Double excitations in finite systems

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Time-dependent density-functional theory (TDDFT) is widely used in the study of linear response properties of finite systems. However, there are difficulties in properly describing excited states, which have double- and higher-excitation characters, which are particularly important in molecules with an open-shell ground state. These states would be described if the exact TDDFT kernel were used; however, within the adiabatic approximation to the exchange-correlation (xc) kernel, the calculated excitation energies have a strict single-excitation character and are fewer than the real ones. A frequency-dependent xc kernel could create extra poles in the response function, which would describe states with a multiple-excitation character. We introduce a frequency-dependent xc kernel, which can reproduce, within TDDFT, double excitations in finite systems. In order to achieve this, we use the Bethe–Salpeter equation with a dynamically screened Coulomb interaction $W(\omega)$, which can describe these excitations, and from this we obtain the xc kernel. Using a two-electron model system, we show that the frequency dependence of W does indeed introduce the double excitations that are instead absent in any static approximation of the electron-hole screening. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3065669]

I. INTRODUCTION

Excitation energies in finite systems have been extensively studied within time-dependent density-functional theory (TDDFT).[1] In this approach the excitation energies of the system are obtained from those of the noninteracting Kohn–Sham (KS) system through the following Dyson-type equation:

$$\chi(x_1,x_2,\omega) = \chi_s(x_1,x_2,\omega) + \int dx_3 dx_4 \chi_s(x_1,x_3,\omega)$$
$$\times \left[\frac{1}{|x_3 - x_4|} + f_{xc}(x_3,x_4,\omega) \right] \chi(x_4,x_2,\omega), \quad (1)$$

where χ and χ_s are the response functions of the interacting and the KS systems, respectively. Here the set of variables (x_1) comprises position and spin coordinates: $(x_1) = (\mathbf{r}_1, \sigma_1)$. The poles of the true response function give the excitation energies of the interacting system, where the excited states can be a mixture of single, double, and higher-multiple excitations, whereas the poles of the KS response function are just at single KS excitation energies. Therefore χ_s has fewer poles than χ. The KS excitation energies are mapped to the true excitation energies by the Coulomb potential and the exchange-correlation (xc) kernel f_{xc}. Hence, in principle, the exact spectrum of the interacting system can be obtained. However, in practice, both the ground-state xc potential and the xc kernel have to be approximated. The most used approximation for f_{xc} is the simple adiabatic local-density ap-

proximation (ALDA), which is local in time and in space. Although this approximation is surprisingly successful, there are some deficiencies. In particular, ALDA fails to create new poles, which would describe excited states with a multiple-excitation character. This deficiency is a problem particularly for open-shell systems.[2] However, there are also problems for closed-shell molecules: for example, the lowest-lying singlet state of polyenes is not a simple highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO-LUMO) one-electron excitation but has a HOMO^2-LUMO^2 double-excitation character.[3,4]

Several solutions have been proposed in literature in the framework of TDDFT. Wang and Ziegler[5,6] used a noncollinear representation of the xc energy. This means that the xc energy, instead of being a functional of the density alone or of the spin-up and spin-down densities, is a functional of the density and of the magnetization $\mathbf{m} = \Sigma_i \psi_i^\dagger \boldsymbol{\sigma} \psi_i$, where $\boldsymbol{\sigma}$ is the vector of Pauli matrices. This allows one to describe spin flip in the systems and, hence, to formally include doubly excited states into a linear response theory. In practice, however, only if the appropriate excited state is used as reference can double excitations from the ground state be described.

Another possible solution is to go beyond the adiabatic approximation. The inclusion of a frequency dependence in the xc kernel can indeed create extra poles. Casida[7] proposed a nonadiabatic correction to the xc kernel by using the formalism of superoperators. As a central result, he obtained a formal equation that gives the correction to the adiabatic

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kernel used in TDDFT. The correction term comes from a Bethe–Salpeter-type equation (BSE), which contains one-electron excitation contributions and higher-excitation contributions. The general formula introduced includes as a special case the "dressed TDDFT" derived by Maitra et al.[8] for closed-shell systems. These authors showed that near states with a double-excitation character, the exact xc kernel has a strong dependence on frequency. They derived the exact frequency-dependent kernel for the case of a double excitation mixed with a single excitation and well separated from the other excitations, and calculated the first excited state of butadiene and hexatriene, which is largely dominated by a double excitation.[4] However, for the application of the dressed treatment, the mixing single and double excitations must be identified *a priori*, which is not straightforward based on TDDFT results only. Recently Giesbertz et al.[9] formulated an adiabatic time-dependent density-matrix-functional theory in which double excitations can be accounted for. In this paper we wish to remain in the TDDFT framework and go beyond the adiabatic approximation and to have a general formulation in which the frequency-dependent kernel can reproduce double excitations. In order to obtain this, we exploit the BSE, where the kernel can be approximated in a more systematic and transparent way. The BSE approach has already been used to find better approximations to the xc kernel of TDDFT in the case of solids.[10–15] In all these previous studies, the BSE kernel has been taken to be static. There are some works in which a dynamical screening is employed.[16,17] Recently Marini and Del Sole[18] discussed the effects of a frequency-dependent BSE kernel on the absorption spectra of copper, silver, and silicon. They showed that dynamical effects are important for metals and that a good description of the spectral intensity of their absorption spectra can be obtained if both dynamical excitonic and self-energy effects are taken into account in the calculation of the response functions. In this article we are interested in the number and position of the poles of the response function in finite systems. Therefore we will start by considering dynamical effects only in the kernel. Once the suitable BSE kernel is found, we can obtain the xc kernel for TDDFT.[19,20]

The paper is organized as follows. In Sec. II first we give a brief introduction to the main equations used in TDDFT for the calculation of excitation energies in molecules, known also as Casida's equations, and we show the problems that arise if ALDA is used. Then we introduce the BSE, where the kernel is approximated by the frequency-dependent screened Coulomb interaction $W(\omega)$. We show that this BSE kernel can describe double excitations by calculating excitation energies of a two-electron model system. However, this kernel, in the current formulation based on the random phase approximation (RPA), produces also unphysical poles, which we attribute to the self-screening problem that the description of the screening suffers from. From this BSE kernel, we derive the frequency-dependent xc kernel. Finally in Sec. IV we draw our conclusions.

II. THEORY

A. TDDFT within Casida's formulation

Excitation energies are obtained in TDDFT as a solution of the following eigenvalue equation:[21]

$$\begin{pmatrix} A & B \\ -B^* & -A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega \begin{pmatrix} X \\ Y \end{pmatrix}, \tag{2}$$

with

$$A_{ia\sigma,jb\tau} = \delta_{\sigma\tau}\delta_{ab}\delta_{ij}(\epsilon_{a\sigma} - \epsilon_{i\tau}) + K_{ia\sigma,jb\tau}, \tag{3}$$

$$B_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}, \tag{4}$$

$$\begin{aligned} K_{ia\sigma,jb\tau} = \int\int \psi_{i\sigma}^*(\mathbf{r})\psi_{a\sigma}(\mathbf{r})\Bigg[\frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ + f_{xc}^{\sigma\tau}(\mathbf{r},\mathbf{r}',\omega) \Bigg]\psi_{b\tau}^*(\mathbf{r}')\psi_{j\tau}(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \end{aligned} \tag{5}$$

Here $a, b, \dots$ are indices for virtual orbitals, $i, j, \dots$ are indices for occupied orbitals, σ and τ are indices for the spin, ϵ and ψ are the KS energies and orbitals, and $f_{xc}^{\sigma\tau}(\mathbf{r},\mathbf{r}',\omega)$ is the xc kernel. Although the matrix above spans only the single KS excitations, in principle the eigenvalue equation yields all the excitation energies of the interacting system. However, for the number of eigenvalues to be larger than the size of the matrix (i.e., the number of single KS excitations), the kernel K must be frequency dependent. Hence, within the adiabatic approximation, TDDFT can only account for singly excited configurations. This means that excited states with a double-excitation character are, in general, not described with the correct energy or are even completely absent. In particular, the problem is evident in open-shell systems if using the three-orbital model of Ref. 2, with one orbital doubly occupied, another one singly occupied, and the third one empty. If $[\hat{H},\hat{S}_z] = [\hat{H},\hat{S}^2] = 0$, then the Hamiltonian $\hat{H}$ and the spin operators $\hat{S}_z$ and $\hat{S}^2$ of the system have common eigenstates. Single Slater determinants of KS orbitals, with the same spatial behavior for different spins (restricted formulation), are always eigenfunctions of $\hat{S}_z$ but not, in general, of $\hat{S}^2$. In this case one can produce spin-adapted wave functions by a linear combination of Slater determinants using Clebsch–Gordan coefficients. In Ref. 2 it is shown that excitations in which the singly occupied molecular orbital is a spectator are problematic. In this case, indeed, among the possible eigenstates of $\hat{S}^2$, there are a quartet and a doublet state, which can be described only if double excitations are included. Hence these two excited states will not be described using a frequency-independent xc kernel. In place of these two states, ALDA yields instead only one state, a combination of two singly excited determinants, which is unphysical.

Our aim is hence to go beyond the adiabatic approximation and include in the xc kernel a frequency dependence which can produce double-excitation energies. We will derive this kernel from the kernel of the BSE. Passing through many-body perturbation theory (MBPT) has the advantage that excitations of the system enter the formulation explicitly.

Therefore approximations with a clear physical meaning can be more easily designed than in the context of DFs and introduced into TDDFT in a second step.

B. Reduced space

In general, an $(m \times m)$ eigenvalue problem can be reduced to a lower-dimensional one by writing it as

$$\begin{pmatrix} S & C_1 \\ C_2 & D \end{pmatrix}\begin{pmatrix} e_1 \\ e_2 \end{pmatrix} = \omega \begin{pmatrix} e_1 \\ e_2 \end{pmatrix}, \tag{6}$$

where S is an $n \times n$ matrix, D is a $t \times t$ matrix, and $m = n + t$. In fact, solving for $e_2 = (\omega \mathbb{1} - D)^{-1} C_2 e_1$ and substituting into the equation for e_1, one gets

$$[S + C_1(\omega \mathbb{1} - D)^{-1} C_2] e_1 = \omega e_1, \tag{7}$$

provided that $(\omega \mathbb{1} - D)$ is invertible. The latter is an $(n \times n)$ eigenvalue problem for a frequency-dependent matrix. In particular, the eigenvalues obtained from Eq. (7) are the same as those of Eq. (6).

This conversion of spatial degrees of freedom into frequency dependence is very general.[20] For example, when solving the BSE in the space of single excitations, the frequency-dependent kernel has folded in it all the many-excitation effects. We are interested, in particular, in double excitations. In this case, the matrix S spans the space of single excitations, and it has the same structure reported in Eq. (2) within a static approximation to the kernel; the matrix D spans the space of double excitations, and the matrices C_1 and C_2 represent the interaction between single and double excitations. Equation (7) shows that an eigenvalue problem formulated in the basis of single and double excitations can be solved in the space of single excitations only by adding to a general static matrix an ω-dependent matrix, which takes into account double excitations. It is this frequency dependence representing additional excitations that we are interested in.

It should be noticed that the kernel acquires an additional ω-dependence when one transforms the four-point BSE to the two-point TDDFT equation. In this case the ω-dependence represents simply the reduction in space.

C. Bethe–Salpeter equation

We consider the BSE for the two-particle propagator L,[22]

$$L(1,2,1',2') = L_0(1,2,1',2') + \int d3d4d5d6 L_0(1,4,1',3)$$
$$\times \Xi(3,5,4,6)L(6,2,5,2'), \tag{8}$$

where L_0 is given in terms of one-particle Green's functions as $L_0(1,2,1',2') = -iG(1,2')G(2,1')$ and the four-point kernel $\Xi(3,5,4,6)$ is given by

$$\Xi(3,5,4,6) = i\frac{\delta[v_H(3)\delta(3,4) + \delta\Sigma(3,4)]}{\delta G(6,5)}, \tag{9}$$

with $v_H(1) = -i\int d3v(1,3)G(3,3^+)$ as the Hartree potential. Here the set of variables (1) comprises position, spin, and time coordinates: $(1) = (x_1, t_1) = (\mathbf{r}_1, \sigma_1, t_1)$. For simplicity, in the following the spatial and spin dependence will not be specified, if not necessary. We will use the so-called GW approximation to the self-energy, $\Sigma(1,2) = iG(1,2)W(1^+,2)$, and hence the BSE kernel reduces to $\Xi(3,5,4,6) = \delta(3,4)\delta(5,6)v(3,6) - \delta(3,6)\delta(4,5)W(3,4)$. Here we neglected the term $i\delta W/\delta G$ in the functional derivative of the self-energy.[23–25] In Ref. 26 it is shown that L naturally depends on the symmetric combinations of time variables $[\tau = (t_1 + t_{1'})/2 - (t_2 + t_{2'})/2; \tau_1 = t_1 - t_{1'}; \tau_2 = t_2 - t_{2'}]$. Usually the screened Coulomb interaction W is taken to be instantaneous, i.e., $W(3,4) = W(x_3, x_4)\delta(t_3 - t_4)$. In this case one can contract the time variables $t_{1'} \to t_1$ and $t_{2'} \to t_2$ in Eq. (8), and thus the propagator L depends only on the time difference $\tau = t_1 - t_2$.[27–32] Instead, if one takes into account the time dependence of the screening, $W(t_3 - t_4)$, the contraction $t_{1'} \to t_1$ is not possible anymore. In Appendix A we show that the Fourier transform of $L(\tau, \tau_1, \tau_2)$ with respect to τ, τ_1, and τ_2 is given by

$$L(\omega, \omega', \omega'')$$
$$= L_0(\omega, \omega', \omega'') - iG(\omega' + \omega/2)G(\omega' - \omega/2)v$$
$$\times \int \frac{d\tilde{\omega}}{2\pi}L(\omega, \tilde{\omega}, \omega'') + iG(\omega' + \omega/2)G(\omega' - \omega/2)$$
$$\times \int \frac{d\tilde{\omega}}{2\pi}W(\omega' - \tilde{\omega})L(\omega, \tilde{\omega}, \omega''), \tag{10}$$

with $L_0(\omega, \omega', \omega'') = -2\pi i \delta(\omega' - \omega'')G(\omega' + \omega/2)G(\omega'' - \omega/2)$. In the following we approximate the one-particle Green's function as

$$G(x_1, x_2, \omega) = \sum_n \frac{\phi_n(x_1)\phi_n^*(x_2)}{\omega - \epsilon_n + i\eta\,\mathrm{sgn}(\epsilon_n - \mu)}, \tag{11}$$

where $\phi_n(x)$ are a complete set of (orthonormal) single-particle wave functions, ϵ_n are the quasiparticle energies, and μ is the chemical potential. Note that we neglect the frequency dependence of the self-energy in the Green's function, and we concentrate on the frequency dependence of the screening W only. It has been shown that the two kinds of dynamical effects tend to cancel each other with an improvement of the spectral intensity and of the f-sum rule in solids.[15,33] In this paper, however, we are interested in the effects of a dynamical screening.

1. Static screening $W(\omega=0)$

It is immediate to see that if we consider a static screening $W(\omega=0)$, as it is done in most of current calculations,[29,31,32] Eq. (10) reduces to

$$\tilde{L}(\omega) = \tilde{L}_0(\omega) + \tilde{L}_0(\omega)K\tilde{L}(\omega), \tag{12}$$

where $K = (v - W)$, $\tilde{L}(\omega) = \int (d\omega'd\omega''/(2\pi)^2)L(\omega, \omega', \omega'')$ and analogously for $\tilde{L}_0(\omega)$. Note that $\tilde{L}(\omega)$ is the quantity that is usually calculated in nowadays applications.[29,31,32] In this work we are interested in the particle-hole portion of the

propagator L (i.e., the part corresponding to the time order-ings which describe the propagation of an electron and a hole); therefore in the following our discussion will refer only to this contribution. Using the change of basis

$$\tilde{L}_{(n_1{'}n_1)(n_2n_2{'})} = \int dx_1 dx_2 dx_1{'} dx_2{'} \tilde{L}(x_1,x_2,x_1{'},x_2{'},\omega)$$
$$\times \phi_{n_1{'}}^*(x_1)\phi_{n_1}(x_1{'})\phi_{n_2{'}}(x_2{'})\phi_{n_2}^*(x_2), \quad (13)$$

the BSE (12) can be mapped into an effective two particle equation,[10,28,34]

$$\tilde{L}_{(n_1{'}n_1)(n_2n_2{'})} = [H^{2p} - I\omega]^{-1}_{(n_1{'}n_1)(n_2n_2{'})}(f_{n_2} - f_{n_2{'}}), \quad (14)$$

with the two-particle Hamiltonian H^{2p} defined as

$$H^{2p}_{(n_1{'}n_1)(n_2n_2{'})} = (\epsilon_{n_1} - \epsilon_{n_1{'}})\delta_{n_1,n_2}\delta_{n_1{'},n_2}$$
$$+ (f_{n_1{'}} - f_{n_1})K_{(n_1{'}n_1)(n_2{'}n_2)}. \quad (15)$$

Note that due to the orthonormality of the basis set wave functions, $\tilde{L}_{0(n_1{'}n_1)(n_2n_2{'})} = \delta_{n_1{'}n_2}\delta_{n_1n_2{'}}(f_{n_1{'}} - f_{n_1})[\omega - (\epsilon_{n_1} - \epsilon_{n_1{'}}) + i\eta \, \mathrm{sgn}(\epsilon_{n_1} - \epsilon_{n_1{'}})]^{-1}$ is diagonal. Here f_k are Fermi occupan-cies ($f_k = 1$ if $\epsilon_k < \mu$ and $f_k = 0$ if $\epsilon_k > \mu$, with μ as the chemi-cal potential). The presence of $(f_{n_2{'}} - f_{n_2})$ selects only a part of the Hamiltonian H^{2p}, which is referred to as excitonic Hamiltonian $H^{2p,\mathrm{exc}}$,

$$H^{2p,\mathrm{exc}} = \begin{pmatrix} H^{2p,\mathrm{reso}}_{(vc)(v{'}c{'})} & K^{\mathrm{coupling}}_{(vc)(c{'}v{'})} \\ -[K^{\mathrm{coupling}}_{(vc)(c{'}v{'})}]^* & -[H^{2p,\mathrm{reso}}_{(vc)(v{'}c{'})}]^* \end{pmatrix}, \quad (16)$$

with v, $v{'}$ and c, $c{'}$ as occupied and unoccupied quasiparticle states, respectively. The matrix $H^{2p,\mathrm{reso}}$ only involves positive energy transitions, and it is given by

$$H^{2p,\mathrm{reso}}_{(vc)(v{'}c{'})} = (\epsilon_c - \epsilon_v)\delta_{v,v{'}}\delta_{c,c{'}} + v_{(vc)(v{'}c{'})} - W_{(vc)(v{'}c{'})},$$
$$(17)$$

with

$$v_{(vc)(v{'}c{'})} = \int dx dx{'} \, \phi_c^*(x)\phi_v(x)\frac{1}{|x - x{'}|}\phi_{c{'}}(x{'})\phi_{v{'}}^*(x{'}),$$
$$(18)$$

$$W_{(vc)(v{'}c{'})} = \int dx dx{'} \, \phi_c^*(x)\phi_{c{'}}(x)W(x,x{'})\phi_v(x{'})\phi_{v{'}}^*(x{'}).$$
$$(19)$$

The lower-right block $-[H^{2p,\mathrm{reso}}_{(vc)(v{'}c{'})}]^*$ is the antiresonant part of the excitonic Hamiltonian, which only involves negative energy solutions, while the off-diagonal terms couple the ei-genvalue equations of the resonant and antiresonant Hamil-tonians. The particle-hole propagator $\tilde{L}$ can be obtained as

$$\tilde{L}(x_1,x_2,x_1{'},x_2{'},\omega)$$
$$= \sum_{\lambda\lambda{'}} \left[\sum_{n_1n_1{'}} \frac{A_\lambda^{(n_1{'}n_1)}\phi_{n_1}(x_1)\phi_{n_1{'}}^*(x_1{'})}{\omega_\lambda - \omega + i\eta \, \mathrm{sgn}(\epsilon_{n_1{'}} - \epsilon_{n_1})} \right.$$
$$\left. \times S_{\lambda\lambda{'}}^{-1} \sum_{n_2n_2{'}} A_{\lambda{'}}^{*(n_2n_2{'})}\phi_{n_2}(x_2)\phi_{n_2{'}}^*(x_2{'})(f_{n_2{'}} - f_{n_2}) \right], \quad (20)$$

where $A_\lambda^{(n_1{'}n_1)}$ and ω_λ are the eigenvectors and eigenvalues of the excitonic Hamiltonian,

$$H^{2p,\mathrm{exc}}_{(n_1{'}n_1)(n_2n_2{'})}A_\lambda^{(n_2n_2{'})} = \omega_\lambda A_\lambda^{(n_1{'}n_1)}, \quad (21)$$

and $S_{\lambda\lambda{'}} = \sum_{n_1n_1{'}} A_\lambda^{*(n_1{'}n_1)}A_{\lambda{'}}^{(n_1{'}n_1)}$ is the overlap matrix. From the particle-hole propagator, we can obtain the two-point po-larizability $\chi(x_1,x_2,\omega) = \tilde{L}(x_1,x_2,x_1,x_2,\omega)$. [Note that all the quantities we have defined so far are time ordered. Analytic continuation to retarded quantities can eventually be per-formed by replacing $-i\eta$ with $i\eta$ in the denominator of Eq. (20) when $\epsilon_{n_1{'}} < \epsilon_{n_1}$.] The excitonic Hamiltonian [Eq. (21)] has the same structure as the TDDFT eigenvalue equation [Eq. (2)]; hence also here a kernel that is frequency depen-dent is needed in order to describe double excitations.

2. Eigenvalue equation with a frequency-dependent screening W

The mapping of the BSE with a frequency-dependent screened Coulomb interaction $W(\omega)$ into an effective two particle equation is not as straightforward as for the static case. However, following Ref. 22, we can obtain an eigen-value equation analogous to Eq. (21),

$$H^{2p,\mathrm{exc}}_{(n_1{'}n_1)(n_2n_2{'})}(\omega_\lambda)A_\lambda^{(n_2n_2{'})}(\omega_\lambda) = \omega_\lambda A_\lambda^{(n_1{'}n_1)}(\omega_\lambda), \quad (22)$$

where now

$$H^{2p,\mathrm{exc}}_{(n_1{'}n_1)(n_2n_2{'})}(\omega_\lambda) = (\epsilon_{n_1} - \epsilon_{n_1{'}})\delta_{n_1{'}n_2}\delta_{n_1n_2{'}} + (f_{n_1{'}} - f_{n_1})$$
$$\times [v_{(n_1{'}n_1)(n_2n_2{'})} - \tilde{W}_{(n_1{'}n_1)(n_2n_2{'})}(\omega_\lambda)], \quad (23)$$

with

$$\tilde{W}_{(n_1{'}n_1)(n_2n_2{'})}(\omega_\lambda) = i\int \frac{d\omega}{2\pi} W_{(n_1{'}n_1)(n_2n_2{'})}(\omega)$$
$$\times \left[\frac{1}{\omega_\lambda - \omega - (\epsilon_{n_2{'}} - \epsilon_{n_1{'}}) + i\eta} \right.$$
$$\left. + \frac{1}{\omega_\lambda + \omega - (\epsilon_{n_1} - \epsilon_{n_2}) + i\eta} \right]. \quad (24)$$

Note that Eq. (22) has been derived assuming spectra with poles ω_λ well isolated from each other. In the present study, in which we deal with molecules, this hypothesis is not severe. Furthermore it is assumed that the poles of L_0 are different from ω_λ.

We now approximate the screened electron-hole interaction $W_{(n_1'n_1)(n_2n_2')}(\omega)$ in Eq. (23). In principle the screening should self-consistently contain multiple excitations. However, as a starting point we can approximate it using only

single excitations, such as in RPA or using some static approximation. We, therefore, first solve Eq. (15) with a static screening and use the corresponding eigenvalues and eigenvectors in Eq. (20) to obtain the two-point response function $\chi(x_1, x_2, \omega) = \widetilde{L}(x_1, x_2, x_1, x_2, \omega)$. The poles of the response function give the excitation energies of the system and, within a static approximation to the screening, are as many as the number of single e-h excitations (v, c) and (c, v). From the equation $W = v + v\chi v$, we then obtain

$$W(x_1, x_2, \omega) = v(x_1, x_2) + \sum_\lambda \int dx_{1'} dx_{2'} v(x_1, x_{1'}) \left\{ \frac{\Sigma_{vc,v'c'} A_\lambda^{(vc),\text{static}} \phi_v^*(x_{1'}) \phi_c(x_{1'}) \phi_{v'}(x_{2'}) \phi_{c'}^*(x_{2'}) A_\lambda^{*(v'c'),\text{static}}}{\omega - \omega_\lambda^{\text{static}} + i\eta} \right.$$

$$\left. - \frac{\Sigma_{cv,c'v'} A_\lambda^{(cv),\text{static}} \phi_c^*(x_{1'}) \phi_v(x_{1'}) \phi_{c'}(x_{2'}) \phi_{v'}^*(x_{2'}) A_\lambda^{*(c'v'),\text{static}}}{\omega + \omega_\lambda^{\text{static}} - i\eta} \right\} v(x_{2'}, x_2), \tag{25}$$

from where it immediately follows that

$$W_{(n_1'n_1)(n_2n_2')}(\omega) = v_{(n_2'n_1)(n_2n_1')} + \sum_\lambda \sum_{\widetilde{v}\widetilde{c},\widetilde{v}'\widetilde{c}'} v_{(n_2'n_1)(\widetilde{v}\widetilde{c})} \frac{A_\lambda^{(\widetilde{v}\widetilde{c}),\text{static}} A_\lambda^{*(\widetilde{v}'\widetilde{c}'),\text{static}}}{\omega - \omega_\lambda^{\text{static}} + i\eta} v_{(\widetilde{v}'\widetilde{c}')(n_2n_1')}$$

$$- \sum_\lambda \sum_{\widetilde{c}\widetilde{v},\widetilde{c}'\widetilde{v}'} v_{(n_2'n_1)(\widetilde{c}\widetilde{v})} \frac{A_\lambda^{(\widetilde{c}\widetilde{v}),\text{static}} A_\lambda^{*(\widetilde{c}'\widetilde{v}'),\text{static}}}{\omega + \omega_\lambda^{\text{static}} - i\eta} v_{(\widetilde{c}'\widetilde{v}')(n_2n_1')}. \tag{26}$$

Note that we used the notation ω_λ for the positive energies and $-\omega_\lambda$ for the negative energies. Furthermore we neglected the coupling between positive and negative energy equations (Tamm–Dancoff approximation). In this case, since the excitonic Hamiltonian is Hermitian, the eigenstates A_λ are mutually orthogonal, and hence the overlap matrix $S_{\lambda\lambda'}$ in Eq. (20) equals the identity matrix.

Inserting Eq. (26) into Eq. (24), we can solve analytically the frequency integration. We arrive at

$$\widetilde{W}_{(n_1'n_1)(n_2n_2')}(\omega_\lambda) = v_{(n_2'n_1)(n_2n_1')} + \sum_{\lambda'} \sum_{\widetilde{v}\widetilde{c},\widetilde{v}'\widetilde{c}'} v_{(n_2'n_1)(\widetilde{v}\widetilde{c})} \frac{A_{\lambda'}^{(\widetilde{v}\widetilde{c}),\text{static}} A_{\lambda'}^{*(\widetilde{v}'\widetilde{c}'),\text{static}}}{\omega_\lambda - \omega_{\lambda'}^{\text{static}} - (\epsilon_{n_2'} - \epsilon_{n_1'}) + i\eta} v_{(\widetilde{v}'\widetilde{c}')(n_2n_1')}$$

$$+ \sum_{\lambda'} \sum_{\widetilde{v}\widetilde{c},\widetilde{v}'\widetilde{c}'} v_{(n_2'n_1)(\widetilde{c}\widetilde{v})} \frac{A_{\lambda'}^{(\widetilde{c}\widetilde{v}),\text{static}} A_{\lambda'}^{*(\widetilde{c}'\widetilde{v}'),\text{static}}}{\omega_\lambda - \omega_{\lambda'}^{\text{static}} - (\epsilon_{n_1} - \epsilon_{n_2}) + i\eta} v_{(\widetilde{c}'\widetilde{v}')(n_2n_1')}. \tag{27}$$

Note that the frequency-dependent term on the right-hand side of Eq. (27) has the same form as the term $C_1(\omega\mathbb{1} - D)^{-1} C_2$ in Eq. (7), in which D plays the role of $\omega^{\text{static}} + \Delta\epsilon$. In Sec. III we will show, using a simple model system, that this frequency-dependent kernel produces double excitations, although with some deficiencies that we will explain later. In the space of single excitations the TDDFT equation and the BSE have the same four-point structure. In particular the xc kernel and the BSE kernel play the same role (besides the quasiparticle shift). Therefore we can compare the kernel in

Eq. (27) with the xc kernel obtained by Maitra et $al.$ in Ref. 8: within the single pole approximation and considering only the resonant part of Eq. (27), we obtain the same structure as Eq. (15) of Ref. 8, with $(\omega^{\text{static}} - (\epsilon_c - \epsilon_v))$ playing the role of $(H_{DD} - H_{00})$.

D. From BSE to TDDFT

In transition space both the TDDFT equation and the BSE are four-point equations. In this case, solving the TD-

DFT equation costs as much as solving the BSE. In real space, instead, the TDDFT equation is a two-point equation, unlike the BSE, which remains four point. Therefore it is worthwhile to try to derive an xc kernel from BSE. An approximate expression for the xc kernel in real space has been obtained from the BSE kernel in several ways, all yielding the same result.[11,13–15,19,20,35,36] However, all these previous derivations assume a static screening. Here, instead, we will

use a dynamical screening in order to obtain an xc kernel, which can describe double excitations. We will follow Refs. 19 and 20. We are interested in positive frequencies. In this case there is no difference between time-ordered and causal response functions. We also assume that both in TDDFT and BSE the starting point is L_0, which already includes quasiparticle corrections. Starting from Eq. (9) of Ref. 20, we then arrive at

$$
f_{xc}(x_1,x_2,\omega) = -\int dx_3 dx_4 dx_5 dx_6 \chi_0^{-1}(x_1,x_3,\omega)\left[\int \frac{d\omega' d\omega''}{(2\pi)^2}L_0(x_3,x_6,x_3,x_5,\omega,\omega',\omega'')\right.
$$
$$
\left. \times \int \frac{d\omega''' d\widetilde{\omega}}{(2\pi)^2}W(x_5,x_6,\omega'-\widetilde{\omega})L_0(x_5,x_4,x_6,x_4,\omega,\widetilde{\omega},\omega''')\right]\chi_0^{-1}(x_4,x_2,\omega),
\tag{28}
$$

with $\chi_0(1,2)=L_0(1,2,1,2)$. As a dynamical screening $W(\omega'-\widetilde{\omega})$ we insert the expression given in Eq. (25), and we obtain

$$
f_{xc}(x_1,x_2,\omega) = \sum_{kk',ss'}\int dx_3 dx_4 dx_5 dx_6 \chi_0^{-1}(x_1,x_3,\omega)\frac{\phi_k(x_3)\phi_k^*(x_5)\phi_{k'}(x_6)\phi_{k'}^*(x_3)}{\omega-(\epsilon_k-\epsilon_{k'})+i\eta\,\mathrm{sgn}(\epsilon_k-\epsilon_{k'})}
$$
$$
\times\left\{v(x_5,x_6)+\int\frac{d\omega'}{2\pi}\left[\frac{1}{\omega'+\omega/2-\epsilon_k+i\eta\,\mathrm{sgn}(\epsilon_k-\mu)}-\frac{1}{\omega'-\omega/2-\epsilon_{k'}+i\eta\,\mathrm{sgn}(\epsilon_{k'}-\mu)}\right]\right.
$$
$$
\times\sum_\lambda\int dx_{1'}dx_{2'}v(x_5,x_{1'})\int\frac{d\widetilde{\omega}}{2\pi}\left[\frac{\sum_{\overline{vc},\overline{v}'\overline{c}'}A_\lambda^{(\overline{v}\overline{c}),\mathrm{static}}\phi_{\overline{v}}^*(x_{1'})\phi_{\overline{c}}(x_{1'})\phi_{\overline{v}'}(x_{2'})\phi_{\overline{c}'}^*(x_{2'})A_\lambda^{*(\overline{v}'\overline{c}'),\mathrm{static}}}{\omega'-\widetilde{\omega}-\omega_\lambda^{\mathrm{static}}+i\eta}\right.
$$
$$
\left.-\frac{\sum_{\overline{cv},\overline{c}'\overline{v}'}A_\lambda^{(\overline{c}\overline{v}),\mathrm{static}}\phi_{\overline{c}}^*(x_{1'})\phi_{\overline{v}}(x_{1'})\phi_{\overline{c}'}(x_{2'})\phi_{\overline{v}'}^*(x_{2'})A_\lambda^{*(\overline{c}'\overline{v}'),\mathrm{static}}}{\omega'-\widetilde{\omega}+\omega_\lambda^{\mathrm{static}}-i\eta}\right]v(x_{2'},x_6)
$$
$$
\left.\times\left[\frac{1}{\widetilde{\omega}+\omega/2-\epsilon_s+i\eta\,\mathrm{sgn}(\epsilon_s-\mu)}-\frac{1}{\widetilde{\omega}-\omega/2-\epsilon_{s'}+i\eta\,\mathrm{sgn}(\epsilon_{s'}-\mu)}\right]\right\}
$$
$$
\times\frac{\phi_s(x_5)\phi_s^*(x_4)\phi_{s'}(x_4)\phi_{s'}^*(x_6)}{\omega-(\epsilon_s-\epsilon_{s'})+i\eta\,\mathrm{sgn}(\epsilon_s-\epsilon_{s'})}\chi_0^{-1}(x_4,x_2,\omega).
\tag{29}
$$

Since we consider only positive energy solution, we select only the terms with $\epsilon_k,\epsilon_s>\mu$ and $\epsilon_{k'},\epsilon_{s'}<\mu$, and after integration in $\widetilde{\omega}$ and ω', we arrive at

$$
f_{xc}(x_1,x_2,\omega)=-\sum_{vc,v'c'}\int dx_3 dx_4 dx_5 dx_6\chi_0^{-1}(x_1,x_3,\omega)\widetilde{L}_0^{vc}(x_3,x_6,x_3,x_5,\omega)\widetilde{W}_{v'c'}^{vc}(x_5,x_6,\omega)\widetilde{L}_0^{v'c'}(x_5,x_4,x_6,x_4,\omega)\chi_0^{-1}(x_4,x_2,\omega),
\tag{30}
$$

where we defined

$$
\widetilde{W}_{v'c'}^{vc}(x_5,x_6,\omega)=v(x_5,x_6)+\sum_\lambda\int dx_{1'}dx_{2'}v(x_5,x_{1'})\left[\frac{\sum_{\overline{vc},\overline{v}'\overline{c}'}A_\lambda^{(\overline{v}\overline{c}),\mathrm{static}}\phi_{\overline{v}}^*(x_{1'})\phi_{\overline{c}}(x_{1'})\phi_{\overline{v}'}(x_{2'})\phi_{\overline{c}'}^*(x_{2'})A_\lambda^{*(\overline{v}'\overline{c}'),\mathrm{static}}}{\omega-\omega_\lambda^{\mathrm{static}}-(\epsilon_{c'}-\epsilon_v)+i\eta}\right.
$$
$$
\left.+\frac{\sum_{\overline{cv},\overline{c}'\overline{v}'}A_\lambda^{(\overline{c}\overline{v}),\mathrm{static}}\phi_{\overline{c}}^*(x_{1'})\phi_{\overline{v}}(x_{1'})\phi_{\overline{c}'}(x_{2'})\phi_{\overline{v}'}^*(x_{2'})A_\lambda^{*(\overline{c}'\overline{v}'),\mathrm{static}}}{\omega-\omega_\lambda^{\mathrm{static}}-(\epsilon_c-\epsilon_{v'})+i\eta}\right]v(x_{2'},x_6),
\tag{31}
$$

which can be obtained from Eq. (27), and $\widetilde{L}_0^{vc}$ such that $\widetilde{L}_0 = \Sigma_{vc}\widetilde{L}_0^{vc}$. Equation (30) is the central result of this article. Unlike previous derivations based on the BSE, here we used a BSE kernel which is frequency dependent.

It has been shown that a static approximation to the factor $\chi_0^{-1}L_0$ can reproduce good spectra for solids in the case when a static screening is used.[37] The same is observed for the spectrum of silicon calculated using only two k points in the Brillouin zone.[13] The latter discrete case can be considered as a simulation of a calculation in a molecule. Therefore, if we suppose the factor $\chi_0^{-1}L_0^{vc}$ to be static, the xc kernel in Eq. (30) will have the same poles of the screened electron-hole interaction $\widetilde{W}$, and hence it will have also the same advantages and the same deficiencies, which will be pointed out in the next section.

1. Exact constraints

Several exact properties of the xc kernel are known, and it is desirable to satisfy as many of them as possible when constructing an approximate kernel.[38,39] In Ref. 40 van Leeuwen and Dahlen showed that, starting from the time-dependent Sham–Schlüter equation,

$$\int d2G_s(1,2)G(2,1)v_{xc}(2) = \int d2d3G_s(1,2)\Sigma(2,3)G(3,1),$$
(32)

its functional derivative with respect to the density yields an xc kernel of TDDFT that satisfies important exact constraints. This is true also if the linearized form of Eq. (32) is employed, where all Green's functions, including those contained in the expression for Σ, are replaced by KS Green's functions.[40,41] In this case, when the GW approximation to the self-energy is used, the xc kernel is given by the diagrammatic expression in Fig. 2 of Ref. 41. The class of xc kernels used in the present paper differs from the conserving kernel of Ref. 41 in three aspects:

- the derivative of W with respect to the total potential V is neglected; i.e., W is treated as an externally given interaction;

- the quasiparticle correction is included in the energies of the independent polarizability χ_0, and it is not linearized as part of the kernel;

- consequently all Green's functions are built with quasiparticle eigenvalues instead of KS eigenvalues.

The term $\delta W/\delta V$, which gives rise to the two last diagrams of the conserving kernel, is usually neglected in the BSE without deteriorating the results, which is our motivation to adopt this approximation. The linearization of the quasiparticle correction term would give the first four diagrams of the conserving kernel[42] instead of dressed Green's functions throughout. However, the linearized quasiparticle correction term is numerically unstable and gives rise to scattered spectra;[42] therefore it is preferable to use the nonlinearized version. Finally, the use of KS Green's functions instead of quasiparticle Green's functions in Eq. (28) is consistent

with that choice; this point is, moreover, not fundamental for the discussion of this paper. Equation (28) gives the fifth diagram of the conserving kernel when KS Green's functions are used.

The kernel in Eq. (28) is, therefore, closely related to conserving approximations to the xc kernel. In fact, if a static screening is used, then the linearized form of Eq. (28) is conserving.[41] This is not sufficient to ensure that the kernel (28) obeys the known exact constraints. However, although the violation of these constraints can cause some instabilities,[43,44] the observance of them does not guarantee that good results will be obtained.[45,46] Indeed, the class of kernels (28) has been derived from a pragmatic point of view by imposing TDDFT to reproduce the two-point polarizability of BSE in a limited frequency range: this is our constraint. The static version of Eq. (28) has been successfully used in solids.[11–13] In this work we release the static approximation, and we investigate the effect of a dynamical screening. As already stressed, other dynamical effects, which might be important for the spectrum, are not taken into account since the goal of the present work is to elucidate the contributions arising from the excitations contained in the dynamically screened electron-hole interaction.

III. APPLICATIONS

We will now study a model system with two energy levels, ϵ_v and ϵ_c, and two paired electrons.

A. Solution of the excitonic Hamiltonian

We calculate the eigenvalues of the Hamiltonian (22), within the Tamm–Dancoff approximation. These eigenvalues give the poles of the four-point polarizability L and hence the excitation energies of the system.

First we need to specify the spin structure of the excitonic Hamiltonian.[32] Since we neglect spin-orbit interaction as well as spin flip, the basis set consists of the particle-hole pairs with spin-up ($v\uparrow c\uparrow$) and of those with spin-down ($v\downarrow c\downarrow$). Furthermore, we will consider a spin-restricted ground state, i.e., $\phi_{i\uparrow} = \phi_{i\downarrow}$. We then have to solve the following eigenvalue problem:

$$(\Delta\epsilon + V - \widetilde{W} - \omega)^2 - V^2 = 0,$$
(33)

where $\Delta\epsilon = (\epsilon_{c\sigma} - \epsilon_{v\sigma})$, $V = v_{(vc\sigma)(vc\sigma')}$, and $\widetilde{W} = \widetilde{W}_{(vc\sigma)(vc\sigma)}$, with $\sigma = \uparrow, \downarrow$. Using a static screening, we obtain two solutions for this model: the singlet solution $\omega_1^{static} = \Delta\epsilon + 2V - W^{static}$ with eigenvector $A_1^{static} = 1/\sqrt{2}(11)^T$ and the triplet solution $\omega_2^{static} = \Delta\epsilon - W^{static}$ with eigenvector $A_2^{static} = 1/\sqrt{2}(1-1)^T$. Using these solutions in Eq. (27), one constructs the frequency-dependent screening $\widetilde{W} = A + B/(\omega - \omega_1^{static} - \Delta\epsilon)$, with $A = v_{(cc)(vv)}$ and $B = 2\Re[v_{(cc)(vc)}v_{(vc)(vv)}]$. From the structure of $\widetilde{W}$, one can already anticipate that the eigenvalue of Eq. (33) has four solutions, although one expects only three for this system, i.e., a singlet single excitation, a triplet single excitation, and a singlet double excitation. One of the four is an unphysical state. We argue that the occurrence of this extra pole is related to the self-screening interaction that the GW approximation to the self-energy suffers from:[47] W is the

TABLE I. Excitation energies ω_1, ω_2, and ω_3 calculated for He atom using the excitonic Hamiltonian and the exact Hamiltonian. All the quantities are given in eV.

$H^{2p,\text{exc}}$	$\Delta\epsilon$(IP-EA)[a]	ω_1^{static}	V	A	B				ω_1[a]	ω_2	ω_3[a]
	24.507	25.304	0.398	4.689	~0				20.615	49.811	19.818
H^{exact}	ϵ_v	ϵ_c	V_{vvvv}	V_{vvvc}	V_{vvcc}	V_{cvvc}	V_{cvcc}	V_{cccc}	ω_1	ω_2	ω_3
	−54.40	−13.60	34.01	4.86	1.19	11.42	0.47	8.18	23.77	58.02	19.22

[a]Experimental values taken from Refs. 48 and 49.

test charge–test charge screening, whereas the charges to be screened are fermions, not classical charges.[19] This could be cured by a vertex correction to the self-energy. Indeed, if one considers only one electron in this model system, then Eq. (22) produces two poles, one corresponding to a single excitation and the other one, unphysical, corresponding to a double excitation. In this case, there are no dynamical self-energy effects involved, and the extra pole arises, indeed, from the fact that the electron screens itself. We can recognize the spurious solution by solving Eq. (33) independently of the dynamical structure of $\widetilde{W}$. We then obtain two groups of solutions: one for singlet states, $\omega = \Delta\epsilon + 2V - \widetilde{W}$, and one for triplet states, $\omega = \Delta\epsilon - \widetilde{W}$. Since the excited state involving a double excitation is a singlet, the correct double-excitation energy is that coming from the singlet-group solutions. The four solutions ($\omega_{1,2}$, the singlet solutions, and $\omega_{3,4}$, the triplet solutions) are

$$\omega_{1,2} = \frac{2\Delta\epsilon + \omega_1^{\text{static}} + 2V - A \pm \sqrt{(\omega_1^{\text{static}} - 2V + A)^2 - 4B}}{2},$$

$$\omega_{3,4} = \frac{2\Delta\epsilon + \omega_1^{\text{static}} - A \pm \sqrt{(\omega_1^{\text{static}} + A)^2 - 4B}}{2}. \tag{34}$$

In order to analyze this result, we can assume that the system has localized wave functions. In this case the overlap between valence and conduction orbitals can be small, and therefore the term $B = 2\Re[v_{(cc)(vc)}v_{(vc)(vv)}]$ is such that $(\omega_1^{\text{static}} + A - 2V)^2 \gg 4B$. The solutions become

$$\omega_1 = \Delta\epsilon + 2V - A,$$

$$\omega_2 = \Delta\epsilon + \omega_1^{\text{static}} = 2\Delta\epsilon + 2V - W^{\text{static}},$$

$$\omega_3 = \Delta\epsilon - A,$$

$$\omega_4 = \Delta\epsilon + \omega_1^{\text{static}} = 2\Delta\epsilon + 2V - W^{\text{static}}.$$

The solutions ω_1 and ω_3 are the energies of the singlet and triplet single excitations, respectively, already described using a static screening, ω_2 is identified as the energy of a singlet double excitation, and ω_4 is the spurious energy.

To give a numerical example, we consider the He atom, where we select only the HOMO, which is a 1s orbital, and the LUMO, which is a 2s orbital. Equation (34) links the singlet and triplet excitation energies (ω_1 and ω_3, respectively) to the parameters A and B. Therefore we use the experimental values for $\Delta\epsilon$, ω_1, and ω_3 from Refs. 48 and 49 to evaluate A and B. Furthermore we approximate $2V = \omega_1 - \omega_3$, which follows from Eq. (33) with a static screening, and we use $\omega_1^{\text{static}} = \omega_1^{\text{RPA}} = \Delta\epsilon + 2V$. All these values are then used in Eq. (34) to calculate the double-excitation energy ω_2. In Table I we reported the results. In particular, the double-excitation energy is calculated to be $\omega_2 = 49.81$ eV. This energy falls in the continuum; therefore we cannot compare our result with experimental data. However, we can show that we obtain a reasonable result by comparing it with the solution of the exact Hamiltonian, which is described in the following.

B. Solution of the exact Hamiltonian

We can compare our result with the eigenstates and eigenvalues of the exact Hamiltonian

$$\hat{H} = \sum_i \hat{h}(x_i) + \frac{1}{2}\sum_{i \neq j} v(x_i, x_j), \tag{35}$$

where the terms on the right-hand side are the noninteracting Hamiltonian and the two-electron interaction, respectively. In Appendix B we show that in second quantization the eigenvalues and eigenvectors of our model can be obtained by diagonalizing the following matrix:

$$H^{\text{exact}} = \begin{pmatrix} & |v\uparrow v\downarrow\rangle & |v\uparrow c\downarrow\rangle & |v\downarrow c\uparrow\rangle & |c\uparrow c\downarrow\rangle \\ |v\uparrow v\downarrow\rangle & 2\epsilon_v + V_{vvvv} & V_{vvvc} & -V_{vvvc} & V_{vvcc} \\ |v\uparrow c\downarrow\rangle & V_{vvvc} & \epsilon_v + \epsilon_c + V_{cvvc} & -V_{vvcc} & V_{cvcc} \\ |v\downarrow c\uparrow\rangle & -V_{vvvc} & -V_{vvcc} & \epsilon_v + \epsilon_c + V_{cvvc} & -V_{cvcc} \\ |c\uparrow c\downarrow\rangle & V_{vvcc} & V_{cvcc} & -V_{cvcc} & 2\epsilon_c + V_{cccc} \end{pmatrix}, \tag{36}$$

where $\epsilon_i = \int dx\, \phi_i^*(x) h(x) \phi_i(x)$, $V_{ijkl} = \int dx\, dx'\, \phi_i^*(x) \phi_j^*(x')$ $\times v(x,x') \phi_k(x') \phi_l(x)$, and ϕ_i are the eigenstates of the non-interacting Hamiltonian. Note that here the terms such as $|v\uparrow c\downarrow\rangle$ indicate Slater determinants and not electron-hole excitations ($v\uparrow c\downarrow$). To keep contact with the notation used in the rest of the paper, we notice that $V_{ijkl} = v_{(li)(jk)}$. In our model the valence orbital v and the conduction orbital c are the hydrogenic wave functions $1s$, i.e., $\phi_{n=1 l=0 m=0}(r)$ $= (Z^{3/2}/\pi^{1/2}) \exp(-Zr)$, and $2s$, i.e., $\phi_{n=2 l=0 m=0}(r)$ $= [Z^{3/2}/(32\pi)^{1/2}](2-Zr)\exp(-Zr/2)$, respectively. Note that since the orbitals are real, then $V_{ijkl} = V_{klij}$ and, in particular, $V_{cvvc} = V_{vvcc}$. The one-electron energies are computed from the Bohr model, i.e., $E_n = -13.6 Z^2/n^2$ eV, with Z as the atomic number and n as the principal quantum number. The two-electron repulsion integrals V_{ijkl} are evaluated analytically. Direct and exchange terms are checked against analytical ones reported in Refs. 50 and 51. Diagonalization of matrix (36) produces four eigenvalues: one at -76.99 eV corresponding mainly to the singlet state $|1s\uparrow 1s\downarrow\rangle$, one at -57.77 eV corresponding mainly to the triplet combination ($|1s\uparrow 2s\downarrow\rangle + |1s\downarrow 2s\uparrow\rangle$) (note that the symmetric combination of the two determinants implies an antisymmetric combination of the spatial orbitals and a symmetric combination of the spin functions and vice versa for the antisymmetric combination of the two determinants), one at -53.23 eV corresponding mainly to the singlet combination ($|1s\uparrow 2s\downarrow\rangle - |1s\downarrow 2s\uparrow\rangle$),[27] and the last one at -18.98 eV corresponding mainly to the singlet state $|2s\uparrow 2s\downarrow\rangle$. The excitation energies for the transitions from the ground state $|1s\uparrow 1s\downarrow\rangle$ to the other (excited) states are reported in Table I. In particular the double-excitation energy is $\omega_3 = 58.02$ eV, which, although larger than the value calculated with the excitonic Hamiltonian, has the same order of magnitude. We also observe that the singlet-triplet splitting and the singlet single excitation are larger than the experimental values. Therefore we can consider the two double-excitation energies calculated with the two methods to be consistent.

IV. CONCLUSIONS

In this article we derive a frequency-dependent xc kernel, which can reproduce, within TDDFT, double excitations in finite systems. In order to achieve this, we get insight from MBPT, where the excitations of the system enter the formulation explicitly and approximations with a clear physical meaning can be more easily designed. We use the BSE, and we approximate the kernel with the dynamically screened Coulomb interaction $W(\omega)$. From this BSE kernel, we can derive a frequency-dependent xc kernel. The frequency dependence of this xc kernel has a double origin: it stems from the frequency dependence of the BSE kernel, which has
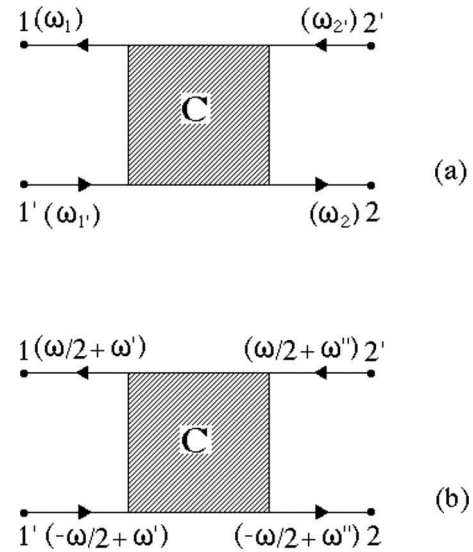

FIG. 1. (a) A generic four-point function $C(1,2,1',2')$ in Fourier (frequency) space. (b) Due to energy conservation, only three frequencies need to be specified [see Eqs. (A1) and (A2)].

folded in it the effect of double excitations, and from the folding of the four-point BSE to the two-point TDDFT equation. If the latter ω-dependence is neglected, the xc kernel exhibits the same frequency dependence as the BSE kernel. This frequency dependence indeed introduces excitations beyond the singles. In particular, we show that in a two-electron model system, the dynamical screening can reproduce double excitations. We obtain also an unphysical excitation energy. We analyze the origin of this spurious excitation, and we relate it to the self-screening problem that the GW approximation to the self-energy suffers from. Vertex corrections are needed in order to overcome the problems of the test charge–test charge approximation to the kernel.

APPENDIX A: BETHE–SALPETER IN FREQUENCY SPACE

Let us consider a four-point function as depicted in Fig. 1(a). At each time variable is associated a frequency. For the energy-conservation principle, we must have $\omega_1 - \omega_{1'} = \omega_{2'} - \omega_2$, which can be satisfied by the following choices:

$$\omega_1 = \frac{\omega}{2} + \omega', \quad \omega_1' = -\frac{\omega}{2} + \omega',$$

$$\omega_2' = \frac{\omega}{2} + \omega'', \quad \omega_2 = -\frac{\omega}{2} + \omega'', \tag{A1}$$

i.e., only three frequencies are needed to be specified [Fig. 1(b)]. Therefore the function $C(t_1, t_2, t_{1'}, t_{2'})$ can be written as

$$C(t_1, t_2, t_{1'}, t_{2'}) = \int \frac{d\omega\, d\omega'\, d\omega''}{(2\pi)^3} C(\omega, \omega', \omega'') e^{-i[(\omega/2+\omega')t_1 + (-\omega/2+\omega'')t_2 - (-\omega/2+\omega')t_{1'} - (\omega/2+\omega'')t_{2'}]}$$

$$= \int \frac{d\omega\, d\omega'\, d\omega''}{(2\pi)^3} C(\omega, \omega', \omega'') e^{-i\omega\tau} e^{-i\omega'\tau_1} e^{-i\omega''\tau_2}, \tag{A2}$$
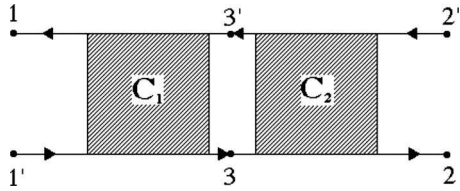
FIG. 2. Frequency convolution of two four-point functions, such as those entering the BSE with a frequency-dependent kernel [see Eqs. (A3) and (A4)].

with $\tau=[(t_1+t_1')/2-(t_2+t_2')/2]$, $\tau_1=t_1-t_{1'}$, and $\tau_2=t_2-t_{2'}$. Note that choice (A1) is done in order to obtain the time combinations of Eq. (A2). If we have two four-point functions $[C_1C_2](\tau,\tau_1,\tau_2)$, as in Fig. 2, the corresponding function $[C_1C_2](\omega,\omega',\omega'')$ in frequency space is

$$[C_1C_2](\omega,\omega',\omega'') = \int \frac{d\omega'''}{2\pi} C_1(\omega,\omega',\omega''')C_2(\omega,\omega''',\omega'').$$

(A3)

Something similar can be obtained for three four-point functions and so on. In particular, if we consider the BSE with the frequencies as in Fig. 1(b), then we have

$$L(\omega,\omega',\omega'') = L_0(\omega,\omega',\omega'') + \int \frac{d\omega'''d\omega^{iv}}{(2\pi)^2} L_0(\omega,\omega',\omega''')$$

$$\times \Xi(\omega,\omega''',\omega^{iv})L(\omega,\omega^{iv},\omega''). \quad (A4)$$

Using for the single-particle Green's functions the inverse Fourier transform,

$$G(1,2) = G(x_1,x_2,t_1-t_2) = \int \frac{d\omega}{2\pi} G(x_1,x_2,\omega)e^{-i\omega(t_1-t_2)},$$

(A5)

one can show that

$$L_0(\omega,\omega',\omega'') = -2\pi i\delta(\omega'-\omega'')G(\omega'+\omega/2)G(\omega''-\omega/2).$$

(A6)

It then follows that

$$L(\omega,\omega',\omega'') = -2\pi i\delta(\omega'-\omega'')G(\omega'+\omega/2)G(\omega''-\omega/2)$$

$$-iG(\omega'+\omega/2)G(\omega'-\omega/2)$$

$$\times \int \frac{d\tilde{\omega}}{2\pi}\Xi(\omega,\omega',\tilde{\omega})L(\omega,\tilde{\omega},\omega''). \quad (A7)$$

If we choose $\Xi(3,5,4,6)=\delta(3,4)\delta(5,6)v(3,6)$
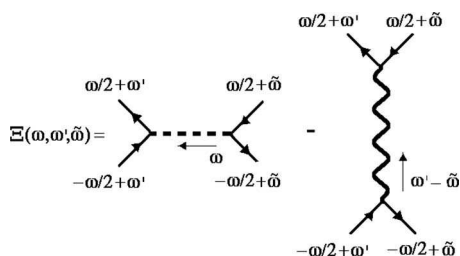

FIG. 3. The Bethe–Salpeter kernel $\Xi(3,5,4,6)=\delta(3,4)\delta(5,6)v(3,6)$ $-\delta(3,6)\delta(4,5)W(3,4)$, explicitly showing frequency arguments in its exchange and Coulomb terms [see Eqs. (10) and (A7)].

$-\delta(3,6)\delta(4,5)W(3,4)$, then it is easy to see in Fig. 3 that in order for the energy to be conserved, the exchange v should bring the frequency ω, while the Coulomb term W should bring the frequency $\omega'-\tilde{\omega}$. Within this approximation to the kernel, the BSE is given by Eq. (10).

APPENDIX B: EXACT SOLUTION

One can compute the ground and excited states and relative energies for the two-level–two-electron model system by starting from the exact Hamiltonian

$$\hat{H} = \sum_i \hat{h}(x_i) + \frac{1}{2}\sum_{i\neq j} v(x_i,x_j), \quad (B1)$$

where the first term on the right-hand side is the noninteracting Hamiltonian

$$\hat{H}_0 = \sum_i \left(-\frac{1}{2}\nabla_i^2 + v(x_i)\right), \quad (B2)$$

with

$$\hat{H}_0\phi_i = \epsilon_i\phi_i, \quad (B3)$$

and the second term is the two-electron interaction. Hamiltonian (B1) can be written in second quantization as

$$\hat{H} = \sum_{ij} h_{ij}\hat{a}_i^\dagger\hat{a}_j + \frac{1}{2}\sum_{ijkl} V_{ijkl}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l, \quad (B4)$$

with

$$h_{ij} = \int dx\phi_i^*(x)h(x)\phi_j(x) = \epsilon_j\delta_{ij},$$

$$V_{ijkl} = \int dxdx'\,\phi_i^*(x)\phi_j^*(x')v(x,x')\phi_k(x')\phi_l(x), \quad (B5)$$

and $V_{ijkl}=V_{klij}^*$. Note that as a complete set of orthonormal one-particle orbitals in which the creation and annihilation operators are expressed, we used the eigenstates ϕ_i's of the noninteracting Hamiltonian. We can construct any state of the noninteracting Hamiltonian $\hat{H}_0$ by acting with the creation operators on the vacuum: $\hat{a}_i^\dagger\hat{a}_j^\dagger|0\rangle$, with $i\neq j$. The energies of the interacting Hamiltonan (B1) can be found by evaluating matrix elements of the form

$$\langle\hat{a}_r\hat{a}_s|\hat{H}|\hat{a}_{s'}^\dagger\hat{a}_{r'}^\dagger\rangle = \sum_i \epsilon_i\langle\hat{a}_r\hat{a}_s\hat{a}_i^\dagger\hat{a}_i\hat{a}_{s'}^\dagger,\hat{a}_{r'}^\dagger\rangle$$

$$+ \frac{1}{2}\sum_{ijkl} V_{ijkl}\langle\hat{a}_r\hat{a}_s\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l\hat{a}_{s'}^\dagger,\hat{a}_{r'}^\dagger\rangle. \quad (B6)$$

We can now use Wick's theorem and rewrite the strings of annihilation and creation operators as an expansion of normal-ordered strings. However, the only terms that need to be retained in this expansion are those that are fully contracted. For the first string on the right-hand side, we get

$$\hat{a}_r\hat{a}_s\hat{a}_i^\dagger\hat{a}_i\hat{a}_{s'}^\dagger\hat{a}_{r'}^\dagger = \delta_{ri}\delta_{ss'}\delta_{ir'} - \delta_{ri}\delta_{sr'}\delta_{is'} + \delta_{rr'}\delta_{si}\delta_{is'}$$
$$- \delta_{rs'}\delta_{si}\delta_{ir'}, \qquad (B7)$$

while for the second one we have

$$\hat{a}_r\hat{a}_s\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l\hat{a}_{s'}^\dagger\hat{a}_{r'}^\dagger = \delta_{ri}\delta_{sj}\delta_{ks}\delta_{lr'} - \delta_{ri}\delta_{sj}\delta_{kr'}\delta_{ls'}$$
$$- \delta_{rj}\delta_{si}\delta_{ks'}\delta_{lr'} + \delta_{rj}\delta_{si}\delta_{kr'}\delta_{ls'}. \quad (B8)$$

The Hamiltonian $\hat{H}_0$ is diagonal on the basis of its eigenstates; i.e., the nonzero matrix elements are those with $r = r'$ and $s = s'$ as

$$\sum_i \epsilon_i\langle\hat{a}_r\hat{a}_s\hat{a}_i^\dagger\hat{a}_i\hat{a}_{s'}^\dagger\hat{a}_{r'}^\dagger\rangle = (\epsilon_r + \epsilon_s)\delta_{rr'}\delta_{ss'}. \quad (B9)$$

For the electron-electron interaction, we have

$$\frac{1}{2}\sum_{ijkl} V_{ijkl}\langle\hat{a}_r\hat{a}_s\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l\hat{a}_{s'}^\dagger\hat{a}_{r'}^\dagger\rangle = V_{rss'r'} - V_{rsr's'}, \qquad (B10)$$

where we considered $V_{srr's'} = V_{rss'r'}$ and $V_{srs'r'} = V_{rsr's'}$. Since the model system we are considering has only two electrons and two energy levels, which will be called v (valence) and c (conduction), we will have the energy matrix of Eq. (36).

Note that since we are not considering spin flip, we have not considered the Slater determinants $|v\uparrow c\uparrow\rangle$ and $|v\downarrow c\downarrow\rangle$ in the evaluation of the matrix elements (B6). Notice that here the notation $|v\uparrow c\uparrow\rangle$ is a Slater determinant, and it indicates a state with an electron in the valence orbital with spin up and the other electron in the conduction electron with spin up. This is different from the notation $(v\uparrow c\uparrow)$ used so far in the paper, which means that an electron with spin up is promoted from the valence orbital to the conduction orbital, thus leading to a state $|v\downarrow c\uparrow\rangle$.

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