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Electronic correlations in oligo-thiophene molecular crystals

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Abstract

The Coulomb interaction between two holes on oligo-thiophene molecules is studied systematically as a function of the oligomer length using first principles density function calculations. The effect of molecular geometry relaxation upon this interaction is found to be small. In contrast, electronic polarization of the molecules that surround the charged oligomer in the crystal lattice reduces the bare Coulomb repulsion between the holes by approximately a factor of 2. In all cases, the effective hole–hole repulsion is much larger than the valence band width, which means that at high doping levels, strong correlation effects should become important.

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1. Introduction

A unique aspect of organic molecular crystals is that the electronic properties of these solids bear the marks of both molecular and condensed matter physics. In a crystal, the organic molecules preserve their identity, since molecular crystals are held together by Van der Waals interactions without the formation of intermolecular covalent bonds. This results in a small overlap between the wave functions of electrons located on adjacent molecules, which leads to rather narrow electronic bandwidths. This makes it quite possible for the energy associated with interaction effects (e.g. electron–phonon or electron–electron interaction) to dominate the kinetic energy of the charge carriers.

An undoped molecular crystal generally is a wide band gap semiconductor, so it is the doped form that is of main interest for electronic transport. The amount of doping, either by chemical or electrostatic means, then

determines the carrier concentration. Different interactions play a dominating role in different regimes of carrier density. For instance, at low carrier density the interaction between charge carriers and molecular vibrations seems to dominate the physical properties of the system, due to the formation of polarons [1]. The situation is likely to be different in the high-density regime where electron–electron interactions become important and correlations between carriers cannot be neglected.

We focus on the strength of carrier–carrier interaction in organic molecular crystals, in order to determine whether in the high density regime a description in terms of a weakly interacting electron gas is appropriate, or whether electronic correlations are dominant. We consider crystals of a particular class of organic molecules, oligo-thiophenes, which consist of a linear chain of thiophene rings. Oligo-thiophenes of various lengths have been synthesized and good quality molecular crystals have been grown [2], which enables us to study a class, rather than a single example. An example of an oligo-thiophene molecule is shown in Fig. 1.

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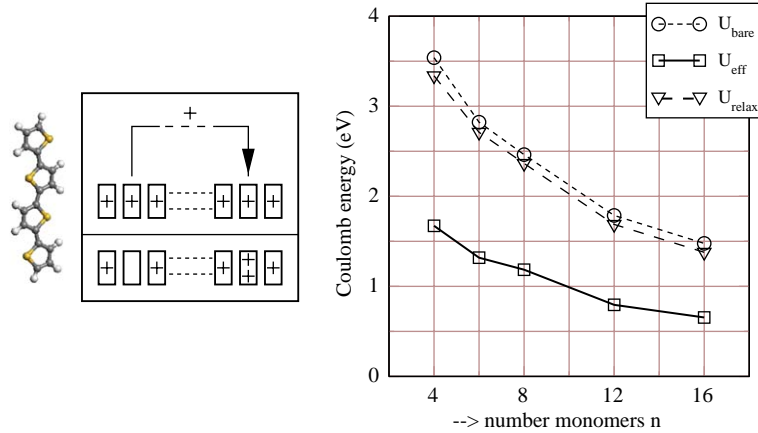


Fig. 1. Left: molecular structure of 4-thiophene. Middle: schematic representation of the procedure to calculate the Coulomb interaction U_{eff} from the ground state energies of (charged) molecules. We remove one hole from the system with singly ionized thiophene molecules and place this hole on a molecule far away (top), so that we end up with one neutral and one doubly ionized thiophene (bottom). The energy associated with this process is U_{eff} . Right: Bare, relaxed and effective molecular Coulomb interactions for n -thiophene in the molecular crystal as a function of conjugation length n . Lines are guides for the eye.

2. Bare molecular Coulomb interactions

We first present the results on the first principles calculations of the Coulomb interaction strength U_{bare} between holes on a single, isolated oligo-thiophene molecules of different sizes. The latter are indicated by nT , where n is the number of thiophene rings comprising the oligomer, cf. Fig. 1. To establish the value of U_{bare} , we first consider two singly charged nT^+ molecules infinitely far apart: in this case there is no interaction of any kind between molecules. The bare, molecular, Coulomb interaction is then determined by the process in which a single electron is moved from one molecule to the other, i.e. $2nT^+ \rightarrow nT + nT^{2+}$, see Fig. 1. Consequently, the molecular Coulomb repulsion for two holes can be expressed in terms of the total energies of the neutral, doubly and singly charged molecules as $U_{\text{bare}}(n) = E(nT) + E(nT^{2+}) - 2E(nT^+)$. In these considerations, only the ground state energies of individual (charged) molecules enter which can be calculated with high accuracy using density functional theory (DFT).

The results shown in this paper have been obtained using the local density approximation [3]; tests with a generalized gradient functional gave only small differences for the total energies [4]. Norm-conserving pseudo-potentials are used to represent the ion cores [5] and the valence electronic wave functions are expanded in a plane wave basis set, including all plane waves up to a kinetic energy cutoff of 40 Ry. Molecular calculations are performed by enclosing the molecule in a finite box [6], whereas the crystal calculations (see below) use the conventional periodic boundary conditions. This scheme has proved to yield accurate results for molecular crystals [7], poly-thiophene [8] and

Table 1

Bare, relaxed and effective Coulomb interaction between two holes on an n -thiophene molecule and the ionization, relaxation and polarization energy (all in eV)

n	U_{bare}	U_{relax}	U_{eff}	E_{relax}^+	E_{relax}^{++}	E_{pol}^+
4	3.54	3.34	1.43	0.115	0.431	0.95
6	2.82	2.71	1.10	0.106	0.323	0.80
8	2.46	2.37	0.98	0.069	0.235	0.69
12	1.79	1.69	0.64	0.048	0.195	0.52
16	1.48	1.38	0.50	0.036	0.171	0.44

oligo-thiophene dimers [9]. For technical details and convergence tests, we refer to these papers.

The calculated bare Coulomb interaction U_{bare} between two holes on an nT oligo-thiophene molecule consisting of n thiophene rings, n ranging from 4 to 16, is listed in Table 1. U_{bare} ranges from 3.5 to 1.5 eV; it decreases as the length n of the oligo-thiophene increases. On a conjugated molecule like an oligo-thiophene, the holes are delocalized over the whole molecule; so, their average distance is larger on a larger molecule, which of course lowers their Coulomb repulsion.

3. Molecular relaxations

So far, we have not considered the fact that the presence of a charge on a molecule can relax the molecular geometry. This relaxation will be larger than the charge and will therefore effectively reduce, i.e.

screen, the Coulomb interaction. If we denote the relaxation energy for singly/doubly charged molecules by $E_{\text{relax}}^{+/2+}$, the “relaxed” Coulomb interaction is then defined as $U_{\text{relax}} = U_{\text{bare}} - (E_{\text{relax}}^{2+} - 2E_{\text{relax}}^{+})$. The energy gained when optimizing the geometries of the charged molecules, starting from the geometries in their neutral state, defines the relaxation energy. It can be obtained from a standard DFT calculation by minimizing the Hellmann–Feynman forces operating on the atoms. The calculated relaxation energies and their effect upon the Coulomb interaction are shown in Table 1. We observe that molecular relaxations reduces the Coulomb interaction by 0.1–0.2 eV, which is an order of magnitude smaller than the typical bare Coulomb interactions.

It is known that DFT tends to overestimate the delocalization of a charge on a conjugated chain [10]. Therefore, we have also calculated the relaxation energies using the AM1 semi-empirical Hartree–Fock method [11], which tends to overestimate relaxation effects. Indeed, we find relaxation energies that are larger [12], which lead in the end to an additional reduction of the Coulomb interaction by 0.5 eV or less for the short thiophenes. This does not affect our conclusions.

4. Screened Coulomb interactions

In the following, we explicitly consider the situation where the molecular crystal responds to the creation of holes. In the presence of excess charges, the electronic system reacts to effectively reduce, i.e. screen, the Coulomb interaction between the charges. We model the screening by a discrete dipole model, i.e. we put a charge on one molecule and calculate the polarization of all surrounding molecules [13]. Denoting the electronic polarization energy due to singly/doubly charged molecules by $E_{\text{pol}}^{+/2+}$, the effective screened Coulomb interaction is then given by $U_{\text{eff}} = U_{\text{relax}} - (E_{\text{pol}}^{2+} - 2E_{\text{pol}}^{+})$. Within a discrete dipole model $E_{\text{pol}}^{Z+} = Z^2 E_{\text{pol}}^{+}$, because it involves the interaction of excess charges with a screening cloud that is induced by the excess charges themselves. So, we only have to explicitly calculate E_{pol}^{+} .

To evaluate the polarization energy E_{pol}^{+} , one needs to perform a lattice sum which involves the induced electric dipole moments on all molecules due to the charge present on one of the molecules [13]. The strength of an induced moment is proportional to the local electric field, which is the sum of the field due to the charge and of that due to all the induced dipoles. The proportionality factor is the molecular polarizability tensor, whose values for oligo-thiophenes are taken from Ref. [14]. The lattice sum is determined by the crystal structures, which are taken from Ref. [2]. One practical problem with discrete dipole models is that large molecules, such as oligo-thiophenes, are not very well represented by point

charges or polarizabilities. A pragmatic solution is to use the so-called sub-molecular approach in which a (sub-molecular) charge or polarizability is assigned to (the center of) each thiophene ring [1]. One complicating factor is that for 4T and 6T, two different crystal structures exist that are (meta)stable at room temperature, called the LT and HT phases, respectively. In practice E_{pol}^{+} turns out to be the same within 0.01 eV for these two phases. For 12T and 16T, no experimental crystal structures are available to our knowledge. We construct these by starting from the relatively simple HT phase of 6T and enlarging the crystal axis that points along the long molecular axis, such as to accommodate the longer 12T or 16T molecule.

The results for the polarization energy E_{pol}^{+} are shown in Table 1. The values are in a range that is similar to that of other molecular crystals [1]. Increasing the length n of the oligo-thiophene decreases the polarization energy E_{pol}^{+} . Basically, this is because for a larger molecule the charge is distributed over a larger volume, whereas the polarizability per unit volume has a very weak dependence upon the size of the molecule [14]. Note that the electronic screening due to electrons on the molecule itself has to be excluded because it is already implicitly accounted for in the calculation of U_{bare} . At this point we are able to determine the effective Coulomb interaction U_{eff} and the results are shown in Table 1. One observes that screening due to polarization of the surrounding molecules has an effect on the Coulomb interaction which is almost an order of magnitude larger than that of molecular relaxation. In fact, the screening is such, that the screened Coulomb interaction U_{eff} is less than half U_{bare} .

5. Coulomb interaction versus band width

To determine the correlation strengths, the effective Coulomb interaction U_{eff} for holes should be compared to the valence bandwidth W . The bandwidths W tend to fall in the range of 0.3–0.4 eV for this type of molecular crystal on the basis of semi-empirical calculations [15]. It is immediately obvious from Fig. 1 that $U_{\text{eff}} > W$ for all oligo-thiophenes. As the length of the molecule increases U_{eff} becomes smaller, but it does not drop below W for any length which is likely to be of practical interest. On the contrary, the molecules for which the experimental effort is largest, i.e. 4T and 6T, have $U_{\text{eff}} \gg W$. Our main conclusion therefore is that, in the high carrier density regime, these systems have to be strongly correlated. Similar calculations show that this conclusion also holds for other organic molecular crystals, e.g. for the *oligo-acenes*, a second class of molecules that is widely studied experimentally [12].

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