orbitals (not only $\Theta_{l}^{[i]}$) and between arbitrary virtual orbitals (not only $\Theta_{v}^{[i]}$). As shown in Appendix B, however (and as must be true physically), all response terms proportional to $\Theta_{j}^{[i]}$ (where neither $i$ nor $j$ is the HOMO) vanish after cancellation with Eq. (32), as do all response terms proportional to $\Theta_{v}^{[i]}$ (where neither $a$ nor $b$ is the LUMO). Finally, all terms proportional to $S_{ab}^{[i]}$ [i.e., all of the terms in $\Gamma_{ab}^{[i]}$ in Eq. (43)] arise in Eq. (34) where we differentiate the CIS-1D basis functions (i.e., the non-Hellman–Feynman terms). These terms reflect an error introduced by the Born–Oppenheimer approximation when we ignore nuclear translation and ultimately lead to a lack of translational invariance of the final derivative coupling result. At bottom, these $\Gamma_{ab}^{[i]}$ terms are the only source of translational variance in the calculations. To see how this effect arises, imagine calculating the quantity $\sum_{i,j} d_{ij}$ (denotes the derivative coupling along the nuclear coordinate $x_{i}$), which corresponds to the derivative coupling associated with total translation. Note that $\sum_{i,j} d_{ij} = \sum_{i,j} S_{ij}^{[i]} = 0$. However, $\sum_{i} S_{ii}^{[i]} \neq 0$, which indeed leads to translational variance of the derivative coupling. In practice, this translational variance has no physical meaning as far as nonadiabatic dynamics are concerned, and in practice, with proper insertion of electron translation factors, these terms vanish. In other words, the contribution $\sum_{i,j} \Gamma_{ij}^{[i]} S_{ij}^{[i]}$ must be included when comparing analytic vs finite difference derivative couplings, but this quantity should not be included when running nonadiabatic calculations.47,48

VI. GrAdIent

In order to calculate the gradient on PES $E^{[i]}$, we start with differentiating both sides of $E^{[i]} = \sum_{K,K'} X_{K} H_{KK'} X_{K'}$, so $E^{[x]} = \sum_{K,K'} X_{K} H_{KK'}^{x} X_{K'}$ in the derivative coupling, which is what we calculate in Appendix B. The only differences are that (i) $f = I$ and (ii) the term involving $E_{0}$ no longer vanishes, that is, $\sum_{K,K'} \chi_{K}^{x} E_{0} \chi_{K'}^{x}$, = $E_{0}^{[x]}$ also contributes. Thus, Eq. (42) can be used to generate the gradient as well as the derivative coupling; for the gradient, all terms proportional to $S_{ab}^{[x]}$ vanish, and the factor $1/(E^{[i]} - E^{[j]})$ disappears.

VII. RESULTS

To demonstrate that the theory above is correct in practice, we will now compare analytic values with finite difference calculations. For a reasonably difficult, representative example, we choose a water molecule near a linear geometry. In a previous calculation, we showed that TDDFT-1D predicts a conical intersection here; so does CIS-1D [see Fig. 1(a) for a definition of our coordinate...
CIS-1D predicts a conical intersection around (−1.83, 0) for the H\(^3\) coordinate. To test the algorithm presented above, we will compare the analytic results vs finite difference results when we move H\(^3\) along the vertical dashed line from −0.05 Å to 0 (which is very close to the conical intersection but not directly on top of it) and then to 0.05. Note that calculating derivative couplings near a conical intersection is always a very challenging task due to the small energy gap and the intense orbital mixing. In Table I, we compare the analytic derivative couplings with the finite difference results at three different points: A (y = −0.03 20), B (y = −0.01 140), and C (y = −0.00 429).

TABLE I. Comparison of derivative couplings between analytic calculations and finite difference (FD) results. We investigate points A, B, and C as well as the equilibrium geometry (Equil). The subscripts of atoms label the directions for calculating derivative couplings. Precise results can be observed over all calculations. All calculations are performed with a 6-31g basis. The threshold for convergence of E\(_d\) is set to 10\(^{-11}\).

|        | \(H_x\) | \(H_y\) | \(H_z\) | \(O_x\) | \(O_y\) | \(O_z\) | \(H_x\) | \(H_y\) | \(H_z\) |
|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| A, analytic | −0.202 66 | 5.938 72 | 0       | −2.948 48 | −9.204 86 | 0       | 3.158 25 | 3.354 69 | 0       |
| A, FD    | −0.202 51 | 5.939 63 | 0       | −2.948 74 | −9.206 26 | 0       | 3.158 36 | 3.355 17 | 0       |
| B, analytic | −1.883 92 | 92.845 98 | 0      | −14.780 23 | −142.515 06 | 0       | 16.666 22 | 49.757 82 | 0       |
| B, FD    | −1.880 41 | 92.848 50 | 0       | −14.783 26 | −142.518 69 | 0       | 16.665 73 | 49.759 20 | 0       |
| C, analytic | −0.004 29 | 27.513 58 | 0      | −0.065 29 | −42.233 03 | 0       | 0.069 59  | 14.808 31 | 0       |
| C, FD    | −0.004 09 | 27.518 58 | 0      | −0.065 39 | −42.237 24 | 0       | 0.069 49  | 14.807 58 | 0       |
| Equil, analytic | 0       | 0       | 0.110 40 | 0        | 0       | −0.070 17 | 0       | 0       | 0.110 40 |
| Equil, FD | 0       | 0       | 0.110 40 | 0        | 0       | −0.070 17 | 0       | 0       | 0.110 40 |

*For the calculations at point C, the threshold for converging E\(_d\) is set to 10\(^{-12}\), so as to recover enough digits to show indisputable agreement with finite difference calculations at this difficult point, so close to the conical intersection in the configuration space. Note that the equilibrium geometry used here is the DFT equilibrium geometry (functional: B3LYP and basis: 6-31g), not the CIS-1D equilibrium geometry.
and C (γ = −0.00013) [see Fig. 1(c)]. In almost all cases we have tested (including very close to the CI), the error is less than 1%. In Table I, we also provide the results for the water molecule at equilibrium, far away from the CI, with bond length 0.96 Å and bond angle 104.5°. Here, the analytic derivative coupling is extremely precise.

In Table II, we provide the complementary results for the gradient of the ground state. For the gradient, we find the same precision as for the derivative couplings. (Note that one must multiply the derivative coupling results by the corresponding energy gaps if one wishes to compare the precision of the derivative couplings vs the precision of the gradients; after all the derivative coupling and the gradient can be expressed as ⟨|I|∇H|J⟩/(E₂ − E₁) and ⟨|I|∇H|I⟩, respectively.)

| TABLE II: Comparison of gradients between analytic calculations and finite difference (FD) results at points A, B, and C. The subscripts of atoms label the directions for calculating derivative couplings. Precise results can be observed for all of the calculations. All calculations are performed with a 6-31g basis. The threshold for convergence of E₂ is set to 10⁻¹¹. |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                 | H₁x            | H₁y            | H₁z            | O₂x            | O₂y            | O₂z            | H₂x            |
| A, analytic     | −0.055 21      | 0.964 21       | 0              | −0.095 63      | −1.480 98      | 0              | 0.150 86       |
| A, FD           | −0.055 24      | 0.964 01       | 0              | −0.095 58      | −1.480 68      | 0              | 0.150 82       |
| B, analytic     | −0.012 47      | 0.515 14       | 0              | 0.067 02       | −0.789 54      | 0              | −0.054 55      |
| B, FD           | −0.012 45      | 0.515 16       | 0              | 0.067 00       | −0.789 57      | 0              | −0.054 52      |
| C, analytic     | −0.001 28      | 0.001 73       | 0              | 0.125 78       | −0.002 65      | 0              | −0.124 50      |
| C, FD           | −0.001 28      | 0.001 70       | 0              | 0.125 78       | −0.002 59      | 0              | −0.124 50      |
| Equil, analytic | 0.005 88       | 0.011 91       | 0              | −0.015 94      | −0.020 58      | 0              | 0.010 06       |
| Equil, FD       | 0.005 88       | 0.011 91       | 0              | −0.015 94      | −0.020 58      | 0              | 0.010 06       |

VIII. DISCUSSION: STABILITY AND COST

Sections II–V have demonstrated that one can derive gradients and derivative couplings for CIS-1D in perfect analogy to a CIS calculation. Moreover, the final equations found do not have terribly more terms than a usual CIS gradient/derivative coupling calculation, and so we expect that a very efficient implementation of the algorithm should be possible. This work is currently ongoing.

Now, one crucial item that we have not yet discussed regarding CIS-1D (or equivalently TDDFT-1D) is the question of numerical stability. The entire premise of constructing a multireference wave function is to allow the chemist to treat curve crossings, especially S₀–S₁ curve crossings, for which it is difficult to find a robust and useful reference state. For this reason, we have analyzed the linear water case above, as it should represent a very difficult problem for a single-reference case.

In Fig. 1(b), we plot the S₀ and S₁ PESs as obtained from diagonalizing the CIS-1D Hamiltonian. Note that near ±0.01, the energy gap reaches a minimum, which should correspond to a maximum in the derivative coupling calculation; recall that the derivative coupling is proportional to the inverse of the energy gap. Unfortunately, plotting and visualizing the full derivative coupling is difficult to do; after all, at each geometry, there are nine derivative couplings (three directions for each of the three atoms). That being said, along the vertical dashed line in Fig. 1(a), empirically we find that the y-direction derivative coupling O² always gives the largest absolute value among the nine possible matrix elements. Therefore, in Fig. 1(c), we plot the y-direction derivative coupling of O². The solid line represents the analytical derivative coupling as calculated from Eq. (42). Interestingly, the dashed line shows the same calculation “without” considering all the intra-subspace response terms; clearly, though it is entirely absent within CIS theory, here intra-subspace response plays a crucial role in calculations near a crossing. Note that all of the curves are smooth and do not display any hiccups that we might fear from a single reference calculation.

The results above are very encouraging, insofar as the fact that not only can we construct gradients/derivative couplings to match finite difference, but those quantities appear smooth. For a seasoned practitioner of quantum chemistry, however, it should come as no surprise that near a CI, one must pay close attention when choosing convergence criteria for a configuration interaction routine; in our case, one must be very careful when evaluating the optimized orbitals. To demonstrate this fact, Fig. 1(d), we analyze the point B in Fig. 1(c) and plot both finite difference and analytic results for different convergence thresholds for E₄ from 10⁻¹¹ to 10⁻⁹. At this difficult point, we require a reasonably tight convergence threshold (∼10⁻⁸) for the double optimization in order to reach quantitative accuracy; in practice, we believe such thresholds should be easily achievable for modern SCF packages.

Finally, before concluding, we want to highlight another interesting fact about the CIS-1D algorithm and its underlying stability. In pondering Fig. 1 and Table I, one might be curious: if there is a very close S₀–S₁ crossing, how in the world can the CIS-1D gradient algorithm be even close to smooth and numerically stable? After all, there is no state-averaging and must not the reference state change discontinuously? To that end, it is helpful to investigate orbital energies. Interestingly, for the linear water case, the HOMO and LUMO energies do not touch. Now, on the one hand, one might assume that such a gap might help to guarantee stability of the CIS-1D algorithm. On the other hand, one might also argue that even if the h and 1 orbitals were to cross, the CIS-1D algorithm should be stable as one includes a CAS(2,2) space. In the future, we would like to investigate this question, and yet the number of molecules where the RHF HOMO and LUMO energies cross appears to be very small.
and does not include the usual candidates (ethylene, lithium fluoride, etc.). Thus, given the current examples focusing on a restricted reference states, the question of \( h \) and 1 crossing may in fact be moot.

Returning to the case of water molecule, even though the \( h \) and 1 energies do not cross, Fig. 2(a) shows that the \( h \) and \( h-1 \) energies do cross. In Fig. 2(a), we plot the \( h \) and \( h-1 \) orbital energies along the vertical dashed line from Fig. 1(a); for linear water, the \( h \) and \( h-1 \) orbitals become degenerate at \( y=0 \), which is a high-symmetry point (point B). Thus, once again, one might presume that such a degeneracy would cause enormous problems for the CIS-1D algorithm; after all, if \( h \) and \( h-1 \) cross, should not there be difficulties in solving the coupled equations for response matrices [Eq. (31)]? Or more specifically, one might expect that the submatrix \([\mathcal{D} \varepsilon; \varepsilon T \mathcal{F}]\) should have a zero eigenvalue, and so inversion of such a matrix should be unstable. Indeed, in Fig. 2(b), we plot the smallest eigenvalues of \([\mathcal{D} \varepsilon; \varepsilon T \mathcal{F}]\) (dashed line) and we do observe very small values (on the order of \( 10^{-16} \)) at \( y=0 \).

How are we to reconcile the facts above? On the one hand, empirically the algorithm is numerically stable here, and yet on the other hand, we are forced to invert a potentially unstable matrix. Apparently, near a conical intersection, one multiplies together very large and very small matrices, but if convergence is tight enough, stability is maintained. The same conclusion can be obtained from Fig. 2(b). For the same matrix block \([\mathcal{D} \varepsilon; \varepsilon T \mathcal{F}]\), we plot the condition number (solid line), which is the largest eigenvalue divided by the smallest eigenvalue and is a measure of the precision needed to invert a matrix actually. Indeed, near the conical intersection (\( y = \pm 0.00 \text{013 Å} \)), the condition number reaches a maximum (on the order of \( 10^{8} \)).

In summary, we have provided the necessary equations for deriving analytic gradients and derivative couplings for the CIS-1D approach. Future work will report the analogous matrix elements for TDDFT-1D. We find that smooth and precise gradients/couplings can be achieved, and the theory is not much more complicated than standard CIS/TDDFT theory. The only new twist is that when one includes HOMO and LUMO frontier orbitals, one must take great care when differentiating such orbitals, in particular, there is a non-vanishing, non-standard intra-subspace response that arises because we do not use the canonical definitions of HOMO and LUMO. However, this intra-subspace response is of a small dimension and is uncoupled from the inter-subspace response; there is no meaningful additional cost.

Looking forward, once an efficient algorithm of the CIS-1D/TDDFT-1D algorithm becomes available, the present approach should be an immediate competitor for standard spin–flip approaches\(^{[50–53]} \) as far as generating the electronic structure as relevant for nonadiabatic simulations in the presence of \( S_0 \to S_1 \) crossings. This represents an exciting new direction of study for this field of research.

### IX. CONCLUSIONS

This work was supported by the U.S. Air Force Office of Scientific Research (USAFOSR) under Grant Nos. FA9550-18-1-0497 and FA9550-18-1-0420. Computational support was provided by the High Performance Computing Modernization Program of the Department of Defense. Computational support was provided by the High Performance Computing Modernization Program (HPCMP) of the Department of Defense. J.E.S. acknowledges a Camille Dreyfus Teacher-Scholar award.

### APPENDIX A: SOLVING EQ. (31) FOR \( \Theta^{[x]} \)

In this appendix, we provide more details about how to solve Eq. (31) for \( \Theta^{[\alpha]} , \Theta^{[\beta]} \), and \( \Theta^{[\gamma]} \). To do so, we present Eq. (31) again,
According to Eqs. (45) and (46), our task is to find \(-\sum_k \Theta^{[s]}_{kh} Z_k - \sum_k \Theta^{[s]}_{kh} W_c\). Note that \(-\Sigma_{\alpha} \Theta^{[s]}_{\alpha k} Y_{ak}\) has already been addressed in Eq. (19). To that end, note also that

\[
\begin{pmatrix}
\Theta^{[s]}_{kh} \\
\Theta^{[s]}_{ci}
\end{pmatrix} = \begin{pmatrix} D & E \\ E^T & F \end{pmatrix}^{-1} \begin{pmatrix} \zeta_i \\ \eta_a \end{pmatrix} = \begin{pmatrix} \zeta_i \\ \eta_a \end{pmatrix} - \left( \begin{pmatrix} D \\ E^T \end{pmatrix} \begin{pmatrix} \zeta_i \\ \eta_a \end{pmatrix} \right) \cdot \begin{pmatrix} B \\ C \end{pmatrix}.
\]

We want to emphasize that since the matrix \(\begin{pmatrix} D & E \\ E^T & F \end{pmatrix}\) is symmetric and the size is only \((N_a + N_v - 2) \times (N_a + N_v - 2)\), the inverse is very cheap and stable. Then, if we multiply by \((Z^T W^T)\), we recover the necessary equations,

\[
(Z^T W^T) \begin{pmatrix} \Theta^{[s]}_{kh} \\ \Theta^{[s]}_{ci} \end{pmatrix} = -(Z^T W^T) \begin{pmatrix} D & E \\ E^T & F \end{pmatrix}^{-1} \begin{pmatrix} \zeta_i \\ \eta_a \end{pmatrix}
\]

\[
+ (Z^T W^T) \begin{pmatrix} D & E \\ E^T & F \end{pmatrix}^{-1} \begin{pmatrix} B \\ C \end{pmatrix} A^{-1} \xi_{by},
\]

where \(V\) is an \(1 \times (N_a N_v)\) column. Calculating the first term above is straightforward. For the second term, we utilize the same trick as in Eq. (19), calculating \(V A^{-1}\) first and then second operating on \(\xi_{by}\).

**APPENDIX B: DETAILS OF THE FIRST TERM \(\sum_k \lambda_{ik} \chi^{[s]}_k \lambda_{ik}^{[s]}\)**

In this appendix, we will provide more details regarding the first term in Eq. (32). By using Eqs. (35) and (36), we can calculate the derivatives of all the Hamiltonian matrix elements and obtain \(\sum_{k\nu} \chi^{[s]}_k \lambda_{ik}^{[s]} \lambda^{[s]}_{ik}\), which are composed of several different components.

(i) Inter-subspace response terms \(\Theta^{[s]}_{kh}\):

\[
\sum_{k,i} \Theta^{[s]}_{kh} \left\{ \sum_{iab} \lambda_{ik}^{[s]} \left( \pi_{ihbc} + \pi_{ihck} \right) - \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \left( \pi_{ihj} + \pi_{ihji} \right) - \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \pi_{ij} \right\} - \sum_{iab} \lambda_{ik}^{[s]} \pi_{ij} \Theta^{[s]}_{ki} + \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \pi_{ij} \Theta^{[s]}_{ki}
\]

After converting these expressions into the AO basis and utilizing the definitions in Eqs. (16), (17) and (37)–(41), along with the intra-subspace response in Eq. (34), we recover \(Y_{ak}\) in Eq. (44).

(ii) Intra-subspace response terms \(\Theta^{[s]}_{0i}\):

\[
-(\chi^{[s]}_i \chi^{[s]}_j) \sum_{k} \pi_{nk11} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} + \sum_{k} \chi^{[s]}_i \chi^{[s]}_j \left( \sum_{k} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} \right) - \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \left( \sum_{k} \pi_{nk11} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} \right)
\]

\[
+ \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \left( \sum_{k} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} \right) \sum_{k} \pi_{nk11} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki}
\]

\[
= \sum_{k} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} \sum_{\mu \nu} \phi_{\mu}^{1} \phi_{\nu}^{1} \left( X^{[s]}_i X^{[s]}_j \right) \frac{1}{N_a N_v} C_{\nu k} C_{\mu k} + \sum_{\mu \nu} \phi_{\mu}^{1} \phi_{\nu}^{1} \left( F - G \right) \frac{1}{N_a N_v} C_{\nu k} C_{\mu k}
\]

\[
+ \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \left( \sum_{k} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} \right) \sum_{k} \pi_{nk11} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki}
\]

\[
+ \sum_{iab} \chi^{[s]}_i \chi^{[s]}_j \left( \sum_{k} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki} \right) \sum_{k} \pi_{nk11} \Theta^{[s]}_{0i} \Theta^{[s]}_{ki}.
\]
In order to simplify the last three terms, which apparently depend on all kinds of occupied intra-subspace responses, let us focus on the Schrödinger equation for the singly excited eigenstates [using the Hamiltonian Eq. (11)],

$$\sum_{jb}(f_{ab}\delta_{ij} - f_i\delta_{ab} + \pi_{ijab})X_{jb} + \sqrt{2}(\delta_{ij}n_{ab11} + \delta_{ib}n_{ah11})X_{jd} = (E' - E_0)X_{ia}$$

$$\Rightarrow \sum_{jb}\pi_{ijab}X_{jb} = (E' - E_0)X_{ia} - \sum_{i}f_{ia}X_{ib} + \sum_{j}f_{ib}X_{ia} + \sqrt{2}(\delta_{ij}n_{ab11} + \delta_{ib}n_{ah11})X_{jd},$$

where $E'$ is the energy of the electronic eigenstate $I$. (This expression also works for the eigenstate $I'$ by substituting $I$ with $I'$.) Therefore,

$$- \sum_{j}X_{ia}\sum_{k}\Theta_{ij}^{[x]} + \pi_{ijab}\Theta_{ij}^{[x]} = - \sum_{j}X_{ia}X_{ib}'(E' - E_i')\Theta_{ij}^{[x]} - \sum_{j}X_{ia}X_{ib}'(f_{ia}\Theta_{ij}^{[x]} + f_{ib}\Theta_{kj}^{[x]})$$

$$- \sum_{j}\sqrt{2}(X_{ia}'X_{jd} + X_{ib}'X_{jd})\Theta_{ij}^{[x]}.$$

As a result, the last three terms become

$$- \sum_{j}X_{ia}\sum_{k}\Theta_{ij}^{[x]} + \sqrt{2}\sum_{a}\Theta_{ij}^{[x]}X_{ia}X_{ia}'X_{id}X_{id}X_{jd} \sum_{\mu\nu\lambda} C_{ia}\Theta_{ij}^{[x]},$$

where the first term, along with the factor $1/(E' - E_i')$, cancels with the occupied intra-subspace response in Eq. (34). Thus, there is only intra-subspace responses between $h$ and other occupied orbitals $k\neq h$ in $Z_i$.

(iii) Intra-subspace response terms $\Theta_{ij}^{[x]}$:

$$- (X_{ia}'X_{id} + X_{ia}'X_{id})\sum_{c}\tau_{abc1}\Theta_{ij}^{[x]} = - \sum_{ia}X_{ia}'X_{ia}'\left[\sum_{c}(f_{ic}\Theta_{ia}^{[x]} + f_{ia}\Theta_{ic}^{[x]})\right] - \sum_{ia}X_{ia}'X_{ia}'\left[\sum_{c}\tau_{abc1}\Theta_{ij}^{[x]} + \tau_{abc1}\Theta_{ij}^{[x]}\right]$$

$$+ \sqrt{2}\sum_{a}(X_{ia}'X_{id} + X_{ia}'X_{id})\sum_{abc1}\tau_{abc1}\Theta_{ij}^{[x]} - \sqrt{2}\sum_{a}(X_{ia}'X_{id} + X_{ia}'X_{id})\sum_{abc1}\tau_{abc1}\Theta_{ij}^{[x]} + \sum_{abc1}\tau_{abc1}\Theta_{ij}^{[x]}$$

$$= \sum_{c,\mu\nu\lambda}\pi_{\mu\nu\lambda}\left[-2(X_{ia}'X_{id} + X_{ia}'X_{id})\Theta_{ij}^{[x]} - \sqrt{2}\Theta_{ij}^{[x]}\right] + \sqrt{2}(F - G)_{\mu\nu\lambda}C_{ia}\Theta_{ij}^{[x]}$$

$$- \sum_{ia}X_{ia}'X_{ia}'\left[\sum_{\mu\nu\lambda}\pi_{\mu\nu\lambda}\left[-2(X_{ia}'X_{id} + X_{ia}'X_{id})\Theta_{ij}^{[x]} - \sqrt{2}\Theta_{ij}^{[x]}\right] + \sum_{\mu\nu\lambda}\pi_{\mu\nu\lambda}\Theta_{ij}^{[x]}\right].$$

Here, in a fashion analogous to the manipulations above, we have used the Schrödinger equation to recover the last two terms; furthermore, again in analogy to the case above, the last term along with a factor of $1/(E' - E_i')$ cancels with the virtual intra-subspace response in Eq. (34). Therefore, in $W$, there is intra-subspace response only between frontier orbital $1$ and other virtual orbitals $c \neq 1$.

(iv) One-electron derivative terms $h_{\mu\nu\lambda}^{[x]}$:

$$\sum_{\mu\nu\lambda}\pi_{\mu\nu\lambda}\left[\sum_{ia}X_{ia}'X_{ia}'\Theta_{ia}^{[x]}C_{ia} + \sum_{ia}X_{ia}'X_{ia}'\Theta_{ia}^{[x]}C_{ia} + \sum_{ia}X_{ia}'X_{ia}'\Theta_{ia}^{[x]}C_{ia} + \sum_{ia}X_{ia}'X_{ia}'\Theta_{ia}^{[x]}C_{ia}\right] + \sum_{ia}X_{ia}'X_{ia}'\left[-2C_{ia}\Theta_{ia}^{[x]} + 2C_{ia}\Theta_{ia}^{[x]}\right].$$

These terms become $\Gamma_{\mu\nu\lambda}^{[x]}$ when written in the AO basis.

(v) Two-electron derivative terms $\pi_{\mu\nu\lambda}^{[x]}$:

$$\sum_{\mu\nu\lambda}\pi_{\mu\nu\lambda}\left\{X_{ia}'X_{ia}'C_{ia} + X_{ia}'X_{ia}'C_{ia} + \sum_{ia}X_{ia}'X_{ia}'C_{ia}C_{ia}C_{ia} + \sum_{ia}X_{ia}'X_{ia}'C_{ia}C_{ia}C_{ia} + \sum_{ia}X_{ia}'X_{ia}'C_{ia}C_{ia}C_{ia} + \sum_{ia}X_{ia}'X_{ia}'C_{ia}C_{ia}C_{ia} \right.$$

$$- \sqrt{2}\sum_{a}(X_{ia}'X_{ia}' + X_{ia}'X_{ia}')C_{ia}C_{ia}C_{ia} + \sqrt{2}\sum_{a}(X_{ia}'X_{ia}' + X_{ia}'X_{ia}')C_{ia}C_{ia}C_{ia}$$

$$+ \sqrt{2}\sum_{a}(X_{ia}'X_{ia}' + X_{ia}'X_{ia}')C_{ia}C_{ia}C_{ia}$$

$$+ \sum_{ia}X_{ia}'X_{ia}'\left[-2C_{ia}\Theta_{ia}^{[x]} + 2C_{ia}\Theta_{ia}^{[x]}\right] + \sum_{ia}X_{ia}'X_{ia}'\left[-2C_{ia}\Theta_{ia}^{[x]} + 2C_{ia}\Theta_{ia}^{[x]}\right] + \sum_{ia}X_{ia}'X_{ia}'\left[-2C_{ia}\Theta_{ia}^{[x]} + 2C_{ia}\Theta_{ia}^{[x]}\right].$$

These terms become $\pi_{\mu\nu\lambda}^{[x]}$ after utilizing the definitions in Eqs. (16), (17), and (37)–(41).
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Interestingly, however, whereas the non-Hellman–Feynman contribution produces only $S_{ax}$ terms within the context of CIS or TD-DFT derivative couplings, here for CIS-1D, Eq. (34) also leads to nonvanishing (physically real) matrix elements proportional to $\Theta_{ia}$ and $\Theta_{hl}$.