Optical saturation driven by exciton confinement in molecular-chains: a TDDFT study

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We have identified excitonic confinement in one-dimensional molecular chains (i.e. polyacetylene and H2) 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 performed with a new derived exchange–correlation kernel. The failure of simple local and semi–local functionals is shown to be related to the lack of memory effects, spatial ultranonlocality, and self–interaction corrections. These effects get smaller as the gap of the system 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. Exciton confinement explains, for example, the size–dependent color of semiconducting quantum dots used as fluorescent markers in biology [1]. Highly localized excitons (solitons) play also a fundamental role in describing the process of vibrational energy transfer in complex proteins [2]. 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 non conducting polymers the longitudinal linear polarizability per monomer unit α(N)/N tends to a constant in the large–N limit [3]. This optical saturation stems from the polarization of the electrons along the chain that tends to counteract the external field and manifest itself in the dependence of the optical absorption spectra on the polymer size. The present Letter aims to provide a consistent description of this saturation within density–functional based schemes.

The commonly used local (LDA) and semilocal (GGA) approximations to Density–Functional–Theory (DFT) and Time–Dependent DFT (TDDFT) that successfully describe the electronic properties of many different physical systems [4], fail dramatically for the case of semiconducting one–dimensional molecular chains. ALDA do not describe the main features of the absorption spectra and strongly overestimates the polarizability with respect to quantum chemical calculations [5,6,7]. The reason for this poor performance of ALDA is still not settled, and it has been traced back to the need of long-range(LR) terms (ultra non–locality) in the exchange-correlation functionals [8] or to the lack of self–interaction correction (SIC) [9,10]. 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 H2 chain (reproducing the Hartree–Fock results [9]) it fails in reproducing the absorption spectrum of the infinite trans-polyacetylene chain [11]. On the contrary CDFT provides quite good results for finite π-conjugated polymers [12,13], while it breaks down for the H2 chain.

In TDDFT all the effects beyond the non interacting particles approximation are embodied in the exchange–correlation (xc) kernel fxc ≡ δvxc/δn, with vxc the xc–potential and n the exact ground state electronic density. The recent developments in merging many–body perturbation–theory (MBPT) [14] and TDDFT [13,10] open the path to unravel the physical origin of the response properties of one-dimensional systems. Here 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, available local or 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 a hyper-non local behavior and memory dependence that is at least one order of magnitude stronger than in solids. The static and dynamical polarizabilities are both well described in simple H2 or in more sophisticated trans–polyacetylene molecular chains.

The polarizability of low-dimensional systems is proportional to the spatial average of the reducible polarization function, χ(r,r′;ω) that can be obtained from the solution of the TDDFT equation

$$\hat{\chi}(\omega) = \chi_0(\omega) \left[ 1 + \int f_{Hxc}(\omega) \hat{\chi}(\omega) \right].$$  (1)

The exchange–correlation part of the kernel fHxc =
In chain B the inter-molecular distance is reduced to 2.05 a.u. and the LDA gap gets very small (0.26 eV). In Fig. 1 we compare the calculated TDDFT absorption spectra for chains A and B in the ALDA and MBPT–$f_{xc}^{LR}$. As the electronic density is more homogeneous in chain B than in chain A the ALDA gives an almost indistinguishable dynamical polarizability if compared to the BS calculations (see Fig. 1 right panel). For the chain A, however, the ALDA performance worsens considerably, and the main absorption peak is not at all reproduced. The $f_{xc}^{LR}$ kernel, instead, yields a dynamical polarizability in both chains almost indistinguishable from the BS calculations. Similarly to the case of wide gap insulators the correct description of excitonic states require the $f_{xc}^{LR}$ kernel to have non local Fourier components. This means that $f_{xc}^{LR} (\omega, \mathbf{q})$ is a matrix, whose size (a few hundred reciprocal space vectors in the present case) is intimately related to the localisation of the excitonic state.

The failure of the ALDA can be understood by looking at the spatial dispersion of the excitonic state corresponding to the main absorption peaks shown at the bottom of Fig. 1 for both chains. In chain A, where ALDA does not work, the exciton is confined within few $H_x$-monomers ($\approx 36$ a.u.). Consequently, the excitonic dispersion introduces a characteristic length given by the exciton linear extension. In chain B the exciton is basically spread all over the chain. If we now look at the xc–kernel $f_{xc}^{LR}$ 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 $\beta \sim 0.45$ eV$^{-2}$, which is more than one order of magnitude larger than in solids, where $\gamma \sim 0.1 - 1.5$, while $\beta \sim 1 - 34 \times 10^{-3}$ eV$^{-2}$. This large value of $\beta$ reflects the dynamical renormalization of the excitonic energy, due to memory effects. More importantly the static limit of the long–range part of the total TDDFT kernel, $\lim_{q \to 0} f_{Hxc} (\omega, \mathbf{q}) \sim (4\pi - \gamma)/|\mathbf{q}|^2$ is negative. This means that the spatial non locality of $f_{xc}^{LR}$ is stronger than the Hartree term. This hyper non locality and the memory effects in $f_{xc}^{LR}$ cannot be captured by any static, local or semi-local approximation.

Turning now to finite-size effects, we show in Fig. 2 the results for the static polarizability of finite length $H_x$ chains within different approximations for the xc–kernel. Both ALDA and CDFT yields 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 $f_{xc}^{LR}$ 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 to the lack of SIC in the LDA wavefunctions used to construct the xc–kernel. This can be easily corrected by recomputing the kernel, $f_{xc}^{LR}$–SIC using...
Hartree–Fock (HF) self–interaction–free wavefunctions to build $\chi_0$.

This new kernel yields axial polarizabilities in excellent agreement with the CCSD(T) results. The SIC increases the $\chi_0$–kernel spatial non locality factor $\gamma$, which translates into further confinement of the excitonic states, compared to the LDA-based $f^{LR}_{xc}$ 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 central hydrogen molecule bond, are also showed.

The $H_2$ chain represents an extreme case of system with few electrons, where confinement is crucial, while electronic screening is negligible (this is the reason why time–dependent HF works fine). For these 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 (PA) molecular chain. The PA chain has been extensively studied in the past within the BS scheme. It has been showed 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 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, which is clearly inconsistent. For finite length chains, as in polyethylene, EXX results are, again, very

![Graph](image-url)  
**FIG. 2:** (color on-line) Axial polarizability per monomer of the molecular $H_2$ chains. TDDFT calculations within the ALDA, $f^{LR}_{xc}$, and $f^{LR+\text{SIC}}_{xc}$ (see text) are compared with coupled cluster CCSD(T) results and CDFT using the VK kernel. The real–space excitonic wavefunctions of selected chains, with the hole placed in the middle of the central hydrogen molecule bond, are also showed.

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**FIG. 3:** (color on-line) Calculated absorption spectra for the infinite (left frame) and polarizability per monomer for the finite (right frame) trans–polyacetylene chain. ALDA is compared with the $f^{LR}_{xc}$. The quasi-particle gap and the position of the experimental absorption at 1.7 eV are also showed. The axial polarizability for the finite chains calculated within HF and MP2 are also reported. In the bottom we show the excitonic wave function corresponding to the bright 1.69 eV peak of the infinite chain.
similar to HF [8] that, in the case of PA largely overestimates the quantum chemistry MP2 results (inset of Fig. 3). As shown in Fig. 3 the present $f^{LR}_{xc}$ kernel, instead, is in very good agreement with the MP2 results in the finite length case and with the experimental absorption peak position in the infinite length case [20]. MP2 calculations [8] predicts the PA chain polarizability to saturate around 15 monomers, in excellent agreement with the excitonic extension obtained with the present $f^{LR}_{xc}$ kernel (shown in the bottom of Fig. 2 for the bright PA exciton at 1.69 eV). As a result even in the more complex PA chain the polarizability saturation naturally correlates with the excitonic localisation length fully confirming the physical picture that emerged from the previous results for the $H_2$ chains.

In conclusion we have shown that TDDFT successfully explains the optical saturation in molecular chains in terms of excitonic confinement. The Many-Body based $xc$-kernel, with the correct long–range tail and including, in the $H_2$ chains, self–interaction corrections yields static and dynamical polarizabilities in excellent agreement with accurate quantum chemical calculations. We have proved that there exists a 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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