

Interactions between two identical polymer chains studied with first-principles calculations

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Results of parameter-free calculations on the interactions between two otherwise isolated, infinite, linear, polymeric chains are reported and discussed. The systems considered are (i) two hydrogen fluoride chains (as an example of a hydrogen-bonded polymer) and (ii) two carbon chains (as an example of a conjugated polymer). It is demonstrated that the interactions are larger than usually assumed for such systems. As a consequence of the results it is suggested that a soliton initially confined to a single chain will lead to distortions of neighboring chains and thus become a three-dimensional defect.

Most polymeric compounds can be idealized as infinite, noninteracting macromolecules. For many of the compounds a single, isolated, infinite chain has two (energetically degenerate or nondegenerate) highly symmetric configurations. The two configurations differ in the way a subset of the nuclei is placed relative to the rest of the nuclei.

Two important classes of such polymers are (i) hydrogen-bonded polymers, where the positions of the protons relative to those of the rest of the nuclei define the two configurations, and (ii) conjugated polymers, where the positions of a part of the carbon atoms relative to those of the others are the parameters defining the configurations.

For those polymers where the two configurations are degenerate, solitonic excitations have been proposed.¹⁻⁴ These are domain walls between two parts of the polymer with different configurations. The domain wall has a finite width, and inside it there is a continuous crossover from one configuration to the other. Independently of the relative total energy of the two configurations, polaronic excitations have been proposed. These are domain walls separating two parts of the polymer with the same configuration and containing a smaller finite part with the other configuration.

Although a single-chain approximation for most purposes is excellent, nonvanishing interchain interactions have important consequences, especially for solitonic excitations. Consider two parallel chains for which the total energy per unit cell is ΔE higher when the two chains are parallel than when they are antiparallel. When the two chains are infinite, $\Delta E \neq 0$, and solitons are true single-chain defects, it is only possible to create solitons in pairs: one soliton on each chain. Furthermore, the creation energy for such a pair is roughly $|N \Delta E|$ plus a constant, where N is the number of unit cells separating the two solitons. This puts some upper bounds on the length of finite chains that can contain solitons, and on the capability of the solitons to move independently of each other, when they are confined to single chains.

Detailed and precise investigations of the interactions between different polymer chains are accordingly of ulti-

mate importance in understanding the properties of solitonic defects. However, except for some investigations on the superconducting poly(sulfur nitride) [(SN)_x; see, e.g., Ref. 5], parameter-free investigations of interchain interactions are to a large extent lacking for polymeric compounds.

The purpose of the present communication is to report results of first-principles calculations on the interaction between two identical, linear, infinite polymer chains for two different systems. For both systems a single, isolated chain has two degenerate configurations. The chosen systems are (i) linear hydrogen fluoride chains and (ii) linear carbon chains as examples of hydrogen-bonded polymers and conjugated polymers, respectively. Although the two systems at a first sight seem very different they possess properties that make them valuable and interesting to compare.

Experimentally, hydrogen fluoride (HF) chains possess a zigzag structure,^{6,7} but first-principles calculations on both linear and zigzag forms have shown^{8,9} that in most respects the results are very similar for the two forms. Similarly, most conjugated polymers have alternating single and double carbon-carbon bonds (see, e.g., Ref. 10), whereas the (nonexisting) linear carbon (CC) chain has alternating single and triple bonds. However, since most of the physical properties of both the more conventional conjugated polymers and of the linear CC chains are related to a dimerization by which the carbon-carbon bond lengths become alternating, the CC chains constitute an excellent model system for examining interchain interactions for conjugated polymers.

Using the experimental values of the dipole moment and the bond length of an isolated HF monomer¹¹ one can estimate an electron transfer of 0.4 electrons from hydrogen to fluorine. This value (only slightly modified for the polymer) implies large electrostatic interactions between the HF chains. On the other hand, since all carbon atoms of a single, isolated CC chain are equivalent, a similar transfer does not exist for the CC chains. The number of valence electrons per diatomic unit is however the same for the two systems such that a comparison between them makes it possible to gain insight into the

effect of electrostatic interactions and that of electronic interactions separately.

We have here considered five different relative arrangements (or configurations) of the two chains of which the four are schematically shown in Fig. 1. In the first set of calculations we only considered the four arrangements of Fig. 1. These can be described as a parallel (I,III) or antiparallel (II,IV), and as an in-phase (I,II) or in-antiphase (III,IV) configuration. In the first set of calculations two fixed values of the interchain distance D were chosen (5.0 and 8.0 a.u.). These are to be compared with the experimental values 6.05 a.u. and 8.01 a.u., respectively, for crystalline hydrogen fluoride⁶ and *trans*-polyacetylene,¹² respectively. Since we expect hypothetical linear HF chains and CC chains to be more compact, we have here chosen slightly smaller values. The next-nearest-neighbor distance h along the chains (which equals the length of the unit cells) was set to 4.8 a.u. for HF and 5.1 a.u. for CC chains, which are reasonable values.^{8,9,13,14} Finally, the dimerization amplitude d was varied from 0.0 to 0.8 a.u. in steps of 0.2 a.u. for hydrogen fluoride and from 0.0 to 0.3 a.u. in steps of 0.1 a.u. for carbon chains.

Whereas the dimerization amplitude in the first set of calculations was varied simultaneously on both chains, we fixed it on one of the chains and varied it only on the other chain in the second set of calculations. In this set we moreover only considered that value of D (5.0 a.u. or 8.0 a.u.) and that phase (i.e., the in-phase or the in-antiphase configuration) which resulted in the lowest total energy in the first set of calculations. The fixed dimerization amplitude of the one chain was chosen close to the optimal value of an isolated chain, i.e., equal to 0.60 a.u. for HF chains and to 0.20 a.u. for CC chains. In this set of calculations we thus focus on the crossover from parallel to antiparallel configurations.

In the third and last set of calculations we varied D for the optimal relative arrangement of the two chains as found in the first set. In this set the values of d and h were fixed.

The first-principles method is based on the density functional formalism in a local approximation and on the Born-Oppenheimer approximation. The eigenfunctions to the Kohn-Sham equations are expanded in linear muffin-tin orbitals, but the full potential is included in the calculations. The method has been described elsewhere in detail,^{15,16} and has with success been applied both on isolat-

ed HF chains^{8,9} and on isolated CC chains,^{13,14} as well as on other systems (see, e.g., Ref. 16).

The calculated relative total energy per diatomic unit is depicted in Fig. 2 for the HF chains and in Fig. 3 for the CC chains. We will now discuss these results.

The results for the HF chains (Fig. 2) show a strong dependence on D , such that the two degenerate minima for $D = 8.0$ a.u. are 10.3 eV below those for $D = 5.0$ a.u. Also the position of the minima is slightly shifted being $d = \pm 0.58$ a.u. for $D = 5.0$ a.u. and $d = \pm 0.56$ a.u. for $D = 8.0$ a.u. In the limit $D \rightarrow \infty$ the earlier reported results [Refs. 8 and 9; for comparison included in Fig. 2(e)] give $d = \pm 0.51$ a.u. For both values of D there is a large difference between the results for the in-phase and the in-antiphase arrangements. Due to slightly different treatments of the in-phase and the in-antiphase configurations we cannot put absolute numbers on the energy difference between them, but it is of the order of some eV per diatomic unit with the in-phase arrangement being preferred. The energy differences between parallel and antiparallel forms are much smaller being 0.4 eV (0.2 eV) for the in-phase forms for $D = 8.0$ a.u. (5.0 a.u.) with the antiparallel arrangement having the lower total energy. It is surprising that we find this difference to be largest for the largest interchain distance. The barrier for a collective displacement of all protons (i.e., $d \rightarrow -d$) is seen to be largest in Fig. 2(a); i.e., for the smallest interchain distance as should be expected; and due to the larger total energy for the in-antiphase configurations the barrier is also larger for the in-phase than for the in-antiphase configurations. For $D = 8.0$ a.u. [Figs. 2(c) and 2(d)] the average between the barriers for the parallel and antiparallel configurations is close to the barrier for $D \rightarrow \infty$ [Fig. 2(e)], as could be expected. The finding of a preferred antiparallel configuration of HF chains is in agreement with the results of Santry and co-workers^{17,18} obtained by using a semiempirical method in examining solid HF. They predict the energy difference to be about 0.1 eV per monomer, which is in good agreement with our results although there are many differences in the structures considered. The results contradict however experimental ones on solid DF.¹⁹ The results of the second set of calculations [Fig. 2(f)] show the surprising result that the dimerization is almost suppressed, and only a very weak preference for antiparallel configurations remain. We have no direct explanation of this but will return to it un-

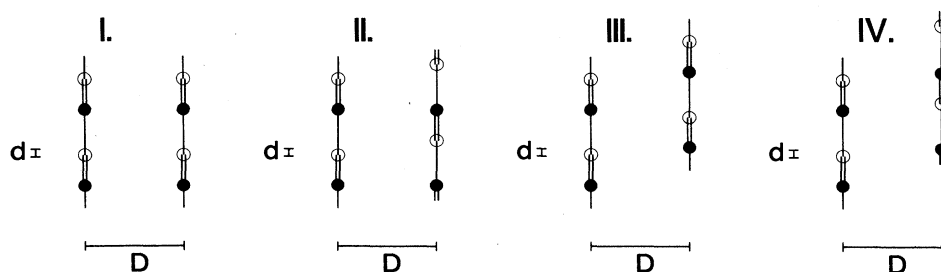


FIG. 1. Different interchain configurations: Parallel (I and III) and antiparallel (II and IV); in-phase (I and II) and in-antiphase (III and IV). The interchain distance D and the displacement d of half the nuclei away from the symmetric positions are also shown. For carbon chains all atoms are identical and the double (single) lines represent triple (single) bonds. For hydrogen fluoride the open (closed) circles represent hydrogen (fluorine) atoms, and the double (single) lines represent molecular (hydrogen) bonds.

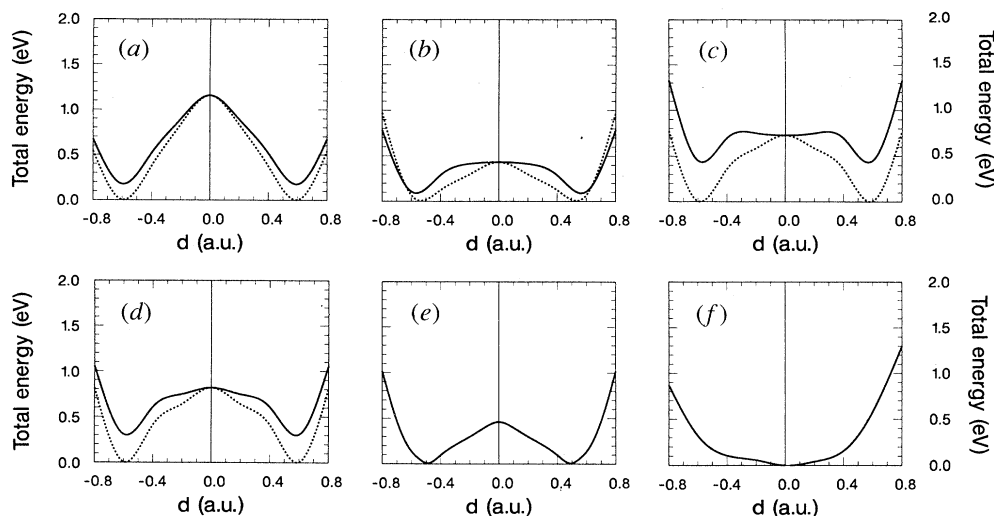


FIG. 2. Relative total energy per diatomic unit for two hydrogen fluoride chains as a function of d . $D = 5.0$ a.u. in (a) and (b), and 8.0 a.u. in (c) and (d). In (a) and (b) the results are shown for in-phase configurations, and in (c) and (d) for in-antiphase configurations. In (a)–(d) the solid (dashed) lines represent results for parallel (antiparallel) configurations. For comparison results for a single chain ($D \rightarrow \infty$) are shown in (e). The results in (f) are for $D = 8.0$ a.u., and the in-phase configuration. The dimerization amplitude of one chain is here fixed at 0.60 a.u., whereas that of the other chain is gradually varied such that for $d = -0.60$ a.u. the chains are parallel and for $d = +0.60$ a.u. they are antiparallel.

der the discussion of the results for the carbon chains. In this figure we notice, however, that the total energy depends only weakly on d for $|d|$ roughly smaller than the optimal value of an isolated value of an isolated chain, and the finding of a suppressed dimerization is therefore connected with some uncertainty.

The results on the CC chains show some different dependences on the relative arrangement of the two chains compared with the results for the HF chains. Thus, the minima for $D = 8.0$ a.u. are only 6.4 eV per diatomic unit below those for $D = 5.0$ a.u. On the other hand, the energy differences between the in-phase and the in-antiphase configurations are as those for HF. In contrast to the case for the HF chains, the dimerization of

the CC chains depends strongly on the relative arrangement of the two chains. For the energetically unfavorable situation of two close-by chains [$D = 5.0$ a.u.; Figs. 3(a) and 3(b)] the calculations indicate a remarkable suppressed dimerization. Moreover, for well-separated chains [$D = 8.0$ a.u.; Figs. 3(c) and 3(d)] the barrier for the collective shift $d \rightarrow -d$ is found significantly larger than in the limit $D \rightarrow \infty$ [Ref. 20; for comparison included in Fig. 3(e)]. The lack of electrostatic interactions leads to the parallel configuration being preferred for the in-antiphase configuration and to the antiparallel configuration being preferred for the in-phase configuration since the electronic interactions will be dominating without long-range electrostatic interactions.

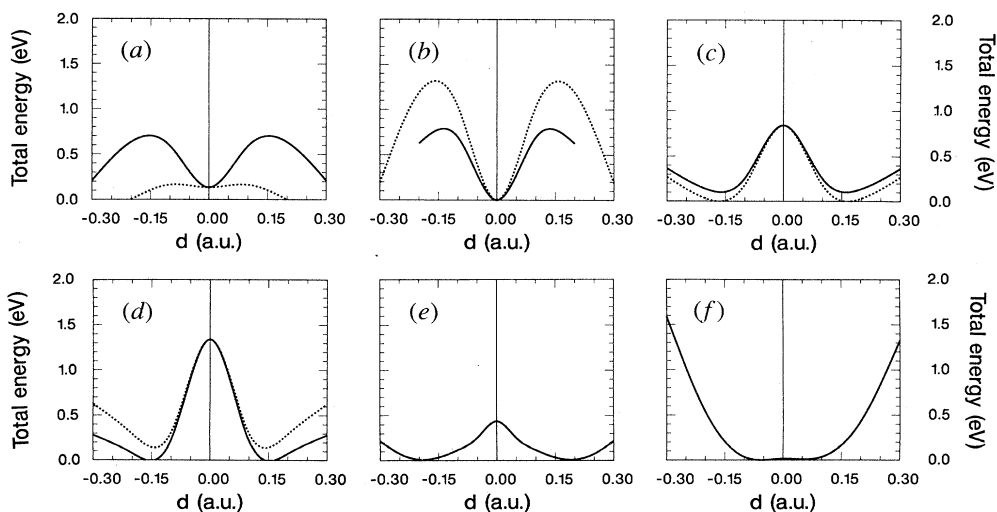


FIG. 3. As Fig. 2 but for two carbon chains. The fixed dimerization amplitude in (f) is here set equal to 0.20 a.u.

The energy difference between the parallel and the antiparallel configuration is for the in-phase configuration roughly half that for HF, i.e. 0.1 eV. This value is about one order of magnitude larger than that found by Vogl *et al.*²¹ from first-principles calculations on an assumed crystalline structure of *trans*-polyacetylene, and they furthermore predict the parallel configuration to be preferred. On the other hand, Zemach *et al.*²² have argued that the experimental optical properties of *trans*-polyacetylene agree best with their first-principles results for a structure with antiparallel chains. Also they report a small total-energy difference for the two structures. However, it should be pointed out that although we have argued that the carbon chains can be considered representative for the class of conjugated polymers, there is one important difference between the carbon chains and most other conjugated polymers: the bond length alternation is considerably larger for the former than for the latter (roughly a factor of 3), and, accordingly, also the dimerization energy is larger for the carbon chains than for the other conjugated polymers. It should finally be added that experimentally it is not yet established whether the chains prefer parallel or antiparallel configurations.^{23,24} The latter can be understood from the present results when assuming a more or less random distribution of the lining-up of neighboring (finite) chains. Finally, the second set of calculations [Fig. 3(f)], where we considered the in-phase configuration with $D = 8.0$ a.u. and with the dimerization amplitude of one chain fixed at 0.20 a.u., led to an almost complete suppression of the dimerization as also was the case for the HF chains. The reason for this result as well as for that for the HF chains might be the same as that proposed by Ashkenazi *et al.*²⁵ in explaining their results for *trans*-polyacetylene. They reported the results of a first-principles investigation of the dimerization amplitude of crystalline, three-dimensional polyacetylene and these indicated a significant underestimate of this amplitude. They proposed that this could be due to interchain interactions as well as to strong correlation effects beyond those of the density-functional formalism with a local approximation.

The finding in the first set of calculations of the in-phase configuration (in contrast to the in-antiphase configuration) to be the stable one for two interacting polymer chains is in agreement with the results of *ab initio* Hartree-Fock calculations on two polyoxymethylene chains.²⁶ These calculations represent to our knowledge the only other parameter-free examinations of the interactions between two chains except for the above-mentioned calculations on sulphur nitride chains.

In the last set of calculations we varied the interchain distance D for the antiparallel in-phase configuration with $d = 0.6$ (0.2) a.u. for the HF (CC) chains. It turned out that the total energy was a monotonically decreasing function of D in the range 5–9 a.u. This can be understood as due to electrostatic interactions for HF as well as to electronic interactions for both systems. For the latter the total electronic energy of completely filled bonding and antibonding combinations of atomic orbitals is a decreasing function of the overlap between the orbit-

als, according to the simplest Hückel theory. We should finally mention that the lack of a stable structure for two linear chains might be modified when considering a complete two-dimensional array of chains, which furthermore do not need to be linear and lying in parallel planes. However, in a recent paper Ishii *et al.*²⁷ examined the interactions between various *trans*- or *cis*-polyacetylene chains using a semiempirical approach and considering structures closely related to those of crystalline polyacetylene. Their results indicate a lacking stability of seven or three interacting chains compared with isolated chains. Furthermore, a significant difference between results for seven and three interacting chains implies multichain effects to be important.

Let us now turn to a discussion of the interactions between the electronic orbitals. One way of estimating these is to examine the splittings of the single-particle energy levels. In such an approach the absolute shifts of the levels are not included, which, however, are non-negligible as we shall see.

In Fig. 4 we show the band structures for two interacting HF chains as calculated in the first set of calculations. d was fixed at 0.60 a.u. and only in-phase arrangements are considered. The band structures can be understood by analyzing a single hydrogen fluoride monomer. For this there are four doubly occupied valence orbitals of which two (the π_1 orbitals) are degenerate.^{8,9} The lowest one (σ_1) is strongly localized to the region between the two nuclei. Of the other three, one (σ_2) is mainly a fluorine p orbital parallel to the molecular axis, and the other two (π_1) are largely fluorine p orbitals perpendicular to this axis. Upon forming a single linear chain the band formed by the σ_2 orbitals shows the largest dispersion (≈ 5 eV), whereas those of the others are much smaller (< 1 eV). The symmetry is lowered when approaching two chains to each other, thereby splitting the doubly degenerate π_1 bands into a σ_3 and a π_1 band. Near the zone center this π -derived σ_3 band interacts with the σ_2 band and a unique identification is difficult (see Fig. 4). But at the zone edge the splittings of the bands can be used as measures of the interactions of the orbitals.

In Fig. 4 we see only small changes in the band structures as functions of the relative arrangement of the two chains. Most noticeable is the decrease in the splittings of the σ_3 and π_1 bands upon increasing D , and a simultaneous shift of all bands towards lower energies. The latter we will ascribe to electrostatic effects. In general the splittings are small (some few tenths of an eV) as expected from the localization of the orbitals to a single chain.

Similar to Fig. 4 for the HF chains we show in Fig. 5 the band structures for two interacting CC chains with $d = 0.20$ a.u. and in-phase arrangements. For a single carbon chain the two lowest lying (σ_1 and σ_2) bands can be interpreted as related to the carbon sp hybrids along the chains. The other two valence bands are the doubly degenerate π_1 bands formed by carbon p orbitals perpendicular to the chain. As for HF, the π_1 bands split up into a σ_3 and a π_1 band when approaching two chains to each other. The bands of the same symmetry and derived from different single-chain bands are well separated throughout the Brillouin zone and the splittings can easi-

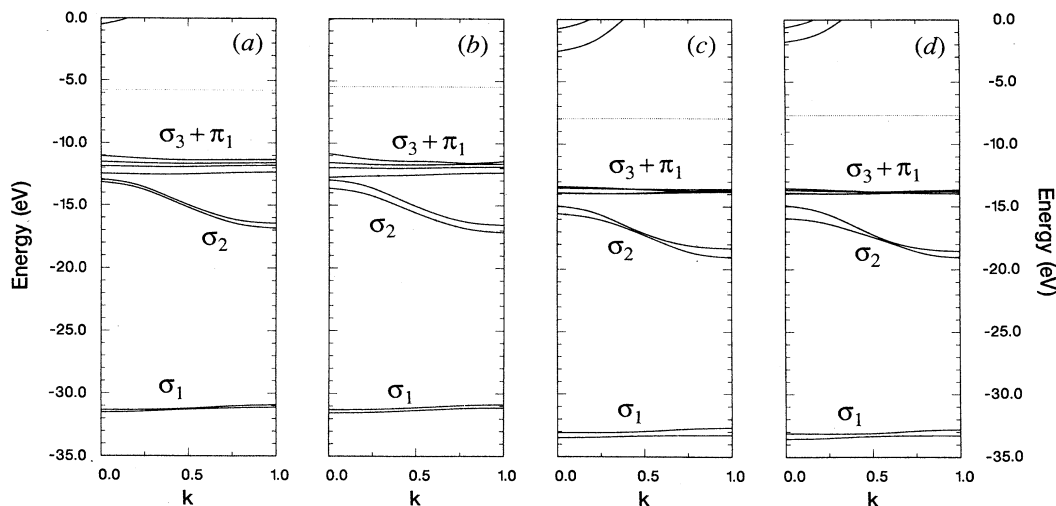


FIG. 4. Band structures for four different in-phase configurations of two hydrogen fluoride chains with $d=0.60$ a.u. $D=5.0$ a.u. in (a) and (b), and 8.0. a.u. in (c) and (d). The two chains are parallel in (a) and (c) and antiparallel in (b) and (d). The labeling of the bands refer to that of a single, isolated chain, except that the single-chain, doubly degenerate π_1 band has been split into a σ_3 and a π_1 band. The dotted lines represent the Fermi level.

ly be extracted from the results of the calculations as can be seen in Fig. 5. Compared with the band structures for the two HF chains in Fig. 4 we notice in Fig. 5 significantly larger splittings, which, furthermore, depend strongly upon the relative arrangement of the two chains. Moreover, the π -derived σ_3 and π_1 bands clearly show splittings about common levels due to the formation of antibonding and bonding orbitals, with the largest splittings for the σ_3 bands as expected. As for the HF chains, the bands are in unison shifted towards lower energies when increasing D , but the lack of strong electrostatic effects makes the shift smaller. In Fig. 5 we finally notice that both the nature and the size of the gap depend sensitively on the two-chain configuration for small values of D .

For the conjugated polymers the interchain interaction is most often included by simply adding a tight-binding

term for the interaction of the orbitals of the otherwise noninteracting chains (see, e.g., Refs. 28 and 29) to a Hamiltonian which includes explicit (tight-binding) descriptions of only the π electrons. Typically, the intra-chain hopping integrals (t_0) are assumed roughly 25 times larger than the interchain hopping integrals (t_1). Within this simple picture our calculated splittings equal $2t_1$. However, as can be seen in Fig. 5, our splittings are clearly k dependent. This is not included in the simplest model. Furthermore, especially for hydrogen fluoride but also for the carbon chains the interchain hopping integrals do depend on the dimerization amplitude d .

With the simple two-chain tight-binding model one can estimate³⁰ the total-energy difference between parallel and antiparallel configurations to be $\Delta E=(2t_1^2)/(\pi t_0)$ per diatomic unit. For reasonable values ($t_0 = 2.5$ eV, $t_1 = 0.1$ eV) this becomes 0.003 eV, i.e., significantly small-

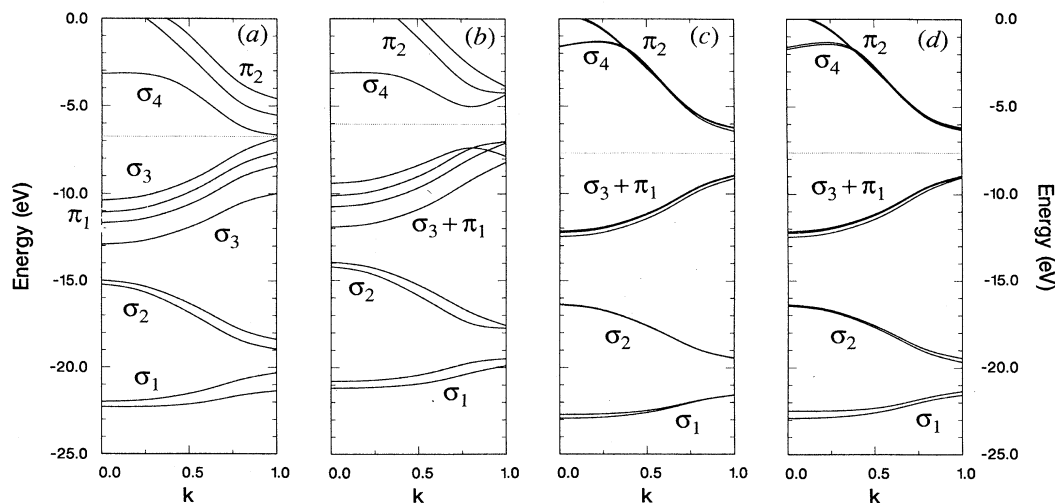


FIG. 5. As Fig. 4 but for two carbon chains with $d=0.20$ a.u.

er than the total-energy differences found in the present first-principles calculations [typically 0.1 eV; see Figs. 3(c) and 3(d)], also when multiplying by four in order to take all four valence bands into account. Thus, the simple model of adding an extra tight-binding term is not sufficient to describe the parallel vs antiparallel difference.

In concluding the presentation of the first-principles results we mention that they have been obtained from parameter-free calculations on nonexistent model compounds and should therefore be taken with some caution. However, we believe that the examined systems contain the main physical properties important for understanding the interactions between two chains. We will now summarize the central results.

The results suggest that for systems without long-range electrostatic interactions and with relatively delocalized orbitals (as the CC chains) the relative stability of the parallel and antiparallel configuration depends on the lining up of the chains, but the in-phase configuration is preferred. Moreover, for small interchain distances the dimerization might be suppressed. For systems with long-range electrostatic interactions and with orbitals fairly well localized to single chains (as the HF chains) the antiparallel configuration becomes overall preferred and the chains prefer the dimerized structure. For both types of systems the interchain interactions lead to splittings of the electronic levels which depend both on the relative arrangement of the chains as well as on the k number. Moreover, the interchain interactions are found to be significantly larger than predicted by the simplest models. Finally, significantly different results are obtained when letting the dimerization amplitude vary on only one chain.

The large interchain interactions as found in the first

set of calculations suggest that solitons are to be considered many-chain defects: A single solitonic defect assumed initially generated on one chain will influence the neighboring chains strongly and change their geometrical structure in order to reduce the total energy. This "polarization" effect will increase the probability for the center of the defect to jump from one chain to the next, and can thus account for the observed doping-induced increase in conductivity for conjugated polymers also observed in samples containing less oriented chains of limited lengths. On the other hand, these results seem somewhat contrasted by those of the second set of calculations. Whereas we in the first set varied the dimerization amplitude d simultaneously on both chains, d was in the second set fixed on one chain and only varied on the other. The second set might thus be of more relevance when discussing solitons assumed confined to a single chain. The results of this set suggest that due to interchain couplings the total energy as a function of the dimerization amplitude of a single — but not isolated — chain varies much less than for the isolated chain, thus making it easier to generate solitons. The results of both sets of calculations agree however upon the importance of interchain couplings, and only further studies on more realistic compounds can reveal whether the interchain interactions are so strong that they lead to instability of solitons or to "solitons" being many-chain defects. But carrying these studies through using first-principles methods is a very large and difficult task and beyond the scope of this communication.

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