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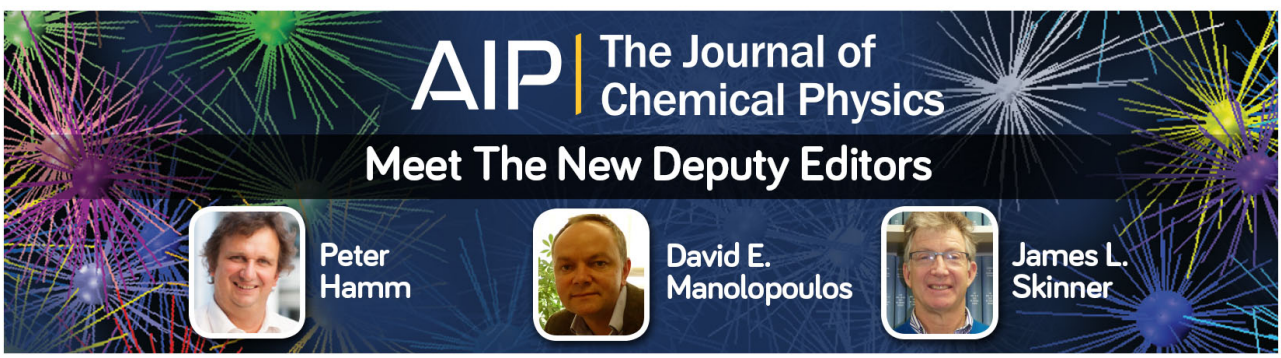
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First-order derivative couplings between excited states from adiabatic TDDFT response theory

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We present a complete derivation of derivative couplings between excited states in the framework of adiabatic time-dependent density functional response theory. Explicit working equations are given and the resulting derivative couplings are compared with derivative couplings from a pseudo-wavefunction *ansatz*. For degenerate excited states, i.e., close to a conical intersection (CI), the two approaches are identical apart from an antisymmetric overlap term. However, if the difference between two excitation energies equals another excitation energy, the couplings from response theory exhibit an unphysical divergence. This spurious behavior is a result of the adiabatic or static kernel approximation of time-dependent density functional theory leading to an incorrect analytical structure of the quadratic response function. Numerical examples for couplings close to a CI and for well-separated electronic states are given. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4906941]

I. INTRODUCTION

In the past few decades, great efforts in the field of quantum chemistry have been expended to study nonadiabatic processes. Going beyond the Born-Oppenheimer approximation, nonadiabatic processes are ubiquitous and cover many interesting modern topics—including charge transfer, electronic excitation quenching, and spin-forbidden transitions. And, at the bottom, modeling most of these processes requires computing the derivative coupling.[1–6]

Today, time-dependent density functional theory (TDDFT)[7–10] is a mainstay of computational photochemistry. The popularity of TDDFT is owed to a compromise between accuracy and computational efficiency that holds up well in many (although not all) applications. However, the evaluation of TDDFT derivative couplings is complicated by the fact that interacting wavefunctions are inaccessible in TDDFT.[11] This led to a plethora of approaches for evaluating both the ground-excited state couplings[12–18] and excited-excited state couplings.[19–24] In 2010, Send and Furche solved the ground-excited state problem definitively by relating the TDDFT derivative coupling to a residue from linear response theory and calculating the residue in a finite atomic orbital (AO) basis.[18] The resulting coupling reduces to the exact expression derived by Chernyak and Mukamel[12] in the complete basis set limit, which guarantees convergence to the exact result as better and better approximations to the time-dependent exchange-correlation (XC) potential are used. These developments have enabled efficient TDDFT-based nonadiabatic molecular dynamics simulations for systems in the first excited state.[25]

In this article, our focus will be exclusively on excited state-excited state couplings. In this case, TDDFT recovers the correct dimensionality of a conical intersection (CI) branching plane[26–28] and should thus be even more useful. To our knowledge, there have been three different proposed methods to evaluate TDDFT excited state derivative couplings. First, Tavernelli *et al.* proposed evaluating $\langle \Psi_I | \frac{\partial}{\partial R} \Psi_J \rangle = \frac{1}{\Omega_{JI}} \langle \Psi_I | \frac{\partial F}{\partial R} | \Psi_J \rangle$, where F is a generalized Kohn-Sham (KS) Fock operator and Ω_{JI} is the energy gap between state J and state I. In Refs. 29 and 23, we show that the Tavernelli formalism neither obeys the correct symmetries around a CI nor agrees with the exact Chernyak-Mukamel expression in the limit of infinite basis.[30]

A second approach is the direct differentiation of pseudo-wavefunctions that we offered in Ref. 23. This approach is identical to what Li and Liu have recently called the equation-of-motion (EOM) TDDFT derivative coupling.[22] While Li and Liu hypothesized this approach based on differentiating the RPA particle-hole operator, we began by guessing a TDDFT/time-dependent Hartree-Fock (TDHF) ground state wavefunction of the form

$$|\Psi_0\rangle \approx \left(1 + \sum_I \hat{X}^I \hat{Y}^I\right) |\Psi_{\mathrm{DFT}}\rangle. \tag{1}$$

Here, $\hat{X}^I$ and $\hat{Y}^I$ are the excitation operators defined as

$$\hat{X}^I \equiv \sum_{ia} X_i^{Ia} a_i a_a^\dagger, \tag{2}$$

$$\hat{Y}^I \equiv \sum_{ia} Y_i^{Ia} a_i a_a^\dagger. \tag{3}$$

The derivative coupling vectors given by our pseudo-wavefunction *ansatz* recover the desired behaviors near a CI point and agree with the Chernyak-Mukamel equality in the limit of an infinite basis set near a CI point.

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Finally, the third approach is to calculate TDDFT derivative couplings via time-dependent response theory. To date, this is the only known approach that can provide exact couplings from TDDFT. An added advantage is the straightforward treatment of Pulay forces, which is essential when atom-centered basis sets are used. In July 2014, Li and Liu presented an abstract approach from time-dependent response theory for computing the excited states derivative couplings, which is applicable for TDDFT, but they did not present working equations or any numerical investigations of the methodology.[22]

Our goal in this work is to provide a detailed derivation of TDDFT/RPA derivative couplings from time-dependent response theory and to give working equations that can easily be implemented. (Note that while the present article was under review, Li and Liu have published a similar article exploring numerical examples that are in close agreement with the present manuscript.[31]) Moreover, we will also compare our response theory derivative couplings with those from a pseudo-wavefunction *ansatz*. (See also the article by Zhang and Herbert.[32])

An outline of this paper is as follows. In Sec. II, we present a self-consistent derivation of TDDFT/RPA derivative couplings from time-dependent response theory. In Sec. III, we present a numerical comparison of response theory results with our pseudo-wavefunction results for two cases: (a) two electronic states near a CI point and (b) two well-separated electronic states. In Sec. IV, we conclude. In Appendix A, we provide some necessary definitions, and in Appendix B, we demonstrate the equivalence of response theory and pseudo-wavefunction derivative couplings near a CI point.

Unless otherwise specified, we use lowercase latin letters to denote spin molecular orbitals (MO) (a, b, c, d for virtual orbitals, i, j, k, l, m for occupied orbitals, p, q, r, s, w for arbitrary orbitals), greek letters ($\alpha, \beta, \gamma, \delta, \lambda, \sigma, \mu, \nu$) denote AOs. Many-electron excited states are denoted by Ψ (with uppercase latin indices I, J). We use atomic units and set $\hbar = 1$. Q denotes nuclear coordinate and superscript $[Q]$ denotes the differentiation with respect to Q.

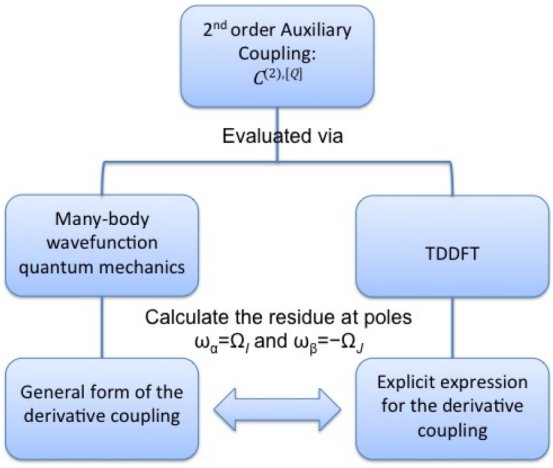


FIG. 1. Summary for evaluating the TDDFT/RPA derivative coupling from time-dependent response theory.

II. THEORY

Fig. 1 gives a summary of how derivative couplings can be calculated with response theory. One calculates the second-order auxiliary coupling from exact many-body wavefunction quantum mechanics with response theory according to a sum-over-states (SOS), and then one calculates the matrix element with TDDFT. By comparing a given residue, one can extract the derivative coupling.

One might wonder if the thus obtained couplings are physical, because the time-dependent Kohn-Sham (TDKS) system is fictitious. However, as long as the Chernyak-Mukamel expression for the coupling is recovered in the infinite basis set limit, the couplings converge to the exact result as better and better approximations are used for the exchange-correlation functional.

A. Exact many-body wavefunction quantum mechanics (nothing to do with TDDFT)

1. Zeroth-, first-, and second-order response of the exact, many-body wavefunction to a time-dependent field according to perturbation theory

Consider an electronic system with the perturbed Hamiltonian

$$H = H_0 + \lambda H_1(t), \tag{4}$$

$$H_1(t) = \sum_\alpha (V^{(\alpha)} e^{i\omega_\alpha t} + V^{(\alpha)*} e^{-i\omega_\alpha t}). \tag{5}$$

The time-dependent Schrödinger equation is

$$H|\Psi(t)\rangle = i\frac{\partial}{\partial t}|\Psi(t)\rangle. \tag{6}$$

Here, $|\Psi(t)\rangle$ is the exact time-dependent wavefunction for the perturbed system (to the second-order) and can be expressed perturbatively as

$$|\Psi(t)\rangle = |\Psi^{(0)}(t)\rangle + \lambda|\Psi^{(1)}(t)\rangle + \lambda^2|\Psi^{(2)}(t)\rangle + \cdots. \tag{7}$$

To construct $|\Psi(t)\rangle$ in terms of $\{|\Psi_I\rangle\}$, the eigenstates of H_0, we take the following steps.

1. The zeroth-order wavefunction is obtained by turning off the field ($V^{(\alpha)} \to 0$)

$$H_0|\Psi^{(0)}(t)\rangle = i\frac{\partial}{\partial t}|\Psi^{(0)}(t)\rangle, \tag{8}$$

$$|\Psi^{(0)}(t)\rangle = e^{-iE_0 t}|\Psi_0\rangle, \tag{9}$$

   where $|\Psi_0\rangle$ is the unperturbed ground state.
2. The first-order wavefunction is obtained by equating all terms linear in λ on both sides of Eq. (6),

$$H_1(t)|\Psi^{(0)}(t)\rangle + H_0|\Psi^{(1)}(t)\rangle = i\frac{\partial}{\partial t}|\Psi^{(1)}(t)\rangle. \tag{10}$$

   Here, the first-order wavefunction $|\Psi^{(1)}(t)\rangle$ does not contain the contribution from $|\Psi_0\rangle$ and can thus be expanded in the basis of eigenstates of H_0 as follows:

$$|\Psi^{(1)}(t)\rangle = e^{-iE_0 t}\sum_{I\neq 0} b_I^{(1)}(t)|\Psi_I\rangle, \tag{11}$$

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where the first-order coefficient $b_I^{(1)}(t)$ has the form

$$b_I^{(1)}(t) = \sum_\alpha W_I^{(1)}(\omega_\alpha) e^{i\omega_\alpha t} + W_I^{(1)}(-\omega_\alpha) e^{-i\omega_\alpha t}. \quad (12)$$

Plugging Eqs. (9) and (11) into Eq. (10), one has

$$e^{-iE_0 t} H_1(t)|\Psi_0\rangle + e^{-iE_0 t} \sum_{I\neq 0} b_I^{(1)}(t) H_0 |\Psi_I\rangle$$

$$= i\frac{\partial}{\partial t} e^{-iE_0 t} \sum_{I\neq 0} b_I^{(1)}(t)|\Psi_I\rangle. \quad (13)$$

Left-multiplying by $\langle\Psi_I|$ gives (after relabeling the indices)

$$\langle\Psi_I|H_1(t)|\Psi_0\rangle + \Omega_I b_I^{(1)}(t) - i\frac{\partial}{\partial t} b_I^{(1)}(t) = 0, \quad (14)$$

where $\Omega_I = E_I - E_0$ is the excitation energy for state I. Now substituting $b_I^{(1)}(t)$ with the expression in Eq. (12) and collecting the coefficient of $e^{i\omega_\alpha t}$, one obtains the expression for $W_I^{(1)}(\omega_\alpha)$,

$$W_I^{(1)}(\omega_\alpha) = -\frac{\langle\Psi_I|V^{(\alpha)}|\Psi_0\rangle}{\Omega_I + \omega_\alpha}, \quad (15)$$

$$W_I^{(1)}(-\omega_\alpha) = -\frac{\langle\Psi_I|V^{(\alpha)}|\Psi_0\rangle}{\Omega_I - \omega_\alpha}. \quad (16)$$

3. Second order: the second-order equation can be written as

$$H_1(t)|\Psi^{(1)}(t)\rangle + H_0|\Psi^{(2)}(t)\rangle = i\frac{\partial}{\partial t}|\Psi^{(2)}(t)\rangle, \quad (17)$$

where $|\Psi^{(2)}(t)\rangle$ is the second-order wavefunction with the expansion coefficient $b_I^{(2)}(t)$,

$$|\Psi^{(2)}(t)\rangle = e^{-iE_0 t}\sum_{I\neq 0} b_I^{(2)}(t)|\Psi_I\rangle, \quad (18)$$

$$b_I^{(2)}(t) = \sum_{\alpha\beta}\Big[W_I^{(2)}(\omega_\alpha,\omega_\beta)e^{i(\omega_\alpha+\omega_\beta)t} + W_I^{(2)}(\omega_\alpha,-\omega_\beta)e^{i(\omega_\alpha-\omega_\beta)t} + W_I^{(2)}(-\omega_\alpha,\omega_\beta)e^{i(-\omega_\alpha+\omega_\beta)t} + W_I^{(2)}(-\omega_\alpha,-\omega_\beta)e^{i(-\omega_\alpha-\omega_\beta)t}\Big]. \quad (19)$$

Similar to the first-order case, the following expression for $W_I^{(2)}(\omega_\alpha,\omega_\beta)$ can be obtained by comparing the coefficients of $e^{i(\omega_\alpha+\omega_\beta)t}$:

$$W_I^{(2)}(\omega_\alpha,\omega_\beta) = \frac{1}{\Omega_I+\omega_\alpha+\omega_\beta} \times \sum_{J\neq 0}\left[\frac{\langle\Psi_J|V^{(\beta)}|\Psi_0\rangle\langle\Psi_I|V^{(\beta)}|\Psi_J\rangle}{\Omega_J+\omega_\beta} + \frac{\langle\Psi_J|V^{(\alpha)}|\Psi_0\rangle\langle\Psi_I|V^{(\alpha)}|\Psi_J\rangle}{\Omega_J+\omega_\alpha}\right]. \quad (20)$$

Similar expression exists for $W_I^{(2)}(\omega_\alpha,-\omega_\beta)$, etc.

2. Second-order auxiliary coupling

The second-order auxiliary coupling matrix element is defined as

$$C^{[Q],(2)}(t) \equiv \langle\Psi^{(2)}(t)|\frac{\partial}{\partial Q}\Psi^{(0)}(t)\rangle + \langle\Psi^{(0)}(t)|\frac{\partial}{\partial Q}\Psi^{(2)}(t)\rangle + \langle\Psi^{(1)}(t)|\frac{\partial}{\partial Q}\Psi^{(1)}(t)\rangle \quad (21)$$

$$\equiv C_1^{[Q],(2)}(t) + C_2^{[Q],(2)}(t) + C_3^{[Q],(2)}(t) \quad (22)$$

and we define

$$C^{[Q],(2)}(t) \equiv \sum_{\alpha\beta}\tilde{C}^{[Q],(2)}(\omega_\alpha,\omega_\beta)e^{i(\omega_\alpha+\omega_\beta)t} + \tilde{C}^{[Q],(2)}(\omega_\alpha,-\omega_\beta)e^{i(\omega_\alpha-\omega_\beta)t} + \tilde{C}^{[Q],(2)}(-\omega_\alpha,\omega_\beta)e^{i(-\omega_\alpha+\omega_\beta)t} + \tilde{C}^{[Q],(2)}(-\omega_\alpha,-\omega_\beta)e^{i(-\omega_\alpha-\omega_\beta)t}. \quad (23)$$

Let us now show that, in most circumstances, the derivative coupling between state I and state J can be found by evaluating the residue of $\tilde{C}^{[Q],(2)}(\omega_\alpha,\omega_\beta)$ at poles $\omega_\alpha = \Omega_I$ and $\omega_\beta = -\Omega_J$. To prove this statement, note that the first two terms in Eq. (21), $C_1^{[Q],(2)}(t)$ and $C_2^{[Q],(2)}(t)$, have residues at $\omega_\alpha = \pm\Omega_J$ and $\omega_\alpha + \omega_\beta = \pm\Omega_J$; as such, these terms are not expected to contribute to the pole of $\tilde{C}^{[Q],(2)}(\omega_\alpha,\omega_\beta)$.

Therefore to isolate the derivative coupling, we will now focus on $C_3^{[Q],(2)}(t)$, which involves only the first-order wavefunctions. According to Eq. (11), the nuclear derivative of the first-order wavefunction can be expressed as

$$\frac{\partial}{\partial Q}|\Psi^{(1)}(t)\rangle = \frac{\partial}{\partial Q}e^{-iE_0 t}\sum_{I\neq 0} b_I^{(1)}(t)|\Psi_I\rangle \quad (24)$$

$$= -iE_0^{[Q]}t|\Psi^{(1)}(t)\rangle + e^{-iE_0 t}\sum_{J\neq 0} b_J^{(1),[Q]}(t)|\Psi_J\rangle + e^{-iE_0 t}\sum_{J\neq 0} b_J^{(1)}(t)|\Psi_J^{[Q]}\rangle. \quad (25)$$

$C_3^{[Q],(2)}(t)$ can be obtained after multiplying by $\langle\Psi^{(1)}(t)|$,

$$C_3^{[Q],(2)}(t) = \langle\Psi^{(1)}(t)|-iE_0^{[Q]}t|\Psi^{(1)}(t)\rangle + e^{-iE_0 t}\sum_{I\neq 0}\langle\Psi^{(1)}(t)|b_J^{(1),[Q]}(t)|\Psi_J\rangle + e^{-iE_0 t}\sum_{I\neq 0}\langle\Psi^{(1)}(t)|b_J^{(1)}(t)|\Psi_J^{[Q]}\rangle. \quad (26)$$

Inserting the SOS representation for the first-order wavefunction, one has

$$C_3^{[Q],(2)}(t) = \sum_{I,J\neq 0}\left(-iE_0^{[Q]}tb_J^{(1)}(t) + b_I^{(1),[Q]}(t)e^{-iE_0 t}\right) \times b_I^{(1)*}(t)\langle\Psi_I|\Psi_J\rangle + \sum_{I,J\neq 0} b_I^{(1)*}(t)b_J^{(1)}(t)\langle\Psi_I|\Psi_J^{[Q]}\rangle. \quad (27)$$

According to the orthogonality of $\{|\Psi_I\rangle\}$,

$$C_3^{[Q],(2)}(t) = \sum_{I\neq 0} b_I^{(1)*}(t)\left(-iE_0^{[Q]}tb_I^{(1)}(t) + b_I^{(1),[Q]}(t)e^{-iE_0 t} + \sum_{J\neq 0} b_J^{(1)}(t)\langle\Psi_I|\Psi_J^{[Q]}\rangle\right). \quad (28)$$

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When evaluating the residue of $\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta)$ at poles $\omega_\alpha=\Omega_I$ and $\omega_\beta=-\Omega_J$, one finds that only the last term in $C_3^{[Q],(2)}(t)$ contributes. Plugging in the expression of $b_I^{(1)*}(t)$ and $b_J^{(1)}(t)$, we find that $\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta)$ can be written as (omitting the non-contributing part)

$$\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta)=\sum_{I,J\neq 0}\frac{\langle\Psi_0|V^{(\alpha)}(\omega_\alpha)|\Psi_I\rangle\langle\Psi_J|V^{(\beta)}(\omega_\beta)|\Psi_0\rangle}{(\Omega_I-\omega_\alpha)(\Omega_J+\omega_\beta)}\langle\Psi_I|\Psi_J^{[Q]}\rangle+\cdots. \tag{29}$$

Thus, the residue of $\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta)$ at poles $\omega_\alpha=\Omega_I$ and $\omega_\beta=-\Omega_J$ is therefore

$$\begin{aligned}&Res[\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]\\&=\langle\Psi_0|V^{(\alpha)}(\omega_\alpha)|\Psi_I\rangle\langle\Psi_J|V^{(\beta)}(\omega_\beta)|\Psi_0\rangle\langle\Psi_I|\Psi_J^{[Q]}\rangle \qquad (30)\\&\equiv V_{0I}V_{J0}\langle\Psi_I|\Psi_J^{[Q]}\rangle. \qquad (31)\end{aligned}$$

Note that the factor $2\pi i$ is omitted when evaluating all the residues. The final residue of the second-order auxiliary couplings is then just the residue of $\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta)$,

$$\begin{aligned}&Res[\tilde{C}^{[Q],(2)}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]\\&=Res[\tilde{C}_3^{[Q],(2)}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]=V_{0I}V_{J0}\langle\Psi_I|\Psi_J^{[Q]}\rangle. \qquad (32)\end{aligned}$$

Up to this point, all of the above theory is simple time-dependent perturbation theory, and we have discussed nothing having to do with TDDFT.

B. TDDFT

As shown in Sec. II A 2, a derivative coupling is related to the residue of the second-order auxiliary coupling at certain frequencies according to perturbative time-dependent quantum mechanics. In this section, we will derive an explicit expression for such a residue via TDDFT.

1. First- and second-order TDKS orbitals

According to the usual TDDFT framework, the general eigenvalue equation for a closed electronic system is

$$F|\Psi_{\mathrm{DFT}}\rangle=E_{\mathrm{DFT}}|\Psi_{\mathrm{DFT}}\rangle, \tag{33}$$

where $|\Psi_{\mathrm{DFT}}\rangle$ is the non-interacting Kohn-Sham ground state with energy E_{DFT}. Here, $|\Psi_{\mathrm{DFT}}\rangle$ is

$$|\Psi_{\mathrm{DFT}}\rangle=|\phi_1\phi_2\ldots\phi_n\rangle, \tag{34}$$

where $|\phi_i\rangle$ is the ith non-interacting KS orbital with energy ε_i. The Fock operator is

$$F_{pq}=h_{pq}+\sum_{rs}\langle\phi_p\phi_s|\phi_q\phi_r\rangle\gamma_{rs}^{(0)}, \tag{35}$$

where $\gamma_{rs}^{(0)}$ is the time-independent density matrix

$$\gamma_{rs}^{(0)}=\langle\Psi_{\mathrm{DFT}}|a_r^\dagger a_s|\Psi_{\mathrm{DFT}}\rangle=\sum_j\langle\phi_r|\phi_j\rangle\langle\phi_j|\phi_s\rangle=\delta_{rs}^{occ}. \tag{36}$$

Now, when a time-dependent field is applied (as in Eq. (6)), the system is perturbed and the time-dependent KS orbitals (denoted by $|\tilde{\phi}_i\rangle$) can be expanded as (to second-order)

$$|\tilde{\phi}_i(t)\rangle=e^{-i\varepsilon_i t}\left(|\phi_i\rangle+|\phi_i^{(1)}(t)\rangle+|\phi_i^{(2)}(t)\rangle\right), \tag{37}$$

where $|\phi_i^{(1)}(t)\rangle$ and $|\phi_i^{(2)}(t)\rangle$ are first- and second-order orbital corrections, respectively. The TDKS density matrix is

$$\begin{aligned}\tilde{\gamma}(t)&=\sum_i|\tilde{\phi}_i(t)\rangle\langle\tilde{\phi}_i(t)| \qquad (38)\\&\equiv\gamma^{(0)}+\tilde{\gamma}^{(1)}(t)+\tilde{\gamma}^{(2)}(t), \qquad (39)\end{aligned}$$

where

$$\begin{aligned}\tilde{\gamma}^{(1)}(t)&=\sum_i\left(|\phi_i\rangle\langle\phi_i^{(1)}(t)|+|\phi_i^{(1)}(t)\rangle\langle\phi_i|\right), \qquad (40)\\\tilde{\gamma}^{(2)}(t)&=\sum_i\Big(|\phi_i^{(2)}(t)\rangle\langle\phi_i|+|\phi_i\rangle\langle\phi_i^{(2)}(t)|\\&\quad+|\phi_i^{(1)}(t)\rangle\langle\phi_i^{(1)}(t)|+|\phi_i^{(1)}(t)\rangle\langle\phi_i^{(1)}(t)|\Big). \qquad (41)\end{aligned}$$

At this point, we want to express the first- and second-order orbital corrections in terms of first- and second-order density matrices, $\tilde{\gamma}^{(1)}(t)$ and $\tilde{\gamma}^{(2)}(t)$. We perform this transformation because the density matrices are the central objects in most TDDFT development.[33] Let us define

$$\tilde{\gamma}^{(1)}(t)\equiv\sum_\alpha\gamma^{(1)}(\omega_\alpha)e^{i\omega_\alpha t}+\gamma^{(1)}(-\omega_\alpha)e^{-i\omega_\alpha t}. \tag{42}$$

In the frequency domain, the first-order density matrix response is

$$\begin{aligned}\gamma^{(1)}(\omega)&=\sum_\alpha\gamma^{(1)}(\omega_\alpha)\delta(\omega-\omega_\alpha), \qquad (43)\\\gamma^{(1)}(\omega_\alpha)&=\sum_{ia}\tilde{X}_{ia}(\omega_\alpha)|\phi_a\rangle\langle\phi_i|+\tilde{Y}_{ia}(\omega_\alpha)|\phi_i\rangle\langle\phi_a|, \qquad (44)\end{aligned}$$

where $\tilde{X}_{ia}(\omega_\alpha)$ and $\tilde{Y}_{ia}(\omega_\alpha)$ are the *virt-occ* and *occ-virt* matrix elements of $\gamma^{(1)}(\omega_\alpha)$, respectively.[33] If we substitute Eq. (40) for $\tilde{\gamma}^{(1)}(t)$ and then sandwich everything by $\langle\phi_j|$ and $|\phi_a\rangle$, we find

$$\langle\phi_i^{(1)}(t)|\phi_a\rangle=\sum_{a\alpha}\left(\tilde{Y}_{ia}(\omega_\alpha)e^{i\omega_\alpha t}+\tilde{Y}_{ia}(-\omega_\alpha)e^{-i\omega_\alpha t}\right). \tag{45}$$

Given that $\tilde{X}_{ia}(\omega_\alpha)=\tilde{Y}_{ia}^*(-\omega_\alpha)$,[34] one arrives at the final expression for the first-order TDKS orbital correction,

$$|\phi_i^{(1)}(t)\rangle=\sum_{a\alpha}\left(\tilde{X}_{ia}(\omega_\alpha)e^{i\omega_\alpha t}+\tilde{X}_{ia}(-\omega_\alpha)e^{-i\omega_\alpha t}\right)|\phi_a\rangle. \tag{46}$$

Our next step is to deal with the second-order density matrix response $\gamma^{(2)}$ in order to get an expression for the second-order orbital correction. The time-dependence of $\gamma^{(2)}$ is given by

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$$\tilde{\gamma}^{(2)}(t) \equiv \sum_{\alpha\beta} \gamma^{(2)}(\omega_\alpha, \omega_\beta) e^{i(\omega_\alpha+\omega_\beta)t} + \gamma^{(2)}(\omega_\alpha, -\omega_\beta) e^{i(\omega_\alpha-\omega_\beta)t} + \gamma^{(2)}(-\omega_\alpha, \omega_\beta) e^{i(-\omega_\alpha+\omega_\beta)t} + \gamma^{(2)}(-\omega_\alpha, -\omega_\beta) e^{i(-\omega_\alpha-\omega_\beta)t}. \quad (47)$$

Sandwiching Eq. (41) by *occ* and *virt* orbitals, one finds the different components of $\tilde{\gamma}^{(2)}(t)$:

1. occ-occ

$$\tilde{\gamma}^{(2)}_{ij}(t) = 2\langle \phi_i | \phi^{(2)}_j(t) \rangle; \quad (48)$$

2. occ-virt

$$\tilde{\gamma}^{(2)}_{ia}(t) = \langle \phi^{(2)}_i(t) | \phi_a \rangle; \quad (49)$$

3. virt-occ

$$\tilde{\gamma}^{(2)}_{ai}(t) = \langle \phi_a | \phi^{(2)}_i(t) \rangle; \quad (50)$$

4. virt-virt

$$\tilde{\gamma}^{(2)}_{ab}(t) = \langle \phi_a | \phi^{(1)}_i(t) \rangle \langle \phi^{(1)}_i(t) | \phi_b \rangle + \langle \phi_a | \phi^{(1)}_i(t) \rangle \langle \phi^{(1)}_i(t) | \phi_b \rangle. \quad (51)$$

From Eq. (51), it is clear that the second-order orbital correction ($|\phi^{(2)}_i(t)\rangle$) has no explicit dependence on $\tilde{\gamma}^{(2)}_{ab}(t)$. According to Eqs. (48) and (49) (or (50)), the expression for $|\phi^{(2)}_i(t)\rangle$ is

$$|\phi^{(2)}_i(t)\rangle = \frac{1}{2}\sum_j \tilde{\gamma}^{(2)}_{ij}(t)|\phi_j\rangle + \sum_a \tilde{\gamma}^{(2)}_{ai}(t)|\phi_a\rangle \quad (52)$$

$$= \frac{1}{2}\sum_{j\alpha\beta}\Big[\gamma^{(2)}_{ij}(\omega_\alpha, \omega_\beta)e^{i(\omega_\alpha+\omega_\beta)t} + \gamma^{(2)}_{ij}(\omega_\alpha, -\omega_\beta)e^{i(\omega_\alpha-\omega_\beta)t} + \gamma^{(2)}_{ij}(-\omega_\alpha, \omega_\beta)e^{i(-\omega_\alpha+\omega_\beta)t} + \gamma^{(2)}_{ij}(-\omega_\alpha, -\omega_\beta)e^{i(-\omega_\alpha-\omega_\beta)t}\Big]|\phi_j\rangle + \sum_{a\alpha\beta}\Big[\gamma^{(2)}_{ai}(\omega_\alpha, \omega_\beta)e^{i(\omega_\alpha+\omega_\beta)t} + \gamma^{(2)}_{ai}(\omega_\alpha, -\omega_\beta)e^{i(\omega_\alpha-\omega_\beta)t} + \gamma^{(2)}_{ai}(-\omega_\alpha, \omega_\beta)e^{i(-\omega_\alpha+\omega_\beta)t} + \gamma^{(2)}_{ai}(-\omega_\alpha, -\omega_\beta)e^{i(-\omega_\alpha-\omega_\beta)t}\Big]|\phi_a\rangle. \quad (53)$$

2. Auxiliary coupling matrix elements for the TDKS determinant

We are now prepared to evaluate the second-order auxiliary coupling using the perturbed TDKS orbitals

$$C^{[Q],(2)}_{\mathrm{KS}} = \sum_j \Big(\langle \phi^{(2)}_j(t)|\phi_j{}^{[Q]}\rangle + \langle \phi_j|\phi^{(2)}_j(t)^{[Q]}\rangle + \langle \phi^{(1)}_j(t)|\phi^{(1)}_j(t)^{[Q]}\rangle\Big) \quad (54)$$

$$\equiv T1 + T2 + T3. \quad (55)$$

Note that the derivative of the exponential part $e^{-i\varepsilon_i t}$ of $\tilde{\phi}_i(t)$ (as shown in Eq. (37)) is not included in the above expression since that term will have no effect on the final result (which is easy to prove). We will now treat the three terms in $C^{[Q],(2)}_{\mathrm{KS}}$ separately.

1. $T1$: $\sum_j \langle \phi^{(2)}_j(t)|\phi_j{}^{[Q]}\rangle$ and $T2$: $\sum_j \langle \phi_j|\phi^{(2)}_j(t)^{[Q]}\rangle$

To evaluate these terms, we plug in the expressions for $|\phi^{(2)}_j(t)\rangle$ (Eq. (52)) and $T1$ becomes

$$T1 = \frac{1}{2}\sum_{ij}\tilde{\gamma}^{(2)*}_{ij}(t)O^{\mathrm{R}[Q]}_{ij} + \sum_{aj}\tilde{\gamma}^{(2)*}_{aj}(t)O^{\mathrm{R}[Q]}_{aj}, \quad (56)$$

where we define the "right" spin-orbital derivative overlap $O^{\mathrm{R}[Q]}_{pq}$ the same way as in Ref. 23,

$$O^{\mathrm{R}[Q]}_{pq} \equiv \langle \phi_p | \phi^{[Q]}_q \rangle \quad (57)$$

$$= \left(\sum_\mu C_{\mu p}\langle\mu|\right)\left(\sum_\nu |\nu\rangle C^{[Q]}_{\nu q} + \sum_\nu \left|\nu^{[Q]}\right\rangle C_{\nu q}\right) \quad (58)$$

$$= \sum_{\mu\nu} C_{\mu p} S_{\mu\nu} C^{[Q]}_{\nu q} + \sum_{\mu\nu} C_{\mu p} S^{\mathrm{R}[Q]}_{\mu\nu} C_{\nu q} \quad (59)$$

$$= \sum_{\mu\nu} C_{\mu p}\left(S^{\mathrm{R}[Q]}_{\mu\nu} - \frac{1}{2}S^{[Q]}_{\mu\nu}\right)C_{\nu q} - \Theta^{[Q]}_{pq} \quad (60)$$

$$\equiv \sum_{\mu\nu} C_{\mu p} S^{\mathrm{A}[Q]}_{\mu\nu} C_{\nu q} - \Theta^{[Q]}_{pq}. \quad (61)$$

Here, $C_{\mu p}$ denotes the MO coefficients, Θ_{pq} stands for an orbital rotation matrix, $S^{[Q]}_{\mu\nu} \equiv \langle\mu|\nu\rangle^{[Q]}$ are meaningful overlap derivatives contributing to Pulay forces, and $S^{\mathrm{R}[Q]}_{\mu\nu} \equiv \langle\mu|\nu^{[Q]}\rangle$. $S^{\mathrm{A}[Q]}_{\mu\nu} \equiv S^{\mathrm{R}[Q]}_{\mu\nu} - \frac{1}{2}S^{[Q]}_{\mu\nu} = \frac{1}{2}(\langle\mu|\nu^{[Q]}\rangle - \langle\mu^{[Q]}|\nu\rangle)$ are artificial matrix elements that can be ignored if we introduce electron-translation factors.[35] (The detailed derivation of $O^{\mathrm{R}[Q]}_{pq}$ can be found in Ref. 35.) The $(\omega_\alpha+\omega_\beta)$ Fourier coefficient of $T1$ is

$$\mathcal{T}1 = \frac{1}{2}\sum_{ij}\gamma^{(2)}_{ij}(\omega_\alpha, \omega_\beta)O^{\mathrm{R}[Q]}_{ij} + \sum_{aj}\gamma^{(2)}_{aj}(\omega_\alpha, \omega_\beta)O^{\mathrm{R}[Q]}_{aj}, \quad (62)$$

where $\gamma^{(2)}_{ji}(\omega_\alpha, \omega_\beta)$ and $\gamma^{(2)}_{ja}(\omega_\alpha, \omega_\beta)$ correspond to the $(\omega_\alpha+\omega_\beta)$ Fourier transforms of $\gamma^{(2)}_{ji}(t)$ and $\gamma^{(2)}_{ja}(t)$, respectively. Similarly, the $(\omega_\alpha+\omega_\beta)$ Fourier coefficient for $T2$ is

$$\mathcal{T}2 = \frac{1}{2}\sum_j \gamma^{(2),[Q]}_{jj}(\omega_\alpha, \omega_\beta) + \frac{1}{2}\sum_{ij}\gamma^{(2)}_{ji}(\omega_\alpha, \omega_\beta)O^{\mathrm{R}[Q]}_{ji} + \sum_{aj}\gamma^{(2)}_{ja}(\omega_\alpha, \omega_\beta)O^{\mathrm{R}[Q]}_{ja}. \quad (63)$$

2. $T3$: $\sum_j \langle \phi^{(1)}_j(t)|\phi^{(1)}_j(t)^{[Q]}\rangle$

To evaluated this term, we plug in the expression for the first-order orbital corrections (Eq. (46)) into $T3$. One finds

$$T3 = \sum_j\Big[\sum_{a\gamma}\big(\tilde{X}_{ja}(\omega_\gamma)e^{i\omega_\gamma t} + \tilde{X}_{ja}(-\omega_\gamma)e^{-i\omega_\gamma t}\big)^*\langle\phi_a|\frac{\partial}{\partial Q}\sum_{b\delta}\big(\tilde{X}_{jb}(\omega_\delta)e^{i\omega_\delta t} + \tilde{X}_{jb}(-\omega_\delta)e^{-i\omega_\delta t}\big)\phi_b\rangle\Big]. \quad (64)$$

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Recall that $\tilde{X}_{ia}(\omega) = \tilde{Y}^*_{ia}(-\omega)$, and it is easy to write down the $(\omega_\alpha + \omega_\beta)$ Fourier transform of $T3$,

$$\mathcal{T}3 = \sum_{ja}\Big(\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}^{[Q]}_{ja}(\omega_\beta) + \sum_b \tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{jb}(\omega_\beta)O^{\mathrm{R}[Q]}_{ab} + \tilde{Y}_{ja}(\omega_\beta)\tilde{X}^{[Q]}_{ja}(\omega_\alpha) + \sum_b \tilde{Y}_{ja}(\omega_\beta)\tilde{X}_{jb}(\omega_\alpha)O^{\mathrm{R}[Q]}_{ab}\Big). \tag{65}$$

The total $(\omega_\alpha + \omega_\beta)$ Fourier coefficient of the second-order auxiliary coupling given by TDDFT can thus be expressed as

$$\begin{aligned}
&\mathcal{T}1 + \mathcal{T}2 + \mathcal{T}3 \\
&= \sum_{ij}\gamma^{(2)}_{ij}(\omega_\alpha,\omega_\beta)O^{\mathrm{R}[Q]}_{ij} + \frac{1}{2}\sum_j \gamma^{(2),[Q]}_{jj}(\omega_\alpha,\omega_\beta) \\
&\quad + \sum_{jab}\big(\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{jb}(\omega_\beta) + \tilde{Y}_{ja}(\omega_\beta)\tilde{X}_{jb}(\omega_\alpha)\big)O^{\mathrm{R}[Q]}_{ab} \\
&\quad + \sum_{ja}\Big(\gamma^{(2)}_{aj}(\omega_\alpha,\omega_\beta) - \gamma^{(2)}_{ja}(\omega_\alpha,\omega_\beta)\Big)O^{\mathrm{R}[Q]}_{aj} \\
&\quad + \sum_{ja}\Big(\tilde{X}^{[Q]}_{ja}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta) + \tilde{X}^{[Q]}_{ja}(\omega_\beta)\tilde{Y}_{ja}(\omega_\alpha)\Big).
\end{aligned} \tag{66}$$

As a result of the idempotency of the Kohn-Sham density matrix,[33] the virt-virt and occ-occ pieces of the second-order density matrix $\gamma^{(2)}_{ab}(\omega_\alpha,\omega_\beta)$ satisfy

$$\gamma^{(2)}_{ab}(\omega_\alpha,\omega_\beta) = \sum_j(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{jb}(\omega_\beta) + \tilde{X}_{ja}(\omega_\beta)\tilde{Y}_{jb}(\omega_\alpha)), \tag{67}$$

$$\gamma^{(2)}_{ij}(\omega_\alpha,\omega_\beta) = -\sum_a(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{ia}(\omega_\beta) + \tilde{X}_{ja}(\omega_\beta)\tilde{Y}_{ia}(\omega_\alpha)). \tag{68}$$

If we apply these expressions to Eq. (66), the total Fourier coefficient becomes

$$\begin{aligned}
\mathcal{T}1 + \mathcal{T}2 + \mathcal{T}3 &= \sum_{ij}\gamma^{(2)}_{ij}(\omega_\alpha,\omega_\beta)O^{\mathrm{R}[Q]}_{ij} \\
&\quad + \sum_{ab}\gamma^{(2)}_{ab}(\omega_\alpha,\omega_\beta)O^{\mathrm{R}[Q]}_{ab} \\
&\quad + \sum_{ja}\Big(\gamma^{(2)}_{aj}(\omega_\alpha,\omega_\beta) - \gamma^{(2)}_{ja}(\omega_\alpha,\omega_\beta)\Big)O^{\mathrm{R}[Q]}_{aj} \\
&\quad + \frac{1}{2}\sum_{ja}\Big[\tilde{X}^{[Q]}_{ja}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta) \\
&\quad + \tilde{X}^{[Q]}_{ja}(\omega_\beta)\tilde{Y}_{ja}(\omega_\alpha) - \tilde{X}_{ja}(\omega_\alpha)\tilde{Y}^{[Q]}_{ja}(\omega_\beta) \\
&\quad - \tilde{X}_{ja}(\omega_\beta)\tilde{Y}^{[Q]}_{ja}(\omega_\alpha)\Big] \qquad (69) \\
&\equiv O + \mathcal{XY}, \qquad (70)
\end{aligned}$$

where we define

$$\begin{aligned}
O &\equiv \sum_{ij}\gamma^{(2)}_{ij}(\omega_\alpha,\omega_\beta)O^{\mathrm{R}[Q]}_{ij} + \sum_{ab}\gamma^{(2)}_{ab}(\omega_\alpha,\omega_\beta)O^{\mathrm{R}[Q]}_{ab} \\
&\quad + \sum_{ja}\Big(\gamma^{(2)}_{aj}(\omega_\alpha,\omega_\beta) - \gamma^{(2)}_{ja}(\omega_\alpha,\omega_\beta)\Big)O^{\mathrm{R}[Q]}_{aj}, \qquad (71) \\
\mathcal{XY} &\equiv \frac{1}{2}\sum_{ja}\Big[\tilde{X}^{[Q]}_{ja}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta) + \tilde{X}^{[Q]}_{ja}(\omega_\beta)\tilde{Y}_{ja}(\omega_\alpha) \\
&\quad - \tilde{X}_{ja}(\omega_\alpha)\tilde{Y}^{[Q]}_{ja}(\omega_\beta) - \tilde{X}_{ja}(\omega_\beta)\tilde{Y}^{[Q]}_{ja}(\omega_\alpha)\Big]. \qquad (72)
\end{aligned}$$

3. Residues of the coefficient derivative terms

We must now evaluate the residues of the O and $\mathcal{XY}$ terms.

1. Residue of $\mathcal{XY}$

We begin with the residue of the $\tilde{X}(\omega_\alpha)$ and $\tilde{Y}(\omega_\alpha)$ derivatives. Start with the general working equation for RPA,[36]

$$\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} + \omega_\alpha\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right]\begin{pmatrix}\tilde{X}(\omega_\alpha)\\ \tilde{Y}(\omega_\alpha)\end{pmatrix} = -\begin{pmatrix}V^{(\alpha)}\\ V^{(\alpha)}\end{pmatrix}. \tag{73}$$

We note that $\tilde{X}(\omega_\alpha)$ and $\tilde{Y}(\omega_\alpha)$ can be obtained by

$$\begin{pmatrix}\tilde{X}(\omega_\alpha)\\ \tilde{Y}(\omega_\alpha)\end{pmatrix} = -\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} + \omega_\alpha\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right]^{-1}\begin{pmatrix}V^{(\alpha)}\\ V^{(\alpha)}\end{pmatrix}. \tag{74}$$

According to Ref. 33, the inverse of the supermatrix is equivalent to

$$\begin{aligned}
\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} + \omega_\alpha\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right]^{-1} &= \sum_I\left[\frac{1}{\Omega_I + \omega_\alpha}\begin{pmatrix}X_I\\ Y_I\end{pmatrix}\begin{pmatrix}X_I & Y_I\end{pmatrix}\right. \\
&\quad \left. + \frac{1}{\Omega_I - \omega_\alpha}\begin{pmatrix}Y_I\\ X_I\end{pmatrix}\begin{pmatrix}Y_I & X_I\end{pmatrix}\right].
\end{aligned} \tag{75}$$

Therefore, if $V^{(\alpha)} = \mu^{(\alpha)}$ (the dipole operator), $\tilde{X}$ and $\tilde{Y}$ can be expressed as

$$\tilde{X}_{ja}(\omega_\alpha) = \sum_I\left(\frac{X^{Ia}_j\mu^{(\alpha)}_{0I}}{\Omega_I + \omega_\alpha} + \frac{Y^{Ia}_j\mu^{(\alpha)}_{I0}}{\Omega_I - \omega_\alpha}\right), \tag{76}$$

$$\tilde{Y}_{ja}(\omega_\alpha) = \sum_I\left(\frac{Y^{Ia}_j\mu^{(\alpha)}_{0I}}{\Omega_I + \omega_\alpha} + \frac{X^{Ia}_j\mu^{(\alpha)}_{I0}}{\Omega_I - \omega_\alpha}\right). \tag{77}$$

Thus, the residues of $\tilde{X}$ and $\tilde{Y}$ at poles $\omega_\alpha = \Omega_I$ and $\omega_\beta = -\Omega_J$ are

$$Res[\tilde{X}_{ja}(\omega_\alpha);\Omega_I] = Y^{Ia}_j\mu^{(\alpha)}_{I0}, \tag{78}$$

$$Res[\tilde{Y}_{ja}(\omega_\alpha);\Omega_I] = X^{Ia}_j\mu^{(\alpha)}_{I0}, \tag{79}$$

$$Res[\tilde{X}_{ja}(\omega_\alpha);-\Omega_J] = X^{Ja}_j\mu^{(\alpha)}_{0J}, \tag{80}$$

$$Res[\tilde{Y}_{ja}(\omega_\alpha);-\Omega_J] = Y^{Ja}_j\mu^{(\alpha)}_{0J}, \tag{81}$$

and the derivatives of $\tilde{X}$ and $\tilde{Y}$ are

$$\begin{aligned}
\tilde{X}^{[Q]}_{ja}(\omega_\alpha) &= \sum_I\left[\frac{X^{Ia[Q]}_j\mu^{(\alpha)}_{0I} + X^{Ia}_j\mu^{(\alpha),[Q]}_{0I}}{\Omega_I + \omega_\alpha}\right. \\
&\quad + \frac{Y^{Ia[Q]}_j\mu^{(\alpha)}_{I0} + Y^{Ia}_j\mu^{(\alpha),[Q]}_{I0}}{\Omega_I - \omega_\alpha} \\
&\quad \left. - \frac{X^{Ia}_j\mu^{(\alpha)}_{0I}\Omega^{[Q]}_I}{(\Omega_I + \omega_\alpha)^2} - \frac{Y^{Ia}_j\mu^{(\alpha)}_{I0}\Omega^{[Q]}_I}{(\Omega_I - \omega_\alpha)^2}\right],
\end{aligned} \tag{82}$$

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$$\tilde{Y}_{ja}^{[Q]}(\omega_\alpha) = \sum_I \left[\frac{Y_j^{Ia[Q]}\mu_{0I}^{(\alpha)} + Y_j^{Ia}\mu_{0I}^{(\alpha),[Q]}}{\Omega_I + \omega_\alpha} + \frac{X_j^{Ia[Q]}\mu_{I0}^{(\alpha)} + X_j^{Ia}\mu_{I0}^{(\alpha),[Q]}}{\Omega_I - \omega_\alpha} - \frac{Y_j^{Ia}\mu_{0I}^{(\alpha)}\Omega_I^{[Q]}}{(\Omega_I + \omega_\alpha)^2} - \frac{X_j^{Ia}\mu_{I0}^{(\alpha)}\Omega_I^{[Q]}}{(\Omega_I - \omega_\alpha)^2} \right], \quad (83)$$

where $\mu_{0I}^{(\alpha)} = \sum_{ja}(X_j^{Ia} + Y_j^{Ia})V_j^{(\alpha)a}$. We can now write down the residue of $\mathcal{XY}$ at the poles $\omega_\alpha = \Omega_I$ and $\omega_\beta = -\Omega_J$,

$$\begin{aligned} &Res[\mathcal{XY};\Omega_I,-\Omega_J] \\ &= \frac{1}{2}\sum_{ja}\Big[\left(Y_j^{Ia[Q]}\mu_{I0}^{(\alpha)} + Y_j^{Ia}\mu_{I0}^{(\alpha),[Q]}\right)Y_j^{Ja}\mu_{0J}^{(\beta)} \\ &\quad + \left(X_j^{Ja[Q]}\mu_{0J}^{(\beta)} + X_j^{Ja}\mu_{0J}^{(\beta),[Q]}\right)X_j^{Ia}\mu_{I0}^{(\alpha)} \\ &\quad - Y_j^{Ia}\mu_{I0}^{(\alpha)}\left(Y_j^{Ja[Q]}\mu_{0J}^{(\beta)} + Y_j^{Ja}\mu_{0J}^{(\beta),[Q]}\right) \\ &\quad - X_j^{Ja}\mu_{0J}^{(\beta)}\left(X_j^{Ia[Q]}\mu_{I0}^{(\alpha)} + X_j^{Ia}\mu_{I0}^{(\alpha),[Q]}\right)\Big] \quad (84) \\ &= \frac{1}{2}\sum_{ja}\Big[\left(X_j^{Ia}X_j^{Ja} - Y_j^{Ia}Y_j^{Ja}\right) \\ &\quad \times \left(\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta),[Q]} - \mu_{I0}^{(\alpha),[Q]}\mu_{0J}^{(\beta)}\right) \\ &\quad + \left(X_j^{Ia}X_j^{Ja[Q]} - Y_j^{Ia}Y_j^{Ja[Q]} - X_j^{Ia[Q]}X_j^{Ja}\right. \\ &\quad \left. + Y_j^{Ia[Q]}Y_j^{Ja}\right)\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta)}\Big]. \quad (85) \end{aligned}$$

Recalling the orthogonality condition

$$\sum_{ja}\left(X_j^{Ia}X_j^{Ja} - Y_j^{Ia}Y_j^{Ja}\right) = \delta_{IJ}, \quad (86)$$

we find that the first term in Eq. (85) vanishes. Taking the derivative on each side of Eq. (86), one finds (for $I \neq J$)

$$\begin{aligned} &\sum_{ja}\left(X_j^{Ia[Q]}X_j^{Ja} - Y_j^{Ia[Q]}Y_j^{Ja}\right. \\ &\qquad \left. + X_j^{Ia}X_j^{Ja[Q]} - Y_j^{Ia}Y_j^{Ja[Q]}\right) = 0, \quad (87) \end{aligned}$$

$$\begin{aligned} &\sum_{ja}\left(-X_j^{Ia[Q]}X_j^{Ja} + Y_j^{Ia[Q]}Y_j^{Ja}\right) \\ &\quad = \sum_{ja}\left(X_j^{Ia}X_j^{Ja[Q]} - Y_j^{Ia}Y_j^{Ja[Q]}\right). \quad (88) \end{aligned}$$

Plugging Eq. (87) into Eq. (85) and taking out the first term, we get the final result for the residue of $\mathcal{XY}$,

$$\begin{aligned} &Res[\mathcal{XY};\Omega_I,-\Omega_J] \\ &= \sum_{ja}\left(X_j^{Ia}X_j^{Ja[Q]} - Y_j^{Ia}Y_j^{Ja[Q]}\right)\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta)}. \quad (89) \end{aligned}$$

2. Residue of O

The residues of the occ-occ and virt-virt part in O are straightforward. Using Eqs. (68) and (78)–(81), the residues of the occ-occ and virt-virt parts at $\omega_\alpha = \Omega_I$ and $\omega_\beta = -\Omega_J$ are just

$$\begin{aligned} &Res\left[\sum_{ij}\gamma_{ij}^{(2)}(\omega_\alpha,\omega_\beta)O_{ij}^{R[Q]};\Omega_I,-\Omega_J\right] \\ &= -\sum_{ija}\left(X_i^{Ia}X_j^{Ja} + Y_j^{Ia}Y_i^{Ja}\right)O_{ij}^{R[Q]}\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta)}, \quad (90) \\ &Res\left[\sum_{ab}\gamma_{ab}^{(2)}(\omega_\alpha,\omega_\beta)O_{ab}^{R[Q]};\Omega_I,-\Omega_J\right] \\ &= \sum_{abj}\left(X_j^{Ib}X_j^{Ja} + Y_j^{Ia}Y_j^{Jb}\right)O_{ab}^{R[Q]}\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta)}. \quad (91) \end{aligned}$$

For the virt-occ ($\gamma_{vo}^{(2)}(\omega_\alpha,\omega_\beta)$) and occ-virt ($\gamma_{ov}^{(2)}(\omega_\alpha,\omega_\beta)$) pieces of the second-order density matrix, these matrix elements must satisfy[33]

$$\begin{aligned} &\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} + (\omega_\alpha+\omega_\beta)\begin{pmatrix}\mathbf{I} & 0\\ 0 & -\mathbf{I}\end{pmatrix}\right]\begin{pmatrix}\gamma_{vo}^{(2)}(\omega_\alpha,\omega_\beta)\\ \gamma_{ov}^{(2)}(\omega_\alpha,\omega_\beta)\end{pmatrix} \\ &= -\begin{pmatrix}\tilde{L}^{vo}(\omega_\alpha,\omega_\beta)\\ \tilde{L}^{ov}(\omega_\alpha,\omega_\beta)\end{pmatrix}. \quad (92) \end{aligned}$$

See Appendix B 1 for explicit expressions of $\tilde{L}^{vo}(\omega_\alpha,\omega_\beta)$ and $\tilde{L}^{ov}(\omega_\alpha,\omega_\beta)$. Note that $\tilde{L}^{vo}(\omega_\alpha,\omega_\beta)$ and $\tilde{L}^{ov}(\omega_\alpha,\omega_\beta)$ are bilinear in $\tilde{X}_{ja}(\omega_\alpha)$ and $\tilde{Y}_{ja}(\omega_\beta)$[33] (or some permutations thereof).

The residue of $\gamma_{vo}^{(2)}(\omega_\alpha,\omega_\beta)$ and $\gamma_{ov}^{(2)}(\omega_\alpha,\omega_\beta)$ at $\omega_\alpha = \Omega_I$ and $\omega_\beta = -\Omega_J$ are γ_{IJ}^{vo} and γ_{IJ}^{ov}, with

$$\begin{pmatrix}\gamma_{IJ}^{vo}\\ \gamma_{IJ}^{ov}\end{pmatrix} = -\left[\begin{pmatrix}\mathbf{A} & \mathbf{B}\\ \mathbf{B} & \mathbf{A}\end{pmatrix} + \Omega_{JI}\begin{pmatrix}\mathbf{I} & 0\\ 0 & -\mathbf{I}\end{pmatrix}\right]^{-1}\begin{pmatrix}L_{IJ}^{vo}\\ L_{IJ}^{ov}\end{pmatrix}. \quad (93)$$

L_{IJ}^{vo} and L_{IJ}^{ov} are the virt-occ and occ-virt Lagrangians, $L_{IJ}^{vo} = Res[\tilde{L}^{vo}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]$ and $L_{IJ}^{ov} = Res[\tilde{L}^{ov}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]$ (see Appendix B 1 for explicit expressions). Thus, the overall residue of O can be written as

$$\begin{aligned} &Res[O;\Omega_I,-\Omega_J] \\ &= \Big[-\sum_{ija}\left(X_i^{Ia}X_j^{Ja} + Y_j^{Ia}Y_i^{Ja}\right)O_{ij}^{R[Q]} \\ &\quad + \sum_{abj}\left(X_j^{Ib}X_j^{Ja} + Y_j^{Ia}Y_j^{Jb}\right)O_{ab}^{R[Q]} \\ &\quad + \sum_{ja}\left(\gamma_{IJ}^{vo} - \gamma_{IJ}^{ov}\right)_{aj}O_{aj}^{R[Q]}\Big]\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta)}. \quad (94) \end{aligned}$$

C. Final expression for TDDFT derivative couplings

Thus, the total residue for the $(\omega_\alpha+\omega_\beta)$ Fourier transform of the auxiliary couplings obtained from TDDFT is

$$\begin{aligned} &Res[O+\mathcal{XY};\Omega_I,-\Omega_J] \\ &= \Big[\sum_{ja}\left(X_j^{Ia}X_j^{Ja[Q]} - Y_j^{Ia}Y_j^{Ja[Q]}\right) \\ &\quad - \sum_{ija}\left(X_i^{Ia}X_j^{Ja} + Y_j^{Ia}Y_i^{Ja}\right)O_{ij}^{R[Q]} \\ &\quad + \sum_{abj}\left(X_j^{Ib}X_j^{Ja} + Y_j^{Ia}Y_j^{Jb}\right)O_{ab}^{R[Q]} \\ &\quad + \sum_{ja}\left(\gamma_{IJ}^{vo} - \gamma_{IJ}^{ov}\right)_{aj}O_{aj}^{R[Q]}\Big]\mu_{I0}^{(\alpha)}\mu_{0J}^{(\beta)}. \quad (95) \end{aligned}$$

Comparing Eqs. (31) and (95), we can write down the Response Theory derivative coupling between state I and

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state J ($\mathbf{d}_{IJ}^{\mathrm{RT}}$),

$$\begin{aligned}\langle\Psi_I|\Psi_J^{[Q]}\rangle &= \sum_{ia}\left(X_i^{Ia}X_i^{Ja[Q]} - Y_i^{Ia}Y_i^{Ja[Q]}\right)\\ &\quad - \sum_{ija}\left(X_i^{Ia}X_j^{Ja} + Y_j^{Ia}Y_i^{Ja}\right)O_{ij}^{\mathrm{R}[Q]}\\ &\quad + \sum_{abj}\left(X_j^{Ib}X_j^{Ja} + Y_j^{Ia}Y_j^{Jb}\right)O_{ab}^{\mathrm{R}[Q]}\\ &\quad + \sum_{ja}\left(\gamma_{IJ}^{\mathrm{vo}} - \gamma_{IJ}^{\mathrm{ov}}\right)_{aj}O_{aj}^{\mathrm{R}[Q]} \qquad (96)\\ &\equiv \mathbf{d}_{IJ}^{\mathrm{RT}}. \qquad (97)\end{aligned}$$

Comparing $\mathbf{d}_{IJ}^{\mathrm{RT}}$ with our derivative coupling based on a pseudo-wavefunction *ansatz* ($\mathbf{d}_{IJ}^{\mathrm{PW}}$, Eqs. (18) and (24) in Ref. 23), we find that the difference between two approaches is no more than

$$\mathbf{d}_{IJ}^{\mathrm{RT}} = \mathbf{d}_{IJ}^{\mathrm{PW}} + \sum_{ja}\left(\gamma_{IJ}^{\mathrm{vo}} - \gamma_{IJ}^{\mathrm{ov}}\right)_{aj}O_{aj}^{\mathrm{R}[Q]}. \qquad (98)$$

This result agrees with the recent work by Li and Liu.[22] Plugging in the final expression for $\mathbf{d}_{IJ}^{\mathrm{PW}}$ (Eq. (47) in Ref. 23) and the expression of $O_{aj}^{\mathrm{R}[Q]}$ given by Eq. (61), one can write down $\mathbf{d}_{IJ}^{\mathrm{RT}}$ in a finite AO basis as

$$\begin{aligned}&\langle\Psi_I|\Psi_J^{[Q]}\rangle\\ &= \frac{1}{\Omega_{JI}}\Bigg\{\sum_{\mu\nu}D_{\mu\nu}^{IJ}\tilde{h}_{\mu\nu}^{[Q]} + \sum_{\mu\nu\lambda\sigma}\Bigg[\begin{pmatrix}R_{\mu\lambda}^{XI}R_{\sigma\nu}^{XJ} + R_{\mu\lambda}^{YI}R_{\sigma\nu}^{YJ}\\ + R_{\mu\lambda}^{XI}R_{\nu\sigma}^{YJ} + R_{\mu\lambda}^{YI}R_{\nu\sigma}^{XJ}\end{pmatrix}\tilde{G}_{\mu\nu\lambda\sigma}^{[Q]}\\ &\quad + D_{\mu\lambda}^{IJ}P_{\sigma\nu}\Pi_{\mu\nu\lambda\sigma}^{[Q]}\Bigg] - \frac{1}{2}\sum_{\alpha\beta\mu\nu}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}\left(D_{\beta\nu}^{IJ} + D_{\nu\beta}^{IJ}\right)F_{\alpha\beta}\\ &\quad - \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}\begin{pmatrix}R_{\nu\gamma}^{XI}R_{\delta\beta}^{XJ} + R_{\nu\gamma}^{YI}R_{\delta\beta}^{YJ}\\ + R_{\delta\beta}^{XI}R_{\nu\gamma}^{XJ} + R_{\delta\beta}^{YI}R_{\nu\gamma}^{YJ}\\ + R_{\nu\gamma}^{XI}R_{\beta\delta}^{YJ} + R_{\nu\gamma}^{YI}R_{\beta\delta}^{XJ}\\ + R_{\beta\delta}^{XI}R_{\nu\gamma}^{YJ} + R_{\beta\delta}^{YI}R_{\nu\gamma}^{XJ}\end{pmatrix}G_{\alpha\beta\gamma\delta}\\ &\quad - \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}\begin{pmatrix}R_{\nu\gamma}^{XI}R_{\delta\beta}^{XJ} + R_{\nu\gamma}^{YI}R_{\delta\beta}^{YJ}\\ + R_{\delta\beta}^{XI}R_{\nu\gamma}^{XJ} + R_{\delta\beta}^{YI}R_{\nu\gamma}^{YJ}\\ + R_{\nu\gamma}^{XI}R_{\beta\delta}^{YJ} + R_{\nu\gamma}^{YI}R_{\beta\delta}^{XJ}\\ + R_{\beta\delta}^{XI}R_{\nu\gamma}^{YJ} + R_{\beta\delta}^{YI}R_{\nu\gamma}^{XJ}\end{pmatrix}G_{\alpha\beta\gamma\delta}\\ &\quad - \sum_{\mu\nu\alpha\beta\gamma\delta\lambda\sigma}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\lambda}P_{\nu\sigma}\begin{pmatrix}R_{\alpha\gamma}^{XI}R_{\delta\beta}^{XJ} + R_{\alpha\gamma}^{YI}R_{\delta\beta}^{YJ}\\ + R_{\delta\beta}^{XI}R_{\alpha\gamma}^{XJ} + R_{\delta\beta}^{YI}R_{\alpha\gamma}^{YJ}\\ + R_{\alpha\gamma}^{XI}R_{\beta\delta}^{YJ} + R_{\alpha\gamma}^{YI}R_{\beta\delta}^{XJ}\\ + R_{\beta\delta}^{XI}R_{\alpha\gamma}^{YJ} + R_{\beta\delta}^{YI}R_{\alpha\gamma}^{XJ}\end{pmatrix}\frac{\Xi_{\alpha\beta\gamma\delta\lambda\sigma}}{2}\\ &\quad + \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}P_{\nu\delta}\left(D_{\gamma\beta}^{IJ} + D_{\beta\gamma}^{IJ}\right)G_{\alpha\beta\gamma\delta}\Bigg\}\\ &\quad - \sum_{\mu\nu iab}\left(X_i^{Ia}X_i^{Jb} - Y_i^{Ia}Y_i^{Jb}\right)C_{\nu a}C_{\mu b}S_{\mu\nu}^{\mathrm{A}[Q]}\\ &\quad - \sum_{\mu\nu ija}\left(X_i^{Ia}X_j^{Ja} - Y_i^{Ia}Y_j^{Ja}\right)C_{\nu i}C_{\mu j}S_{\mu\nu}^{\mathrm{A}[Q]}\\ &\quad + \sum_{ja}\left(\gamma_{IJ}^{\mathrm{vo}} - \gamma_{IJ}^{\mathrm{ov}}\right)_{aj}\sum_{\mu\nu}C_{\mu a}C_{\nu j}S_{\mu\nu}^{\mathrm{A}[Q]}\\ &\quad - \sum_{ja}\left[\left(\gamma_{IJ}^{\mathrm{vo}} - \gamma_{IJ}^{\mathrm{ov}}\right)_{aj} + \frac{1}{\Omega_{JI}}L_{aj}\right]\Theta_{aj}^{\mathrm{R}[Q]}. \qquad (99)\end{aligned}$$

After simplifying the orbital response (i.e., those terms involving $\Theta_{aj}^{\mathrm{R}[Q]}$ in the last line of Eq. (99); see Appendix B 2 for details), and invoking the "z-vector" trick,[37] the final TDDFT/RPA derivative coupling between state I and state J given by response theory is then

$$\begin{aligned}&\langle\Psi_I|\Psi_J^{[Q]}\rangle\\ &= \frac{1}{\Omega_{JI}}\Bigg\{\sum_{\mu\nu}D_{\mu\nu}^{IJ}\tilde{h}_{\mu\nu}^{[Q]} + \sum_{\mu\nu\lambda\sigma}\Bigg[\begin{pmatrix}R_{\mu\lambda}^{XI}R_{\sigma\nu}^{XJ} + R_{\mu\lambda}^{YI}R_{\sigma\nu}^{YJ}\\ + R_{\mu\lambda}^{XI}R_{\nu\sigma}^{YJ} + R_{\mu\lambda}^{YI}R_{\nu\sigma}^{XJ}\end{pmatrix}\tilde{G}_{\mu\nu\lambda\sigma}^{[Q]}\\ &\quad + D_{\mu\lambda}^{IJ}P_{\sigma\nu}\Pi_{\mu\nu\lambda\sigma}^{[Q]}\Bigg] - \frac{1}{2}\sum_{\alpha\beta\mu\nu}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}\left(D_{\beta\nu}^{IJ} + D_{\nu\beta}^{IJ}\right)F_{\alpha\beta}\\ &\quad - \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}\begin{pmatrix}R_{\nu\gamma}^{XI}R_{\delta\beta}^{XJ} + R_{\nu\gamma}^{YI}R_{\delta\beta}^{YJ}\\ + R_{\delta\beta}^{XI}R_{\nu\gamma}^{XJ} + R_{\delta\beta}^{YI}R_{\nu\gamma}^{YJ}\\ + R_{\nu\gamma}^{XI}R_{\beta\delta}^{YJ} + R_{\nu\gamma}^{YI}R_{\beta\delta}^{XJ}\\ + R_{\beta\delta}^{XI}R_{\nu\gamma}^{YJ} + R_{\beta\delta}^{YI}R_{\nu\gamma}^{XJ}\end{pmatrix}G_{\alpha\beta\gamma\delta}\\ &\quad - \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}\begin{pmatrix}R_{\gamma\nu}^{XI}R_{\beta\delta}^{XJ} + R_{\gamma\nu}^{YI}R_{\beta\delta}^{YJ}\\ + R_{\beta\delta}^{XI}R_{\gamma\nu}^{XJ} + R_{\beta\delta}^{YI}R_{\gamma\nu}^{YJ}\\ + R_{\gamma\nu}^{XI}R_{\beta\delta}^{YJ} + R_{\gamma\nu}^{YI}R_{\beta\delta}^{XJ}\\ + R_{\beta\delta}^{XI}R_{\gamma\nu}^{YJ} + R_{\beta\delta}^{YI}R_{\gamma\nu}^{XJ}\end{pmatrix}G_{\alpha\beta\gamma\delta}\\ &\quad - \sum_{\mu\nu\alpha\beta\gamma\delta\lambda\sigma}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\lambda}P_{\nu\sigma}\begin{pmatrix}R_{\alpha\gamma}^{XI}R_{\delta\beta}^{XJ} + R_{\alpha\gamma}^{YI}R_{\delta\beta}^{YJ}\\ + R_{\delta\beta}^{XI}R_{\alpha\gamma}^{XJ} + R_{\delta\beta}^{YI}R_{\alpha\gamma}^{YJ}\\ + R_{\alpha\gamma}^{XI}R_{\beta\delta}^{YJ} + R_{\alpha\gamma}^{YI}R_{\beta\delta}^{XJ}\\ + R_{\beta\delta}^{XI}R_{\alpha\gamma}^{YJ} + R_{\beta\delta}^{YI}R_{\alpha\gamma}^{XJ}\end{pmatrix}\frac{\Xi_{\alpha\beta\gamma\delta\lambda\sigma}}{2}\\ &\quad + \frac{1}{2}\sum_{\mu\nu\alpha\beta\gamma\delta}S_{\mu\nu}^{[Q]}\tilde{P}_{\mu\alpha}P_{\nu\delta}\left(D_{\gamma\beta}^{IJ} + D_{\beta\gamma}^{IJ}\right)G_{\alpha\beta\gamma\delta}\Bigg\}\\ &\quad - \sum_{\mu\nu iab}\left(X_i^{Ia}X_i^{Jb} - Y_i^{Ia}Y_i^{Jb}\right)C_{\nu a}C_{\mu b}S_{\mu\nu}^{\mathrm{A}[Q]}\\ &\quad - \sum_{\mu\nu ija}\left(X_i^{Ia}X_j^{Ja} - Y_i^{Ia}Y_j^{Ja}\right)C_{\nu i}C_{\mu j}S_{\mu\nu}^{\mathrm{A}[Q]}\\ &\quad + \sum_{ja}\left(\gamma_{IJ}^{\mathrm{vo}} - \gamma_{IJ}^{\mathrm{ov}}\right)_{aj}\sum_{\mu\nu}C_{\mu a}C_{\nu j}S_{\mu\nu}^{\mathrm{A}[Q]}\\ &\quad - \frac{1}{2\Omega_{JI}}\sum_{bi}\left(\gamma_{IJ}^{\mathrm{vo}} + \gamma_{IJ}^{\mathrm{ov}}\right)_{bi}M_{bi}^{[Q]}. \qquad (100)\end{aligned}$$

All terms in Eqs. (99) and (100) are defined in Appendix A. This final expression for $\mathbf{d}_{IJ}^{\mathrm{RT}}$ is very similar to the one for $\mathbf{d}_{IJ}^{\mathrm{PW}}$ except for the orbital response terms and the (rather meaningless) $S_{\mu\nu}^{\mathrm{A}[Q]}$ terms.

D. Spurious poles of the adiabatic TDDFT derivative couplings

Despite the appeal of response theory, a crucial aspect of Eq. (100) is unphysical. Consider again Eq. (92), where we solve for the relaxed part of the second-order density matrix response, $\gamma_{\mathrm{vo}}^{(2)}(\omega_\alpha, \omega_\beta)$ and $\gamma_{\mathrm{ov}}^{(2)}(\omega_\alpha, \omega_\beta)$. Because $\tilde{L}^{\mathrm{vo}}(\omega_\alpha, \omega_\beta)$

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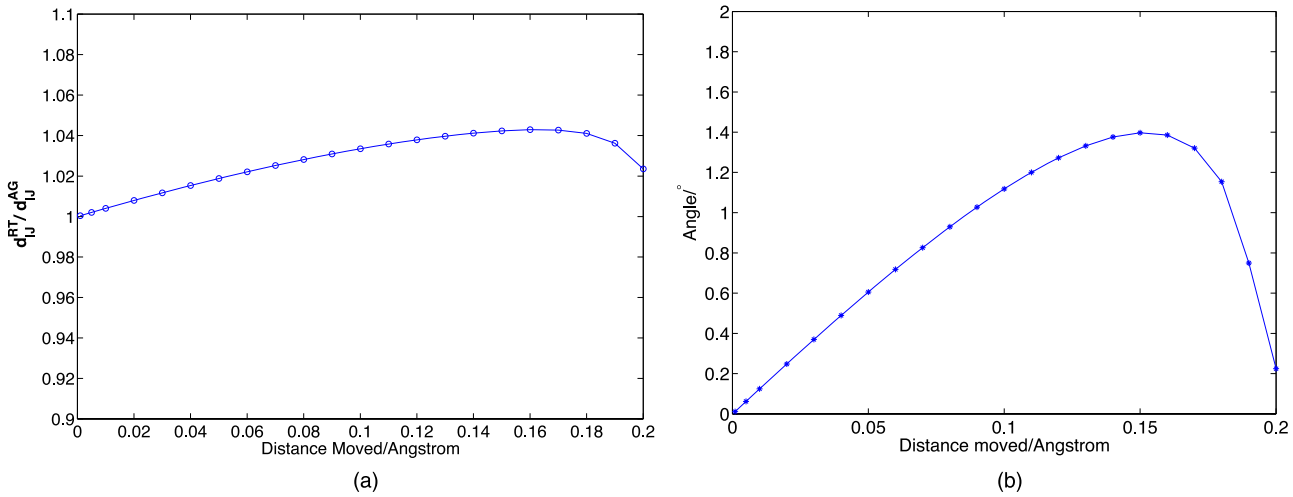


FIG. 2. (a) The norm ratio $\frac{\|\mathbf{d}_{IJ}^{\mathrm{RT}}\|}{\|\mathbf{d}_{IJ}^{\mathrm{PW}}\|}$ and (b) the angle $\frac{\mathbf{d}_{IJ}^{\mathrm{RT}}\cdot\mathbf{d}_{IJ}^{\mathrm{PW}}}{\|\mathbf{d}_{IJ}^{\mathrm{RT}}\|\,\|\mathbf{d}_{IJ}^{\mathrm{PW}}\|}$ between $CH_2NH_2^+$ S_1/S_2 derivative coupling vectors given by a pseudo-wavefunction *ansatz* and response theory at various distances to the CI point.

and $\tilde{L}^{\mathrm{ov}}(\omega_\alpha,\omega_\beta)$ are bilinear in $\tilde{X}_{ja}(\omega_\alpha)$ and $\tilde{Y}_{ja}(\omega_\beta)$ (or some permutations thereof), the pole structure of $\gamma_{\mathrm{vo}}^{(2)}(\omega_\alpha,\omega_\beta)$ (or $\gamma_{\mathrm{ov}}^{(2)}(\omega_\alpha,\omega_\beta)$) is of the form

$$\gamma_{aj}^{(2)}(\omega_\alpha,\omega_\beta) = \sum_{Kbi}\frac{X_j^{Ka}\left[X_i^{Kb}\tilde{L}_{bi}^{\mathrm{vo}}(\omega_\alpha,\omega_\beta)+Y_i^{Kb}\tilde{L}_{bi}^{\mathrm{ov}}(\omega_\alpha,\omega_\beta)\right]}{\Omega_K+\omega_\alpha+\omega_\beta}+\cdots \tag{101}$$

$$= \sum_{IJKbi}\frac{X_j^{Ka}\left[X_i^{Kb}L_{bi}^{\mathrm{vo}}+Y_i^{Kb}L_{bi}^{\mathrm{ov}}\right]}{(\Omega_I-\omega_\alpha)(\Omega_J+\omega_\beta)(\Omega_K+\omega_\alpha+\omega_\beta)}+\cdots, \tag{102}$$

where, again, $L_{IJ}^{\mathrm{vo}} = Res[\tilde{L}^{\mathrm{vo}}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]$ and $L_{IJ}^{\mathrm{ov}} = Res[\tilde{L}^{\mathrm{ov}}(\omega_\alpha,\omega_\beta);\Omega_I,-\Omega_J]$ (see Appendix B 1 for explicit expressions). Thus, for adiabatic TDDFT, $\gamma_{\mathrm{vo}}^{(2)}(\omega_\alpha,\omega_\beta)$ (or $\gamma_{\mathrm{ov}}^{(2)}(\omega_\alpha,\omega_\beta)$) contains products of three poles, which is at variance with the pole structure of the exact time-dependent density response—the latter containing at most products of two poles. The existence of such spurious poles appears to have been recognized previously by Dalgaard[38] in the case of TDHF response theory. We can expect these terms to be problematic when $\pm\Omega_K+\Omega_I-\Omega_J=0$, where Ω_K is any excitation energy; at such a geometry, Eq. (92) cannot be inverted and the interstate transition density matrix will diverge. To see this effect, a numerical example will be given in Sec. III B. Note that Li and Liu independently came to the exact same conclusion in their concurrent paper.[31]

III. NUMERICAL EXAMPLES

A. S_1/S_2 conical intersection of protonated formaldimine

To investigate the derivative couplings ($\mathbf{d}_{IJ}^{\mathrm{RT}}$) derived above, we now study two sample cases: (a) a CI when $\Omega_{JI}\to 0$ and (b) the case of two well separated electronic states ($\Omega_{JI}\gg 0$). In a previous study,[23] we explored the S_1/S_2 derivative coupling of protonated formaldimine ($CH_2NH_2^+$) near its S_1/S_2 CI point and we showed that the derivative coupling vectors obtained from the direct differentiating our pseudo-wavefunction *ansatz* recover all the desired properties along a loop around the CI point: (i) the derivative couplings lie rigorously on the branching plane and are perpendicular to the energy difference gradient direction; (ii) their magnitudes are identical everywhere on the loop in the proper coordinate system; (iii) the path integral gives the Berry's phase. In this work, we will reexamine this molecule as an example to show that the derivative couplings for TDDFT/RPA response theory are identical to those for a pseudo-wavefunction *ansatz* near the CI point.

We numerically implemented Eq. (100) in Q-Chem[39,40] and ωB97X/6-31G** is used to get both $\mathbf{d}_{IJ}^{\mathrm{RT}}$ and $\mathbf{d}_{IJ}^{\mathrm{PW}}$ between S_1 and S_2 of $CH_2NH_2^+$. Taking the **g** direction as an example, we gradually increased the distance moved away from the CI point and computed both derivative couplings at various distances. Then, we compared the norm and the direction for

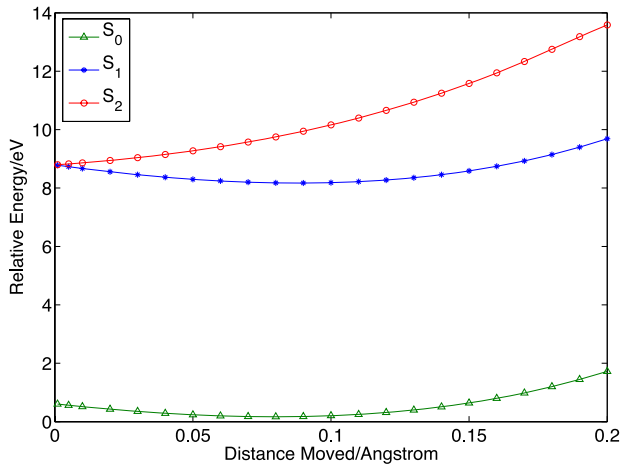


FIG. 3. Relative energies for S_0, S_1, and S_2 states of $CH_2NH_2^+$ versus the distance moved from the CI point.

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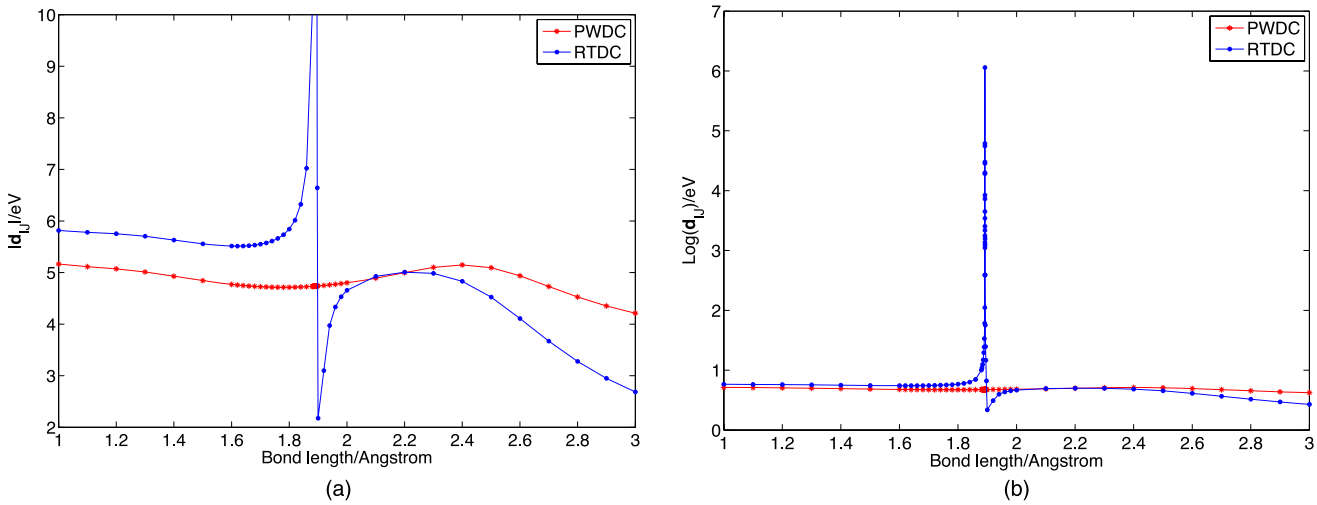


FIG. 4. S_1/S_4 TDHF derivative coupling elements for LiH obtained from a pseudo-wavefunction *ansatz* (PWDC) and response theory (RTDC) as a function of bond length. In (a), we use a linear scale, and in (b), we use a logarithm scale. Note that the two methods basically agree except at 1.9 Å, where RTDC diverges. The absolute value of the derivative coupling with respect to Li_z coordinate is plotted.

two derivative coupling vectors computed at every distance. As shown in Fig. 2, the agreement between the two approaches is very good up to a large distance from the CI point. The relative error for the norm is less than 5% and the angle between two vectors is less than 1.5°. We also plot the S_1/S_2 energy gap with respect to the distance in Fig. 3 for reference. As the distance increased from 0.001 Å to 0.2 Å to the CI point, the energies of S_1 and S_2 become 4 eV separated. Even with such a large energy gap, the derivative couplings given by these two different approaches are just about indistinguishable.

B. S_1/S_4 TDHF derivative coupling of LiH

As we have shown in the previous example, the RPA derivative coupling obtained from the original response theory and our direct differentiation of a pseudo-wavefunction *ansatz* are practically equivalent near a CI point (and pretty far away too).

We now study the opposite case: two well-separated electronic states. LiH is used as the test system and its TDHF S_1/S_4 derivative coupling at different bond lengths is computed with a 6-31G* basis for both approaches. In Fig. 4, we plot the absolute value of the derivative coupling with respect to the z direction of Li atom, using both our direct differentiation of pseudo-wavefunction *ansatz* and response theory. Relative energies of S_0, S_1, and S_4 are plotted in Fig. 5 as reference.

As shown in Fig. 4, when the bond length is increased from 1 Å to 3 Å, both S_1/S_4 TDHF derivative couplings of LiH usually behave similarly. Near 1.9 Å, however, the two couplings behave completely differently. While $\mathbf{d}_{14}^{\mathrm{PW}}$ has a relatively consistent value in this range, $\mathbf{d}_{14}^{\mathrm{RT}}$ changes dramatically in magnitude. This abnormal behavior of $\mathbf{d}_{14}^{\mathrm{RT}}$

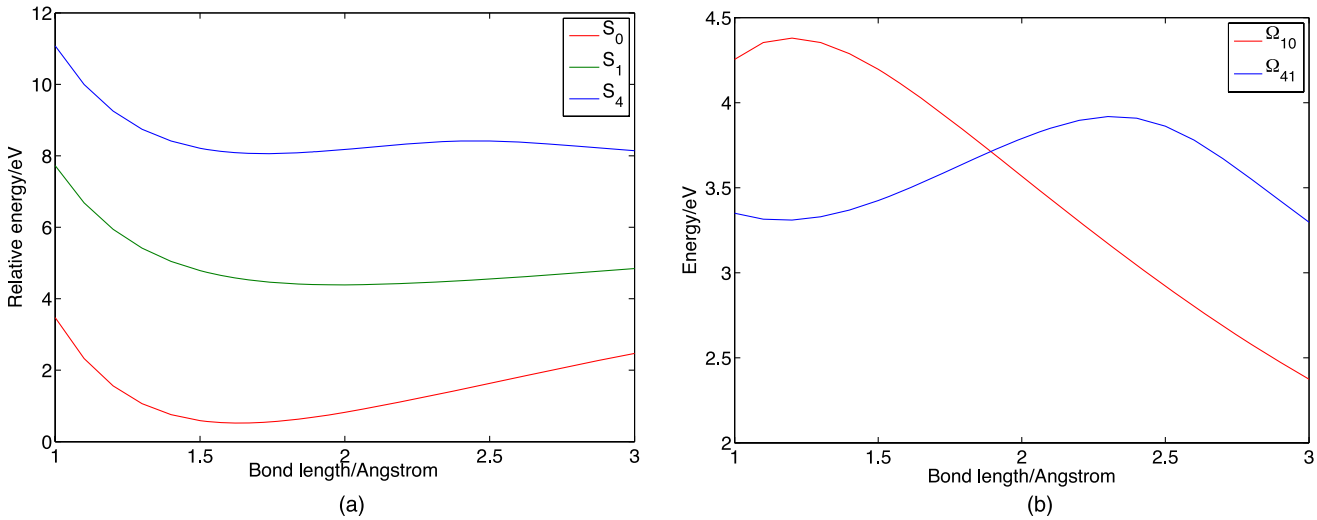


FIG. 5. (a) Relative energies for S_0, S_1, and S_4 states and (b) energy gaps between these three states of LiH as a function of bond length. ($\Omega_{10} = \Omega_1 - \Omega_0$, $\Omega_{41} = \Omega_4 - \Omega_1$.)

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is not hard to explain if we analyze the S_0, S_1, and S_4 relative energies of LiH. As shown in Fig. 5, on the left, the potential energy curves of these three states are smooth and there is no crossing when the bond length changes. However on the right, we plot the two energy gaps, Ω_{10} and Ω_{41}. One can see that the two energy gaps cross when the bond length ≈1.9 Å, which is exactly the case where the derivative coupling from response theory is expected to be unphysical.

IV. CONCLUSION

In this paper, we have presented a detailed derivation for the RPA derivative couplings based on response theory. The final expression has been implemented in Q-Chem, and we have compared the resulting derivative couplings with those based on a pseudo-wavefunction *ansatz* (as obtained in our previous studies[41,23]). For small energy gaps between the two excited states, i.e., close to a CI, both sets of derivative couplings are identical up to an antisymmetric overlap term, see Appendix B 2.

However, when the energy difference between two excited states equals the excitation energy of a third excited state, the derivative couplings from adiabatic TDDFT response theory exhibit a spurious pole. This unphysical behavior appears to be a consequence of an incorrect pole structure of quadratic and higher-order frequency dependent response properties within the adiabatic approximation,[8] which neglects frequency dependence in the XC kernel and its derivatives. This incorrect analytical behavior also calls into question the validity of the adiabatic approximation for other non-linear response properties such as state-to-state transition moments and even non-linear polarizabilities. For TDHF response theory, which has the same analytical structure as adiabatic TDDFT, this problem has been discussed before,[38] but its consequences for excited-state properties appear to have been largely ignored. Li and Liu have independently come to the same realization.[31]

An important conclusion of this work is thus that the adiabatic approximation of TDDFT is less robust for higher-order non-linear response properties than it has been generally assumed. The development of practical frequency-dependent XC kernels beyond the adiabatic approximation is also essential for states with double excitation character.[42]

A remedy of the spurious divergence is to evaluate the relaxed part of the transition density matrix at frequency zero instead of Ω_{JI} in Eq. (B10). This is exact at a CI, where the couplings are largest, and recovers the previously proposed pseudo-wavefunction approximation up to an antisymmetric overlap term. Thus, in the absence of better XC kernels, the pseudo-wavefunction approximation to the couplings may be the best available option for computing excited state to excited state couplings in a TDDFT framework.

ACKNOWLEDGMENTS

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APPENDIX A: DEFINITIONS FOR TERMS IN EQ. (100)

The final expression for response theory derivative couplings that we implemented and used throughout this paper is Eq. (100),

$$
\begin{aligned}
&\langle \Psi_I | \Psi_J^{[Q]} \rangle \\
&= \frac{1}{\Omega_{JI}} \Bigg\{ \sum_{\mu\nu} D_{\mu\nu}^{IJ} \tilde{h}_{\mu\nu}^{[Q]} + \sum_{\mu\nu\lambda\sigma} \Bigg[\begin{pmatrix} R_{\mu\lambda}^{XI} R_{\sigma\nu}^{XJ} + R_{\mu\lambda}^{YI} R_{\sigma\nu}^{YJ} \\ + R_{\mu\lambda}^{XI} R_{\nu\sigma}^{YJ} + R_{\mu\lambda}^{YI} R_{\nu\sigma}^{XJ} \end{pmatrix} \tilde{G}_{\mu\nu\lambda\sigma}^{[Q]} \\
&\quad + D_{\mu\lambda}^{IJ} P_{\sigma\nu} \Pi_{\mu\nu\lambda\sigma}^{[Q]} \Bigg] - \frac{1}{2} \sum_{\alpha\beta\mu\nu} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} \left(D_{\beta\nu}^{IJ} + D_{\nu\beta}^{IJ} \right) F_{\alpha\beta} \\
&\quad - \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} \begin{pmatrix} R_{\nu\gamma}^{XI} R_{\delta\beta}^{XJ} + R_{\nu\gamma}^{YI} R_{\delta\beta}^{YJ} \\ + R_{\delta\beta}^{XI} R_{\nu\gamma}^{XJ} + R_{\delta\beta}^{YI} R_{\nu\gamma}^{YJ} \\ + R_{\nu\gamma}^{XI} R_{\beta\delta}^{XJ} + R_{\nu\gamma}^{YI} R_{\beta\delta}^{XJ} \\ + R_{\beta\delta}^{XI} R_{\nu\gamma}^{YJ} + R_{\beta\delta}^{YI} R_{\nu\gamma}^{XJ} \end{pmatrix} G_{\alpha\beta\gamma\delta} \\
&\quad - \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} \begin{pmatrix} R_{\gamma\nu}^{XI} R_{\beta\delta}^{XJ} + R_{\gamma\nu}^{YI} R_{\beta\delta}^{YJ} \\ + R_{\beta\delta}^{XI} R_{\gamma\nu}^{XJ} + R_{\beta\delta}^{YI} R_{\gamma\nu}^{YJ} \\ + R_{\gamma\nu}^{XI} R_{\delta\beta}^{XJ} + R_{\gamma\nu}^{YI} R_{\delta\beta}^{XJ} \\ + R_{\delta\beta}^{XI} R_{\gamma\nu}^{YJ} + R_{\delta\beta}^{YI} R_{\gamma\nu}^{XJ} \end{pmatrix} G_{\alpha\beta\gamma\delta} \\
&\quad - \sum_{\mu\nu\alpha\beta\gamma\delta\lambda\sigma} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\lambda} P_{\nu\sigma} \begin{pmatrix} R_{\alpha\gamma}^{XI} R_{\delta\beta}^{XJ} + R_{\alpha\gamma}^{YI} R_{\delta\beta}^{YJ} \\ + R_{\delta\beta}^{XI} R_{\alpha\gamma}^{XJ} + R_{\delta\beta}^{YI} R_{\alpha\gamma}^{YJ} \\ + R_{\alpha\gamma}^{XI} R_{\beta\delta}^{YJ} + R_{\alpha\gamma}^{YI} R_{\beta\delta}^{XJ} \\ + R_{\beta\delta}^{XI} R_{\alpha\gamma}^{YJ} + R_{\beta\delta}^{YI} R_{\alpha\gamma}^{XJ} \end{pmatrix} \frac{\Xi_{\alpha\beta\gamma\delta\lambda\sigma}}{2} \\
&\quad + \frac{1}{2} \sum_{\mu\nu\alpha\beta\gamma\delta} S_{\mu\nu}^{[Q]} \tilde{P}_{\mu\alpha} P_{\nu\delta} \left(D_{\gamma\beta}^{IJ} + D_{\beta\gamma}^{IJ} \right) \\
&\quad \times G_{\alpha\beta\gamma\delta} - \frac{1}{2} \sum_{bi} (\gamma_{IJ}^{\mathrm{vo}} + \gamma_{IJ}^{\mathrm{ov}})_{bi} M_{bi}^{[Q]} \Bigg\} \\
&\quad - \sum_{\mu\nu iab} (X_i^{Ia} X_i^{Jb} - Y_i^{Ia} Y_i^{Jb}) C_{\nu a} C_{\mu b} S_{\mu\nu}^{\mathrm{A}[Q]} \\
&\quad - \sum_{\mu\nu ija} \left(X_i^{Ia} X_j^{Ja} - Y_i^{Ia} Y_j^{Ja} \right) C_{\nu i} C_{\mu j} S_{\mu\nu}^{\mathrm{A}[Q]} \\
&\quad + \sum_{ja} \left(\gamma_{IJ}^{\mathrm{vo}} - \gamma_{IJ}^{\mathrm{ov}} \right)_{aj} \sum_{\mu\nu} C_{\mu a} C_{\nu j} S_{\mu\nu}^{\mathrm{A}[Q]}. \qquad \text{(A1)}
\end{aligned}
$$

Terms in the above equation are defined as follows.

1. One- and two-electron integrals
   (a) Total one-electron integral

$$h_{pq} = h_{pq}^0 + g_{pq}, \qquad \text{(A2)}$$

where h_{pq}^0 is the matrix element of the kinetic energy plus the external potential (Eq. (A3)) and g_{pq} is the first derivative of the XC energy functional $E_{xc} = \int d\mathbf{r} f_{xc}(\mathbf{r})$[29] (Eq. (A4)),

$$h_{pq}^0 \equiv \langle \phi_p | h^0 \phi_q \rangle, \qquad \text{(A3)}$$

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$$g_{pq} \equiv \sum_{pq} \int d\mathbf{r} \phi_p(\mathbf{r}) \frac{\partial f_{xc}}{\partial \rho(\mathbf{r})} \phi_q(\mathbf{r}). \tag{A4}$$

(b) Total two-electron integral

$$G_{pqsr} = \Pi_{pqsr} + f_{pqsr}, \tag{A5}$$

where Π_{pqsr} is the Coulomb term plus whatever fraction of Hartree-Fock exchange is included in the DFT functional (c_{HF} in Eq. (A6)), and f_{pqsr} is the second derivative of the XC functional (Eq. (A6))

$$\Pi_{pqsr} \equiv \langle \phi_p \phi_q | \phi_s \phi_r \rangle - c_{\mathrm{HF}} \langle \phi_p \phi_q | \phi_r \phi_s \rangle, \tag{A6}$$

$$\begin{aligned} f_{pqsr} &\equiv \langle \phi_p \phi_q | f''_{xc} | \phi_s \phi_r \rangle \\ &= \sum_{pqsr} \int d\mathbf{r} \phi_p(\mathbf{r}) \phi_q(\mathbf{r}) \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} \phi_r(\mathbf{r}) \phi_s(\mathbf{r}). \end{aligned} \tag{A7}$$

2. Density matrices

(a) The general density matrices

$$P_{\mu\nu} = \sum_m C_{\mu m} C_{\nu m}, \tag{A8}$$

$$\tilde{P}_{\mu\nu} = \sum_p C_{\mu p} C_{\nu p} = P_{\mu\nu} + \sum_a C_{\mu a} C_{\nu a}. \tag{A9}$$

Note that we may express the real-space density as $\rho(\mathbf{r}) = P_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r})$.

(b) The RPA excitation-amplitude matrices

$$R^{XI}_{\mu\nu} = \sum_{ia} C_{\mu a} X^{Ia}_i C_{\nu i}, \tag{A10}$$

$$R^{YI}_{\mu\nu} = \sum_{ia} C_{\mu a} Y^{Ia}_i C_{\nu i}. \tag{A11}$$

(c) The generalized difference-density matrix

$$\begin{aligned} D^{IJ}_{\mu\nu} = &\sum_{iab} C_{\mu a} (X^{Ia}_i X^{Jb}_i + Y^{Ja}_i Y^{Ib}_i) C_{\nu b} \\ &- \sum_{ija} C_{\mu i} (X^{Ja}_i X^{Ia}_j + Y^{Ia}_i Y^{Ja}_j) C_{\nu j}. \end{aligned} \tag{A12}$$

3. Derivative terms

(a) One-electron-integral derivatives

The first derivative of the XC functional $\mathbf{g}^{[Q]}$ is defined as

$$g^{[Q]}_{\mu\nu} \equiv \tilde{g}^{[Q]}_{\mu\nu} + g^{\mathrm{Y}[Q]}_{\mu\nu}, \tag{A13}$$

where

$$\begin{aligned} \tilde{g}^{[Q]}_{\mu\nu} \equiv &\int^{[Q]} d\mathbf{r} \phi_\mu(\mathbf{r}) \frac{\partial f_{xc}}{\partial \rho(\mathbf{r})} \phi_\nu(\mathbf{r}) \\ &+ \int d\mathbf{r} \frac{\partial f_{xc}}{\partial \rho(\mathbf{r})} (\phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}))^{[Q]} \\ &+ \sum_{\lambda\sigma} \int d\mathbf{r} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} \\ &\times P_{\lambda\sigma} (\phi_\lambda(\mathbf{r}) \phi_\sigma(\mathbf{r}))^{[Q]}, \end{aligned} \tag{A14}$$

$$g^{\mathrm{Y}[Q]}_{\mu\nu} \equiv \sum_{\lambda\sigma} P^{[Q]}_{\lambda\sigma} f_{\mu\nu\lambda\sigma}. \tag{A15}$$

Here, $\int^Q$ denotes differentiation with respect to Becke weights.

The total one-electron-integral derivative for TDDFT can be written as

$$\begin{aligned} h^{[Q]}_{\mu\nu} &= h^{0[Q]}_{\mu\nu} + g^{[Q]}_{\mu\nu} \\ &= h^{0[Q]}_{\mu\nu} + \tilde{g}^{[Q]}_{\mu\nu} + g^{\mathrm{Y}[Q]}_{\mu\nu} \\ &\equiv \tilde{h}^{[Q]}_{\mu\nu} + g^{\mathrm{Y}[Q]}_{\mu\nu}. \end{aligned} \tag{A16}$$

(b) Two-electron-integral derivatives

The second derivative of the XC functional $f^{[Q]}$ is defined as

$$f^{[Q]}_{\mu\nu\lambda\sigma} = \tilde{f}^{[Q]}_{\mu\nu\lambda\sigma} + f^{\mathrm{Y}[Q]}_{\mu\nu\lambda\sigma}, \tag{A17}$$

where

$$\begin{aligned} \tilde{f}^{[Q]}_{\mu\nu\lambda\sigma} \equiv &\int^{[Q]} d\mathbf{r} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} \phi_\lambda(\mathbf{r}) \phi_\sigma(\mathbf{r}) \\ &+ \int d\mathbf{r} (\phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}))^{[Q]} \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} \phi_\lambda(\mathbf{r}) \phi_\sigma(\mathbf{r}) \\ &+ \int d\mathbf{r} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{\partial^2 f_{xc}}{\partial \rho(\mathbf{r})^2} (\phi_\lambda(\mathbf{r}) \phi_\sigma(\mathbf{r}))^{[Q]} \\ &+ \sum_{\gamma\delta} \int d\mathbf{r} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{\partial^3 f_{xc}}{\partial \rho(\mathbf{r})^3} \phi_\lambda(\mathbf{r}) \\ &\times \phi_\sigma(\mathbf{r}) P_{\gamma\delta} (\phi_\gamma(\mathbf{r}) \phi_\delta(\mathbf{r}))^{[Q]}, \end{aligned} \tag{A18}$$

$$f^{\mathrm{Y}[Q]}_{\mu\nu\lambda\sigma} \equiv \sum_{\gamma\delta} P^{[Q]}_{\gamma\delta} \Xi_{\mu\nu\lambda\sigma\gamma\delta}, \tag{A19}$$

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

$$\begin{aligned} \Xi_{\mu\nu\lambda\sigma\gamma\delta} \equiv &\int d\mathbf{r} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) \frac{\partial^3 f_{xc}}{\partial \rho(\mathbf{r})^3} \\ &\times \phi_\lambda(\mathbf{r}) \phi_\sigma(\mathbf{r}) \phi_\gamma(\mathbf{r}) \phi_\delta(\mathbf{r}). \end{aligned} \tag{A20}$$

The total two-electron-integral derivative for TDDFT can be written as

$$\begin{aligned} G^{[Q]}_{\mu\nu\lambda\sigma} &= \Pi^{[Q]}_{\mu\nu\lambda\sigma} + f^{[Q]}_{\mu\nu\lambda\sigma} \\ &= \Pi^{[Q]}_{\mu\nu\lambda\sigma} + \tilde{f}^{[Q]}_{\mu\nu\lambda\sigma} + f^{\mathrm{Y}[Q]}_{\mu\nu\lambda\sigma} \\ &\equiv \tilde{G}^{[Q]}_{\mu\nu\lambda\sigma} + \sum_{\gamma\delta} P^{[Q]}_{\gamma\delta} \Xi_{\mu\nu\lambda\sigma\gamma\delta}. \end{aligned} \tag{A21}$$

(c) The mixed derivative $M^{[Q]}_{bi}$

$$\begin{aligned} M^{[Q]}_{bi} \equiv &\sum_{\mu\nu} \left(\frac{\partial^2 E}{\partial \Theta_{bi} \partial h_{\mu\nu}} h^{[Q]}_{\mu\nu} + \frac{\partial^2 E}{\partial \Theta_{bi} \partial S_{\mu\nu}} S^{[Q]}_{\mu\nu} \right) \\ &+ \sum_{\mu\nu\lambda\sigma} \frac{\partial^2 E}{\partial \Theta_{bi} \partial \Pi_{\mu\nu\lambda\sigma}} G^{[Q]}_{\mu\nu\lambda\sigma} \\ = &- \sum_{\mu\nu} (C_{\mu b} C_{\nu i} + C_{\mu i} C_{\nu b}) h^{[Q]}_{\mu\nu} \\ &- (C_{\mu b} P_{\nu\sigma} C_{\lambda i} + C_{\mu i} P_{\nu\sigma} C_{\lambda b}) G^{[Q]}_{\mu\nu\lambda\sigma} \\ &+ \sum_{\mu\nu} [\varepsilon_b C_{\mu b} C_{\nu i} + \varepsilon_i C_{\mu i} C_{\nu b} \\ &+ \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \Pi_{\alpha\beta\gamma\delta} (\tilde{P}_{\beta\mu} P_{\delta\nu} + \tilde{P}_{\beta\nu} P_{\delta\mu}) \\ &\times (C_{\alpha b} C_{\gamma i} + C_{\alpha i} C_{\gamma b})] S^{[Q]}_{\mu\nu}. \end{aligned} \tag{A22}$$

(A23)

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APPENDIX B: ORBITAL RESPONSE

1. Definition of Lagrangians

According to Ref. 33, $\tilde{L}^{\mathrm{vo}}(\omega_\alpha,\omega_\beta)$ and $\tilde{L}^{\mathrm{ov}}(\omega_\alpha,\omega_\beta)$ can be expressed as

$$\begin{aligned}\tilde{L}^{\mathrm{vo}}_{bi}(\omega_\alpha,\omega_\beta) &= \sum_{adj}\Big[\big(\tilde{X}_{id}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{id}(\omega_\beta)\big)G_{abjd}+\big(\tilde{X}_{id}(\omega_\alpha)\tilde{X}_{ja}(\omega_\beta)+\tilde{X}_{ja}(\omega_\alpha)\tilde{X}_{id}(\omega_\beta)\big)G_{adjb}\Big]\\ &-\sum_{ajl}\Big[\big(\tilde{X}_{lb}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{lb}(\omega_\beta)\big)G_{alji}+\big(\tilde{X}_{lb}(\omega_\alpha)\tilde{X}_{ja}(\omega_\beta)+\tilde{X}_{ja}(\omega_\alpha)X_{lb}(\omega_\beta)\big)G_{aijl}\Big]\\ &+\sum_{adjl}\Big[\big(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{ld}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{ld}(\omega_\beta)\big)\Xi_{aljdbi}+\big(\tilde{X}_{ja}(\omega_\alpha)\tilde{X}_{ld}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{Y}_{ld}(\omega_\beta)\big)\Xi_{adjlbi}\Big]\\ &+\sum_{adj}\big(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{jd}(\omega_\beta)+\tilde{Y}_{jd}(\omega_\alpha)\tilde{X}_{ja}(\omega_\beta)\big)G_{abdi}-\sum_{ajl}\big(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{la}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{la}(\omega_\beta)\big)G_{jbli},\end{aligned}\tag{B1}$$

$$\begin{aligned}\tilde{L}^{\mathrm{ov}}_{bi}(\omega_\alpha,\omega_\beta) &= \sum_{adj}\Big[\big(\tilde{Y}_{id}(\omega_\alpha)\tilde{X}_{ja}(\omega_\beta)+\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{id}(\omega_\beta)\big)G_{abjd}+\big(\tilde{Y}_{id}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{Y}_{id}(\omega_\beta)\big)G_{adjb}\Big]\\ &-\sum_{ajl}\Big[\big(\tilde{Y}_{lb}(\omega_\alpha)\tilde{X}_{ja}(\omega_\beta)+\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{lb}(\omega_\beta)\big)G_{alji}+\big(\tilde{Y}_{lb}(\omega_\alpha)\tilde{Y}_{ja}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)Y_{lb}(\omega_\beta)\big)G_{aijl}\Big]\\ &+\sum_{adjl}\Big[\big(\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{ld}(\omega_\beta)+\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{ld}(\omega_\beta)\big)\Xi_{aljdbi}+\big(\tilde{Y}_{ja}(\omega_\alpha)\tilde{Y}_{ld}(\omega_\beta)+\tilde{X}_{ja}(\omega_\alpha)\tilde{X}_{ld}(\omega_\beta)\big)\Xi_{adjlbi}\Big]\\ &+\sum_{adj}\big(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{jd}(\omega_\beta)+\tilde{Y}_{jd}(\omega_\alpha)\tilde{X}_{ja}(\omega_\beta)\big)G_{dbai}-\sum_{ajl}\big(\tilde{X}_{ja}(\omega_\alpha)\tilde{Y}_{la}(\omega_\beta)+\tilde{Y}_{ja}(\omega_\alpha)\tilde{X}_{la}(\omega_\beta)\big)G_{lbji}.\end{aligned}\tag{B2}$$

L^{ov}_{IJ} and L^{vo}_{IJ} are obtained by evaluating the residues of $\tilde{L}^{\mathrm{vo}}(\omega_\alpha,\omega_\beta)$ and $\tilde{L}^{\mathrm{ov}}(\omega_\alpha,\omega_\beta)$ at $\omega_\alpha=\Omega_I$ and $\omega_\beta=-\Omega_J$. In the AO basis, L^{ov}_{IJ} and L^{vo}_{IJ} can be expressed as

$$\begin{aligned}L^{\mathrm{vo}}_{bi} &= \sum_{\mu\nu\lambda\sigma d}C_{\mu b}C_{\lambda d}\begin{pmatrix}R^{XI}_{\sigma\nu}X^{Jd}_i+R^{YJ}_{\sigma\nu}Y^{Id}_i\\ +X^{Jd}_i R^{YI}_{\nu\sigma}+Y^{Id}_i R^{XJ}_{\nu\sigma}\end{pmatrix}G_{\mu\nu\lambda\sigma}\\ &-\sum_{\mu\nu\lambda\sigma\ell}C_{\mu\ell}C_{\lambda i}\begin{pmatrix}R^{XI}_{\sigma\nu}X^{Jb}_\ell+R^{YJ}_{\sigma\nu}Y^{Ib}_\ell\\ +X^{Jb}_\ell R^{YI}_{\nu\sigma}+Y^{Ib}_\ell R^{XJ}_{\nu\sigma}\end{pmatrix}G_{\mu\nu\lambda\sigma}\\ &+\sum_{\mu\nu\lambda\sigma\gamma\delta}C_{\gamma b}C_{\delta i}\begin{pmatrix}R^{XI}_{\mu\lambda}R^{XJ}_{\sigma\nu}+R^{YI}_{\mu\lambda}R^{YJ}_{\sigma\nu}\\ +R^{XI}_{\nu\sigma}R^{YJ}_{\mu\lambda}+R^{YI}_{\nu\sigma}R^{XJ}_{\mu\lambda}\end{pmatrix}\Xi_{\mu\nu\lambda\sigma\gamma\delta}\\ &+\sum_{\mu\nu\lambda\sigma}C_{\nu b}C_{\sigma i}D^{IJ}_{\mu\lambda}G_{\mu\nu\lambda\sigma},\end{aligned}\tag{B3}$$

$$\begin{aligned}L^{\mathrm{ov}}_{bi} &= \sum_{\mu\nu\lambda\sigma d}C_{\mu b}C_{\lambda d}\begin{pmatrix}R^{XJ}_{\sigma\nu}X^{Id}_i+R^{YI}_{\sigma\nu}Y^{Jd}_i\\ +X^{Id}_i R^{YJ}_{\nu\sigma}+Y^{Jd}_i R^{XI}_{\nu\sigma}\end{pmatrix}G_{\mu\nu\lambda\sigma}\\ &-\sum_{\mu\nu\lambda\sigma\ell}C_{\mu\ell}C_{\lambda i}\begin{pmatrix}R^{XJ}_{\sigma\nu}X^{Ib}_\ell+R^{YI}_{\sigma\nu}Y^{Jb}_\ell\\ +X^{Ib}_\ell R^{YJ}_{\nu\sigma}+Y^{Jb}_\ell R^{XI}_{\nu\sigma}\end{pmatrix}G_{\mu\nu\lambda\sigma}\\ &+\sum_{\mu\nu\lambda\sigma\gamma\delta}C_{\gamma b}C_{\delta i}\begin{pmatrix}R^{XI}_{\sigma\nu}R^{XJ}_{\mu\lambda}+R^{YI}_{\sigma\nu}R^{YJ}_{\mu\lambda}\\ +R^{XI}_{\mu\lambda}R^{YJ}_{\nu\sigma}+R^{YI}_{\mu\lambda}R^{XJ}_{\nu\sigma}\end{pmatrix}\Xi_{\mu\nu\lambda\sigma\gamma\delta}\\ &+\sum_{\mu\nu\lambda\sigma}C_{\nu b}C_{\sigma i}D^{IJ}_{\lambda\mu}\Omega_{\mu\nu\lambda\sigma}.\end{aligned}\tag{B4}$$

Finally, we can define a total Lagrangian $L_{bi}\equiv L^{\mathrm{ov}}_{bi}+L^{\mathrm{vo}}_{bi}$.

2. Behavior near a CI

In Ref. 23, we showed that derivative couplings constructed from our pseudo-wavefunction *ansatz* are consistent with the Chernyak-Mukamel equality and time-dependent response theory near an excited crossing in the limit of an infinite atomic orbital basis.[41,23,12] In this subsection, we show that this consistency survives in a finite basis. The key observation is that the only meaningful difference between $\mathbf{d}^{\mathrm{PW}}_{IJ}$ and $\mathbf{d}^{\mathrm{RT}}_{IJ}$ comes from orbital response terms.

a. The orbital response in the pseudo-wavefunction derivative coupling

According to Eqs. (47) and (48) in Ref. 23, the orbital response in $\mathbf{d}^{\mathrm{PW}}_{IJ}$ is

$$-\frac{1}{\Omega_{JI}}\sum_{bi}L_{bi}\Theta^{[Q]}_{bi}=-\frac{1}{\Omega_{JI}}\sum_{bi}(L^{vo}_{bi}+L^{ov}_{bi})\Theta^{[Q]}_{bi}.\tag{B5}$$

This term can be simplified via the coupled-perturbed Hartree Fock (CPHF) equation

$$\Theta^{[Q]}_{aj}=-\sum_{aj}\left(\frac{\partial^2 E}{\partial\Theta_{bi}\partial\Theta_{aj}}\right)^{-1}M^{[Q]}_{bi}\tag{B6}$$

$$=-\frac{1}{2}\sum_{aj}(A+B)^{-1}_{jaib}M^{[Q]}_{bi},\tag{B7}$$

where $M^{[Q]}_{aj}$ refers to the mixed derivative terms (Eq. (A22)). The orbital response in $\mathbf{d}^{\mathrm{PW}}_{IJ}$ finally becomes

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$$-\frac{1}{\Omega_{JI}}\sum_{bi}L_{bi}\Theta_{bi}^{[Q]}=\frac{1}{2\Omega_{JI}}\sum_{jaib}(A+B)^{-1}_{jaib}L_{bi}M_{bi}^{[Q]}. \quad \text{(B8)}$$

b. The orbital response from derivative couplings according to response theory

According to Eq. (99), the orbital response in $\mathbf{d}_{IJ}^{\mathrm{RT}}$ is

$$-\sum_{aj}\left[\left(\gamma_{IJ}^{\mathrm{vo}}-\gamma_{IJ}^{\mathrm{ov}}\right)_{aj}+\frac{1}{\Omega_{JI}}L_{aj}\right]\Theta_{aj}^{\mathrm{R}[Q]}. \quad \text{(B9)}$$

Here, $L_{aj}=L_{aj}^{\mathrm{ov}}+L_{aj}^{\mathrm{vo}}$. $\gamma_{IJ}^{\mathrm{vo}}$ and $\gamma_{IJ}^{\mathrm{ov}}$ are given by

$$\begin{pmatrix}\gamma_{IJ}^{\mathrm{vo}}\\ \gamma_{IJ}^{\mathrm{ov}}\end{pmatrix}=-\left[\begin{pmatrix}\mathbf{A}&\mathbf{B}\\ \mathbf{B}&\mathbf{A}\end{pmatrix}+\Omega_{JI}\begin{pmatrix}\mathbf{I}&0\\ 0&-\mathbf{I}\end{pmatrix}\right]^{-1}\begin{pmatrix}L_{IJ}^{\mathrm{vo}}\\ L_{IJ}^{\mathrm{ov}}\end{pmatrix}, \quad \text{(B10)}$$

and one has

$$\gamma_{IJ}^{\mathrm{vo}}-\gamma_{IJ}^{\mathrm{ov}}=-\frac{1}{\Omega_{JI}}\left[(\mathbf{A}+\mathbf{B})(\gamma_{IJ}^{\mathrm{vo}}+\gamma_{IJ}^{\mathrm{ov}})+(L^{\mathrm{vo}}+L^{\mathrm{ov}})\right]. \quad \text{(B11)}$$

If we substitute Eq. (B11) into Eq. (B9), we find that all L terms are canceled. The orbital response in $\mathbf{d}_{IJ}^{\mathrm{RT}}$ can thus be rewritten as

$$\sum_{jaib}\frac{1}{\Omega_{JI}}(A+B)_{jaib}(\gamma_{IJ}^{\mathrm{vo}}+\gamma_{IJ}^{\mathrm{ov}})_{bi}\Theta_{aj}^{[Q]}. \quad \text{(B12)}$$

After applying the CPHF equation (Eq. (B7)), the final expression of the orbital response in $\mathbf{d}_{IJ}^{\mathrm{RT}}$ becomes

$$\sum_{jaib}\frac{1}{\Omega_{JI}}(A+B)_{jaib}(\gamma_{IJ}^{\mathrm{vo}}+\gamma_{IJ}^{\mathrm{ov}})_{bi}\Theta_{aj}^{[Q]}=-\frac{1}{2\Omega_{JI}}\sum_{bi}(\gamma_{IJ}^{\mathrm{vo}}+\gamma_{IJ}^{\mathrm{ov}})_{bi}M_{bi}^{[Q]}. \quad \text{(B13)}$$

c. Equivalence near a CI point

According to Eq. (B10), in the limit of $\Omega_{JI}\to 0$ (i.e., at a CI point), one has

$$\left(\gamma_{IJ}^{\mathrm{vo}}+\gamma_{IJ}^{\mathrm{ov}}\right)=-(\mathbf{A}+\mathbf{B})^{-1}\left(L_{IJ}^{\mathrm{vo}}+L_{IJ}^{\mathrm{ov}}\right)=-(\mathbf{A}+\mathbf{B})^{-1}L. \quad \text{(B14)}$$

Referring to Eqs. (B13) and (B8), one finds that under such a condition, the orbital responses in $\mathbf{d}_{IJ}^{\mathrm{RT}}$ become exactly the same as the one in $\mathbf{d}_{IJ}^{\mathrm{PW}}$. Therefore at a CI point, $\mathbf{d}_{IJ}^{\mathrm{RT}}$ is equivalent to $\mathbf{d}_{IJ}^{\mathrm{PW}}$ up to a factor of $\mathbf{S}^{\mathrm{A}[Q]}$ (which can be ignored when applying electron-translation factors[35]). This proves the equivalence we hypothesized.

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