

## Ab-initio study of excitonic effects in conventional and organic semiconductors

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The excitonic effects on the optical absorption properties of organic semiconductors as well as gallium nitride are studied from first-principles. The Coulomb interaction between the electron and the hole is accounted for by solving the two-particle Bethe–Salpeter Equation. In the organic semiconductors the exciton binding energies strongly depend on the molecular size, the crystalline packing, as well as the polarization direction of the incoming light. We show that the electron–hole interaction can lead to strongly bound excitons with binding energies of the order of 1 eV or to a mere redistribution of oscillator strength. In several cases, the screening is efficient enough such that free charge carriers govern the optical absorption process. In the inorganic counterparts the sensitivity of the exciton binding energy is tested against the structural parameters and the screening of the electron–hole Coulomb interaction.

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### 1 Introduction

While density functional theory (DFT) has been successfully applied for the parameter-free calculation of ground state properties since more than 30 years, the description of excited state properties is less well settled. Calculating optical spectra within DFT, e.g. utilizing the local density approximation (LDA) for exchange and correlation effects, implies the interpretation of the Kohn–Sham orbitals in terms of single particle states, which is not rigorously justified, but works quite well in many cases. On the one hand, the dielectric tensor is usually determined within the random phase approximation (RPA), which neglects the Coulomb interaction of the electron excited during the absorption process with the remaining hole. This latter problem can be overcome by solving the Bethe–Salpeter Equation (BSE), which is an effective two-particle Schrödinger Equation for the electron–hole (e–h) pair. Thereby, bound singlet and triplet states and/or a redistribution of oscillator strength with respect to the transitions between free charge carriers can be described. We apply this powerful theoretical approach to organic as well as inorganic semiconductors in order to study the excitonic effects on their optical absorption properties. Concerning the organic materials, the experimental side has been focusing on the exciton binding energies in conjugated polymers. Despite many years of intensive research in terms of their opto-electronic properties the nature of the lowest optical transitions is still controversial, e.g., the proposed exciton binding energies range from a few  $k_B T$  up to the order of one eV [1, 2]. To contribute to this ongoing discussion we have solved the BSE for various molecular crystals including oligomers of different type and molecu-

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lar size as well as polymers, i.e., the limit of infinite chain length. The materials under investigation representing the latter group comprise *trans*-polyacetylene (PA), polythiophene (PT), and poly(*para*-phenylene vinylene) (PPV), whereas biphenyl (2P) and bithiophene (2T), as well as the series of linear oligoacenes, i.e. naphthalene (2A), anthracene (3A), tetracene (4A), and pentacene (5A), correspond to the former. Especially, 4A and 5A are promising candidates for opto-electronic devices due to their high charge carrier mobilities [3, 4]. Regarding the inorganic semiconductors, we have chosen Galliumnitride (GaN) as typical representative. In particular, the hexagonal wurtzite phase of GaN has been studied, which is an important compound for opto-electronic applications in the blue/UV range of the spectrum.

## 2 Methods

Groundstate calculations have been mainly performed by the full-potential linearized augmented plane-wave code WIEN2k [5] based on DFT, and a planewave-based code [6] was also employed only for the calculation of single-particle properties of PT and PPV. Exchange and correlation effects have been treated by the generalized gradient approximation. The solution of the BSE [7] has been carried out with the EXC!TiNG@WIEN2k package [8], where the formalism is described in detail in Ref. [9]. Solving the BSE equations results in excitonic correlation functions and eigenenergies (excitation energies), which contain all information necessary to generate optical spectra by means of the imaginary part of the dielectric function  $\varepsilon_2(\omega)$ . For calculating  $\varepsilon_2(\omega)$ , the valence and conduction state energies have been approximated by the Kohn–Sham eigenvalues corrected by a  $\mathbf{k}$ -independent self energy (scissors operator) such that the calculated optical gap matches the experimentally observed one. For the GaN calculations the BSE Hamiltonian was expanded using 6 valence and 8 conduction bands with  $\mathbf{k}$  sampling of  $12 \times 12 \times 8$  in the full Brillouin zone, which leads to a matrix size bigger than 55000. In order to avoid the diagonalization of this huge matrix the *time evolution algorithm* [16] has been utilized.

## 3 Results and discussion

In the following we discuss our findings for the exciton binding energies (BEs) in organic semiconductors and GaN. Before, we would like to point out the general differences between organic materials and the consequences regarding the computational effort required to obtain reasonable results. The organic molecules crystallize in large unit cells with low symmetry, i.e., merely monoclinic and triclinic space groups, whereas the inorganic compounds exhibit comparably simple structures with small unit cells. Despite the rather large range of e–h pair BEs observed in organic materials, i.e., between approximately 0.1 and 1 eV, the inorganic semiconductors exhibit much smaller exciton BEs in the order of a few tens of meV. In contrast to the former, low temperature measurements of samples with very high purity are achievable from the latter. In particular, the polymers cannot be crystallized with such a quality thus leading to higher experimental uncertainties. Therefore, the inorganic semiconductors require calculations to a much higher degree of accuracy for the comparison with the experimental data. Such a high precision can only be obtained by employing a very dense  $\mathbf{k}$  mesh for the computation. Since the effective two-particle Hamiltonian to be solved in the BSE scales with the number of valence and conduction bands as well as the  $\mathbf{k}$  points, it is the  $\mathbf{k}$  grid, which limits its diagonalization and thus the computational time rather than the complexity of the crystal structure. The computational accuracy for the organic compounds is estimated to 0.1 eV.

### 3.1 Organic semiconductors

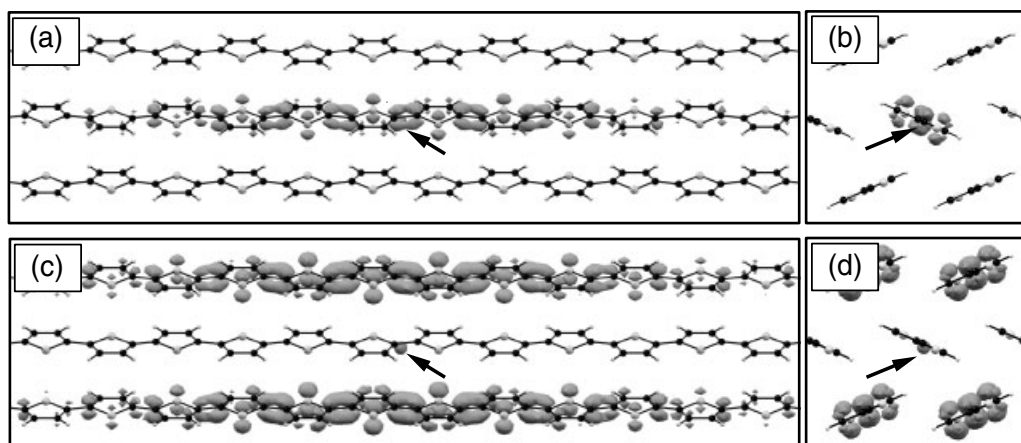
In Table 1 the spin singlet binding energies for the investigated organic materials as a function of the polarization of the incoming light are summarized. For comparison, literature data based on similar calculations for the polymers are included. For the molecular crystals built up by the shortest molecules, i.e. 2P, 2T, and 2A, the lowest optical absorption is due to strongly bound excitons with similar binding energies of 0.7–1.1 eV. With increasing oligomer size, the binding energy is reduced, which is demon-

**Table 1** Singlet (S) binding energies (BEs) in eV for several organic semiconductors, when the response is generated by *b* and *c* polarized light, respectively, and the polarization of the lowest absorption peak (pol.).

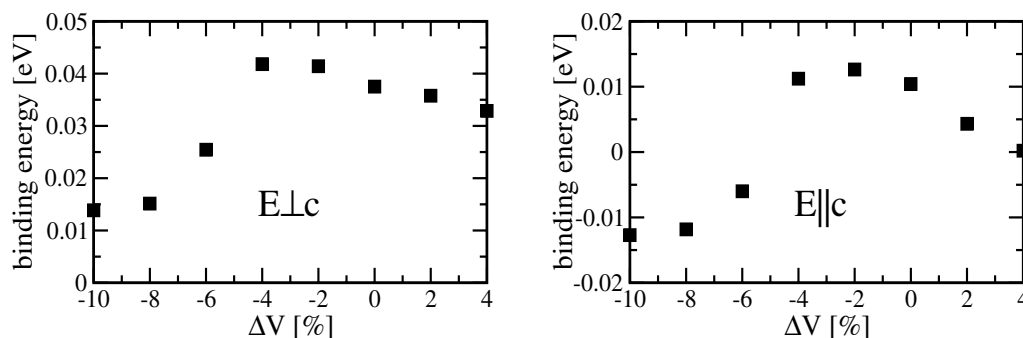
	2P	2T	2A	3A	4A	5A
SBE <sub><i>b</i></sub>	0.7	1.1	0.9	0.7	0.4	0.1
SBE <sub><i>c</i></sub>	0.7	0.8	0.0	0.0	0.0	0.0
pol.	<i>c</i>	<i>c</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
	PT-1D [11]	PT-3D [11, 12]	PA-1D [13]	PA-3D [13]	PPV-1D [14]	PPV-3D [14]
SBE	0.96	0.23/0.17	0.55	0.05	0.6–0.7	0.2
pol.	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>

strated for the oligoacenes from 2A to 5A. For pentacene, it is 0.1 eV only, which is similar to the values found for different polymers, when the 3D structure is taken into account. It should be pointed out that the reduction of the binding energy with increasing oligomer length can be understood in terms of the enhancement of the dielectric screening and the extension of the e–h wavefunction [15]. Our results (see Table) also point out that the polarization of the exciting light plays an important role when analyzing the optical absorption in organic semiconductors; bound excitons as well as free charge carriers can be found by just rotating the polarization from the direction out of the molecular plane (*b*) to one in the plane, which corresponds to *c* [10].

The very effect of the solid state arrangement becomes visible when comparing the results obtained for the 1D polymer chain to calculations taking into account the full 3D crystalline environment. Crystal packing crucially affects the size of the exciton binding energy for two reasons: First, it enhances the screening of the e–h Coulomb interaction and second, it allows for a wider distribution of the e–h wavefunction, as shown in Fig. 1. Therein we plot the excitonic wavefunctions for the two lowest active excitons in PT crystals [12], giving information on the relative positions of electron and hole. Both effects similarly contribute to the lowering of the binding energy with respect to the 1D polymer chain. Actually, the binding energy for PA was found [13] to be reduced by even one order of magnitude. In the same way the significance of the 3D effects has been emphasized for PT [11, 12] as well as PPV [11, 14]. Moreover, due to the typical herringbone packing of the two inequivalent chains in unsubstituted



**Fig. 1** Excitonic wavefunctions for PT representing the probability density to find the electron, when the hole is fixed in the position indicated by the arrow; (a) and (b): lowest direct exciton wavefunction in *x,z*-plane and *x,y*-plane; (c) and (d) same for the lowest charge transfer exciton. The six repeat units depicted in panels (a) and (c) cover a spatial extension of nearly 5 nm.



**Fig. 2** Exciton binding energies as a function of the unit cell volume.

polymer crystals, symmetry effects come into play leading to the presence of several excited states with assorted character below the single particle gap. A real-space analysis [12, 14] of all lowest excitonic states was accomplished and the lowest active exciton turned out to be “direct”, that is, strictly confined to one chain; however, we find also charge-transfer excitons with electron and hole on different chains, that are expected to be dark due to the low probability for radiative recombination.

### 3.2 Gallium nitride

The optical absorption process in GaN is governed by three bound spin singlet excitons: Two of them are energy degenerate for the incoming light with the electromagnetic field vector  $E$  perpendicular to  $c$  and one with  $E$  parallel to  $c$ . Because they are highly localized in  $k$  space, a very fine  $k$  mesh is required. However, only a limited fraction of the Brillouin zone close to the  $\Gamma$  point needs to be sampled. The bound excitons are spanned only by the three highest valence bands and the lowest conduction band. Figure 2 shows the dependence of the exciton binding energies as a function of the unit cell volume. For the experimental equilibrium volume ( $\Delta V = 0\%$ ), the  $c/a$  ratio, and the the Ga–N nearest neighbor distance in  $c$  direction,  $u$ , we calculate spin singlet exciton BEs of 38 meV and 10 meV for  $E \perp c$  and  $E \parallel c$ , respectively. With decreasing unit cell volume it first slightly increases and afterwards significantly decreases. The small increase of the BEs can be explained by the fact that the band gap rises when the GaN unit cell is compressed. Further, the calculations show that bigger band gaps produce deeper lying excitons. For small compressions, this change is not compensated by the effects related to the expansion of the e-h wavefunctions due to the decrease of the interatomic distances. It should be noticed here that the small changes of the  $u$  and the  $c/a$  parameters dramatically influence the calculated BEs, which can be attributed to the change of the valence band splitting due to crystal field. A reduction of the exciton BE with compression has also been previously found for anthracene [10].

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