Excited-state response theory within the context of the coupled-cluster formalism

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Time-dependent response theories are foundational to the development of algorithms that determine quantum properties of electronic excited states of molecules and periodic systems. They are employed in wave-function, density-functional, and semiempirical methods and are applied in an incremental order: linear, quadratic, cubic, etc. Linear response theory is known to produce electronic transitions from ground to excited state, and vice versa. In this work, a linear response approach, within the context of the coupled-cluster formalism, is developed to offer transition elements between different excited states (including permanent elements) and related properties. Our formalism, second linear response theory, is consistent with quadratic response theory and can serve as an alternative to develop and study excited-state theoretical methods, including pathways for algorithmic acceleration. This work also formulates an extension of our theory for general propagations under nonlinear external perturbations, where the observables are given by linked expressions which can predict their time evolution under arbitrary initial states and could serve as a means of constructing general state propagators. A connection with the physics of wave-function theory is developed as well, in which dynamical cluster operator amplitudes are related to wave-function linear superposition coefficients.

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I. INTRODUCTION

Predicting the dynamics of electronic quantum systems, and ensembles of these, is a primary goal in theoretical science for the understanding and discovery of cutting-edge physical and chemical effects [1–3]. Without demanding parameters besides the fundamental physical constants, quantum mechanics (QM) provides all the necessary tools to determine all quantities needed for the theoretical modeling of quantum phenomena. This has led to the development of theoretical methods and algorithms that compute observables connected to excited states, including the development of quantum [4–8] and machine-learning [3,9–12] technologies. Such algorithms are often based on wave function theory or density functional theory, but they could also rely on semiempirical theory, depending on their foundation their range of application varies. There is a growing interest by the scientific community in excited-state phenomena linked to quantum information science [13–16], quantum light emission and absorption [17–23], cavity quantum dynamics [24], and multiphoton processes [25]. Hence, quantum methods to compute properties connected to the modeling and understanding of these phenomena can benefit from advanced theoretical tools.

Because of their useful accuracy and their relatively modest computational power requirements, algorithms based on linear response (LR) time-dependent density functional theory (TDDFT) are commonly used to study the behavior of electrons subject to external perturbations (such as a low-intensity laser field). LR TDDFT techniques [26–29], through a single matrix diagonalization, provide excited-state energies and ground-to-excited-state multipolar transition elements [30], but other similar quantities can be computed as well. These methods are quite suited for excited states mainly composed of single-electron transitions [31]. Excited states that originate from the simultaneous excitation of two or more electrons are challenging to determine numerically. This also includes the study of multireference states [32–34]. Multireference theory [35–38], due to its widespread applicability to systems of strongly correlated character, is to date very actively motivating the development of advanced theoretical methods that could stimulate newer generations of algorithms, which may also encompass density functional techniques.

On the other hand, response theories within the context of wave-function theory deliver information as the aforementioned techniques [39–44]. These demand higher computational power over DFT-based methods, but they are essential due to their natural reliability and improvability. Wave-function and Green's function response theories have also been extended to the multireference case [45–47]. Excited-state methods, derived from response theory, that directly diagonalize a Hamiltonian are of general broad use as they can be computationally convenient. An example of this is the well-known Bethe-Salpeter equation [48,49], capable of yielding highly accurate absorption spectra of extended systems and explaining spectroscopic features seen in a vast family of experiments. Similarly, multireference coupled-cluster (MRCC) theory is among the most advanced tools being developed currently to obtain high accuracy in energetics and wave-function-derived properties [50–55]. MRCC methods are remarkably promising because they integrate both dynamic- and strong-correlation effects. Hence, if computationally efficient MRCC methods are enabled for large systems, they would likely result in enjoying a broad

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productive applicability to critical problems in physics and chemistry.

This work presents the formulation of an extended linear-response approach, within single-reference standard (non-Hermitian) coupled-cluster theory [40,56–66], that leads to the calculation of excited-state properties. This theory relies on a modification to the initial-state wave function of the system so one can extract properties of excited states through linked coupled-cluster (CC) equations. These are quantities such as matrix elements to study transitions between excited states, as well as permanent dipoles of such states. This formulation is based on an alternative linear response theory we developed previously, dubbed the second linear response theory (SLR) [67–69]. We have applied it before within the context of time-dependent (TD) density functional theory to organic semiconductors. The general working principle is founded on exact QM identities and is applicable to wave-function methodologies, as shown in this work, where we develop an SLR approach within the CC formalism and show that it provides excited-state expressions that are fully consistent with established quadratic response (QR) theory. Then, we show SLR theory can be used to compute wave-function amplitudes in the linear regime where the electronic system is initially described by an excited-state wave function. QR theory is based on the analysis of terms that are quadratic in the perturbing external field. In contrast, SLR theory only requires linear terms. The linear quantities of interest are different with respect to QR theory because they are multiplied by an initial wave-function superposition coefficient. However, as we show in this work, SLR theory gives the same result as QR theory for excited-state-to-excited-state transition moments.

Finally, we extend our SLR theory to the nonlinear case, where excited-state information can be extracted from the analysis of generalized time-dependent transition elements. This generalization, which is exact in principle, includes the description of the evolution of an observable starting from an arbitrary initial state, such as a linear superposition of different quantum states. The formalisms we present in this work could be used to further expand the capabilities of response theories in theoretical and numerical contexts, where a different angle on the fundamental problem of wave-function propagation can stimulate further developments in the pursuit of accuracy or to accelerate wave-function-based algorithms to compute excited-state properties.

II. DEFINITIONS AND CONNECTION TO STANDARD LINEAR RESPONSE THEORY

For any operator $\hat{\Omega}$ we write $\bar{\Omega} = \exp(-\hat{T})\hat{\Omega}\exp(+\hat{T})$, where $\hat{T}$ refers to the standard ground-state cluster operator, which is assumed to be given. The symbol $\hat{\Omega}_{\rm N}$ denotes the normal-ordered form of $\hat{\Omega}$, i.e., $\hat{\Omega}_{\rm N} = \{\hat{\Omega}\}$; also, we use the notation $\bar{\Omega}_{\rm N} = \{\bar{\Omega}\}$. The letter μ labels transitions from the (single) ground-state reference of any order: singles, doubles, triples, etc. So $\hat{\tau}_\mu$ is a product of electron-hole creation operators, and $\hat{\tau}_\mu^\dagger$ is its Hermitian conjugate. We use (i) $|0\rangle$ to refer to the reference Hartree-Fock wave function, (ii) $\langle\hat{\Omega}\rangle_0 = \langle 0|\hat{\Omega}|0\rangle$, and (iii) ∂_t as a compact symbol for the partial derivative operator ∂/∂_t.

The (nonrelativistic) TD Hamiltonian of interest in this work is

$$\hat{H}(t) = \hat{H}_0 - f(t)\hat{B}, \tag{1}$$

where $\hat{H}_0$ is the static component, consisting of the kinetic, external (electron-nuclei interaction), and electron-electron repulsion energies. The term $f(t)$ denotes the scalar driving potential the system is subject to, and $\hat{B}$ is the observable operator that couples to that potential. In addition, we are also interested in the evolution of an additional operator, denoted $\hat{A}$. Hence,

$$\langle A(t)\rangle = \langle[\hat{L}_0 + \hat{\lambda}(t)]e^{-\hat{x}(t)}\bar{A}e^{+\hat{x}(t)}\rangle_0, \tag{2}$$

where the operator $\hat{L}_0$ leads to the expression for the ground-state bra $\langle 0|\hat{L}_0\exp(-\hat{T})$. In terms of the well-known λ operator this gives $\hat{L}_0 = 1 + \hat{\Lambda}$. The excitation operators read $\hat{x}(t) = \sum_\mu x_\mu(t)\hat{\tau}_\mu$ and $\hat{\lambda}(t) = \sum_\mu \hat{\tau}_\mu^\dagger\lambda_\mu(t)$, with $x_\mu(t)$ and $\lambda_\mu(t)$ being the excitation and deexcitation TD amplitudes. For the application of SLR theory, the above expression remains the starting point, but the initial conditions of the $\hat{\lambda}(t)$ and $\hat{x}(t)$ terms are different, as we detail in Sec. III.

In this TD CC response formalism the (left) bra of the TD wave function is represented as

$$\langle\Upsilon(t)| = \langle 0|[\hat{L}_0 + \hat{\lambda}(t)]\exp[-\hat{x}(t) - \hat{T} + i\phi(t)], \tag{3}$$

where $\phi(t)$ is a TD phase. The right ket reads

$$|\Phi(t)\rangle = \exp[\hat{T} + \hat{x}(t) - i\phi(t)]|0\rangle. \tag{4}$$

Regarding the Hamiltonian, using normal ordering we can express it as $\bar{H}(t) = E_0 + \bar{H}_{0,\rm N} + \bar{v}(t)$, where $\bar{v}(t) = -f(t)\bar{B}$, and E_0 is the ground-state energy, $\langle\hat{L}_0\bar{H}_0\rangle_0$ (or simply $\langle\bar{H}_0\rangle_0$).

In an ideal CC calculation both the (left) bra and (right) ket solve the full TD Schrödinger equation. In practice, however, the differences between $\langle\Upsilon(t)|$ and $|\Phi(t)\rangle$ are responsible for the non-Hermitian nature of CC response theory. However, they offer the quite desirable property of size extensiveness, required to study large molecular systems and periodic structures.

The motion equations of the $\hat{\lambda}$ and $\hat{x}$ operators can be derived from stationarizing the action functional:

$$\begin{aligned}\mathcal{F}[\boldsymbol{\lambda}, \boldsymbol{x}, \phi] &= \int dt\,\langle[\hat{L}_0 + \hat{\lambda}(t)]\{e^{-\hat{x}(t)}\bar{H}(t)e^{+\hat{x}(t)} \\ &\quad - i\vec{\partial}_t[\hat{x}(t) - i\phi(t)]\}\rangle_0 \\ &= \int dt[\langle\Upsilon(t)|\hat{H}(t)|\Phi(t)\rangle - i\langle\Upsilon(t)|\vec{\partial}_t|\Phi(t)\rangle].\end{aligned} \tag{5}$$

The symbols $\boldsymbol{\lambda}$ and $\boldsymbol{x}$ refer to the "history" of the amplitudes $\{\lambda_\mu(t)\}$ and $\{x_\mu(t)\}$, respectively, whereas $\vec{\partial}_t$ indicates the time derivative is applied to the ket $|\Phi(t)\rangle$. Variations with respect to λ_μ and x_μ give the well-established TD equations:

$$i\partial_t x_\mu(t) = \langle\hat{\tau}_\mu^\dagger e^{-\hat{x}(t)}[\bar{H}_0 + \bar{v}(t)]e^{+\hat{x}(t)}\rangle_0 \tag{6}$$

and

$$-i\partial_t\lambda_\mu(t) = \langle[\hat{L}_0 + \hat{\lambda}(t)]e^{-\hat{x}(t)}[\bar{H}_0 + \bar{v}(t), \hat{\tau}_\mu]e^{+\hat{x}(t)}\rangle_0. \tag{7}$$

Using the solution to the two last equations and by demanding that $\mathcal{F} = 0$, the phase function takes the form

$$\partial_t \phi(t) = \langle [\hat{L}_0 + \hat{\lambda}(t)] e^{-\hat{x}(t)} \bar{H}(t) e^{+\hat{x}(t)} \rangle_0. \quad (8)$$

Because it originates from an action functional, the phase factor we use is different from that employed in other TD CC response formalisms. For convenience we define

$$\Delta\phi(t) = \int_0^t ds \langle [\hat{L}_0 + \hat{\lambda}(s)] e^{-\hat{x}(s)} [\bar{H}_{0,N} + \bar{v}(s)] e^{+\hat{x}(s)} \rangle_0, \quad (9)$$

so $\phi(t) = E_0 t + \Delta\phi(t)$. Even though this phase does not influence the calculation of observables, it is important for the interpretation of the right and left wave functions.

Now we specialize the above equations to the standard form of linear response theory, and then to the SLR case (see Sec. III). For the latter, however, we consider a few additional terms that are due to the different type of initial condition that we use. We start by linearizing the TD CC equations with respect to $\hat{x}$, $\hat{\lambda}$, and $\hat{v}$. This gives the following equation for the excitation amplitudes:

$$i\partial_t x_\mu(t) = \langle \hat{\tau}_\mu^\dagger (\bar{v}(t) + [\bar{H}_0, \hat{x}(t)]) \rangle_0. \quad (10)$$

Now we define the following operators:

$$\bar{H}^0_{\tau,\mu} = [\bar{H}_0, \hat{\tau}_\mu] \quad (11)$$

and

$$\bar{v}_{\tau,\mu}(t) = [\bar{v}(t), \hat{\tau}_\mu]. \quad (12)$$

In general, $\bar{\Omega}_{\tau,\mu} = \bar{\Omega}\hat{\tau}_\mu - \hat{\tau}_\mu \bar{\Omega}$.

Using the above definitions we obtain the following equation:

$$-i\partial_t \lambda_\mu(t) = \left\langle \hat{L}_0 \left(\bar{v}_{\tau,\mu}(t) + \left[\bar{H}^0_{\tau,\mu}, \hat{x}(t) \right] \right) + \hat{\lambda}(t) \bar{H}^0_{\tau,\mu} \right\rangle_0. \quad (13)$$

To derive the above result one uses the fact that $\langle \hat{L}_0 [\bar{H}_0, \hat{\tau}_\mu] \rangle_0 = 0$. Let us introduce the matrix:

$$(\mathcal{A})_{\mu\nu} = \left\langle \hat{\tau}_\mu^\dagger \bar{H}^0_{\tau,\nu} \right\rangle_0. \quad (14)$$

Because this is a nonsymmetric (square) matrix, we assume there is a complete set of left and right eigenvectors $\{\mathbf{\Lambda}^I, \mathbf{X}^I\}$ and eigenvalues (excitation energies) $\{\Omega_I\}$ such that $\mathcal{A}\mathbf{X}^I = \Omega_I \mathbf{X}^I$ and $\mathcal{A}^{\mathrm{T}} \mathbf{\Lambda}^I = \Omega_I \mathbf{\Lambda}^I$. Following the steps shown in the Supplemental Material [70], we find the well-known linear response expressions (or assignments) for the ground-state-to-excited-state transition matrix elements:

$$\langle \Psi_I | \hat{A} | \Psi_0 \rangle = \sum_\mu \Lambda^I_\mu \langle \hat{\tau}_\mu^\dagger \bar{A} \rangle_0 \quad (15)$$

and

$$\langle \Psi_0 | \hat{A} | \Psi_I \rangle = \sum_\mu \langle \hat{L}_0 \bar{A}_{\tau,\mu} \rangle_0 X^I_\mu - \sum_J \frac{F^{IJ} (\mathbf{\Lambda}^J \cdot \bar{\mathbf{A}})}{\Omega_I + \Omega_J}, \quad (16)$$

where Ψ_0 denotes the exact standard ground-state wave function of the system, and Ψ_I denotes an arbitrary excited-state wave function. F^{IJ} is the matrix element:

$$F^{IJ} = \sum_{\mu\nu} X^I_\mu F_{\mu\nu} X^J_\nu, \quad (17)$$

where $F_{\mu\nu} = \langle \hat{L}_0 [\bar{H}^0_{\tau,\mu}, \hat{\tau}_\nu] \rangle_0$, and $\mathbf{\Lambda}^J \cdot \bar{\mathbf{A}} = \sum_\mu \Lambda^J_\mu \langle \hat{\tau}_\mu^\dagger \bar{A} \rangle_0$. This result holds for the observable B as well.

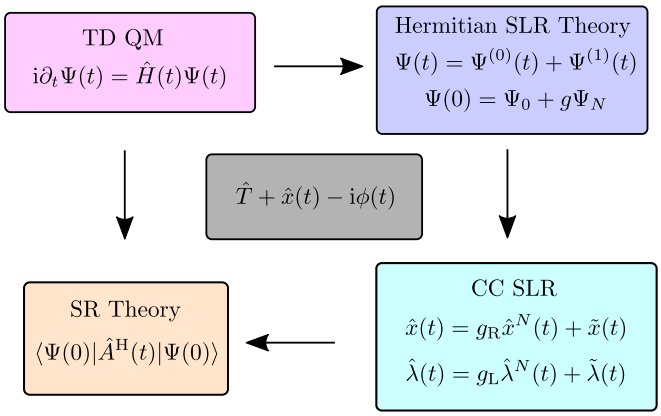

FIG. 1. Theoretical components explored in this work. Standard TD QM defines the quantities that are to be represented by our CC approaches. The starting point is the use of LR QM where the initial state is not the ground state, but a combination of its ground-state wave function with an excited state of interest (Ψ_N). A LR CC theory is formulated to cover this situation and is then extended to consider cases beyond the linear response regime, yielding SR theory, in which an observable is propagated for a general initial state (not purely ground state). In the center frame we show the combined set of operators used to examine the response of the system to external perturbations.

III. SECOND LINEAR RESPONSE THEORY

In this section we develop an alternative formalism to compute excited-state transition elements. We observe, as in the linear response case, that the left response vector contributes counterclockwise and clockwise elements [terms proportional to $\exp(i\omega t)$ and $\exp(-i\omega t)$, respectively, where ω denotes frequency in the Fourier analysis we perform below], whereas the right vector does so only for counterclockwise ones. Although we follow different theoretical steps, the matrix elements we predict are consistent with QR theory. We remark, however, that the phase expression we utilize differs from other CC-based response theories. This phase does not affect the transition elements. However, as we show in Sec. IV, our phase equation is useful to interpret wave-function amplitudes that emerge from our second response (SR) theory. The steps followed are pictorially summarized in Fig. 1.

From standard quantum mechanics, we apply linear response analysis to the case where the system is initially described by a linear combination of the following form:

$$|\Psi(t = 0; g)\rangle = |\Psi_0\rangle + g|\Psi_N\rangle. \quad (18)$$

Here Ψ_0 refers to the exact standard ground-state wave function, and Ψ_N denotes an excited state of interest. We assume the symbols Ψ_I and Ψ_J denote exact standard (non-CC) excited-state wave functions with labels "I" and "J". The linear-response TD WF is

$$|\Psi(t; g)\rangle = |\Psi^{(0)}(t; g)\rangle + |\Psi^{(1)}(t; g)\rangle, \quad (19)$$

where

$$|\Psi^{(0)}(t; g)\rangle = e^{-i\hat{H}_0 t} |\Psi(0; g)\rangle \quad (20)$$

and

$$|\Psi^{(1)}(t;g)\rangle = -i\int_0^t ds e^{-i\hat{H}_0(t-s)}\hat{V}(s)e^{-i\hat{H}_0 s}|\Psi^{(0)}(0;g)\rangle, \tag{21}$$

where $\hat{V}(s) = -f(s)\hat{B}$. The response function now reads

$$\mathcal{R}(\omega;g) = \int_{-\infty}^{+\infty} dt e^{i(\omega\pm i\eta)t}\frac{\delta}{\delta f(s)}\{\langle\Psi^{(0)}(t;g)|\hat{A}|\Psi^{(1)}(t;g)\rangle + \text{c.c.}\}\Big|_{s=0,f=0}. \tag{22}$$

Using these equations and taking $\eta \to 0^+$, we find the following:

$$\lim_{g\to 0}\frac{\partial}{\partial g}\mathcal{R}(\omega;g) = -\sum_J\left[\frac{\langle\Psi_0|\hat{A}|\Psi_J\rangle(\langle\Psi_J|\hat{B}|\Psi_N\rangle - \delta_{JN}\langle\Psi_0|\hat{B}|\Psi_0\rangle)}{\omega-\Omega_J} - \frac{\langle\Psi_J|\hat{A}|\Psi_0\rangle(\langle\Psi_N|\hat{B}|\Psi_J\rangle - \delta_{NJ}\langle\Psi_0|\hat{B}|\Psi_0\rangle)}{\omega+\Omega_J}\right]. \tag{23}$$

Although we used a single variable (g) for the above equations, we now split the analysis into a left and a right mathematical problem by using one superposition variable (g_L) for the counterclockwise component and a second variable (g_R) for the clockwise one, where variations with respect to either give the information of interest. Starting from Eqs. (19)–(21), we consider the wave functions $\langle\Psi(t;g_\text{L})|$, $|\Psi(t;g_\text{R})\rangle$ and their zero- and first-order components. For example, $\langle\Psi^{(0)}(t=0;g_\text{L})| = \langle\Psi_0| + g_\text{L}\langle\Psi_N|$, where $\langle\Psi^{(0)}(t;g_\text{L})| = \langle\Psi^{(0)}(t=0;g_\text{L})|\exp(i\hat{H}_0 t)$. In a similar way we obtain the wave function $|\Psi^{(0)}(t;g_\text{R})\rangle$.

Henceforth, we introduce the function

$$R_2(\omega;g_\text{L},g_\text{R}) = \int_{-\infty}^{+\infty} dt e^{i(\omega\pm i\eta)t}\frac{\delta}{\delta f(s)}\{\langle\Psi^{(0)}(t;g_\text{L})|\hat{A}|\Psi^{(1)}(t;g_\text{R})\rangle + \langle\Psi^{(1)}(t;g_\text{L})|\hat{A}|\Psi^{(0)}(t;g_\text{R})\rangle\}\Big|_{s=0,f=0}. \tag{24}$$

In agreement with the function $\mathcal{R}$, R_2 satisfies

$$\lim_{\omega\to\Omega_I}\lim_{g_\text{L},g_\text{R}\to 0} -(\omega-\Omega_I)\frac{\partial}{\partial g_\text{R}}R_2 = \langle\Psi_0|\hat{A}|\Psi_I\rangle(\langle\Psi_I|\hat{B}|\Psi_N\rangle - \delta_{IN}\langle\Psi_0|\hat{B}|\Psi_0\rangle) \tag{25}$$

and

$$\lim_{\omega\to-\Omega_I}\lim_{g_\text{L},g_\text{R}\to 0}(\omega+\Omega_I)\frac{\partial}{\partial g_\text{L}}R_2 = \langle\Psi_I|\hat{A}|\Psi_0\rangle(\langle\Psi_N|\hat{B}|\Psi_I\rangle - \delta_{NI}\langle\Psi_0|\hat{B}|\Psi_0\rangle). \tag{26}$$

We now proceed to solve the CC linear response equations under the initial condition where the system is in a linear combination of the ground state and some excited state of interest. We label this excited state as N.

If the system is unperturbed then it must behave as a stationary state that satisfies the standard linear response equations. Therefore, we seek for a solution set as shown below:

$$\begin{aligned}\hat{x}(t;g_\text{R}) &= g_\text{R}\hat{x}^N(t) + \tilde{x}(t;g_\text{R}),\\ \hat{\lambda}(t;g_\text{L},g_\text{R}) &= g_\text{L}\hat{\lambda}^N(t) + \tilde{\lambda}(t;g_\text{L},g_\text{R}),\\ \phi(t;g_\text{L},g_\text{R}) &= g_\text{R}\phi^N(t) + \tilde{\phi}(t;g_\text{L},g_\text{R}).\end{aligned} \tag{27}$$

The operators $\hat{x}^N(t)$ and $\hat{\lambda}^N(t)$ and the phase $\phi^N(t)$ represent the stationary state that would occur in the absence of an external perturbation [$\hat{v}(t) = 0$]. The terms $\tilde{x}(t)$, $\tilde{\lambda}(t)$, and $\tilde{\phi}(t)$ are the "new" response operators and phase; they provide information about the evolution of the system. We express the operators as $\tilde{x}(t) = \sum_\mu \tilde{x}_\mu(t)\hat{\tau}_\mu$ and $\tilde{\lambda}(t) = \sum_\mu \hat{\tau_\mu}^\dagger\tilde{\lambda}_\mu(t)$. As we show later on, the operator $\tilde{\lambda}$ depends on both g_L and g_R, in addition to time. For the phase we use the right amplitude g_R only as the operator $\hat{x}^N(t)$ determines this object, besides E_0. Its response part, $\tilde{\phi}$, on the other hand, depends on $\tilde{x}$ and $\tilde{\lambda}$, and thereby on g_L and g_R.

The vectors $\hat{x}^N(t)$ and $\hat{\lambda}^N(t)$ stationarize their respective equations. Equation (10) reads

$$i\partial_t x_\mu^N(t) = \sum_\nu \mathcal{A}_{\mu\nu}x_\nu^N(t). \tag{28}$$

So we naturally take $x_\mu^N(t) = X_\mu^N\exp(-i\Omega_N t)$. The vector $\lambda_\mu^N(t)$ follows a different relation:

$$-ig_\text{L}\partial_t\lambda_\mu^N(t) = \left\langle g_\text{R}\hat{L}_0\left[\bar{H}^0_{\tau,\mu},\hat{x}^N(t)\right] + g_\text{L}\hat{\lambda}^N(t)\bar{H}^0_{\tau,\mu}\right\rangle_0. \tag{29}$$

The solution to this equation when both g_L and g_R are different from zero is possible to obtain. But in this section, we are interested in the case where (after derivatives with respect to g_L or g_R are taken in our formalism) $g_\text{R} = 0$ and $g_\text{L} \neq 0$, and then the limit $g_\text{L} \to 0$. Thus we take $\lambda_\mu^N(t) = \Lambda_\mu^N\exp(i\Omega_N t)$. The phase $\phi^N(t)$ satisfies

$$\phi^N(t) = E_0 t + \Delta\phi^N(t) \tag{30}$$

in the above equation $\Delta\phi^N(t) = \int_0^t ds\langle\hat{L}_0[\bar{H}_0,\hat{x}^N(s)]\rangle_0$.

To derive the linearized time-dependent equations from Eqs. (6)–(8), we include terms that are proportional to g_{L} or g_{R} (for example, a term like $g_{\mathrm{R}}[\bar{v}(t), \hat{x}^N(t)]$ needs to be included), as such terms, for the purpose of applying linear response analysis, are required and remain nonzero after completing the limiting procedures that we apply. Any term that is quadratic in g_{L} or g_{R} in the weak perturbation limit is neglected because these vanish.

The SLR equation for the components of the operator $\tilde{x}$ reads

$$i\partial_t \tilde{x}_\mu(t) = \langle \hat{\tau}^\dagger_\mu\{[\bar{H}_0, \tilde{x}(t)] + \bar{v}(t) + g_{\mathrm{R}}[\bar{v}(t), \hat{x}^N(t)] + g_{\mathrm{R}}\hat{M}(t)\}\rangle_0, \tag{31}$$

where

$$\hat{M}(t) = [[\bar{H}_0, \hat{x}^N(t)], \tilde{x}(t)]. \tag{32}$$

The conjugate operator $\tilde{\lambda}(t)$ follows the equation

$$-i\partial_t \tilde{\lambda}_\mu(t) = \left\langle \hat{L}_0\left(\bar{v}_{\tau,\mu}(t) + \left[\bar{H}^0_{\tau,\mu}, \tilde{x}(t)\right]\right) + \tilde{\lambda}(t)\bar{H}^0_{\tau,\mu} + g_{\mathrm{R}}\hat{L}_0[\bar{v}_{\tau,\mu}(t), \hat{x}^N(t)] + g_{\mathrm{L}}\hat{\lambda}^N(t)\bar{v}_{\tau,\mu}(t) + \hat{Q}_\mu(t)\right\rangle_0, \tag{33}$$

where

$$\hat{Q}_\mu(t) = g_{\mathrm{R}}\hat{L}_0\left[\left[\bar{H}^0_{\tau,\mu}, \hat{x}^N(t)\right], \tilde{x}(t)\right] + g_{\mathrm{L}}\hat{\lambda}^N(t)\left[\bar{H}^0_{\tau,\mu}, \tilde{x}(t)\right] + g_{\mathrm{R}}\tilde{\lambda}(t)\left[\bar{H}^0_{\tau,\mu}, \hat{x}^N(t)\right]. \tag{34}$$

The SLR phase is given by

$$\partial_t\tilde{\phi}(t) = (1 - g_{\mathrm{R}})E_0 + \partial_t\Delta\tilde{\phi}(t), \tag{35}$$

where

$$\begin{aligned}\Delta\tilde{\phi}(t; g_{\mathrm{L}}, g_{\mathrm{R}}) = \int_0^t ds\langle & g_{\mathrm{L}}\hat{\lambda}^N(s)\bar{v}(s) + g_{\mathrm{L}}\hat{\lambda}^N(s)[\bar{H}_0, \tilde{x}(s)] + g_{\mathrm{R}}\tilde{\lambda}(s)[\bar{H}_0, \hat{x}^N(s)] \\ & + \hat{L}_0\{[\bar{H}_0, \tilde{x}(s)] + \bar{v}(s) + g_{\mathrm{R}}[\bar{v}(s), \hat{x}^N(s)] + g_{\mathrm{R}}\hat{M}(s)\}\rangle_0\end{aligned} \tag{36}$$

The last three SLR equations are fully consistent with standard LR when $g = 0$.

For these SLR equations, it is important to note the initial conditions $\tilde{\lambda}_\mu(t = 0) = \tilde{x}_\mu(0) = 0$, and this holds regardless of the values of g_{L} and g_{R}. After carrying out the mathematical analysis of the response functions, as shown in the Supplemental Material [70], we obtain the following relation:

$$\langle\Psi_I|\hat{B}|\Psi_N\rangle = \delta_{IN}\langle\hat{L}_0\bar{B}\rangle_0 + \langle\hat{\Lambda}^I\bar{B}_{X,N}\rangle_0 + \sum_J\left[\frac{C_{IN,J}}{\Omega_I - \Omega_J - \Omega_N}\right](\mathbf{\Lambda}^J\cdot\bar{\mathbf{B}}), \tag{37}$$

where

$$C_{IN,J} = \langle\hat{\Lambda}^I[[\bar{H}_0, \hat{X}^N], \hat{X}^J]\rangle_0 \tag{38}$$

and $\hat{X}^J = \sum_\mu X^J_\mu\hat{\tau}_\mu$ and $\hat{\Lambda}^I = \sum_\mu \Lambda^I_\mu\hat{\tau}^\dagger_\mu$. Both the left and right evaluations give the same element, one only has to swap the N and I indices.

In the limit where the CC excited state problem is solved to all orders, the last term in Eq. (37) eliminates $\langle\hat{\Lambda}^I\hat{X}^N\hat{B}\rangle_0$, so the matrix element is given by $\langle\hat{\Lambda}^I\bar{B}\hat{X}^N\rangle$. This implies that the last term in Eq. (37) is in such a limit finite, but not necessarily otherwise. For this reason, it may be important to apply a regularization scheme in case there is a term $\Omega_I - \Omega_J - \Omega_N$ that is quite close to zero. Alternatively, as an additional approximation, not explored in this work, for the sake of eliminating divergences one can neglect the difference $\Omega_I - \Omega_N$. It holds true for the case of permanent-dipole determination, but not for transition elements.

IV. INTERPRETATION OF WAVE-FUNCTION AMPLITUDES

In this section we approach with approximations the interpretation of wave-function amplitudes.

Although the initial state we employed before is a quantum mixture of ground and excited states, one can also analyze through such an initial state the situation where the system begins evolving from the excited state N, and the response to a weak perturbation can be determined. Note that $\partial/\partial g|\Psi^{(0)}(t = 0; g)\rangle = |\Psi_N\rangle$, where the first derivative of the initial of state with respect to g gives the excited-state wave function. When we apply the same operation to the first response wave function, it is found that

$$\frac{\partial}{\partial g}|\Psi^{(1)}(t; g)\rangle = -i\int_0^t ds e^{-i\hat{H}_0(t-s)}\hat{V}(s)e^{-i\hat{H}_0 s}|\Psi_N\rangle. \tag{39}$$

This is equivalent to the result of applying the standard linear response, where the initial state is entirely described by Ψ_N.

Let us introduce the following expansion:

$$\partial_g|\Psi^{(1)}(t)\rangle = \sum_I \mathcal{C}_I(t)|\Psi_I\rangle, \tag{40}$$

where the amplitude $\mathcal{C}_I(t)$ is given by $\mathcal{C}_I(t) = \langle\Psi_I|\partial_g\Psi^{(1)}(t)\rangle$ ($\partial_g = \partial/\partial g$). This object then describes the contribution of state I to the response of the initial excited state to a perturbation, and it can be related to response CC coefficients. But before proceeding to show this, for a function h of the

coefficients $g_{\rm L}$ and $g_{\rm R}$, the following notation is used:

$$h_{\rm r} = \lim_{g_{\rm L},g_{\rm R}\to 0} \frac{\partial h}{\partial g_{\rm R}}, \qquad h_{\rm l} = \lim_{g_{\rm L},g_{\rm R}\to 0} \frac{\partial h}{\partial g_{\rm L}}. \tag{41}$$

In addition, if h is time dependent, $h(t;0)$ refers to the function evaluated at time t in the case where $g_{\rm L}=0$ and $g_{\rm R}=0$. So $\tilde{x}(t;0)$ is essentially the same object as the operator $\hat{x}(t)$ for an arbitrary driving scalar field f and where the system is initially at the ground state. Now let us consider the starting ansatz

$$|\Phi(t;g_{\rm R},g_{\rm L})\rangle = \exp\{\hat{T} + g_{\rm R}\hat{x}^N(t) + \tilde{x}(t) - i[g_{\rm R}\phi^N(t) + \tilde{\phi}(t)]\}|0\rangle. \tag{42}$$

On the basis of the previous analysis, we derive from this wave function the following:

$$|\Phi_{\rm r}(t)\rangle = \lim_{g_{\rm L},g_{\rm R}\to 0} \frac{\partial}{\partial g_{\rm R}}|\Phi(t;g_{\rm R})\rangle \approx \left|\Phi_{\rm r}^{(0)}(t)\right\rangle + \left|\Phi_{\rm r}^{(1)}(t)\right\rangle, \tag{43}$$

where

$$\left|\Phi_{\rm r}^{(0)}(t)\right\rangle = e^{\hat{T}-iE_0t}[\hat{x}^N(t) - i\Delta\phi^N(t)]|0\rangle \tag{44}$$

and $|\Phi_{\rm r}^{(1)}(t)\rangle$ is assigned as

$$\left|\Phi_{\rm r}^{(1)}(t)\right\rangle = [\tilde{x}_{\rm r}(t) - i\Delta\tilde{\phi}(t;0)\hat{x}^N(t) - i\Delta\tilde{\phi}_{\rm r}(t)]e^{\hat{T}-iE_0t}|0\rangle, \tag{45}$$

where $\Delta\phi^N$ is a relatively small residual term that would vanish in a formally exact calculation. In the above we neglected $\exp[\tilde{x}(t;0)]$ and a few quadratic terms. Similarly, the left ansatz reads

$$\langle\Upsilon(t;g_{\rm L},g_{\rm R})| = \langle 0|[\hat{L}_0 + g_{\rm L}\hat{\lambda}^N(t) + \tilde{\lambda}(t)]\exp\{-\hat{T} - g_{\rm R}\hat{x}^N(t) - \tilde{x}(t) + i[E_0t + g_{\rm R}\Delta\phi^N(t) + \Delta\tilde{\phi}(t;g_{\rm L},g_{\rm R})]\}. \tag{46}$$

From this (left) bra the approximated state is derived as

$$\langle\Upsilon_{\rm l}(t)| = \lim_{g_{\rm L},g_{\rm R}\to 0} \frac{\partial}{\partial g_{\rm L}}\langle\Upsilon(t;g_{\rm L},g_{\rm R})| \approx \left\langle\Upsilon_{\rm l}^{(0)}(t)\right| + \left\langle\Upsilon_{\rm l}^{(1)}(t)\right|, \tag{47}$$

where

$$\left\langle\Upsilon_{\rm l}^{(0)}(t)\right| = \langle 0|\hat{\lambda}^N(t)e^{-\hat{T}+iE_0t}, \qquad \left\langle\Upsilon_{\rm l}^{(1)}(t)\right| = \langle 0|[\tilde{\lambda}_{\rm l}(t) + i\Delta\tilde{\phi}(t;0)\hat{\lambda}^N(t) + i\hat{L}_0\Delta\tilde{\phi}_{\rm l}(t)]e^{-\hat{T}+iE_0t}. \tag{48}$$

The left bra and right ket can be expanded in their respective eigenbasis [$\tilde{x}(t) = \sum_I \tilde{c}_I(t)\hat{X}^I$, $\tilde{\lambda}(t) = \sum_I \tilde{d}_I(t)\hat{\Lambda}^I$], giving

$$\left|\Phi_{\rm r}^{(1)}(t)\right\rangle = \left\{\sum_I [\tilde{c}_{{\rm r},I}(t) - \delta_{NI}i\Delta\phi(t)]\hat{X}^I - i\Delta\tilde{\phi}_{\rm r}(t)\right\}e^{\hat{T}-iE_0t}|0\rangle \tag{49}$$

and

$$\left\langle\Upsilon_{\rm l}^{(1)}(t)\right| = \langle 0|e^{-\hat{T}+iE_0t}\left\{\sum_I \hat{\Lambda}^I[\tilde{d}_{{\rm l},I}(t) + \delta_{NI}i\Delta\phi(t)] + \hat{L}_0 i\Delta\tilde{\phi}_{\rm l}(t)\right\}, \tag{50}$$

where

$$\tilde{c}_{{\rm r},I}(t) = \left.\frac{\partial\tilde{c}_I}{\partial g_{\rm R}}\right|_{g_{\rm R}=0}, \qquad \tilde{d}_{{\rm l},I}(t) = \left.\frac{\partial\tilde{d}_I}{\partial g_{\rm L}}\right|_{g_{\rm L}=0,g_{\rm R}=0}. \tag{51}$$

From the above equation we extract the following approximated excited-state wave function, $\langle\Upsilon^I| = \langle 0|\hat{\Lambda}^I\exp(-\hat{T})$, which leads to

$$\left\langle\Upsilon^I\middle|\Phi_{\rm r}^{(1)}(t)\right\rangle = [\tilde{c}_{{\rm r},I}(t) - \delta_{NI}i\Delta\phi(t)]e^{-iE_0t} \approx \mathcal{C}_I(t). \tag{52}$$

Analogously, using $|\Phi^I\rangle = \hat{X}^I\exp(\hat{T})|0\rangle$ we see that $\langle\Upsilon_{\rm l}^{(1)}(t)|\Phi^I\rangle = [\tilde{d}_{{\rm l},I}(t) + \delta_{NI}i\Delta\phi(t)]\exp(iE_0t) \approx \mathcal{C}_I^*(t)$.

The motion equations in this case follow from Eqs. (31) and (33):

$$i\partial_t\tilde{x}_{{\rm r},\mu}(t) = \langle\hat{\tau}_\mu^\dagger\{[\bar{H}_0,\tilde{x}_{\rm r}(t)] + [\bar{v}(t),\hat{x}^N(t)] + [[\bar{H}_0,\hat{x}^N(t)],\tilde{x}(t;0)]\}\rangle_0 \tag{53}$$

and

$$-i\partial_t\tilde{\lambda}_{{\rm l},\mu}(t) = \left\langle\tilde{\lambda}_{\rm l}(t)\bar{H}^0_{\tau,\mu} + \hat{\lambda}^N(t)\bar{v}_{\tau,\mu}(t) + \hat{\lambda}^N(t)\left[\bar{H}^0_{\tau,\mu},\tilde{x}(t;0)\right]\right\rangle_0. \tag{54}$$

In the eigenbasis representation we then have that

$$(i\partial_t - \Omega_I)\tilde{c}_{{\rm r},I}(t) = e^{-i\Omega_{N^I}t}\left\langle\hat{\Lambda}^I[\bar{v}(t),\hat{X}^N] + \sum_J\hat{\Lambda}^I[[\bar{H}_0,\hat{X}^N],\hat{X}^J]c_J(t)\right\rangle_0,$$
$$(-i\partial_t + \Omega_I)\tilde{d}_{{\rm l},I}(t) = e^{i\Omega_{N^I}t}\left\langle\hat{\Lambda}^N[\bar{v}(t),\hat{X}^I] + \sum_J\hat{\Lambda}^N[[\bar{H}_0,\hat{X}^I],\hat{X}^J]c_J(t)\right\rangle_0. \tag{55}$$

Even though these two equations involve similar objects, they are different. Hence, the left ($\tilde{d}_{\mathrm{l},I}$) and right ($\tilde{c}_{\mathrm{r},I}$) amplitudes differ from one another.

The assignment deduced above can be applied to derive the excited-state transition elements in a different way, by simply taking the functional derivatives and extracting the information from this. Such a feature can be seen if variations with respect to $f(t)$ are taken for coefficients such as $\mathcal{C}_J$ and $\tilde{c}_{\mathrm{r},I} - \delta_{NI} i\Delta\phi(t)$, where one would derive an equation identical to Eq. (37). Not only do quantum terms such as $\mathcal{C}_J$ lead to transition matrix elements but also they are an integral component in predicting the course of a photostimulated physical process, or driven by other factors. Hence, a connection between the CC analog is relevant to bridge electronic structure algorithms with photophysical models.

V. GENERAL EVOLUTION EQUATIONS

A. Extension of the SLR framework

We consider a more general propagation from an excited state, i.e., $\hat{U}(t)|\Psi_N\rangle$, where $\hat{U}(t) = \mathcal{T}\exp[-i\int_0^t ds\,\hat{H}(s)]$ ($\mathcal{T}$ being the time-ordering superoperator), and extend our formalism beyond the linear response; we refer to this as SR theory. First, we write $|\Psi(t;g_{\mathrm{R}})\rangle = \hat{U}(t)[|\Psi_0\rangle + g_{\mathrm{R}}|\Psi_N\rangle]$, and $\langle\Psi(t;g_{\mathrm{L}})| = [\langle\Psi_0| + g_{\mathrm{L}}\langle\Psi_N|]\hat{U}^\dagger(t)$. We also define

$$\langle A(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle = \langle\Psi(t;g_{\mathrm{L}})|\hat{A}|\Psi(t;g_{\mathrm{R}})\rangle. \tag{56}$$

Hence,

$$\lim_{g_{\mathrm{L}},g_{\mathrm{R}}\to 0}\left[\frac{\partial}{\partial g_{\mathrm{L}}}+\frac{\partial}{\partial g_{\mathrm{R}}}\right]\langle A(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle = \langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle + \mathrm{c.c.}, \tag{57}$$

where $\hat{A}^{\mathrm{H}}(t) = \hat{U}^\dagger(t)\hat{A}\hat{U}(t)$. Note that the derivative above has information about propagation of both the excited state of interest *and* the ground state of the system. In this case, a full normalization of the left and right initial states $[\Psi(t;g_{\mathrm{L}}),\ \Psi(t;g_{\mathrm{R}})]$ is not required as such a normalization as no effect on the final result.

The same notation applied before (see Secs. IV and III) is used in this section to derive the SR equations. We start with the set shown in Eq. (27) and insert these in Eqs. (6)–(8), where no further assumptions are taken. So the response operators $\tilde{x}(t)$ and $\tilde{\lambda}(t)$ and the phase $\tilde{\phi}(t)$ are now valid for arbitrary strengths of the perturbation. It is important to bear in mind that the operators $\hat{\lambda}(t)$ and $\hat{x}(t)$, when the system does not initiate completely from a ground-state configuration, are functions of the numbers g_{L} and g_{R}, allowing us to compute variations of these operators with respect to such parameters at any time t, including $t = 0$, leading to the equations discussed below.

In the present case, the expectation value reads $\langle A(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle = \langle\Upsilon(t;g_{\mathrm{L}},g_{\mathrm{R}})|\hat{A}|\Phi(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle$, so it satisfies

$$\begin{aligned}\lim_{g_{\mathrm{L}},g_{\mathrm{R}}\to 0}&\left[\frac{\partial}{\partial g_{\mathrm{L}}}+\frac{\partial}{\partial g_{\mathrm{R}}}\right]\langle A(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle\\ &= \langle\hat{\lambda}_{\mathrm{l}}(t)e^{-\tilde{x}(t;0)}\bar{A}e^{+\tilde{x}(t;0)}\rangle_0\\ &\quad+\langle[\hat{L}_0+\tilde{\lambda}(t;0)]e^{-\tilde{x}(t;0)}[\bar{A},\hat{x}_{\mathrm{r}}(t)]e^{+\tilde{x}(t;0)}\\ &\quad+\hat{\lambda}_{\mathrm{r}}(t)e^{-\tilde{x}(t;0)}\bar{A}e^{+\tilde{x}(t;0)}\rangle_0.\end{aligned} \tag{58}$$

Because we distinguish the parameters g_{L} and g_{R}, we assign the term $\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle$ as $\langle\hat{\lambda}_{\mathrm{l}}(t)e^{-\tilde{x}(t;0)}\bar{A}e^{+\tilde{x}(t;0)}\rangle_0$, and we assign the other quantity containing the right-handed derivatives as $\langle\Psi_0|\hat{A}^{\mathrm{H}}(t)|\Psi_N\rangle$ (in the numerical calculations shown in the next section we found they are visually identical, but in more practical contexts they are not expected to be so). Where the general equations of motion are

$$\begin{aligned}i\partial_t x_{\mathrm{r},\mu}(t) &= \langle\hat{\tau}_\mu^\dagger e^{-\tilde{x}(t;0)}[\bar{H}(t),\hat{x}_{\mathrm{r}}(t)]e^{+\tilde{x}(t;0)}\rangle_0,\\ -i\partial_t\lambda_{\mathrm{l},\mu}(t) &= \langle\hat{\lambda}_{\mathrm{l}}(t)e^{-\tilde{x}(t;0)}[\bar{H}(t),\hat{\tau}_\mu]e^{+\tilde{x}(t;0)}\rangle_0,\\ -i\partial_t\lambda_{\mathrm{r},\mu}(t) &= \langle[\hat{L}_0+\tilde{\lambda}(t;0)]e^{-\tilde{x}(t;0)}[\bar{H}_{\tau,\mu}(t),\hat{x}_{\mathrm{r}}(t)]e^{+\tilde{x}(t;0)}\\ &\quad+\hat{\lambda}_{\mathrm{r}}(t)e^{-\tilde{x}(t;0)}\bar{H}_{\tau,\mu}(t)e^{+\tilde{x}(t;0)}\rangle_0,\\ \Delta\phi_{\mathrm{r}}(t) &= \int_0^t ds\langle[\hat{L}_0+\tilde{\lambda}(s;0)]e^{-\tilde{x}(s;0)}[\bar{H}(s),\hat{x}_{\mathrm{r}}(s)]e^{+\tilde{x}(s;0)}\\ &\quad+\hat{\lambda}_{\mathrm{r}}(s)e^{-\tilde{x}(s;0)}\bar{H}(s)e^{+\tilde{x}(s;0)}\rangle_0,\\ \Delta\phi_{\mathrm{l}}(t) &= \int_0^t ds\langle\hat{\lambda}_{\mathrm{l}}(s)e^{-\tilde{x}(s;0)}\bar{H}(s)e^{+\tilde{x}(s;0)}\rangle_0.\end{aligned} \tag{59}$$

recall that $\bar{H}_{\tau,\mu}(t) = [\bar{H}(t),\hat{\tau}_\mu]$ refers to the full Hamiltonian. The operators $\tilde{\lambda}(t;0)$ and $\tilde{x}(t;0)$ refer to the solution of Eqs. (6) and (7) in the case where the system is initially at the ground state, so $\tilde{x}(t=0;0) = \tilde{\lambda}(t=0;0) = 0$. Also note the equations for the phases correspond to taking the derivatives of the quantity $\Delta\phi(t)$, not $\tilde{\phi}$. The initial conditions of the (de)excitation amplitudes are $\hat{\lambda}_{\mathrm{l}}(t=0) = \hat{\lambda}^N(t=0)$ and $\hat{x}_{\mathrm{r}}(t=0) = \hat{x}^N(t=0)$, and for $\hat{\lambda}_{\mathrm{r}}$ we have

$$\hat{\lambda}_{\mathrm{r}}(t=0) = -\sum_I \frac{F^{NI}}{\Omega_N+\Omega_I}\hat{\Lambda}^I. \tag{60}$$

These initial conditions ensure that at the initial time, the transition moment $\langle\Psi_N|\hat{A}|\Psi_0\rangle$ is consistent with the standard CC linear response result. On the other hand, for the energy $\langle E(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle = \langle\Upsilon(t;g_{\mathrm{L}},g_{\mathrm{R}})|\hat{H}(t)|\Phi(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle$, using the phases above we obtain

$$\lim_{g_{\mathrm{L}},g_{\mathrm{R}}\to 0}\left[\frac{\partial}{\partial g_{\mathrm{L}}}+\frac{\partial}{\partial g_{\mathrm{R}}}\right]\langle E(t;g_{\mathrm{L}},g_{\mathrm{R}})\rangle = \partial_t[\Delta\tilde{\phi}_{\mathrm{l}}(t)+\Delta\tilde{\phi}_{\mathrm{r}}(t)]. \tag{61}$$

This result provides a connection between the phase response and the energy evolution.

Equation (58) is advantageous as it provides linked expressions for quantities such as $\langle\Psi_N|\hat{A}^{\mathrm{H}}|\Psi_0\rangle$, in which the ground- and excited-state propagations are present together. The resolution of the identity can be inserted on both sides of the operator $\hat{A}$, which gives, for instance, $\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle = \sum_{IJ}\langle\Psi_N|\hat{U}^\dagger(t)|\Psi_I\rangle A_{IJ}\langle\Psi_J|\hat{U}(t)|\Psi_0\rangle$, where $A_{IJ} = \langle\Psi_I|\hat{A}|\Psi_J\rangle$. Therefore, the expression above has contributions from the solutions to the excited- and ground-state problems. The excited-state component can be extracted through a frequency space analysis or a related technique.

Alternatively, a single resolution operation can be applied, giving

$$\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle = \sum_J \mathcal{C}_J^*(t)\langle\Psi_J|\hat{A}\hat{U}(t)|\Psi_0\rangle \tag{62}$$

$[\mathcal{C}_J^*(t) = \langle\Psi_N|\hat{U}(t)|\Psi_J\rangle]$. If this idea is applied to the first term on the right-hand side of Eq. (58), we obtain the following two elements: $\delta_{NJ}\exp(i\Omega_N t) + \tilde{d}_{\mathrm{l},J}(t)$ and $\langle\hat{\Lambda}^J \exp[-\tilde{x}(t;0)]\bar{A}\exp[+\tilde{x}(t;0)]\rangle_0$. These resemble in appearance their parent linear (quantum mechanical) counterparts, from Eq. (57). Hence, it is plausible to approximate $C_J^*(t)$ using $\tilde{d}_{\mathrm{l},J} + i\delta_{JN}\Delta\phi(t)$, where $\tilde{d}_{\mathrm{l},J}(t) = \langle\tilde{\lambda}_{\mathrm{l}}(t)\hat{X}^J\rangle_0$. Although the right-hand contribution is more interconnected than the left one, it may be associated approximately with the term $\langle\Psi_0|\hat{A}^{\mathrm{H}}(t)|\Psi_N\rangle$. In the next section we use a numerical model to discuss the right-hand expression for $C_J(t)$.

Although the assignment above might serve useful for interpretation and for quantitative analysis, it could result in more rigorous formulas for a direct comparison in frequency space based on the specific form of the perturbation used. A robust determination of the TD element $\langle\Psi_I|\hat{U}(t)|\Psi_N\rangle$ for manyfold N and I states in turn provides a nonsymmetric representation of the operator $\hat{U}(t)$ and by extension a propagator for general initial states of the form $|\Psi(t=0)\rangle = \sum_J C_{J,0}|\Psi_J\rangle$. This supposes that the propagator is represented in the eigenbasis of the Hamiltonian. It is possible, however, to change the basis representing the operators, such as that corresponding to the bare single orbital excitations, characterized by the indices μ and ν. The choice is largely dependent on the potential numerical approach of interest. We pursue the excited-state energy picture because of its connection to physical models, where a state-by-state perspective becomes convenient and leads to the calculation and understanding of optical and/or magnetic spectra.

B. Propagation from an arbitrary initial state

It is possible to obtain the time evolution of an observable average where the system is an initial state described by a linear combination of eigenstates. We thus denote $|\Psi_{\mathrm{R}}\rangle = \mathcal{N}^{-1/2}[|\Psi_0\rangle + g_{\mathrm{R}}|\Psi(0)\rangle]$ and $\langle\Psi_{\mathrm{L}}| = \mathcal{N}^{-1/2}[\langle\Psi_0| + g_{\mathrm{L}}\langle\Psi(0)|]$, where $\mathcal{N}$ is the normalization factor

$$\mathcal{N} = 1 + g_{\mathrm{L}}S + g_{\mathrm{R}}S^* + g_{\mathrm{L}}g_{\mathrm{R}} \tag{63}$$

and S is the overlap between the ground-state and the initial wave functions: $S = \langle\Psi(0)|\Psi_0\rangle$. The initial wave function reads

$$|\Psi(0)\rangle = \sum_N C_N|\Psi_N\rangle. \tag{64}$$

The set $\{C_N\}$ represents normalized complex-valued coefficients ($\sum_N |C_N|^2 = 1$). Contrary to the case of expressing $\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle$, in this instance the normalization function $\mathcal{N}$ is of crucial relevance.

To obtain the element $\langle\Psi(0)|\hat{A}^{\mathrm{H}}|\Psi(0)\rangle$ we apply the following limit to the mixed second-degree derivative, which gives

$$\lim_{g_{\mathrm{L}},g_{\mathrm{R}}\to 0}\frac{\partial^2}{\partial g_{\mathrm{L}}\partial g_{\mathrm{R}}}\langle\Psi_{\mathrm{L}}|\hat{A}^{\mathrm{H}}(t)|\Psi_{\mathrm{R}}\rangle = \langle\Psi(0)|\hat{A}^{\mathrm{H}}(t)|\Psi(0)\rangle - \langle\Psi_0|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle - \mathcal{I}(t), \tag{65}$$

where

$$\mathcal{I}(t) = [S\langle\Psi(0)|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle + \mathrm{c.c.}] - 2S\times S^*\langle\Psi_0|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle. \tag{66}$$

In the standard picture the element $\langle\Psi(0)|\hat{A}^{\mathrm{H}}(t)|\Psi(0)\rangle$ is equivalent to $\langle\Psi(t)|\hat{A}|\Psi(t)\rangle$, with $|\Psi(t)\rangle = \hat{U}(t)|\Psi(0)\rangle$. In this case we then use a different initial condition for the cluster operators, so $\hat{\lambda}_{\mathrm{l}}(t=0) = \sum_M C_M^*\hat{\Lambda}^M$ and $\hat{x}_{\mathrm{r}}(t=0) = \sum_N C_N\hat{X}^N$. The superposition of operators does not translate into a superposition of symmetrized wave function, but instead it ensures that at the end of the calculation one obtains $\langle\Psi(0)|\hat{A}^{\mathrm{H}}|\Psi(0)\rangle = \sum_{M,N} C_M^*C_N\langle\Psi_M|\hat{A}^{\mathrm{H}}|\Psi_N\rangle$.

With the initial conditions defined we derive the following expression:

$$\lim_{g_{\mathrm{L}},g_{\mathrm{R}}\to 0}\frac{\partial^2}{\partial g_{\mathrm{L}}\partial g_{\mathrm{R}}}\langle\Upsilon(t;g_{\mathrm{L}},g_{\mathrm{R}})|\hat{A}|\Phi(t;g_{\mathrm{L}},g_{\mathrm{R}}\rangle = \langle\hat{\lambda}_{\mathrm{l}}(t)e^{-\tilde{x}(t;0)}[\bar{A},\hat{x}_{\mathrm{r}}(t)]e^{+\tilde{x}(t;0)} + \hat{\lambda}_{\mathrm{l,r}}(t)e^{-\tilde{x}(t;0)}\bar{A}e^{+\tilde{x}(t;0)}\rangle_0, \tag{67}$$

where $\hat{\lambda}_{\mathrm{l,r}}$ is the mixed derivative $(\partial^2\hat{\lambda}/\partial g_{\mathrm{L}}\partial g_{\mathrm{R}})$ with respect to g_{L} and g_{R} evaluated at $g_{\mathrm{L}} = g_{\mathrm{R}} = 0$, and it follows the motion equation

$$-i\partial_t\lambda_{\mathrm{l,r},\mu}(t) = \langle\hat{\lambda}_{\mathrm{l,r}}(t)e^{-\tilde{x}(t;0)}\bar{H}_{\tau,\mu}(t)e^{+\tilde{x}(t;0)} + \hat{\lambda}_{\mathrm{l}}(t)e^{-\tilde{x}(t;0)}[\bar{H}_{\tau,\mu}(t),\hat{x}_{\mathrm{r}}(t)]e^{+\tilde{x}(t;0)}\rangle_0, \tag{68}$$

in which

$$\hat{\lambda}_{\mathrm{l,r}}(t=0) = \sum_J Y_J\hat{\Lambda}^J \tag{69}$$

and

$$Y_J = \sum_{M,N} C_M^*(0)C_N(0)\frac{\langle\hat{\Lambda}^M[[\bar{H}_0,\hat{X}^N],\hat{X}^J]\rangle_0}{\Omega_M - \Omega_J - \Omega_N}. \tag{70}$$

This initial condition guarantees that at the initial propagation time the element $\langle\Psi(0)|\hat{A}^{\mathrm{H}}(0)|\Psi(0)\rangle$ is consistent with QR theory.

Using the standard TD CC equations for ground-state propagation $[\langle\Psi_0|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle]$, we find the relation

$$\langle\Psi(0)|\hat{A}^{\mathrm{H}}(t)|\Psi(0)\rangle = \langle[\hat{L}_0 + \tilde{\lambda}(t;0)]e^{-\tilde{x}(t;0)}\bar{A}e^{+\tilde{x}(t;0)}\rangle_0 + \langle\hat{\lambda}_{\mathrm{l}}(t)e^{-\tilde{x}(t;0)}[\bar{A},\hat{x}_{\mathrm{r}}(t)]e^{+\tilde{x}(t;0)} + \hat{\lambda}_{\mathrm{l,r}}(t)e^{-\tilde{x}(t;0)}\bar{A}e^{+\tilde{x}(t;0)}\rangle_0 + \mathcal{I}(t). \tag{71}$$

If the ground-state wave function Ψ_0 is orthogonal to the initial state, then $\mathcal{I} = 0$, otherwise this term, $\mathcal{I}(t)$, can be computed using Eqs. (10) and (13). Our method is also applicable to obtain an element such that $\langle\Psi_J|\hat{A}^{\mathrm{H}}(t)|\Psi_I\rangle$. This only requires changing the initial conditions of the left and right cluster operators and a simple adaptation of Eq. (70) where $C_M^*(0)$ and $C_N(0)$ are replaced by δ_{JM} and δ_{IN}, correspondingly, and the same applies to the initial conditions. In fact one can analyze propagating the wave functions $\langle\Psi_{\mathrm{L}}| = \langle\Psi_0| + g_{\mathrm{L}}\langle\Psi_J|$ and $|\Psi_R\rangle = |\Psi_0\rangle + g_{\mathrm{R}}|\Psi_I\rangle$ and conclude that our formalism gives the element $\langle\Psi_J|\hat{A}^{\mathrm{H}}(t)|\Psi_I\rangle$ in terms of the equations shown above, with the mentioned required adaptations. This would in turn justify the initial conditions for cluster operators we applied to obtain the general evolution of a quantum mechanical observable under an arbitrary initial state, $\langle\Psi(0)|\hat{A}^{\mathrm{H}}(t)|\Psi(0)\rangle$.

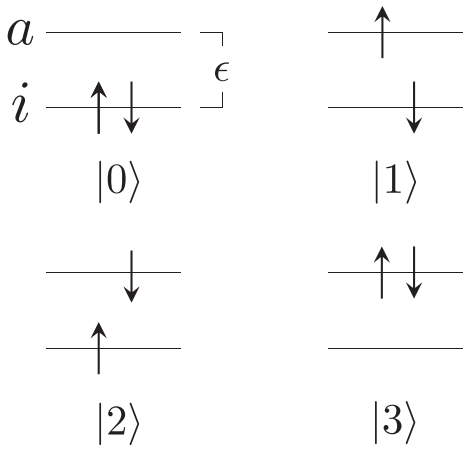

FIG. 2. Sketch of the two-level system considered for the numerical illustration.

VI. NUMERICAL ILLUSTRATION

Here we examine the application of our generalized SR method to a two-electron two-level system, where we examine in total four levels. It is studied here how the quantum system evolves under the presence of an external TD driving field that is strong. The Hamiltonian of the system is

$$\hat{H}(t) = \sum_{\sigma} \epsilon \hat{a}_{\sigma}^{\dagger}\hat{a}_{\sigma} + \sum_{\sigma} b[\hat{\tau}_{\sigma} + \hat{\tau}_{\sigma}^{\dagger}] + w[\hat{\tau}_{\uparrow}\hat{\tau}_{\downarrow} + \hat{\tau}_{\downarrow}^{\dagger}\hat{\tau}_{\uparrow}^{\dagger}] + \hat{v}(t). \tag{72}$$

We denote the occupied level as i and the unoccupied one as a, so $\hat{\tau}_{\sigma} = \hat{a}_{\sigma}^{\dagger}\hat{i}_{\sigma}$. The external driving term reads $\hat{v}(t) = -f(t)\mu_0 \sum_{\sigma}[\hat{\tau}_{\sigma} + \hat{\tau}_{\sigma}^{\dagger}]$. The function $f(t)$ describes a Gaussian pulse $f(t) = f_0 \exp[-(t-t_0)/2\sigma_0^2]$. In our simulation we take ϵ as 1 eV, b and w as 0.25 eV, $\mu_0 = 0.5$ a.u., $f_0\mu_0$ as 1 eV (so $f_0 \approx 0.0735$ a.u., which is approximately 3.8×10^{10} V/m), $\sigma_0 = 5$ fs, and $t_0 = 2.5 \times \sigma_0$. This corresponds to applying a strong pulse to the system.

In Fig. 2 we show the four mentioned quantum levels, which form the linear space we consider: the ground-state configuration $|0\rangle$, two separate single-electron promoted states, $|1\rangle$ and $|2\rangle$, respectively, and the a doubly excited configuration $|3\rangle$. All our wave functions are constrained to the space $\mathcal{L}$ spanned by the set of mentioned states, $\{|0\rangle, |1\rangle, |2\rangle, |3\rangle\}$. We then translate all the required operators, such as the Hamiltonian and the cluster operators, into matrix form over the basis shown in Fig. 2; this allows us to perform all the operations numerically. The diagonalization of the Hamiltonian matrix reveals a considerable mixing between the states in the generation of the eigenvectors; such mixing ensures that our model is *nontrivial*, which leads to the characteristic asymmetries of non-Hermitian CC approaches, discussed below. The eigenvectors of the unperturbed Hamiltonian matrix are referred to as Ψ_0, Ψ_1, Ψ_2, and Ψ_3, where $\mathbf{H}_0|\Psi_J\rangle = E_J|\Psi_J\rangle$ (for $J = 0$, 1, 2, and 3). The ground state is composed approximately of 92% $|0\rangle$ and 8% of the singles configurations. The first-excited state contains 13% of the doubles configuration $|3\rangle$, 6% of $|0\rangle$, and the rest is an equal mix of singles. The second-excited state is a triplet state with equal amounts of the $|1\rangle$ and $|2\rangle$ states. And the third-excited state is dominated by the doubles state $|3\rangle$ with a weight of 87%, the combined states $|1\rangle$ and $|2\rangle$ give a weight of 10%, and the rest corresponds to $|0\rangle$. Therefore, there is considerable interaction by the configurations that we selected (Fig. 2). The standard unitary operations based on the operator $\hat{U}(t)$ were performed using a simple midpoint rule, where we discretize the whole time interval as a grid and propagate step by step using $|\Psi(t+\delta t)\rangle \approx \exp[-i\hat{H}(t+\delta t/2)\delta t]|\Psi(t)\rangle$. For the TD CC equations we use the second-order Runge-Kutta methodology, over the same grid for the unitary propagation, which consists of 60 000 points.

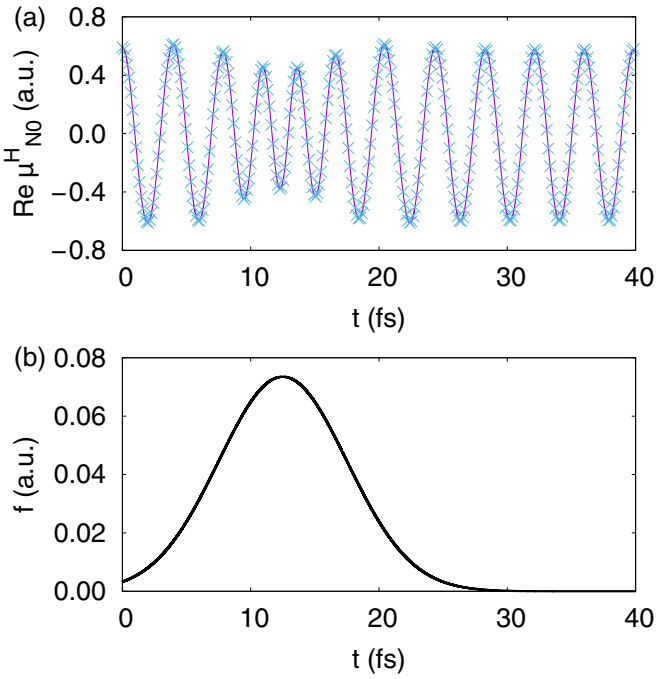

FIG. 3. (a) Computed element $\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle$ ($\hat{A} = \hat{\mu}$) for $N = 1$ in the interval of time between 0 and 40 fs. The purple line corresponds to our second response calculations, whereas the blue "X" symbols correspond to sample points of full standard propagation, from computing $\hat{U}(t)$ in matrix representation and applying it to the states Ψ_N and Ψ_0, which are eigenfunctions of the Hamiltonian matrix derived from Eq. (72).

Let us begin considering the computation of the element $\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle$, where $\hat{A}$ corresponds to the dipole operator, which we take in this work as $\hat{\mu} = \mu_0(\hat{\tau}_{\uparrow} + \hat{\tau}_{\downarrow} + \mathrm{H.c.})$, and denote $\langle\Psi_N|\hat{\mu}^{\mathrm{H}}(t)|\Psi_0\rangle$ as μ_{N0}^{H}. The term $\langle\Psi_N|\hat{A}^{\mathrm{H}}(t)|\Psi_0\rangle$ is an important quantity because in the Heisenberg representation, for a general initial state that is a linear combination of eigenstates, a quantity of this kind is required. For this reason we propose a model for this type of object, because it would be needed for a propagation from an initial state that includes a portion of the ground state. We take $N = 1$, so our simulation is based on propagating with the SR equations both the ground state and the excited state. Ψ_1 is a singlet excited state of the system. Our basis misses the two paramagnetic states in which the second level is occupied with an electron with the same z-spin as the electron in the first level. However, we focus on singlet states. Figure 3(a) shows the time dependency of the real part of this object (its imaginary component behaves in

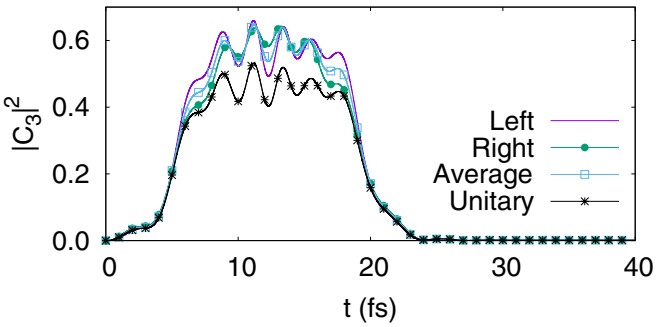

FIG. 4. Probability of finding the system in the doubly excited state Ψ_3, when the quantum system evolves from state Ψ_1 and in the presence of the pulse shown in Fig. 3. The black line with stars is obtained from the unitary propagation, the purple solid line is obtained from $\tilde{d}^*_{1,3}(t)$, the green line with solid circles is obtained from $c'_3(t)$, and the blue line with squares corresponds to the average $1/2[c'_3(t) + \tilde{d}^*_{1,3}(t)]$.

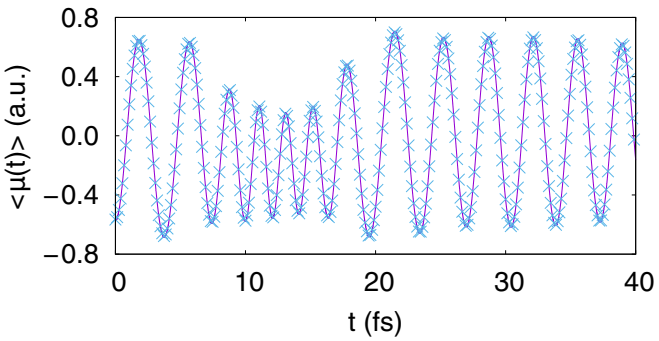

FIG. 5. Comparison between SR theory and unitary propagation for the calculation of the time-dependent dipole of the system $\langle\mu(t)\rangle = \langle\Psi(0)|\hat{U}^\dagger(t)\hat{\mu}\hat{U}(t)|\Psi(0)\rangle$, where $|\Psi(0)\rangle$ is a linear combination of the states $|\Psi_1\rangle$ and $|\Psi_3\rangle$: $|\Psi(0)\rangle = \sqrt{3/4}|\Psi_1\rangle + \sqrt{1/4}|\Psi_3\rangle$. The purple line represents SR theory. The blue "X" symbols represent samples from the unitary propagation.

a similar fashion), and Fig. 3(b) shows the shape of the pulse applied to the system. As expected, given that the TD CC theory is robust if the cluster operators cover all excitation orders, the SR theory and the standard unitary solution yield visually identical results. Both the SR theory left and right expressions for the matrix element in the Heisenberg representation offer the same results. This would not hold if the cluster operators were truncated, which happens in practice; in that case the expressions may differ.

If this two-electron quantum system initiated evolution from the first-excited state, then one can ask about the probability of finding the system in the third-excited state at some given time. Such probability is determined by the squared modulus of the coefficient $C_3(t) = \langle\Psi_3|\hat{U}(t)|\Psi_1\rangle$. This coefficient is approximated as $\tilde{d}^*_{1,J}(t)$ $(J = 3)$, which is discussed in the previous section. For the right-hand contribution, we noted that the coefficient $c_J(t)$ often underestimates C_3 by a significant margin. As an alternative to this, we compute $c'_J(t) = \langle\hat{\Lambda}^J\hat{x}_r(t)\exp(\tilde{x}(t;0))\rangle_0/\|\hat{x}_r(t)\exp(\tilde{x}(t;0))|0\rangle\|$ and denote that as our right-hand estimator. Computing the norm of $\hat{x}_r(t)\exp(\tilde{x}(t;0))|0\rangle$ is not practical for molecular systems due to the need for Hermitian conjugation, but in this case the small size of the system allows for its computation. We refer to $c'_J(t)$ as the right-hand approximation to the standard coefficient $\langle\Psi_J|\hat{U}(t)|\Psi_1\rangle$. Figure 4 shows the result of this procedure. As discussed before, at short times our assignment holds, but as the pulse action becomes more significant some deviations are present. Part of the reason for such behavior is the non-negligible cluster amplitudes associated with the operator $\hat{T}$. We noticed that upon reducing the parameters b and w to about 0.1 eV, the agreement with respect to C_3 is quite improved, especially for the averaged value $c_{\text{avg},3}(t) = 1/2 \times [c'_3(t) + \tilde{d}^*_{1,3}(t)]$, but we believe it important to emphasize potential deviations over closer agreements.

Now we show the application of the SR theory to compute the evolution of an observable such as the dipole in the case where the system does not initiate at the ground state, but at a linear combination of two excited states. We then choose the following as the initial state:

$$|\Psi(0)\rangle = \sqrt{3/4}|\Psi_1\rangle + \sqrt{1/4}|\Psi_3\rangle, \tag{73}$$

where the wave functions $|\Psi_1\rangle$ and $|\Psi_3\rangle$, in the basis shown in Fig. 2, correspond to the first- and third-excited states obtained from the diagonalization of the unperturbed system Hamiltonian matrix. As in the case for calculating $\langle\Psi_N|\hat{\mu}^H(t)|\Psi_0\rangle$, the SR expression, Eq. (71) with $\hat{A} = \hat{\mu}$, for $\langle\mu(t)\rangle = \langle\Psi(t)|\hat{\mu}|\Psi(t)\rangle$ [where $\hat{U}(t)|\Psi(0)\rangle = |\Psi(t)\rangle$] is fully consistent with respect to the unitary propagation (Fig. 5), confirming the possibility of propagating an observable based on a general initial state.

The effect of increasing the intensity of the electric field is presented in Fig. 6, where the unitary propagation results are reproduced for the observable. Despite this, however, the terms c'_3 and $\tilde{d}^*_{1,3}$ display deviations and an oscillatory behavior at longer times. This is caused by the non-Hermitian nature of our time-dependent CC wave functions. Because the left bra and the right ket are different, there is likely an imbalance in the projections we extracted from such TD CC kets. However, we believe that with all the tools developed here an alternative more accurate route to compute eigenstate probabilities may be found, possibly by analyzing the behavior of the system under different initial conditions. Non-Hermitian CC theories are the subject of asymmetries that can cause small deviations from the unitary calculations. The matrix elements that are inferred from unitary standard quantum mechanics are identified in nonsymmetric non-Hermitian TD CC theory; however, matrix elements from CC do not conjugate as expected [43], resulting in disparities. In our simulations these are small. There are differences between the SR CC and the unitary calculations that do not meet the eye and are below 0.1%, but they persist for very fine time grids. For this reason, a potential alternative is to formulate our theory within unitary coupled-cluster theory, which has quite desirable properties in terms of the assignment of transition elements. On the other hand, for convenience we employed a simplified two-electron two-level approach which was tuned to feature non-negligible couplings between the configurations that span the linear space of interest. However, future work could focus on the

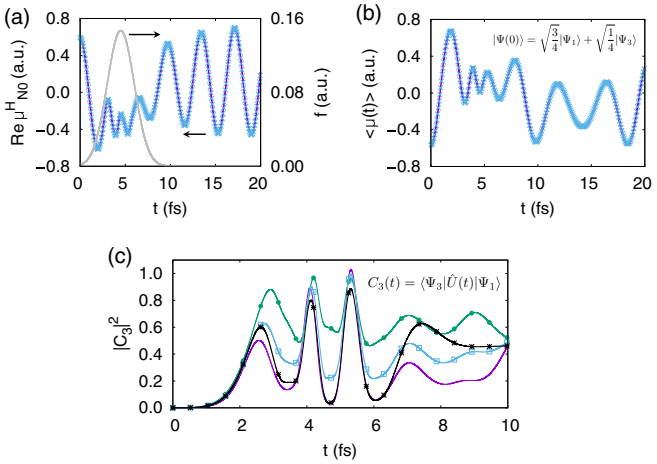

FIG. 6. Response of the system to a stronger driving pulse in which $f_0\mu_0 = 2$ eV (so $f_0 \approx 7.6 \times 10^{10}$ V/m), $\sigma_0 = 1.5$ fs, and $t_0 = 4.5$ fs. Panel (a) shows the shape of the pulse (light gray) and time dependency of the real part of the element $\langle\Psi_N|\hat{\mu}^{\mathrm{H}}(t)|\Psi_0\rangle$, $N = 1$. The purple line denotes SR calculations and the blue "X" symbols denote unitary reference results. Panel (b) shows the element $\langle\Psi(0)|\hat{\mu}^{\mathrm{H}}|\Psi(0)\rangle$. The purple line refers to SR calculations and the blue "X" symbols refer to unitary reference results. Panel (c) displays the evolution of the coefficient C_3, and our CC estimators. The purple solid line is the left-hand estimator, the green line with solid circles is the right-handed estimator, the blue line with squares is their average, and the black line with stars is the exact result.

application of our initial-state modifications within the context of Lipkin models [71–75], which are often employed to gain a critical understanding of many-body systems and may offer in-depth insights regarding the numerical performance of the proposed methodologies.

VII. CONCLUSION

An extended linear response theory (or second linear response theory) was formulated to determine properties of excited states through the time-dependent coupled-cluster formalism, where the generalization to cases beyond that of linear perturbations was considered. From the theoretical generalization we derived a set of equations that characterize the time-dependent evolution of transition elements in the Heisenberg representation, so these could support propagations that rely on such kinds of transition objects or to derive nonlinear properties that rely on linked coupled-cluster expressions. The proposed second response theories can be used to study quantities such as multipolar matrix elements, magnetic transition amplitudes, and electronic densities. In the case of the second linear response theory, we found it gives results fully consistent with the well-known coupled-cluster quadratic response theory. On the other hand, because our theory examines excited states in a step-by-step fashion, it allows us to identify wave-function time-dependent linear-combination coefficients, so bridging the second linear response and general response theory expressions with standard wave-function theory. These connections could serve useful in the computation of excited-state coherent interferences and their response to driving fields in either the linear or the nonlinear regime.

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