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Coulomb parameters and photoemission for the molecular metal TTF-TCNQ

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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 find significant longer-range Coulomb interactions along the molecular stacks, as well as inter-stack coupling. We show that the long-range Coulomb term of the extended Hubbard model leads to a broadening of the spectral density, likely resolving the problems with the interpretation of photoemission experiments using a simple Hubbard model only.

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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 [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 . Yet, despite their importance for a correct description of the electronic properties, more quantitative values for the Coulomb parameters of TTF-TCNQ are to date not available.

In addition, a description of TTF-TCNQ in terms of a pure one-dimensional Hubbard model with only on-site Coulomb interaction seems to have problems. For the interpretation of recent 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 spectral function cannot be understood [10, 11]. These calculations, however, neglect the inter-molecular Coulomb repulsion V , the relevance of which was already suggested by Hubbard [7] and through diffusive X-ray scattering experiments, which display Wigner-type fluctuations [2].

Our aim in this Letter is to provide a realistic model for the description of TTF-TCNQ and to understand the

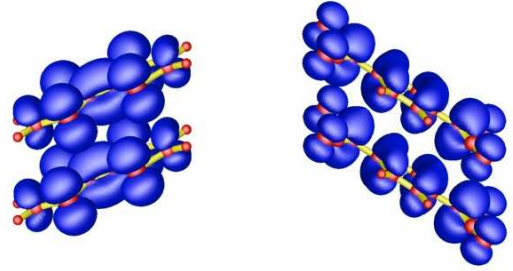


FIG. 1: (Color online) TTF-HOMO (left) and TCNQ-LUMO (right) of two neighboring molecules in TTF-TCNQ. Since both are planar π -orbitals, the molecules facing each other in a stack are quite close. This gives rise to the hopping t and also implies a strong nearest-neighbor Coulomb repulsion V .

spectral function. To calculate the screened Coulomb parameters for an extended Hubbard model, we proceed in two steps. Using density-functional theory (DFT), we first determine the screening due to the electrons on the same molecule (intra-molecular screening). To also include the inter-molecular screening we describe the other molecules in the lattice by point polarizabilities and check this electrostatic approach against constrained-DFT calculations for small clusters. Our calculations yield a sizable coupling between neighboring molecules on different stacks, as well as important longer-range Coulomb interactions V along the stacks. Focusing on the effect of V on the spectral density, we find that it leads to a broadening consistent with photoemission experiments.

We start our calculation of the Coulomb matrix elements from the bare Coulomb integrals between molecular orbitals (MOs) on two molecules a distance l apart $V_{\text{bare}}^l = \int d^3\mathbf{r} \int d^3\mathbf{r}' \rho_0(\mathbf{r}) \rho_l(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$, with $V_{\text{bare}}^0 = U_{\text{bare}}$. We calculate the charge density $\rho(\mathbf{r})$ of the highest occupied molecular orbital (HOMO) of TTF and the lowest unoccupied MO (LUMO) of TCNQ from all-electron

	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

TABLE I: Hubbard parameters for TTF-TCNQ. U_{bare} is the direct Coulomb integral, U_0 includes the renormalization due to 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. For comparison, the band-width is about 0.7 eV.

density-functional theory (DFT) using Gaussian orbitals [12] and 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 listed in Table I. We notice that V_{bare} is substantial, being of the order of $U_{\text{bare}}/2$. This can be understood from Fig. 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, V_{bare}^l is given by e^2/l . As a side-product we obtain from the bonding-antibonding splitting for a pair of neighboring molecules the hopping matrix elements along the stacks: $|t| = 0.15$ eV for TTF and 0.18 eV for TCNQ.

The on-site Coulomb parameter U_0 including intra-molecular screening is obtained by calculating the DFT total energy of an isolated molecule, putting charge q in the HOMO or LUMO, respectively, and fitting to $E_U(q) = a_0 + a_1q + U_0q^2/2$. The results are listed in Table I and agree well with previous calculations for TCNQ [14]. We note that intra-molecular screening reduces U_{bare} by more than 1 eV. In order to obtain the Coulomb parameters V_0^l , we calculate the total energy of two molecules at distance l , putting charge $q/2$ on each and fitting to $E_V(q) = 2E_U(q/2) + b_0 + b_1q + V_0q^2/4$. In contrast to the on-site term, we find hardly any screening of the V_{bare} 's, since 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 allows to obtain U , while constraining it to two molecules at a distance l provides the different V_l . Unfortunately, such constrained DFT calculations [15] can only be done for very small clusters of molecules. In order to reach the infinite-system limit, we therefore evaluate the reliability of approaches which represent the molecules by their polarizabilities. To determine the polarizability tensor of the isolated molecules, we calculate, with DFT, the dipole moments in a homogeneous external field along the principal axes and extract the linear response. The results are given in Table II and are consistent with estimates derived from the experimental dielectric constant through the Clausius-Mossotti relation.

One might then replace a molecule in the lattice by

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

TABLE II: Principal elements of the polarizability tensor of the TTF and the TCNQ molecule in atomic units (bohr³). x (y) is the long (short) axis of the molecule, while z is perpendicular to the molecular plane.

a point polarizability at the molecule's center of gravity. Such an approach, which works nicely, e.g., in the case of C₆₀ [16], 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 approximation. To avoid this problem we distribute the polarizability uniformly over the non-hydrogen atoms of the molecule [17]. To test the reliability of this approach, we compare the screening due to the nearest molecules, where the distributed dipole approach should work least well, to constrained DFT calculations, using an implementation of the method in DMol³ [18]. Calculating the reduction δU of the on-site Coulomb term due to screening of 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. A similarly good agreement is found when taking also the second nearest neighbors on the stack into account: The constrained DFT calculation for this 5 molecule system gives $\delta U = 1.7$ eV, compared to 1.6 eV from the distributed-dipole approach. This points at a quite small error, in particular when considering that the screening due to the more distant molecules along the stack will be increasingly well described by the dipole approximation.

We therefore employ the distributed-dipole approach to compute the screening of the Coulomb interaction in a lattice of polarizable points with the experimental crystal structure of Ref. [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 $|\mathbf{E}^{\text{ext}}\rangle$ is given by $\langle \mathbf{p} | \alpha^{-1} - \mathbf{\Gamma} | \mathbf{p} \rangle / 2 - \langle \mathbf{p} | \mathbf{E}^{\text{ext}} \rangle$, where α is the polarizability tensor. The configuration that minimizes the energy follows from the variational principle: $|\mathbf{p}\rangle = (\alpha^{-1} - \mathbf{\Gamma})^{-1} |\mathbf{E}^{\text{ext}}\rangle$. As the energy is quadratic in the external field we can focus on pairs of electrons.

Writing the field of two point charges located at lattice sites n and m as $\mathbf{E}^{\text{ext}} = \mathbf{E}_n + \mathbf{E}_m$, we find that screening lowers the energy by

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

where in the first term, which gives the screening of each individual charge, we have used translational invariance, and in the second term, which describes the screening of the interaction, we have used inversion symmetry. If the two point-charges are located at the same position, we get the screening of the on-site interaction $\delta U = -\langle \mathbf{E}_0 | (\alpha^{-1} - \mathbf{\Gamma})^{-1} | \mathbf{E}_0 \rangle$, while for $|n - m| = l$ we find $\delta V^l = -\langle \mathbf{E}_0 | (\alpha^{-1} - \mathbf{\Gamma})^{-1} | \mathbf{E}_l \rangle$. We have performed these calculations for clusters of up to 400 molecules. Extrapolating to the infinite lattice limit gives the results compiled in Table I. We find that for TTF-TCNQ the screening is very efficient, reducing $U = U_0 - \delta U$ by more than 2 eV, while for the longer range interactions the screening is somewhat smaller.

Comparing to the band-width W of about 0.7 eV [9], we find that U/W is larger than 2, and also the longer range interaction is substantial, with the nearest neighbor interaction V being about $U/2$. Even the interaction between third nearest neighbors is still comparable to W . The parameters for the TTF and TCNQ stacks are quite similar, with TTF, having smaller hopping and larger Coulomb parameters, being slightly more correlated. 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, which is still comparable to the band-width.

Our results therefore show that a realistic description of TTF-TCNQ requires an extended Hubbard model, including both inter-stack, as well as longer-range Coulomb interactions along the stacks. This is in stark contrast to existing pure one-dimensional Hubbard models with on-site term only (t - U -model) [6, 10, 11]. Due to the inter-chain coupling we expect Coulomb-drag effects [21], giving rise to interesting correlated dynamics of the individual stacks. Treating this coupling at mean-field level, one arrives at a one-dimensional Hubbard model, with Coulomb-parameters renormalized by the metallic neighboring chains. This will somewhat reduce U and V , while the longer-range interactions are suppressed more efficiently [7]. In the following we study the importance of the longer-range Coulomb interaction along the stacks by considering the extended Hubbard model of a single TTF or TCNQ chain

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

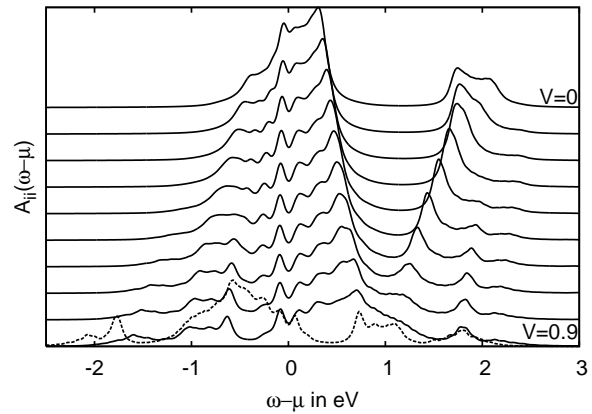


FIG. 2: Spectral function for the one-dimensional t - U - V model on 20 sites. The full lines show the effect of V for a TCNQ chain with $n = 0.6$, $t = 0.18$, $U = 1.7$, and V increasing from 0 to 0.9 eV. The dotted line is for a TTF chain with $n = 1.4$, $t = -0.15$, $U = 2.0$, and $V = 1.0$ eV.

using the values for U and V given in Table I (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 of the spectral function for a chain of TCNQ and applies therefore correspondingly to TTF.

Since U is more than twice the band-width W , it seems safe to assume that in a TCNQ-chain double occupancies are completely suppressed. The effect of V is then to maximize the distance between occupied sites. For filling 0.6 this results in a Hubbard-Wigner state with occupations $\dots 1101011010 \dots$ with a periodicity of 5 lattice sites [7]. However, such a state would be an insulator with a gap opening with V . This is, indeed, what we find solving the t - U - V Hubbard chain for $U \rightarrow \infty$. For $U = 1.7$ eV, however, the chain is metallic, indicating that double occupancies can not be neglected. Indeed, for $V = 0$ we find that the probability d of a doubly occupied site is $d \approx 0.01$, to be compared to $d = 0.09$ for $U = 0$. The effect of V is to further increase d . For $V = 0.9$ eV we have $d \approx 0.027$. To obtain the same value in the t - U 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 $U - V$. This can be translated to an effective hopping $t_{\text{eff}} \approx tU/(U - V)$ for a corresponding t_{eff} - U model. For our parameters we find $t_{\text{eff}} \approx 0.38$ eV.

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 Ref. [11] and is reminiscent of what happens when we increase t in the t - U model as proposed in Ref. [6]. 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 energy of the many-body states changes 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 position 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. Thus the further a pole is from the Fermi level, the more it moves with V , leading to the observed broadening of the spectrum.

We finally illustrate an interesting effect of the polarizability α on the screening of the Coulomb 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, 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

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

where $\text{Li}_2(z)$ and $\text{Li}_3(z)$ is the di- and trilogarithm, respectively [22]. 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. TTF-TCNQ should be very close to the transition. Hence it would be exciting to see what happens to the electronic correlations in TTF-TCNQ under sufficient hydrostatic pressure.

In conclusion, we have calculated a realistic set of Coulomb parameters for TTF-TCNQ. We find that the commonly used values for the on-site interaction U are correct, but that interactions between electrons on neighboring sites are significant and must be taken into account. Including the nearest neighbor interaction V on a TCNQ or TTF chain, we find that the spectra are broadened, an effect that can also be mimicked by increasing the hopping term 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, possibly giving rise to interesting

Coulomb-drag effects.

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