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Comparison of the INDO band structures of polyacetylene, polythiophene, polyfuran, and polypyrrole

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Abstract

The intermediate neglect of differential overlap (INDO) band structures of polythiophene, polyfuran, and polypyrrole are analyzed in terms of the band structure of polyacetylene. This is done by decoupling the INDO Fock operator to obtain the band structure of the carbon system and of the heteroatoms. For all three polymer systems, the highest valence band is essentially a pure carbon band, whereas the lowest conduction band is a strong mixture of carbon and heteroatom bands. This suggests that the electron and hole should show distinct properties. This difference between the electron and hole can be understood in terms of coupling between the respective Wannier functions of polyacetylene and the heteroatoms. Polypyrrole shows a stronger coupling between the carbon and heteroatom bands than polythiophene or polyfuran. © 2001 Published by Elsevier Science B.V.

Keywords: Semiempirical models and model calculations; Polythiophene and derivatives; Polypyrrole and derivatives

1. Introduction

Much of our current understanding of conjugated polymers is based on the two-band model, such as that appropriate for the π-electronic structure of polyacetylene. Studies on the two-band model system have led to a rather detailed understanding of the electronic structure, including the effects of bond alternation and electron-electron interactions on the photophysics [1,2]. However, most conjugated polymers exhibit a number of π-bands, and the question arises as to what extent the properties of these multi-band systems can be understood within the context of the simpler two-band model [3]. One new aspect of the multi-band system is the presence of a variety of excitations, arising from excitations between the various bands [4–7]. Here, we consider a different issue, namely, the extent to which the π-band structure of polythiophene, polypyrrole and polyfuran can be understood in terms of a perturbed polyacetylene band structure. Such a connection may allow our knowledge of the two-band system to be transferred to these systems [3].

2. Computational approach

All results reported here were obtained using a computer program we recently developed that solves for the band structure of a one-dimensional periodic system using the INDO Hamiltonian. The INDO model includes both σ and π electrons and has been quite successful in predicting the electronic structure of medium-size organic molecules [8], and polythiophene oligomers [9].

The calculations are done on a polymer chain with N unit cells and periodic boundary conditions, such that there are N allowed values of the wave vector k in the region from $-\pi$ to π. Since the energy is only a function of the absolute value of k, the figures below show only the $(N+1)/2$ values of k between 0 and π. The band structure is obtained at the Hartree–Fock level, such that the band energies are equivalent to the Hartree–Fock orbital energies that would be obtained in a calculation on a circular ring containing N unit cells [10]. The Wannier functions are obtained through the standard inverse Fourier transform of the Hartree–Fock orbitals, with phases of the molecular orbitals chosen to minimize the size of the Wannier function.

The chemical structures of the unit cell were obtained by performing a geometry optimization of an oligomer at the AM1 level [11], and extracting the geometry of the central unit cell. In the geometry optimization, the system was constrained to remain planar. This was done to allow a rigorous separation of σ and π electrons, thereby allowing us to focus on the effects of the heteroatom on the π-electronic structure.

In the following analysis, it will be useful to decouple the π-electronic structure into that of the carbon atoms and that

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of the heteroatoms. This decoupling is done at the Hartree–Fock level as follows. Since the systems are planar, the Fock operator is block diagonal in σ and π electrons, with no matrix elements connecting the σ and π spaces. We begin by taking the π-electron block of the Fock matrix, and transforming it back to the atomic p_z orbitals. We then extract the submatrix corresponding to the carbon p_z orbitals, and that corresponding to the heteroatom p_z orbitals, and diagonalize these submatrices. The resulting orbitals are then π-orbitals residing either on the carbon atoms or the heteroatoms. The carbon and heteroatom band structures have thus been decoupled at the Hartree–Fock level. Note that the Fock operator connects these two subspaces, such that diagonalization would lead to the full π-electronic structure.

The Fock operator is a function of the electronic density matrix, such that it includes the interaction between an electron and the average charge density of the remaining electrons. In the above decoupling procedure, the Fock operator is that for the full (coupled) electronic structure. The electrons in the carbon π-electronic structure therefore move in the potential of both the carbons and the heteroatoms. Thus, Coulomb interactions with the heteroatoms are included even in the decoupled band structure.

3. Results

3.1. Polyacetylene

Our goal is to consider the extent to which the band structure of the heteroatom containing polymers may be understood within the context of polyacetylene. The INDO band structure of polyacetylene is shown in Fig. 1. Note that the bandwidth of the valence and conduction bands are not equal. This breaking of electron–hole symmetry arises from electron-transfer terms in the INDO Hamiltonian that go beyond next nearest neighbors.

A unit cell of polythiophene is shown in Fig. 2. The unit cell contains eight carbon atoms, with alternating single and double bonds. One effect of the heteroatoms is therefore to increase the size of the unit cell from two carbons, in polyacetylene, to eight carbons, in polythiophene. Fig. 3 shows the band structure of polyacetylene obtained by expanding the unit cell by a factor of four. We will refer to this as the band structure of PA4. This expansion of the unit cell corresponds to a reduction in the size of the Brillioun zone by a factor of four. The valence band of polyacetylene then becomes four valence bands. Note that this is simply an alternative view of the band structure in Fig. 1, with the single valence band folded into the reduced Brillioun zone. Similarly, the conduction band becomes four conduction bands in the reduced Brillioun zone.

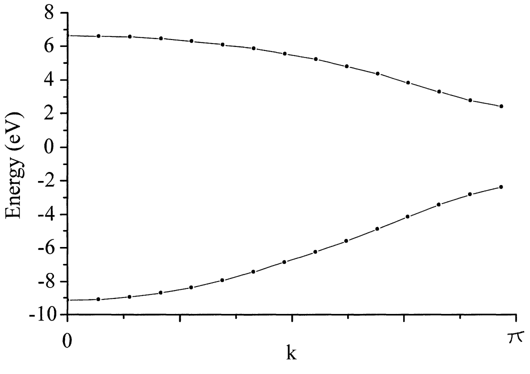

Fig. 1. The π band structure of polyacetylene, obtained from an INDO calculation on a polymer with 29 unit cells (58 carbon atoms) and translational symmetry. The lower band is the valence band and the upper band is the conduction band.

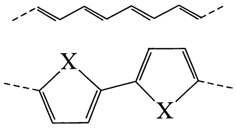

Fig. 2. Chemical structure of the unit cell of polythiophene ($X = S$), polyfuran ($X = O$), and polypyrrole ($X = N$), compared to that of PA4. (PA4 is polyacetylene with the unit cell expanded by a factor of four). To allow for rigorous separation of σ and π electrons, the polymers are constrained to remain planar in these studies.

3.2. Polythiophene

Fig. 4 shows the π-band structure of polythiophene. While the four conduction bands resemble those PA4, the valence bands show additional structure. Each of the two sulfurs in the unit cell has a p_z orbital, and this causes there to be six valence bands, as compared to the four of PA4. The two relatively flat bands near −10 eV can be qualitatively attributed to these sulfur orbitals.

Fig. 5 shows the π-band structure decoupled into the carbon and sulfur π-orbitals, using the procedure described above. The carbon bands resemble those of PA4, and the sulfur bands are flat bands at −10.8 eV. Comparison with the

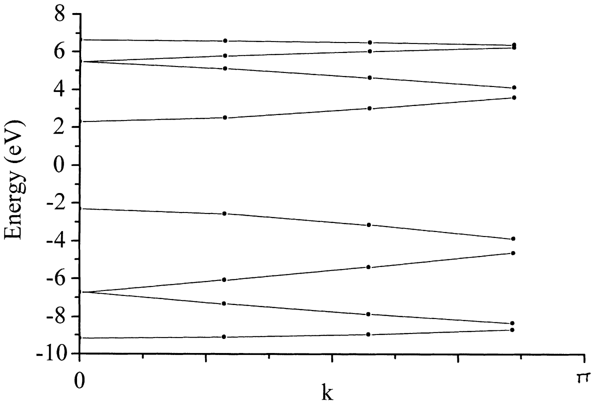

Fig. 3. The INDO π-band structure of PA4 (see Fig. 2), obtained from a calculation on a polymer with seven unit cells (56 carbon atoms). The expansion of the unit cell of polyacetylene by a factor of four, leads to a four fold reduction in the Brillioun zone. The bands are equivalent to those of Fig. 1, folded into this reduced Brillioun zone.

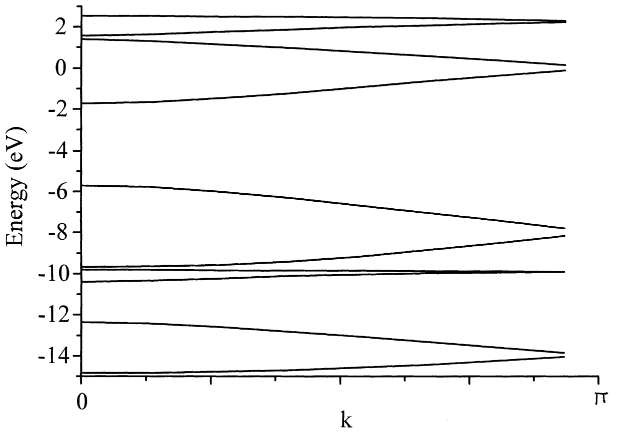

Fig. 4. The INDO π-band structure of polythiophene, obtained from a calculation on a polymer with 15 unit cells and translational symmetry. The top four bands are conduction bands and the bottom six bands are valence bands.

full band structure, shown as dotted lines in Fig. 5, indicated that the sulfur bands interact strongly with the lowest two carbon bands.

Comparison of the decoupled and full band structures reveals an interesting difference between the highest valence band and lowest conduction band. (These bands are the analog of the HOMO and LUMO orbitals). The highest valence band is essentially unaltered by coupling to the sulfur, while the lowest conduction band shifts up in energy by about 0.7 eV. This can be understood by comparing the Wannier functions of polythiophene with those of PA4 (Fig. 6). Note that the Wannier functions of polythiophene and PA4 exhibit similar nodal patterns on the carbon atoms. Next, we consider the carbon atoms that are bonded to the sulfur, since these likely dominate the coupling between the carbon and sulfur bands. In the highest valence band of PA4, the Wannier function has roughly equal magnitude on these carbons but opposite phase. When this band is coupled to the sulfur, the change in phase causes the coupling to cancel. This is shown both by the energy of the highest valence band being unaffected by the coupling with sulfur, and by the Wannier function of the highest valence band of polythiophene having little amplitude on the sulfur atom. The opposite is true for the lowest valence band, where the Wannier function of PA4 has roughly equal magnitude and phase on the carbons that are bonded to the sulfur. This leads to strong coupling with the sulfur, as shown by the 0.7 eV increase in energy of the lowest conduction band on coupling with the sulfur, and by the Wannier function of this band of polythiophene having a relatively large magnitude on the sulfur atom.

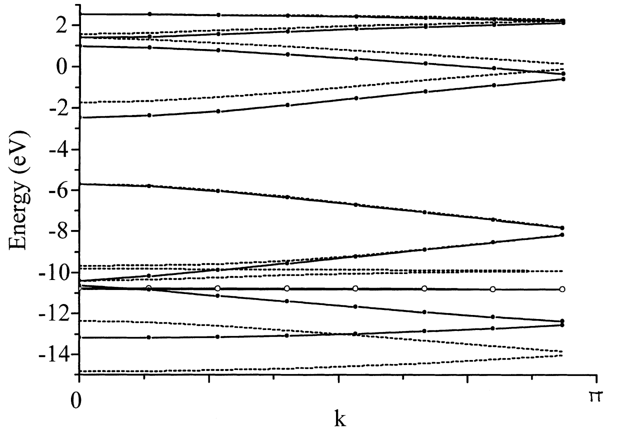

Fig. 5. The INDO π-band structure of polythiophene decoupled into carbon and sulfur bands as described in the text. The dotted lines are the full band structure of Fig. 4. The filled circles are the carbon bands, and the open circles are the sulfur bands.

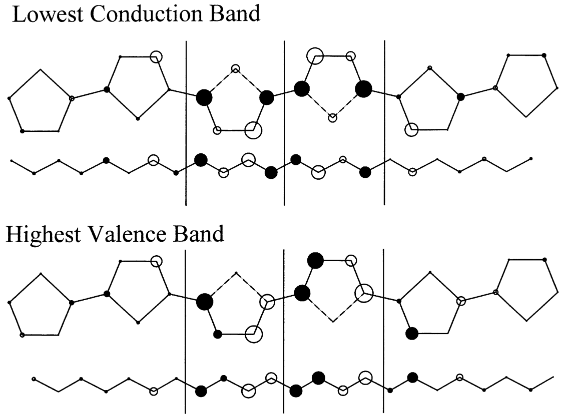

Fig. 6. The Wannier functions of PA4 and polythiophene, corresponding to the band structures of Figs. 3 and 4.

3.3. Comparison with polypyrrole and polyfuran

Figs. 7 and 8 show both the full and decoupled band structures of polypyrrole and polyfuran, respectively. The effects are similar to those seen in polythiophene. In particular, the highest valence band is relatively unaffected by coupling with the heteroatom, while the lowest conduction band is substantially shifted to higher energy.

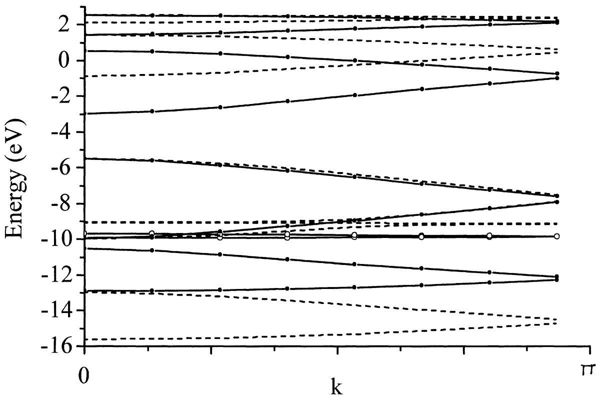

Fig. 7. The INDO π-band structure of polypyrrole. The lines are labeled as in Fig. 5.

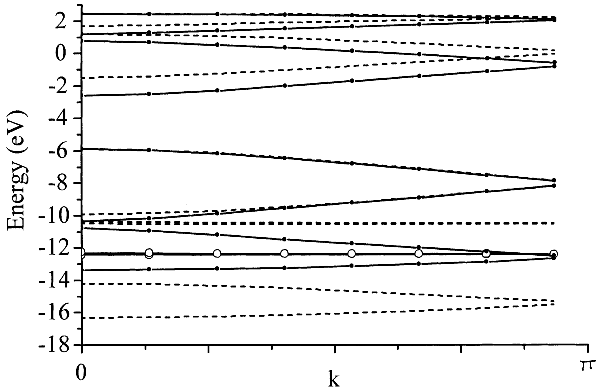

Fig. 8. The INDO π-band structure of polyfuran. The lines are labeled as in Fig. 5.

The Huckel theory of polyacetylene can be used to interpret the decoupled carbon bands. In Huckel theory, polyacetylene is described by two parameters, the transfer integrals for the double and single bonds, t_2 and t_1. The total width of the bands, from the bottom of the valence band to the top of the conduction band, is set by the average of these transfer integrals. In all three systems, the total width of the decoupled carbon bands is about 15.5 eV, suggesting the average strength of the carbon–carbon π-bonds is the same in all three systems. In Huckel theory, the band gap is set by the bond alternation, $|t_2 - t_1|$. The band gap of the decoupled carbon bands is 3.2 eV in polythiophene, 3.3 eV in polyfuran, and 2.5 eV in polypyrrole. This suggests that polypyrrole has a significantly smaller effective bond alternation than the other two systems.

The strength of the coupling between the carbon and heteroatom bands is revealed by the shift of the respective bands. Coupling with the heteroatom raises the lowest conduction band by 0.7 eV in polythiophene, 1.0 eV in polyfuran and 2.1 eV in polypyrrole. This suggests that polypyrrole has much stronger effects from the presence of the heteroatom, than in the other two systems. This is also observed in the lowest two valence bands, which are more strongly perturbed in polypyrrole, than in the other two systems.

4. Discussion

The above calculations decouple the carbon and heteroatom and structures at the level of the Fock operator for the π-electrons. The Fock operator is based on the full electronic density matrix, such that the electrons move in the averaged charge distribution of the entire polymer. Thus the electrons in the carbon band structure experience the charge distribution of the entire σ bonding network, and the π-electron charge distribution on the heteroatoms.

In all three systems studied, the highest valence band is essentially a pure carbon band and shows little effects on coupling of the carbon and heteroatom band structures. The lowest conduction band, however, shows strong effects due to this coupling. This strong braking of electron-hole symmetry suggests that the electron and hole should show distinct properties in these systems. This difference between the electron and hole can be understood simply in terms of the nodal pattern of the respective Wannier functions of polyacetylene (PA4).

It was also found that the decoupled carbon bands of polypyrrole exhibit a smaller effective bond alternation than that of polythiophene and polyfuran. (The non-planarity of these systems, ignored in this work, will also alter the effective bond alternation). Polypyrrole also exhibits much stronger coupling between the carbon and heteroatoms bands, than that seen in the other two systems.

The results shown here indicate that is it is possible to understand certain aspects of the band structure in heteroatom containing polymers via a model where the heteroatom perturbs the π-electronic structure of the carbons. This suggests that it may be possible to transfer some of our understanding of the two-band model, such as the effects of electron–electron interactions and bond alternation on the excited states, to these systems.

Acknowledgements

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