Exciton–plasmon states in nanoscale materials: breakdown of the Tamm–Dancoff approximation

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Within the Tamm–Dancoff approximation ab initio approaches describe excitons as packets of electron-hole pairs propagating only forward in time. However, we show that in nanoscale materials excitons and plasmons hybridize, creating exciton–plasmon states where the electron-hole pairs oscillate back and forth in time. Then, as exemplified by the trans-azobenzene molecule and carbon nanotubes, the Tamm–Dancoff approximation yields errors as large as the accuracy claimed in ab initio calculations. Instead, we propose a general and efficient approach that avoids the Tamm–Dancoff approximation, and correctly describes excitons, plasmons and exciton–plasmon states.

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The Bethe–Salpeter (BS) and the Time-Dependent Density Functional Theory (TDDFT) equations allow the accurate calculation of the polarization function of many physical systems without relying on external parameters. Within these frameworks neutral excitations are described as combination of electron-hole (e-h) pairs of a noninteracting system. However for nanoscale materials, the huge number of e-h pairs involved makes the solution of the BS/TDDFT equation extremely cumbersome. Consequently, the increasing interest in the excitation properties of such materials has justified the use of ad-hoc approximations. The most important and widely-used is the Tamm-Dancoff approximation (TDA) where only positive energy e-h pairs are considered. Within the TDA the interaction between e-h pairs at positive and negative (antipairs) energies is neglected, and only one e-h pair is assumed to propagate in any time interval. The main advantage of the TDA is that the non-Hermitian BS/TDDFT problem reduces to a Hermitian problem, that can be solved with efficient and stable iterative methods.

In Solid State Physics—a major field of application of the BS/TDDFT equation—the success of TDA is based on the sharp distinction between excitonic and plasmonic excitations. Excitons are localized packets of e-h pairs bound together by the Coulomb attraction and are observed in optical absorption experiments. Plasmons are, instead, delocalized collective oscillations of the electronic density that induce a macroscopic polarization effect and are observed in electron energy loss (EEL) experiments. In contrast to the case of excitons, the TDA is known to misdescribe plasmons in solids as the density oscillations involve the excitation of e-h antipairs. Nevertheless, the success in describing optical absorption of solids and the remarkable numerical advantages have motivated the application of the TDA to very different systems. Nowadays the BS/TDDFT equation within the TDA is becoming a standard tool to study excitations in nanostructures, and in molecular systems.

In this Letter we argue that for confined systems—such as nanostructures or π-conjugated molecules—the excitations appearing in the response function show a mixed excitonic–plasmonic behavior. As a consequence the e-h pair-antipair interaction becomes crucial and the TDA does not hold anymore. A paradigmatic example is the trans-azobenzene molecule, where the TDA overestimates the static polarizability by ~40%. This error is larger than the claimed accuracy in ab initio calculations. Even more intriguing is the case of carbon nanotubes that, because of the quasi-one-dimensional (1D) structure, behave either as extended or isolated system depending on the direction of the perturbing field. Thus, for transverse perturbations the excitons acquire a plasmonic nature and the TDA overestimates the position of the π plasmon peak appearing in both absorption and EEL spectra by almost 1 eV. By exploiting the symmetry properties of the BS and TDDFT kernels we devise a robust and efficient iterative approach to calculate the frequency-dependent response, beyond the TDA. This approach benefits from the same numerical advantages of Hermitian techniques, and correctly describes excitons, plasmons and exciton–plasmon states.

To introduce and understand the reasons beyond the breakdown of the TDA we need to study in detail the structure of the TDDFT and BS equations. These are commonly rewritten as a Hamiltonian problem by expanding the single particle states in the Kohn–Sham basis. Then, the BS/TDDFT Hamiltonian \( H \) is a matrix in the Fock space of the e-h pairs \(|eh⟩\) and antipairs \(|he⟩\), and it has the block-form

\[
H = \begin{pmatrix}
R & C \\
-C^* & -R^*
\end{pmatrix}.
\]
The resonant block \( R \) is Hermitian and the coupling block \( C \) is symmetric (see Appendix B of Ref. [9]). The dielectric function \( \varepsilon(\omega) \) is written in terms of the resolvent of \( H \), \( (\omega - H)^{-1} \), as \( \varepsilon(\omega) = 1 - (8\pi i)/\Omega |P(\omega - H + i0^+)^{-1}|P \), where \( \Omega \) is the simulation volume. In the limit of large \( \Omega \) the polarizability is given by \( \alpha(\omega) \propto \varepsilon(\omega) \). \( |P \) is a ket whose components along the \( \{eh\} \) space are the optical oscillators: \( \langle P|eh \rangle \sim \langle e \rangle \hat{d} \cdot \hat{\xi} \hat{h} \), with \( \hat{d} \) the electronic dipole, and \( \hat{\xi} \) the light polarization factor.

TDA is known to fail for plasmonic excitations [5] that, causing an oscillation of the density, involve the creation of e-h pairs and antipairs.

The electronic density of confined systems, like molecules and nanostructures, is typically strongly inhomogeneous. Moreover the excitons can be spread all over the molecule, involving the excitations of most of the electrons. Thus, in contrast to solids, it is not possible to distinguish between excitonic and plasmonic excitations, and the arguments commonly used to sustain the TDA fail.

Indeed, the striking failure of the TDA is clearly demonstrated by the dynamical polarizability \( \Im [\alpha(\omega)] \) of trans-azobenzene, calculated within the time-dependent local density approximation (TDLDA) [10, 11]. In Fig. 1 we compare \( \Im [\alpha(\omega)] \) calculated either using the TDA, or by solving the full \( H \) eigenproblem. TDA yields a blueshift of 0.2 eV and a large overestimation of the intensity of the main peak. More importantly the TDA causes a 40% underestimation of the static polarizability, \( \Re [\alpha(\omega = 0)] \). The reason for this failure can be understood looking at the amplitude function \( A^\lambda(\omega) \) of the eigenstates \( |\lambda\rangle \) of \( H \), defined as \( A^\lambda(\omega) = \sum_{\eta=\{eh\}} |\langle \eta |\lambda \rangle|^2 \delta (\omega - E_\eta) \). The \( A^{\lambda_{\text{max}}} \) function for the state \( \lambda_{\text{max}} \) corresponding to the most intense peak of the \( \alpha \) spectrum is shown in the inset of Fig. 1. In the TDA, the \( \lambda_{\text{max}} \) state is decomposed only in positive e-h pairs. However, the solution the full Hamiltonian reveals an important contribution from the spatially extended e-h antipair with energy \( \sim -2.7 \) eV.

The example of the trans-azobenzene makes clear that a proper description of the electron-electron correlations in confined systems requires the solution of the full BS/TDDFT Hamiltonians, beyond the TDA. However, for larger nanostructures with many degrees of freedom, the size of the \( H \) matrix can be as large as \( 10^6 \times 10^6 \) and consequently the problem is impossible to treat if not using iterative methods. The TDA reduces \( H \) to a Hermitian Hamiltonian, and makes possible to use the efficient and stable Hermitian iterative approaches [3]. Therefore we need an iterative approach for calculating the resolvent of the full non-Hermitian Hamiltonian \( H \) as efficient and stable as for the Hermitian case.

In what follows, we show that it is indeed possible to design such an iterative approach by observing that \( H \) belongs to a class of non-Hermitian Hamiltonians with a real spectrum—that is real eigenvalues. As established by Mostafazadeh [12], the reality of the spectrum is re-
lated to the existence of a positive-definite inner product with respect to which the Hamiltonian is Hermitian. We show that for the BS (TDDFT) Hamiltonian—and in general for all the Hamiltonians of this form—this inner product does exist (thus the spectrum is real) and, more importantly, it is explicitly known. The knowledge of this product allows one to conveniently transform the iterative approach designed for the Hermitian TDA Hamiltonian to treat the full non-Hermitian Hamiltonian.

Following Zimmermann [13] we can write $H$ as the product of two noncommuting Hermitian matrices,

$$H = FH = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} R & C^* \\ C & R^* \end{pmatrix}. \tag{2}$$

One can check that $HH = H^1HH$. This key property of $H$ is called $\bar{H}$-pseudo-Hermiticity [14]. Through the $\bar{H}$ operator, we can define a positive-definite $\bar{H}$-inner product [15] $\langle \cdot | \bar{H} | \cdot \rangle$ and a corresponding $\bar{H}$-expectation value $\langle \cdot | \bar{O} | \cdot \rangle := \langle \cdot | \bar{H} O | \cdot \rangle$. With respect to this $\bar{H}$-expectation value, $H$ is Hermitian as can be verified by using the $\bar{H}$-pseudo-Hermiticity,

$$\langle v | H | v' \rangle_{\bar{H}} = \langle v' | H^1 \bar{H} | v \rangle^* = \langle v' | \bar{H} H | v \rangle^* = \langle v' | H | v \rangle_{\bar{H}}^* \tag{3}$$

It follows that the $\bar{H}$-expectation value of the resolvent of $H$, $(\omega - H)^{-1}$, is Hermitian as well. Then, to evaluate $\langle P | (\omega - H)^{-1} | P \rangle_{\bar{H}}$, and thus $\epsilon(\omega)$, we rewrite it in terms of Hermitian $\bar{H}$-expectation values by using completeness relationship $I = \sum_k |q_k\rangle \langle q_k| H \bar{H}$

$$\langle P | (\omega - H)^{-1} | P \rangle = \sum_k \langle P | q_k \rangle \langle q_k | (\omega - H)^{-1} | P \rangle_{\bar{H}}, \tag{4}$$

where $\{ |q_k\rangle \}$ is a complete basis, orthonormal with respect to the $\bar{H}$-inner product. The $\langle q_k | (\omega - H)^{-1} \rangle_{\bar{H}}$ are conveniently calculated within the standard Lanczos–Haydock (LH) iterative method [16]—the same used in the TDA Hermitian case [17]—provided that the $\bar{H}$-inner product replaces the standard one. The LH method recursively builds the $\{ |q_k\rangle \}$ basis in which $H$ is represented by a one-dimensional semi-infinite chain of sites with only nearest-neighbors interactions. For such a system, the evaluation of the matrix elements of $(\omega - H)^{-1}$ reduces to the calculation of a continued fraction.

This approach allows us to treat systems as large as commonly done using the TDA, but using the full Hamiltonian. Computationally, it requires a single matrix–vector multiplication at each iteration—as in the Hermitian case [13]. Since $\langle P | (\omega - H)^{-1} | P \rangle$ in Eq. (4) is converged after a number of iterations much smaller than the dimension of $H$, this method is far more efficient than performing the diagonalization of the Hamiltonian. Specifically, for the trans-azobenzene, the number of operations performed in the diagonalization is about two orders of magnitude larger than in our approach [19], while the results are indistinguishable (Fig. 1).

As an application we consider the frequency-dependent response of carbon nanotubes (CNTs) within the BS equation. Recently, experimental studies have shown CNTs to be characterized by strongly anisotropic electronic and optical properties [21,22]. Moreover, the measured optical and EEL spectra have revealed that excitations appearing at energies higher than $4 \, \text{eV}$ have a collective character [21,22]. Using the present method we show that the external field polarization and the excitonic–plasmonic character of the optical excitations of CNTs are intimately related.

So far ab initio studies have been limited to the excitonic effects appearing below $4 \, \text{eV}$ and only for longitudinal polarized light [7]. In fact, calculations of the optical response to transverse perturbing fields are extremely challenging, as the plasmonic character of the excitation requires the inclusion of a huge number of e-h pairs. Using the method proposed in this work we were able to include up to $\sim 1.4 \times 10^5 \, \text{e-h pairs}$ in the solution of the BS equation, without using the TDA.

Figure 2 shows the absorption (left stack) and $q \rightarrow 0$ EEL (right stack) spectrum of CNTs calculated within the BS [14,20] equation as a function of the angle $\phi$ that the perturbing field forms with the tube axis. We compare the full solution of the BS equation (full line)
with the result of the TDA (dashed line).

For a parallel perturbing field (φ = 0) the CNT behaves as an extended solid. As expected, in this case the TDA describes well the excitonic peaks in the absorption spectrum [1]. On the contrary the TDA completely fails in reproducing the longitudinal plasmonic peak, overestimating its frequency by 1.5 eV. By increasing the φ angle the perturbing field acquires a perpendicular component, and a peak at ∼ 6 eV appears in the ϵ(ω) function. The very same peak occurs in the EEL spectrum, confirming that it corresponds to a mixed excitonic–plasmonic excitation. This mixed behavior is misdescribed by the TDA both in the absorption and in the EEL spectra. The TDA performs even worse for a transverse perturbing field (φ = 90°), where the excitations are confined within the tube radius. The ϵ(ω) and ϵ₋₁(ω) functions become very similar—that is, the system behaves as an isolated molecule. Thus, like in the case of the trans-azobenzene, the contribution from e-h antipairs cannot be neglected, and the TDA yields an error on the position of the main peak in the absorption/EEL spectra of ∼ 0.6 eV.

Our results for the CNT show that, in contrast to the common belief, the excitations appearing in 3(ε) are not all purely excitonic. When the excitation is forced to be spatially confined, it acquires a mixed excitonic–plasmonic character, and the TDA breaks down. The TDA performs well only for purely excitonic states that are dominant only when the perturbing field is polarized along the tube axis. However, in practice it is not possible to measure selectively only longitudinal polarization as CNTs are generally randomly oriented in a sample. Even in the case of vertical aligned CNTs the tubes are found to form angles of ∼ 25° [22].

Finally, an important confirmation of the accuracy of the present approach is given by the position of the plasmon peaks in the EEL spectra. Using the full solution of the BS equation, the plasmon energy is found to blueshift of ∼ 0.5 eV by moving from φ = 0° to φ = 90°. This is in striking agreement with the 0.5 eV value measured in momentum dependent EEL experiments [22]. On the contrary, the TDA causes an energy redshift of the plasmon, in disagreement with the experimental results.

In summary, we have shown that the TDA breaks down in nanoscale systems where dimensionality effects confine the optical excitation, inducing a mixed excitonic–plasmonic behavior. We propose a novel approach to solve the BS/TDDFT equations beyond the TDA, keeping the numerical advantages of a Hermitian formulation. This approach successfully explains the experimental features in the optical and EEL spectra of CNTs, and opens the way to a truly ab initio approach to linear response properties of nanoscale materials.

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