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Ab-initio study of Coulomb-correlated optical properties in conjugated polymers

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Abstract

The spatial extension and binding energy of excitons in semiconducting conjugated polymers are still the subject of a great debate. We address this problem through first-principles calculations (within DFT-LDA, plane-waves and ab-initio pseudopotentials), which allow to include electron-hole correlation effects in a fully three-dimensional approach through the density-matrix formalism. We show results for the correlated optical spectrum and the exciton wavefunctions of single-chain poly(*para*)phenylene-vinylene (PPV), that support the picture of a strongly bound anisotropic exciton localized over $\sim 4\text{--}5$ monomers.

Key words: Density functional calculations, Optical absorption, Poly(phenylenevinylene)

Poly(phenylenevinylene) (PPV) and its derivatives have been the subject of numerous investigations, due to their use as the active component in polymer-based optoelectronic devices[1]. For optical applications, the emitting polymer must be cast or assembled into films: in this case, there is an on-going controversy about the character of the optically active species. There is a general consensus that the emissive species is a dipole-allowed singlet 1B_u , and that the triplet species is dark, but this exciton description also has controversial points, mainly the binding energy (estimated range from $E_b \simeq 0.4$ to 0.8eV for PPV films [3,4]) and the spatial extension (generally estimated as $R \sim 5\text{--}6$ monomers [5] but reported also as $R \sim 2$ monomers or smaller [6]).

Theory is therefore needed to help sort the controversial points. However, theoretical studies for the optical properties are mostly carried through semiempirical Hartree-Fock techniques, which are known to give accurate results but for isolated,

small oligomers [7]; semiempirical band-structure techniques, useful for infinite isolated chains, are not reliable for excited states; ab-initio Density-Functional techniques are also known to fail in the description of excited states. Very recently the first-principles optical spectrum for PPV was calculated [8], within a Green's Function GW-Bethe-Salpeter (BS) approach, for infinite isolated chains. We propose a novel method to investigate optical properties, which can be easily applied also to more complex systems (e.g. polymer crystals) and avoids the very demanding calculations required by the Green's Function method. Here we present results for isolated planar PPV, which can be compared to the GW+BS results; we will focus on the exciton binding energies, and on the effect of Coulomb-correlation on the optical spectrum.

We use a standard DFT/LDA calculation, to obtain the PPV single-particle properties, i.e. the electron (hole) states $\phi_\mu^e(\mathbf{r})$ ($\phi_\nu^h(\mathbf{r})$) available for adding one additional electron to the conduction-band, (removing one electron from the valence-band). In the presence of an external light field, the dynamics of the photogenerated electron-hole

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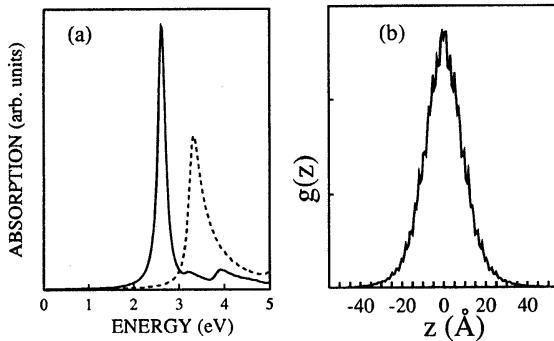


Fig. 1. (a) Optical absorption spectrum for single-chain PPV. The dashed line corresponds to the non-interacting optical spectrum polarized along the polymer chain, while the solid line corresponds to the correlated optical absorption lineshape. (b) Electron-hole correlation function along the chain direction.

pair is governed also by the attractive electron-hole Coulomb interaction, V . In linear response, the optical absorption is characterized by the *interband polarizations* $p_{\mu\nu}(t) = \langle d_{\nu} c_{\mu} \rangle_t$, which describe the properties of the virtual electron-hole pair (the operators c_{μ}^{\dagger} and d_{ν}^{\dagger} are the Fermionic creation operators and the labels $\mu = (m, \mathbf{k})$ and $\nu = (n, -\mathbf{k})$ stand for both the band index and the wavevector). The polarization $p_{\mu\nu}$ is given by the semiconductor Bloch equations [9]:

$$(E_{\nu}^e + E_{\nu}^h)p_{\mu\nu} + \sum_{\mu'\nu'} V_{\mu\nu, \mu'\nu'}^{eh} p_{\mu'\nu'} = E_x p_{\mu\nu}. \quad (1)$$

The term V^{eh} in Eq. 1 includes the direct Coulomb potential and the exchange interaction between electron and hole, both terms being screened by an effective $\epsilon(\mathbf{r}, \mathbf{r}')$, which accounts for the truncation of the Hilbert space. We calculate $\epsilon(\mathbf{r}, \mathbf{r}')$ from first-principles calculation for each tensor component ($\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}$), taken as homogeneous within an effective volume which is determined selfconsistently according to the typical e-h interaction distances.

We have thus calculated the absorption spectrum and the exciton binding energy for infinite, single-chain PPV, by correcting the LDA band gap for self-interaction effects (“scissors”-operator taken from Ref [8]).

We show in Fig. 1(a) the uncorrelated absorption spectrum (dashed lines) and the excitonic spectrum (solid line) obtained for PPV. The uncorrelated spectrum shows a behavior $\alpha(\omega) \sim 1/\sqrt{E}$, typical of 1D systems; electron-hole correlation suppresses the van Hove singularity[10] and introduces a bound exciton state in the gap. This confirms that the binding energy cannot be extracted from one-photon experiments, but should be derived from parallel transport and optical

measurements[4].

The exciton binding energy E_b is defined as the difference $E_b = E_{gap} - E_x$ where E_{gap} is the lowest direct energy-gap, and E_x is the exciton energy (Eq. 1). Our data for the lowest exciton binding energy is $E_b = 0.7$ eV, in fair agreement with the result of Ref.[8] ($E_b = 0.9$ eV) for the same system. Our results are higher than the experimental results of Alvarado et al. [4] ($E_b \simeq 0.4$ eV) for polymer films. It must be noted, however, that our results are for isolated chains; since it has been shown that interchain screening effects will decrease E_b [11], this difference is in the correct direction.

The eigenvectors $p_{\mu\nu}$ (Eq.1) are directly related to the exciton wavefunction $\Psi^{exc}(\mathbf{r}_e, \mathbf{r}_h) \propto \sum_{\mu\nu} p_{\mu\nu} \psi_{\mu}^e(\mathbf{r}_e) \psi_{\nu}^{h*}(\mathbf{r}_h)$, that averaged over the center-of-mass coordinates gives information about typical e-h correlation distances. We obtain a highly anisotropic exciton wavefunction, which extends over 4-5 monomer units along the chain direction (Fig. 1(b)).

This approach proves suitable for investigations of crystalline 3D systems, which are now in progress.

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