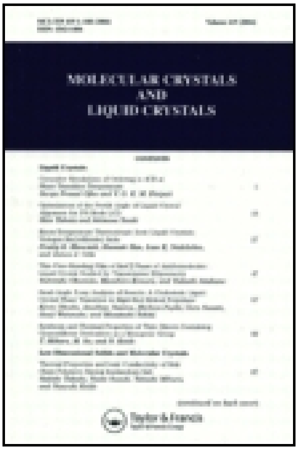

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Screening of Coulomb Interactions in Quasi one Dimensional Conductors

C. Noguera [a]
[a] Laboratoire de Physique des Solides, Université Paris-Sud, 91405, Orsay, France

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SCREENING OF COULOMB INTERACTIONS IN QUASI ONE DIMENSIONAL CONDUCTORS.

C. Noguera
Laboratoire de Physique des Solides, Université Paris-Sud
91405 Orsay (France).

Abstract - We present qualitative arguments based on studies of the charge transfer, the Madelung energy and the phase diagram of charge transfer organic conductors which indicate the important role played by the molecular and metallic polarizability in the physical properties of these compounds.

Quasi One Dimensional conductors such as TTF-TCNQ, which are built with large molecules possess an important polarizability due to the many possible molecular and metallic excitations. As a consequence, all the Coulomb interactions in these compounds are expected to have a low or moderate strength. Different kinds of Coulomb interactions may be distinguished : the electron-electron interactions on a given stack are of importance in determining the nature of the instability of the one dimensional electron gas, the conductivity, the enhancement of the magnetic susceptibility..; the Coulomb interactions between (non distorted) stacks play a major role in the cohesion of the crystals and in the establishment of its structure; at low temperature, interactions between possible charge density waves on different stacks make a phase transition possible through the development of three dimensional correlations.

Nevertheless, the strength of these interactions has been a subject of controversy along the years, especially as concerns the value of the electron-electron repulsion on a stack. Although many arguments have been given from both sides, no agreement exists and two main reasons may explain this situation : i) first, no existing computer is large enough to allow the metallic and molecular virtual excitations to be accounted for in an ab initio calculation and ii) when simplified models are used, one generally cannot solve them exactly for the whole range of values of the interactions.

We present here some new qualitative arguments concerning the role of screening and polarization effects in reducing the bare Coulomb repulsion, by focusing mainly on the interchain couplings. We will not be able to describe at length the calculations underlying each argument ; but we will summarize their assumptions and results and how they bring elements of answer on this problem.

Existence of fractional charge transfers : The charge transfer ρ which occurs between donor and acceptor molecules in two chain compounds with 1:1 stoechiometry, such as in the TTF and TSeF families, may be determined by minimizing the ρ-dependent part of the cohesive energy $\mathcal{E}_{coh}$. We have considered [1] four major contributions to $\mathcal{E}_{coh}$: the ionization, band, Madelung and Van der Waals energies. By assuming that the transverse hopping may be neglected, that the ρ dependent part of the Van der Waals energy is due mainly to the metallic polarizability [2] and that the Madelung energies varies as ρ^2, we have written :

$$\mathcal{E}_{coh} = (I_1-A_1)\rho - E_B \sin\frac{\pi\rho}{2} - E_M\rho^2 - \frac{E_{VW}}{\sin\pi\rho/2}$$

Considering the quantities (I_1-A_1), E_B, E_M and E_{VW} as parameters, we have been able to derive charge transfer maps such as the one of figure 1, on which one may read the value of ρ which minimizes $\mathcal{E}_{coh}$ for selected values of the parameters. Aside several other interesting but non related features, these maps give a criterion for the existence of a non integer value of ρ which is :

$$E_M < E_B \quad \underline{\text{and}} \quad (I_1 - A_1) < 1.5\, E_B$$

In other words the Coulomb energies E_M and $(I_1 - A_1)$ (respectively Madelung and ionization energies) must be of the order of, or less than the band energy E_B (which is equal to $4/\pi$ times the sum of the hopping integrals on both stacks). In TTF-TCNQ for example, it is well established that $\rho = .59$ and $E_B \sim .4$ eV, while it is believed that $I_1 - A_1 \sim 4$ eV and $E_M \sim 2$ eV.[3] But these two latter values correspond to bare Coulomb interactions : $I_1 - A_1$ was measured in the gas phase and E_M was calculated without taking into account screening and polarization effects. The charge transfer maps suggest that in the crystals these values are reduced by a factor of about 5 to 10.

Screening of the Madelung interactions : Because it was not clear from the literature whether one should use a dielectric constant in evaluating a Madelung energy, we have searched[1] under which conditions the second order terms in interchain coupling give a vanishing contribution when summed over the lattice. By denoting ψ_n^A the wave function of an electron on a chain A in a state n of energy E_n^A, this lattice summation reads :

$$\mathcal{E} = \sum_{ABM} \sum_{\substack{n\ \mathrm{occ} \\ m\ \mathrm{occ}}} \sum_{\substack{n_1 \mathrm{occ} \\ n_2 \mathrm{empty}}} < \psi_n^A \psi_{n_1}^M \left| \frac{1}{|\vec{r}-\vec{r}\,'|} \right| \psi_{n_2}^M \psi_n^A > \frac{1}{E_{n_1}^M - E_{n_2}^M} < \psi_{n_2}^M \psi_m^B \left| \frac{1}{|\vec{r}-\vec{r}\,'|} \right| \psi_{n_1}^M \psi_m^B >$$

We found that three conditions have to be fulfilled simultaneously: i) the chains A, B and M must be far enough so that only dipolar terms in the development of $1/|\vec{r}-\vec{r}\,'|$ could be kept ; ii) the extent of the orbitals ψ_n^A.. must be small enough so that the polarization field created by M could be taken uniform upon A and B and iii) enough symmetry of the lattice is needed. It is clear that in the organic compounds upon consideration in which the molecular orbitals are large compared to the interatomic distances, the two first conditions break down while they don't, to a good approximation, in simple ionic crystals such as NaCl. As a consequence, in charge transfer organic conductors the virtual excitations of the molecular and metallic type are expected to reduce the Madelung energy, the more effectively as the polarizability of the compound is larger.

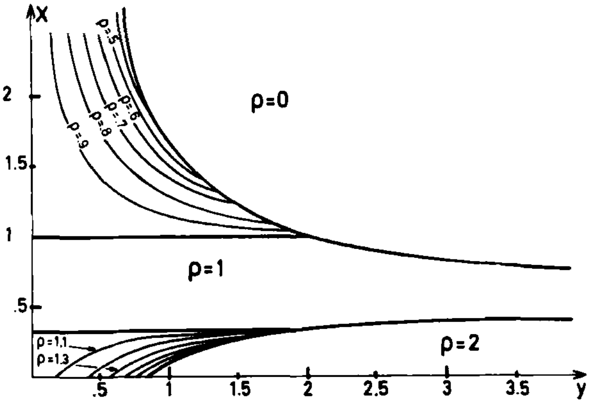

FIGURE 1

Charge transfer map as a function of $x=I_1-A_1/2E_M$ and $y=2E_M/E_B$. ($E_{VW} = 0$)

Phase-diagram of TTF-TCNQ under pressure : TTF-TCNQ presents a rich variety of phase transitions corresponding to the appearance of charge density waves on the stacks (Figure 2). It was shown that the high temperature part of the phase diagram could be explained by considering only two order parameters χ_F and χ_Q related respectively to the distortions on the TTF and TCNQ chains and emphasis [4] was put on the importance of the fourth order terms in the Landau expansion $\chi_F^2\chi_Q^2$ and $\chi_F\chi_Q^3 + \chi_Q\chi_F^3$ necessary to understand the rapid variation of the second transition temperature T_M under pressure.

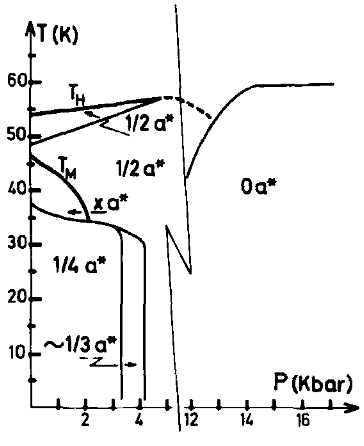

FIGURE 2 - Phase diagram of TTF-TCNQ from S. Metgert [4]. The component along a* of the wave vector of the modulation is indicated.

Using a microscopic approach in which the interchain interactions are treated in the mean field approximation, we have shown [5] that the opening of a gap on the TTF and TCNQ chains decreases the strength of the screening and Van der Waals processes through a decrease (in absolute value) of the one dimensional electronic susceptibilities. Assuming for simplicity that the lattice is orthorhombic[6] we have found that the $\psi_F^2\psi_Q^2$ terms come from a development of the Van der Waals energy while the $\psi_F\psi_Q^3$ and $\psi_Q\psi_F^3$ terms come from mediated interchain interactions. This study suggests again that the metallic polarizability plays an important role in the physics of TTF-TCNQ.

Conclusion : We have presented here new arguments supporting the idea that polarization and screening effects are large in conducting charge transfer compounds. This seems a natural conclusion considering that they possess many molecular and band states available for excitation just above the Fermi level. But it is also in agreement with determination of the dielectric constant by optic measurements [7] in TTF-TCNQ which indicate $\varepsilon(\omega) \sim 2.8$ in the region of molecular excitations while $\varepsilon(\omega) >> 2.8$ for ω below the plasma edge where the metallic polarizability is large. The requested reduction (at ω=0) of the Coulomb interactions by a factor 5 to 10 thus does not seem unreasonable. Our conclusion seems also to support the idea that the Van der Waals interaction is large enough to help in stabilizing the TTF-TCNQ-type lattice.[2] Finally it gives hints that electron-electron interactions should also be screened, in agreement with the good metallic character of these compounds. In this context a 'Wigner-type lattice' explanation [8] is not necessary to account neither for the non integer charge transfer, nor for the existence of $4k_F$ distortions[9].

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