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Modifying polyacetylene

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Abstract

Using a parameter-free density-functional method for infinite, periodic, isolated, helical chains, we study the electronic and structural properties of polyacetylene and various modifications of this conjugated polymer. First, we study the bond-length alternation and how the properties of the material are changed upon different substitutions. Subsequently, structural defects (solitons) are studied, and it is shown how model parameters can be extracted from the calculations. Finally, charged chains and the effects of external electrostatic fields are discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Nobel Prize in Chemistry 2000 was awarded to Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa for the work that in some sense defined the beginning of the research in the materials often called synthetic metals [1-3]. These materials combine mechanical properties as those of ordinary plastics with electronic properties as conventional semiconductors. This combination makes them interesting materials for special-purpose applications, where soft semiconductor devices that can be given any desirable shape are sought and they have been the subject of an intensive research activity during the last two decades (see, e.g. Refs. [4-7] and references therein).

In the original work [1-3], MacDiarmid, Heeger, and Shirakawa together with their co-workers found that *trans* polyacetylene could increase its macroscopic electrical conductivity upon doping by more

than 11 orders of magnitude. In the meantime, even larger increases have been obtained and similar behaviors (both in regard to the doping-induced increase in conductivity and in regard to other electronic properties) have been found for other related materials. In more recent years, parts of the interest in those materials is due to their large linear and, in particular, non-linear responses to external electromagnetic field.

In order to obtain a detailed understanding of these properties, one encounters the fundamental problem that a macroscopic sample is rather ill defined. A typical sample contains a more or less random distribution of tubes that more resembles a bowl of spaghetti. Each tube contains approximately parallel polymers, each consisting of roughly 100 monomers. A detailed theoretical description requires thus that the properties of one polymer chain are understood, as also is the case for the interactions between different polymer chains of one tube and for those between the different tubes. As a part of this process, we shall here

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Fig. 1. Different structures of *trans* polyacetylene. (a) The structure of the chain without C-C bond-lengths alternation, whereas these bond length alternate for the two energetically degenerate structures (b) and (c). (d) The structure shows a soliton and (e) a polaron. White and black circles represent hydrogen and carbon atoms, respectively.

report results of theoretical studies of the properties of one isolated polymer chain.

The prototype of the conjugated polymers is polyacetylene (CH)_x. In its simplest form, i.e. the *trans* isomer, see Fig. 1, a single polymer chain consists of a zigzag backbone of carbon atoms. One hydrogen atom is bonded to each carbon atom, so that every carbon atom is threefold coordinated. The chemical bonds are formed first of all by σ bonds between sp² hybrids of the carbon atoms and the 1s orbitals of the hydrogen atoms. The last valence electron per carbon atom occupies a p orbital perpendicular to the plane of the nuclei, and these orbitals lead to weaker π bonds between the carbon atoms. The occupied σ orbitals appear at deep energies far away from the Fermi level and, equivalently, the unoccupied σ orbitals are far above the Fermi level. Both the occupied and the unoccupied π orbitals are those occurring closest to the Fermi level. Thus, in some sense, *trans* polyacetylene can be considered as having one (i.e. a π) electron per repeated (i.e. CH) unit.

In the neutral case, the ground state is found for a structure with alternating C-C bond lengths. When approximating the material as having one electron per repeated unit, the occurrence of a bond-length alternation can be interpreted as being a physical realization of a Peierls distortion [8].

Su et al. [9,10] proposed that when electrons are added or removed from an infinite *trans* polyacetylene chain, structural distortions, the so-called solitons, are generated (see Fig. 1(d)). The extra charge is localized to the solitons and since the solitons are highly mobile the charge can be transported through the chain. Thereby, they proposed an explanation for the dopinginduced increase in electrical conductivity. The existence of solitons is closely related to the fact that two energetically degenerate structures exist (Fig. 1(b) and (c)). Without this degeneracy polarons (Fig. 1(e)) might be generated, as is the case for most other conjugated polymers.

Many other conjugated polymers can, in principle, be obtained by modifying *trans* polyacetylene in one or more ways: the hydrogen atoms may be replaced by other side groups like alkyl or phenyl groups, heteroatoms like sulfur, nitrogen, or transition-metals may be incorporated into the backbone, or phenyl groups or heterocycles may be built into the backbone.

In the present contribution, we shall use a parameter-free density-functional method to study how a single *trans* polyacetylene chain responds to different types of changes. The method that has been developed explicitly for studies of infinite, periodic, helical, isolated polymer chains shall be briefly discussed in Section 2. In Section 3, we shall examine whether such calculations can describe the occurrence of the bond-length alternation mentioned earlier. Subsequently, we study the changes when substituting every second CH group with an N atom (Section 4), when substituting the hydrogen atoms with halogen atoms (Section 5), when substituting every second

hydrogen atom with a cyano group (Section 6), or when substituting the hydrogen atoms pairwise with a selenium atom (Section 7). After having discussed these different neutral, periodic systems, we shall turn to distorted systems. First, we study chains containing solitons for which we in Section 8 present a simple scheme for estimating the energies of the orbitals localized near the structural distortion. Next, we show in Section 9 how density-functional calculations on periodic chains can be used in extracting parameters for model Hamiltonians that subsequently can be used for studying dynamic properties or distorted or charged systems. Periodic, infinite, charged chains is the topic of Section 10, and, finally, we discuss briefly in Section 11 how one may treat infinite chains, when they are exposed to external electrostatic fields. Section 12 contains a summary.

2. Computational method

Our computational method has been described in detail elsewhere [11-13] and, therefore, we shall here give only a brief description. We assume that the Born-Oppenheimer approximation is valid and seek accordingly the properties of the electrons moving in the external field of the nuclei. To this end, we apply the density-functional formalism of Hohenberg, Kohn, and Sham [14,15]. Then the total electronic energy of the ground state is a functional of the electron density,

$$E_{\text{tot}} = E_{\text{tot}}[\{\vec{R}_i\}, \rho(\vec{r})], \tag{1}$$

where we have specified that different structures, characterized by the coordinates of the nuclei $\{\vec{R}_i\}$, lead to different total energies.

The electron density is given by

$$\rho(\vec{r}) = \sum_{i=1}^{\text{occ}} |\psi_i(\vec{r})|^2,$$
(2)

and the single-particle wavefunctions ψ_i are obtained by solving the Kohn–Sham equations (in Hartree a.u.)

$$\hat{h}_{\rm eff}\psi_i(\vec{r}) = \left[-\frac{1}{2}\nabla^2 + V_{\rm eff}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}).$$
(3)

The effective potential V_{eff} is a sum of the electrostatic potential of the nuclei, that of the electrons, and the exchange-correlation potential

$$V_{\rm eff} = V_{\rm N} + V_{\rm C} + V_{\rm xc}.$$
(4)

In the calculations to be reported below, we have most often used a local-density approximation for $V_{\rm xc}$ but in some few cases also a generalized-gradient approximation. In those cases, essentially no changes were found in the calculated physical properties.

In solving Eq. (3), we expand the eigenfunctions in some basis functions,

$$\psi_i(\vec{r}) = \sum_j c_{ij} \chi_j(\vec{r}).$$
(5)

We have used linearized muffin-tin orbitals (LMTOs) as basis functions. These atom-centered functions are defined as spherical Hankel functions times harmonics,

$$h_{l}^{(1)}(\kappa | \vec{r} - \vec{R} |) Y_{lm} \left(\frac{\vec{r} - \vec{R}}{|\vec{r} - \vec{R}|} \right).$$
(6)

Here, \vec{R} is the position of the atom and κ is a decay constant. Inside atom-centered, non-overlapping, socalled muffin-tin spheres these functions are augmented continuously and differentiably with numerical functions that are obtained by solving Eq. (3) numerically when keeping only the spherically symmetric part of the potential. Through this construction, we end up with a set of basis functions that constitutes good approximations to the exact solutions to Eq. (3) but still being of finite size. It shall be stressed that although the basis functions are eigenfunctions to a muffin-tin potential (spherically symmetric around the nuclei, constant outside the spheres), we use the full potential in the calculations.

Finally, our computational code has been developed for treating polymer chains that are assumed being infinite, periodic, helical, isolated, and having a straight polymer axis (notice that translational and zigzag symmetries are special cases). The periodicity is utilized in generating Bloch waves from the equivalent basis functions of different unit cells,

$$\chi_{jL\kappa}^{k}(\vec{r}) = \lim_{N \to \infty} \frac{1}{\sqrt{2N+1}} \sum_{n=-N}^{N} \chi_{jnL\kappa}(\vec{r}) e^{i\pi kn},$$
 (7)

where n labels the unit cells, j the atom inside one





Fig. 2. (a) and (b) *trans* polyacetylene and (c)-(e) *cis* polyacetylene without ((a) and (c)) and with ((b), (d), and (e)) a bond-length alternation. White and black circles represent hydrogen and carbon atoms, respectively.

repeated unit, L = (l, m) describes the angular dependence, and κ the radial dependence. Thereby, the wavefunctions become *k* dependent

$$\psi_i^k(\vec{r}) = \lim_{N \to \infty} \frac{1}{\sqrt{2N+1}} \sum_{n=-N}^N \sum_{jL\kappa} c_{i,jL\kappa}^k \chi_{jnL\kappa}(\vec{r}) e^{i\pi kn},$$
(8)

and the orbital energies are continuous functions of k, $\epsilon_i(k)$. As is well-known, the band structures are obtained by depicting ϵ_i as a function of k, whereas the density of states $[D(\epsilon)]$ is obtained by depicting the number of orbitals in the interval $[\epsilon; \epsilon + d\epsilon]$.

Below we shall use the crystal orbital overlap populations (COOP [16]) and the crystal orbital Hamilton populations (COHP [17]) in analyzing the bond-length alternation. These are defined as follows. By using that ψ_i^k is normalized, we have immediately

$$1 = \langle \Psi_{i}^{k} | \Psi_{i}^{k} \rangle$$

= $\sum_{n} \sum_{j_{1}j_{2}} \bigg[\sum_{L_{1}L_{2}\kappa_{1}\kappa_{2}} c_{ij_{1}L_{1}\kappa_{1}}^{k*} c_{ij_{2}L_{2}\kappa_{2}}^{k} e^{i\pi kn} \langle \chi_{j_{1}0L_{1}\kappa_{1}} | \chi_{j_{2}nL_{2}\kappa_{2}} \rangle \bigg].$
(9)

The term in the square brackets describes the interaction between the j_1 th atom of the 0th unit cell and the j_2 th atom of the *n*th unit cell. It is positive (negative) for bonding (antibonding) interactions. The COOP is obtained by modulating the density of states with these for fixed (j_1, j_2, n) .

Equivalently, the COHP is obtained by modulating the density of states with quantities that are defined through the single-particle energies,

$$\epsilon_{i}^{k} = \langle \psi_{i}^{k} | \hat{h}_{\text{eff}} | \psi_{i}^{k} \rangle = \sum_{n} \sum_{j_{1}j_{2}} \sum_{k_{1}L_{1}\kappa_{1}} c_{ij_{1}L_{1}\kappa_{1}}^{k} c_{ij_{2}L_{2}\kappa_{2}}^{k} e^{i\pi kn} \langle \chi_{j_{1}0L_{1}\kappa_{1}} | \hat{h}_{\text{eff}} | \chi_{j_{2}nL_{2}\kappa_{2}} \rangle \Big].$$
(10)

The COHP is positive (negative) for antibonding (bonding) interactions.

3. The dimerization

As a first example of the application of the method of Section 2, we discuss the electronic and structural



Fig. 3. The band structures for the five structures of Fig. 2. The dashed lines mark the Fermi level.

properties of two isomers of polyacetylene, i.e. the trans and cis isomers of Fig. 2. In Fig. 3, we show the band structures for the five structures of Fig. 2 [18]. In all cases, the orbitals closest to the Fermi level are of π symmetry. Moreover, the difference between the *cis* and the *trans* isomers that the smallest gap appears at k = 0 for the *cis* isomers and at k = 1 for the *trans* isomers is non-physical but due to the difference between the translational symmetry for the trans isomers and the zigzag symmetry for the cis isomers. In the figure, we see also that the bond-length alternation leads to the opening up of a gap at the Fermi level for the trans isomer (i.e. the Peierls distortion mentioned in Section 1), whereas for the cis isomer the gap is non-vanishing for all structures (although being very small for the *trans-cis* isomer of



Fig. 4. Total energy, E_{tot} , the sum of the energies of the occupied π orbitals, E_{π} , and the remaining part of the total energy, E_{σ} , for *trans* polyacetylene as functions of the C–C bond-length alternation.

Fig. 2(e)). Nevertheless, also for the *cis* isomer, it is known that the structure of the lowest total energy is one with a C–C bond-length alternation (actually, the *cis–trans* isomer of Fig. 2(d)).

In a further study, we explored the bond-length alternation of *trans* polyacetylene in more detail [12]. We first optimized the geometrical parameters for the structure without bond-length alternation and subsequently moved every CH unit rigidly in alternating direction parallel to the polymer axis. When denoting the amplitude of the displacement of the *n*th CH unit u_n , we have

$$u_n = (-1)^n u_0. (11)$$

Fig. 4 shows the variation in the total energy E_{tot} as a function of the difference in lengths between the carbon nearest neighbors, Δd . This is related to u_0 through

$$\Delta d \simeq 4u_0 \cos(\alpha/2) \tag{12}$$

where α is the C–C–C bond angle. In the figure, we also show the variation in the sum of the energies of the occupied π orbitals, E_{π} , and the difference between the two, E_{σ} . The lowest total energy is found for structures with $\Delta d \neq 0$, and E_{π} is a decreasing function of $|u_0|$, whereas E_{σ} is an increasing function. All these findings are in accord with interpreting the occurrence of the C–C bondlength alternation as a Peierls distortion.



Fig. 5. Calculated/experimental (when available) structural parameters (in Å and $^{\circ}$) for *trans* polyacetylene.

In a recent work, we calculated the forces (i.e. the derivatives of the total energy with respect to the nuclear coordinates) analytically and used this possibility in optimizing all structural degrees of freedom for *trans* polyacetylene [13]. The results are shown in Fig. 5 together with experimental findings [19,20]. It is seen that there is a good agreement between the calculated and the experimental results. However, the results of Fig. 4 show that the energy gain upon the bond-length alternation is very small, i.e. only some 0.01 eV per CH unit, so that small differences in the computational details may easily lead to differences in the optimized values of the structural parameters, in particular for the size of the bond-length alternation. This may be part of the explanation for the large scatter in the calculated values of the size of the bond-length alternation although also other reasons like the approximate density functionals, many-body effects, or the finite number of the k points used in the calculations may be held responsible (see, e.g. Refs. [13,21-23] and references therein).

Although the energy gain upon the C–C bondlength alternation is small, the COOP and the COHP are very sensitive to this alternation. Fig. 6 shows these populations for the interactions along the C–C bonds. Here, it is clear that for the orbitals closest to the Fermi level (i.e. the π orbitals), the bond-length alternation leads to a larger bonding interaction along the shorter C–C bonds and more antibonding interactions along the longer C–C bonds compared



Fig. 6. The COOP (solid curves) and COHP (dashed curves) for the interactions between nearest C–C neighbors for (a) the structure without C–C bond-length alternation and (b) and (c) the one with a such alternation. In (b) ((c)), the interactions along the shorter (longer) bonds are shown. The vertical dashed lines mark the Fermi level and the curves have been broadened with Gaussians. The panels have only approximately the same vertical scales.

to the case for the structure without C-C bond-length alternation.

4. Polycarbonitrile

Polycarbonitrile, also called polymethineimine, can be considered as a modification of polyacetylene obtained by replacing every second CH unit by a nitrogen atom. As a consequence, the two materials are isoelectronic. However, although the material has been known for some decades [24], it has only marginally been the subject of experimental studies within the concept of synthetic metals, but due to its simple structure it is a popular material for theoretical studies.

For *trans* polyacetylene, we saw in Section 3 that the C–C bond-length alternation leads to a gap at the Fermi level as a consequence of the lowering of the symmetry (from a zigzag symmetry with one CH unit per unit cell to a translational symmetry with two CH units per unit cell). But for polycarbonitrile, a bondlength alternation will not lead to a larger unit cell and, accordingly, the existence of a such cannot directly be interpreted as being due to a Peierls



distortion. On the other hand, for *cis* polyacetylene, we saw that a bond-length alternation exists.

For the planar *trans* polycarbonitrile system, we found [25] that the lowest total energy is found for a structure with a C–N bond-length alternation, Fig. 7. The band structures, Fig. 8, show that the bond-length alternation is accompanied by an increase of the gap around the Fermi level. By comparing the band structures with those of *trans* polyacetylene, we observe the further differences that a σ band (due to N lone-pair orbitals) appears just below the top of the occupied π band, as well as the fact that the bands for polycarbonitrile are narrower than those of polyace-tylene: for the former the orbitals are more localized to either the CH units or the N atoms.

5. Halogen-substituted polyacetylene

Returning to polyacetylene, its electronic proper-

Table 1

The optimized structural parameters (bond lengths in a.u., bond angles in °) for the *trans* form of $(CX)_x$. In the order of their appearance, the three values for the C–C bond lengths correspond to the lengths of the long bonds and the short bonds for the structure with a bond-length alternation and to the lengths for the structure without a such alternation, respectively

	X = H	X = F	X = Cl
C-X	2.064	2.652	3.281
C-C	2.636	2.653	
C-C	2.520	2.509	
C-C	2.576	2.581	2.578
C-C-C	124	130	133



Fig. 8. As Fig. 3(a) and (b), but for polycarbonitrile.

ties may also be modified by replacing the hydrogen atoms with other side groups. These can, e.g. be alkyl chains or phenyl rings but also sidegroups containing heteroatoms like N, S, or O are common. More recently, Gould et al. [26] replaced all hydrogen atoms with halogen atoms, these being fluorine or chlorine. These atoms are more electronegative than the other sidegroups and the question arises then whether the materials synthesized by Gould et al. still can be considered synthetic metals. More specifically, do π orbitals still appear closest to the Fermi level, do the C-C bond length alternate, do the materials prefer the trans or cis form, and, for the material with 50% fluorine and 50% chlorine substitution, does the material have nearest F-F and Cl-Cl neighbors or nearest F-Cl neighbors? In order to address these issues, we performed density-functional calculations with the method of Section 2 [27].

First we considered the *trans* forms of $(CH)_x$, $(CF)_x$, and $(CCI)_x$ and for these we optimized the structural parameters. In Table 1, we list the results. The table shows first of all that the C–C bond lengths are only marginally affected by the substitutions, but that the larger sizes of Cl compared with F, which in turn is larger than H, leads to differences in the C–X bond lengths and in the C–C–C bond angles. Finally, and most important, we see that for X = Cl we do not find any C–C bond-length alternation.

Fig. 9, that shows the band structures for the *trans* isomers without the bond-length alternation, gives an explanation for the absence of a bond-length

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Fig. 9. Band structures for the *trans* forms of (a) $(CH)_x$, (b) $(CF)_x$, (c) $(CCI)_x$, and (d) $(CFCCI)_x$ without C-C bond-length alternations. In all cases, one unit cell contains two C atoms, and the horizontal dashed lines represent the Fermi level.

alternation for X = Cl: not only π bands but also σ bands cross the Fermi level, and the bond-length alternation would not open up a gap at the Fermi level. Also for X = F, we observe some extra bands compared to X = H, but they appear at deeper energies.

Turning to the *cis* isomers, we found [27] that the results found for the *trans* isomers prevail: for X = F, the band structures are similar to those for X = H (except for some extra bands at lower energies), but for X = CI more bands cross the Fermi level.

Finally, we studied also polymers of the form $(CFCCI)_x$, i.e. chains where every second H atom has been substituted by an F atom and every other second by a Cl atom. The band structures of Fig. 9(d) are representative for the results: In all cases, both σ and π bands appear close to the Fermi level. We did not carry a full geometry optimization through, but by comparing with the experimental information of Gould et al. [26] we found that the *trans* isomer most likely was the one synthesized by Gould et al.



Fig. 10. Different structures of polyacetylene with every second H atom replaced by a cyano group. Black circles, white circles, and black squares represent carbon, hydrogen, and nitrogen atoms, respectively.

6. Cyano-substituted polyacetylene

An interesting system is obtained by replacing every second H atom of *trans* polyacetylene by a cyano group, CN. In this case (Fig. 10), two fundamentally different structures may occur, i.e. either a polyacetylene-like structure (Fig. 10(a) and (b)) or a structure consisting of fused rings (Fig. 10(c)-(e)). And for each of those, a bond-length alternation may exist (Fig. 10(b), (d), and (e)) or not (Fig. 10(a) and (c)).

We performed a partly restricted geometry optimization and studied subsequently whether the total energy could be lowered through a bond-length alternation [28]. As seen in Fig. 11, this is indeed



Fig. 11. Variation in the total energy for $(CHCCN)_x$ as a function of the bond-length alternation for different structures of Fig. 10. The structures I and III of that figure corresponds to vanishing displacement.



Fig. 12. Variation in the total energy for $(CHCCN)_x$ as a function of a parameter describing the transition between structure I (N displacement = 0) and structure III (N displacement = 1) of Fig. 10.

the case. Fig. 11 shows also that all types of bondlength alternation in Fig. 10 lead to a lowering of the total energy.

In another set of calculations, we considered a (maybe artificially chosen) transition between the polyacetylene-like structure and the structure consisting of fused rings. The variation in the total energy, Fig. 12, shows that the fused-ring structure has the lowest total energy, but also that the polyacetylene-like structure corresponds to a metastable structure.

The band structures, Fig. 13, show finally that all materials are semiconductors with π bands closest to the Fermi level. For some of the structures (most notably the transition structure between structure I and III), some extra orbitals of σ symmetry appear



Fig. 14. Structure of a C_2 Se polymer. Black and white circles represent carbon and selenium atoms, respectively.

close to the Fermi level. Moreover, it is interesting to notice that for the structure of fused rings the highest occupied orbital is localized to the C–C zigzag chain, whereas the lowest unoccupied orbital is localized to the C–N zigzag chain. This implies that upon excitation a charge separation can take place.

7. Selenium-substituted polyacetylene

Kobayashi et al. [29,30] and Iqbal et al. [31,32] polymerized CSe₂. The resulting material was, however, ill defined and despite a detailed experimental, Iqbal et al. [32] were not able to characterize the material completely. In fact, not only the structure but also the stoichiometry of the polymer chains was not fully resolved. As a complementary study to the experimental work, we



Fig. 13. Band structures for the different structures of Fig. 10, as well as for an intermediate structure between those of structures I and III of Fig. 10 (labeled I–III). The horizontal dashed lines mark the Fermi level.





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Fig. 15. Variation in total energy per monomer for the $(C_2Se)_x$ polymer as a function of the difference in the C–C bond lengths. Only a limited geometry variation has been carried through.

applied [33,34] the density-functional method on various polymers proposed by Iqbal et al.

Fig. 14 shows a $(C_2Se)_x$ polymer that was considered interesting by Iqbal et al. [31] although the experimental study showed that this structure was inconsistent with some of the experimental data. Nevertheless, they proposed that this structure could exist and have interesting properties. In some sense, this polymer can be thought of as being cis polyacetylene with pairs of hydrogen atoms replaced by bridging Se atoms. Then, one might expect the cis-trans isomer, and not the trans-cis isomer, as was suggested by Iqbal et al. [31], to be the stabler form. Our density-functional calculations [34] showed (Fig. 15) in fact that the *cis-trans* form is stabler. Moreover, the band structures, depicted in Fig. 16, show that this polymer has three π bands closest to the Fermi level of which two are occupied. As for *cis* polyacetylene, the smallest gap occurs at k = 0, but the highest occupied band at k = 1 is also of π symmetry and has the largest contributions from the selenium atoms. Moreover, in contrast to cis polyacetylene, for the present system, the cis-trans form has a smaller gap than the *trans-cis* form.

8. Solitons

In the previous sections, we have discussed the properties of infinite, periodic chains. We have seen how the properties can be modified through modification of the structure and/or composition of the material, but that the overall properties in most cases prevail: the materials are semiconductors with orbitals



Fig. 16. Band structures for the $(C_2Se)_x$ polymer. The horizontal dashed line marks the Fermi level.

of π symmetry closest to the Fermi level and the backbone consists mainly of carbon atoms and possesses a bond-length alternation.

However, as discussed in Section 1, the interest in those materials originates from their transport and their (linear and non-linear) optical properties. The strong coupling between electrons and phonons has as one consequence that excitation or charging may lead to structural changes. As one example we shall here discuss the orbitals that are induced by a soliton, Fig. 1(d).

A soliton breaks the translational symmetry and, accordingly, cannot be treated directly with the method of Section 2. Since, moreover, it is extended (i.e. the parameter u_n describing the position of the *n*th CH unit, Section 3, varies over a larger *n* interval), neither a supercell calculation nor a finite-system calculation is straightforward. On the other hand, a large part of the interest in the solitons is devoted to identifying the energies of the orbitals localized to the region of the soliton and an important contribution would therefore be to be able, from parameter-free calculations, to predict these energies.

We shall here use the density-functional calculations for the periodic chains in giving qualitative and quantitative information on the energies of the orbitals localized to the region of some structural defect in an otherwise infinite and regular polymer





Fig. 17. Calculated density of states (lower curve) together with experimental UPS spectra (upper curves) recorded at different photon energies (given on the curves) for *trans* polyacetylene.

chain. To this end, we have developed a simple scheme [35-37] and shall, as a specific example, apply this to the energies of the soliton-induced orbitals in polyacetylene and polycarbonitrile. Before, however, describing the scheme we shall argue that the density-functional calculations give orbital energies that are of experimental relevance and, accordingly, that our approach is of practical use. In Fig. 17, we show therefore the density of states for the valence orbitals together with experimental ultraviolet photoelectron spectra (UPS) of Rasmusson et al. [38] for *trans* polyacetylene. The good agreement between the two sets of results should be obvious.

A straightforward way of using density-functional calculations on periodic chains to give information on the properties of the structural defects like solitons is to perform several such calculations on different, but related structures, map the results on a suitable model Hamiltonian (in Section 9, we shall discuss this approach in more detail), and finally apply the model Hamiltonian in studying the defect-containing system. Thus, the results of the final model calculations are, although indirectly, determined from the density-functional results on the periodic chains. An obvious question is hence whether it is possible to predict the results of the model calculations directly from the



Fig. 18. The left part shows, schematically, the variation of the band structures for periodic *trans*-polyacetylene chains as function of a bond-length alternation parameter (structure), and the right part shows, also schematically, the density of states for a soliton-containing chain. For further details, see the text.

results of the density-functional calculations without first having to define the model Hamiltonian, determine the parameter values, and perform the model calculations. The answer is that in some cases this is possible [35-37]. Specifically, when the defect is extended (as is the case for the solitons in the present work) and many-body effects are less important (this may be questionable here; Section 9), the energies of the orbitals induced by the defects can be estimated quite accurately. We shall here not repeat the mathematical arguments behind the scheme (see Refs. [35-37]) but instead demonstrate its use for solitons in polyacetylene and polycarbonitrile.

A soliton in trans polyacetylene involves a local transition from the structure of Fig. 1(b) via that of Fig. 1(a) to that of Fig. 1(c). Instead, we study periodic structures that span the structure of Fig. 1(b) via that of Fig. 1(a) to that of Fig. 1(c). For any of those structures, we obtain band structures like those of Fig. 3(a) and (b). We will here focus on the occupied and unoccupied π bands closest to the Fermi level and can then depict the results of all the calculations for the periodic structures as in the left-hand part of Fig. 18. For any periodic structure (a specific value on the 'structure' axis), we will have band orbitals only inside the hatched area. The panel shows accordingly also how the band gap closes for the structure without bond-length alternation, whereas it has a finite value for the structures of Fig. 1(b) and (c) (these structures correspond to the vertical dashed lines). The density of states for the defect-free system is therefore given as shown in the right-hand part of the figure when



Fig. 19. As Fig. 18, but for polycarbonitrile.

excluding the small peak in the middle between the valence and the conduction bands. This small peak is the soliton-induced state as predicted by the simple scheme. The scheme states that for a structural defect, where the structure locally spans a certain interval (the one between the vertical dashed line in the lefthand part of the figure), any energy within the hatched region is possible as the energy of a defect-induced orbital. Out of this manifold, one chooses the single one or the few ones that are energetically most far away from those of the band orbitals of the defect-free system. In this case, this gives the mid-gap state of the right-hand panel of Fig. 18. Actually, this finding is well known, since the model studies of Su et al. [9,10] but is here presented in a different and more general way.

For polycarbonitrile, the situation is similar with, however, the important difference that the band gap does not vanish for the structure without a C–N bondlength alternation, Fig. 8. Fig. 18 is therefore to be modified as shown in Fig. 19, and it is then seen that the soliton leads to not one but two gap states at the positions of the band edges for the structure without a bond-length alternation. Also this result has been found through more detailed model studies [25,39].

9. Model parameters

As a more complicated, but also more exact alternative to the approach of Section 8, the densityfunctional calculations may be used in determining values of parameters of model Hamiltonians that subsequently may be used in studying defects, excitations, or dynamical and transport properties. In the spirit of the model of Su et al. [9,10] we split the total Hamiltonian for a single chain into two parts,

$$\hat{H} = \hat{H}_{\pi} + \hat{H}_{\sigma},\tag{13}$$

where the first part describes the electronic part for the π electrons and the second part everything else. Thereby we assume that each site of the chain consists of one CH unit and provides one (π) orbital (neglecting spin, *s*). Labeling the sites *n* we will consider the Hubbard-like Hamiltonian

$$H_{\pi} = \left[\sum_{n,s} \epsilon_n \hat{c}_{n,s}^{\dagger} \hat{c}_{n,s} - \sum_{n < m,s} t_{n,m} \left(\hat{c}_{n,s}^{\dagger} \hat{c}_{m,s} + \hat{c}_{m,s}^{\dagger} \hat{c}_{n,s} \right) \right] + \left[\sum_n U_n \hat{\rho}_{n,\uparrow} \hat{\rho}_{n,\downarrow} + \sum_n V_{n,n+1} \hat{\rho}_n \hat{\rho}_{n+1} \right], \quad (14)$$

with

$$\hat{\rho}_{n,s} = \hat{c}_{n,s}^{\dagger} \hat{c}_{n,s} \tag{15}$$

and

$$\hat{\rho}_n = \hat{\rho}_{n,\uparrow} + \hat{\rho}_{n,\downarrow}.$$
(16)

For an infinite, periodic *trans*-polyacetylene chain, we have

$$\boldsymbol{\epsilon}_{n} = \boldsymbol{\epsilon}_{0}, \qquad t_{n,m} = t_{0,m-n} \equiv t_{m-n},$$

$$U_{n} = U_{0} \equiv U, \qquad V_{n,n+1} = V_{0,1} \equiv V.$$
(17)

(Notice that, e.g. t_1 takes two values when the C–C bond lengths alternate.)

The density-functional calculations for the infinite, periodic chains can now be used in determining these parameter values. However, there is a conceptual problem: the model Hamiltonian assumes implicitly the existence of a minimal set of orthonormal, sitecentered basis functions (Wannier functions), whereas the density-functional method employs a larger set of non-orthonormal basis functions. In the latter case, it is therefore non-trivial to split the orbitals into atomic components, which, however, is required when extracting the values of the model parameters. Moreover, the values of the single-particle parameters (those of the first square bracket in Eq. (14)) can be extracted from, e.g. the band structures, but the determination of the values for the many-body parameters (those of the second square bracket in

Table 2

Parameter values for the model Hamiltonian of Eq. (12) for *trans* and *cis-trans* polyacetylene as obtained with constrained density-functional calculations

Parameter	Trans	Cis-trans
t_1 (eV)	3.35, 2.88	3.44, 2.59
t_2 (eV)	-0.25	-0.16
U(eV)	10.7	10.5
V(eV)	0.3	0
$t_0 (eV)$	3.12	3.02
$\alpha (eV/Å)$	2.98	5.39

Eq. (14)) requires determining the energy responses of the system to redistributing the electrons among the sites.

We have found [40] that by transforming the basis functions of the density-functional calculations into an orthonormal one using Löwdin's symmetric orthonormalization [41] the final results (to be discussed later) depend the least sensitive to the details of the definition of the basis set of the densityfunctional calculations. Subsequently, so-called constrained density-functional calculations [42] can be used in modifying the number of electrons at the different sites. Such calculations yield accordingly the orbital energies and the total energy as functions of the distribution of the electrons. By performing model calculations (in our case, we use the Hartree-Fock approximation for the model calculations) with the same electronic distribution, the parameter values can be adjusted until an optimal agreement between the density-functional and the model calculations is obtained.

We applied this approach to the *trans* and *cistrans* isomers of polyacetylene of Fig. 2(b) and (d), respectively [43]. Table 2 lists the resulting parameter values. It is seen that U is large, whereas V is essentially vanishing. The large value of U (it is larger than what usually is assumed realistic) may, however, partly be due to the Hartree–Fock approximation employed in the model calculations. In accordance with the effective screening of the many-body interactions, also t_2 is considerably smaller than t_1 . Finally, it is customary to assume that the nearestneighbor hopping integrals depend linearly on the bond lengths which in turn are approximated as a linear function of the displacement parameters u_n ,

$$t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n), \tag{18}$$

and the table contains also the values for t_0 and α for the two isomers.

10. Charged chains

In the last two sections, we shall discuss how density-functional calculations can be of use when studying two of those areas, where conjugated polymers have attracted the most attention. Both areas were discussed in Section 1, and whereas the large doping-induced increase in electrical conductivity is the subject of the present section, Section 11 is devoted to the (linear and non-linear) responses of the materials to external electromagnetic fields.

When trying to study theoretically infinite chains with extra or less electrons, one encounters a



Fig. 20. (a) The optimized value of the parameter u_0 describing the bond-length alternation in *trans* polyacetylene and (b) the energy gain upon the bond-length alternation as a function of added (solid curves) and removed (dashed curves) electrons.

fundamental problem: the extra charge may be localized (e.g. to structural defects like solitons) whereby the periodicity is broken, or the extra charge is added periodically whereby the electrostatic potential diverges. In the analogous case where infinite, periodic, three-dimensional crystalline solids are treated, it has become practice to compensate the charge of the extra or less electrons through a constant background density of the same total charge (but opposite in sign). For the chains, however, the threedimensional volume of one unit cell is diverging, making such an approach not possible. We have instead chosen to add the compensating charge only inside the muffin-tin spheres (see Section 2) and shall here consider the special case of trans polyacetylene [22].

In Section 3, we showed that the occurrence of a bond-length alternation in *trans* polyacetylene can be interpreted as a physical realization of a Peierls distortion, so that its existence is closely related to the half-filled π band for the neutral structure without a bond-length alternation. Accordingly, it may be expected that adding or removing electrons would gradually suppress the bond-length alternation. That this in fact is so, is seen in Fig. 20, where it also is observed that first for about 0.05 extra or less electrons per CH unit is the bond-length alternation vanishing.

The results of Fig. 20 were found by considering a number of different amplitudes of the bond-length alternation parameter u_0 , as well as many different cases of added or removed electrons up to ± 0.1 electrons/CH unit. Subsequently, the results were analyzed with a model of the type of Eq. (13) [22]. For \hat{H}_{σ} we assumed

$$\hat{H}_{\sigma} = \frac{K_2}{2} \sum_{n} (u_{n+1} - u_n)^2 + \frac{K_4}{4} \sum_{n} (u_{n+1} - u_n)^4 + \cdots$$
(19)

The analysis gave $K_2 = 70 \text{ eV}/\text{Å}^2$, whereas K_4 was essentially vanishing.

Fitting the energies of the lowest π band (i.e. of the band that for the neutral system is occupied—notice, however, that we also consider the cases of added charge) led to $t_0 = 3.09 \text{ eV}$ and $\alpha = 4.28 \text{ eV}/\text{\AA}$ for the parameters of Eq. (18). Whereas the value of t_0 is very similar to that of Table 2, that of α differs

significantly. Notice, however, that the results of Table 2 were obtained by fitting total energies with the Hubbard-like Hamiltonian of Eq. (14), but here we used the band structures in the fitting process.

An important finding of Fig. 20 is that there is a difference between adding and removing electrons. We used that difference in estimating the Hubbard parameters U and V of Eq. (17) and found [22] $(U/2) + V \approx 12.5$ eV. Assuming that V is very small (Table 2), this leads to a value of U much larger than that of Table 2. It should, however, be remembered that in the present calculations the charge is added periodically so that screening effects are abandoned, ultimately leading to a large value of U. In fact, for an isolated C atom we estimated [22] that U = 29.6 eV, i.e. close to the value obtained here.

11. External electrostatic fields

The π valence electrons of the conjugated polymers are not as strongly bonded to the nuclei as are the σ valence electrons, but on the other hand not so loosely bonded that they can be considered fully freeelectron like. This combination leads to large linear and non-linear responses to external electromagnetic fields. In particular, the large values of the non-linear responses, also as functions of frequencies of the external fields, have led to a significant research activity in those properties for the conjugated polymers.

Considering a single polymer chain, the responses may be quantified through the dipole moment in the external field \vec{E} ,

$$\mu_{i} = \mu_{i}^{(0)} + \sum_{j} \alpha_{ij}E_{j} + \sum_{jk} \beta_{ijk}E_{j}E_{k}$$

$$+ \sum_{jkl} \gamma_{ijkl}E_{j}E_{k}E_{l} + \cdots$$
(20)

where i, j, k, l, ... equals x, y, or z. Moreover, $\mu_i^{(0)}$ is the static dipole moment in the absence of the external field, and we have introduced the polarizabilities α_{ij} and the hyperpolarizabilities $\beta_{ijk}, \gamma_{ijkl}, ...$ that are frequency-dependent.

The quantities of interest are α_{ij} , β_{ijk} , and γ_{ijkl} or, rather, for a finite oligomer of N monomers, α_{ij}/N , β_{ijk}/N , and γ_{ijkl}/N . It turns out that, as functions of N,





Fig. 21. Relative total energy (squares), Fermi energy (diamonds), band gap (circles), and x component of the dipole moment (triangles) for (a) *trans* polyacetylene and (b) polycarbonitrile as functions of strength of an external electrostatic field in the (x, z) plane of the polymer backbone but perpendicular to the polymer axis.

 γ_{ijkl}/N converges much slower than β_{ijk}/N that in turn converges much slower than α_{ii}/N .

For the static case (i.e. all frequencies vanishing), one may study finite systems in the external field. By gradually increasing the length of the system, one may hope to reach the $N \rightarrow \infty$ limit, which, however, as mentioned earlier may be reached first for quite large values of N. Alternatively, one may consider the infinite system theoretically, but in that case one encounters the problem that when the field has a non-vanishing component along the polymer axis, the periodicity is broken and, moreover, the potential diverges at both ends of the polymer.

Despite these problems, there exist different, more or less accurate, ways of studying the responses of an infinite polymer to an external electrostatic field. As a first approximation one may concentrate on the special case that the field has no component along the polymer axis, so that a translational symmetry prevails. Although the responses are significantly larger for the components along the polymer axis, such studies give a first insight into the properties of the polymers when exposed to electrostatic fields. As an example of such studies, we show in Fig. 21 different properties for *trans* polyacetylene and polycarbonitrile as functions of the strength of a field perpendicular to the polymer axis but in the plane of the polymer [44]. The largest values of the field are larger than those usually used in experiments, so that it is clear from the figure that most properties change only weakly as a function of field strength. Also the band structures (not shown) are hardly affected by also the strongest fields [44]. Subsequently, results like those of Fig. 21 can be fitted with expressions of the form of Eq. (20) giving the polarizabilities and hyperpolarizabilities.

Since the responses of the system to the external field are small, an alternative would be to use perturbation theory in the calculation of the polarizabilities and hyperpolarizabilities, which also would permit the study of their frequency dependencies. This leads to expressions of the form

$$\alpha_{ij}(\omega;\omega) \sim \sum_{m}^{\text{occ}} \sum_{n}^{\text{unocc}} \frac{A_{nm,ij}}{(\epsilon_n - \epsilon_m) - \omega}$$
(21)

where we have explicitly included the frequency dependencies and where $A_{nm,ij}$ is some matrix element. Since usual density-functional calculations



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Fig. 22. Results of model calculations for a Hückel-like model for different approximate treatments of an external electrostatic potential. The panels (a), (b), (e), and (f) corresponds to the approximations of Eqs. (25), (22), (26), and (27), respectively. In (c) and (d), Eq. (24) has been used with the further approximation that in (c) the terms $k_1 \neq k_2$ have been ignored, and in (d) only the second term on the right-hand side has been included. The four sets of results of each panel corresponds to Born von Kármán cells of 24, 204, 408, and 612 sites, respectively. The largest system is the one for which the total energy deviates fastest from 0 as a function of increasing field strength.

lead to an underestimate in the optical gap, this expression will predict an absorption onset at a too low energy, at least in a standard calculation employing a finite basis set. Therefore, although this expression and the related ones for the hyperpolarizabilities are useful in the study of the frequencydependent properties, it would be of value to have an alternative approach not suffering from the abovementioned band-gap problem, i.e. to be able to include the field directly in the calculations.

If we assume that the z axis is the polymer axis, the simplest approximation is to replace z by

$$\hat{z}_1 = z - [z/h]h \tag{22}$$

where [x] is the integral part of x, and where h is the length of one unit cell. \hat{z}_1 is a saw-tooth curve with the periodicity h.

A very similar approach has been suggested by Otto [45]. Using the formulation of Bloch, any electronic wavefunction in the absence of the external field can be written as

$$\psi_j^k(\vec{r}) = e^{ikz} u_j^k(\vec{r}) \tag{23}$$

where u_i^k is a periodic function. Then,

$$\left\langle \psi_{j_{1}}^{k_{1}}|z|\psi_{j_{2}}^{k_{2}}\right\rangle = \left\langle \psi_{j_{1}}^{k_{1}}\right| - i\frac{\partial}{\partial k}\left|\psi_{j_{2}}^{k_{2}}\right\rangle$$
$$- \left\langle \psi_{j_{1}}^{k_{1}}\right|e^{ikz}\frac{\partial}{\partial k}\left|e^{-ik_{2}z}\psi_{j_{2}}^{k_{2}}\right\rangle.$$
(24)

The second term on the right-hand side has nonvanishing matrix element only for $k_1 = k_2$ and only this term is kept.

In a somewhat different context, Resta [46] observed that in an actual calculation, one employs $N_k k$ points in the first Brillouin zone, which, when the k points are equidistant, corresponds to imposing periodicity with the Born von Kármán cell. An improvement would therefore be to replace Eq. (22)



Fig. 23. Wannier functions along the polymer axis for *trans* polyacetylene for the four highest occupied ((a)-(c) and (g)) and four lowest unoccupied bands ((d)-(f) and (h)). (a)–(f) show Wannier functions of σ symmetry, and (g) and (h) functions of π symmetry. For the latter, an offset of 1 a.u. away from the polymer axis has been introduced. The length of one unit cell (with two CH units) is 4.543 a.u.

(25)

by

$$\hat{z}_2 = z - [z/(N_k h)]N_k h.$$

Closer related to the suggestions of Resta [46] (who, however, only examined the calculation of matrix elements and not of directly including an external field in a calculation) is to use trigonometric functions and we shall therefore also consider the following two approximations

$$\hat{z}_3 = \frac{N_k h}{2\pi} \sin\left(\frac{2\pi z}{N_k h}\right) \tag{26}$$

and

$$\hat{z}_4 = \frac{N_k h}{\pi} \sin\left(\frac{\pi z}{N_k h}\right),\tag{27}$$

We have constructed a simple Hückel-like model (with, however, alternating hopping integrals as in *trans* polyacetylene) and studied the different approximations [47]. The results are shown in Fig. 22. Without an external field, the system has a band gap at the Fermi level. When the field becomes so large that unoccupied orbitals at one end become occupied and occupied orbitals at the other end become unoccupied, the total energy varies rapidly as a function of field strength, whereas before this the variation is weak. This is first of all the case when N_k is large. The results of Fig. 22 show furthermore that there are strong dependences on the way the field is treated and in particular including only the second term on the right-hand side of Eq. (24) (Fig. 22(d)) leads to results in conflict with those of all the other approaches.

Since the operator \hat{z}_2 destroys the periodicity of the system, orbitals of different *k* may interact. On the other hand, we saw that the effects of the electrostatic field are small. Therefore, the orbitals of the unperturbed system for the occupied and the lowest unoccupied bands provide good starting points for the

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inclusion of \hat{z}_2 . Of computational reasons, it is then most convenient to use not Bloch but Wannier functions as the basis functions. These are defined as

$$w_{jp}(\vec{r}) = \frac{1}{\sqrt{N_k}} \sum_k e^{i\phi_j(k)} \psi_j^k(\vec{r}) e^{-ikp}$$
 (28)

where *j* is a band index and *p* labels the unit cell of the Wannier function. The phases $\phi_j(k)$ are determined so that the integral $\int_{0 \le z \le h} |w_{i0}(\vec{r})|^2 z^2 d\vec{r}$ is minimized.

The Wannier functions are of interest also in other context and, therefore, we show in Fig. 23 those for a *trans* polyacetylene chain obtained from $N_k = 20 \ k$ points [48]. As seen in the figure, we obtain thereby functions that are more or less well localized. In all cases, the Wannier functions have, however, long-ranged oscillations around the value 0.

The next step will be to perform a self-consistent calculation with the Wannier functions as basis functions for different field strengths and from the results of the total energy extract the static polarizabilities and hyperpolarizabilities. Thereby also different directions of the field shall be considered. However, the computer program for these calculations is not yet completely developed and, therefore, the results of these calculations will have to await a future publication.

12. Conclusions

Polyacetylene is the prototype of the conjugated polymers/synthetic metals. It has in addition a fairly simple structure making it an excellent system for theoretical studies. In the present contribution, we have therefore concentrated on this material but want to emphasize that many of the results we have obtained are valid for the larger class of conjugated polymers.

After the presentation of our parameter-free density-functional scheme, that has been developed explicitly for studies of infinite, periodic, isolated, helical chains, we studied first pure polyacetylene and saw how the calculations could reproduce and also throw more light on (e.g. through the crystal orbital populations, COOP and COHP) the experimentally observed bond-length alternation.

Subsequently, we studied a number of periodic,

undistorted conjugated polymers obtained from polyacetylene through different types of substitution. For these, it was obvious that in many cases (but not all, see, e.g. $(CCl)_x$), the general properties of the conjugated polymers prevail: they are semiconductors with π orbitals closest to the Fermi level and they possess a bond-length alternation along the backbone. But we also saw that there were system-specific differences that, ultimately, allow for a fine-tuning of the materials properties.

Finally, we studied the materials when the assumption that they are infinite, periodic, and neutral no longer is valid. We presented a general scheme that allows for a detailed and accurate determination of the energies of defect-induced orbitals and applied the scheme to solitons in polyacetylene and polycarbonitrile. Moreover, we showed how parameter values for many-body Hamiltonians could be extracted from constrained calculations and presented also a scheme for studying charged chains. Finally, we presented some preliminary results addressing the problems related to the calculation of the response of the polymer to external electromagnetic fields.

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