

## Optical Saturation Driven by Exciton Confinement in Molecular Chains: A Time-Dependent Density-Functional Theory Approach

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We identify excitonic confinement in one-dimensional molecular chains (i.e., polyacetylene and  $H_2$ ) as the main driving force for the saturation of the chain polarizability as a function of the number of molecular units. This conclusion is based on first principles time-dependent density-functional theory calculations using a recently developed exchange-correlation kernel that accounts for excitonic effects. The failure of simple local and semilocal functionals is shown to be linked to the lack of memory effects, spatial ultranonlocality, and self-interaction corrections. These effects get smaller as the gap reduces, in which case such simple approximations do perform better.

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The electronic quantum confinement occurring in low-dimensional systems is often responsible for the peculiar spectroscopic properties exhibited by molecules and nanostructures [1]. Exciton confinement explains, for example, the size-dependent color of semiconducting quantum dots used as fluorescent markers in biology. Highly localized excitons (solitons) also play a fundamental role in describing the process of vibrational energy transfer in complex proteins. In this context, one-dimensional polymers and molecular chains constitute an excellent playground to analyze the interplay between correlation effects and quantum confinement. For example, in nonconducting polymers the longitudinal linear polarizability per monomer unit  $\alpha(N)/N$  tends to a constant in the large- $N$  limit [2]. This optical saturation stems from the polarization of the electrons along the chain that tends to counteract the external field. This Letter aims to provide a consistent description of this saturation within a density-functional scheme.

The widely used local density approximation (LDA) and semilocal approximations to density-functional theory (DFT) and time-dependent DFT (TDDFT) that successfully describe the electronic properties of many different physical systems [3] fail dramatically for the case of semiconducting one-dimensional molecular chains. ALDA does not provide a good absorption spectra and strongly overestimates the polarizability with respect to quantum chemical calculations [4,5]. The reason for this poor performance of ALDA has been traced either to the need of long-range terms (*ultranonlocality*) in the exchange-

correlation functionals [6] or to the lack of self-interaction correction (SIC) [7,8]. Exact-exchange (EXX) or current-density-functional (CDFT) approaches capture some of the effects, but not all: while EXX works fairly well in the case of the finite  $H_2$  chain [reproducing the Hartree-Fock (HF) results [7]], it fails in reproducing the absorption spectrum of the infinite trans-polyacetylene (PA) chain [9]. On the contrary, CDFT provides quite good results for some finite  $\pi$ -conjugated polymers [10], while it breaks down for the  $H_2$  chain.

In TDDFT all effects beyond noninteracting particles are embodied in the exchange-correlation (xc) kernel  $f_{xc} \equiv \delta v_{xc} / \delta n$ , with  $v_{xc}$  the xc potential and  $n$  the exact ground state electronic density. The recent developments in merging many-body perturbation theory (MBPT) [11] and TDDFT [12] open the path to unravel the physical origin of the response properties of one-dimensional systems. Below we show that exciton confinement dictates the evolution (saturation) of the optical response of one-dimensional chains as a function of the chain length. Therefore the failure of EXX, local, semilocal, or CDFT approximations is related to their inability to describe strong excitonic effects in anisotropic low-dimensional systems. We show that the xc kernel has an *ultranonlocal* behavior and memory dependence that is at least 1 order of magnitude stronger than in solids. The static and dynamical polarizabilities are both well described in the simple  $H_2$  or in the more sophisticated trans-polyacetylene molecular chains.

To guide the discussion, we remind the reader that the polarizability  $\alpha$  is obtained from the imaginary part of the microscopical reducible polarization function  $\hat{\chi}(\omega)$  that can be obtained from the solution of the standard TDDFT equation in matrix form [3]:

$$\hat{\chi}(\omega) = \hat{\chi}_0(\omega)[1 + \hat{f}_{Hxc}(\omega)\hat{\chi}(\omega)]. \quad (1)$$

$\hat{\chi}_0(\omega)$  is the noninteracting response function, and  $\hat{f}_{Hxc} = \hat{f}_{Hartree} + \hat{f}_{xc}$ . All quantities are two-point functions (matrices in reciprocal space). The  $f_{xc}$  kernel used in this work has been derived in Ref. [12] imposing the TDDFT equation to reproduce the results of the Bethe-Salpeter (BS) equation for  $\hat{\chi}$  within MBPT [11]. The BS equation describes the excitonic dynamics in terms of  $W$ , the screened electron-hole interaction. Consequently, the leading term in the perturbative expansion of the xc kernel turns out to be  $\hat{f}_{xc} = \hat{\chi}_0^{-1}\hat{\chi}_1\hat{\chi}_0^{-1}$ , where  $\hat{\chi}_0$  is the noninteracting quasiparticle response function [13], and  $\hat{\chi}_1$  the first order correction in  $W$  to  $\hat{\chi}_0$ . This kernel is *ab initio* and, in spite of its simplicity, it fully captures excitonic features in the absorption spectra of bulk semiconductors, insulators, as well as surfaces [3], in contrast to EXX and CDFT. Moreover,  $f_{xc}$  includes the correct behavior  $\lim_{\mathbf{q} \rightarrow 0} f_{xc}(\omega, \mathbf{q}) \sim -(\gamma + \beta\omega^2)/|\mathbf{q}|^2$  in the long-range regime [12,14]. The two constants,  $\gamma$  and  $\beta$ , measure, respectively, the degree of spatial nonlocality and memory effects.

In order to illustrate how the kernel  $f_{xc}$  solves the failure of ALDA (and of any semilocal approximations), we consider two Peierls distorted infinite molecular  $H_2$  chains [15]. In chain A (see Fig. 1) the intermolecular distance is set to 2.5 a.u. and the intramolecular distance is 2.0 a.u. (as in previous works [5,7,10]). This chain is a semiconductor with a LDA gap of 2.28 eV. In chain B the intermolecular distance is reduced to 2.05 a.u. and the LDA gap gets very small (0.26 eV). In Fig. 1 we compare the TDDFT absorption spectra for both chains calculated within ALDA and the  $f_{xc}$  kernel. As the electronic density is more homogeneous in chain B than in chain A, the ALDA gives an almost indistinguishable dynamical polarizability from the BS calculations (see Fig. 1, right panel). Instead, in chain A the ALDA performance worsens considerably, failing to reproduce the main absorption peak. However, the  $f_{xc}$  kernel yields a dynamical polarizability in both chains almost indistinguishable from the BS calculations. To gain more insight we plot in Fig. 1 the excitonic wave function corresponding to the main absorption peaks for both chains. We see that for chain A, where ALDA fails, the exciton is confined within few  $H_2$  monomers ( $\approx 36$  a.u.), while in B it is basically spread all over the chain.

This simple example brings up the main conclusion of the Letter, namely, to link the failure of the ALDA to the exciton spatial localization. The crucial difference between quasimetallic and semiconducting chains is reflected in the structure of the TDDFT kernel. If we look at the long-range

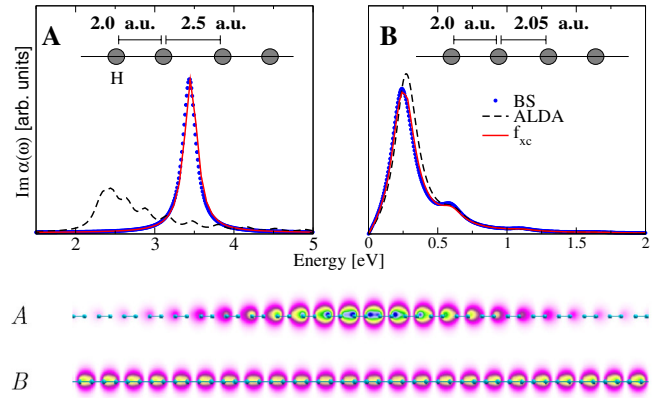


FIG. 1 (color online). Axial optical absorption spectra for the molecular  $H_2$  chain A (Peierls distorted, left-hand frame) and chain B (nearly equally spaced H atoms, right-hand frame). While the present  $f_{xc}$  kernel yields an excellent agreement with the many-body calculations in both cases, ALDA works only in the small gap case when the exciton is not localized. The excitonic wave functions [22] corresponding to the main absorption peak are also shown by fixing the hole in the middle of the central hydrogen molecular bond. A delocalized exciton wave function in chain B is connected with a successful description of the spectra by the ALDA (see text).

limit of  $f_{xc}$  for the two chains we see very drastic differences: whereas in chain B both  $\gamma$  and  $\beta$  are almost zero, in chain A  $\gamma \sim 16.92$  and  $\beta \sim 0.45 \text{ eV}^{-2}$  [16], which is more than 1 order of magnitude larger than in solids, where  $\gamma \sim 0.1\text{--}1.5$ , while  $\beta \sim 1\text{--}34 \times 10^{-3} \text{ eV}^{-2}$  [14]. The huge values of  $\gamma$  and  $\beta$  are due to the strong confinement of the excitonic state caused by the correlation effects in the  $f_{xc}$  kernel. In addition, the  $\beta$  constant is related to the energy-dependent part of  $f_{xc}$  that measures the strength of the memory effects. Another fingerprint of the relevance of correlation effects in the  $f_{xc}$  of chain A is that the static limit of the long-range part of the total TDDFT kernel,  $\lim_{\omega \rightarrow 0} f_{Hxc}(\omega, \mathbf{q}) \sim (4\pi - \gamma)/|\mathbf{q}|^2$ , is negative. This means that the spatial nonlocality of  $f_{xc}$ , linked again to the excitonic localization, is stronger than the Hartree term [17] that measures, instead, the degree of inhomogeneity of the electronic density. The *ultranonlocality* and the memory effects described by the many-body  $f_{xc}$  cannot be captured by any static, local, or semilocal approximation.

The effect of exciton confinement is enhanced in finite length  $H_2$  chains, whose static polarizability is shown in Fig. 2 for different approximations of the xc kernel. Both ALDA and CDFT yield a very slow saturation of  $\alpha$  as a function of the chain length and a strong overestimation of the static polarizability compared to accurate quantum chemical coupled cluster results CCSD(T). The TDDFT results obtained using the  $f_{xc}$  kernel partially reduce the ALDA and CDFT overestimation, showing a faster saturation. However the agreement with CCSD(T) is not yet satisfactory. We have traced the residual discrepancy back to the presence of self-interaction effects in the LDA wave functions used to construct the xc kernel, that

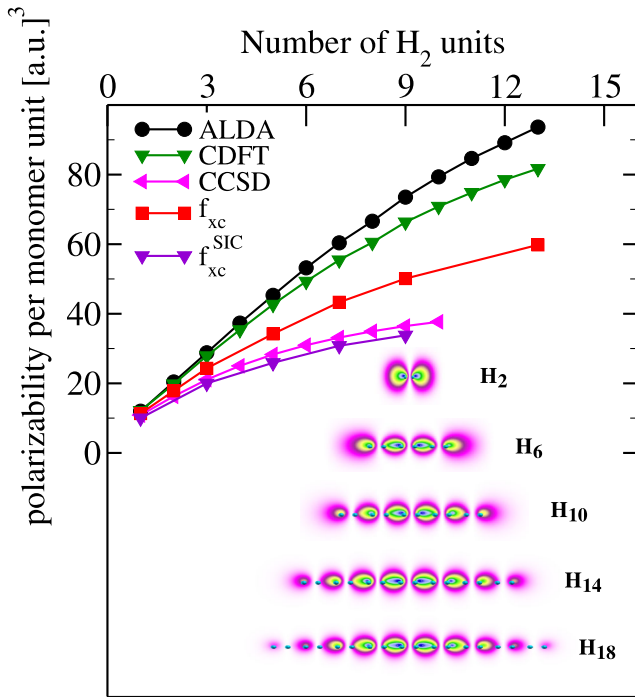


FIG. 2 (color online). Axial polarizability per monomer of the molecular  $H_2$  chains. TDDFT calculations within the ALDA,  $f_{xc}$ , and  $f_{xc}^{SIC}$  (see text) are compared with coupled cluster CCSD (T) [5] and CDFT [10] results. The real-space excitonic wave functions of selected chains, with the hole placed in the middle of the central hydrogen molecule bond, are also shown.

counteract the spatial localization of the excitonic states. This is because the LDA states are too delocalized, and the process of localization of the electron-hole packets induced by  $f_{xc}$  is more difficult. This drawback of the LDA can be easily corrected by recomputing the kernel (named  $f_{xc}^{SIC}$  in Fig. 2) using HF self-interaction-free wave functions.

This new kernel yields axial polarizabilities in excellent agreement with the CCSD(T) results. The SIC increases the xc kernel spatial nonlocality factor  $\gamma$ , which translates into further confinement of the excitonic states, compared to the LDA-based  $f_{xc}$  results. This can be rationalized by looking at the excitonic wave functions shown in the bottom of Fig. 2. The probability of finding an electron at the end of the chain when the hole is placed in the middle of the bond of the central  $H_2$  molecule (that measures excitonic confinement) quickly decreases while increasing the chain length, being almost zero for  $N = 9$ . The polarizability follows the same trend, exhibiting saturation when the extension of the excitonic wave function is smaller than the chain length [18]. The reason that ALDA gives good results for small chains is again related to the fact that the excitonic wave function is spread over the whole molecule (like in the case of chain *B* discussed above). It is then clear that exciton confinement plays a major role in the determination of the response properties of  $H_2$  chains providing microscopic support to the relevance of the ultranlocality and memory concepts in exchange-correlation functionals.

The  $H_2$  chain represents an extreme case of system with few electrons, where confinement is crucial, while electronic screening is negligible. For this reason TDDFT kernels that work in the case of  $H_2$  chain may fail in more complex molecular systems where electronic screening becomes more important. This is the case of the trans-polyacetylene molecular chain. The PA chain has been extensively studied in the past within the BS scheme [19]. It has been shown that the main absorption peak observed experimentally is excitonic, with 0.44 eV binding energy. On the contrary, all available calculations within TDDFT do not reproduce the experimental results: ALDA spectra (see left inset of Fig. 3) is too low in energy and the main absorption peak shape is more similar to a van Hove singularity than to an isolated excitonic peak. Within an EXX calculation it is possible to obtain a good agreement with the experiment only by *neglecting the x kernel*, i.e., in the independent particle approximation [9], which is clearly inconsistent. As shown in Fig. 3, our  $f_{xc}$  kernel [20], instead, is in good agreement with the second order Møller-Plesset (MP2) results in the finite length case and with the experimental absorption peak position in the infinite length case (left inset) [21]. MP2 calculations [4]

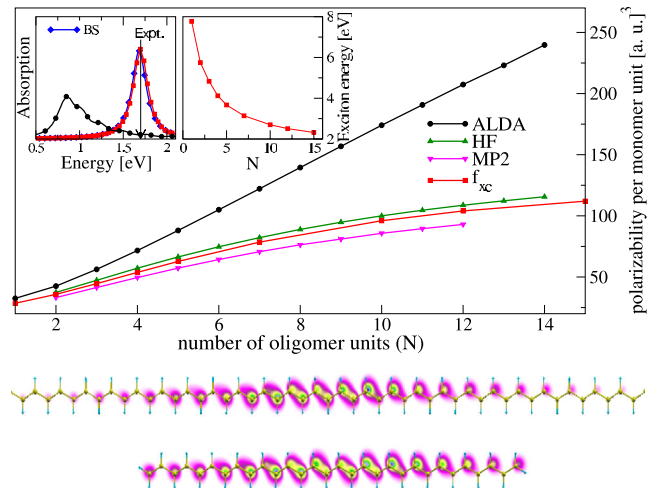


FIG. 3 (color online). Calculated axial polarizability of the finite trans-polyacetylene chain with alternating C-C distances of 1.339 and 1.451 Å. We also show the result of HF [23], MP2 [4], and ALDA calculations. In the insets we report the absorption spectrum of the infinite chain (left inset) and dependence of the excitonic energy ( $E_{exc}$ ) as a function of the number of monomers ( $N$ ). In contrast to the ALDA, the experimental absorption at 1.7 eV [24] is perfectly reproduced by either the BS or the present TDDFT calculations. At difference with the ALDA, the axial polarizability calculated with the present  $f_{xc}$  correctly saturates at 15 monomers, in excellent agreement with the MP2 results. At the same time, the excitonic energy saturates towards the infinite chain experimental peak position. Bottom: Excitonic wave functions corresponding to the most intense and bright peak of the infinite and 15 monomers long chains, respectively. It is significant to note that in both cases the exciton extends over the same number of neighbors.

predict the PA chain polarizability to saturate around 15 monomers, in excellent agreement with the excitonic extension obtained in the present work and with the observed saturation of the dependence of the calculated main absorption peak and static polarizability with respect to the length of the chain. At the bottom of Fig. 3 we show the excitonic wave function in the infinite chain corresponding to the PA exciton at 1.69 eV, together with the wave function of the predominant state in the 15 monomers long chain. The saturation of the static polarizability is reflected in the complete localization of the excitonic wave function that, in the finite length case, extends over the same number of monomers of the infinite chain. At the same time the exciton energy  $E_{\text{exc}}$  saturates towards the infinite chain experimental peak position (see right-hand inset of Fig. 3). This confirms the result found in the  $\text{H}_2$  chains and transforms the link between exciton localization and optical saturation in a general property of molecular chains and confined quantum systems.

In conclusion, we have shown that a many-body derived  $f_{\text{xc}}$  kernel within TDDFT successfully explains the optical saturation in molecular chains in terms of excitonic confinement. The  $\text{H}_2$  and the, more realistic, trans-polyacetylene molecular chains are very well described by the many-body based xc kernel, both in the finite and infinite length regime, yielding static and dynamical polarizabilities in excellent agreement with accurate quantum chemical calculations. We have proved that there exists a general close link between the excitonic spatial extension and the axial polarizability in the TDDFT framework, giving a sound interpretation of the severe breakdown of the local-density approximation in anisotropic structures.

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- [16] In low-dimensional systems the constants  $\gamma$  and  $\beta$  scale linearly as a function of the simulation volume. Nevertheless the  $f_{Hxc}\chi_0$  product entering in the TDDFT equation [Eq. (1)] is always finite.
- [17] In solids, the optical absorption  $\epsilon$  differs from the polarizability  $\alpha$ .  $\epsilon$  is proportional to the spatial average of the modified reducible polarization  $\bar{\chi}$ , solution of Eq. (1) with no long-range component in the Hartree term. Thus, even small values of  $\gamma$  yield large modifications of the non-interacting absorption spectrum. In the infinite  $\text{H}_2$  chain, instead,  $f_{\text{xc}}$  must counteract the nonzero Hartree term to yield similar effects on the polarizability spectrum.
- [18] As the dynamical polarizability of the  $\text{H}_2$  chains is dominated by a single peak at energy  $E_{\text{exc}}$ , it is straightforward to show from the energy and  $f$  sum rules that the static polarizability per monomer unit goes as  $\alpha(N)/N \sim E_{\text{exc}}^{-2}$ . Therefore both quantities  $E_{\text{exc}}$  and  $\alpha$  are closely linked as functions of the excitonic spatial extension.
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