Plasmon spectra and cohesion of the mixed stack organic conductors
P. Zupanovic, S. Barisic, A. Bjelis

To cite this version:
P. Zupanovic, S. Barisic, A. Bjelis. Plasmon spectra and cohesion of the mixed stack organic conductors. Journal de Physique, 1985, 46 (10), pp.1751-1761. <10.1051/jphys:0198500460100175100>. <jpa-00210127>

HAL Id: jpa-00210127
https://hal.archives-ouvertes.fr/jpa-00210127
Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
1. Introduction.

The theory of the one-dimensional electron gas accounts for many low temperature properties of quasi one-dimensional organic conductors and it is tempting to describe their cohesion within the same scheme. In fact, such an attempt focused on the relative stability of the TTF-TCNQ (T) and HMTTF-TCNQ (H) lattices was made recently [1]. The Coulomb interaction was treated as the perturbation and the second order correction to the ground state energy was cast in the form of a Van der Waals-type (VdW) energy between metallic chains. Extrapolating this weak coupling result to intermediate couplings, it was suggested that the competition between this VdW energy and the Madelung energy of charged chains is responsible for the different stacking patterns of the TTF-TCNQ and HMTTF-TCNQ lattices. In the latter lattice the Madelung energy was assumed dominant, leading to alternation of chains in both directions perpendicular to the chains. In contrast, for TTF-TCNQ the metallic VdW energy was taken to favour the formation of sheets in the c-direction, which alternate then along the a-axis (Fig. 1). The main purpose of this paper is to check this idea using the method of bosonization [2] which supposedly treats the intermediate coupling regime more accurately. The obtained result agrees in sign with the perturbation result. However, for realistic values of the coupling constant, the change of the plasmon energy, which corresponds to the change of the VdW energy, is much smaller than the concomitant change of the Madelung energy on going from one to the other structure. This result reopens the problem of cohesion of organic metals without providing an answer to it. However, a byproduct of our discussion is the detailed
Fig. 1. — Stacking patterns of the orthorhombic counter-parts of the TTF-TCNQ (a) and HMTTF-TCNQ (b) lattices.

Form of the plasmon dispersion relations for the considered structures. These spectra are not only interesting by themselves, but also provide experimental challenges relevant to the problem of cohesion.

In section 2 the Hamiltonian of the system is described. The weak coupling limit results of reference [1] are completed with the on-chain terms in section 3. The Tomonaga model is developed in section 4. The plasmon dispersion relations are found and the overall zero-point plasmon energy is calculated in this section. In section 5 the relationship between the ground state energy of the Tomonaga model and perturbation scheme is established. Finally, the relative stability of the TTF-TCNQ and HMTTF-TCNQ lattices is considered in section 6.

2. Description of the Hamiltonian.

A 1:1 quasi one-dimensional charge transfer complex is usually described by assuming that bands on both kind of chains arise from π orbitals of donor and acceptor molecules. Since the overlap of these orbitals is very small, the tight binding approach is appropriate. The highest energy level of the neutral donor molecule is assumed to be doubly occupied, and electrons which are transferred to the acceptor chain leave the same number of holes on the donor chain. The electron to hole transformation performed on the donor states enables one to replace all electrostatic interactions (ion-ion, electron-ion, and electron-electron) with the electron-hole interaction only. Assuming further that the intraband transitions are the only relevant ones, phase space is restricted to the conduction bands and

\[ \hat{H} = \hat{H}_0 + E \]  

with

\[ \hat{H}_0 = -2 \sum_{s,\alpha,\beta} t_s \cos(qb) \hat{a}^\alpha_s(q) \hat{a}_\beta(q) + \frac{1}{2N_0} \sum_{n,m,k,k',q,h,a,a'} V_{n,m}(q) \hat{a}^+_{n,k}(q) \hat{a}^+_{m,k}(q + q) \hat{a}_{m,k}(k + q) \]  

and

\[ \frac{E}{N} = (1 - \rho) U + \rho E^0_Q + (2 - \rho) E^2_T. \]  

The wave vectors \( k, k', q \) and the chain indices \( n, m \) are the longitudinal and transverse coordinates, respectively. In \( \hat{H}_0 \), \( t_s \) is the transfer integral between nearest neighbour sites, \( b \) is the lattice constant in the stacking direction, \( \hat{a}_\alpha(q) \) is the destruction operator of an electron (hole) on the acceptor (donor) chain in the Bloch state of wave vector \( q \) and spin \( s \). \( N_0 \) is the number of molecules per chain and \( V_{n,m}(q) \) is the interaction matrix element. Assuming for simplicity that the electrons and holes are located on the centres of the donor and acceptor molecules the point charge approximation [3] is used for the Coulomb matrix element

\[ V_{n,m}(q) = \begin{cases} \frac{2e^2}{b} K_0(q | r_n - r_m|) & n \neq m \\ -\frac{e^2}{b} \ln(2(1 - \cos qb)) + U(1 - \delta_{s,a}) & n = m. \end{cases} \]  

Here \( K_0 \) is the modified Bessel function [4], and the Kronecker symbol \( \delta_{s,a} \) describes the spin dependent nature of the on-site interaction \( U \). The constant term \( E \) in equation (3) is calculated per donor or acceptor molecule, where \( N \) is the number of donors or acceptors, and \( \rho \) is the charge transfer per molecule. The first term in this equation is the electron self-energy due to the electron on-site interaction on the donor and acceptor molecules assuming for simplicity the same \( U \) for both of them. This simplification is
unessential once we restrict ourselves to the Tomonaga model, which assumes that the local interactions are small with respect to the (long range) off-site terms. The other two terms in equation (3) are the negative values of the electron affinity energy and second ionization potential of the acceptor and donor molecules, respectively.

The cohesive energy is the difference in the ground state energy between the gas and the solid phase. Consistently with the separation of equations (1)-(3) it can be written as

$$E_c/N = \rho (E_0^0 - E_F^+ - U) +$$

$$+ \frac{1}{2} \rho^2 U + (E_B + E_{HF} + E_{COR})/N + E_{el}/N. \ (5)$$

The first term is the ionization-affinity energy, since $U$ is the disproportionation energy \[5\] for the reaction $2 \text{TTF}^+ \rightarrow \text{TTF}^0 + \text{TTF}^2$, so that $E_F^+ + U$ is the negative value of the first ionization potential. $E_B$ is the band energy defined as usually,

$$E_B/N = -\frac{4}{\pi} \left( |t_F| + |t_Q| \right) \sin \rho \frac{\pi}{2}, \ (6)$$

where $t_F$ and $t_Q$ are the transfer integrals on the donor and acceptor chains, respectively. The Hartree-Fock energy $E_{HF}$ and the correlation energy $E_{COR}$ are defined in the usual way. Their particularities associated with the chain structure will be discussed in what follows. Finally $E_{el}$ involves all energies not related to the band formation and the charge transfer.

### 3. Weak coupling limit

The aim of this section is to review briefly the weak coupling results of reference [1] and to complete them with the on-chain terms, omitted there.

$$E_{HF}^M/N = 4 \frac{\rho^2 e^2}{a} \left\{ - \ln 2 + \sum_{n_1, n_2 \neq 0} e^{i\pi n_1} \sum_{L=0, \pm 1, \ldots} K_0 \left[ \frac{2 \pi}{a} (1 + 2L) (b^2 n_1^2 + (c/2)^2 n_2^2)^{1/2} \right] \right\}. \ (8)$$

Here $a$ and $c$ are the perpendicular lattice constants, where $\gamma = 0$ for TTF-TCNQ and $\gamma = n_3$ for HMTTF-TCNQ.

$E_{ex}$ is an on-chain term when the interchain overlap is neglected, and following reference [6] we obtain easily

$$E_{ex}/N = \frac{e^2}{\pi^2} b \int_0^{2k_F} (2k_F - q) \ln 2(1 - \cos qb) \, dq =$$

$$= \frac{e^2}{b} \left( -3 + \ln \rho \pi - \frac{\pi^2 \rho^2}{144} \right) \rho^2 + o(\rho^6). \ (9)$$

Here $k_F$ is the Fermi wave vector related to the charge transfer by

$$k_F = \rho \frac{\pi}{2}. \ (10)$$

The exchange energy $E_{ex}$ exhibits electron-hole symmetry, so that for the more than half-filled band case $\rho$ refers to the hole density. The on-site interaction $U$ does not contribute to the exchange energy, as the
latter arises from electrons with parallel spins, whereas \( U \) involves only electrons with antiparallel spins. \( E_{ex} \) turns out to be also independent of the transfer integrals \( t_{Q,F} \). It tends to stabilize the lattice by achieving its minimum which amounts to approximately \( -e^2/2b \) per pair of molecules for a half filled band. However, this value is somewhat too large since the point charge approximation overestimates the intrachain matrix element.

The second order perturbation energy can be cast in the form of a VdW-like energy. The VdW energy between two chains is [1]

\[
E_{\text{vaw}}(n, m) \approx -\frac{e^4}{\pi^2 R_{nm}^2} \frac{n_p^m n_p^n}{n_p^p + n_p^n}. \tag{11}
\]

Here \( R_{nm} \) is a distance between the chains and \( n_p^n \) is the density of electron states at the Fermi level on the \( n \)-th chain related to the Fermi velocity \( v_F \) of the electron on this chain by

\[
n_p^n = \frac{b}{2 \pi n_p^p}. \tag{12}
\]

The infinite sum of the pair interactions (11) over all chains diverges, but the screening effect suppresses this divergence by restricting the sum to a circle of radius \( k_{TF}^{-1} \), where \( k_{TF} \) is the Thomas-Fermi wave vector. \( k_{TF} \) is related to the mean density of electronic states at the Fermi level by

\[
k_{TF}^2 = 16 \pi n_F \frac{e^2}{abc}. \tag{13}
\]

Replacing the actual lattice by its orthorhombic counterpart the total interchain VdW energy \( E'_{\text{vaw}} \) becomes [1]

\[
E'_{\text{vaw}}/N = \frac{n_p e^4}{ac} C_1 \ln (1/c_1 k_{TF} \sqrt{ac}). \tag{14}
\]

The constants \( C_1 \) and \( C_2 \) are of the order of unity and their numerical values are given in Appendix B. The expression (14) for the interchain VdW energy is obviously valid for \( 1/2 k_{TF} \sqrt{ac} \leq 1 \), since the notion of screening is meaningful only if the screening length \( 1/k_{TF} \) exceeds the nearest neighbour chain distance. In terms of the interaction parameter \( v = e^2 n_p/b \), the expression (14) is thus valid for \( v \ll 1 \).

The on-chain long-wavelength VdW energy is easily found to be

\[
E_{0\text{vaw}}/N = -\frac{2 n_p e^4}{ac} C_0, \tag{15}
\]

where

\[
C_0 = \frac{\rho^2 ac}{16 b^2} \left[ 4 \ln \frac{\rho \pi/2 - 2(2 + Ub/e^2)}{2(2 + Ub/e^2)} \times \ln \frac{\rho \pi/2 + 2 + Ub/e^2(1 + Ub/2 e^2)}{2(2 + Ub/e^2)} \right]. \tag{16}
\]

The value of \( C_0 \) is calculated using the long-wavelength limit for the on-chain interaction matrix element (4), and assuming that \( k_F > k_{TF} \). The ratio \( E_{0\text{vaw}}/E_{0\text{vaw}} \) is a decreasing function of the interaction parameter \( v \) due to the screening effect. Neglecting the on-site interaction \( U \) and using appropriate values for the parameters \( a, b, c \) and \( \rho \) in TTF-TCNQ (see Appendix B) \( C_0 \) becomes approximately \( \rho^2 ac/8 b^2 \approx 0.7 \), indicating that \( E_{0\text{vaw}} \) and \( E_{0\text{vaw}} \) are of the same order of magnitude for \( \ln (1/C_J) k_{TF} \sqrt{ac} \approx 1 \) i.e. already for \( v \approx 0.01 \). For larger \( v \) the intrachain term \( E_{0\text{vaw}} \) dominates.

Two similar molecules TTF and HMTTF lead to quite different stacking patterns when forming compounds with TCNQ(Q) (Figs. 1a and 1b). In order to explain the simultaneous existence of these lattices within the present model in nature, the Madelung energy loss \( \Delta E_{M} \) on going from the HMTTF-TCNQ to the TTF-TCNQ lattice should be compensated by various band corrections. The change of the metallic VdW energy (14) is

\[
\Delta E_{\text{vaw}} = (E'_{\text{vaw}} - E_{\text{vaw}})/N = \frac{e^4}{2 \pi ac} \left( n_p - n_p^o \right)^2 (n_p + n_p^o) \ln (1 - k^2), \tag{17}
\]

where \( k \) is related to \( c/a \) through the elliptic integral \( K \) [4]

\[
\frac{c}{a} = \frac{K(\sqrt{1 - k^2})}{K(k)}. \tag{18}
\]

Considering the signs of \( \Delta E_{M} \) and \( \Delta E_{\text{vaw}} \) it follows that \( \Delta E_{\text{vaw}} \) tends to compensate for the change in \( \Delta E_{M} \). Concerning the values it was found in [1] that the absolute value of the ratio \( \Delta E_{\text{vaw}}/\Delta E_{M} \) is of the order \( n_p^2 \omega_0^2 \) where \( \omega_0 \) is the maximum plasma frequency [7],

\[
\omega_0^2 = \frac{16}{ac} (v_F^2 + v_F^2). \tag{19}
\]

Here \( v_F^p \) and \( v_F^o \) are the Fermi velocities on the donor and acceptor chain respectively. The assumption that \( \Delta E_{\text{vaw}}/\Delta E_{M} \) is of the order of \( n_p^2 \omega_0^2 \) not only in the weak coupling limit \( n_p \omega_0 < 1 \) but also for intermediate couplings \( n_p \omega_0 \approx 1 \) led to the suggestion that the TTF-TCNQ lattice results from the VdW cohesion.

We wish to point out here that \( \Delta E_{\text{vaw}}/\Delta E_{M} \approx n_p^2 \omega_0^2 \) is only a qualitative result even in the weak coupling limit. Solving equation (18) approximately for \( k \) it was found that \( n_p \omega_0 < 1 \) and \( 2 \omega_0 \approx -1/2 \) (for numerical values of the perpendicular lattice constants see Appendix B). However, a better solution can be found by iteration. Keeping in mind that \( c/a \approx 3/2, k^2 \) in (18) should be less than \( 1/2 \) since \( K(m) \) is an increasing function of \( m \). Therefore, \( \ln (1 - k^2) \approx k^2 < 1/2 \). This procedure gives \( k^2 \approx 0.16 \), so that \( \Delta E_{\text{vaw}}/\Delta E_{M} \) is closer to \( 0.1 n_p^2 \omega_0^2 \) than to \( n_p^2 \omega_0^2 \). Although the possibility that for intermediate couplings \( \Delta E_{\text{vaw}} \) becomes of the order of
I f E_M is still not excluded this requires a careful investigation which is carried out in the forthcoming sections.

4. The Tomonaga model.

The main features of the Tomonaga model [8] are the assumptions that the electron spectrum in the vicinity of the Fermi vector is linear in k and that the long-range part of the interaction dominates over all other interactions. Both assumptions were also tacitly used in reference [1] on dealing with cohesion, and the Tomonaga model is thus a natural extension of those calculations. After a lengthy but straightforward procedure the Hamiltonian (1) of the Tomonaga model can be bosonized to become

$$\hat{H} = \hat{H}_F + \hat{H}_Q + \hat{H}_i + E_b + E + E_{ax} + E_M + \frac{1}{2} \rho^2 NU + \hat{U},$$  

where

$$\hat{H}_{F(Q)} = \sum_{q > 0, \alpha_i} q \{ [V_1(q, \alpha_i)] [b_{1F(Q)}^* b_{1F(Q)} + b_{2F(Q)}^* b_{2F(Q)}] +$$

$$+ V_1(q, \alpha_i) [b_{1F(Q)} b_{2F(Q)} + b_{1F(Q)}^* b_{2F(Q)}^* + 1] \},$$  

$$\hat{H}_i = - \sum_{q > 0, \alpha_i} q V_2(q, \alpha_i) [b_{1F} b_{1Q}^* + b_{1F} b_{2Q} + b_{2F} b_{1Q}^* + b_{2F} b_{2Q} +$$

$$+ b_{1F}^* b_{1Q} + b_{1F}^* b_{2Q} + b_{2F} b_{1Q} + b_{2F} b_{2Q}],$$

$$V_{1(2)}(q, \alpha_i) = \frac{b}{\pi} \sum_{m(n)} \cos q_{\alpha_i} r_{m(n)} V_{m(n),0}(q),$$  

$$E_{ax} = \frac{e^2}{\pi^2} b \int_{\omega_0}^{\infty} 2 k_F \ln (1 - \cos q\beta) dq,$$

and

$$\hat{U} = - \frac{1}{2} U \sum_{n,k,k', \alpha \neq 0, \alpha} a_{n\alpha}^*(k) a_{n\alpha}(k + q) a_{n\alpha}^*(k') + q a_{n\alpha}(k').$$

The sum in equation (23) for $V_{1(2)}$ is performed over the transverse coordinates corresponding to the same (different) kind of chains as the one at the origin. $E_{ax}$ appears in the Hamiltonian as a result of the anticommutation relations on arranging the products of the annihilation and creation operators into the $p(q) \rho(-q)$ form. The on-site interaction (25) is the most prominent part of the short-range interactions. As already mentioned in section 2 the Tomonaga model assumes this term small, i.e. avoids the related complications.

The Hamiltonians $\hat{H}_{F(Q)}$ correspond to the sublattices associated with the two kinds of chains. They are the usual Tomonaga Hamiltonians [9], and can be easily diagonalized leading to the plasmon dispersion relations

$$\omega_{F(Q)}(q, \alpha_i) = q \{ v_{F(Q)}^2 + 2 V_1(q, \alpha_i) \}^{1/2}.$$  

The interaction between sublattice plasmons is introduced through $\hat{H}_i$. The total plasmon part of the Hamiltonian can be diagonalized by means of the standard method [10], with the result

$$\hat{P} = \hat{P}_F + \hat{P}_Q + \hat{P}_i = \sum_{q > 0, \alpha_i} \left[ \omega_1(q, \alpha_i) (d_1^* d_1 + \hat{e}_1^* \hat{e}_1 + 1) +
\omega_2(q, \alpha_i) (d_2^* d_2 + \hat{e}_2^* \hat{e}_2 + 1) - q(v_F^2 + v_0^2) \right]$$

where

$$\omega_1,2(q, \alpha_i) = \frac{d}{\sqrt{2}} \left( v_F^2 + 2 V_1(q, \alpha_i) \right) \pm$$

$$\pm \left( (v_F^2 + 2 V_1(q, \alpha_i) + v_0^2 + 2 V_1(q, \alpha_i))^2 + 16 V_2^2(q, \alpha_i) v_F^2 v_0^2 \right)^{1/2}. $$
The dispersion relations in equation (28) are intricate for general values of \(q + q_1\). However, in the long-wavelength limit all matrix elements (see Appendix A) diverge as \(1/(q^2 + q^2_1)\) and this part of spectrum can be easily found, revealing the nature of the two plasmon branches. The first branch is

\[
\omega_1(q, q_1) = \omega_0 \frac{q}{\sqrt{q^2 + q^2_1}},
\]

where \(\omega_0\) is already defined in equation (19). The second branch is the acoustic one [7, 11]. The corresponding velocity is of the order of the Fermi velocity,

\[
\omega_2(q, q_1) = |q| \left\{ \frac{v_F^2}{v_F^2 + v_F^2} \right\}^{1/2}.
\]

The dispersion relations can be calculated numerically for the orthorhombic counterparts of the TTF-TCNQ and HMTTF-TCNQ lattices and are meaningful in the forward part of the Brillouin zone. The result of numerical calculations is displayed in figures 3 and 4. It is interesting to notice that TTF-TCNQ and HMTTF-TCNQ dispersion surfaces cross at \(q_c = \pm \frac{\pi}{c}\) (see Fig. 4). This fact will play later an important role in the considerations on the relative stability of those lattices.

The zero-point plasmon energy \(E_p\) is easily obtained by summing up the plasmon frequencies (28) in the

---

**Fig. 3.** — The plasmon dispersion surfaces \(\omega_1\) for \(q_a = 0\) (a) and \(q_a = \pi/2\) a (b). At the edge of the Brillouin zone \(q_e = 2\pi/c\) the upper surfaces correspond to the HMTTF-TCNQ structure. The difference between these surfaces is hardly perceptible on the scale of these figures. The units of energy and wave number are \(5t_F \sin \pi/2 \approx 0.5\) eV and 0.1 Å⁻¹, respectively.

**Fig. 4.** — The dispersion surfaces \(\omega_2\) for \(q_a = 0\) (a) and \(q_a = \pi/2\) a (b). The larger \(\omega_2\) along q axis corresponds to the HMTTF-TCNQ structure. The unit of energy is \(0.5t_F \sin \pi/2 \approx 0.05\) eV, while the unit of wave number is same as in figure 3.
forward part of the Brillouin zone

\[ E_p = \sum_{k_p > q = 0, q_z} \left[ \omega_1(q, q_z) + \omega_2(q, q_z) - q(v_F^2 + v_D^2) \right] \]

(31)

The dispersion relations are rather intricate for a general value of the wave vector in equation (31) and we had to resort to numerical integration (1). The dependence of the plasmon energy \( E_p \) and the Madelung energy \( E_M \) calculated within the same approximation (8) are shown in figure 5. The crossing \( E_p \approx E_M \) occurs only in TTF-TCNQ for \( v \approx 3 \).

5. Relationship between the Tomonaga model and perturbation scheme.

In this section we wish to discuss the correspondence between the perturbation theory results and the results of the Tomonaga model. For the sake of simplicity we shall consider here a lattice of equivalent stacks. The ground state energy of the Tomonaga model is

\[ E_0 = E_p + E_{\text{ex}} + E_B + E_M + \frac{1}{2} \rho^2 N U + E + E_{\text{el}}. \]

(32)

In the preceding section the zero-point energy \( E_p \) was calculated by taking the cut-off at the Fermi wave vector \( k_F \), in accordance with the assumption that the long-range part of the interaction is dominant in the cohesive energy. Therefore only the long-wavelength part of the exchange energy (9) can be contained in the ground state energy of the Tomonaga model,

\[ E_{\text{ex}}/N = \frac{e^2 b}{\pi^2} \int_0^{k_F} (2 k_F - q) \ln 2(1 - \cos qb) dq. \]

(33)

Indeed the expansion of the plasmon energy \( E_p \) in a Taylor series in powers of the interaction parameter \( v \) gives

\[ E_p = E_{\text{ex}} - E_{\text{ex}}^1 + \frac{1}{2} \sum_{m,n} (1 + \delta_{m,n}) E_{v\text{dW}}(m,n) + \cdots \]

(34)

\[ E_{\text{COR}} = E_p - E_{\text{ex}} - E_{\text{ex}}^1 \]

(35)

where \( E_{\text{ex}}^1 \) is given by equation (24). This expansion shows that \( E_p \) contains a small part of the long-wavelength exchange energy \( E_{\text{ex}} \). Combined with other terms in (32) equation (34) brings us back to the second order perturbation calculation. The VdW energy of two chains in equation (11) is proportional to the inverse square of the interchain distance. Therefore the sum of the VdW energies in equation (34) diverges, but we have to keep in mind that higher order corrections remove this divergence as in equation (14). Through its cut-off \( k_F \), equation (14) represents a much better approximation to \( E_p \) than the second order perturbation theory itself. As for \( E_{\text{COR}} \), it is the correlation energy which is due to correlation effects tending to keep the electrons apart. Therefore it should be negative. Indeed,

\[ E_{\text{COR}} = E_p - E_{\text{ex}} - E_{\text{ex}}^1 \leq 0. \]

(37)

The equality holds for a system of noninteracting fermions when all correlations except those due to the exchange effect vanish.

In order to establish a precise correspondence between \( E_{\text{COR}} \) and the intra and interchain VdW energies \( E_{\text{vdW}}^0 \) and \( E_{\text{vdW}}^- \) it is interesting to separate out the value of the plasmon energy \( E_p^0 \) due to the intra-chain interactions only. In the perturbation theory limit \( E_p^0 \) contains the contributions \( E_{\text{ex}} - E_{\text{ex}}^1 \) and \( E_{\text{vdW}}^- \), whereas the interchain term \( E_p = E_p - E_p^0 \) corresponds to the interchain energy \( E_{\text{vdW}}^- \) of equation (14). It turns out that \( E_p^0 \) makes up approximately ten percent of \( E_p \) in the physical case under consideration (\( v \approx 3 \)). This amounts to 0.01 eV (2). In short the main contribution to \( E_p \) for \( v \approx 3 \), when \( E_p \approx E_M \) in figure 5, comes from \( E_p^0 \) rather than from \( E_p^0 \). This shows that the weak coupling situation is preserved for intermediate couplings. For small \( v \) the leading contribution in \( E_p = E_{\text{ex}} - E_{\text{ex}}^1 + E_{\text{vdW}}^- \) comes from the on-chain term \( E_{\text{ex}} - E_{\text{ex}}^1 \). (2) \( E_p \) was calculated numerically in reference [11] and the obtained value agrees with the one mentioned above.

\((1)\) Details of this procedure are presented in Appendix B.
In addition the ratio \( E_{wV}/E_{wV}^0 \) was found to be a decreasing function of \( v \), becoming small for \( v > 0.01 \).

In spite of the above qualitative agreement between the perturbation theory results and the numerical result for \( v \approx 3 \), the detailed comparison shows that these results coincide only up to \( v \approx 0.1 \). This value of \( v \) corresponds to \( k_F \approx 2/\alpha \), the condition discussed in section 3. The discrepancy between the two kinds of results which occurs for \( v > 0.1 \) is to be attributed to the breakdown of the perturbation theory \([12]\), whereas the results for \( E_p \) can be trusted up to \( v \approx 4 \), according to the usual criterion for the validity of the Tomonaga model \([13]\). This criterion is obtained on requiring that the occupation number of the single particle state at the bottom of the band is of the order of unity in the Tomonaga ground state. The latter requirement is satisfied if

\[
\frac{(N\rho)^2}{4} \sum_{\rho > 0} \left\{ \left[ 1 + \rho \frac{V_{s,n}(q)}{2\epsilon_F} \right]^{1/2} + \left[ 1 + \rho \frac{V_{s,n}(q)}{2\epsilon_F} \right]^{-1/2} \right\} q^2 \frac{N\beta}{N^2} \tag{38}
\]

where \( N \) is the number of unit cells and \( \epsilon_F \) is the Fermi energy. After some simple algebra the inequality (38) transforms into

\[
\frac{2}{N\rho} \sum_{\rho > 0} \left\{ v_F^2 q + \frac{E_p}{N\rho} \epsilon_F \right\} v_F q + \frac{E_p}{N\rho} \epsilon_F \tag{39}
\]

A sufficient condition for the validity of the Tomonaga model is thus

\[
E_p \leq N\rho \epsilon_F \tag{40}
\]

With our values of the parameters \( a, b, c, \rho \) this amounts to \( v < 4 \), as stated above. It should be noted however that the Tomonaga model gives correctly the 4 \( k_F \) correlation function only up to \( v \approx 1/2 \) \([2]\).

In summary, the results of the perturbation calculation and the Tomonaga model coincide up to \( v \approx 0.1 \), while the Tomonaga model is internally consistent up to \( v \approx 4 \), when \( E_{M} \) and \( E_p \) are of the same order of magnitude.

### 6. Relative stability in the Tomonaga model

It was already mentioned in section 2 that the competition between the metallic VdW and the Madelung energy was regarded responsible for different stacking patterns of the TTF-TCNQ and HMTTF-TCNQ lattices \([1]\). Following this idea the Madelung energy loss \( \Delta E_{M} \) on going from the HMTTF-TCNQ to TTF-TCNQ lattice should be compensated with the corresponding gain \( \Delta E_p \) in the zero-point plasmon energy. This can be hardly expected since we have seen in the previous section that when \( E_p \approx E_m \) (for \( v = 3 \)) the interchain contribution \( E_p \) to \( E_p \) represents only about ten percent of \( E_p \). As a rule of thumb the change of \( E_p \) \( \Delta E_p \) should not then represent more than ten percent of the change in \( E_{me} \).

\[
\Delta E_p = \Delta E_{M} \text{ It will turn out now that } \Delta E_p \text{ is even smaller than that.}
\]

For the same reason as in the calculations of \( E_p \) we shall find \( \Delta E_p \) by numerical integration. The result is given in figure 6. It can be seen from this figure that the difference between \( \Delta E_{M} \) and \( -\Delta E_p \) is an increasing function of the interaction parameter \( v \). For \( v \approx 3 \) \( |\Delta E_p| \) is three orders of magnitude smaller than \( |\Delta E_{M}| \). Such energy difference \( |\Delta E_p| \) is smaller than \( E_p \), the interchain contribution to \( E_p \) by two orders of magnitude. This is surprising and in order to find the cause of such a strong cancelation we shall inspect closer the plasmon dispersion relations for the orthorhombic counterpart of both, TTF-TCNQ and HMTTF-TCNQ, lattices. For convenience we consider \((\omega_1 + \omega_2)^2 \) for a given wave vector \( q + q_L \)

\[
(\omega_1 + \omega_2)^2 \alpha \{ \nu_F^2 + \nu_F^2 + 2(\nu_F^2 + \nu_F^2) V_1(q, q_L) + [4 \nu_F^2 \nu_F^2 + 8 \nu_F^2 \nu_F^2 (\nu_F^2 + \nu_F^2) V_1(q, q_L) + + 16 \nu_F^2 \nu_F^2 (V_1(q, q_L) + V_2(q, q_L)) (V_1(q, q_L) - V_2(q, q_L))]^{1/2} \} \tag{41}
\]
Since the sum $V_1(q, q_1) + V_2(q, q_1)$ does not depend on the chain arrangement, the sign of the difference $V_2(q, q_1) - V_2(q, q_1')$ determines the sign of $\Delta E_p$. It follows from (A1) and (A2) that $V_2^{\text{H}} = V_2^{\text{L}}$ for $q_x = \pi/c$ and $V_2^{\text{H}} > V_2^{\text{L}}$ for $|q_x| < \pi/c$ and $q_x = \pm \pi/a$. The plausible assertion confirmed by numerical calculation is that $V_2^{\text{H}} > V_2^{\text{L}}$ for $|q_x| < \pi/c$. The energy associated with plasmons is larger for HMTTF-TCNQ (TTF-TCNQ) like structure in the outer (inner) part of the Brillouin zone (see Figs. 3 and 4). Although the outer part of the Brillouin zone along the c-axis dominates the final sum, in agreement with the perturbation argument [1], the partial cancellation of this effect by the contribution of the inner part of the Brillouin zone explains why $\Delta E_p$ is so much smaller than $E_p$ itself.

In order to check the validity of the point charge approximation we have divided the one electron density originally situated at the centres of the molecules in two channels separated by $d = 4$ Å in the c-direction. As a result $E_p$ and $\Delta E_p$ are increased by less than ten percent due to compensating effects similar to those described above. On the other hand the increase in $E_M$ with electron delocalization on the molecule [14] is much larger, since the point charge approximation overestimates the repulsive intrachain interactions. Such delocalization of the charge reinforces therefore $E_M$ with respect to $E_p$ in these crystals.

In short, in the Tomonaga model the metallic VdW interaction cannot be responsible for the different stacking patterns of TTF-TCNQ and HMTTF-TCNQ observed in the nature.

7. Concluding remarks.

The validity of the perturbation results for the cohesive energy of the charge transfer complexes has been examined here by comparison with the Tomonaga model, which can be solved accurately by the method of bosonization. It turned out that perturbation theory breaks down for the values of the coupling constant $v$ considerably smaller than unity and not (as was expected earlier [1]) of the order of unity. The departure is such that it rules out the explanation of the relative stability of the TTF-TCNQ vs. HMTTF-TCNQ structures by the band metallic model with long range forces. This opens once again the question of cohesion of the mixed stack organic metals.

It should be noted in this respect that the crystal fields in these materials, of the order of 1 V/Å [15], are remarkably large. Therefore they can affect the band structure considerably i.e. move the centres of the tight binding bands with respect to the energy levels of the free (ionized) molecules. This might increase the intra-molecular polarizability in the crystalline phase. The latter appears as inter-band polarizability in the band picture and was thus ignored here. The intra-molecular polarizabilities determined experimentally for some Bechgaard salts are indeed surprisingly large. Large intra-molecular polarizabilities result in the first place in the reduction of the effective $U$'s in the crystalline phase with respect to the disproportionation energies. This effect enters in the absolute cohesion of TTF-TCNQ and HMTTF-TCNQ. Moreover, the intra-molecular polarizabilities are involved into the relative cohesion of the mentioned materials. Actually the early explanations [16] of the stability of the TTF-TCNQ relative to the HMTTF-TCNQ structure were invoking the intramolecular rather than the metallic intrachain polarizabilities. The extension of the approach discussed here to include the intra-molecular polarizabilities in the form of inter-band processes therefore deserves further attention.

Acknowledgments.

It is a pleasure to thank S. Kilić and D. Hunjet for their assistance in the numerical work. The generous computing support of the Department of Civil Engineering, University of Split, and CIPRAG-INA-Projekt-Elektrotehna (Zagreb) is gratefully acknowledged. This work was partially supported by the YU-US collaboration project DOE 438.

Appendix A.

The matrix elements of equation (23) are given as double series which converge very poorly for a small value of the wave vector component parallel to the chain axis. Since we had to perform the numerical integration it was necessary to improve the convergence of these series. Using the symmetry arguments $V_2^{\text{L}}$ of equation (23) becomes

$$V_2^{\text{L}}(q, q_1) = \frac{2 e^2}{\pi} \sum_{m,n} \cos \left( m + \frac{1}{2} \right) a q_x \cos \left( n q_x \frac{c}{2} \right) K_0 \left\{ q \left[ \left( m + \frac{1}{2} \right)^2 a^2 + n^2 c^2 \right]^{1/2} \right\}.$$

Replacement of the summation over one direction of the direct space (e.g. along the c-axis) with a corresponding one in the reciprocal space [3] enables us to sum up over the other direction of the direct space (i.e. a-direction).
reducing in that way the double series to the single sum

\[ V'_1(q, q_a) = \frac{4 \alpha^2}{c} \sum_n \frac{1}{\left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2}} \frac{\sinh \frac{a}{2} \left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2} \cos \frac{aq_c}{2}}{\sinh^2 \frac{a}{2} \left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2} + \sin^2 \frac{aq_c}{2}}. \quad (A.1) \]

The resulting convergence is better than the original one. In the same way one obtains for the HMTTF-TCNQ structure:

\[ V'_2(q, q_a) = \frac{2 \alpha^2}{c} \sum_n \frac{1}{\left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2}} \frac{\sinh \frac{a}{2} \left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2} \cos \frac{aq_c}{2}}{\sinh^2 \frac{a}{2} \left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2} + \sin^2 \frac{aq_c}{2}} + \frac{2 \alpha^2}{a} \sum_n \frac{1}{\left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2}} \frac{\sinh \frac{c}{2} \left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2} \cos \frac{cq_a}{2}}{\sinh^2 \frac{c}{2} \left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2} + \sin^2 \frac{cq_a}{2}}. \quad (A.2) \]

The matrix elements \( V^{I, H}(q, q_a) \) are somewhat more intricate due to the on-chain contribution. The same procedure gives

\[ V'_1(q, q_a) = \frac{4 \alpha^2}{c} \sum_n \frac{1}{\left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2}} \left\{ \frac{\sinh \frac{a}{2} \left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2}}{\cosh \frac{a}{2} \left[ q^2 + \left( q_c + n \frac{4 \pi}{c} \right)^2 \right]^{1/2} - \cos \frac{aq_c}{2}} - 1 \right\} + \frac{2 \alpha^2}{\pi} C + \frac{2 \alpha^2}{\pi} \ln \frac{q_c}{8 \pi} + \frac{4 \alpha^2}{c(q^2 + q_a^2)^{1/2}} + 2 \alpha^2 \sum_{n=1}^{\infty} \frac{1}{\left[ \left( q_c \right)^2 + \left( 2 \pi n - q_c \right)^2 \right]^{1/2}} + \left( \frac{q_c}{c} \right)^2 + \left( 2 \pi n - q_c \right)^2 \right]^{1/2} \right]^{1/2} - \frac{1}{\left( \frac{q_c}{c} \right)^2 + \left( 2 \pi n - q_c \right)^2 \right]^{1/2} \right]^{1/2} \} - \frac{e^2 \alpha^2}{\pi} \ln 2(1 - \cos qb) + \frac{Ub}{a} \quad (A.3) \]

\[ V'_H(q, q_a) = \frac{\alpha^2}{a} \sum_n \frac{1}{\left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2}} \frac{\cos q_c - \exp \left\{ - c \left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2} \right\}}{\sinh^2 \frac{c}{2} \left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2} + \sin^2 \frac{q_c}{2}} + \frac{2 \alpha^2}{a} \sum_n \frac{(-1)^n}{\left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2}} \frac{\sinh \frac{c}{2} \left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2} \cos \frac{q_c}{2}}{\sinh^2 \frac{c}{2} \left[ q^2 + \left( q_a + \frac{4 \pi}{a} \right)^2 \right]^{1/2} + \sin^2 \frac{q_c}{2}} + \frac{2 \alpha^2}{\pi} C + \frac{2 \alpha^2}{\pi} \ln \frac{qa}{4 \pi} + \frac{2 \alpha^2}{b(q^2 + q_a^2)^{1/2}} + 2 \alpha^2 \sum_{n=1}^{\infty} \left( \frac{1}{\left( qa \right)^2 + \left( 2 \pi n - q_a \right)^2 \right]^{1/2}} + \left( \frac{qa}{c} \right)^2 + \left( 2 \pi n - q_a \right)^2 \right]^{1/2} \right]^{1/2} \right]^{1/2} - \frac{1}{\left( \frac{qa}{c} \right)^2 + \left( 2 \pi n - q_a \right)^2 \right]^{1/2} \right]^{1/2} \} - \frac{e^2 \alpha^2}{\pi} \ln 2(1 - \cos qb) + \frac{Ub}{a} \quad (A.4) \]
Here $C$ is Euler's constant. It follows from (A.1), (A.2), (A.3), and (A.4) that $V_1^{H}(q, q_j)$ and $V_2^{H}(q, q_j)$ are of the order of $e^2$ except in the long-wavelength limit, when all of them diverge like $1/(q^2 + q_j^2)$. Therefore the expansion of $\Delta E_p$ in a Taylor series is meaningful for $2e^2/\nu_F < 1$ (see (26)) i.e. $\nu < 1/4 \pi \approx 0.1$, in accordance with the numerically determined value in section 6.

Appendix B

The numerical integration of the plasmon energies $E_p$ for the TTF-TCNQ like lattice and the plasmon energy difference $\Delta E_p$ was performed using two routines. The first was based on the Gauss twelve point rule while the second one was D01FCE taken from the NAG Library Mark 8. The routines were used on different computers and obtained values differed by less than five percent. The results presented in this paper are those obtained by means of D01FCE routine since it gives a relative error.

By means of comparison of $E_{vaw}$ in (14) and $E_p'$ it is found that $C_1 \approx 2.15$ and $C_2 \approx 2.5$.

We put $U = e^2/2 b$, $t_F = 0.12$ eV, $t_Q/t_F = 3$, $a = 12.2 \text{ Å}$, $b = 3.73 \text{ Å}$, $c = 18.3 \text{ Å}$, and $\rho = 0.6$ in all numerical calculations.

References