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Spectral broadening due to long-range Coulomb interactions in the molecular metal TTF-TCNQ

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Abstract. We employ density-functional theory to calculate realistic parameters for an extended Hubbard model of the molecular metal TTF-TCNQ. Considering both intra- and intermolecular screening in the crystal, we confirm the importance of the suspected longer-range Coulomb interactions along the molecular stacks, as well as inter-stack coupling. Contrary to past belief, these terms do not lead to the formation of a Wigner lattice, but simply broaden the spectral function.

PACS. 71.10.Fd Lattice fermion models (Hubbard model, etc.) – 71.15.-m Methods of electronic structure calculations – 71.10.Pm Fermions in reduced dimensions (anyons, composite fermions, Luttinger liquid, etc.) – 79.60.Fr Polymers; organic compounds

As the first realization of a molecular metal, the quasi one-dimensional molecular crystal TTF-TCNQ has been studied thoroughly for more than thirty years [1]. The different electro-negativity of the two molecules leads to charge transfer of about $0.6e$ from TTF to TCNQ, effectively doping molecular stacks of like molecules, which become conducting. Low dimensionality and strong Coulomb repulsion [2] lead to many-body effects which appear in spin susceptibility [3] and angular-resolved photoemission experiments (ARPES) [4,5]. Most prominently, TTF-TCNQ is one of the few systems in which spectroscopic signatures of spin-charge separation have been clearly observed (at temperatures above the charge-density wave state) [6]. The interpretation of the measured spectra relies, however, on rough estimates of the Coulomb parameters, which come from early experimental [3] and theoretical [7,8] works. They suggest that the Coulomb repulsion U between two electrons on a molecule is larger than the band-width W.

Recent attempts to describe TTF-TCNQ in terms of a Hubbard model with only on-site Coulomb interaction have, however, run into severe problems: for the interpretation of ARPES data [6] the hopping matrix element t within a molecular chain has to be taken about twice of what is estimated from band structure [9] and experiment [2]. Moreover, using these parameters, the temperature dependence of the spectra cannot be understood [10,11].

A frequently suspected reason for these shortcomings is the neglect of inter-molecular Coulomb repulsions V, the relevance of which was already suggested by Hubbard and others [7,8]. In this Note we therefore give a systematic method to quantitatively calculate these Coulomb parameters from first-principles and confirm that long-range Coulomb terms are indeed significant. Moreover and quite surprisingly, we find that they do not lead to the anticipated formation of a Hubbard-Wigner-lattice [7], but simply broaden the spectral function, thereby likely resolving the problems with the interpretation of the experiments using a simple Hubbard model only.

For a realistic description of TTF-TCNQ we first calculate the screened Coulomb parameters for an extended Hubbard model. Starting from the bare Coulomb integrals, this requires to evaluate both the screening due to the electrons on the same molecule (intra-molecular screening) and due to the other molecules in the lattice (inter-molecular screening). The bare Coulomb integrals between molecular orbitals (MOs) on two molecules a distance l apart are given as $V^l_{\mathrm{bare}} = \int d^3\mathbf{r} \int d^3\mathbf{r}' \rho_0(\mathbf{r})\rho_l(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ with $V^0_{\mathrm{bare}} = U_{\mathrm{bare}}$. The charge density $\rho(\mathbf{r})$ of the highest occupied MO (HOMO) of TTF and the lowest unoccupied MO (LUMO) of TCNQ is calculated with all-electron DFT [12] and using the Perdew-Burke-Ernzerhof functional [13]. The results for the on-site, U_{bare}, and the first, V_{bare}, second, V'_{bare}, and third, V''_{bare}, nearest neighbor Coulomb terms on the TTF/TCNQ stacks are compiled in Table 1. We notice that V_{bare} is substantial, being of the order of $U_{\mathrm{bare}}/2$,

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Table 1. Hubbard parameters for TTF-TCNQ. U_{bare} is the direct Coulomb integral, U_0 includes intra-molecular screening, and U is the screened on-site Coulomb term in the crystal. Correspondingly, V gives the first, V' the second, and V'' the third nearest-neighbor Coulomb interaction between molecules on the same TTF or TCNQ stack. All energies are in eV.

	TTF	TCNQ		TTF	TCNQ		TTF	TCNQ		TTF	TCNQ
U_{bare}	5.9	5.4	V_{bare}	3.1	2.9	V'_{bare}	1.8	1.7	V''_{bare}	1.2	1.2
U_0	4.7	4.3	V_0	2.9	2.8	V'_0	1.8	1.7	V''_0	1.2	1.2
U	2	1.7	V	1	0.9	V'	0.55	0.4	V''	0.4	0.3

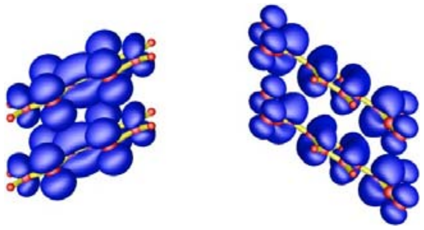

Fig. 1. (Color online) TTF-HOMO (left) and TCNQ-LUMO (right) of two neighboring molecules in TTF-TCNQ. Since both are planar π-orbitals, the molecules facing each other in a stack are quite close. This gives rise to the hopping t and also implies a strong nearest-neighbor Coulomb repulsion V.

which can be understood from Figure 1: the π-molecular orbitals stick out of the molecular planes so that the charges from the two molecules repel strongly. For distances l larger than twice the molecular radius, the corresponding V^l_{bare} (from $l = 3$, i.e. V''_{bare} on) are simply given by e^2/l. From the bonding-antibonding splitting for a pair of neighboring molecules we obtain the hopping matrix elements along the stacks: $|t| = 0.15$ eV for TTF and 0.18 eV for TCNQ.

Proceeding to the Coulomb parameters including intra-molecular screening, the on-site term U_0 is determined from the DFT total energy of an isolated molecule with various charges q in the HOMO or LUMO, and fitting to $E_U(q) = a_0 + a_1 q + U_0 q^2/2$. The results are listed in Table 1 and agree well with previous calculations for TCNQ [14]. The corresponding Coulomb parameters V^l_0 between different sites are obtained in a similar way, by calculating the total energy of two molecules at distance l, putting charge $q/2$ on each and fitting to $E_V(q) = 2E_U(q/2)+b_0+b_1 q+V_0 q^2/4$. Inspecting Table 1, we see that intra-molecular screening already noticeably reduces U_{bare} by more than 1 eV, while we find hardly any screening of the V_{bare}'s, i.e. the molecules mainly screen their own charge.

Determination of the inter-molecular screening contribution requires calculations of the energy of an infinite lattice of molecules. Constraining a charge q to a single molecule gives U, while constraining it to two molecules at a distance l provides the different V_l. In order to reach the infinite-system limit, we employ an electrostatic approach and represent the molecules by their polarizabilities. The polarizability tensor of the isolated molecules is calculated with DFT, by evaluating the dipole moments in homogeneous external fields along the principal axes and extracting the linear response. The results in Table 2 are consistent with estimates derived from the experimental dielectric constant through the Clausius-Mossotti relation. In a most reduced approach, one might then replace each molecule in the lattice by a point polarizability at the molecule's center of gravity. While this works nicely, e.g., in the case of C_{60} [16], it fails in the present case, since the molecules in a TTF/TCNQ stack come so close that they are inside the convergence radius of the dipole expansion. To avoid this we instead distribute the polarizability uniformly over the non-hydrogen atoms of the molecule [17]. Since such a representation by distributed dipoles works best in the far-field, the most stringent test is to compare the screening due to the closest neighboring molecules to constrained-DFT calculations [15,18], which take the full charge distribution into account. Calculating this way the reduction δU of the on-site Coulomb term due to screening by just the two nearest neighbors of a TTF molecule in a stack, we find $\delta U = 1$ eV, while the distributed-dipole approach yields 0.9 eV. This error is not increased when additionally taking the second nearest neighbors into account: The constrained-DFT calculation for the corresponding 5-molecule system gives $\delta U = 1.7$ eV, compared to 1.6 eV from the distributed-dipole approach. Since the screening by more distant molecules will be described even better, we can therefore conclude that the uncertainty in the parameters due to the approximate electrostatic approach is about 5%, which does not affect any of the physics and conclusions discussed below.

Table 2. Principal elements of the polarizability tensor of the TTF and the TCNQ molecule in atomic units (bohr^3). x (y) is the long (short) axis of the molecule, while z is perpendicular to the molecular plane.

	α_{xx}	α_{yy}	α_{zz}
TTF	226	160	88
TCNQ	440	184	82

In order to compute the inter-molecular screening of the Coulomb interaction we thus employ the distributed-dipole approach in a lattice with the experimental crystal structure of reference [19]. We use the notation of Allen [20], where a configuration of dipole moments on the lattice is denoted by a vector $|\mathbf{p}\rangle$ and the dipole-dipole interaction on the lattice is described by a matrix $\mathbf{\Gamma}$. If the dipoles arise via polarization, their energy in an external field $|\mathbf{E}^{\mathrm{ext}}\rangle$ is given by $\langle\mathbf{p}|\alpha^{-1} - \mathbf{\Gamma}|\mathbf{p}\rangle/2 - \langle\mathbf{p}|\mathbf{E}^{\mathrm{ext}}\rangle$, where α is the polarizability tensor. The configuration that minimizes the energy follows from the variational principle: $|\mathbf{p}\rangle = (\alpha^{-1} - \mathbf{\Gamma})^{-1}|\mathbf{E}^{\mathrm{ext}}\rangle$. As the energy is quadratic in the external field we can focus on pairs of electrons. With $\mathbf{E}^{\mathrm{ext}} = \mathbf{E}_n + \mathbf{E}_m$ the field of two point charges located at lattice sites n and m, screening lowers the energy by

$$\delta W = -\langle \mathbf{E}_n|(\alpha^{-1} - \mathbf{\Gamma})^{-1}|\mathbf{E}_n\rangle - \langle \mathbf{E}_m|(\alpha^{-1} - \mathbf{\Gamma})^{-1}|\mathbf{E}_n\rangle\,,$$

where the first term gives the screening of each charge individually, and the second term describes the screening of the interaction. If the two point-charges are located at the same position, the screening of the on-site interaction is $\delta U = -\langle \mathbf{E}_0|(\alpha^{-1} - \mathbf{\Gamma})^{-1}|\mathbf{E}_0\rangle$, while for $|n-m| = l$ we find $\delta V^l = -\langle \mathbf{E}_0|(\alpha^{-1} - \mathbf{\Gamma})^{-1}|\mathbf{E}_l\rangle$. Corresponding calculations for δU and δV^l were performed for clusters of up to 400 molecules and then extrapolated to the infinite-lattice limit. Inspecting the results compiled in Table 1, we notice that for TTF-TCNQ the screening is very efficient and further reduces $U = U_0 - \delta U$ by more than 2 eV. For the longer-range interactions the screening is somewhat smaller, but still substantial.

The finally obtained set of quantitative Hubbard parameters in Table 1 confirms the importance of correlations and longer-range Coulomb interactions in the TTF-TCNQ system. Compared to the band-width W of about 0.7 eV [9], U/W is larger than 2, and the nearest neighbor interaction V is about $U/2$. Even the interaction between third nearest neighbors is still comparable to W. While the electronic structure in the absence of inter-stack Coulomb interaction is essentially one-dimensional, we find that there is also a sizable coupling between neighboring molecules on different stacks. For two neighboring TTF stacks we find $V_{\text{bare}} = 1.6$ eV, the same for neighboring TCNQ stacks, while the interaction between TTF and TCNQ stacks is about 2.1 eV. Screening reduces all these values to about 0.4 eV.

A realistic description of TTF-TCNQ thus requires a 3-dimensional extended Hubbard model, including both inter-stack, as well as longer-range Coulomb interactions along the stacks. These terms have been neglected in previous calculations [6,10,11] using a simple *t-U* Hubbard model. To make contact to these calculations which treat only a single stack of molecules explicitly, we have to include the screening due to the neighboring stacks. This will somewhat reduce U and V, while the longer-range interactions are suppressed much more efficiently by the metallic screening [7]. Since the neighboring chains are strongly correlated this renormalization of the parameters is itself a complicated many-body problem that we presently cannot solve exactly. We therefore focus on the effect of the nearest-neighbor Coulomb term V, and consider a *t-U-V*-model of a single TTF or TCNQ chain

$$H = -t\sum_{\langle ij\rangle,\sigma}(c^\dagger_{i\sigma}c_{j\sigma} + H.c.) + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{\langle ij\rangle} n_i n_j,$$

using the values for U and V given in Table 1 (*t-U-V*-model). With filling $n \approx 0.6$ and 1.4 and very similar parameters, the models for a chain of TCNQ and TTF are closely related by an electron-hole transformation, with TTF being somewhat more correlated than TCNQ. The following discussion is for a chain of TCNQ but applies equally to TTF.

Following Hubbard [7], one might expect that the longer-range Coulomb terms completely change the physics of the model: since U is more than twice the band-width W, it seems safe to assume that double-occupancies are completely suppressed. The effect of the V's is then to maximize the distance between occupied sites. For filling 0.6 this results in a Hubbard-Wigner state with occupations ...1101011010... and a periodicity of 5 lattice sites. We can indeed interpret the spectral function for the *t-U-V* Hubbard chain with $U \to \infty$ using this reasoning. Nevertheless, even then the ground state is not a true Hubbard-Wigner lattice, since there are defect states that differ in Coulomb energy only when including the 4th nearest neighbor Coulomb term [21].

Using the actual value $U = 1.7$ eV of TCNQ we find that, even though $U \gg W$, double-occupancies are *essential.* For $V = 0$ the probability d of a doubly occupied site (calculated by exact diagonalization for a chain of 20 sites) is indeed only $d \approx 0.01$, to be compared to $d = 0.09$ for $U = 0$. However, the effect of V is to increase d, and for the actually calculated $V = 0.9$ eV of TCNQ we find $d \approx 0.027$. To obtain the same value in a *t-U* only model, we would have to double t from 0.18 eV to about 0.37 eV. Evidently, the nearest-neighbor Coulomb term encourages hopping. To understand this, consider what happens when two electrons pass each other: first they must become neighbors (energy V), then, to pass, they must form a doubly occupied site (energy U), to finally end up in a configuration where the neighbors have exchanged roles. This process thus involves effectively an energy $U - V$ (cf. Fig. 2 of Ref. [8]). This can be translated into an effective hopping $t_{\text{eff}} \approx t\,U/(U-V)$ for a corresponding t_{eff}-U model. Varying t in the *t-U*-model and V in the *t-U-V* model, we find that the double-occupancies as a function of t and t_{eff} are indeed very similar. For our TCNQ-parameters we find $t_{\text{eff}} \approx 0.38$ eV — almost exactly the value used to fit experiment [6].

Figure 2 shows the spectral function $A_{ii}(\omega)$ of the *t-U-V* chain as function of V. We see that the main effect of V is to broaden the spectrum around the Fermi level. A similar broadening has also been observed in reference [11] and is reminiscent of what happens when we increase t in the *t-U* Hubbard-model. Remarkably, the broadening can already be understood in first-order Rayleigh-Schrödinger perturbation theory: if we consider the V-term in the *t-U-V* Hamiltonian as a perturbation, then, to first order, the energies of the many-body states change by $V\sum_{\langle ij\rangle}\langle n_i n_j\rangle$, while the wave-functions remain unchanged. From the Lehmann representation we thus see that the positions of the spectral peaks shift linearly in V. This shift is proportional to $\sum_{\langle ij\rangle}\langle n_i n_j\rangle$, which, for the low energy states, tends to increase with the energy. This linearity also ensures that the physics does not critically depend on the exact values of the Coulomb parameters. It is quite surprising that perturbation theory gives such a good description for V as large as $U/2$. For larger V, however, it breaks down as the system changes phase (cf. Fig. 4 of Ref. [22]).

Returning to the model describing the molecules in the lattice by polarizable points, we illustrate an interesting effect of the polarizability α on the screening of the Coulomb

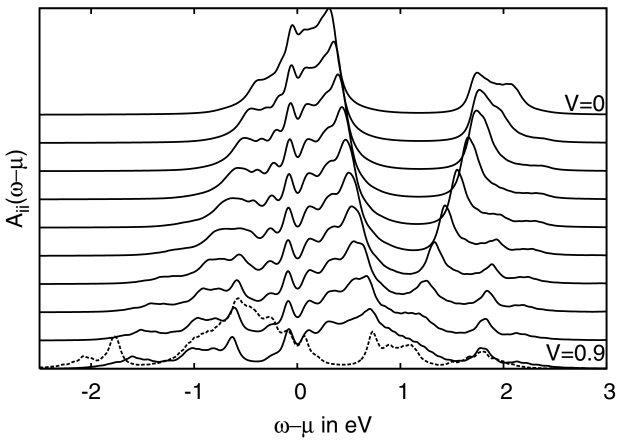

Fig. 2. Spectral function for the one-dimensional t-U-V model on 20 sites with periodic boundary conditions calculated by the Lanczos method (Lorentzian broadening 0.055 eV). The full lines show the effect of V for a TCNQ chain with $n = 0.6$, $t = 0.18$, $U = 1.7$, and V increasing from 0 to 0.9 eV. The dotted line is for a TTF chain with $n = 1.4$, $t = -0.15$, $U = 2.0$, and $V = 1.0$ eV.

interaction. For this, we consider a one-dimensional chain of polarizable points with lattice spacing b, which we can solve analytically. For $\alpha < b^3/4\zeta(3)$, where $\zeta(n)$ is the Riemann zeta function, such a system is stable against spontaneous polarization [20], so we can use translational invariance of the dipole-dipole interaction matrix to diagonalize $1/\alpha - \mathbf{\Gamma}$ in a plane-wave basis [20]. From the spectral representation we then obtain

$$\delta V^l = -\frac{e^2}{2\pi b}\int_{-\pi}^{\pi} dk\; cos(lk)\;\frac{\Im(\mathrm{Li}_2(e^{ik}))^2}{b^3/4\alpha - \Re(\mathrm{Li}_3(e^{ik}))}\,,$$

where $\mathrm{Li}_2(z)$ and $\mathrm{Li}_3(z)$ is the di- and trilogarithm, respectively [23]. From this solution we find that the screening is less efficient for larger l, even showing *antiscreening* for $l \geq 2$ and α not too close to the ferroelectric instability. Approaching the critical α, we find that the interactions V^l become almost independent of the distance l. Thus close to the ferroelectric instability electronic correlations are lost. With $\alpha_{zz} \approx 85\, a_0^3$ and $b = 3.819$ Å, TTF-TCNQ should be very close to this transition and it would be exciting to see what happens under sufficient hydrostatic pressure.

In conclusion, we have calculated a realistic set of Coulomb parameters for TTF-TCNQ, putting the commonly used values for the on-site interaction U and the estimates given by Hubbard [7] on a solid footing. We find that including long-range Coulomb terms does not lead to Hubbard-Wigner-type states. Instead, the effect of the nearest neighbor interaction V is a simple broadening of the spectra, an effect that has been mimicked in previous works by increasing t. Not having to assume an enhanced t to obtain the proper width of the low-temperature spectral function, should also lower the estimate of the temperature scale T_J, above which the signs of spin-charge separation are lost, to the experimentally observed range. In addition we have found that the Coulomb terms couple different chains.

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