

## Self-consistent linear-combination-of-Gaussian-orbitals approach for polymers: Application to *trans*-(CH)<sub>x</sub>

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A self-consistent linear-combination-of-Gaussian-orbitals (SCLCGO) method for calculating electronic properties of semiconducting crystalline polymers is presented. The method is based on the division of the electron density  $\rho$  into the sum  $\rho_0$  of spherically symmetric atom densities compensating the nuclear charges and the neutral deformation density  $\Delta\rho$ .  $\rho_0$  is expanded in terms of atom-centered Gaussians and  $\Delta\rho$  in terms of plane waves. This procedure avoids the multipole expansion, keeps the effective potential (in the local-density approximation) fully general, and allows the analytic calculation of the matrix elements between the LCGO's. The SCLCGO energy bands and  $\rho$  are presented for the dimerized all-*trans*-polyacetylene chain. Close agreement with optical and x-ray photoemission spectroscopy experiments is found. The results are also compared with those of other calculations.

### I. INTRODUCTION

Polymers are attracting extensive interest as a result of their unusual combination of electrical, magnetic, and optical properties under doping.<sup>1-8</sup> This has increased theoretical efforts to understand the basic electronic structure of crystalline polymers. Such knowledge has been obtained from both semiempirical and nonempirical calculations of restricted Hartree-Fock (RHF) type as well as from band calculations based on the local-density approximation. The traditional linear-combination-of-atomic-orbitals (LCAO) RHF approach of quantum chemistry suffers from describing the energy spectra of extended systems insufficiently because of the missing correlation. As a consequence, e.g., the RHF gaps are far too large. Although the local-density approximation improves the description of the combined exchange and correlation, there still remains the difficulty of representing the anisotropic bonding of crystalline polymers. Methods based on muffin-tin-type approximations [like the cellular, augmented-plane-wave (APW), and Korringa-Kohn-Rostoker (KKR) methods] are not expected to be suitable for this purpose. The orthogonalized-plane-wave (OPW) method is not expected to converge well because of the lack of *p* states in the atomic cores of light polymers. The pseudopotential (PSP) method suffers from using the pseudo-electron-density instead of the true electron density  $\rho$ .

The purpose of this paper is to present a self-consistent (SC) linear-combination-of-Gaussian-orbitals (LCGO) method for calculating the electronic structure of semiconducting crystalline polymers and to apply it to a

dimerized all-*trans*-polyacetylene chain, which is a much studied fundamental polymer system of wide interest. Our method is based on the exact division of  $\rho$  into the sum  $\rho_0$  of the spherically symmetric atomic densities compensating the nuclear charges and the neutral deformation density  $\Delta\rho$ .<sup>9,10</sup>  $\rho_0$  is expanded in terms of atom-centered Gaussians and  $\Delta\rho$  in terms of plane waves.

This procedure avoids the multipole expansion,<sup>11,12</sup> keeps  $\rho$  and the effective potential (in the local-density approximation) fully general, and allows the analytic calculation of the matrix elements between the LCGO's.

The format of this paper is as follows. The basic formalism is presented in Sec. II, the numerical methods are presented in Sec. III, the energy bands and  $\rho$  for the dimerized all-*trans*-polyacetylene chain are presented and analyzed in Sec. IV, and the conclusions are drawn in Sec. V.

### II. FORMALISM

The effective Schrödinger equation reads, in the local-density approximation,

$$H\Psi_{kn}(\mathbf{r}) = E_{kn}\Psi_{kn}(\mathbf{r}), \quad (1)$$

where the effective Hamiltonian  $H$  in Hartree atomic units is of the form

$$H = -\frac{1}{2}\nabla^2 + V_C[\rho(\mathbf{r})] + V_{xc}[\rho(\mathbf{r})]. \quad (2)$$

$V_C$  in Eq. (2) is the Coulombic potential

$$V_C = -\sum_{m,i} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_m - \boldsymbol{\tau}_i|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r', \quad (3)$$

where  $Z_i$  is the nuclear charge of the atom at site  $\tau_i$  of the primitive unit cell at  $\mathbf{R}_m$  and  $\rho$  is the electron density

$$\rho = 2 \sum_{k,n}^{\text{occ}} \Psi_{kn}^* \Psi_{kn} . \quad (4)$$

The Gáspar-Kohn-Sham exchange approximation<sup>13,14</sup> is used for the exchange-correlation potential  $V_{xc}$  in Eq. (2)

$$V_{xc} = - \left[ \frac{3\rho(\mathbf{r})}{\pi} \right]^{1/3} . \quad (5)$$

The main idea of the present method is to divide  $\rho$  exactly into two parts,<sup>9</sup>

$$\rho = \rho_0 + \Delta\rho . \quad (6)$$

The atomic density  $\rho_0$  in Eq. (6) consists of spherically symmetric atomic densities  $\rho_0^i$ :

$$\rho_0(\mathbf{r}) = \sum_{m,i} \rho_0^i(|\mathbf{r} - \mathbf{R}_m - \tau_i|) , \quad (7)$$

where the  $\rho_0^i$ 's compensate the nuclear charges

$$\int \rho_0^i(r) d^3r = Z_i . \quad (8)$$

$\rho_0$  is held fixed during the calculation. The deformation density  $\Delta\rho$  in Eq. (6) accounts for bonding.  $\Delta\rho$  is neutral,

$$\int \Delta\rho(\mathbf{r}) d^3r = 0 . \quad (9)$$

$\Delta\rho$  is relatively smooth and has the symmetry of the crystal. It is therefore convenient to expand  $\Delta\rho$  in terms of plane waves

$$\Delta\rho(\mathbf{r}) = \sum_{\mathbf{G}(\neq 0)} \Delta\rho(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}} , \quad (10)$$

where the  $\mathbf{G}$ 's are reciprocal-lattice vectors. The division of  $\rho$  [Eq. (6)] divides the crystal potential  $V = V_C + V_{xc}$  [Eqs. (2)–(5)] further into the corresponding parts

$$V = V_0 + \Delta V . \quad (11)$$

$V_0$  in Eq. (11) is produced by  $\rho_0$  and is of the form

$$V_0(\mathbf{r}) = V_{0,C}(\mathbf{r}) + V_{0,xc}(\mathbf{r}) = \sum_{m,i} V_0^i(|\mathbf{r} - \mathbf{R}_m - \tau_i|) , \quad (12)$$

where

$$V_0^i(r) = V_{0,C}^i(r) + V_{0,xc}^i(r) \quad (13)$$

and

$$V_{0,C}^i(r) = -\frac{Z_i}{r} + 4\pi \left[ \frac{1}{r} \int_0^r (r')^2 \rho_0^i(r') dr' + \int_r^\infty r' \rho_0^i(r') dr' \right] , \quad (14)$$

$$V_{0,xc}^i(r) = - \left[ \frac{3\rho_0^i(r)}{\pi} \right]^{1/3} . \quad (15)$$

$\Delta V = \Delta V_C + \Delta V_{xc}$  in Eq. (11) is produced by  $\Delta\rho$ ,

$$\Delta V_C(\mathbf{r}) = \int \frac{\Delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \quad (16)$$

and

$$\Delta V_{xc}(\mathbf{r}) = V_{xc}[\rho(\mathbf{r})] - V_{0,xc}(\mathbf{r}) . \quad (17)$$

The relatively smooth  $\Delta V$  [Eq. (11)] having the symmetry of the crystal is expanded in terms of plane waves:

$$\Delta V_C(\mathbf{r}) = \sum_{\mathbf{G}} \Delta V_C(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}} , \quad (18)$$

$$\Delta V_{xc}(\mathbf{r}) = \sum_{\mathbf{G}} \Delta V_{xc}(\mathbf{G}) e^{-i\mathbf{G}\cdot\mathbf{r}} . \quad (19)$$

The Fourier coefficients  $\Delta V_C(\mathbf{G})$  in Eq. (18) are obtained for  $\mathbf{G} \neq \mathbf{0}$  via Poisson's equation,

$$\Delta V_C(\mathbf{G}) = \frac{4\pi}{G^2} \Delta\rho(\mathbf{G}) , \quad \mathbf{G} \neq \mathbf{0} . \quad (20)$$

For  $\Delta V_C(\mathbf{G} = \mathbf{0})$  we use the approximation<sup>15</sup>

$$\Delta V_C(\mathbf{G} = \mathbf{0}) = -\frac{2\pi}{3\Omega_0} \int_{\Omega_0} \Delta\rho(\mathbf{r}) r^2 dr , \quad (21)$$

where  $\Omega_0$  is the volume of the primitive unit cell. The Fourier coefficients  $\Delta\rho(\mathbf{G})$  [Eq. (10)] and  $\Delta V_{xc}(\mathbf{G})$  [Eq. (19)] are calculated from the respective  $\Delta\rho(\mathbf{r})$  and  $\Delta V_{xc}(\mathbf{r})$  values in a fine regular mesh of the primitive unit cell as will be discussed in more detail below.

The rapidly varying parts  $V_0^i$  [Eqs. (12)–(15)] of  $V$  around the atom sites are expanded in terms of Gaussians:

$$V_0^i(r) = -\frac{Z_i}{r} e^{-\alpha_1 r^2} + \sum_{j=2}^N c_j e^{-\alpha_j r^2} . \quad (22)$$

In this way  $V$  contains only terms of the form  $e^{-i\mathbf{G}\cdot\mathbf{r}}$ ,  $r^{-1}e^{-\alpha r^2}$ , and  $e^{-\alpha r^2}$  and therefore the matrix elements between Gaussian orbitals can be calculated analytically as will be discussed in more detail below. [One could also include Gaussians of the form  $r^2 e^{-\alpha r^2}$  in Eq. (22)].

The basis Bloch functions are of the form

$$\phi_{ki}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_m e^{i\mathbf{k}\cdot\mathbf{R}_m} \chi_i(\mathbf{r} - \mathbf{R}_m - \tau_i) , \quad (23)$$

where  $N$  is the number of the primitive unit cells in the region defined by the periodic boundary conditions and  $\chi_i$  is an atomic basis functions expressed further in terms of Gaussian orbitals:

$$\chi_i(\mathbf{r} - \tau_i) = \sum_{s=1}^N a_s^i G(\beta_s^i, l_s^i, m_s^i, n_s^i, \tau_i) , \quad (24)$$

$$G(\beta, l, m, n, \tau) = (x - \tau_x)^l (y - \tau_y)^m (z - \tau_z)^n e^{-\beta(r - \tau)^2} . \quad (25)$$

The eigenfunctions of Eq. (1) are expanded in terms of  $\phi_{ki}$ :

$$\Psi_{kn} = \sum_i \phi_{ki} c_{kni} . \quad (26)$$

The use of the Rayleigh-Ritz variational principle gives the matrix eigenvalue equation

$$\underline{H}_{k\mathbf{C}} \underline{C}_{kn} = E_{kn} \underline{\Delta}_{k\mathbf{C}} \underline{C}_{kn} , \quad (27)$$

where the column matrices  $\underline{C}_{kn}$  contain the coefficients  $c_{kni}$ ,

$$H_{\mathbf{k},ij} = \sum_m e^{i\mathbf{k}\cdot\mathbf{R}_m} H_{ij}(\mathbf{R}_m), \quad (28)$$

$$\Delta_{\mathbf{k},ij} = \sum_m e^{i\mathbf{k}\cdot\mathbf{R}_m} \Delta_{ij}(\mathbf{R}_m), \quad (29)$$

and

$$H_{ij}(\mathbf{R}_m) = \langle \chi_i(\mathbf{r}-\tau_i) | H \chi_j(\mathbf{r}-\mathbf{R}_m-\tau_j) \rangle, \quad (30)$$

$$\Delta_{ij}(\mathbf{R}_m) = \langle \chi_i(\mathbf{r}-\tau_i) | \chi_j(\mathbf{r}-\mathbf{R}_m-\tau_j) \rangle. \quad (31)$$

$H_{ij}(\mathbf{R}_m)$  is the sum of its parts:

$$H_{ij}(\mathbf{R}_m) = T_{ij}(\mathbf{R}_m) + V_{0,ij}(\mathbf{R}_m) + \Delta V_{C,ij}(\mathbf{R}_m) + \Delta V_{xc,ij}(\mathbf{R}_m), \quad (32)$$

where  $T$  denotes  $-\frac{1}{2}\nabla^2$ . Since the atomic basis functions  $\chi_i$  are expressed in terms of Gaussian orbitals [Eq. (24)] the calculation of the matrix elements in Eqs. (30)–(32) reduces to the calculation of the matrix elements between Gaussian orbitals of the form  $\langle G(i) | G(j) \rangle$ ,  $\langle G(i) | -\frac{1}{2}\nabla^2 G(j) \rangle$ ,  $\langle G(i) | G(k)G(j) \rangle$ ,  $\langle G(i) | r_k^{-1}G(k)G(j) \rangle$ , and  $\langle G(i) | e^{-i\mathbf{G}\cdot\mathbf{r}}G(j) \rangle$ . The analytic expressions for these matrix elements as well as their detailed derivations are given in Ref. 16 and will not be reproduced here.

In the self-consistent iteration the solution of the eigenvalue equation (27) gives a new  $\rho$  [Eqs. (4) and (6)] and thus a new  $V$  [Eqs. (11), (17)–(21)] that gives again a new eigenvalue equation to be solved. The matrix elements between the  $\chi_i$ 's as well as the fixed  $\rho_0$  and  $V_0$  [Eqs. (7) and (22)] must be calculated only at the beginning. Only the Fourier coefficients  $\Delta V_C(\mathbf{G})$  and  $\Delta V_{xc}(\mathbf{G})$  [Eqs. (18) and (19)] vary during the iteration. The iteration may be started by assuming that  $\rho = \rho_0$  (as we did).

### III. NUMERICAL METHODS

The carbon  $1s$ ,  $2s$ ,  $2p_x$ ,  $2p_y$ ,  $2p_z$ , and hydrogen  $1s$  atomic orbitals from Ref. 17 were used as the atomic basis functions  $\chi_i$ . They are given in Table I in terms of the Gaussian orbitals [see Eqs. (24) and (25)]. The long-range Gaussian orbitals were neglected because they contribute little to a band calculation for a crystal, cause extensive overlap and may cause linear dependences in the basis function set.<sup>18</sup> The  $\rho_0^i$ 's in Eq. (7) were calculated from the atomic basis functions  $\chi_i$  (Table I) in a logarithmic mesh consisting of about 80 points. The corresponding spherically symmetric potentials  $V_0^i$  were calculated with the 50 points Gaussian quadrature formula in the same mesh [see Eqs. (12)–(15)]. The  $V_0^i$ 's were then fitted to the Gaussian expansion (22) using Hartley's method.<sup>19</sup> The resulting parameters are given in Table II. The error

$$\left[ \sum_{j=1}^N (V_{0j}^{\text{fit}} - V_{0j})^2 / (N^2 - N) \right]^{1/2}$$

of the fit was 0.0018 for C and 0.00046 for H.

The  $7^3 = 343$  Fourier coefficients  $\Delta\rho(\mathbf{G})$  for  $\Delta V_C(\mathbf{G})$  [Eqs. (10) and (20)] were calculated from  $\rho(\mathbf{r})$  and (the fixed)  $\rho_0$  using a regular mesh of  $11^3 = 1331$   $\mathbf{r}_{ijk}$  points of the primitive unit cell with the equation

TABLE I. The atomic basis functions  $\chi_i$  (Ref. 17).  $a$  and  $\beta$  denote the expansion coefficients and exponents of the Gaussians, respectively [see Eqs. (24) and (25)].

$\chi_i$	$a$	$\beta$
C $1s$	1.309 607 06	$4.869\,669 \times 10^2$
	2.206 190 73	$7.337\,109 \times 10^1$
	2.521 594 37	$1.641\,346 \times 10^1$
	1.204 354 22	4.344 984
C $2s$	−0.437 237 286	8.673 525
	−0.282 307 698	2.096 619
	0.579 189 861	$6.046\,513 \times 10^{-1}$
C $2p$	1.348 244 37	8.673 525
	1.072 619 91	2.096 619
	0.579 208 747	$6.046\,513 \times 10^{-1}$
H $1s$	0.163 506 877	$1.300\,773 \times 10^1$
	0.277 338 720	1.962 079
	0.315 740 334	$4.445\,290 \times 10^{-1}$

$$\begin{aligned} \Delta\rho(\mathbf{G}) &= \frac{1}{\Omega_0} \int_{\Omega_0} [\rho(\mathbf{r}) - \rho_0(\mathbf{r})] e^{i\mathbf{G}\cdot\mathbf{r}} d^3\mathbf{r} \\ &\approx \frac{1}{1331} \sum_{i=1}^{11} \sum_{j=1}^{11} \sum_{k=1}^{11} [\rho(\mathbf{r}_{ijk}) - \rho_0(\mathbf{r}_{ijk})] e^{i\mathbf{G}\cdot\mathbf{r}_{ijk}}, \end{aligned} \quad (33)$$

where

$$\mathbf{G}\cdot\mathbf{r}_{ijk} = 2\pi \left[ \frac{i}{11}n_1 + \frac{j}{11}n_2 + \frac{k}{11}n_3 \right] \quad (34)$$

and  $n_1$ ,  $n_2$ , and  $n_3$  are the components of  $\mathbf{G}$ . The 343 coefficients  $\Delta V_{xc}(\mathbf{G})$  [Eq. (19)] were calculated in the same way.

The eigenvalue equation (27) was solved with the Cholesky decomposition, Householder tridiagonalization–bisection–inverse-iteration method<sup>20</sup> at ten regularly spaced  $\mathbf{k}$  vectors of the one-dimensional Brillouin zone. The electron density  $\rho$  [Eq. (4)] was calculated with a sum over these  $\mathbf{k}$  vectors weighted with the nearest volumes in the Brillouin zone.

The convergence was improved by mixing 70% of the previous  $\Delta V_C(\mathbf{G})$  and  $\Delta V_{xc}(\mathbf{G})$  coefficients into the new ones. The neutrality condition (9) was fulfilled with the

TABLE II. The coefficients of the Gaussian expansion for the  $V_0^i$ 's.  $c_j$  and  $\alpha_j$  denote the expansion coefficients and the exponents of the Gaussians, respectively [Eq. (22)].

Atom	$j$	$c_j$	$\alpha_j$
C	1	$Z_C = 6$	1.391 585
	2	2.363 669	28.341 33
	3	3.216 698	6.627 048
	4	5.395 517	2.203 240
	5	0.968 2283	1.040 296
	6	−1.090 826	0.378 1194
H	1	$Z_H = 1$	0.228 747
	2	0.450 533	0.791 728
	3	0.105 379	0.251 564

accuracy  $\Delta\rho(\mathbf{G}=0)=0.006$  that should be compared with the number of ten valence electrons in the primitive unit cell. Typically five to ten iteration cycles were needed for a practically full convergence.

#### IV. RESULTS AND DISCUSSION

*Trans*-polyacetylene [*trans*-(CH)<sub>x</sub>] consists of weakly coupled chains of CH units forming a quasi-one-dimensional lattice. Due to the Peierls instability<sup>21</sup> *trans*-(CH)<sub>x</sub> is expected to dimerize. The dimerization (C—C bond alternation) was recently confirmed experimentally.<sup>22</sup> In this paper we consider electronic properties of a single dimerized *trans*-(CH)<sub>x</sub> chain the structure of which is shown in Fig. 1.<sup>23</sup> The dimensions of the primitive unit cell in the *y*- and *z* directions,  $b=12a_0$  and  $c=8a_0$  ( $a_0$  is the Bohr radius  $\cong 0.529$  Å), respectively, were chosen so large that the chains are essentially noninteracting.

Our calculated SCLCGO band structure is shown in Fig. 2 and the key quantities are compared with the other calculations using local-density approximations<sup>13,14,24,25</sup> in Table III.<sup>11,12,26–34</sup> The five averaged valence bands (VB1–VB5) of the three-dimensional SC bands<sup>32,33</sup> from  $\Gamma$  along the chain direction are used in Table III (columns 9 and 10).<sup>35</sup>

The second and third columns of Table III show the effect of the self-consistency in our bands. The valence bands VB2–VB4 (see Fig. 2) undergo a considerable change under the SC iteration which also affects the density of states significantly (see below). Our bands agree most closely with the “weakly alternating” bands of Grant and Batra (fourth columns in Table III). Our uppermost valence band (VB5) agrees closely with those of the other SC calculations with  $u_0=0.03$  Å (columns 7 and 9–11 in Table III) whereas there are considerable differences in the lower valence bands.

According to the orbital analysis of our eigenfunctions  $\Psi_{kn}$  the uppermost valence band (VB5) and the lowest conduction band (CB1) are pure bonding and antibonding carbon  $2p_z$  bands, respectively. The total width of these bands—measuring the delocalization and mobility in the chain—is 11 eV in close agreement with the corresponding widths in Refs. 12, 28, and 29. Our minimum optical

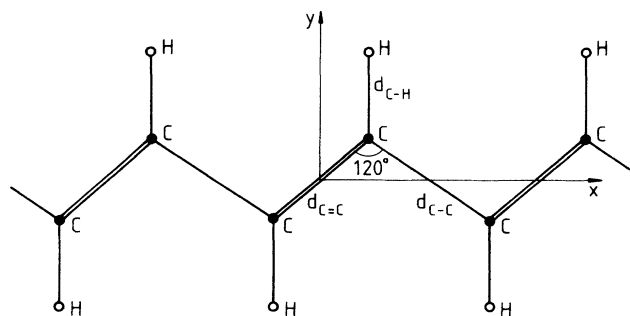


FIG. 1. The structure of the dimerized *trans*-polyacetylene chain. The closed and open circles denote the carbon and hydrogen atoms, respectively. The structure parameters  $d_{C=C}=1.35$  Å,  $d_{C-C}=1.46$  Å,  $\angle(C-C-C)=120^\circ$ , and  $d_{C-H}=1.09$  Å are taken from the paper of Good *et al.* (Ref. 23).

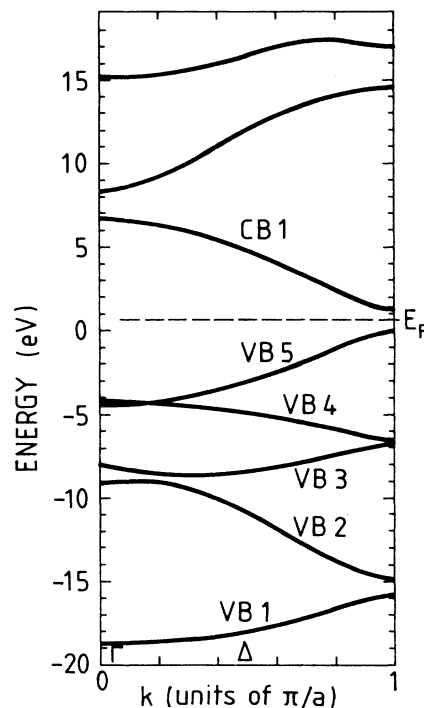


FIG. 2. The SCLCGO band structure of the dimerized *trans*-polyacetylene chain. VB1–VB5 denote the five valence bands, CB1 denotes the lowest conduction band, and  $E_F$  denotes the Fermi level.

gap (the dimerization gap) of 1.3 eV agrees within  $\pm 0.5$  eV with the other gaps calculated at the same degree of dimerization  $u_0 \approx 0.03$  Å (Table III). Our gap is in good accordance with the experimental gap of 1.7–1.8 eV for a single isolated dimerized chain.<sup>36</sup> The somewhat smaller value of our gap is consistent with the fact that the local-density approximation for the exchange and correlation tends to underestimate the gap.

Our SCLCGO density of states (DOS) is presented in Fig. 3. The effect of the self-consistency on the DOS is as follows: the peaks at 7,  $-5$  (with a deep valley),  $-12$ ,  $-17$ , and  $-19$  eV of the non-SCDOS<sup>27</sup> become the peaks at 6,  $-5$  (without a valley),  $-9$ , and  $-19$  eV of the SCDOS. Our DOS resembles most the weakly alternating DOS of Grant and Batra.<sup>28,29</sup>

The positions of the peaks of our DOS agree closely with those of the SCDOS of Mintmire and White<sup>11,12</sup> (6,  $-6$ ,  $-10$ , and  $-17$  eV) but the heights of our peaks decrease less for decreasing energy due to the different grouping of the valence bands. Our DOS also agrees closely with the SC three-dimensional DOS by Ashkenazi *et al.*<sup>33</sup> except that their peaks at  $-5$  and  $-10$  eV contain deep valleys. Figure 3 shows the close agreement of our DOS with the experimental x-ray photoemission (XPS) spectrum of Brundle.<sup>37</sup> Even the shoulder at  $-1$  eV, the small intermediate peak at  $-7$  eV and the shoulder at  $-14$  eV of the XPS spectrum can be found in our DOS.

Our SCLCGO electron density  $\rho$  and the non-SC density  $\rho_0$  are shown in Fig. 4 along the *x* axis of the chain (see

TABLE III. The key quantities of the calculations using the local-density approximation for exchange and correlation for *trans*-(CH) $_x$ .  $\alpha = \frac{2}{3}$ , 1, and BH denote the Gaspar-Kohn-Sham, Slater, and von Barth-Hedin approximations, respectively (Refs. 13, 14, 24, and 25). The structure parameters  $d_{C=C}$ ,  $d_{C-H}$  and  $\angle(C-C-C)$  are explained in Fig. 1.  $\alpha$  denotes the dimension of the primitive unit cell along the chain axis and  $u_0$  measures the degree of the dimerization (see Refs. 3 and 5). VB1-VB5,  $E_g$ , and CBI denote the five valence bands, the fundamental gap, and lowest conduction band, respectively. The energies are given in units eV.

Property	Present Study and Ref. 26	Ref. 27	Refs. 28 and 29	Refs. 28 and 29	Refs. 11 and 12	Refs. 11 and 12	Refs. 30 and 31	Ref. 32	Ref. 33	Ref. 34
$\alpha$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	1			
Dimensionality	1	1	1	1	1	1	1			1
Self-consistency	SC	non-SC	non-SC	non-SC	SC	SC	non-SC	SC	SC	SC
$d_{C=C}$ (Å)	1.35	1.35	1.36	1.34	1.377	1.35	1.34			1.35
$d_{C-C}$ (Å)	1.46	1.46	1.43	1.54	1.54	1.46	1.46			1.46
$d_{C-H}$ (Å)	1.09	1.09			1.08	1.08	1.09			1.09
$\angle(C-C-C)$	120°	120°			120°	120°	125°			120°
$a$ (Å)	2.43	2.43			2.435	2.435	2.48	2.46		2.43
$u_0$ (Å)	0.03	0.03			0.02	0.03	0.03	0.03		0.03
VB1	2.8	2.8	3.2			3.8		3.9		3.4
Gap VB1→VB2	1.0	0.4	1.0	3.0		1.3		3.7		0.8
VB2	5.8	0.7	5.7	4.4		2.6		1.3		3.5
Gap VB2→VB3	0.3	4.1	0.4	0.6		0.8		4.0		1.2
VB3 + VB4 + VB5	8.7	12.0	8.9	8.0		8.3		9.9		9.4
VB5	4.3	4.5	4.4	3.8		4.4		4.6		5.0
$E_g$	1.3	1.6	0.8	2.3	0.6	1	1.6	0.8		1.7
CBI	5.3	5.5	5.8	4.4		4.6				1.1

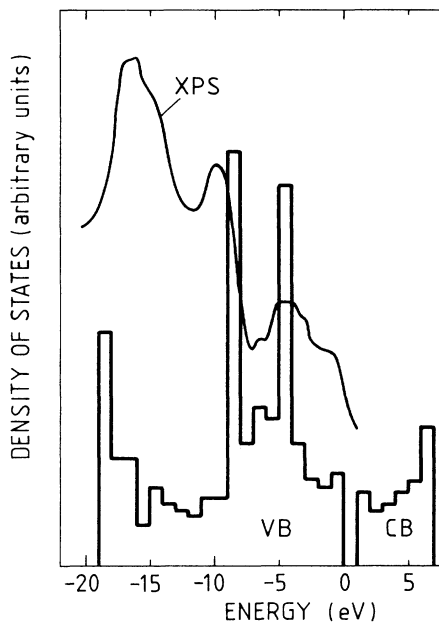


FIG. 3. The SCLCGO density of states (DOS) of the dimerized *trans*-polyacetylene chain. The thick and thin lines represent the SCLCGO DOS and the experimental x-ray photoemission spectrum of Brundle (Ref. 37), respectively.

Fig. 1). The maximum at  $x \approx 1.0a_0$  is due to the close location of a C atom (see Fig. 1). The electron density changes from  $\rho_0$  to  $\rho$  in the formation of bonding. The electron density increases everywhere on the  $x$  axis (Fig. 4). The maximum increase occurs in the middle of the double C=C bond where the density more than doubles.

Our  $\rho$  is qualitatively similar to the contour plot of the density of Kasowski *et al.*<sup>31</sup> Our  $\rho$  (Fig. 4) agrees closely

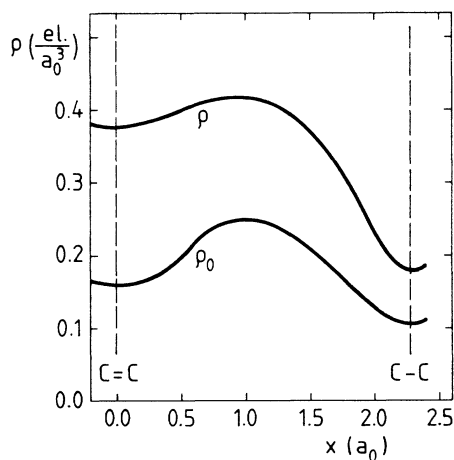


FIG. 4. The SCLCGO electron density  $\rho$  along the  $x$  axis of the *trans*-polyacetylene chain. Also the non-SCLCGO density  $\rho_0$  is shown. The densities are given in the units electrons/ $a_0^3$ .

with the (continued) density  $\bar{\rho}$  of Springborg:<sup>34</sup> the densities are in the middle of the C=C bond twice as large as in the middle of the (single) C—C bond and the densities have a maximum at the closest point to the near C atom. Our  $\rho$  differs somewhat from the (three-dimensional) SC pseudopotential (PSP) density of Grant and Batra.<sup>32</sup> The PSP density is in the middle of the C=C bond only 1.1 times as large as in the middle of the C—C bond and in place of the maximum of our  $\rho$  at  $x \approx 1.0a_0$  (Fig. 4) the PSP density has a minimum. These differences may be due to the fact that the PSP density has a tendency to vary too slowly.<sup>38</sup>

The Hartree-Fock (HF) calculations for the isolated *trans*-(CH)<sub>x</sub> chain<sup>39–47</sup> result in band structures that are significantly broader than those obtained using the local-density approximation for exchange and correlation (Table III) or the experimental band structures. For example, the widths of the HF valence bands<sup>39,40,43,46</sup> are about 2–14 eV broader than the widths of the valence bands obtained with the local-density approximation (Table III) and about 7–12 eV broader than the width of the XPS spectrum of Brundle.<sup>37</sup> Specifically, the fundamental HF energy gaps<sup>39–42,44,45,47</sup> of 6–10 eV are much larger than the gap of 1–2 eV obtained with the local-density approximation (Table III) and the experimental gap of 1.7–1.8 eV.<sup>36</sup> The necessary correlation correction to the HF gap has been elaborated by Suhai.<sup>48,49</sup> He found that inclusion of the full correlation corrects the gap down to  $\sim 2.5$  eV which is still  $\sim 0.7$  eV higher than the experimental value.<sup>49</sup>

## V. CONCLUSIONS

We have developed a self-consistent linear-combination-of-Gaussian orbitals method for calculating the electronic properties of semiconducting crystalline polymers. Our method (using the local-density approximation for exchange and correlation) is based on the exact division of the electron density  $\rho$  into the sum  $\rho_0$  of spherically symmetric atom densities compensating exactly the nuclear charges and the neutral deformation density  $\Delta\rho$ . The fixed  $\rho_0$  is expanded in terms of atom-centered Gaussians and the relatively smooth  $\Delta\rho$  in terms of plane waves. Our method has the following advantages: (1) the electron density and the effective potential (in the local-density approximation) can be kept fully general, (2) the matrix elements between the basis functions can be calculated analytically and (3) the multipole expansion is avoided. We feel that the last point is quite essential because the LCAO results are sensitive to the truncation errors in the multipole expansion. The method is not limited to polymers but can be applied to any light periodic crystals. The method can be straightforwardly extended to the calculation of the total energy, optical response, etc.

We have applied our method to the dimerized *trans*-polyacetylene chain. The band structure and the electron density are presented for this system. Our energy spectrum (the fundamental gap and the density of states) agrees closely with the experimental spectra. Our bands

agree quite closely with the other calculations in the region of the fundamental gap whereas our lower valence bands show considerable differences as compared with the corresponding bands of the other calculations. According to our self-consistent density (when compared with the non-self-consistent atomic density) the electron density grows everywhere on the chain axis in the formation of bonding the maximum pileup being in the middle of the double C=C bond.

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