Determination of screened Coulomb repulsion energies in organic molecular crystals: A real space approach

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Abstract

We present a general method for determining screened Coulomb parameters in molecular assemblies, in particular organic molecular crystals. This allows us to calculate the interaction parameters used in a generalized Hubbard model description of correlated organic materials. In such a model only the electrons in levels close to the Fermi level are included explicitly, while the effect of all other electrons is included as a renormalization of the model parameters. For the Coulomb integrals this renormalization is mainly due to screening. For molecular materials we can split the screening into intra- and inter-molecular screening. Here we demonstrate how the inter-molecular screening can be calculated by modeling the molecules by distributed point-polarizabilities and solving the resulting self-consistent electrostatic screening problem in real space. For the example of the quasi one-dimensional molecular metal TTF-TCNQ we demonstrate that the method gives remarkably accurate results.

Keywords: Hubbard model, correlated organics, molecular crystals

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1. Introduction

Low dimensional organic molecular compounds based on the BEDT-TTF, TTF and TCNQ molecules are narrow band systems, where the Coulomb repulsion is large compared to the bandwidth. This leads to many-body effects which are manifest, e.g., in the spin susceptibility [1] or angular-resolved photoemission experiments [2, 3, 4]. While theoretical works suggest the importance of Coulomb parameters in these materials [5], only rough theoretical estimates of these parameters do exist [6]. The use of modern techniques, such as density-functional theory (DFT), gives accurate results of the parameters for individual molecules [7, 8], improving previous quantum chemistry calculations [9, 10]. However, there is a lack of accurate theoretical estimates of the Coulomb repulsion screened inside the crystal. These are needed for a more realistic description of organic molecular compounds.

In the present paper we introduce a systematic method for calculating these Coulomb parameters in low-dimensional organic molecular crystals. In Sec. 2 we construct the minimal model and give details of the general formalism. This is applied to TTF-TCNQ salts in Sec. 3, where we discuss the distributed-dipole approach. In Sec. 4 we give our results for Coulomb parameters.

2. Model and Formalism

The minimal model generally used to describe the low-energy electronic properties of low-dimensional organic systems is the Hubbard model [11], where transfer integrals between neighboring sites and on-site Coulomb interactions are taken into account. Such a simple Hubbard model is, however, usually not sufficient to describe strongly correlated organics, as long-range Coulomb repulsion energies can rarely be neglected [4, 12]. In the generalized model

\[ H = -t \sum_{\langle i,j,\sigma \rangle} (c^+_i c_{j,\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i,j} V_{ij} n_i n_j, \]  

we include hopping integrals between nearest-neighbors, \( t \), on-site Coulomb energies, \( U \), and longer-range Coulomb interactions, \( V_{ij} \). While transfer integrals can be obtained from ab initio DFT calculations [2, 13, 14], Coulomb parameters are more difficult to obtain, as they include the screening correction due to different high-energy processes inside the crystal, the main mechanism being the polarization of the surrounding, usually highly polarizable, molecules. By realizing that organic molecules preserve their identity inside the crystal, we may estimate the screening energy, by describing the molecular interactions through classical electrostatics.

In BEDT-TTF and TTF-TCNQ families of organic conductors [15], flat molecules crystallize forming low-dimensional anisotropic structures. Considering such a lattice of organic molecules, we ask what happens when a charge is added to one molecule. The electric field of that charge will induce a dipole moment on the surrounding highly polarizable molecules. Solving this electrostatic problem assuming fixed polarizabilities, we obtain the screening of the charged molecule in linear response. This gives the screening contribution of the lattice that is needed for renormalizing the bare Coulomb integral.

Modelling each molecule as a polarizable point with charge \( q_i \), dipole moment \( \mathbf{p}_i \), and polarizability \( \alpha_i \), the energy of the
The Coulomb parameters for a single molecule are calculated with DFT [7, 8]. Defining the on-site Coulomb screening, \( \delta \), the dipole, dipole-monopole and monopole-monopole interactions [16]. For molecules without net charge (the electrons involved in charge transfer are explicitly included in the Hubbard model), we can simplify Eq. (2). Expressing it in the notation of Allen [17], defining the external field as the composition of anisotropy in the dipole interactions. Such instability influences the screening of a charge in the lattice. For small polarizabilities \( \alpha \) the induced dipoles simply arrange along the field-lines of the central point charge. Increasing \( \alpha \) we, however, observe quite unconventional dipole arrangements as shown in Fig. 1.

This reflects the fact that for this lattice the matrix \( (\alpha^{-1} - \Gamma) \) becomes singular at a critical polarizability \( \alpha_c \), with the eigenvector of the vanishing eigenvalue having non-zero momentum (in this case \( (\pi, \pi, 0) \)). Hence the ferroelectric instability happens before the critical value \( \alpha_{CM} \) obtained from the Clausius-Mossotti relation [17].

### 3. Submolecular approach

In a real molecular crystal the molecules typically form stacks, i.e., they are quite closely packed. Consequently, approximating the polarizability of a molecule by just one point-polarizability is not a good approximation. It only works outside a sphere containing the charge density of the molecule, which for typical \( \pi \)-bonded molecules will intersect the neighboring molecules, but it becomes accurate at large distances. To obtain a better description of the molecular response, we model it as point-polarizabilities distributed over the non-hydrogen atoms of the molecule [19]. The accuracy of this submolecular approach is tested for TTF-TCNQ salts.

We consider a small system of only three or five molecules in a TTF chain. For such small systems we can perform constrained density-functional calculations [7, 20], constraining the added charge to the central molecule. This gives us the screening due to the molecules in this small assembly. We compare to the results of the screening calculated using the distributed point-polarizability approach. Since this approach works least well in the near-field, this is a critical test of the method. Nevertheless, both approaches agree within 5%. If we included more distant molecules, for which the computational cost of constrained density-functional calculations would be prohibitive, the agreement would improve further, as the multi-pole approximation becomes exact in the far-field. Thus, using polarizability tensors obtained with DFT [7] in our submolecular approach essentially reproduces the results of full quantum mechanical treatment of the screening.

### 4. Screening parameters in TTF-TCNQ

To obtain the screened parameters for a TTF-TCNQ crystal, we perform calculations for crystal fragments (clusters) of increasing sizes to extrapolate to the infinite-size limit. To obtain the parameters for the extended Hubbard model [17] we consider the Coulomb screening between two charges at the same or at neighbor molecules placed in the center of the cluster. For simplicity, the clusters of \( N \) molecules are constructed as spheres of radius \( R \), where \( R \) is the distance between the doped molecule (or center of the pair of molecules) and the farthest neighbor in the cluster, hence \( \Omega = \frac{4\pi R^3}{3} \) being the volume of the sphere [21]. For large enough \( R \) we can linearly extrapolate the screening energy \( \delta U \) or \( \delta V \), respectively, versus \( 1/R \) to the thermodynamic limit \( R \to \infty \). This is shown in Fig. 2 where clusters of
up to 400 molecules are studied. Calculations for TTF-TCNQ salts up to the third nearest-neighbors are performed and results are given in Table 1. The ratio of the radius of the sphere, $R$, to the distance between third nearest-neighbors, $d$, where we still can make the extrapolation to the thermodynamic limit is $d/R = 0.43$. However for longer range interactions, the cluster size should be increased towards this convergence ratio, reaching a linear dependence with the inverse of the volume, which allows the extrapolation to the bulk value.

### Table 1: Screening Coulomb energies for TTF-TCNQ.

|        | $\delta U$ (eV) | $\delta V$ (eV) | $\delta V'$ (eV) | $\delta V''$ (eV) |
|--------|----------------|----------------|-----------------|------------------|
| TTF    | 2.7            | 1.9            | 1.25            | 0.8              |
| TCNQ   | 2.6            | 1.9            | 1.3             | 0.9              |

### 5. Conclusions

We have presented a general method for obtaining accurate values of Coulomb parameters in organic molecular compounds, where molecules interact weakly, and shown how it works for TTF-TCNQ. We are currently extending this method to other crystals like quasi-bidimensional salts based on the BEDT-TTF molecule.

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