

Excitation Energies in Time-Dependent (Current-) Density-Functional Theory: A Simple Perspective

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Abstract: This paper gives a simple and pedagogical explanation, using density matrices of two-level systems, how to calculate excitation energies with time-dependent density-functional theory. The well-known single-pole approximation for excitation energies is derived here in an alternative way and extended to time-dependent current-density-functional theory.

1. Introduction

Time-dependent density-functional theory (TDDFT)¹ is a universal approach to electronic dynamics and excitations. Just like ground-state density-functional theory (DFT), where the rigorous theorems by Hohenberg, Kohn, and Sham^{2,3} prove a one-to-one correspondence between ground-state densities and potentials, there is a similar existence theorem for TDDFT, due to Runge and Gross,⁴ which establishes the time-dependent density as a fundamental variable.

Many of the concepts that were pioneered by John Perdew for ground-state DFT have now begun to make an important impact also in TDDFT: two prime examples are the self-interaction correction⁵ and the discontinuity of the exchange-correlation (XC) potential upon change of particle number.⁶ These concepts now find an important place in the discussion of the dynamics of electronic systems.^{7–11} Therefore, it seems not inappropriate that the following article, dedicated to honor John Perdew's scientific achievements, addresses a topic in the area of TDDFT.

Many areas in science require an understanding of the electronic excitations of atomic or molecular systems, nanostructures, mesoscopic systems, or bulk materials.^{12–15} A wide variety of spectroscopic techniques is being used to characterize the electronic structure and dynamics of these systems by probing their excitation spectra. The performance of any nanoelectronic device, such as a molecular junction, is dominated by its electronic excitation characteristics.^{16,17}

The usage of TDDFT as a practical tool to calculate excitation energies started in the mid-90s with the ground-breaking work of Petersilka et al.¹⁸ and Casida.¹⁹ In the Casida-formalism, the excitation energies are obtained from

the following eigenvalue problem (in this paper we use Hartree atomic units, $e = m = \hbar = 1$):

$$\begin{pmatrix} \mathbf{A} & \mathbf{K} \\ \mathbf{K}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (1)$$

Where the matrices \mathbf{A} and \mathbf{K} are defined as follows:

$$A_{ia\sigma, i'a'\sigma'} = \delta_{ii'} \delta_{aa'} \delta_{\sigma\sigma'} (\epsilon_{a\sigma} - \epsilon_{i\sigma}) + K_{ia\sigma, i'a'\sigma'} \quad (2)$$

and

$$K_{ia\sigma, i'a'\sigma'} = \int d^3r \int d^3r' \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc, \sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) \right] \varphi_{i'\sigma'}(\mathbf{r}') \varphi_{a'\sigma'}^*(\mathbf{r}') \quad (3)$$

Here, $\varphi_{i\sigma}$ and $\epsilon_{i\sigma}$ are the Kohn–Sham orbitals and eigenvalues coming from a self-consistent ground-state DFT calculation; we use the standard convention that i, i', \dots and a, a', \dots are indices of occupied and unoccupied orbitals, respectively. The term $f_{xc, \sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega)$ is the so-called XC kernel,²⁰ defined as the Fourier transform of

$$f_{xc, \sigma\sigma'}(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta V_{xc, \sigma}(\mathbf{r}, t)}{\delta n_{\sigma'}(\mathbf{r}', t')} \right|_{n_{\sigma}(\mathbf{r}, t) = n_{0\sigma}(\mathbf{r})} \quad (4)$$

where $V_{xc, \sigma}(\mathbf{r}, t)$ is the XC potential of TDDFT, and $n_{0\sigma}(\mathbf{r})$ is the ground-state spin density. In general, $f_{xc, \sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega)$ is a frequency-dependent quantity, but in practice, it is often approximated using frequency-independent expressions. This is known as the adiabatic approximation.

The eigenvalues ω of eq 1 are, in principle, the *exact* excitation energies of the system, provided one starts from an exact Kohn–Sham ground-state calculation and then uses the exact $f_{xc, \sigma\sigma'}$. In practice, of course, static and dynamical

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XC functionals need to be approximated. The formalism of eqs 1–3 can also be recast in the shape of an eigenvalue problem for the squares of the excitation energies:

$$\sum_{a'i'\sigma'} [\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}\omega_{ia\sigma}^2 + 2\sqrt{\omega_{ia\sigma}\omega_{i'a'\sigma'}}K_{ia\sigma,i'a'\sigma'}]\xi_{a'i'\sigma'} = \omega^2\xi_{ia\sigma} \quad (5)$$

where $\omega_{ia\sigma} = \varepsilon_{a\sigma} - \varepsilon_{i\sigma}$.

This TDDFT formalism for excitation energies has become very popular for practical applications, due to its unique balance between accuracy and efficiency, allowing the user to study systems that would be impossible to treat with traditional wave function methods, for example in all-electron studies of the photochemistry of large biomolecules.^{21,22} The broad spectrum of applications of TDDFT for excited states has been recently reviewed by Elliott et al.²³ From the large body of available literature, the following trends for molecules have emerged. Transition frequencies, calculated with standard gradient-corrected XC functionals, are typically good to within 0.4 eV. Excited-states structural properties such as bond lengths, vibrational frequencies, and dipole moments are essentially as good as those of ground-state calculations (about 1% for bond lengths and about 5% for dipoles and vibrational frequencies). Most importantly for large systems, the computational costs scale as N^3 versus N^5 for wave function methods of comparable accuracy.

While there exist efficient iterative algorithms for solving the full eigenvalue problem (1), it is nevertheless useful to consider approximations, since these can lead to further insight and sometimes even better results. One such method is the Tamm–Dancoff approximation (TDA), which has been known for a long time in nuclear physics.²⁴ The TDA can be viewed as an approximation to the so-called random-phase approximation (RPA), limited to single particle–hole pairs that are propagating forward in time. In the context and language of quantum chemistry, this approximation is formally identical to the configuration interaction singles (CIS) method. The TDA has been adopted in TDDFT,²⁵ but with a somewhat different meaning than originally in nuclear physics: one simply neglects the off-diagonal matrices \mathbf{K} in eq 1 but keeps the matrix \mathbf{A} as it is; see eq 2. This results in the simpler eigenvalue problem

$$\mathbf{A}\mathbf{X} = \omega_{\text{TDA}}\mathbf{X} \quad (6)$$

This TDDFT/TDA approach has some technical advantages over the full TDDFT linear response formalism away from ground-state equilibrium geometry, as shown by Casida et al.²⁶ The physical meaning of the TDDFT/TDA will become clear when we discuss two-level systems.

In an even more drastic approximation, eq 5 is truncated down to a 1×1 matrix. This yields the so-called small-matrix approximation (SMA),²⁷ which for spin-saturated systems is given by

$$\omega_{\text{SMA}}^2 = \omega_{ia}^2 + 4\omega_{ia}K_{ia,ia} \quad (7)$$

This can be further approximated if the correction to the bare Kohn–Sham excitation energy $\omega_{ia\sigma}$ is small, which is known as single-pole approximation (SPA):^{18,27}

$$\omega_{\text{SPA}} = \omega_{ia} + 2K_{ia,ia} \quad (8)$$

This approximation can also be viewed as a TDA for a two-level system, as we shall show below.

The original derivation of the SPA¹⁸ proceeded along a different line of thought. The excitation energies of a many-body systems can be represented as the poles of its density–density response function. If the excitation of interest is sufficiently well “isolated” from neighboring excitations, one can focus on a single pole of the response function—hence the name SPA. Carrying out a Laurent expansion in the TDDFT linear response equation then leads to eq 8, where $f_{xc,\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega)$ in the matrix element $K_{ia,ia}$ is evaluated at the bare Kohn–Sham excitation energy $\omega_{ia\sigma}$. Evaluating $f_{xc,\sigma\sigma'}$ in eqs 7 and 8 self-consistently at the frequencies ω_{SMA} and ω_{SPA} , respectively, has been termed “dressed” SMA and SPA in the literature.²⁸ Needless to say, this distinction is irrelevant unless one uses a nonadiabatic approximation for $f_{xc,\sigma\sigma'}$.

It turns out that the SMA and SPA can perform surprisingly well for systems with well-separated excitations, such as simple closed-shell atomic systems²⁹ or semiconductor nanostructures such as quantum wells.^{30,31} We will give a brief example at the end of this paper. From a practical point of view, the SMA and SPA might be seen as merely a curiosity—after all, even large molecular systems can be described with the full Casida TDDFT formalism without resorting to such drastic approximations. Instead, the main importance of the SMA and SPA is as analytical tools that give us insight into how the TDDFT linear response formalism works in combining Kohn–Sham single-particle excitations to form the true excitations.^{18,27} Furthermore, they can be extended to treat more complicated processes where excitations involve two close-lying poles³² or as starting point for the analysis of double or charge-transfer excitations.^{28,33}

The main purpose of this paper is to present an alternative, more direct way to derive simplified TDDFT approaches to excitation energies such as SMA and SPA. Instead of starting from Casida’s equations or the TDDFT linear response equation and eliminating all excitations except for a single pole, we will simply work with two-level Kohn–Sham systems from the very beginning. This has the advantage that the derivation is very transparent and does not require familiarity with linear response theory; only a basic knowledge of static DFT.

We will show that our two-level system derivation of the SMA and SPA can be extended to systems with phenomenological dissipation in a straightforward manner. Next, we will consider the case of time-dependent current-DFT (TDCDFT), where one deals with XC vector potentials coupling to currents. A generalization of the SMA and SPA for TDCDFT will be derived. To give an example, we will show results for intersubband plasmon excitations in doped quantum wells.

2. Excitation Energies of a Two-Level Kohn–Sham System

2.1. Scalar Potential. Let us consider a two-level system consisting of two orbitals $\varphi_1(\mathbf{r})$ and $\varphi_2(\mathbf{r})$ which are eigenstates of the static Kohn–Sham Hamiltonian

$$H^0 = -\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[n_0](\mathbf{r}) \quad (9)$$

where V_{xc} is the static XC potential, a functional of the ground-state density $n_0(\mathbf{r})$. We assume that initially φ_1 is doubly occupied and φ_2 is empty, and both orbitals are chosen to be real. Now consider a weak perturbation $\lambda H'(\mathbf{r}, t)$ acting on the system. According to time-dependent perturbation theory, the time evolution of the system is given by

$$\varphi(\mathbf{r}, t) = c_1(t)\varphi_1(\mathbf{r}) + \lambda c_2(t)\varphi_2(\mathbf{r}) \quad (10)$$

Let us construct the density matrix of the system as follows:

$$\rho(t) = \begin{pmatrix} \rho_{11} & \lambda \rho_{12} \\ \lambda \rho_{21} & \lambda^2 \rho_{22} \end{pmatrix} = \begin{pmatrix} |c_1|^2 & \lambda c_1 c_2^* \\ \lambda c_1^* c_2 & \lambda^2 |c_2|^2 \end{pmatrix} \quad (11)$$

where we explicitly indicate the order of the perturbation through orders of λ . The density matrix obeys the following equation of motion:

$$\dot{\rho} = -i[H, \rho] = -i[H^0 + \lambda H'(t), \rho] \quad (12)$$

Dropping terms of order λ^2 , this yields the time evolution of the off-diagonal elements of the density matrix as follows:

$$\dot{\rho}_{12} = -i[(H_{11}^0 - H_{22}^0)\rho_{12} - H'_{12}\rho_{11}] \quad (13)$$

$$\dot{\rho}_{21} = i[(H_{11}^0 - H_{22}^0)\rho_{21} - H'_{21}\rho_{11}] \quad (14)$$

where $H_{11}^0 = \int d^3r \varphi_1(\mathbf{r})H^0\varphi_1(\mathbf{r})$ and similar for all other matrix elements of H^0 and H' . Since $\rho_{11} = 1 + \mathcal{O}(\lambda^2)$ and defining $H_{22}^0 - H_{11}^0 = \omega_{21}$ (the bare Kohn–Sham excitation energy), this simplifies to

$$\dot{\rho}_{12} = i[\omega_{21}\rho_{12} + H'_{12}] \quad (15)$$

$$\dot{\rho}_{21} = -i[\omega_{21}\rho_{21} + H'_{21}] \quad (16)$$

Next, we make the ansatz (which will be justified later)

$$\rho_{12}(t) = \tilde{\rho}_{12}(\omega)e^{-i\omega t} + \tilde{\rho}_{12}(-\omega)e^{i\omega t} \quad (17)$$

and similar for ρ_{21} , H'_{12} , and H'_{21} . This gives

$$-\omega \tilde{\rho}_{12}(\omega) = [\omega_{21}\tilde{\rho}_{12}(\omega) + \tilde{H}'_{12}(\omega)] \quad (18)$$

$$-\omega \tilde{\rho}_{21}(\omega) = -[\omega_{21}\tilde{\rho}_{21}(\omega) + \tilde{H}'_{21}(\omega)] \quad (19)$$

and an additional two equations for $\tilde{\rho}_{12}(-\omega)$ and $\tilde{\rho}_{21}(-\omega)$ which do not contain any new information. Adding eqs 18 and 19 gives

$$\tilde{\rho}_{12}(\omega) + \tilde{\rho}_{21}(\omega) = -\frac{\tilde{H}'_{12}(\omega)}{\omega_{21} + \omega} - \frac{\tilde{H}'_{21}(\omega)}{\omega_{21} - \omega} \quad (20)$$

Let us now consider the perturbing Hamiltonian:

$$H'(\mathbf{r}, \omega) = \int d^3r' \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right] \delta n(\mathbf{r}', \omega) \quad (21)$$

where $\delta n(\mathbf{r}, \omega)$ is the density response. From eqs 10 and 11, we have

$$\delta n(\mathbf{r}, t) = 2|\varphi(\mathbf{r}, t)|^2 = 2\rho_{11}(t)\varphi_1(\mathbf{r})^2 + 2\lambda[\rho_{12}(t) + \rho_{21}(t)]\varphi_1(\mathbf{r})\varphi_2(\mathbf{r}) + 2\lambda^2\rho_{22}(t)\varphi_2(\mathbf{r})^2 \quad (22)$$

where the factor 2 comes from the double occupancy of $\varphi(\mathbf{r}, t)$. Taking the first-order term in λ and Fourier transforming, we get

$$\delta n(\mathbf{r}, \omega) = 2\varphi_1(\mathbf{r})\varphi_2(\mathbf{r})[\tilde{\rho}_{12}(\omega) + \tilde{\rho}_{21}(\omega)] \quad (23)$$

Notice that we do not consider an external perturbation, only the linearized Hartree and XC potentials. We are thus looking for an “eigenmode” of the system in a steady state. This justifies the ansatz (17) made above. We define the double matrix element [cf. eq 3]

$$K_{12,12}(\omega) = \int d^3r \int d^3r' \varphi_1(\mathbf{r})\varphi_2(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right] \varphi_1(\mathbf{r}')\varphi_2(\mathbf{r}') \quad (24)$$

and eq 20 becomes

$$\tilde{\rho}_{12}(\omega) + \tilde{\rho}_{21}(\omega) = -2K_{12,12}(\omega)[\tilde{\rho}_{12}(\omega) + \tilde{\rho}_{21}(\omega)] \left[\frac{1}{\omega_{21} + \omega} + \frac{1}{\omega_{21} - \omega} \right] \quad (25)$$

Canceling $\tilde{\rho}_{12} + \tilde{\rho}_{21}$ on both sides results in

$$1 = -\frac{4\omega_{21}}{\omega_{21}^2 - \omega^2} K_{12,12}(\omega) \quad (26)$$

which gives the final result

$$\omega^2 = \omega_{21}^2 + 4\omega_{21}K_{12,12}(\omega) \quad (27)$$

This is the same as the “dressed” SMA, eq 7. From the point of view of a two-level system, our derivation shows that the SMA considers the excitation $1 \rightarrow 2$ (absorption) as well as the de-excitation $2 \rightarrow 1$ (stimulated emission). The SPA, eq 8, on the other hand, only includes the excitation $1 \rightarrow 2$ (it is obtained by ignoring the first pole in eq 25). In general, the TDA (6) ignores all de-excitations.

The formalism of this section can easily be extended to the spin-dependent case. Assuming, for simplicity, that the ground-state is spin-unpolarized, we find

$$\omega_{\pm}^2 = \omega_{21}^2 + 2\omega_{21}[K_{12\sigma,12\sigma}(\omega) \pm K_{12\sigma,12\bar{\sigma}}(\omega)] \quad (28)$$

where the spin-dependent double matrix elements $K_{12\sigma,12\sigma}(\omega)$ are defined in eq 3.

2.2. Scalar Potential with Phenomenological Dissipation. In many practical situations, it is desirable to introduce dissipation in a simple phenomenological manner.^{34,35} Although this sounds easy enough, it is not straightforward

at all for the time-dependent Kohn–Sham equation, but if we work with the Kohn–Sham density matrix, all one needs to do is simply add a relaxation term to the equation of motion. For our two-level system, we have

$$\dot{\rho} = -i[H, \rho] - R \quad (29)$$

where

$$R = \begin{pmatrix} \frac{\rho_{11} - \rho_{11}^0}{T_1} & \frac{\rho_{12} - \rho_{12}^0}{T_2} \\ \frac{\rho_{21} - \rho_{21}^0}{T_2} & \frac{\rho_{22} - \rho_{22}^0}{T_1} \end{pmatrix} \quad (30)$$

T_1 and T_2 are phenomenological parameters whose physical meaning is a population relaxation time and a dephasing time. ρ_{jk}^0 are the equilibrium values of the density matrix; in our case, we have $\rho_{11}^0 = 1$ and $\rho_{12}^0 = \rho_{21}^0 = \rho_{22}^0 = 0$. The relaxation term does not introduce any difficulties in the linearization, and eqs 15 and 16 become

$$\dot{\rho}_{12} = i[\Omega_{21}\rho_{12} + H'_{12}] \quad (31)$$

$$\dot{\rho}_{21} = -i[\Omega_{21}^*\rho_{21} + H'_{21}] \quad (32)$$

where $\Omega_{21} = \omega_{21} + i/T_2$. The subsequent derivation then goes through in the same way as in the previous section, and the excitation energies are obtained as

$$\omega = \sqrt{\omega_{21}^2 + 4\omega_{21}K_{12,12}(\omega)} - \frac{i}{T_2} \quad (33)$$

The dephasing rate $1/T_2$ thus produces a negative imaginary part of the excitation energy (27), i.e. a finite line width, as expected. In the resulting spectrum, $1/T_2$ is the half-width at half-maximum of the spectral line at the real part of ω . The population relaxation time T_1 does not play any role for excitation energies but becomes important in the nonlinear dynamics of strongly driven systems.^{34,35}

2.3. More than Two Levels. Let us briefly sketch how the density matrix formalism works in a subspace with more than two levels. For example, in the case of a spin-unpolarized three-level system, the doubly occupied time-dependent Kohn–Sham orbital is $\varphi(\mathbf{r}, t) = c_1(t)\varphi_1(\mathbf{r}) + \lambda c_2(t)\varphi_2(\mathbf{r}) + \lambda c_3(t)\varphi_3(\mathbf{r})$, which gives the following density matrix

$$\rho(t) = \begin{pmatrix} \rho_{11} & \lambda\rho_{12} & \lambda\rho_{13} \\ \lambda\rho_{21} & \lambda^2\rho_{22} & \lambda^2\rho_{23} \\ \lambda\rho_{31} & \lambda^2\rho_{32} & \lambda^2\rho_{33} \end{pmatrix} = \begin{pmatrix} |c_1|^2 & \lambda c_1 c_2^* & \lambda c_1 c_3^* \\ \lambda c_1^* c_2 & \lambda^2 |c_2|^2 & \lambda^2 c_2^* c_3^* \\ \lambda c_1^* c_3 & \lambda^2 c_2^* c_3 & \lambda^2 |c_3|^2 \end{pmatrix} \quad (34)$$

extending the expressions in eqs 10 and 11. Going through a similar procedure as in section 2.1, considering only the first order in λ , we arrive at

$$\tilde{\rho}_{12} + \tilde{\rho}_{21} = -\frac{4\omega_{21}}{\omega_{21}^2 - \omega^2}[(\tilde{\rho}_{12} + \tilde{\rho}_{21})K_{12,12} + (\tilde{\rho}_{13} + \tilde{\rho}_{31})K_{12,13}] \quad (35)$$

$$\tilde{\rho}_{13} + \tilde{\rho}_{31} = -\frac{4\omega_{31}}{\omega_{31}^2 - \omega^2}[(\tilde{\rho}_{12} + \tilde{\rho}_{21})K_{13,12} + (\tilde{\rho}_{13} + \tilde{\rho}_{31})K_{13,13}] \quad (36)$$

The off-diagonal matrix elements $K_{12,13}$ and $K_{13,12}$ come in because the first-order density response

$$\delta n(\mathbf{r}, \omega) = 2\varphi_1(\mathbf{r})\varphi_2(\mathbf{r})(\tilde{\rho}_{12} + \tilde{\rho}_{21}) + 2\varphi_1(\mathbf{r})\varphi_3(\mathbf{r})(\tilde{\rho}_{13} + \tilde{\rho}_{31}) \quad (37)$$

which enters in the perturbing Hamiltonian (21) and involves products of the first and second as well as the first and third single-particle orbitals. This shows how the TDDFT linear-response formalism mixes independent single-particle excitations between individual Kohn–Sham levels.

We now define $\xi_{12} = (\tilde{\rho}_{12} + \tilde{\rho}_{21})/(\omega_{21})^{1/2}$ and $\xi_{13} = (\tilde{\rho}_{13} + \tilde{\rho}_{31})/(\omega_{31})^{1/2}$ and end up with

$$(\omega_{21}^2 + 4\omega_{21}K_{12,12})\xi_{12} + 4\sqrt{\omega_{21}\omega_{31}}K_{12,13}\xi_{13} = \omega^2\xi_{12} \quad (38)$$

$$4\sqrt{\omega_{21}\omega_{31}}K_{13,12}\xi_{12} + (\omega_{31}^2 + 4\omega_{31}K_{13,13})\xi_{13} = \omega^2\xi_{13} \quad (39)$$

This is a 2×2 eigenvalue problem which yields two excitation energies, correcting the Kohn–Sham excitation energies ω_{21} and ω_{31} . Equations 38 and 39 can also be directly obtained from the general TDDFT response equation (5) in the case of three spin-unpolarized Kohn–Sham levels. It is thus straightforward to see how Casida's linear response formalism follows from a generalization of our density matrix formalism for $N \rightarrow \infty$ spin-dependent levels.

3. Vector Potentials and TDCDFT

Let us now consider the case where the time-dependent Hamiltonian has the following form:

$$H(t) = \frac{1}{2}\left(\frac{\nabla}{i} + \lambda\frac{1}{c}\mathbf{A}(\mathbf{r}, t)\right)^2 + V_{\text{ext}}(\mathbf{r}) + \int d^3r' \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{\text{xc}}[n_0](\mathbf{r}) \quad (40)$$

i.e., the perturbation is given by a vector potential, with the linear term

$$H'(t) = \frac{1}{2ic}(\nabla \cdot \mathbf{A}(t) + \mathbf{A}(t) \cdot \nabla) \quad (41)$$

To obtain the excitation energies in a two-level system, we carry out a similar density-matrix calculation as in the previous section where we considered scalar perturbations. After Fourier transformation, have the following matrix element of the perturbing Hamiltonian:

$$H'_{12}(\omega) = \frac{1}{2ic} \int d^3r A(\omega) \cdot [\varphi_1(\mathbf{r})\nabla\varphi_2(\mathbf{r}) - \varphi_2(\mathbf{r})\nabla\varphi_1(\mathbf{r})] \quad (42)$$

The general form of the vector potential is $\mathbf{A} = \mathbf{A}_{\text{ext}} + \mathbf{A}_{\text{H}} + \mathbf{A}_{\text{xc}}$, where \mathbf{A}_{ext} is the external vector potential, e.g., associated with an electromagnetic wave, \mathbf{A}_{H} is the Hartree vector potential

$$\mathbf{A}_H(\mathbf{r}, \omega) = \frac{\nabla}{(i\omega)^2} \int d^3r' \frac{\nabla' \cdot \delta \mathbf{j}(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} \quad (43)$$

and the XC vector potential is in general given by

$$\mathbf{A}_{xc}(\mathbf{r}, \omega) = \int d^3r' f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \delta \mathbf{j}(\mathbf{r}', \omega) \quad (44)$$

where f_{xc} is the tensorial XC kernel of TDCDFT.

Again, we will assume that the external perturbation \mathbf{A}_{ext} is absent and that we only consider eigenmodes of the system, driven by the dynamical self-consistent vector potentials \mathbf{A}_H and \mathbf{A}_{xc} . Let us now take the following explicit form for \mathbf{A}_{xc} , proposed by Vignale et al.:³⁶

$$\mathbf{A}_{xc,i}(\mathbf{r}, \omega) = \frac{c}{i\omega} \nabla \int d^3r' f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}', \omega) - \frac{c}{i\omega n_0} \sum_j \nabla_j \sigma_{xc,ij}(\mathbf{r}, \omega) \quad (45)$$

where $f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}')$ is the XC kernel in adiabatic local-density approximation (ALDA)¹ and the XC viscoelastic stress tensor is defined as a function of the gradients of the velocity field $\mathbf{u}(\mathbf{r}, \omega) = \delta \mathbf{j}(\mathbf{r}, \omega)/n_0(\mathbf{r})$:

$$\sigma_{xc,ij} = \eta_{xc} \left(\nabla_j u_i + \nabla_i u_j - \frac{2}{3} \nabla \cdot \mathbf{u} \delta_{ij} \right) + \zeta_{xc} \nabla \cdot \mathbf{u} \delta_{ij} \quad (46)$$

The quantities η_{xc} and ζ_{xc} are viscosity coefficients of the homogeneous electron gas, defined as³⁶

$$\eta_{xc}(\bar{n}, \omega) = -\frac{\bar{n}^2}{i\omega} f_{xc}^T(\bar{n}, \omega) \quad (47)$$

$$\zeta_{xc}(\bar{n}, \omega) = -\frac{\bar{n}^2}{i\omega} \left[f_{xc}^L(\bar{n}, \omega) - \frac{4}{3} f_{xc}^T(\bar{n}, \omega) - \frac{d^2 e_{xc}(\bar{n})}{d\bar{n}^2} \right] \quad (48)$$

where f_{xc}^L and f_{xc}^T are the longitudinal and transverse XC kernels and e_{xc} is the XC energy density of a homogeneous electron gas of density \bar{n} . In eq 46, η_{xc} and ζ_{xc} are evaluated at the local ground-state density. For our two-level system, the current density can be expressed as

$$\delta \mathbf{j}(\mathbf{r}, \omega) = \frac{1}{i} (\tilde{\rho}_{21}(\omega) - \tilde{\rho}_{12}(\omega)) (\varphi_1(\mathbf{r}) \nabla \varphi_2(\mathbf{r}) - \varphi_2(\mathbf{r}) \nabla \varphi_1(\mathbf{r})) \quad (49)$$

where we ignore any diamagnetic contributions to the current since they are of higher order in the perturbation. The derivation of this expression for $\delta \mathbf{j}(\mathbf{r}, \omega)$ proceeds along similar lines as the derivation of $\delta n(\mathbf{r}, \omega)$, eq 23. The matrix element (42) thus becomes

$$H'_{12} = -\frac{1}{2\omega} \sum_i \int d^3r \left(\nabla_i \int d^3r' \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}') \right] \delta n(\mathbf{r}', \omega) - \frac{1}{n_0} \sum_j \nabla_j \sigma_{xc,ij} \right) P_i \quad (50)$$

where we defined $P_i(\mathbf{r}) = \varphi_1(\mathbf{r}) \nabla_i \varphi_2(\mathbf{r}) - \varphi_2(\mathbf{r}) \nabla_i \varphi_1(\mathbf{r})$. After some straightforward manipulation involving partial integration and introducing the abbreviation

$$S_{12,12}(\omega) = \frac{1}{4i\omega} \int d^3r \left[\frac{\eta_{xc}}{2} \sum_{ij} \left(\nabla_j \frac{P_i}{n_0} + \nabla_i \frac{P_j}{n_0} \right)^2 + \left(\zeta_{xc} - \frac{2}{3} \zeta_{xc} \right) \left(\nabla \cdot \frac{\mathbf{P}}{n_0} \right)^2 \right] \quad (51)$$

we obtain

$$\tilde{H}'_{12} = -2 \frac{\omega_{21}}{\omega} K_{12,12}(\omega) (\tilde{\rho}_{12} + \tilde{\rho}_{21}) + 2 S_{12,12}(\omega) (\tilde{\rho}_{12} - \tilde{\rho}_{21}) \quad (52)$$

Notice that $\tilde{H}'_{12} = -\tilde{H}'_{21}$. From eq 20, we thus get (dropping the subscripts of K and S)

$$\tilde{\rho}_{12} + \tilde{\rho}_{21} = -\frac{-2 \frac{\omega_{21}}{\omega} K(\tilde{\rho}_{12} + \tilde{\rho}_{21}) + 2 S(\tilde{\rho}_{12} - \tilde{\rho}_{21})}{\omega_{21} + \omega} - \frac{2 \frac{\omega_{21}}{\omega} K(\tilde{\rho}_{12} + \tilde{\rho}_{21}) - 2 S(\tilde{\rho}_{12} - \tilde{\rho}_{21})}{\omega_{21} - \omega} \quad (53)$$

and similarly

$$\tilde{\rho}_{12} - \tilde{\rho}_{21} = -\frac{-2 \frac{\omega_{21}}{\omega} K(\tilde{\rho}_{12} + \tilde{\rho}_{21}) + 2 S(\tilde{\rho}_{12} - \tilde{\rho}_{21})}{\omega_{21} + \omega} + \frac{2 \frac{\omega_{21}}{\omega} K(\tilde{\rho}_{12} + \tilde{\rho}_{21}) - 2 S(\tilde{\rho}_{12} - \tilde{\rho}_{21})}{\omega_{21} - \omega} \quad (54)$$

Using the abbreviation $\beta = 4/(\omega_{21}^2 - \omega^2)$, we can write this as a system of two coupled equations:

$$(1 + \beta \omega_{21} K)(\tilde{\rho}_{12} + \tilde{\rho}_{21}) - \beta \omega S(\tilde{\rho}_{12} - \tilde{\rho}_{21}) = 0 \quad (55)$$

$$-\frac{\omega_{21}^2}{\omega} \beta K(\tilde{\rho}_{12} + \tilde{\rho}_{21}) + (1 + \beta \omega_{21} S)(\tilde{\rho}_{12} - \tilde{\rho}_{21}) = 0 \quad (56)$$

The determinant vanishes if

$$\omega^2 = \omega_{21}^2 + 4\omega_{21}(K_{12,12}(\omega) + S_{12,12}(\omega)) \quad (57)$$

which is the desired TDCDFT generalization of the SMA. Again, it is straightforward to repeat the derivation for the spin-dependent case. Assuming, as before, that the ground-state is not spin-polarized, and using the spin-dependent XC vector potential of Qian et al.,³⁷ we find

$$\omega_{\pm}^2 = \omega_{21}^2 + 2\omega_{21}[(K_{12\sigma,12\sigma}(\omega) + S_{12\sigma,12\sigma}(\omega)) \pm (K_{12\sigma,12\bar{\sigma}}(\omega) + S_{12\sigma,12\bar{\sigma}}(\omega))] \quad (58)$$

where

$$S_{12\sigma,12\sigma}(\omega) = \frac{1}{i\omega} \int d^3r \left[\frac{\eta_{xc,\sigma\sigma'}}{2} \sum_{ij} \left(\nabla_j \frac{P_{i\sigma}}{n_0} + \nabla_i \frac{P_{j\sigma}}{n_0} \right)^2 + \left(\zeta_{xc,\sigma\sigma'} - \frac{2}{3} \eta_{xc,\sigma\sigma'} \right) \left(\nabla \cdot \frac{\mathbf{P}_{\sigma}}{n_0} \right)^2 \right] + \frac{2\delta_{\sigma\sigma'} - 1}{4i\omega} \int d^3r \rho_{\uparrow\downarrow} |\mathbf{P}_{\sigma}|^2 \quad (59)$$

Table 1. Lowest Intersubband Excitation Energy ω and Linewidth Γ (both in millielectronvolts) of an n -Doped 40-nm GaAs/AlGaAs Quantum Well^a

	KS	ALDA (full)	ALDA (eq 27)	VUC (full)	VUC (eq 57)
ω	7.7445	10.0309	10.0323	10.0950	10.0967
Γ				0.0663	0.0677

^a VUC stands for the XC vector potential of Vignale et al.³⁶

Here, $\rho_{\uparrow\downarrow}(\mathbf{r}, \omega)$ is the so-called spin transresistivity,³⁸ which is a measure of the spin Coulomb drag effect.³⁹ It affects only the spin-density excitations.

We point out that eqs 57 and 58 had been derived earlier in an alternative way,^{31,40} leading to the same result, except that $S_{12,12}(\omega)$ and $S_{12\sigma,12\sigma}(\omega)$ are multiplied with ω^2/ω_{21}^2 . This difference arises because the alternative derivation starts from an approximation of the Kohn–Sham current–current response function, where the prefactor ω^2/ω_{21}^2 is needed to ensure that the formalism reduces to eq 27 in the appropriate limit. In that sense, the present density-matrix formalism is more consistent: once we have selected a 2-level subspace, no further approximations are involved. Therefore, although the prefactor ω^2/ω_{21}^2 causes only corrections to the excitation energies of order S^2 (which are usually small), eqs 57 and 58 are to be preferred.

In Table 1, we present some results to illustrate the performance of the two-level system approximation. We consider the lowest intersubband transition energy of an n -doped 40 nm square GaAs/AlGaAs quantum well with parabolic subbands and an electron concentration of 10^{11} cm^{-2} , using the standard effective-mass approximation.³⁰

Table 1 compares the KS transition energy ω_{21} with the ALDA and TDCDFT results. We see that the results using the full TDDFT response equation agree extremely well with the simple SMA approximations, eqs 27 and 57. A more systematic study for closed-shell atoms by Vasiliev et al.²⁹ came to similar conclusions, although the agreement between SMA and full TDDFT was not as close as for quantum wells. This has to do with the structure and distribution of the quantum well subband levels, which are much better separated than in atoms: the level spacing is $\sim n^2$ for the lowest-lying levels, where n is the subband index, and there is no Rydberg series.

For quantum wells, the finite line width Γ reflects the fact that collective electronic excitations can decay into incoherent single-particle excitations of the electron gas in the (infinite) quantum well plane. Unfortunately, the same physics also leads to a line width for excitations of finite systems such as atoms.⁴⁰ To avoid this unphysical effect, approximate XC vector potentials based on the electron gas^{36,37} should be applied to extended systems only.^{31,41,42}

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