

## SELF-CONSISTENT CRYSTAL POTENTIAL AND BAND STRUCTURE OF THREE-DIMENSIONAL TRANS-POLYACETYLENE

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**Résumé** — Nous avons calculé la structure des bandes à trois dimensions d'un cristal parfait de *trans*-polyacétylène en utilisant une technique self-consistante de pseudopotentiel. Nous avons obtenu la distribution de la densité de charge dans la cellule élémentaire. Nous trouvons que les propriétés à un électron sont extrêmement anisotropes dans le *trans*-polyacétylène. Nous suggérons que les interactions des solitons (ou <<kink>>) entre chaînes pourraient être assez faibles.

**Abstract** — We have calculated the three-dimensional band structure of ideally crystalline *trans*-polyacetylene using a self-consistent pseudopotential technique and have obtained the charge density distribution within the unit cell. We find *trans*-(CH)<sub>x</sub> to be highly anisotropic in its one-electron properties and therefore suggest that the interchain soliton/kink interactions might be quite weak.

**1. Introduction.**— Although much attention has been given the one-dimensional aspects of *trans*-polyacetylene, *trans*-(CH)<sub>x</sub>, notably in the area of topological excitations, *i.e.*, solitons or phase kinks[1], little has been done to investigate the magnitude of the interchain interaction. From an experimental point of view, the problem appears almost intractable given the high degree of disorder present in current samples of the material. One has then mainly to rely on computational results. For *cis*-(CH)<sub>x</sub>, Grant and Batra[2] were able to perform a first principles, three-dimensional, extended tight-binding band structure calculation on an idealized <<crystal structure>> obtained by Baughman, *et al.*[3], using packing analysis techniques. Until recently, on the other hand, even crude estimates of possible 3D crystal structures for *trans*-(CH)<sub>x</sub> were difficult due to the paucity of good x-ray data. However, Fincher, *et al.*[4], have now been able to obtain from oriented *trans*-(CH)<sub>x</sub> samples data of sufficient quality to permit estimating the unit cell parameters and symmetry, and the quantitative amount of bond alternation. Given these data, it is straightforward to determine the atomic positions to be used as input to a 3D calculation of *trans*-(CH)<sub>x</sub>. We have done such a calculation and report here our results for the interchain bandwidth and unit cell charge density distribution.

**Computational details.**— Our calculations were performed using a local density functional theory and the self-consistent pseudopotential method[5-8]. We employed non-local norm-conserving ionic pseudopotentials tabulated by Bachelet, *et al.*[8] All plane waves (PW) with kinetic energy up to 12 Ry (163 eV) (367 at  $\Gamma$ ) were treated exactly and another 125 PW's (KE up to 15 Ry (204 eV)) were included via Lowdin's perturbation scheme. During the self-consistency iterations electronic valence charge was sampled at 16 k-points in the irreducible part of the Brillouin zone. the iterations were continued until the mean square and maximum difference throughout the unit cell between the input and output potentials reached  $10^{-5}$  and  $10^{-2}$  Ry, ( $10^{-4}$  and  $10^{-1}$  eV) respectively. The total (pseudo) energy was evaluated using the expressions developed by Ihm, *et al.*[9] For the above parameters our calculated total pseudo-energy was -48.416 Ry (-658.46 eV) and the bandwidth 1.51 Ry (20.54 eV). We observe that our absolute total pseudo-energy is reasonable because the sum of pseudo-atomic energies is -47.54 Ry (-646.54 eV).[10] We studied the basis set size sensitivity of the calculated results by increasing the number of PW's to be treated via Lowdin's perturbation scheme to 420 (KE up to 20 Ry (272 eV)). Total energy now was

lowered to  $-49.130$  Ry ( $-668.17$  eV) but the bandwidth only increased by  $0.04$  Ry ( $0.544$  eV). Thus we seem to have reached convergence in one electron eigenvalues and probably in total energy (but this needs to be investigated further). Because the alternating bond length structure should provide the minimum ground state energy, we also performed a calculation for an undimerized chain in the same unit cell as above using the larger basis set but could not find any convincing increase in total pseudo-energy. This may be due to our lack of convergence in computational parameters or the arbitrary imposition of equal bond lengths within an unchanged unit cell. Therefore we focus here primarily on one electron properties postponing serious discussion about energetics to a future publication.

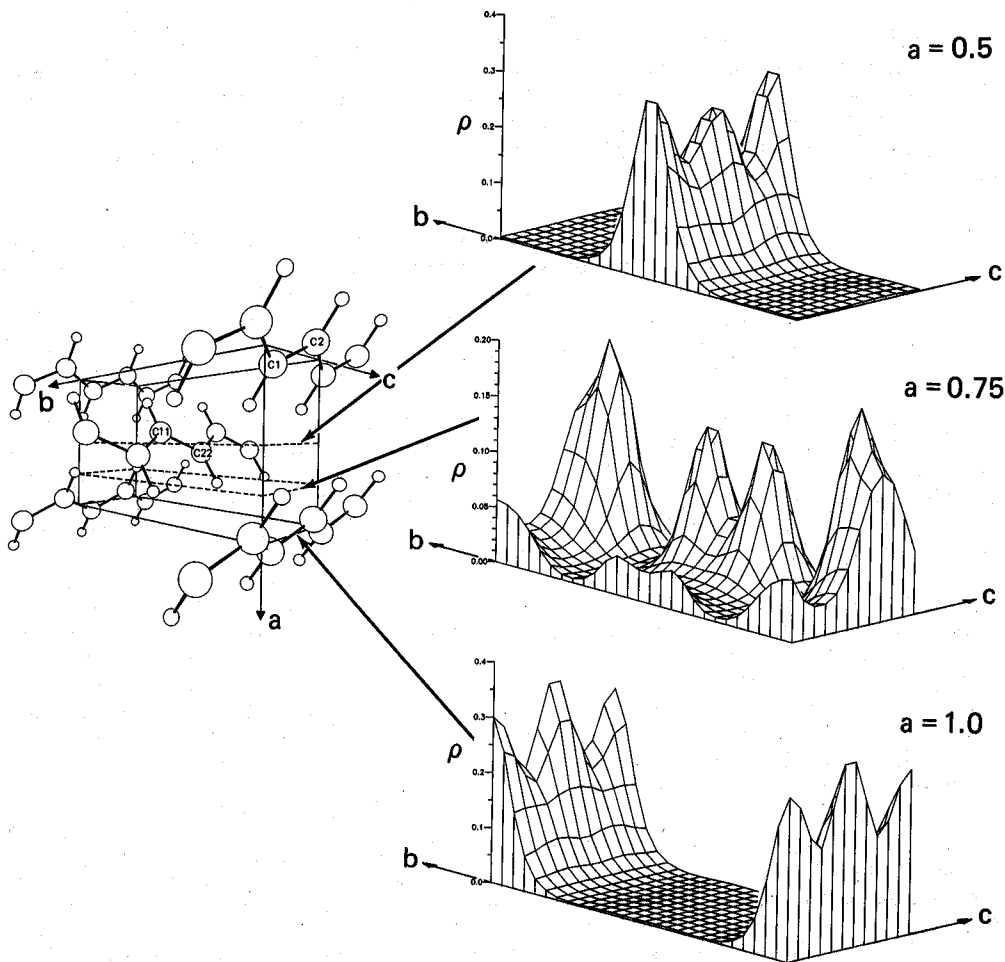


Fig. 1. Charge density surfaces on three sections perpendicular to the  $a$ -axis within the  $trans-(CH)_x$  unit cell. The units of charge density are au/unit cell.

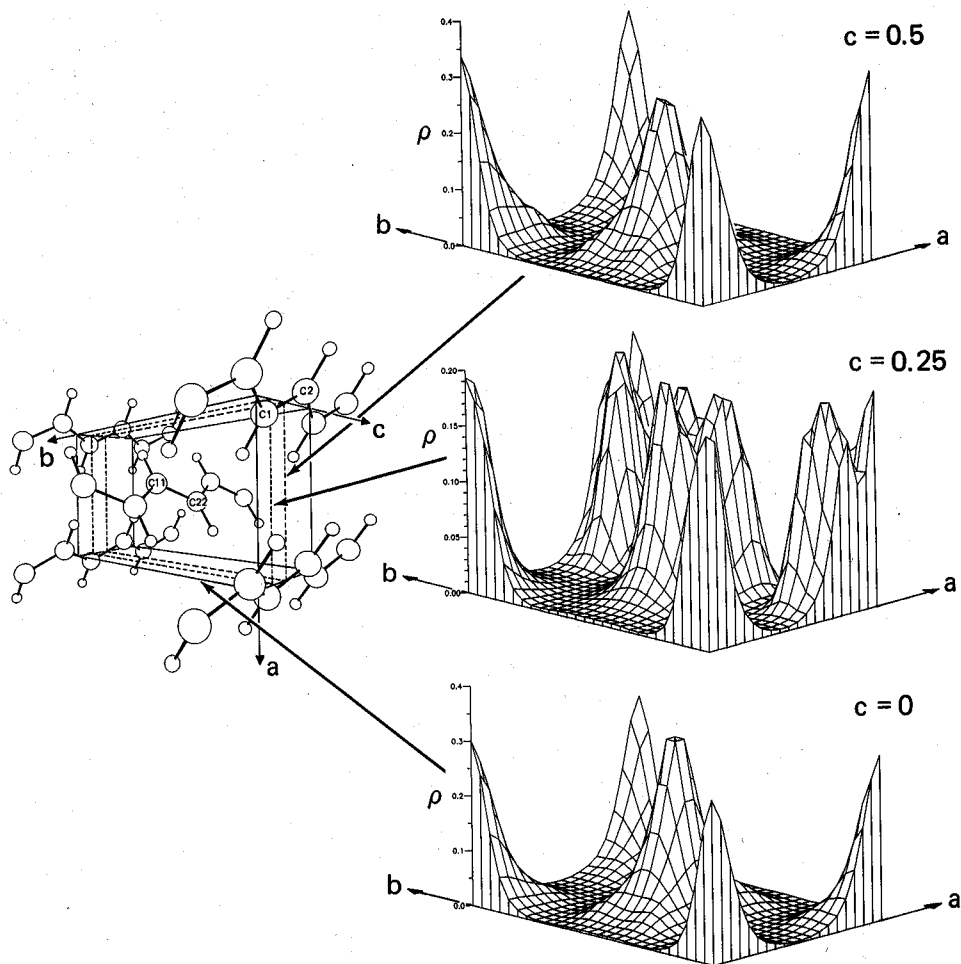


Fig. 2. Charge density surfaces on three sections perpendicular to the  $c$ -axis.

**Results and conclusions.**— Figures 1 and 2 show the charge density distribution in the  $\text{trans}(\text{CH})_x$  unit cell derived by solving Poisson's equation using the calculated self-consistent crystal potential. The effect of bond alternation is readily seen in the  $a = 1.0$  and  $a = 0.5$  sections as manifested by the unequal charge density peaks. Particularly significant is the very low level ( $< 0.01$  au/unit cell) of charge between chains suggesting good interchain isolation with weak interaction. This point is made especially clear in Fig. 2 which shows charge density sections down the  $c$ -axis which explicitly contain the regions between the C1-C2 and C11-C22 chains. One gets the qualitative feeling from Figs. 1 and 2 that neutral solitons or kinks moving down these two chains could pass each other rather easily with relatively little Coulomb interaction. Figure 3 contains the band structure of  $\text{trans}(\text{CH})_x$  plotted along its principal Brillouin zone directions. Note that the direct energy gap at D is only about 0.5 eV, whereas experiment places it near 1.4 eV[11]. This discrepancy arises from the fact that the local density functional exchange term,  $\rho^{1/3}$ , does not completely cancel the self-energy term of the Hartree potential, as would be the case for an exact Hartree-Fock calculation.

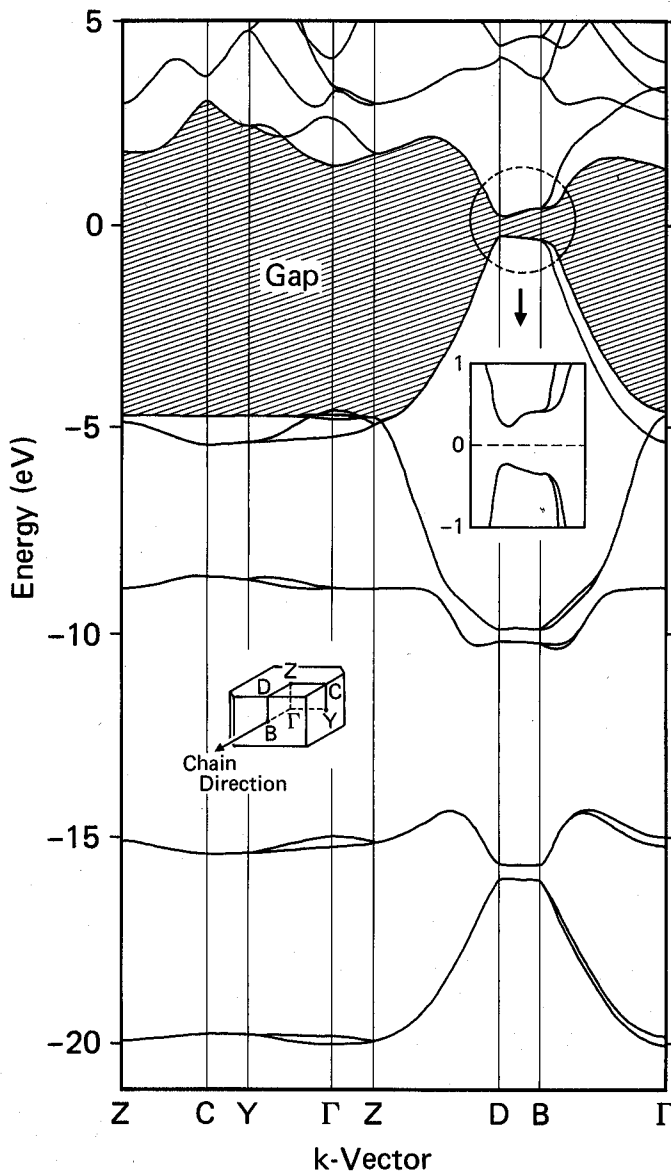


Fig. 3. Three-dimensional band structure and Brillouin zone of  $trans-(CH)_x$ . The inset shows details of the dispersion around the direct energy gap at D. The energy origin has been set at midgap.

However, the dispersion character of the bands is little affected by this problem. In a single-particle sense, Fig. 3 shows  $trans-(CH)_x$  to be very anisotropic. Taking the valence band dispersion along D-B (see Fig. 3 inset) as a measure of the interchain interaction, we find a bandwidth ( $4t_{\perp}$ )  $\approx$  100 meV implying a tight-binding transfer integral of around 25 meV. This leads to an anisotropy in the range 50-100 depending on how one defines the intrachain valence bandwidth. Thus,  $trans-(CH)_x$  is much more anisotropic than many other low-dimensional organic systems of current interest, in particular, the 2:1 Bechgaard salts of TMTSF which have anisotropies of order 10-20[12]. On the other hand, the magnitude of  $t_{\perp}$  in  $trans-(CH)_x$  is of the same order as found in these latter compounds. Only recently have the effects of interchain interaction in  $trans-(CH)_x$  begun to be considered theoretically, particularly regarding its influence on soliton/kink formation and propagation. Brazovskii, *et al.*[13], have derived a criterion on  $t_{\perp}$  in terms of soliton creation energy for the formation of a coherent 2D soliton/kink wall perpendicular to the chain axis which requires  $t_{\perp} \geq 2\Delta/\pi c$ , where  $2\Delta$  is the single-particle band gap and  $c$  a lattice geometric parameter of order unity. Using the experimental  $2\Delta = 1.4$  eV, we obtain  $\sim 450$  meV as the critical value for  $t_{\perp}$ . This hopping energy is considerably greater than our computed  $t_{\perp}$  and we would have to conclude that the existence of such a soliton/kink wall in  $trans-(CH)_x$  is unlikely. Jouanin and Albert[14] have investigated the effect of a finite interchain coupling on the density-of-states and found the expected suppression of the 1D band edge singularity as also seen by Grant and Batra[2] in their 3D *cis-(CH)\_x* calculation. The most thorough study to date on the effect of interchain interaction on soliton properties has been done by Baughman and Moss[15]. However, they approach the problem through a bond-specific interaction methodology which makes comparison with band theory difficult. They assume that interaction between solitons on neighboring chains will invariably lead to mutual annihilation via crosslinking, regardless of the degree of interchain coupling, in contrast to the model of Brazovskii, *et al.*[13], which would establish a coherent soliton wall for sufficiently strong interaction. Our charge density distribution results seen in Figs. 1-2 would suggest the soliton-soliton interaction energy to be very weak. More work is in progress to clarify the nature and conditions underlying soliton/kink interchain interactions.

**Acknowledgements.**— We are grateful to T. C. Clarke for several useful discussions. Nous faisons des remerciements à J. Voiron pour le résumé français.

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