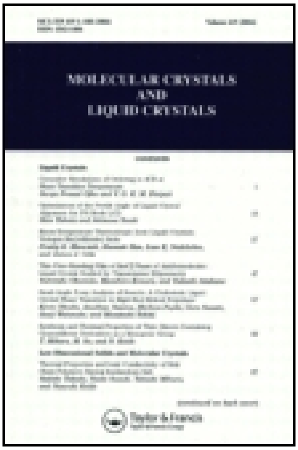

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Self-Consistent GÁspár-Kohn-Sham Electronic Structure of Dimerized Trans-Polyacetylene-Chain

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Version of record first published: 17 Oct 2011.

To cite this article: P. Kuivalainen , J. Von Boehm & J.-L. Calais (1985): Self-Consistent GÁspár-Kohn-Sham Electronic Structure of Dimerized Trans-Polyacetylene-Chain, Molecular Crystals and Liquid Crystals, 117:1, 197-200

To link to this article: http://dx.doi.org/10.1080/00268948508074623

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 197-204
0026-8941/85/1174-0197/$10.00/0

SELF-CONSISTENT GÁSPÁR-KOHN-SHAM ELECTRONIC STRUCTURE OF DIMERIZED TRANS-POLYACETYLENE-CHAIN

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Abstract The electronic structure of the dimerized trans-polyacetylene-chain is calculated with the self-consistent (SC) linear combination of atomic orbitals method using the Gáspár-Kohn-Sham-approximation for exchange and correlation. The SC gap 1.3 eV and the SC density of states agree closely with the experimental data.

INTRODUCTION

Recent interest in conducting polymers has also increased the efforts to understand the basic electronic structure of these materials. Thus far such knowledge has mainly been obtained theoretically by empirical or semiempirical methods which, however, suffer from the fundamental deficiency of containing adjustable parameters and various approximations giving sometimes unreliable results. Due to the omission of correlation effects the Hartree-Fock calculations, which have been applied to undoped polymers (see Ref. (1) and refs. therein), typically give also incorrect band structure for extended systems. On the other hand, the local approximation for exchange and correlation works surprisingly well in the solids. The purpose of this paper is to present the results of a self-consistent linear combination of atomic orbitals (SL-LCAO) calculation for a trans-polyacetylene $(CH)_x$ chain using the Gáspár-Kohn-Sham (GKS) potential[2] for exchange and correlation.

COMPUTATIONAL METHOD

The X_α-SC-LCAO-method has recently been applied to $(CH)_x$ by Mintmire and White[3] and by Grant and Batra[4] in the pseudopotential approximation. The method we have chosen differs from these two approaches to some extent. Our LCAO's are generated from atom centered s and p type Gaussians given in the paper of Ditchfield et al[5]. We neglect the long range Gaussians, which has been shown to be a good approximation[6]. The most essential feature of our SC-LCAO method is the division of the total electron density into two parts: $\rho(\vec r) = \rho_o(\vec r) + \Delta\rho(\vec r)$, where the fixed charge density $\rho_o(\vec r)$, which is a superposition of radial atomic charge densities, exactly compensates the charges of the nuclei and $\Delta\rho = \rho - \rho_o$ is a relatively smooth difference density whose total charge equals zero. The radial atomic densities are calculated from the atomic orbitals of Ditchfield et al[5]. in a logarithmic mesh consisting of about 80 points. $\Delta\rho(\vec r)$ is expanded as a Fourier series. The division of $\rho(\vec r)$ causes further a division of the effective crystal potential into two parts: $V(\vec r) = V_o(\vec r) + \Delta V(\vec r)$ where

$$V_o(\vec r) = \sum_{jm} V_o^j \left(|\vec r - \vec\tau_j - \vec R_m|\right) \qquad (1)$$

$$\Delta V(\vec r) = V(\vec r) - V_o(\vec r) = \sum_G \Delta V(\vec G)\, e^{-i\vec G.\vec r} \qquad (2)$$

Here j denotes the sum over all atoms, $\vec\tau_j$ is the position of the j th atom in the primitive unit cell $\vec R_m$, and $\vec G$ is the reciprocal lattice vector. The fixed Coulombic potentials in Eq. (1) are calculated numerically from the radial atomic charge densities using a 50 points Gaussian quadrature formula in the mesh mentioned above. The total radial atomic potentials were then accurately fitted to a Gaussian expansion. The Fourier coefficients of the Coulombic part of $\Delta V(\vec r)$ are updated during the SC iteration from Poisson's equation $\Delta V_c(\vec G) = 4\pi G^{-2}\Delta\rho(\vec G)$, where $\Delta\rho(\vec G)$ are the Fourier coefficients of $\Delta\rho(\vec r)$. The 343 exchange-correlation coefficients $\Delta V_{xc}(\vec G)$ and the 343 coefficients $\Delta\rho(\vec G)$ are calculated for every SC iteration cycle from $\rho(\vec r)$ and $o_o(\vec r)$ by integrating in a mesh of a $11 \times 11 \times 11 =$

1331 regularly spaced points of the primitive unit cell. Due to the non-linearity of the GKS potential we have to add a relatively smooth correction to $\Delta V_{xc}(\vec{r})$:

$$\Delta V_{GKS}(\vec{r}) = -\left[-\frac{3}{\pi}\sum_{jm}\rho_o^j(|\vec{r}-\vec{\tau}_j-\vec{R}_m|)\right]^{1/3}-\sum_{jm}\left\{-\left[-\frac{3}{\pi}\rho_o^j(|\vec{r}-\vec{\tau}_j-\vec{R}_m|)\right]^{1/3}\right\} \tag{3}$$

where ρ_o^j is the atomic charge density. This correction may, however, cause quite large shifts in energy, for example in copper about 30 eV[7]. The 343 Fourier coefficients $\Delta V_{GKS}(\vec{G})$ are computed in the above mesh of 1331 points.

Due to the combined Fourier and Gaussian representation the integration of all the matrix elements of the effective Schrödinger equation can be performed analytically. The advantage of our method is that it entirely avoids the multipole expansions (cf. Mintmire and White[3]) needed due to the long range of Coulombic potentials. Our method also gives the real charge densities instead of the pseudocharge densities of the pseudopotential method.

RESULTS AND DISCUSSION

The SC-LCAO band structure for the dimerized trans-$(CH)_x$ chain ($d_{C=C}$ = 1.35 Å, d_{c-c} = 1.46 Å, ∢ ccc = 120°, d_{c-H} = 1.09 Å, Ref.(8)) obtained using the GKS (α = 2/3) potential for exchange and correlation is shown in Figure 1. The minimum band gap E_g is direct and located at the boundary of the first Brillouin zone. The calculated value E_g = 1.27 eV agrees closely with the experimental value 1.4 eV[9]. It is well known that in the local density approximations the gap remains slightly smaller than the experimental one.

The calculated SC density of states (DOS) is shown in Fig. 2. The SC valence DOS has three main peaks located at -4 → -5, -8 → -9 and -18 → -19 eV. These compare favourably both with the SC LCAO valence DOS calculated by Mintmire and White[3] (peaks at -6, -10 and -17 eV) and with the X-ray photoemission spectrum of Brundle[10] (peaks at -6, -11 and -18 eV).

As a conclusion our SC LCAO approach using the GKS-approximation for exchange and correlation seems to be well suited to calculations of the basic electronic structure of the linear polymers. The method can in a straightforward manner be extended to the total energy calculations as well as to the calculation of the electronic structure of a polaron lattice.

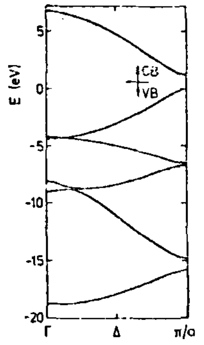

FIGURE 1. The SC LCAO band structure of the dimerized trans-polyacetylene chain. VB and CB denote valence and conduction bands, respectively.

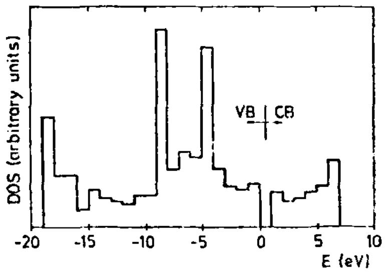

FIGURE 2. The SC LCAO density of states of the dimerized trans-polyacetylene chain. DOS denotes density of states.

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