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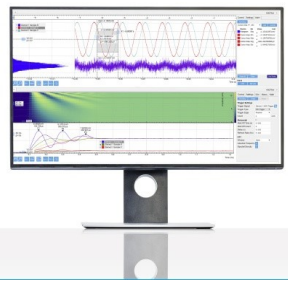
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Hung-Hsuan Teh[a] and Joseph E. Subotnik[b]

AFFILIATIONS

University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, USA

[a]Author to whom correspondence should be addressed: teh@sas.upenn.edu
[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,[1] the generalized Langevin equation,[2] or the mixed quantum–classical Liouville formalism[3]—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[4]), 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,[5] to estimate electron transfer rates in singlet fission processes,[6] to quantify energy dissipation in gas–metal interfaces,[7] to simulate charge recombination in mixed perovskites,[8,9] and to model photo-induced charge transfer in graphene layers.[10] 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,[11,12] 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;[13,14] in particular, there still remains today the need for accurate and inexpensive $S_1 \rightarrow S_0$ nonadiabatic couplings.[15]

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

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likely possible candidate to produce the needed electronic structure matrix elements, with a reasonable balance between accuracy and computational cost.[16,17] 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[13,14,18] 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,[19,20] ideally with a balanced reference set of orbitals.[21] 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.[22–25]

Very recently, we have proposed an alternative means of merging DFT with configuration interaction to address the S_0–S_1 failure of DFT,[26] following the previous ideas of Maitra *et al.*[27] Our *Ansatz* is to build a configuration interaction space 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 $|\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle$ is chosen through a self-consistent field (SCF) procedure for minimizing the energy $\langle\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}|H|\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle$. Here, $\mathtt{h}$ is the optimized HOMO (to be determined), $\mathtt{l}$ is the optimized LUMO (also to be determined), and H is an effective Hamiltonian. In principle, if we make the Tamm–Dancoff approximation,[28] 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*.[26] 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.[29–32]

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,[33] 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[34] 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 ($\mathtt{h}$) and the optimized LUMO ($\mathtt{l}$): 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, $\{\mu, \nu, \sigma, \lambda, \alpha, \beta\}$ 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 $\{|\Phi^a_i\rangle\}$ and one doubly excited configuration from the frontier HOMO orbital $\mathtt{h}$ to the frontier LUMO orbital $\mathtt{l}$: $|\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle$. We consider only singlet systems here so that we can focus on spin-allowed $S_1 \to S_0$ crossings; the case of triplets will be addressed in a forthcoming paper. The set $\left\{|\Phi_0\rangle, |S^a_i\rangle \equiv \left(|\Phi^a_i\rangle + |\Phi^{\bar{a}}_{\bar{i}}\rangle\right)/\sqrt{2}, |\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle\right\}$ includes all of the configurations that we must treat. The CIS-1D wave function can be written down as

$$|\Psi\rangle = X_0|\Phi_0\rangle + \sum_{ia} X^a_i|S^a_i\rangle + X_{\mathrm{d}}|\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle,$$

where $\{X_0, X^a_i, X_{\mathrm{d}}\}$ are variational parameters.

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

$$\mathbf{H} = E_0 + \begin{array}{c} \begin{matrix} \langle\Phi_0| & \langle S^b_j| & \langle\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}| \end{matrix} \\ \begin{pmatrix} 0 & 0 & \pi_{\mathtt{hhll}} \\ 0 & f_{ab}\delta_{ij} - f_{ji}\delta_{ab} + \pi_{ajib} & \sqrt{2}(-\delta_{a\mathtt{l}}\pi_{\mathtt{h}ji\mathtt{l}} + \delta_{i\mathtt{h}}\pi_{\mathtt{h}a\mathtt{ll}}) \\ \pi_{\mathtt{hhll}} & \sqrt{2}(-\delta_{b\mathtt{l}}\pi_{\mathtt{hh}j\mathtt{l}} + \delta_{j\mathtt{h}}\pi_{\mathtt{h}b\mathtt{ll}}) & -2f_{\mathtt{hh}} + 2f_{\mathtt{ll}} + \pi_{\mathtt{llll}} + \pi_{\mathtt{hhhh}} - 2\pi_{\mathtt{lhlh}} \end{pmatrix} \end{array} \begin{array}{l} |\Phi_0\rangle \\ |S^a_i\rangle \\ |\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle \end{array}. \quad (1)$$

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Here, $f_{pq} = \mathtt{h}_{pq} + \sum_i \pi_{ipiq}$ is a Fock matrix element and $\pi_{pqrs} \equiv 2(pr|qs) - (ps|qr)$. We use chemist notation $(pq|rs) = \int d\mathbf{r}_1 d\mathbf{r}_2\, \phi_p^*(\mathbf{r}_1)\phi_q(\mathbf{r}_1) r_{12}^{-1} \phi_r^*(\mathbf{r}_2)\phi_s(\mathbf{r}_2)$ so that $(pr|qs)$ and $(ps|qr)$ 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. $\mathbf{H}$ 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 $\mathbf{H}$ matrix in Eq. (1). Note, however, that this will require taking the derivative of the CIS-1D optimized orbitals, in particular, the $|\mathtt{h}\rangle$ and $|\mathtt{l}\rangle$ frontier orbitals, which are at the heart of CIS-1D theory. We emphasize that here, as in Ref. 26, the indices $\mathtt{h}$ and $\mathtt{l}$ label the optimized orbitals, which minimize the energy of the doubly excited state $E_d = \langle \Phi_{\mathtt{h}\bar{\mathtt{h}}}^{\mathtt{l}\bar{\mathtt{l}}} | H | \Phi_{\mathtt{h}\bar{\mathtt{h}}}^{\mathtt{l}\bar{\mathtt{l}}} \rangle$; these are not canonical orbitals, and it will be necessary to differentiate these orbitals with respect to other optimized occupied $\{i\}$ and virtual $\{a\}$ orbitals. To that end, before working out the relevant derivative couplings, we must extensively review both (i) standard orbital response (i.e., the response of canonical orbitals to nuclear displacement) and (ii) optimized orbital response (i.e., especially, the response of the $|\mathtt{h}\rangle$ and $|\mathtt{l}\rangle$ orbitals) to nuclear displacements. These tasks are described in Secs. III and IV. Fortunately, we will find that the optimized orbital responses can be calculated with only minimal changes to (and minimal cost beyond) standard coupled-perturbed HF theory. For the reader who is not concerned with how one generates orbital response, one may skip directly to Sec. V for the final form of the CIS-1D derivative coupling.

III. BRIEF REVIEW OF STANDARD ORBITAL RESPONSE THEORY AND COUPLED-PERTURBED HARTREE–FOCK THEORY

Before deriving CIS-1D derivative couplings and gradients, it will be helpful to review standard analytic response theory, which dictates how one can calculate the change in molecular orbitals (especially, the $\mathtt{h}$ and $\mathtt{l}$ 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 $\mathbf{C}_0$ be the MO coefficient at a reference nuclear position x_0, and let $\mathbf{C}$ 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 $\mathbf{C}_0^{[x]}$ (the superscript $[x]$ representing the total derivative). One (non-unique) means of rigorously parameterizing $\mathbf{C}$ in terms of $\mathbf{C}_0$ is as follows:[40,41]

$$\mathbf{C} = \mathbf{C}_0 \left(\mathbf{C}_0^\dagger \mathbf{S} \mathbf{C}_0 \right)^{-1/2} e^{-\mathbf{\Theta}}, \tag{2}$$

where $\mathbf{S}$ is the atomic orbital (AO) overlap matrix (that depends on the nuclear coordinate x) and $\mathbf{\Theta}$ is the rotation angle matrix. The factor $\left(\mathbf{C}_0^\dagger \mathbf{S} \mathbf{C}_0 \right)^{-1/2}$ enters into Eq. (2) as a way of enforcing the normalization condition: $\mathbf{C}^\dagger \mathbf{S} \mathbf{C} = \mathbf{I}$. The exponential describes how the MO coefficient $\mathbf{C}$ is rotated away from the reference $\mathbf{C}_0$, and the exponent $\mathbf{\Theta}$ 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

$$\mathbf{\Theta} = \begin{pmatrix} 0 & -\Theta_{21} & \dots \\ \Theta_{21} & 0 & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \tilde{\Theta}_{11} & \tilde{\Theta}_{12} & \dots \\ \tilde{\Theta}_{21} & \tilde{\Theta}_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{3}$$

In other words, consider a system with an orbital basis of dimension N. When convenient, we will refer to the not independent N^2 elements of $\mathbf{\Theta}$ as having tildes (and where antisymmetry is not enforced), whereas we will refer to the $N(N-1)/2$ independent elements of $\mathbf{\Theta}$ as not having tildes (and where antisymmetry is enforced).

Let us now investigate the total derivative of the MO coefficient at the reference point x_0 by using the chain rule,

$$\left(\frac{dC_{\mu p}}{dx} = \sum_{\alpha\beta} \frac{\partial C_{\mu p}}{\partial S_{\alpha\beta}} S_{\alpha\beta}^{[x]} + \sum_{st} \frac{\partial C_{\mu p}}{\partial \tilde{\Theta}_{st}} \tilde{\Theta}_{st}^{[x]} \right)_{\mathbf{S}=\mathbf{S}_0, \mathbf{\Theta}=\mathbf{0}}. \tag{4}$$

Here, we treat $S_{\alpha\beta}$, $S_{\beta\alpha}$, $\tilde{\Theta}_{st}$, and $\tilde{\Theta}_{ts}$ as independent variables and will apply the symmetric/antisymmetric condition for $\mathbf{S}/\mathbf{\Theta}$ after taking the derivatives. The total derivative of the overlap matrix, $S_{\alpha\beta}^{[x]}$, can be calculated analytically since all AOs used in practice will be Gaussian functions, and the other total derivative, $\tilde{\Theta}_{st}^{[x]}$, will be discussed in detail in Subsections III C and IV B and Appendix A.

By utilizing the *Ansatz* in Eq. (2), we recover the partial derivatives,

$$\left(\frac{\partial C_{\mu p}}{\partial S_{\alpha\beta}} \right)_{\mathbf{S}=\mathbf{S}_0, \mathbf{\Theta}=\mathbf{0}} = -\frac{1}{2} \sum_q C_{0,\mu q} C_{0,\alpha q} C_{0,\beta p}, \tag{5}$$

$$\left(\frac{\partial C_{\mu p}}{\partial \tilde{\Theta}_{st}} \right)_{\mathbf{S}=\mathbf{S}_0, \mathbf{\Theta}=\mathbf{0}} = -C_{0,\mu s} \delta_{tp}. \tag{6}$$

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 $\mathbf{\Theta} = \mathbf{0}$ relative to an updated set of MO coefficients.

B. $a_r^{[x]}$ and $O_{rs}^{R[x]}$

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

$$a_r^{[x]} = -\sum_p O_{rp}^{R[x]} a_p, \tag{7}$$

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where $O^{R[x]}_{rs} \equiv \langle r|s^{[x]}\rangle$ and r and p label spin orbitals. To prove this identity, consider the identity $\langle rL|sL\rangle = \delta_{rs}$, 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

$$\begin{aligned}&\langle L^{[x]}|a_r|sL\rangle + \langle L|a^{[x]}_r|sL\rangle + \langle L|a_r|s^{[x]}L\rangle + \langle L|a_r|sL^{[x]}\rangle\\ &= \langle L^{[x]}|L\rangle\delta_{rs} + \langle L|a^{[x]}_r|sL\rangle + \langle L|a_r|s^{[x]}L\rangle + \delta_{rs}\langle L|L^{[x]}\rangle\\ &= 0,\end{aligned}$$

which implies that

$$\begin{aligned}\langle L|a^{[x]}_r|sL\rangle &= -\langle L|a_r|s^{[x]}L\rangle = -O^{R[x]}_{rs}\\ &= -\sum_p \delta_{ps}O^{R[x]}_{rp} = \langle L|\left\{-\sum_p O^{R[x]}_{rp}a_p\right\}|sL\rangle.\end{aligned}$$

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

$$a^{\dagger[x]}_r = \sum_p O^{R[x]}_{pr}a^\dagger_p.$$

Having expressed the derivatives of creation/annihilation operators in terms of $O^{R[x]}_{rs}$, the only problematic item is to compute $O^{R[x]}_{rs}$ explicitly. If the orbitals r and s have different spins, $O^{R[x]}_{rs}$ 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

$$\begin{aligned}O^{R[x]}_{rs} &= \left(\sum_\mu C_{\mu r}\langle\mu|\right)\left(\sum_\nu C^{[x]}_{\nu s}|\nu\rangle + \sum_\nu C_{\nu s}|\nu^{[x]}\rangle\right)\\ &= \sum_{\mu\nu} C_{\mu r}C^{[x]}_{\nu s}S_{\mu\nu} + \sum_{\mu\nu} C_{\mu r}C_{\nu s}S^{R[x]}_{\mu\nu}\\ &= \sum_{\alpha\beta} C_{\alpha r}C_{\beta s}\left(S^{R[x]}_{\alpha\beta} - \frac{1}{2}S^{[x]}_{\alpha\beta}\right) + \tilde{\mathbf{\Theta}}^{[x]}_{rs},\end{aligned}$$

where $S^{R[x]}_{\alpha\beta} \equiv \langle\alpha|\beta^{[x]}\rangle$. Here, we have utilized Eqs. (4)–(6).

C. Inter-subspace response $\Theta^{[x]}_{ck}$

The central item of standard response theory is the calculation of $\Theta^{[x]}_{ck}$, 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 being 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

$$\begin{aligned}E_0 &= 2\sum_i (i|h|i) + \sum_{ij}\pi_{ijij}\\ &= 2\sum_i\sum_{\mu\nu} h_{\mu\nu}C_{\mu i}C_{\nu i} + \sum_{ij}\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}C_{\mu i}C_{\nu j}C_{\sigma i}C_{\lambda j}.\end{aligned} \tag{8}$$

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

$$\begin{aligned}\frac{\partial E_0}{\partial\tilde{\mathbf{\Theta}}_{st}} &= -2\sum_{i\mu\nu} h_{\mu\nu}(C_{\mu s}\delta_{it}C_{\nu i} + C_{\mu i}C_{\nu s}\delta_{it})\\ &\quad - \sum_{ij}\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}\big(C_{\mu s}\delta_{it}C_{\nu j}C_{\sigma i}C_{\lambda j} + C_{\mu i}C_{\nu s}\delta_{jt}C_{\sigma i}C_{\lambda j}\\ &\quad + C_{\mu i}C_{\nu j}C_{\sigma s}\delta_{it}C_{\lambda j} + C_{\mu i}C_{\nu j}C_{\sigma i}C_{\lambda s}\delta_{jt}\big).\end{aligned}$$

Recall that the value of $\partial E_0/\partial\tilde{\mathbf{\Theta}}_{st}$ will depend strongly on the nature of the orbitals s and t. For instance, if t in $\tilde{\mathbf{\Theta}}_{st}$ is an occupied orbital, say k, then

$$\frac{\partial E_0}{\partial\tilde{\mathbf{\Theta}}_{sk}} = -2(f_{sk} + f_{ks}).$$

In contrast, if t is a virtual orbital, say c,

$$\frac{\partial E_0}{\partial\tilde{\mathbf{\Theta}}_{sc}} = 0.$$

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 $\partial^2E_0/\partial\Theta_{ak}\partial\Theta_{bj}$. Note that inverting a singular matrix is always unstable, and so it will be necessary to work with the independent variables Θ_{pq} rather than the dependent variables $\tilde{\mathbf{\Theta}}_{pq}$. To calculate the relevant matrix ($\partial^2E_0/\partial\Theta_{ak}\partial\Theta_{bj}$, which will be symmetric), we can simply use the derivatives above plus the chain rule,

$$\begin{aligned}\frac{\partial E_0}{\partial\Theta_{ij}} &= \left[\frac{\partial E_0}{\partial\tilde{\mathbf{\Theta}}_{ij}} + \frac{\partial E_0}{\partial\tilde{\mathbf{\Theta}}_{ji}}\frac{\partial\tilde{\mathbf{\Theta}}_{ji}}{\partial\tilde{\mathbf{\Theta}}_{ij}}\right]_{\tilde{\mathbf{\Theta}}_{ji}=-\tilde{\mathbf{\Theta}}_{ij}}\\ &= -2(f_{ij} + f_{ji}) - 2(f_{ij} + f_{ji})(-1) = 0.\end{aligned} \tag{9}$$

Similarly,

$$\frac{\partial E_0}{\partial\Theta_{ab}} = 0, \tag{10}$$

$$\frac{\partial E_0}{\partial\Theta_{ai}} = -2(f_{ai} + f_{ia}). \tag{11}$$

In all that follows, we will work with the independent variables Θ_{pq} rather than the constrained variables $\tilde{\mathbf{\Theta}}_{pq}$.

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 $f_{ia} = 0$, 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 occupied orbitals (or of course virtual and virtual orbitals).[42] 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 $\Theta^{[x]}$ by differentiating Eq. (11),

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$$\left(\frac{\partial E_0}{\partial \Theta_{ai}}\right)^{[x]} = -4f_{ai}^{[x]} = \sum_{ck}\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial\Theta_{ck}}\Theta_{ck}^{[x]} + \sum_{\alpha\beta}\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial S_{\alpha\beta}}S_{\alpha\beta}^{[x]} + \sum_{\mu\nu}\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial h_{\mu\nu}}h_{\mu\nu}^{[x]} + \sum_{\mu\nu\alpha\lambda}\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial\pi_{\mu\nu\alpha\lambda}}\pi_{\mu\nu\alpha\lambda}^{[x]} = 0. \quad (12)$$

Note that (i) The terms $\sum_{j<k}(\partial^2 E_0/\partial\Theta_{ai}\partial\Theta_{jk})\Theta_{jk}^{[x]}$ and $\sum_{b>c}(\partial^2 E_0/\partial\Theta_{ai}\partial\Theta_{bc})\Theta_{bc}^{[x]}$ do not appear in Eq. (12) because of Eqs. (9) and(10). (ii) The term $\sum_r(\partial^2 E_0/\partial\Theta_{ai}\partial\Theta_{rr})\Theta_{rr}^{[x]}$ also does not appear, since $\boldsymbol{\Theta}$ is antisymmetric.

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

$$\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial S_{\alpha\beta}} = 2\sum_{\mu\nu} f_{\mu\nu}\tilde{P}_{\mu\alpha}(C_{\nu i}C_{\beta a} + C_{\nu a}C_{\beta i}) + 2\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}\tilde{P}_{\nu\alpha}P_{\lambda\beta}(C_{\mu a}C_{\sigma i} + C_{\mu i}C_{\sigma a}), \quad (13)$$

$$\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial h_{\mu\nu}} = -2(C_{\mu a}C_{\nu i} + C_{\mu i}C_{\nu a}), \quad (14)$$

$$\frac{\partial^2 E_0}{\partial\Theta_{ak}\partial\pi_{\mu\nu\sigma\lambda}} = -2P_{\nu\lambda}(C_{\mu a}C_{\sigma i} + C_{\mu i}C_{\sigma a}). \quad (15)$$

Here, we have defined,

$$P_{\mu\nu} \equiv \sum_k C_{\mu k}C_{\nu k}, \quad (16)$$

$$\tilde{P}_{\mu\nu} \equiv \sum_q C_{\mu q}C_{\nu q}. \quad (17)$$

With regard to the second order derivative $\partial^2 E_0/\partial\Theta_{ai}\partial\Theta_{ck} = -2\partial(f_{ai} + f_{ia})/\partial\Theta_{ck}$, we can differentiate the Fock matrix with respect to Θ (not $\tilde{\boldsymbol{\Theta}}$). Following the same procedure as in Eqs. (9)–(11), we obtain

$$\frac{\partial f_{rs}}{\partial\Theta_{ck}} = -f_{cs}\delta_{rk} - f_{rc}\delta_{sk} + f_{ks}\delta_{rc} + f_{rk}\delta_{sc} - \pi_{rcsk} - \pi_{rksc},$$

and therefore,

$$\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial\Theta_{ck}} = 4(f_{ac}\delta_{ik} - f_{ik}\delta_{ac} + \pi_{acik} + \pi_{akic}).$$

Note that $\pi_{rstu} = \pi_{srut} = \pi_{turs} = \pi_{utsr}$ as we consider real MOs. Moreover, $\partial^2 E_0/\partial\Theta_{ai}\partial\Theta_{ck}$ 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 $\Theta_{ck}^{[x]}$,

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

where

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

In principle, according to Eq. (18), one should calculate the inverse of the response matrix $3N$ times (since the matrix element ξ_{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 $\sum_{kc}\Theta_{kc}^{[x]}Y_{ck}$. Below, we will use the standard Z-vector trick of Handy and Schaefer,[37]

$$\sum_{kc}\Theta_{kc}^{[x]}Y_{ck} = \sum_{kc}\sum_{ai}\left(\frac{\partial^2 E_0}{\partial\Theta_{ai}\partial\Theta_{ck}}\right)^{-1}\xi_{ai}Y_{ck} = \sum_{ai}y_{ai}\xi_{ai}, \quad (19)$$

where $y_{ai} \equiv \sum_{kc}(\partial^2 E_0/\partial\Theta_{ai}\partial\Theta_{ck})^{-1}Y_{ck}$. Since Y_{ck} does not depend on the direction of any nuclear displacement, we can first build up y_{ai} and second calculate the single matrix inverse. Using Eqs. (13)–(15), the final result is

$$\sum_{kc}Y_{ck}\Theta_{kc}^{[x]} = -\sum_{\mu\nu}h_{\mu\nu}^{[x]}2A_{\mu\nu} - \sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}^{[x]}2A_{\mu\sigma}P_{\nu\lambda} - \sum_{\alpha\beta}S_{\alpha\beta}^{[x]}\left(-2\sum_{\mu\nu}f_{\mu\nu}\tilde{P}_{\mu\alpha}A_{\nu\beta} - 2\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}A_{\mu\sigma}\tilde{P}_{\nu\alpha}P_{\lambda\beta}\right),$$

where

$$A_{\mu\nu} = \sum_{ai}y_{ai}(C_{\mu a}C_{\nu i} + C_{\mu i}C_{\nu a}).$$

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 $\mathtt{h}$ be our target frontier orbital within the occupied set and $\mathtt{l}$ be our target frontier orbital within the virtual set.

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The energy of the doubly excited configuration $|\Phi^{\mathtt{l}\bar{\mathtt{l}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle$ (in which a pair of electrons is excited from HOMO $\mathtt{h}$ to LUMO $\mathtt{l}$) is

$$\begin{aligned} E_{\mathrm{d}} &= E_0 - 2h_{\mathtt{hh}} + 2h_{\mathtt{ll}} - 2\sum_i \pi_{i\mathtt{h}i\mathtt{h}} \\ &\quad + 2\sum_i \pi_{i\mathtt{l}i\mathtt{l}} + \pi_{\mathtt{hhhh}} + \pi_{\mathtt{llll}} - 2\pi_{\mathtt{hlhl}} \\ &\equiv E_0 + E'_{\mathrm{d}}. \end{aligned} \tag{20}$$

Here, $\mathtt{h}_{rs}$ 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 $|\mathtt{h}\rangle$ and $|\mathtt{l}\rangle$ in terms of the canonical HF occupied orbitals $\{|i_0\rangle\}$ and canonical virtual orbitals $\{|a_0\rangle\}$, respectively,

$$|\mathtt{h}\rangle = \sum_i c_i|i_0\rangle, \quad |\mathtt{l}\rangle = \sum_a \tilde{c}_a|a_0\rangle,$$

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 $\{|i_0\rangle\}$ with a subspace of optimized orbitals spanned by vectors labeled $\{|1\rangle, |2\rangle, \ldots, |i\rangle, \ldots, |\mathtt{h}-1\rangle, |\mathtt{h}\rangle\}$; similarly, the canonical subspace of virtual orbitals $\{|a_0\rangle\}$ is equivalent to a subspace of optimized orbitals spanned by the vector labeled set $\{|\mathtt{l}\rangle, |\mathtt{l}+1\rangle, \ldots, |a\rangle, \ldots, |N-1\rangle, |N\rangle\}$.

Using the invariance of the occupied space under any occupied–occupied unitary transformation, one can easily show that $\sum_i \pi_{iris} = \sum_i \pi_{i_0 r i_0 s}$ so that all HF orbitals in E'_{d} can be expanded in the canonical basis,

$$\begin{aligned} E'_{\mathrm{d}} &= -2\sum_{ij} h_{i_0 j_0} c_i^* c_j + 2\sum_{ab} h_{a_0 b_0} \tilde{c}_a^* \tilde{c}_b - 2\sum_{ijk} \pi_{i_0 j_0 i_0 k_0} c_j^* c_k \\ &\quad + 2\sum_{iab} \pi_{i_0 a_0 i_0 b_0} \tilde{c}_a^* \tilde{c}_b + \sum_{ijkl} \pi_{i_0 j_0 k_0 l_0} c_i^* c_j^* c_k c_l \\ &\quad + \sum_{abcd} \pi_{a_0 b_0 c_0 d_0} \tilde{c}_a^* \tilde{c}_b^* \tilde{c}_c \tilde{c}_d - 2\sum_{ijab} \pi_{i_0 a_0 j_0 b_0} c_i^* \tilde{c}_a^* c_j \tilde{c}_b. \end{aligned}$$

Since we require that both $|\mathtt{h}\rangle$ and $|\mathtt{l}\rangle$ be normalized ($\langle \mathtt{h}|\mathtt{l}\rangle = 0$ is already guaranteed), the Lagrangian function is

$$\mathcal{L} = E'_{\mathrm{d}} - 2\epsilon_{\mathtt{h}}\left(\sum_i c_i^* c_i - 1\right) - 2\epsilon_{\mathtt{l}}\left(\sum_a \tilde{c}_a^* \tilde{c}_a - 1\right),$$

where $\epsilon_{\mathtt{h}}$ and $\epsilon_{\mathtt{l}}$ are Lagrange multipliers. By setting the derivatives of $\mathcal{L}$ with respect to c_m^* and $\tilde{c}_e^*$ to 0, we obtain

$$\langle m_0|f'|\mathtt{h}\rangle = \langle m_0|\epsilon_{\mathtt{h}}|\mathtt{h}\rangle, \tag{21}$$

$$\langle e_0|f'|\mathtt{l}\rangle = \langle e_0|\epsilon_{\mathtt{l}}|\mathtt{l}\rangle, \tag{22}$$

where f' is

$$\begin{aligned} f' &= f - \pi_{\mathtt{h}} + \pi_{\mathtt{l}} \\ \Rightarrow f'_{\mu\nu} &= h_{\mu\nu} + \sum_{r=1,2,\ldots,\mathtt{h}-1,\mathtt{l}} \pi_{r\mu r\nu} = h_{\mu\nu} + \sum_{\sigma\lambda} \pi_{\sigma\mu\lambda\nu} P'_{\lambda\sigma}, \end{aligned} \tag{23}$$

with the definition $[\pi_r]_{st} = \pi_{rsrt}$.

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 $\mathtt{l}$ has replaced $\mathtt{h}$ in the occupied space). The new density matrix satisfies

$$P' \equiv \sum_{r=1,2,\ldots,\mathtt{h}-1,\mathtt{l}} C^*_{\sigma r} C_{\lambda r}. \tag{24}$$

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,

$$\begin{aligned} \langle m|f'|\mathtt{h}\rangle &= \langle m|\epsilon_{\mathtt{h}}|\mathtt{h}\rangle, \\ \langle e|f'|\mathtt{l}\rangle &= \langle e|\epsilon_{\mathtt{l}}|\mathtt{l}\rangle, \end{aligned}$$

which can be further decomposed into the atomic orbital basis,

$$\begin{aligned} &\sum_i \sum_{\mu\nu} C^*_{\mu m} f'_{\mu\nu} C_{\nu i} c_i = \epsilon_{\mathtt{h}} c_m \\ \Rightarrow &\left[\mathbf{C}^\dagger_{\mathrm{occ}} \mathbf{f}' \mathbf{C}_{\mathrm{occ}}\right]\mathbf{c} = \epsilon_{\mathtt{h}}\mathbf{c}, \\ &\sum_a \sum_{\mu\nu} C^*_{\mu e} f'_{\mu\nu} C_{\nu a} c_a = \epsilon_{\mathtt{l}} c_e \\ \Rightarrow &\left[\mathbf{C}^\dagger_{\mathrm{vir}} \mathbf{f}' \mathbf{C}_{\mathrm{vir}}\right]\tilde{\mathbf{c}} = \epsilon_{\mathtt{l}}\tilde{\mathbf{c}}. \end{aligned}$$

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

Although the math above might at first look a bit overwhelming, at bottom the matrix $\mathbf{f}'$ is the same as the normal Fock matrix $\mathbf{f}$ after exchanging the HOMO column and the LUMO column in the MO coefficient $\mathbf{C}$; 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[43,44]), and Morokuma and Iwata's Extended HF approach:[45]

1. Perform a standard HF calculation and generate the canonical MO coefficient $\mathbf{C} = [\mathbf{C}_{\mathrm{occ}}\ \mathbf{C}_{\mathrm{vir}}]$; order the columns of $\mathbf{C}$ according to energy (with $\mathbf{C}_{1\mu}$ having the lowest energy, $\mathbf{C}_{2\mu}$ having the next lowest energy, etc.) For our initial guess, we will let $|\mathtt{h}\rangle$ be approximated by column $\mathtt{h}$ of $\mathbf{C}$, $\mathbf{C}_{\mathtt{h}\mu}$; we will let $|\mathtt{l}\rangle$ be approximated by column $\mathtt{l}$ of $\mathbf{C}$, $\mathbf{C}_{\mathtt{l}\mu}$.
2. Build the density matrix $\mathbf{P}'$ by choosing to occupy the $(1, 2, \ldots, \mathtt{h}-1, \mathtt{l})$-th columns in $\mathbf{C}$, i.e., skip of over column $\mathtt{h}$. Then, construct $\mathbf{f}'$ according to Eq. (23).
3. Calculate $\mathbf{C}^\dagger_{\mathrm{occ}}\mathbf{f}'\mathbf{C}_{\mathrm{occ}}$ and $\mathbf{C}^\dagger_{\mathrm{vir}}\mathbf{f}'\mathbf{C}_{\mathrm{vir}}$, and diagonalize each matrix separately (ordering by energy). Let $\mathbf{U}_{\mathrm{occ}}$ and $\mathbf{U}_{\mathrm{virt}}$ be the respective eigenvector matrices (of dimension $N_{\mathrm{o}} \times N_{\mathrm{o}}$ and $N_{\mathrm{v}} \times N_{\mathrm{v}}$, respectively). The last column of $\mathbf{U}_{\mathrm{occ}}$ will represent the

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frontier orbital $\mathtt{h}$ with the highest eigenvalue $\epsilon_{\mathtt{h}}$ in the occupied subspace ($\mathbf{c}$); the first column of $\mathbf{U}_{\rm vir}$ will represent the frontier orbital $\mathtt{l}$ with the lowest eigenvalue $\epsilon_{\mathtt{l}}$ in the virtual subspace ($\tilde{\mathbf{c}}$).

4. Construct by matrix multiplication: $\mathbf{C}_{\rm occ}^{\rm new} = \mathbf{C}_{\rm occ}\mathbf{U}_{\rm occ}$ and $\mathbf{C}_{\rm vir}^{\rm new} = \mathbf{C}_{\rm vir}\mathbf{U}_{\rm vir}$. The updated MO coefficient is then

$$\mathbf{C}^{\rm new} = \left[\mathbf{C}_{\rm occ}^{\rm new}; \mathbf{C}_{\rm vir}^{\rm new}\right].$$

5. Check whether $|\mathbf{C}^{\rm new} - \mathbf{C}|$ is below a threshold for convergence. If not, set $\mathbf{C} = \mathbf{C}^{\rm new}$ 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), $f_{ij} \neq \epsilon_i\delta_{ij}$ and $f_{ab} \neq \epsilon_a\delta_{ab}$; however, $f_{ia} = 0$ remains zero.

B. Intra-subspace responses $\Theta_{k\mathtt{h}}^{[x]}$ and $\Theta_{c\mathtt{l}}^{[x]}$

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 $E_{\rm d}$; after all, E and $E_{\rm d}$ have the same functional form—just with different orbitals. By utilizing Eqs. (20) and (6) and the chain rule, we can obtain

$$\frac{\partial E_{\rm d}}{\partial \Theta_{ij}} = 2\delta_{\mathtt{h}j}\left(f'_{i\mathtt{h}} + f'_{\mathtt{h}i}\right) - 2\delta_{\mathtt{h}i}\left(f'_{j\mathtt{h}} + f'_{\mathtt{h}j}\right), \tag{25}$$

$$\begin{aligned}\frac{\partial E_{\rm d}}{\partial \Theta_{ab}} &= -2\delta_{\mathtt{l}b}\left(f'_{a\mathtt{l}} + f'_{\mathtt{l}a}\right) + 2\delta_{\mathtt{l}a}\left(f'_{b\mathtt{l}} + f'_{\mathtt{l}b}\right),\\ \frac{\partial E_{\rm d}}{\partial \Theta_{ai}} &= -2\left[f'_{ai} + f'_{ia} - \delta_{\mathtt{h}i}\left(f'_{a\mathtt{h}} + f'_{\mathtt{h}a}\right) - \delta_{\mathtt{l}a}\left(f'_{i\mathtt{l}} + f'_{\mathtt{l}i}\right)\right].\end{aligned} \tag{26}$$

As in Eq. (11), the partial derivatives above are not automatically 0 but do vanish when the optimized orbitals are substituted in. For the purposes of a CIS-1D calculation, we will need to calculate only $\Theta_{i\mathtt{h}}^{[x]}$ and $\Theta_{a\mathtt{l}}^{[x]}$. To that end, we set $j = \mathtt{h}$ ($i \neq \mathtt{h}$) and $b = \mathtt{l}$ ($a \neq \mathtt{l}$) in Eqs. (25) and (26), respectively,

$$\frac{\partial E_{\rm d}}{\partial \Theta_{i\mathtt{h}}} = 2\left(f'_{i\mathtt{h}} + f'_{\mathtt{h}i}\right), \tag{27}$$

$$\frac{\partial E_{\rm d}}{\partial \Theta_{a\mathtt{l}}} = -2\left(f'_{a\mathtt{l}} + f'_{\mathtt{l}a}\right). \tag{28}$$

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

$$\begin{aligned}\left(\frac{\partial E_{\rm d}}{\partial \Theta_{i\mathtt{h}}}\right)^{[x]} &= \sum_{ck}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial\Theta_{ck}}\Theta_{ck}^{[x]} + \sum_{k<\mathtt{h}}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial\Theta_{k\mathtt{h}}}\Theta_{k\mathtt{h}}^{[x]}\\ &\quad + \sum_{c>\mathtt{l}}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial\Theta_{c\mathtt{l}}}\Theta_{c\mathtt{l}}^{[x]} + \zeta_i = 0,\end{aligned} \tag{29}$$

$$\begin{aligned}\left(\frac{\partial E_{\rm d}}{\partial \Theta_{a\mathtt{l}}}\right)^{[x]} &= \sum_{ck}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial\Theta_{ck}}\Theta_{ck}^{[x]} + \sum_{k<\mathtt{h}}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial\Theta_{k\mathtt{h}}}\Theta_{k\mathtt{h}}^{[x]}\\ &\quad + \sum_{c>\mathtt{l}}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial\Theta_{c\mathtt{l}}}\Theta_{c\mathtt{l}}^{[x]} + \eta_a = 0,\end{aligned} \tag{30}$$

where

$$\begin{aligned}\zeta_i &\equiv -\sum_{\alpha\beta}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial S_{\alpha\beta}}S_{\alpha\beta}^{[x]} - \sum_{\mu\nu}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial h_{\mu\nu}}h_{\mu\nu}^{[x]}\\ &\quad - \sum_{\mu\nu\sigma\lambda}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial\pi_{\mu\nu\sigma\lambda}}\pi_{\mu\nu\sigma\lambda}^{[x]},\\ \eta_a &\equiv -\sum_{\alpha\beta}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial S_{\alpha\beta}}S_{\alpha\beta}^{[x]} - \sum_{\mu\nu}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial h_{\mu\nu}}h_{\mu\nu}^{[x]}\\ &\quad - \sum_{\mu\nu\sigma\lambda}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial\pi_{\mu\nu\sigma\lambda}}\pi_{\mu\nu\sigma\lambda}^{[x]}.\end{aligned}$$

All the second-order derivatives above can be computed by taking partial derivatives with respect to Θ over Eqs. (27) and (28),

$$\begin{aligned}\frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial h_{\mu\nu}} &= 2\left(C_{\mu i}C_{\nu\mathtt{h}} + C_{\mu\mathtt{h}}C_{\nu i}\right),\\ \frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial\pi_{\mu\nu\sigma\lambda}} &= 2\left(C_{\mu i}C_{\sigma\mathtt{h}} + C_{\mu\mathtt{h}}C_{\sigma i}\right)P'_{\nu\lambda},\\ \frac{\partial^2 E_{\rm d}}{\partial\Theta_{i\mathtt{h}}\partial S_{\alpha\beta}} &= -2\sum_{\mu\nu}f'_{\mu\nu}\tilde{P}_{\mu\alpha}\left(C_{\nu\mathtt{h}}C_{\beta i} + C_{\nu i}C_{\beta\mathtt{h}}\right)\\ &\quad - 2\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}\tilde{P}_{\nu\alpha}P'_{\lambda\beta}\left(C_{\mu i}C_{\sigma\mathtt{h}} + C_{\mu\mathtt{h}}C_{\sigma i}\right),\\ \frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial h_{\mu\nu}} &= -2\left(C_{\mu a}C_{\nu\mathtt{l}} + C_{\mu\mathtt{l}}C_{\nu a}\right),\\ \frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial\pi_{\mu\nu\sigma\lambda}} &= -2\left(C_{\mu a}C_{\sigma\mathtt{l}} + C_{\mu\mathtt{l}}C_{\sigma a}\right)P'_{\nu\lambda},\\ \frac{\partial^2 E_{\rm d}}{\partial\Theta_{a\mathtt{l}}\partial S_{\alpha\beta}} &= 2\sum_{\mu\nu}f'_{\mu\nu}\tilde{P}_{\mu\alpha}\left(C_{\nu\mathtt{l}}C_{\beta a} + C_{\nu a}C_{\beta\mathtt{l}}\right)\\ &\quad + 2\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}\tilde{P}_{\nu\alpha}P'_{\lambda\beta}\left(C_{\mu a}C_{\sigma\mathtt{l}} + C_{\mu\mathtt{l}}C_{\sigma a}\right).\end{aligned}$$

Note that if we assume $j < k$ (without loss of generality), $\partial^2 E_{\rm d}/\partial\Theta_{ih}\partial\Theta_{jk} = 0$ and $\partial^2 E_{\rm d}/\partial\Theta_{al}\partial\Theta_{jk} = 0$ if $k \neq \mathtt{h}$. In addition, if we assume $b > c$ (without loss of generality), $\partial^2 E_{\rm d}/\partial\Theta_{ih}\partial\Theta_{bc} = 0$ and $\partial^2 E_{\rm d}/\partial\Theta_{al}\partial\Theta_{bc} = 0$ if $c \neq \mathtt{l}$. Therefore, these second order derivatives do not appear.

In the end, Eqs. (29) and (30), along with Eq. (12), form the following coupled expressions:

$$\begin{pmatrix}\mathcal{A} & 0 & 0\\ \mathcal{B} & \mathcal{D} & \mathcal{E}\\ \mathcal{C} & \mathcal{E}^{\rm T} & \mathcal{F}\end{pmatrix}\begin{pmatrix}\Theta_{ck}^{[x]}\\ \Theta_{m\mathtt{h}}^{[x]}\\ \Theta_{d\mathtt{l}}^{[x]}\end{pmatrix} = -\begin{pmatrix}\xi_{bj}\\ \zeta_i\\ \eta_a\end{pmatrix}, \tag{31}$$

where $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, $\mathcal{D}$, $\mathcal{E}$, and $\mathcal{F}$ represent different matrix subblocks of the superoperator,

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$$
\begin{aligned}
\mathcal{A}_{bj,ck} &= 4\big(f_{bc}\delta_{jk} - f_{jk}\delta_{bc} + \pi_{bcjk} + \pi_{bkjc}\big),\\
\mathcal{B}_{i,ck} &= 4\big[-f'_{\mathtt{ch}}\delta_{ik} - f'_{ic}\delta_{\mathtt{hk}} - \pi_{ic\mathtt{h}k} - \pi_{ik\mathtt{h}c} + \delta_{\mathtt{hk}}(\pi_{ic\mathtt{hh}} + \pi_{i\mathtt{hh}c}) + \delta_{\mathtt{1}c}(\pi_{ik\mathtt{h1}} + \pi_{i\mathtt{1}\mathtt{h}k})\big],\\
\mathcal{C}_{a,ck} &= 4\big[-f'_{k\mathtt{1}}\delta_{ac} - f'_{ak}\delta_{\mathtt{1}c} + \pi_{ac\mathtt{1}k} + \pi_{ak\mathtt{1}c} - \delta_{\mathtt{hk}}(\pi_{ac\mathtt{1h}} + \pi_{a\mathtt{h}\mathtt{1}c}) - \delta_{\mathtt{1}c}(\pi_{ak\mathtt{11}} + \pi_{a\mathtt{1}\mathtt{1}k})\big],\\
\mathcal{D}_{im} &= 4\big(-f'_{im} + f'_{\mathtt{hh}}\delta_{im} + \pi_{im\mathtt{hh}} + \pi_{i\mathtt{hh}m}\big),\\
\mathcal{E}_{id} &= 4(-\pi_{id\mathtt{h}\mathtt{1}} - \pi_{i\mathtt{1}\mathtt{h}d}),\\
\mathcal{F}_{ad} &= 4\big(f'_{ad} - f'_{\mathtt{11}}\delta_{ad} + \pi_{ad\mathtt{11}} + \pi_{a\mathtt{11}d}\big),
\end{aligned}
$$

and $\Theta^{[x]}_{ck}$, $\Theta^{[x]}_{k\mathtt{h}}$, and $\Theta^{[x]}_{c\mathtt{1}}$ can be solved efficiently; for more details, see Appendix A. Note that Eq. (31) is shorthand notation for a standard linear matrix equation $\mathbf{Ax} = \mathbf{b}$, where $\mathbf{A}$ operates in a vector space with dimension $N_\mathrm{o}N_\mathrm{v} + N_\mathrm{o} + N_\mathrm{v} - 2$.

V. DERIVATIVE COUPLINGS

With the tools developed in Subsections III A and III B, we can proceed to calculate the derivative couplings. We let I and J represent two different electronic states. The derivative coupling between these two states is

$$
\begin{aligned}
\langle \Psi^I|\Psi^{J[x]}\rangle &= \sum_{KK'}\langle\Phi_K|X^{I*}_K\big(X^J_{K'}|\Phi_{K'}\rangle\big)^{[x]}\\
&= \sum_K X^{I*}_K X^{J[x]}_K + \sum_{KK'} X^{I*}_K X^J_{K'}\langle\Phi_K|\Phi^{[x]}_{K'}\rangle, \qquad (32)
\end{aligned}
$$

where K and K' denote the configurations used in CIS-1D (i.e., the HF configuration, the singly excited configurations, and one lone doubly excited configuration). To begin our analysis, let us focus on the second term: we have to calculate all possible derivative couplings between the configurations (which are real). As an example, the derivative coupling between a singles configuration and the one double configuration can be calculated as follows:

$$
\begin{aligned}
\langle\Phi^a_i|\Phi^{\mathtt{1}\bar{\mathtt{1}}[x]}_{\mathtt{h}\bar{\mathtt{h}}}\rangle &= -\langle\Phi^{a[x]}_i|\Phi^{\mathtt{1}\bar{\mathtt{1}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle\\
&= -\Big(\langle\Phi_0|a^\dagger_i a_a\Big)^{[x]} a^\dagger_{\bar{\mathtt{1}}}a_{\bar{\mathtt{h}}}a^\dagger_{\mathtt{1}}a_{\mathtt{h}}|\Phi_0\rangle\\
&= -\langle\Phi^{[x]}_0|a^\dagger_i a_a a^\dagger_{\bar{\mathtt{1}}}a_{\bar{\mathtt{h}}}a^\dagger_{\mathtt{1}}a_{\mathtt{h}}|\Phi_0\rangle\\
&\quad - \sum_p\langle\Phi_0|O^{R[x]}_{pi}a^\dagger_p a_a a^\dagger_{\bar{\mathtt{1}}}a_{\bar{\mathtt{h}}}a^\dagger_{\mathtt{1}}a_{\mathtt{h}}|\Phi_0\rangle\\
&\quad + \sum_p\langle\Phi_0|a^\dagger_i O^{R[x]}_{ap}a_p a^\dagger_{\bar{\mathtt{1}}}a_{\bar{\mathtt{h}}}a^\dagger_{\mathtt{1}}a_{\mathtt{h}}|\Phi_0\rangle. \qquad (33)
\end{aligned}
$$

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 $\langle\Phi_0|\Phi^{[x]}_0\rangle = 0$. For the singly contracted terms, note that $a^\dagger_i$ and a_a 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, $\overbrace{a^\dagger_i a_a} = 0$ and so 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,

$$
\begin{aligned}
&-\langle\Phi^{[x]}_0|:\overbrace{a^\dagger_i a_a a^\dagger_{\bar{\mathtt{1}}}a_{\bar{\mathtt{h}}}}a^\dagger_{\mathtt{1}}a_{\mathtt{h}}:|\Phi_0\rangle = -\delta_{i\mathtt{h}}\delta_{a\mathtt{1}}\langle\Phi^{[x]}_0|a^\dagger_{\bar{\mathtt{1}}}a_{\bar{\mathtt{h}}}|\Phi_0\rangle\\
&= \delta_{i\mathtt{h}}\delta_{a\mathtt{1}}O^{R[x]}_{\bar{\mathtt{h}}\bar{\mathtt{1}}} = \delta_{i\mathtt{h}}\delta_{a\mathtt{1}}O^{R[x]}_{\mathtt{h}\mathtt{1}}.
\end{aligned}
$$

The other term $\langle\Phi^{\bar{a}}_i|\Phi^{\mathtt{1}\bar{\mathtt{1}}[x]}_{\mathtt{h}\bar{\mathtt{h}}}\rangle$ will give the same contribution. Thus, the derivative coupling between the singlet singles configuration $|S^a_i\rangle$ and the lone doubly excited configuration in Eq. (32) is

$$
\langle S^a_i|\Phi^{\mathtt{1}\bar{\mathtt{1}}[x]}_{\mathtt{h}\bar{\mathtt{h}}}\rangle = \sqrt{2}\delta_{i\mathtt{h}}\delta_{a\mathtt{1}}O^{R[x]}_{\mathtt{h}\mathtt{1}} = -\langle S^{a[x]}_i|\Phi^{\mathtt{1}\bar{\mathtt{1}}}_{\mathtt{h}\bar{\mathtt{h}}}\rangle.
$$

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

$$
\begin{aligned}
\langle\Phi_0|S^{a[x]}_i\rangle &= \sqrt{2}O^{R[x]}_{ia} = -\langle\Phi^{[x]}_0|S^a_i\rangle,\\
\langle S^a_i|S^{b[x]}_j\rangle &= \delta_{ij}O^{R[x]}_{ab} - \delta_{ab}O^{R[x]}_{ji}.
\end{aligned}
$$

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

$$
\begin{aligned}
\sum_{KK'} X^{I*}_K X^J_{K'}\langle\Phi_K|\Phi^{[x]}_{K'}\rangle &= \sqrt{2}\sum_{ia}\big(X^I_0 X^J_{ia} - X^I_{ia}X^J_0\big)\left[\sum_{\alpha\beta}C_{\alpha i}C_{\beta a}\left(S^{R[x]}_{\alpha\beta} - \frac{1}{2}S^{[x]}_{\alpha\beta}\right) - \Theta^{[x]}_{ia}\right] + \sum_{iab}X^I_{ia}X^J_{ib}\left[\sum_{\alpha\beta}C_{\alpha a}C_{\beta b}\left(S^{R[x]}_{\alpha\beta} - \frac{1}{2}S^{[x]}_{\alpha\beta}\right) - \Theta^{[x]}_{ab}\right]\\
&\quad - \sum_{ija}X^I_{ia}X^J_{ja}\left[\sum_{\alpha\beta}C_{\alpha j}C_{\beta i}\left(S^{R[x]}_{\alpha\beta} - \frac{1}{2}S^{[x]}_{\alpha\beta}\right) - \Theta^{[x]}_{ji}\right] + \sqrt{2}\big(X^I_{\mathtt{h}\mathtt{1}}X_{\mathtt{d}} - X^I_{\mathtt{d}}X^J_{\mathtt{h}\mathtt{1}}\big)\left[\sum_{\alpha\beta}C_{\alpha\mathtt{h}}C_{\beta\mathtt{1}}\left(S^{R[x]}_{\alpha\beta} - \frac{1}{2}S^{[x]}_{\alpha\beta}\right) - \Theta^{[x]}_{\mathtt{h}\mathtt{1}}\right], \qquad (34)
\end{aligned}
$$

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where again $S^{R[x]}_{\alpha\beta} \equiv \langle\alpha|\beta^{[x]}\rangle$.

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

$$\sum_K X^{I*}_K X^{J[x]}_K = \frac{1}{E^J - E^I} \sum_{KK'} X^{I*}_K H^{[x]}_{KK'} X^J_{K'}.$$

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 $\sum_{KK'} X^{I*}_K E^{[x]}_0 \delta_{KK'} X^J_{K'} = E^{[x]}_0 \sum_K X^{I*}_K X^J_K = 0$. Thus, we will need to differentiate only π_{rstu} and f_{rs}. By utilizing Eqs. (4)–(6),

$$\begin{aligned}\pi^{[x]}_{rstu} = &\sum_{\mu\nu\sigma\lambda} \pi^{[x]}_{\mu\nu\sigma\lambda} C_{\mu r} C_{\nu s} C_{\sigma t} C_{\lambda u} \\ &- \frac{1}{2} \sum_{\alpha\beta q} C_{\alpha q} \left(\pi_{qstu} C_{\beta r} + \pi_{rqtu} C_{\beta s} + \pi_{rsqu} C_{\beta t} + \pi_{rstq} C_{\beta u}\right) S^{[x]}_{\alpha\beta} \\ &- \sum_q \left(\pi_{qstu} \Theta^{[x]}_{qr} + \pi_{rqtu} \Theta^{[x]}_{qs} + \pi_{rsqu} \Theta^{[x]}_{qt} + \pi_{rstq} \Theta^{[x]}_{qu}\right), \end{aligned} \tag{35}$$

$$\begin{aligned} f^{[x]}_{rs} = &\sum_{\mu\nu} h^{[x]}_{\mu\nu} C_{\mu r} C_{\nu s} + \sum_{i\mu\nu\sigma\lambda} \pi^{[x]}_{\mu\nu\sigma\lambda} C_{\mu r} C_{\nu i} C_{\sigma s} C_{\lambda i} \\ &- \frac{1}{2} \sum_{\alpha\beta q} C_{\alpha q} S^{[x]}_{\alpha\beta} \left(f_{qs} C_{\beta r} + f_{rq} C_{\beta s}\right) \\ &- \frac{1}{2} \sum_{ia\beta q} \left(\pi_{rqsi} + \pi_{risq}\right) C_{\alpha q} C_{\beta i} S^{[x]}_{\alpha\beta} \\ &- \sum_q \left(f_{qs} \Theta^{[x]}_{qr} + f_{rq} \Theta^{[x]}_{qs}\right) - \sum_{iq} \left(\pi_{rqsi} + \pi_{risq}\right) \Theta^{[x]}_{qi}. \end{aligned} \tag{36}$$

Obviously, there will be many terms in the final expression, and one must be careful in the final evaluation. There are two items to emphasize here: (i) $f_{qs} \neq f_{qq}\delta_{qs}$ since we are using the optimized (rather than canonical) orbitals. (ii) The last term on the RHS of Eq. (36) can be shown to be equal to $-\sum_{kc}(\pi_{rcsk} + \pi_{rksc})\Theta^{[x]}_{ck}$ if we invoke the antisymmetric constraint for $\boldsymbol{\Theta}$, since $-\sum_{ki}(\pi_{risk} + \pi_{rksi})\Theta^{[x]}_{ik} = 0$.

For readers who are interested in the details of manipulating this term $\sum_K X^{I*}_K X^{J[x]}_K$, refer to Appendix B. Before presenting the final results of Eq. (32), we will need to define several intermediate matrices,

$$R^I_{\mu\nu} \equiv \sum_{ia} C_{\mu a} X^I_{ia} C_{\nu i}, \tag{37}$$

$$P^{\mathtt{hl}}_{\mu\nu} \equiv C_{\mu\mathtt{h}} C_{\nu\mathtt{l}},\ P^{\mathtt{hh}}_{\mu\nu} \equiv C_{\mu\mathtt{h}} C_{\nu\mathtt{h}},\ P^{\mathtt{ll}}_{\mu\nu} \equiv C_{\mu\mathtt{l}} C_{\nu\mathtt{l}}, \tag{38}$$

$$B_{\mu\nu} \equiv \sum_{iab} C_{\mu a} X^I_{ia} X^J_{ib} C_{\nu b} - \sum_{ija} C_{\mu j} X^I_{ia} X^J_{ja} C_{\nu i}, \tag{39}$$

$$F_{\mu\nu} \equiv C_{\mu\mathtt{h}} F'_\nu,\ F'_\nu \equiv \sum_i \left(X^I_{i\mathtt{l}} X^J_{\mathtt{d}} + X^I_{\mathtt{d}} X^J_{i\mathtt{l}}\right) C_{\nu i}, \tag{40}$$

$$G_{\mu\nu} \equiv G'_\mu C_{\nu\mathtt{l}},\ G'_\mu \equiv \sum_a \left(X^I_{\mathtt{h}a} X^J_{\mathtt{d}} + X^I_{\mathtt{d}} X^J_{\mathtt{h}a}\right) C_{\mu a}. \tag{41}$$

The final derivative coupling [as obtained by combining all equations in Appendix B with Eq. (34)] is presented in the equations below. Here, we have grouped terms with $h^{[x]}_{\mu\nu}$ together, terms with $\pi^{[x]}_{\mu\nu\sigma\lambda}$ together, and so on, and hence,

$$\begin{aligned}\langle\Psi^I|\Psi^{J[x]}\rangle = &\frac{1}{E^J - E^I} \left\{ \sum_{\mu\nu} \Gamma^{h[x]}_{\nu\mu} h^{[x]}_{\mu\nu} + \sum_{\mu\nu\sigma\lambda} \Gamma^{\pi[x]}_{\mu\nu\sigma\lambda} \pi^{[x]}_{\mu\nu\sigma\lambda} \right. \\ &+ \sum_{\alpha\beta} \Gamma^{S[x]}_{\beta\alpha} S^{[x]}_{\alpha\beta} + \sum_{\alpha\beta} \Gamma^{S^A[x]}_{\beta\alpha} S^{A[x]}_{\alpha\beta} \\ &\left. - \sum_{kc} Y_{ck} \Theta^{[x]}_{kc} - \sum_k Z_k \Theta^{[x]}_{\mathtt{kh}} - \sum_c W_c \Theta^{[x]}_{c\mathtt{l}} \right\}, \end{aligned} \tag{42}$$

where

$$S^{A[x]}_{\alpha\beta} \equiv S^{R[x]}_{\alpha\beta} - \frac{1}{2} S^{[x]}_{\alpha\beta}.$$

All the coefficients are listed below,

$$\begin{aligned}
\Gamma^{h[x]}_{\nu\mu} &= B_{\mu\nu} - 2X^I_{\mathtt{d}} X^J_{\mathtt{d}} (P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\nu}, \\
\Gamma^{\pi[x]}_{\mu\nu\sigma\lambda} &= \left[(X^I_0 X^J_{\mathtt{d}} + X^I_d X^J_0) P^{\mathtt{hl}}_{\mu\sigma} - \sqrt{2}(F-G)_{\mu\sigma}\right] P^{\mathtt{hl}}_{\nu\lambda} + \left[B_{\mu\sigma} - 2X^I_{\mathtt{d}} X^J_{\mathtt{d}} (P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\sigma}\right] P_{\nu\lambda} + R^I_{\mu\sigma} R^J_{\lambda\nu} + X^I_{\mathtt{d}} X^J_{\mathtt{d}} (P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\sigma} (P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\nu\lambda}, \\
\Gamma^{S[x]}_{\beta\alpha} &= -(X^I_0 X^J_{\mathtt{d}} + X^I_{\mathtt{d}} X^J_0) \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda} P^{\mathtt{hl}}_{\mu\sigma} (\tilde{P}_{\alpha\nu} P^{\mathtt{hl}}_{\beta\lambda} + \tilde{P}_{\lambda\alpha} P^{\mathtt{hl}}_{\nu\beta}) - \frac{1}{2} \sum_{\mu\nu} f_{\mu\nu} (B_{\beta\nu} + B_{\nu\beta}) \tilde{P}_{\alpha\mu} \\
&\quad + \frac{1}{2} \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda} B_{\mu\sigma} (\tilde{P}_{\alpha\nu} P_{\beta\lambda} + \tilde{P}_{\lambda\alpha} P_{\nu\beta}) - \frac{1}{2} \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda} \left[R^J_{\mu\sigma} (R^I_{\alpha\nu} \tilde{P}_{\beta\lambda} + R^I_{\lambda\alpha} \tilde{P}_{\nu\beta}) + R^I_{\mu\sigma} (R^J_{\alpha\nu} \tilde{P}_{\beta\lambda} + R^J_{\lambda\alpha} \tilde{P}_{\nu\beta})\right] \\
&\quad + \frac{1}{\sqrt{2}} \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda} \left\{ P^{\mathtt{hl}}_{\mu\sigma} \left[\tilde{P}_{\alpha\nu} (F-G)_{\beta\lambda} + \tilde{P}_{\lambda\alpha} (F-G)_{\nu\beta}\right] + (F-G)_{\mu\sigma} (\tilde{P}_{\alpha\nu} P^{\mathtt{hl}}_{\beta\lambda} + \tilde{P}_{\lambda\alpha} P^{\mathtt{hl}}_{\nu\beta}) \right\} \\
&\quad + 2X^I_{\mathtt{d}} X^J_{\mathtt{d}} \left\{ \sum_{\mu\nu} f_{\mu\nu} \tilde{P}_{\alpha\mu} (P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\nu\beta} + \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda} (P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\sigma} \tilde{P}_{\alpha\nu} \left[P - (P^{\mathtt{hh}} - P^{\mathtt{ll}})\right]_{\lambda\beta} \right\}, \\
\Gamma^{S^A[x]}_{\beta\alpha} &= \sqrt{2}\left(X^I_0 R^J_{\beta\alpha} - R^I_{\beta\alpha} X^J_0\right) + B_{\alpha\beta} + \sqrt{2}\left(X^I_{\mathtt{hl}} X^J_{\mathtt{d}} - X^I_{\mathtt{d}} X^J_{\mathtt{hl}}\right) P^{\mathtt{hl}}_{\alpha\beta},
\end{aligned} \tag{43}$$

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$$Y_{ck} = \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda}\Big[-B_{\mu\sigma}(C_{\nu c}C_{\lambda k} + C_{\nu k}C_{\lambda c}) + \sum_i \big(X^I_{ic}R^J_{\mu\sigma} + R^I_{\mu\sigma}X^J_{ic}\big)C_{\nu i}C_{\lambda k}$$
$$- \sum_a \big(R^I_{\mu\sigma}X^J_{ka} + X^I_{ka}R^J_{\mu\sigma}\big)C_{\nu c}C_{\lambda a} + \sqrt{2}\big(X^I_{k\mathtt{l}}X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_{k\mathtt{l}}\big)P^{\mathtt{hl}}_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda c}$$
$$+ \sqrt{2}\big(X^I_{\mathrm{h}c}X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_{\mathrm{h}c}\big)P^{\mathtt{hl}}_{\mu\sigma}C_{\nu k}C_{\lambda\mathtt{l}} + 4X^I_{\mathrm{d}}X^J_{\mathrm{d}}(P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\sigma}C_{\nu k}C_{\lambda c}\Big]$$
$$+ \delta_{k\mathtt{h}}M_{ck} + \delta_{c\mathtt{l}}N_{ck} + \sqrt{2}\big(X^I_0X^J_{kc} - X^I_{kc}X^J_0\big)(E^J - E^I) + \sqrt{2}\big(X^I_{kc}X^J_{\mathrm{d}} - X^I_{\mathrm{d}}X^J_{kc}\big)(E^J - E^I)\delta_{k\mathtt{h}}\delta_{c\mathtt{l}}. \tag{44}$$

Here, we have also defined,

$$M_{c\mathtt{h}} = \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda}\Big[-2\big(X^I_0X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_0\big)C_{\nu c}C_{\lambda\mathtt{l}}P^{\mathtt{hl}}_{\mu\sigma} + \sqrt{2}P^{\mathtt{hl}}_{\mu\sigma}F'_\lambda C_{\nu c}$$
$$+\sqrt{2}(F-G)_{\mu\sigma}C_{\nu c}C_{\lambda\mathtt{l}} - 4X^I_{\mathrm{d}}X^J_{\mathrm{d}}(P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\sigma}C_{\nu c}C_{\lambda\mathtt{h}}\Big]$$

and

$$N_{\mathtt{l}k} = \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda}\Big[2\big(X^I_0X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_0\big)C_{\nu\mathtt{h}}C_{\lambda k}P^{\mathtt{hl}}_{\mu\sigma} + \sqrt{2}P^{\mathtt{hl}}_{\mu\sigma}G'_\nu C_{\lambda k}$$
$$-\sqrt{2}(F-G)_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda k} - 4X^I_{\mathrm{d}}X^J_{\mathrm{d}}(P^{\mathtt{hh}} - P^{\mathtt{ll}})_{\mu\sigma}C_{\nu\mathtt{l}}C_{\lambda k}\Big].$$

Finally, for the intra-subspace response terms,

$$Z_k = \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda}\Big[2\big(X^I_0X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_0\big)P^{\mathtt{hl}}_{\mu\sigma}C_{\nu k}C_{\lambda\mathtt{l}} - \sqrt{2}P^{\mathtt{hl}}_{\mu\sigma}F'_\lambda C_{\nu k}$$
$$-\sqrt{2}(F-G)_{\mu\sigma}C_{\nu k}C_{\lambda\mathtt{l}} + \sqrt{2}P^{\mathtt{hl}}_{\mu\sigma}\sum_a (X^I_{ka}X^J_{\mathrm{d}} + X^J_{ka}X^I_{\mathrm{d}})C_{\nu a}C_{\lambda\mathtt{l}}\Big] \tag{45}$$

and

$$W_c = \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda}\Big[2\big(X^I_0X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_0\big)C_{\nu\mathtt{h}}C_{\lambda c}P^{\mathtt{hl}}_{\mu\sigma} + \sqrt{2}P^{\mathtt{hl}}_{\mu\sigma}G'_\nu C_{\lambda c}$$
$$- \sqrt{2}(F-G)_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda c} - \sqrt{2}\sum_i (X^I_{ic}X^J_{\mathrm{d}} + X^I_{\mathrm{d}}X^J_{ic})P^{\mathtt{hl}}_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda i}\Big]. \tag{46}$$

Note that in Eq. (34), we found the response terms between arbitrary occupied orbitals (not only $\Theta^{[x]}_{k\mathtt{h}}$) and between arbitrary virtual orbitals (not only $\Theta^{[x]}_{c\mathtt{l}}$). As shown in Appendix B, however (and as must be true physically), all response terms proportional to $\Theta^{[x]}_{ji}$ (where neither i nor j is the HOMO $\mathtt{h}$) vanish after cancellation with Eq. (32), as do all response terms proportional to $\Theta^{[x]}_{ab}$ (where neither a nor b is the LUMO $\mathtt{l}$).

Finally, all terms proportional to $S^{A[x]}$ [i.e., all of the terms in $\Gamma^{S^{A[x]}}_{\beta\alpha}$ in Eq. (43)] arise in Eq. (34) where we differentiate the CIS-1D basis functions (i.e., the non-Hellman–Feynman terms).[46] 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 $\Gamma^{S^{A[x]}}_{\beta\alpha}$ terms are the only source of translational variance in the calculations. To see how this effect arises, imagine calculating the quantity $\sum_i d^{x_i}_{IJ}$ ($d^{x_i}_{IJ}$ means the derivative coupling along the nuclear coordinate x_i), which corresponds to the derivative coupling associated with total translation. Note that $\sum_i \pi^{[x_i]}_{\mu\nu\sigma\lambda} = \sum_i h^{[x_i]}_{\mu\nu} = \sum_i S^{[x_i]}_{\alpha\beta} = 0$. However, $\sum_i S^{A[x_i]}_{\alpha\beta} \neq 0$, 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 $\sum_{\alpha\beta}\Gamma^{S^{A[x]}}_{\beta\alpha}S^{A[x]}_{\alpha\beta}$ must be included when comparing analytic vs finite difference derivative couplings, but this quantity should not be included when running nonadiabatic dynamics calculations.[47,48]

VI. GRADIENT

In order to calculate the gradient on PES $E^{[I]}$, we start with differentiating both sides of $E^I = \sum_{KK'} X^{I*}_K H_{KK'} X^I_{K'}$,

$$E^{I[x]} = \sum_{KK'} X^{I*}_K H^{[x]}_{KK'} X^I_{K'} + \sum_{KK'} X^{I*[x]}_K H_{KK'} X^I_{K'} + \sum_{KK'} X^{I*}_K H_{KK'} X^{I[x]}_{K'}$$
$$= \sum_{KK'} X^{I*}_K H^{[x]}_{KK'} X^I_{K'} + \sum_K X^{I*[x]}_K X^I_K E^I + \sum_{K'} E^I X^{I*}_{K'} X^{I[x]}_{K'}$$
$$= \sum_{KK'} X^{I*}_K H^{[x]}_{KK'} X^I_{K'}.$$

Note that $E^{I[x]}$ has exactly the same form as the term $(E^J - E^I)\sum_K X^{I*}_K X^{J[x]}_K$ in the derivative coupling, which is what we calculate in Appendix B. The only differences are that (i) $J = I$ and (ii) the term involving E_0 no longer vanishes, that is, $\sum_{KK'} X^{I*}_K E^{[x]}_0 X^I_{K'} = E^{[x]}_0$ 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 $S^{A[x]}$ vanish, and the factor $1/(E^J - E^I)$ 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,[26] we showed that TDDFT-1D predicts a conical intersection here; so does CIS-1D [see Fig. 1(a) for a definition of our coordinate

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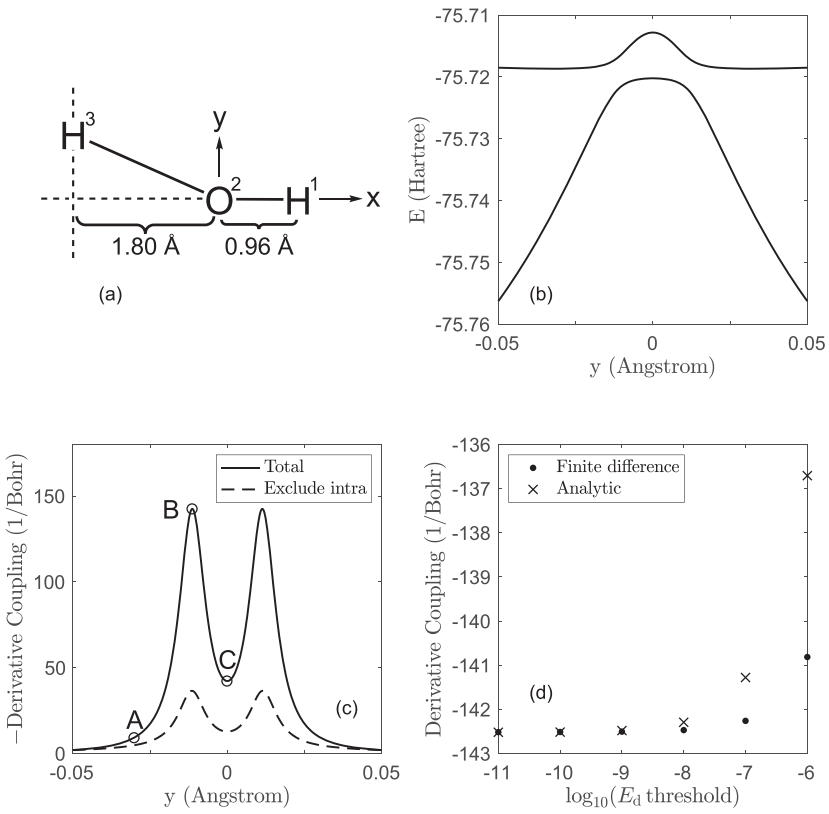


FIG. 1. Results for the water molecule: (a) Definition of the coordinate system. (b) S_0 and S_1 PESs according to the CIS-1D Hamiltonian. (c) *y*-direction derivative couplings of the oxygen corresponding to different *y* positions of the H^3 moving along the vertical dashed line. Solid and dashed lines represent the analytic calculations with and without considering the intra-subspace response, respectively. Details regarding the derivative couplings at points A, B, and C can be found in Table I, where we compare against the finite difference results. (d) Derivative couplings calculated with different thresholds for E_d at point B. In order to obtain highly precise results near CIs, a threshold lower than 10^{-9} is required. All calculations are done with basis 6-31g. The threshold for E_d is set to 10^{-11} in (b) and (c).

system]. 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 ($y = -0.030\,20$), B ($y = -0.01\,140$),

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^1_x	H^1_y	H^1_z	O^2_x	O^2_y	O^2_z	H^3_x	H^3_y	H^3_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[a]	−0.004 29	27.513 58	0	−0.065 29	−42.233 03	0	0.069 59	14.808 31	0
C, FD[a]	−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

[a]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.

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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 E_d is set to 10^{-11}.

	H^1_x	H^1_y	H^1_z	O^2_x	O^2_y	O^2_z	H^3_x	H^3_y	H^3_z
A, analytic	−0.055 21	0.964 21	0	−0.095 63	−1.480 98	0	0.150 86	0.516 77	0
A, FD	−0.055 24	0.964 01	0	−0.095 58	−1.480 68	0	0.150 82	0.516 67	0
B, analytic	−0.012 47	0.515 14	0	0.067 02	−0.789 54	0	−0.054 55	0.274 40	0
B, FD	−0.012 45	0.515 16	0	0.067 00	−0.789 57	0	−0.054 52	0.274 41	0
C, analytic	−0.001 28	0.001 73	0	0.125 78	−0.002 65	0	−0.124 50	0.000 92	0
C, FD	−0.001 28	0.001 70	0	0.125 78	−0.002 59	0	−0.124 50	0.000 90	0
Equil, analytic	0.005 88	0.011 91	0	−0.015 94	−0.020 58	0	0.010 06	0.008 67	0
Equil, FD	0.005 88	0.011 91	0	−0.015 94	−0.020 58	0	0.010 06	0.008 67	0

and C ($y = -0.00\,013$) [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 $\langle I|\nabla H|J\rangle/(E^J - E^I)$ and $\langle I|\nabla H|I\rangle$, respectively.)

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 S_0–S_1 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 S_0 and S_1 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 O^2 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 O^2. 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 E_d from 10^{-11} to 10^{-6}. At this difficult point, we require a reasonably tight convergence threshold ($\sim 10^{-9}$) 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 S_0–S_1 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 l 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

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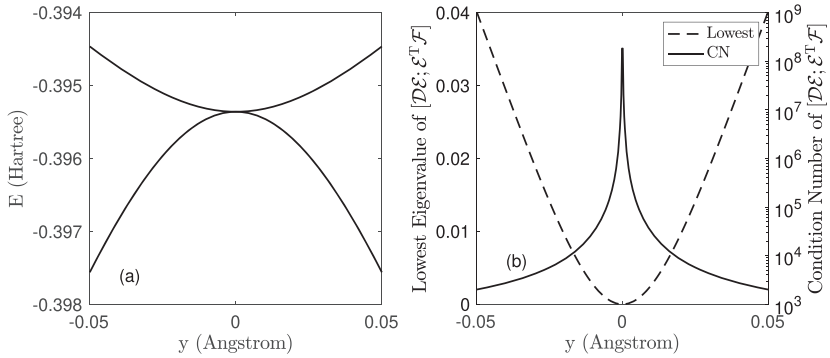


FIG. 2. (a) Orbital energies of h and h − 1 and (b) the lowest eigenvalues (dashed line) and the condition numbers (solid line) of the matrix $[\mathcal{D}\mathcal{E};\mathcal{E}^{\mathrm{T}}\mathcal{F}]$, when moving along the vertical line for H^3 motion, which is plotted in Fig. 1(a). Here, we use a grid spacing 0.00 025 Å. A degeneracy seemly appears around $y = 0$ so that the lowest eigenvalue of the matrix $[\mathcal{D}\mathcal{E};\mathcal{E}^{\mathrm{T}}\mathcal{F}]$ is nearly zero and the condition number of the matrix gets large. In particular, for $y = \pm 0.00\,013$ Å, the condition number of the matrix is 10^8. Nevertheless, this condition number is easily treated with scientific calculations using 16 byte doubles, and the CIS-1D derivative couplings/gradients remain robust.

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 l crossing may in fact be moot.

Returning to the case of water molecule, even though the h and l 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 $[\mathcal{D}\mathcal{E};\mathcal{E}^{\mathrm{T}}\mathcal{F}]$ 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 $[\mathcal{D}\mathcal{E};\mathcal{E}^{\mathrm{T}}\mathcal{F}]$ (dashed line) and we do observe very small values (on the order of 10^{-6}) 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 $[\mathcal{D}\mathcal{E};\mathcal{E}^{\mathrm{T}}\mathcal{F}]$, 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 ($y = \pm 0.00\,013$ Å), the condition number reaches a maximum (on the order of 10^8).[49] Note that, however, 10^8 is much less than 10^{16} (which approximately is the inverse of the precision of a standard IEEE floating point double); thus, we should not (and do not) find any numerical difficulties computing the inverses. In practice, given the accuracy shown in Table I, it appears that for most cases of interest, the CIS-1D *Ansatz* should be able to deliver enough precision to function as a black-box routine.

IX. CONCLUSIONS

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–S_1 crossings. This represents an exciting new direction of study for this field of research.

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

In this appendix, we provide more details about how to solve Eq. (31) for $\Theta^{[x]}_{ck}$, $\Theta^{[x]}_{kh}$, and $\Theta^{[x]}_{c1}$. To do so, we present Eq. (31) again,

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$$\begin{pmatrix} \mathcal{A} & 0 & 0 \\ \mathcal{B} & \mathcal{D} & \mathcal{E} \\ \mathcal{C} & \mathcal{E}^{\mathrm{T}} & \mathcal{F} \end{pmatrix} \begin{pmatrix} \Theta_{ck}^{[x]} \\ \Theta_{\mathrm{kh}}^{[x]} \\ \Theta_{c1}^{[x]} \end{pmatrix} = - \begin{pmatrix} \xi_{bj} \\ \zeta_i \\ \eta_a \end{pmatrix}. \tag{A1}$$

According to Eqs. (45) and (46), our task is to find $-\sum_k \Theta_{\mathrm{kh}}^{[x]} Z_k - \sum_c \Theta_{c1}^{[x]} W_c$. Note that $-\Sigma_{ck}\Theta_{kc}^{[x]} Y_{ck}$ has already been addressed in Eq. (19). To that end, note also that

$$\begin{pmatrix} \Theta_{\mathrm{kh}}^{[x]} \\ \Theta_{c1}^{[x]} \end{pmatrix} = \begin{pmatrix} \mathcal{D} & \mathcal{E} \\ \mathcal{E}^{\mathrm{T}} & \mathcal{F} \end{pmatrix}^{-1} \left\{ - \begin{pmatrix} \zeta_i \\ \eta_a \end{pmatrix} - \begin{pmatrix} \mathcal{B} \\ \mathcal{C} \end{pmatrix} \Theta_{ck}^{[x]} \right\}.$$

We want to emphasize that since the matrix $\left[\mathcal{D}\,\mathcal{E}; \mathcal{E}^{\mathrm{T}}\,\mathcal{F}\right]$ is symmetric and the size is only $(N_{\mathrm{o}} + N_{\mathrm{v}} - 2) \times (N_{\mathrm{o}} + N_{\mathrm{v}} - 2)$, the inverse is very cheap and stable. Then, if we multiply by $(\mathbf{Z}^{\mathrm{T}}\ \mathbf{W}^{\mathrm{T}})$, we recover the necessary equations,

$$\begin{aligned} (\mathbf{Z}^{\mathrm{T}}\mathbf{W}^{\mathrm{T}}) \begin{pmatrix} \Theta_{\mathrm{kh}}^{[x]} \\ \Theta_{c1}^{[x]} \end{pmatrix} &= -(\mathbf{Z}^{\mathrm{T}}\ \mathbf{W}^{\mathrm{T}}) \begin{pmatrix} \mathcal{D} & \mathcal{E} \\ \mathcal{E}^{\mathrm{T}} & \mathcal{F} \end{pmatrix}^{-1} \begin{pmatrix} \zeta_i \\ \eta_a \end{pmatrix} \\ &\quad + \underbrace{(\mathbf{Z}^{\mathrm{T}}\ \mathbf{W}^{\mathrm{T}}) \begin{pmatrix} \mathcal{D} & \mathcal{E} \\ \mathcal{E}^{\mathrm{T}} & \mathcal{F} \end{pmatrix}^{-1} \begin{pmatrix} \mathcal{B} \\ \mathcal{C} \end{pmatrix}}_{\mathbf{V}} \mathcal{A}^{-1} \xi_{bj}, \end{aligned}$$

where $\mathbf{V}$ is an $1 \times (N_{\mathrm{o}} N_{\mathrm{v}})$ column. Calculating the first term above is straightforward. For the second term, we utilize the same trick as in Eq. (19), calculating $\mathbf{V}\mathcal{A}^{-1}$ first and then second operating on ξ_{bj}.

APPENDIX B: DETAILS OF THE FIRST TERM $\sum_K X_K^{I*} X_K^{J[x]}$

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 $\sum_{KK'} X_{K'}^{I*} H_{KK'}^{[x]} X_{K'}^{J}$, which are composed of several different components.

(i) Inter-subspace response terms $\Theta_{kc}^{[x]}$:

$$\begin{aligned} &\sum_{kc} \Theta_{kc}^{[x]} \Bigg\{ \sum_{iab} X_{ia}^I X_{ib}^J (\pi_{acbk} + \pi_{akbc}) - \sum_{ija} X_{ia}^I X_{ja}^J (\pi_{jcik} + \pi_{jkic}) - \sum_{ijb} X_{ic}^I X_{jb}^J \pi_{kjib} - \sum_{ija} X_{ia}^I X_{jc}^J \pi_{ajik} + \sum_{iab} X_{ia}^I X_{kb}^J \pi_{acib} + \sum_{jab} X_{ka}^I X_{jb}^J \pi_{ajcb} \\ &- \sqrt{2}(X_{k1}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{k1}^J)\pi_{\mathrm{hhc1}} - \sqrt{2}(X_{\mathrm{hc}}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{\mathrm{hc}}^J)\pi_{\mathrm{hk11}} - 4X_{\mathrm{d}}^I X_{\mathrm{d}}^J (\pi_{\mathrm{hkhc}} - \pi_{\mathrm{1k1c}}) \Bigg\} \\ &+ \sum_{c} \Theta_{\mathrm{hc}}^{[x]} \Bigg\{ 2(X_0^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_0^J)\pi_{\mathrm{ch11}} - \sqrt{2} \sum_i (X_{i1}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{i1}^J)(\pi_{\mathrm{chi1}} + \pi_{\mathrm{hci1}}) \\ &+ \sqrt{2} \sum_a (X_{\mathrm{ha}}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{\mathrm{ha}}^J)\pi_{\mathrm{ca11}} - 4X_{\mathrm{d}}^I X_{\mathrm{d}}^J (-\pi_{\mathrm{chhh}} + \pi_{\mathrm{1c1h}}) \Bigg\} \\ &+ \sum_{k} \Theta_{k1}^{[x]} \Bigg\{ -2(X_0^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_0^J)\pi_{\mathrm{hhk1}} + \sqrt{2} \sum_i (X_{i1}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{i1}^J)\pi_{\mathrm{hhik}} \\ &- \sqrt{2} \sum_a (X_{\mathrm{ha}}^I X_d^J + X_{\mathrm{d}}^I X_{\mathrm{ha}}^J)(\pi_{\mathrm{hak1}} + \pi_{\mathrm{ha1k}}) - 4X_{\mathrm{d}}^I X_{\mathrm{d}}^J (\pi_{k111} - \pi_{\mathrm{kh1h}}) \Bigg\}. \end{aligned}$$

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_{ck} in Eq. (44).

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

$$\begin{aligned} &- (X_0^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_0^J) 2 \sum_k \pi_{\mathrm{kh11}} \Theta_{\mathrm{kh}}^{[x]} + \sum_{ija} X_{ia}^I X_{ja}^J \left[\sum_k \left(f_{ki} \Theta_{kj}^{[x]} + f_{jk} \Theta_{ki}^{[x]} \right) \right] - \sum_{ijab} X_{ia}^I X_{jb}^J \left[\sum_k \left(\pi_{akib} \Theta_{kj}^{[x]} + \pi_{ajkb} \Theta_{ki}^{[x]} \right) \right] \\ &+ \sqrt{2} \sum_i (X_{i1}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{i1}^J) \left[\sum_k (\pi_{\mathrm{khi1}} + \pi_{\mathrm{hki1}}) \Theta_{\mathrm{kh}}^{[x]} + \sum_k \pi_{\mathrm{hhk1}} \Theta_{ki}^{[x]} \right] \\ &- \sqrt{2} \sum_a (X_{\mathrm{ha}}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{\mathrm{ha}}^J) \sum_k \pi_{\mathrm{ka11}} \Theta_{\mathrm{kh}}^{[x]} \\ = &\sum_k \Theta_{\mathrm{kh}}^{[x]} \sum_{\mu\nu\sigma\lambda} \pi_{\mu\nu\sigma\lambda} \Big\{ -2(X_0^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_0^J) P_{\mu\sigma}^{\mathrm{hl}} C_{\nu k} C_{\lambda 1} + \sqrt{2} P_{\mu\sigma}^{\mathrm{hl}} F_{\lambda}' C_{\nu k} + \sqrt{2} (F - G)_{\mu\sigma} C_{\nu k} C_{\lambda 1} \Big\} \\ &+ \sum_{ija} X_{ia}^I X_{ja}^J \left[\sum_k \left(f_{ki} \Theta_{kj}^{[x]} + f_{jk} \Theta_{ki}^{[x]} \right) \right] - \sum_{ijab} X_{ia}^I X_{jb}^J \left[\sum_k \left(\pi_{akib} \Theta_{kj}^{[x]} + \pi_{ajkb} \Theta_{ki}^{[x]} \right) \right] \\ &+ \sqrt{2} \sum_i (X_{i1}^I X_{\mathrm{d}}^J + X_{\mathrm{d}}^I X_{i1}^J) \left[\sum_k \pi_{\mathrm{hhk1}} \Theta_{ki}^{[x]} \right]. \end{aligned}$$

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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. (1)],

$$\begin{aligned}&\sum_{jb}(f_{ab}\delta_{ij}-f_{ji}\delta_{ab}+\pi_{ajib})X^I_{jb}+\sqrt{2}(-\delta_{a\mathtt{l}}\pi_{\mathtt{hhi}\mathtt{l}}+\delta_{i\mathtt{h}}\pi_{\mathtt{ha}\mathtt{ll}})X^I_{\mathtt{d}}=(E^I-E_0)X^I_{ia}\\ \Rightarrow&\sum_{jb}\pi_{ajib}X^I_{jb}=(E^I-E_0)X^I_{ia}-\sum_b f_{ab}X^I_{ib}+\sum_j f_{ji}X^I_{ja}+\sqrt{2}(\delta_{a\mathtt{l}}\pi_{\mathtt{hhi}\mathtt{l}}-\delta_{i\mathtt{h}}\pi_{\mathtt{ha}\mathtt{ll}})X^I_{\mathtt{d}},\end{aligned}$$

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

$$\begin{aligned}-\sum_{ijab}X^I_{ia}X^J_{jb}\sum_k(\pi_{akib}\Theta^{[x]}_{kj}+\pi_{ajkb}\Theta^{[x]}_{ki})=&-\sum_{jkb}X^I_{kb}X^J_{jb}(E^I-E^J)\Theta^{[x]}_{kj}-\sum_{ijkb}X^I_{ib}X^J_{jb}(f_{ik}\Theta^{[x]}_{kj}+f_{jk}\Theta^{[x]}_{ki})\\&-\sum_{jkb}\sqrt{2}(X^J_{jb}X^I_{\mathtt{d}}+X^I_{jb}X^J_{\mathtt{d}})(\delta_{b\mathtt{l}}\pi_{\mathtt{hhk}\mathtt{l}}-\delta_{k\mathtt{h}}\pi_{\mathtt{hb}\mathtt{ll}})\Theta^{[x]}_{kj}.\end{aligned}$$

As a result, the last three terms become

$$-\sum_{jkb}X^I_{kb}X^J_{jb}(E^I-E^J)\Theta^{[x]}_{kj}+\sum_k\sqrt{2}\sum_a(X^I_{ka}X^J_{\mathtt{d}}+X^J_{ka}X^I_{\mathtt{d}})\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}P^{\mathtt{hl}}_{\mu\sigma}C_{\nu a}C_{\lambda\mathtt{l}}\Theta^{[x]}_{k\mathtt{h}},$$

where the first term, along with the factor $1/(E^J-E^I)$, cancels with the occupied intra-subspace response in Eq. (34). Thus, there is only intra-subspace responses between $\mathtt{h}$ and other occupied orbitals $k\neq\mathtt{h}$ in Z_k.

(iii) Intra-subspace response terms $\Theta^{[x]}_{ab}$:

$$\begin{aligned}&-(X^I_0X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_0)2\sum_c\pi_{\mathtt{hhc}\mathtt{l}}\Theta^{[x]}_{c\mathtt{l}}-\sum_{iab}X^I_{ia}X^J_{ib}\left[\sum_c\left(f_{cb}\Theta^{[x]}_{ca}+f_{ac}\Theta^{[x]}_{cb}\right)\right]-\sum_{ijab}X^I_{ia}X^J_{jb}\left[\sum_c\left(\pi_{cjib}\Theta^{[x]}_{ca}+\pi_{ajic}\Theta^{[x]}_{cb}\right)\right]\\&+\sqrt{2}\sum_i(X_{i\mathtt{l}}X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_{i\mathtt{l}})\sum_c\pi_{\mathtt{hhi}c}\Theta^{[x]}_{c\mathtt{l}}-\sqrt{2}\sum_a(X^I_{\mathtt{h}a}X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_{\mathtt{h}a})\left[\sum_c\pi_{\mathtt{hc}\mathtt{ll}}\Theta^{[x]}_{ca}+\sum_c(\pi_{\mathtt{ha}c\mathtt{l}}+\pi_{\mathtt{ha}\mathtt{l}c})\Theta^{[x]}_{c\mathtt{l}}\right]\\=&\sum_c\Theta^{[x]}_{c\mathtt{l}}\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}\left\{-2(X^I_0X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_0)P^{\mathtt{hl}}_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda c}-\sqrt{2}P^{\mathtt{hl}}_{\mu\sigma}G'_{\nu}C_{\lambda c}+\sqrt{2}(F-G)_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda c}\right\}\\&-\sum_c\Theta^{[x]}_{c\mathtt{l}}\sum_{\mu\nu\sigma\lambda}\pi_{\mu\nu\sigma\lambda}\sqrt{2}\sum_i(X^I_{ic}X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_{ic})P^{\mathtt{hl}}_{\mu\sigma}C_{\nu\mathtt{h}}C_{\lambda i}-\sum_{iac}X^I_{ia}X^J_{ic}(E^I-E^J)\Theta^{[x]}_{ac}.\end{aligned}$$

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 $1/(E^J-E^I)$ cancels with the virtual intra-subspace response in Eq. (34). Therefore, in W_c, there is intra-subspace response only between frontier orbital $\mathtt{l}$ and other virtual orbitals $c\neq\mathtt{l}$.

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

$$\sum_{\mu\nu}h^{[x]}_{\mu\nu}\left\{\sum_{iab}X^I_{ia}X^J_{ib}C_{\mu a}C_{\nu b}-\sum_{ija}X^I_{ia}X^J_{ja}C_{\mu j}C_{\nu i}+X^I_{\mathtt{d}}X^J_{\mathtt{d}}(-2C_{\mu\mathtt{h}}C_{\nu\mathtt{h}}+2C_{\mu\mathtt{l}}C_{\nu\mathtt{l}})\right\}.$$

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

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

$$\begin{aligned}&\sum_{\mu\nu\sigma\lambda}\pi^{[x]}_{\mu\nu\sigma\lambda}\left\{(X^I_0X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_0)C_{\mu\mathtt{h}}C_{\nu\mathtt{h}}C_{\sigma\mathtt{l}}C_{\lambda\mathtt{l}}+\sum_{iabk}X^I_{ia}X^J_{ib}C_{\mu a}C_{\nu k}C_{\sigma b}C_{\lambda k}-\sum_{ijak}X^I_{ia}X^J_{ja}C_{\mu j}C_{\nu k}C_{\sigma i}C_{\lambda k}+\sum_{ijab}X^I_{ia}X^J_{jb}C_{\mu a}C_{\nu j}C_{\sigma i}C_{\lambda b}\right.\\&-\sqrt{2}\sum_i(X^I_{i\mathtt{l}}X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_{i\mathtt{l}})C_{\mu\mathtt{h}}C_{\nu\mathtt{h}}C_{\sigma i}C_{\lambda\mathtt{l}}+\sqrt{2}\sum_a(X^I_{\mathtt{h}a}X^J_{\mathtt{d}}+X^I_{\mathtt{d}}X^J_{\mathtt{h}a})C_{\mu\mathtt{h}}C_{\nu a}C_{\sigma\mathtt{l}}C_{\lambda\mathtt{l}}\\&\left.+X^I_{\mathtt{d}}X^J_{\mathtt{d}}\left(-2\sum_iC_{\mu\mathtt{h}}C_{\nu i}C_{\sigma\mathtt{h}}C_{\lambda i}+2\sum_iC_{\mu\mathtt{l}}C_{\nu i}C_{\sigma\mathtt{l}}C_{\lambda i}+C_{\mu\mathtt{l}}C_{\nu\mathtt{l}}C_{\sigma\mathtt{l}}C_{\lambda\mathtt{l}}+C_{\mu\mathtt{h}}C_{\nu\mathtt{h}}C_{\sigma\mathtt{h}}C_{\lambda\mathtt{h}}-2C_{\mu\mathtt{l}}C_{\nu\mathtt{h}}C_{\sigma\mathtt{l}}C_{\lambda\mathtt{h}}\right)\right\}.\end{aligned}$$

These terms become $\Gamma^{\pi^{[x]}}_{\mu\nu\sigma\lambda}$ after utilizing the definitions in Eqs. (16), (17), and (37)–(41).

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(vi) Overlap derivative terms $S^{[x]}_{\alpha\beta}$:

$$\sum_{\alpha\beta} S^{[x]}_{\alpha\beta}\Bigg\{(X^I_0X^J_{\mathrm{d}}+X^I_dX^J_0)\Bigg[-\sum_q C_{\alpha q}(\pi_{q\mathtt{h}\mathtt{l}\mathtt{l}}C_{\beta\mathtt{h}}+\pi_{\mathtt{h}\mathtt{h}q\mathtt{l}}C_{\beta\mathtt{l}})\Bigg]+\sum_{iab}X^I_{ia}X^J_{ib}\Bigg[-\frac{1}{2}\sum_q C_{\alpha q}(f_{qb}C_{\beta a}+f_{aq}C_{\beta b})-\frac{1}{2}\sum_{qk}C_{\alpha q}(\pi_{aqbk}+\pi_{akbq})C_{\beta k}\Bigg]$$
$$-\sum_{ija}X^I_{ia}X^J_{ja}\Bigg[-\frac{1}{2}\sum_q C_{\alpha q}(f_{qi}C_{\beta j}+f_{jq}C_{\beta i})-\frac{1}{2}\sum_{qk}C_{\alpha q}(\pi_{jqik}+\pi_{jkiq})C_{\beta k}\Bigg]+\sum_{ijab}X^I_{ia}X^J_{jb}\Big(-\frac{1}{2}\Big)\sum_q C_{\alpha q}(\pi_{qjib}C_{\beta a}+\pi_{aqib}C_{\beta j}+\pi_{ajqb}C_{\beta i}+\pi_{ajiq}C_{\beta b})$$
$$-\sqrt{2}\sum_i(X^I_{i\mathtt{l}}X^J_{\mathrm{d}}+X^I_{\mathrm{d}}X^J_{i\mathtt{l}})\Big(-\frac{1}{2}\Big)\sum_q C_{\alpha q}(\pi_{q\mathtt{h}i\mathtt{l}}C_{\beta\mathtt{h}}+\pi_{\mathtt{h}qi\mathtt{l}}C_{\beta\mathtt{h}}+\pi_{\mathtt{h}\mathtt{h}q\mathtt{l}}C_{\beta i}+\pi_{\mathtt{h}\mathtt{h}iq}C_{\beta\mathtt{l}})$$
$$+\sqrt{2}\sum_a(X^I_{\mathtt{h}a}X^J_{\mathrm{d}}+X^I_{\mathrm{d}}X^J_{\mathtt{h}a})\Big(-\frac{1}{2}\Big)\sum_q C_{\alpha q}(\pi_{qa\mathtt{l}\mathtt{l}}C_{\beta\mathtt{h}}+\pi_{\mathtt{h}q\mathtt{l}\mathtt{l}}C_{\beta a}+\pi_{\mathtt{h}aq\mathtt{l}}C_{\beta\mathtt{l}}+\pi_{\mathtt{h}a\mathtt{l}q}C_{\beta\mathtt{l}})$$
$$+2X^I_{\mathrm{d}}X^J_{\mathrm{d}}\Bigg[\sum_q C_{\alpha q}f_{q\mathtt{h}}C_{\beta\mathtt{h}}+\sum_{qi}C_{\alpha q}\pi_{\mathtt{h}q\mathtt{h}i}C_{\beta i}-\sum_q C_{\alpha q}f_{q\mathtt{l}}C_{\beta\mathtt{l}}-\sum_{qi}C_{\alpha q}\pi_{\mathtt{l}q\mathtt{l}i}C_{\beta i}$$
$$-\sum_q C_{\alpha q}\pi_{q\mathtt{l}\mathtt{l}\mathtt{l}}C_{\beta\mathtt{l}}-\sum_q C_{\alpha q}\pi_{q\mathtt{h}\mathtt{h}\mathtt{h}}C_{\beta\mathtt{h}}+\sum_q C_{\alpha q}(\pi_{q\mathtt{h}\mathtt{l}\mathtt{h}}C_{\beta\mathtt{l}}+\pi_{\mathtt{l}q\mathtt{l}\mathtt{h}}C_{\beta\mathtt{h}})\Bigg]\Bigg\}.$$

These terms become $\Gamma^{S^{[x]}}_{\beta\alpha}$ when written in the AO basis and using the definitions in Eqs. (16), (17), and (37)–(41). Note that in order to combine as many terms as possible, we have utilized the symmetry of π many times ($\pi_{rstu}=\pi_{srut}=\pi_{turs}=\pi_{utsr}$).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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