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Letter

Curing the Divergence in Time-Dependent Density Functional Quadratic Response Theory

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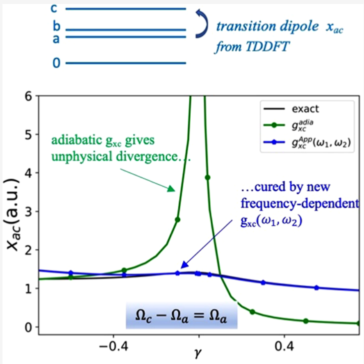
ABSTRACT: The adiabatic approximation in time-dependent density functional theory is known to give an incorrect pole structure in the quadratic response function, leading to unphysical divergences in excited state-to-state transition probabilities and hyperpolarizabilties. We find the form of the exact quadratic response kernel and derive a practical and accurate approximation that cures the divergence. We demonstrate our results on excited state-to-state transition probabilities of a model system and of the LiH molecule.



Until recently, quadratic response has received far less attention than linear response. Most response applications had involved properties related to the optical spectra of a molecule in equilibrium, while relatively few ventured into the nonlinear regime to gain access to properties such as two-photon absorption, sum-frequency generation, and hyperpolarizabilities which can be obtained from the quadratic response of the ground-state system.[1,2] However, in the past few decades, nonlinear optical processes have emerged as key in a number of applications, including optical data storage and switching, for examples. Moreover, an increasingly relevant class of applications involves excited-state dynamics, where a molecule is initially photoexcited and coupled electron−ion motion ensues. Such applications inherently require the response of an excited state, appearing in the form of excited state-to-state transition amplitudes. These amplitudes also appear even without nuclear motion: when simulating the dynamics of a molecule in a nonperturbative laser field by expressing the wavefunction in a superposition of eigenstates, coupled by the laser field.

Response theory offers a way to obtain these quantities by circumventing the expensive calculation of the excited-state wavefunctions and may yield more accurate properties when, inevitably, approximations are used. However, response theories of approximate electronic structure theories suffer from an unphysical divergence problem when the difference between two excitation frequencies is equal to another excitation frequency.[3] This had been first discovered in time-dependent Hartree−Fock (TDHF) 40 years ago[4] but lay relatively dormant until the work of ref 3, which showed the divergence also appears in response theories based on coupled cluster, multiconfiguration self-consistent field, and adiabatic time-dependent density functional theory (TDDFT).[3,5−7]

Addressing this issue for TDDFT[8−11] is of great interest: not only does TDDFT have a favorable system-size scaling enabling the calculation of photoinduced dynamics in complex molecules, it is in principle an exact theory and so offers the possibility of finding more accurate functional approximations that cure the unphysical divergence, which is what we aim to achieve here.

We find the form of the exact quadratic response kernel of TDDFT and show explicitly why the adiabatic approximations used thus far are responsible for the incorrect pole structure of the second-order response function that creates the divergence, and that a relatively gentle linear frequency dependence in the quadratic response kernel corrects the pole structure and tames the divergence. Inspired by this, we derive a frequency-dependent approximation for the quadratic response kernel. Results on a two-electron model system and on the LiH molecule show that our approximation provides a practical and accurate fix to the problem of divergences in the TDDFT quadratic response.

In TDDFT response theory, the central object at each order of response is a density-response function expressed in terms of response functions of the Kohn−Sham (KS) system and

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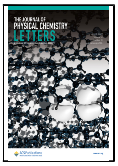

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exchange—correlation kernels.[10,12] The linear density-response function of the interacting system to an external perturbation $\delta v_{\text{ext}}(\mathbf{r}, t)$,

$$\begin{aligned}\chi(\mathbf{r}, \mathbf{r}', t - t') &= \frac{\delta n(\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}'t')} \\ &= -i\theta(t - t')\langle \Psi_0 | [\hat{n}(\mathbf{r}t), \hat{n}(\mathbf{r}'t')] | \Psi_0 \rangle\end{aligned}$$

where $\theta(t - t')$ is the step function, has the spectral representation

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_a \left(\frac{n_{0a}(\mathbf{r})\, n_{a0}(\mathbf{r}')}{\omega - \Omega_a + i0^+} - \frac{n_{0a}(\mathbf{r}')\, n_{a0}(\mathbf{r})}{\omega + \Omega_a + i0^+} \right) \tag{1}$$

where $n_{0a}(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_a \rangle$ is the transition density between the ground state, Ψ_0, and the excited state, Ψ_a, which has excitation frequency $\Omega_a = E_a - E_0$ and $\hat{n}(\mathbf{r})$ is the one-body density operator; the 0^+ indicates the shift of the pole slightly below the real axis to ensure causality and will be omitted hereon. In TDDFT, χ is instead obtained from the non-interacting KS system, through the Dyson-like equation[13,14]

$$\chi_{ij}^{\text{tddft}}(\omega) = \chi_{\text{S},ij}(\omega) + \chi_{\text{S},ik}(\omega)\, f_{\text{HXC},kl}(\omega)\, \chi_{lj}(\omega) \tag{2}$$

where χ_{S} is the density-response function of the KS system and $f_{\text{HXC}}(\omega)$ is the Hartree—exchange—correlation kernel. The indices i, j represent the spatial variables $\mathbf{r}_i$ and $\mathbf{r}_j$ and repeated indices imply integration. While $\chi_{\text{S}}(\omega)$ displays residues given by transition densities between ground and excited states of the KS system and poles given by KS excitation frequencies, the linear response (LR) kernel,

$$f_{\text{HXC},kl}[n_0](t - t') = \frac{\delta(t - t')}{|\mathbf{r}_k - \mathbf{r}_l|} + \left.\frac{\delta v_{\text{XC}}[n](\mathbf{r}_k, t)}{\delta n(\mathbf{r}_l, t')}\right|_{n=n_0}$$

corrects these to those of the true response function. Almost always, an adiabatic approximation is used where the exchange—correlation potential $v_{\text{XC}}[n](\mathbf{r}, t)$ depends only on the instantaneous density and is approximated by the functional derivative of a ground-state energy functional, $E_{\text{XC}}[n]$. This results in a frequency-independent kernel, $f_{\text{XC},ij}^{\text{adia}}[n](\omega) = \frac{\delta^2 E_{\text{XC}}[n]}{\delta n(\mathbf{r}_i)\, \delta n(\mathbf{r}_j)}$. With an adiabatic approximation, LR TDDFT has become a workhorse of electronic structure calculations, yielding excitation spectra with an unprecedented balance between accuracy and efficiency. The adiabatic approximation is known to fail for certain classes of excitations, and improved, frequency-dependent approximations have been derived for some cases, e.g., double excitations.[15,16]

Going to second order in the perturbation defines the quadratic response (QR) function,[12,17,18]

$$\chi^{(2)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, t - t_1, t - t_2) = \frac{\delta^2 n(\mathbf{r}, t)}{\delta v_{\text{ext}}(\mathbf{r}_1, t_1)\, \delta v_{\text{ext}}(\mathbf{r}_2, t_2)}:$$

$$\begin{aligned}&\chi^{(2)}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2; t - t_1, t - t_2) \\ &\quad = \frac{(-i)^2}{2}\theta(t - t_1)\, \theta(t_1 - t_2) \\ &\qquad \times \langle \Psi_0 | [[\hat{n}(\mathbf{r}, t), \hat{n}(\mathbf{r}_1, t_1)], \hat{n}(\mathbf{r}_2, t_2)] | \Psi_0 \rangle + (1 \leftrightarrow 2)\end{aligned} \tag{3}$$

which has the spectral representation[18]

$$\begin{aligned}&\chi^{(2)}(\mathbf{r}, \mathbf{r}_i, \mathbf{r}_j, \omega_i, \omega_j) \\ &= \frac{1}{2}\sum_{a,b} \left(\frac{n_{0a}(\mathbf{r})\, n_{ab}(\mathbf{r}_i)\, n_{b0}(\mathbf{r}_j)}{(\omega_i + \omega_j - \Omega_b)(\omega_j - \Omega_a)} \right. \\ &\quad - \frac{n_{0a}(\mathbf{r}_j)\, n_{ab}(\mathbf{r})\, n_{b0}(\mathbf{r}_i)}{(\omega_i - \Omega_b)(\omega_j + \Omega_a)} \\ &\quad \left. + \frac{n_{0a}(\mathbf{r}_j)\, n_{ab}(\mathbf{r}_i)\, n_{b0}(\mathbf{r})}{(\omega_i + \omega_j + \Omega_b)(\omega_i + \Omega_a)} + (i \leftrightarrow j) \right)\end{aligned} \tag{4}$$

where the state-a to state-b transition density is $n_{ab}(\mathbf{r}) = \langle \Psi_a | \hat{n}(\mathbf{r}) | \Psi_b \rangle$ and can be extracted from double residues of $\chi^{(2)}$. The second-order response may be extracted from TDDFT linear response quantities together with a QR kernel $g_{\text{XC}}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, t - t_1, t - t_2) = \left.\frac{\delta^2 v_{\text{XC}}(\mathbf{r}, t)}{\delta n(\mathbf{r}_1, t_1)\, \delta n(\mathbf{r}_2, t_2)}\right|_{n_0}$ through[12,19,20]

$$\begin{aligned}&\chi_{mnp}^{(2),\text{tddft}}(\omega_1, \omega_2) \\ &\quad = \chi_{mi}(\omega_1 + \omega_2)\, \chi_{\text{S},ij}^{-1}(\omega_1 + \omega_2)\, {\chi_{\text{S},jkl}}^{(2)}(\omega_1, \omega_2) \\ &\qquad \times \chi_{\text{S},lq}^{-1}(\omega_1)\, \chi_{qn}(\omega_1)\, \chi_{\text{S},kr}^{-1}(\omega_2)\, \chi_{rp}(\omega_2) \\ &\qquad + \chi_{mi}(\omega_1 + \omega_2)\, g_{\text{XC},ijk}(\omega_1, \omega_2)\, \chi_{jn}(\omega_1)\, \chi_{kp}(\omega_2)\end{aligned} \tag{5}$$

(again using the index notation for spatial dependences). In the adiabatic approximation, $g_{\text{XC},ijk}^{\text{adia}}(\omega_1, \omega_2) = \left.\frac{\delta^3 E_{\text{XC}}[n]}{\delta n_i\, \delta n_j\, \delta n_k}\right|_{n=n_0}$ is frequency-independent.

Equation 5 is usually recast in terms of a matrix in the space of KS single excitations in molecular codes, e.g., see refs 21 and 22, or written in a Sternheimer formulation,[10,23] which has enabled calculations of a wide range of nonlinear optical properties of complex systems, e.g., see refs 24—28. However, several works encountered greatly exaggerated responses in domains where the difference between two excitation frequencies Ω_b and Ω_c is equal to another excitation frequency, Ω_a; i.e., $\Omega_c - \Omega_b = \Omega_a$,[3,6,7,29,30] which, in this work, we call the "resonance condition". Reference 3 tracked this unphysical divergence to an incorrect pole structure in $\chi^{(2),\text{tddft}}$ when an adiabatic approximation is made, pointing out the similarity to the divergence observed in ref 4 for TDHF, as well as in other response theories. The question arises: Since TDDFT is in principle an exact theory, what is the structure of the exact QR kernel that cures this divergence? And can we build a practical approximation that inherits this behavior?

To answer these questions, we construct the exact $\chi^{(2)}$ in a Hilbert space truncated to contain four many-body states, denoted 0, a, c, and c', and solve for the exact form of the QR kernel in this truncated space by inversion of eq 5. The resonant case is met when $\Omega_c = 2\Omega_a$. We include the possibility of a double-excitation contribution to the many-body states, where the states c and c' are approximately linear combinations of a single KS excitation ν_3 and a double KS excitation $2\nu_1$ (see Figure 1 for a slightly more general truncation and note that in this work we will refer to KS excitations via the symbol ν and true excitations via the symbol Ω). In fact, the resonance condition is suggestive of a state of double-excitation character: $\Omega_c = \Omega_b + \Omega_a$ would have double-excitation character if Ω_a and Ω_b are predominantly single excitations out of a Slater determinant reference and if the TDDFT corrections to the excited-state

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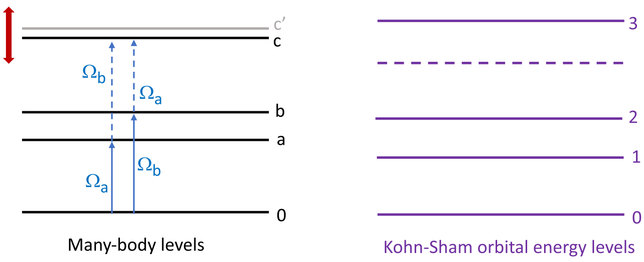

Figure 1. Depiction of a truncated Hilbert space. True interacting system (left) with three excited states of excitation frequencies Ω_a, Ω_b, and Ω_c, with the corresponding KS system (right) with excitation frequencies ν_1, ν_2, and ν_3 with 0 being the HOMO level; $\nu_i = \epsilon_i - \epsilon_0$, where ϵ_i is the orbital energy. The possibility of a KS double excitation of frequency $\nu_1 + \nu_2$ (dashed line) mixing with the single excitation at ν_3 yields an additional excitation $\Omega_{c'}$ (gray on the left); in this case c and c' have both single and double character. Displacement along the red vertical arrow tunes the system out of the resonance condition. In our model, we take the case when $\Omega_b = \Omega_a$ and $\nu_2 = \nu_1$.

energies are small. We will consider the second-order response at frequencies ω_1, ω_2 to be much closer to Ω_a than to Ω_c.

To simplify the inversion, we assume that the KS states have frequencies ν_1, ν_3, well-separated from each other and far enough from the ground state such that the single-pole approximation may be applied.[10,13,31,32] Then, constructing the linear response functions χ and χ_S and the KS quadratic response function $\chi_S^{(2)}$ and using them in eq 5 (see the Supporting Information for detail) gives

$$\begin{aligned}\chi_{mnp}^{(2),\mathrm{tddft}}&(\omega_1, \omega_2)\\ &= \left(\frac{a_{c,mi}}{\omega_1 + \omega_2 - \Omega_c} + \frac{a_{c',mi}}{\omega_1 + \omega_2 - \Omega_{c'}}\right)\\ &\times \left[a_{S3,ij}^{-1}\frac{{\nu_1}^2}{2\Omega_a^2}\left(\frac{A_{S13,jnp}}{\omega_2 - \Omega_a} + \frac{A_{S13,jpn}}{\omega_1 - \Omega_a}\right)\right.\\ &\left.+ \frac{a_{S3,ij}^{-1}\frac{{\nu_1}^2}{{\Omega_a}^2}\langle f_{\mathrm{HXC}}\rangle_1(A_{S13,jnp} + A_{S13,jpn}) + g_{\mathrm{XC},ijk}(\omega_1, \omega_2)a_{a,jn}a_{a,kp}}{(\omega_2 - \Omega_a)(\omega_1 - \Omega_a)}\right]\end{aligned} \tag{6}$$

where $A_{S13,jnp} = n_{S01}(\mathbf{r}_j)n_{S13}(\mathbf{r}_n)n_{S30}(\mathbf{r}_p)$, $a_{S3,ij} = n_{S03}(\mathbf{r}_i)n_{S30}(\mathbf{r}_j)$, defined in terms of the KS transition densities. The residue $a_{c,mi} = n_{0c}(\mathbf{r}_m)n_{c0}(\mathbf{r}_i)$ and

$$\langle f_{\mathrm{HXC}}(\omega_2)\rangle_1 = \int \varphi_0(\mathbf{r})\varphi_1(\mathbf{r})\, f_{\mathrm{HXC}}(\mathbf{r}, \mathbf{r}', \omega)\, \varphi_0(\mathbf{r}')\, \varphi_1(\mathbf{r}')\, \mathrm{d}^3\mathbf{r}\, \mathrm{d}^3\mathbf{r}'$$

All quantities on the right of eq 6 can be obtained from LR TDDFT, from the QR kernel, or from the KS system directly.

When g_{XC} is independent of frequency, the incorrect pole structure is salient, with the last line of eq 6 having a three-pole structure instead of the two appearing in the exact $\chi^{(2)}$ of eq 4.[3,6,30] We note that in most cases the frequencies $\omega_{1,2}$ are in a region dominated by single excitations, where the adiabatic approximation for the linear response XC kernel f_{XC} does a reasonable job; i.e., the exact f_{XC} does not have important frequency dependence in the region it is probed in eq 6. Instead, it follows that g_{XC} must carry a frequency dependence that removes the extra pole, which means the numerator of the last term in eq 6 must be of the following form: $X_{inp}(\omega_1 - \Omega_a) + Y_{inp}(\omega_2 - \Omega_a)$, where X_{inp} and Y_{inp} are functions of $\{\mathbf{r}_i, \mathbf{r}_n, \text{and } \mathbf{r}_p\}$. The permutation symmetry of $\chi^{(2)}$ under $(\mathbf{r}_1, \omega_1) \leftrightarrow (\mathbf{r}_2, \omega_2)$ implies $Y_{inp} = X_{ipn}$, leading to

$$\begin{aligned}X_{inp}&(\omega_1 - \Omega_a) + X_{ipn}(\omega_2 - \Omega_a)\\ &= g_{\mathrm{XC},ijk}(\omega_1, \omega_2)a_{a,jn}a_{a,kp}\\ &\quad + a_{S3,ij}^{-1}\frac{{\nu_1}^2}{{\Omega_a}^2}\langle f_{\mathrm{HXC}}(\omega_2)\rangle_1(A_{S13,jnp} + A_{S13,jpn})\end{aligned} \tag{7}$$

Equation 7 shows that the exact QR kernel g_{XC} in the vicinity of $\omega_{1,2}$ close to Ω_a has a linear frequency dependence. For the general case where $\Omega_a \neq \Omega_b$, a similar analysis leads to $g_{\mathrm{XC}}(\omega_1 \approx \Omega_a, \omega_2 \approx \Omega_b)$ having linear behavior as $X(\omega_1 - \Omega_a) + Y(\omega_2 - \Omega_b)$. It remains now to derive an approximation for X_{inp} that yields a practical approximation for $g_{\mathrm{XC},ijk}(\omega_1, \omega_2)$.

In order to determine X_{inp}, we interpolated between two limiting cases. The first is to set $g_{\mathrm{XC}} \to g_{\mathrm{XC}}^{\mathrm{adia}}$ when $\omega_1 = \omega_2 = 0$ in eq 7, which gives an equation for $X_{inp} + X_{ipn}$. A possible solution is

$$X_{inp} = \frac{-1}{2\Omega_a}\left(g_{\mathrm{XC},ijk}^{\mathrm{adia}}a_{a,jn}a_{a,kp} + a_{S3,ij}^{-1}\frac{{\nu_1}^2}{{\Omega_a}^2}\langle f_{\mathrm{HXC}}(\omega_2)\rangle_1 A_{S13,jnp}\right) \tag{8}$$

Using eq 8 in eq 7 gives $g_{\mathrm{XC}}^{\mathrm{App},1}(\omega_1, \omega_2)$ that corrects the single-excitation contribution $(A_{S13,jnp})$ to the quadratic response but appears not to include double-excitation contributions to the transition density. It is unclear whether the first term captures true double-excitation character because an adiabatic QR kernel yields a response that has poles at sums of LR-corrected single excitations without any mixing with double excitations, and even these poles are missing when only forward transitions are kept.[33,34] Our second limiting case therefore focuses on the double-excitation contribution.

Thus, the second limit is the opposite case when state c is close to a pure double excitation. Considering Figure 1, the KS state 3 is absent, and we denote the KS state with two electrons excited to orbital 1 at the dashed line as d. The KS residue appearing in eq 6, $A_{S1d,ijk} = n_{S01}(\mathbf{r}_i)n_{S1d}(\mathbf{r}_j)n_{Sd0}(\mathbf{r}_k) = 0$ due to the last factor, and equating eq 6 to the true $\chi^{(2)}$ in this limit yields

$$\begin{aligned}a_{c,mi}g_{\mathrm{XC},ijk}^{\mathrm{App},2}a_{a,jn}a_{a,kp} &= \frac{1}{2}[(\omega_1 - \Omega_a)A_{ca,mnp}\\ &\quad + (\omega_2 - \Omega_a)A_{ca,mpn}]\end{aligned} \tag{9}$$

The residue $A_{ca} = n_{0c}n_{ac}n_{a0}$, contains the ground-to-excited transition densities of the true system n_{0a} and n_{0c}, which are accessible from LR, and substituting the KS excited-to-excited transition density n_{1d} for n_{ac} in eq 9 gives the second limit in our approximation for g_{XC}. Our final approximation interpolates between the two limits through the weighting of the double-excitation component to the true state (details in the Supporting Information),

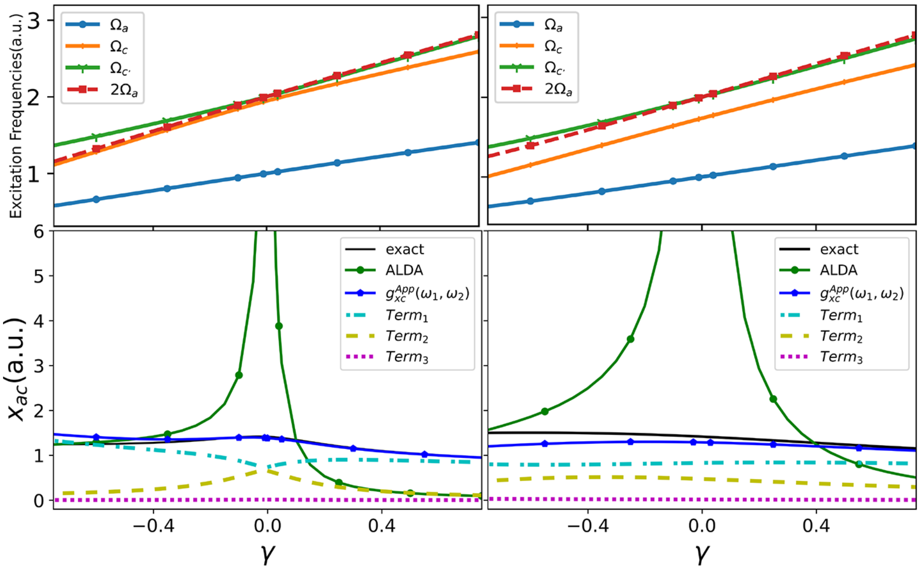

Figure 2. Excitation frequencies (upper) and transition dipole moments (lower panels), $x_{ac} = \langle\Psi_a|\hat{x}|\Psi_c\rangle$, between the first and second excited states of the model system as a function of parameter, γ, for $\lambda = 0.2$ (left) and $\lambda = 1$ (right): exact (black), ALDA (green), and our approximation via eq 12 (blue). The dashed lines term 1, term 2, and term 3 are the respective terms of eq 12.

$$
\begin{aligned}
&g^{\mathrm{App}}_{\mathrm{XC},iqr}(\omega_1, \omega_2)\\
&= -\left(\frac{\omega_1 + \omega_2 - 2\Omega_a}{2\Omega_a}\right)g^{\mathrm{adia}}_{\mathrm{XC},iqr} - \left(a^{-1}_{\mathrm{S3},ij}\frac{\nu_1{}^2}{\Omega_a{}^3}\langle f_{\mathrm{HXC}}(\omega_2)\rangle_1\right.\\
&\quad(\omega_1 A_{\mathrm{S13},jnp} + \omega_2 A_{\mathrm{S13},jpn}) + \frac{a^{-1}_{c,im}}{2}\left(\sqrt{1 - a_c a_{\mathrm{S3}}{}^{-1}}\right)_{mo}\frac{n_{0c}(\mathbf{r}_o)}{2}\\
&\quad\left.\times [(\omega_1 - \Omega_a)n_{d1}(\mathbf{r}_n)\, n_{0a}(\mathbf{r}_p) + (\omega_2 - \Omega_a)n_{d1}(\mathbf{r}_p)\, n_{0a}(\mathbf{r}_n)]\right)\\
&\quad\times a^{-1}_{a,nq}a^{-1}_{a,\mathrm{pr}}
\end{aligned}
\tag{10}
$$

For an excited-state c that has predominantly single-excitation character, the first two terms dominate, while the third term incorporates the effect of its doubly-excited character. As evident from eq 10, all ingredients for our approximation can be obtained from linear response TDDFT or adiabatic QR TDDFT. Turning to the transition density obtained from the double residue

$$
\xi n_{ca}(\mathbf{r}_m) = \lim_{\substack{\omega_2 \to \Omega_a \\ \omega_1 + \omega_2 \to \Omega_c}} (\omega_2 - \Omega_a)(\omega_1 + \omega_2 - \Omega_c)\frac{\chi^{(2)}_{mmm}(\omega_1, \omega_2)}{n_{0c}(\mathbf{r}_m)\, n_{a0}(\mathbf{r}_m)}
\tag{11}
$$

where $\xi = 1$ for the resonant case, and $\xi = \frac{1}{2}$ otherwise, we find

$$
\begin{aligned}
n^{\mathrm{App}}_{ca}(\mathbf{r}) &= \sqrt{1 - \alpha_c^2}\, n_{\mathrm{S1}d}(\mathbf{r})\\
&\quad+ \left(\frac{\nu_1}{\Omega_a}\right)^{3/2}\alpha_c\left(1 - 2\frac{\langle f_{\mathrm{HXC}}(\omega_2)\rangle_1}{\Omega_a}\right)n_{\mathrm{S},13}(\mathbf{r})\\
&\quad- \frac{n_{0a}(\mathbf{r})}{\Omega_a}\int n_{0c}(r_1)\, g^{\mathrm{adia}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, n_{0a}(\mathbf{r}_2)\, n_{0a}(\mathbf{r}_3)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3
\end{aligned}
\tag{12}
$$

Here $\alpha_c{}^2$ is an **r**-independent approximation to $a_c a^{-1}_{\mathrm{S},3}$: α_c ranges from $\nu_3\sqrt{\Omega_c}$ in the case where the state c is predominantly a single excitation to 0 when it is predominantly a double excitation. Equation 12 can be compared with the adiabatic approximation, for which

$$
\begin{aligned}
n^{\mathrm{adia}}_{ca}(\mathbf{r}) &= \left(\frac{\nu_1}{\Omega_a}\right)^{3/2}\alpha_c\left(1 + \frac{\Omega_a - \nu_1}{\Omega_c - 2\Omega_a}\right)n_{\mathrm{S13}}(\mathbf{r})\\
&\quad+ \frac{n_{0a}(\mathbf{r})}{\Omega_c - 2\Omega_a}\int n_{0c}(\mathbf{r}_1)\, g^{\mathrm{adia}}_{\mathrm{XC}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)\, n_{0a}(\mathbf{r}_2)\, n_{0a}(\mathbf{r}_3)\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\mathbf{r}_3
\end{aligned}
\tag{13}
$$

The divergence is evident in the last two terms when the resonant condition $\Omega_c - \Omega_a = \Omega_a$ is satisfied; further, there is no contribution from any double excitation.

In practice, there are several ad hoc workarounds to the unphysical divergence, including applying damping factors,[21] neglecting the kernels in "simplified-TDDFT",[35] setting the term to zero, and the pseudowave-function approximation,[3,5,6,36,37] where orbital relaxation terms in the second-order response are neglected, which is equivalent to solving the second-order response equation at zero frequency. The second term in eq 12 could be viewed as in the pseudowave-function spirit in the sense that it can be obtained by setting ω_1 to zero in the divergent term of eq 13. The connections with the standard pseudowave-function approximation are left for future work, including what the implied underlying g_{XC} kernel, is as our work suggests it also has a linear frequency dependence. In any case, all of the standard workarounds miss any double-excitation contribution to the transition density (the first term in eq 12), which can be significant, as our first example below demonstrates.

Our first example is a model system of two electrons in a one-dimensional harmonic plus linear potential, $v_{\mathrm{ext}}(x) = \frac{1}{2}x^2 + \gamma|x|$ where γ is a parameter in the range $[-1, 1]$; varying γ tunes the system in and out of the resonance condition. The electrons interact via a soft-Coulomb interaction: $\frac{\lambda}{\sqrt{(x_1 - x_2)^2 + 1}}$, where we consider $\lambda = 0.2$ a.u. as a weak interaction in which the assumptions made in eqs 6−12 apply, but we also consider the results at the full coupling strength $\lambda = 1$ a.u. In order to test our approximation for the QR kernel alone, without conflating errors from approximations made to the LR treatment, we use the *exact* KS and LR quantities in the equations. The LR thus

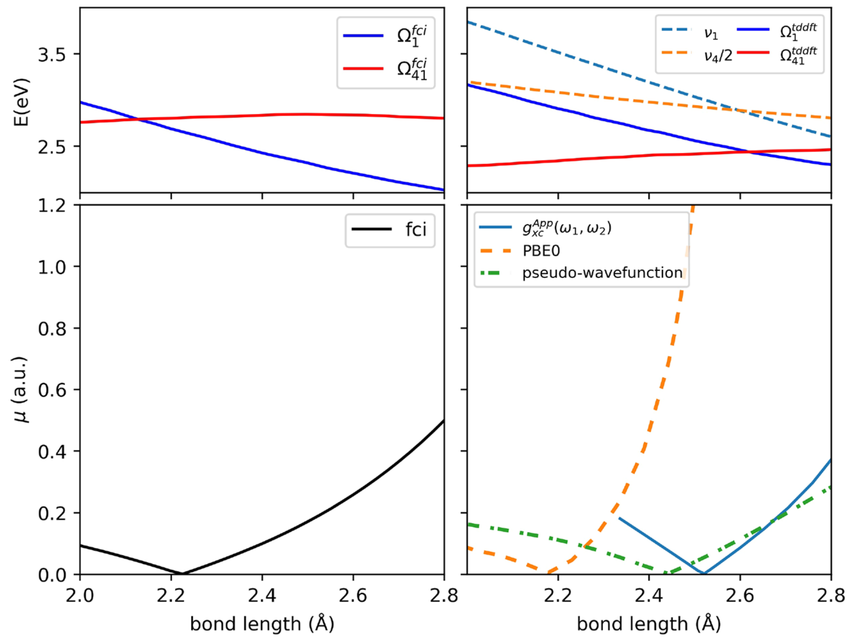

Figure 3. Upper panel: (left) Full configuration interaction (fci) and (right) TDDFT frequencies between the ground and the first excited states (solid blue) and the first and fourth excited states of LiH ($\Omega_{41} = \Omega_4 - \Omega_1$) (solid red). The right panel also shows the KS lowest transition frequency, ν_1 (light blue dotted), and half of the fourth KS frequency, ν_4 (orange dotted). Lower panel: Transition dipole moment, μ_{14}, between the first and fourth excited states as a function of bond length; exact (black), our approximation via eq 12 (light blue), PBE0 (orange dashed), and pseudowave function approximation (green dashed). Note that for bond lengths greater than 2.4 the adiabatic PBE0 is out of the scale of the figure.

includes double-excitation contributions, which would be missing in an adiabatic LR treatment.

Figure 2 shows the transition dipole moment, $\mu_{ac} = \langle\Psi_a|\hat{x}|\Psi_c\rangle$, between the first two excited states, Ψ_a and Ψ_c, for which the resonance condition, in this case $\Omega_c = 2\Omega_a$, holds as $|\gamma| \to 0$. We calculate α_c from the ratio of the matrix element $\langle\Psi_0|\hat{x}^2|\Psi_c\rangle$ to the corresponding matrix element of the KS system. At the weaker coupling strength $\lambda = 0.2$, our approximation of eq 12 clearly cures the divergence of ALDA shown and is barely distinguishable from the exact result in quite a wide region around the divergence. Tuning γ away from $\gamma = 0$, we move away from the resonance condition, and eventually, we expect that our approximation may decrease in quality compared to ALDA: the error in our approximation from neglecting the mixing of other single excitations may no longer be negligible compared to the large error caused by the spurious pole in adiabatic approximations in the resonance region. For the particular case here, our approximation continues to do well for positive γ where the system remains harmonic at large distances, while for negative values a double well develops in v_{ext} which brings the two lowest energy levels closer together as delocalized orbitals, deviating from the more clearly separated levels of a single well and leading to a breakdown of the single-pole-like assumptions in the derivation of eq 12. Although our approximation was derived in the limit of well-separated excitations, we still observe a good performance at full coupling strength $\lambda = 1.0$ (right panel in Figure 2), not only curing the divergence seen in ALDA but also giving predictions close to the exact.

We now turn to LiH, using PBE0[38] with the def2-SVP basis set,[39] within the Turbomole package.[22] The fourth excited-state frequency is close to twice the first excited-state frequency in the region around 2.6 Å in PBE0; the first and fourth excited states correspond to the first two excited states in the A_1 irreducible representation of C_{2v} point group symmetry. Also around this bond length, the frequency of the lowest doubly-excited KS state matches that of the fourth single KS excitation (see top right panel in Figure 3). The PBE0 excitation energies are a little shifted from those of the reference full configuration interaction calculation taken from ref 3, while the transition dipole moment diverges in the resonance region $\Omega_4 = 2\Omega_1$.[3] Our approximation, applied together with adiabatic PBE0 LR, shown in Figure 3 tames this divergence and follows the trend of the exact result, but with an overestimate; the adiabatic LR lacks the double-excitation contribution which, from the upper right panel, could be expected to be significant, so only the second term in eq 12 contributes. Further, we set the third term to zero because we ran into some numerical problems in its extraction from Turbomole; we note that for the two-electron case of the harmonic oscillator where g_X^{adia} is strictly zero and g_C was small, it may be small in this case as well. Likely, including this together with the double-excitation contribution with the LR kernel of ref 15 should improve the performance of our QR kernel; we leave for future work the investigation of oscillator strengths from a modified dressed LR TDDFT[14,40,41] which would be used to determine α_c. The figure shows also the result from the pseudowave-function approximation that is often used,[3,6,37] which, despite being an ad hoc correction, appears to perform a little better than ours when compared with the same relative position in fci. Again, as we move away from the resonance region, our approximation deviates as expected; the prescription would be that we revert to adiabatic PBE0 when the curves meet.

In summary, we found the form of the exact frequency-dependent kernel in QR TDDFT and derived an approximate kernel based on this. Tests on the excited-state transition amplitudes of a model system and on the LiH molecule suggest it is a promising practical cure to the unphysical divergence problem in adiabatic QR TDDFT; eq 10 can be applied also to cure the divergences in other second-order response properties such as hyperpolarizabilities, two-photon absorption, etc. Our approach can be generalized to situations beyond the single-pole type of analysis here, when more than one KS single excitation contributes to a given state. Alternatives to the two limiting approximations that we interpolated between here may lead to improved accuracy and will be explored in future work. This work also stresses the importance of including double-excitation contributions in LR; the kernel of ref 15 needs to be generalized to describe how the oscillator strength gets redistributed in this case.[14,40,41] We note that TDDFT can also be applied in the real-time domain to obtain nonlinear optical properties,[42] and the implications of the frequency-domain divergences for the time domain have yet to be explored. Future work also includes determining whether the divergence is related to the spurious pole shift of generalized LR TDDFT[11,43,44] in the adiabatic approximation, as was previously surmised.[3] The QR kernel is the functional derivative, or response, of the LR kernel evaluated at the ground state and in this sense may be viewed as containing information about the linear response of an excited state. On the other hand, the pole shifting occurs quite generally, not just in situations where the resonance condition is satisfied.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00122.

> Detailed derivations and discussion of eq 6 and the steps in the approximation leading to eq 10 (PDF)

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Notes

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■ REFERENCES

(1) Papadopoulos, M. G., Sadlej, A. J., Leszczynski, J., Eds. *Non-Linear Optical Properties of Matter*; Springer Netherlands, 2006. DOI: 10.1007/1-4020-4850-5.

(2) Mukamel, S. *Principles of Non-Linear Optical Spectroscopy*; Oxford University Press, 1999.

(3) Parker, S. M.; Roy, S.; Furche, F. Unphysical divergences in response theory. *J. Chem. Phys.* **2016**, *145*, 134105.

(4) Dalgaard, E. Quadratic response functions within the time-dependent Hartree-Fock approximation. *Phys. Rev. A* **1982**, *26*, 42−52.

(5) Li, Z.; Liu, W. First-order nonadiabatic coupling matrix elements between excited states: A Lagrangian formulation at the CIS, RPA, TD-HF, and TD-DFT levels. *J. Chem. Phys.* **2014**, *141*, 014110.

(6) Ou, Q.; Bellchambers, G. D.; Furche, F.; Subotnik, J. E. First-order derivative couplings between excited states from adiabatic TDDFT response theory. *J. Chem. Phys.* **2015**, *142*, 064114.

(7) Zhang, X.; Herbert, J. M. Analytic derivative couplings in time-dependent density functional theory: Quadratic response theory versus pseudo-wavefunction approach. *J. Chem. Phys.* **2015**, *142*, 064109.

(8) Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* **1984**, *52*, 997−1000.

(9) Ullrich, C. A. *Time-dependent density-functional theory: concepts and applications*; Oxford University Press, 2011. DOI: 10.1093/acprof:oso/9780199563029.001.0001.

(10) Marques, M. A., Maitra, N. T., Nogueira, F. M., Gross, E. K., Rubio, A., Eds. *Fundamentals of time-dependent density functional theory*; Lecture Notes in Physics, Vol. *837*; Springer, 2012. DOI: 10.1007/978-3-642-23518-4.

(11) Maitra, N. T. Perspective: Fundamental aspects of time-dependent density functional theory. *J. Chem. Phys.* **2016**, *144*, 220901.

(12) Gross, E. K. U.; Dobson, J. F.; Petersilka, M. In *Density Functional Theory II: Relativistic and Time Dependent Extensions*; Nalewajski, R. F., Ed.; Springer: Berlin, Heidelberg, 1996; pp 81−172. DOI: 10.1007/BFb0016643.

(13) Petersilka, M.; Gossmann, U. J.; Gross, E. K. U. Excitation Energies from Time-Dependent Density-Functional Theory. *Phys. Rev. Lett.* **1996**, *76*, 1212−1215.

(14) Casida, M. In *Recent Advances in Density Functional Methods, Part I*; Chong, D., Ed.; World Scientific: Singapore, 1995. DOI: 10.1142/2914.

(15) Maitra, N. T.; Zhang, F.; Cave, R. J.; Burke, K. Double excitations within time-dependent density functional theory linear response. *J. Chem. Phys.* **2004**, *120*, 5932−5937.

(16) Maitra, N. T. Double and Charge-Transfer Excitations in Time-Dependent Density Functional Theory. *Annu. Rev. Phys. Chem.* **2022**, *73*, 117−140.

(17) Wehrum, R. P.; Hermeking, H. On the response of arbitrary finite order and its relation to imaginary-time correlation functions. *Journal of Physics C: Solid State Physics* **1974**, *7*, L107−L110.

(18) Senatore, G.; Subbaswamy, K. Nonlinear response of closed-shell atoms in the density-functional formalism. *Phys. Rev. A* **1987**, *35*, 2440.

(19) Parker, S. M.; Furche, F. In *Frontiers of Quantum Chemistry*; Wójcik, M. J., Nakatsuji, H., Kirtman, B., Ozaki, Y., Eds.; Springer: Singapore, 2018; pp 69−86. DOI: 10.1007/978-981-10-5651-2_4.

(20) Sałek, P.; Vahtras, O.; Helgaker, T.; Ågren, H. Density-functional theory of linear and nonlinear time-dependent molecular properties. *J. Chem. Phys.* **2002**, *117*, 9630−9645.

(21) Aidas, K.; et al. The Dalton quantum chemistry program system. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2014**, *4*, 269−284.

(22) Balasubramani, S. G.; et al. TURBOMOLE: Modular program suite for ab initio quantum-chemical and condensed-matter simulations. *J. Chem. Phys.* **2020**, *152*, 184107.

(23) Gonze, X.; Vigneron, J.-P. Density-functional approach to nonlinear-response coefficients of solids. *Phys. Rev. B* **1989**, *39*, 13120−13128.

(24) Van Gisbergen, S.; Snijders, J.; Baerends, E. Time-dependent density functional results for the dynamic hyperpolarizability of C 60. *Physical review letters* **1997**, *78*, 3097.

(25) Zhu, H.; Wang, J.; Wang, F.; Feng, E.; Sheng, X. Linear and quadratic response TDDFT methods for the excited-state absorption in oligofluorenes. *Chem. Phys. Lett.* **2021**, *785*, 139150.

(26) Norman, P.; Bishop, D. M.; Jensen, H. J. A.; Oddershede, J. Nonlinear response theory with relaxation: The first-order hyperpolarizability. *J. Chem. Phys.* **2005**, *123*, 194103.

(27) Kjaegaard, T.; Jorgensen, P.; Olsen, J.; Coriani, S.; Helgaker, T. Hartree-Fock and Kohn-Sham time-dependent response theory in a second-quantization atomic-orbital formalism suitable for linear scaling. *J. Chem. Phys.* **2008**, *129*, 054106.

(28) Zahariev, F.; Gordon, M. S. Nonlinear response time-dependent density functional theory combined with the effective fragment potential method. *J. Chem. Phys.* **2014**, *140*, 18A523.

(29) Hu, Z.; Autschbach, J.; Jensen, L. Simulating Third-Order Nonlinear Optical Properties Using Damped Cubic Response Theory within Time-Dependent Density Functional Theory. *J. Chem. Theory Comput.* **2016**, *12*, 1294−1304.

(30) Li, Z.; Suo, B.; Liu, W. First order nonadiabatic coupling matrix elements between excited states: Implementation and application at the TD-DFT and pp-TDA levels. *J. Chem. Phys.* **2014**, *141*, 244105.

(31) Grabo, T.; Petersilka, M.; Gross, E. Molecular excitation energies from time-dependent density functional theory. *Journal of Molecular Structure: THEOCHEM* **2000**, *501*, 353−367.

(32) Appel, H.; Gross, E. K.; Burke, K. Excitations in time-dependent density-functional theory. *Physical review letters* **2003**, *90*, 043005.

(33) Elliott, P.; Goldson, S.; Canahui, C.; Maitra, N. T. Perspectives on double-excitations in TDDFT. *Chem. Phys.* **2011**, *391*, 110−119.

(34) Tretiak, S.; Chernyak, V. Resonant nonlinear polarizabilities in the time-dependent density functional theory. *J. Chem. Phys.* **2003**, *119*, 8809−8823.

(35) Bannwarth, C.; Grimme, S. A simplified time-dependent density functional theory approach for electronic ultraviolet and circular dichroism spectra of very large molecules. *Comput. Theor. Chem.* **2014**, *1040-1041*, 45−53.

(36) Ou, Q.; Alguire, E. C.; Subotnik, J. E. Derivative Couplings between Time-Dependent Density Functional Theory Excited States in the Random-Phase Approximation Based on Pseudo-Wavefunctions: Behavior around Conical Intersections. *J. Phys. Chem. B* **2015**, *119*, 7150−7161.

(37) Alguire, E. C.; Ou, Q.; Subotnik, J. E. Calculating derivative couplings between time-dependent Hartree−Fock excited states with pseudo-wavefunctions. *J. Phys. Chem. B* **2015**, *119*, 7140−7149.

(38) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0Model. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

(39) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(40) Mazur, G.; Włodarczyk, R. Application of the dressed time-dependent density functional theory for the excited states of linear polyenes. *J. Comput. Chem.* **2009**, *30*, 811−817.

(41) Carrascal, D. J.; Ferrer, J.; Maitra, N.; Burke, K. Linear response time-dependent density functional theory of the Hubbard dimer. *Eur. Phys. J. B* **2018**, *91*, 142.

(42) Cocchi, C.; Prezzi, D.; Ruini, A.; Molinari, E.; Rozzi, C. A. Ab Initio Simulation of Optical Limiting: The Case of Metal-Free Phthalocyanine. *Phys. Rev. Lett.* **2014**, *112*, 198303.

(43) Fuks, J. I.; Luo, K.; Sandoval, E. D.; Maitra, N. T. Time-Resolved Spectroscopy in Time-Dependent Density Functional Theory: An Exact Condition. *Phys. Rev. Lett.* **2015**, *114*, 183002.

(44) Luo, K.; Fuks, J. I.; Maitra, N. T. Studies of spuriously shifting resonances in time-dependent density functional theory. *J. Chem. Phys.* **2016**, *145*, 044101.