Theory of positive muons in polyacetylene

LETTER TO THE EDITOR

Theory of positive muons in polyacetylene

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Abstract. We calculate the effects of introducing muonium (a positive muon plus one electron) into *trans*-polyacetylene and *cis*-polyacetylene. We find that the energetically favoured site for the muon produces an sp^3 hybridized carbon atom and an associated spin distribution. The spin is bound to the muon in *cis*-polyacetylene but is free to propagate in *trans*-polyacetylene. The presence of the muon acts as a barrier to the motion of mobile electronic defects.

Muon spin rotation (μSR) provides a sensitive test of the local magnetic environment in solids (Cox 1987). In particular, the relaxation rate of the muon spin following implantation probes the spin distribution of the electrons in the vicinity of the positive muon. Recently, this technique has been applied to conducting polymers (Nagamine *et al* 1984, Ishida *et al* 1985, Nagamine and Ishida 1986, Pratt *et al* 1990), which are of considerable interest because they can be electrochemically doped to achieve absolute conductivities and conductivities per unit mass comparable to those of conventional metals (Hayes 1985). Device applications are also being developed (Burroughes *et al* 1988). From a physical point of view the materials are interesting because of their one-dimensionality and strong electron–lattice coupling (Su *et al* 1979, Heeger *et al* 1988).

In this letter we report the first theoretical determination of the structures taken up by implanted muons in conducting polymers and of the associated spin distributions. In order to address this type of issue, it is important to begin with a method which goes beyond simple one-dimensional model Hamiltonians (Su *et al* 1979), since these cannot incorporate the perturbation introduced by the presence of the muon without additional assumptions. We adopt a procedure in which the equations of semi-empirical Hartree–Fock theory at the complete neglect of differential overlap (CNDO) level (Pople and Beveridge 1970) are solved simultaneously with the classical Newtonian dynamical equations of motion for the ions (Wallace 1990, Wallace *et al* 1991a,b). The ionic motion can be damped to find the minimum-energy geometry if desired. While not affording the accuracy of *ab initio* electronic structure methods, this approach has the advantage of employing a calculation of the electronic structure which is well tested for organic materials and which allows typical polymer

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chains to be treated self-consistently in their entirety with modest computational resources. We can then return to a model Hamiltonian to provide a framework for understanding our results, once the nature of the muon site has been established.

Note that our calculation treats the muon itself as a classical object; this approximation will be a poor one if the zero-point motion of the muon is important. However, we shall see that the favoured site for the muon in polyacetylene involves bonding to an sp^3 hybridized carbon atom. The vibrational frequency for such a muon bond is approximately $10\,000$ cm^{-1}, corresponding to a zero-point energy of 0.6 eV. This is small compared with the binding energy of the muon to the polymers (see below). Hence, given that it is unlikely that low-energy paths between equivalent muon binding sites exist with activation energies comparable to the zero-point energy, we conclude that the zero-point motion is unlikely to be important.
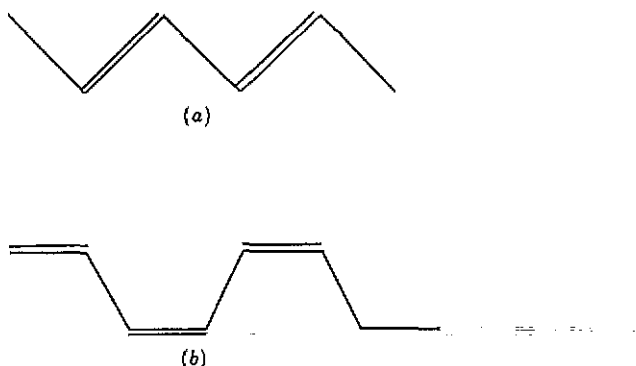

Figure 1. Schematic bonding diagrams for (*a*) the degenerate polymer *trans*-polyacetylene; (*b*) the non-degenerate polymer *cis*-polyacetylene.

It is important to distinguish between degenerate and non-degenerate polymers (Hayes 1985). It is convenient to define the dimerization along the chain by

$$d_n = (-1)^n(b_{n,n+1} - b_{n-1,n}) \tag{1}$$

where $b_{n,n+1}$ is the bond length between atoms n and $n+1$ in the polymer's carbon backbone. For degenerate polymers such as *trans*-polyacetylene (see figure 1(*a*)), two inequivalent bonding configurations of the carbon backbone with dimerizations of opposite sign have the same energy, so mobile defects across which the dimerization changes sign can exist in arbitrarily long chains. In non-degenerate polymers such as *cis*-polyacetylene however, the symmetry between positive and negative dimerizations is broken (see figure 1(*b*)) and only defects across which the dimerization's sign is unchanged are stable.

We shall assume that a positive muon that has come to rest in a polymer will already have captured an electron to form electrically neutral muonium. This point is discussed by Cox (1987). We model the resulting system by adding an additional neutral hydrogen atom to a molecule of the polymer; this is appropriate when performing damped molecular dynamics to find the ground-state molecular geometry because the result is independent of the nuclear masses. (We need only include the muon mass explicitly when performing undamped dynamical calculations.) We have used chains with a length of 32 carbon units for the calculations; the resulting minimum-energy

geometries for the two polymers have a carbon atom converted in each case from sp^2 to sp^3 hybridization. The calculated binding energies of the muon to the polymers are 6.4 eV for *trans*-polyacetylene and 4.0 eV for *cis*-polyacetylene. These may be reduced by the zero-point energy of the bound muon (see above).
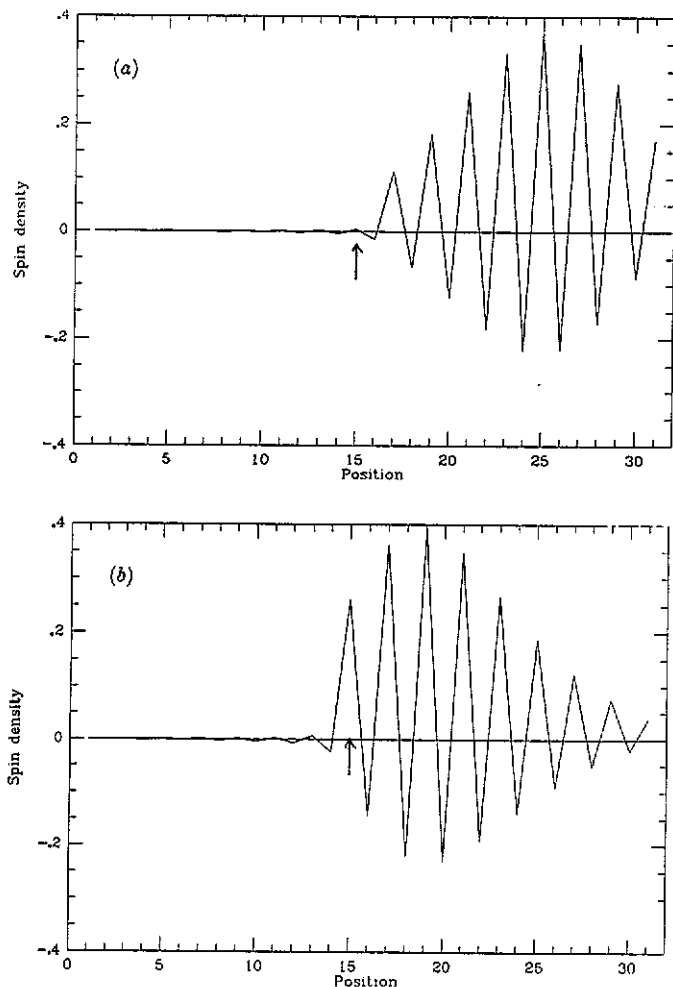

Figure 2. Spin density as a function of position for a muon introduced near the centre of a chain of (*a*) *trans*-polyacetylene; (*b*) *cis*-polyacetylene. The arrow shows the muon site.

The unpaired electron spin introduced by the muonium resides predominantly on the carbon backbone of the molecule. Figure 2 shows the spin density as a function of position along the chain when the muon is introduced into a stable site near the centre of the chain. In each case the spin density is effectively confined to one side of the muon, which therefore acts as a barrier to the propagation of spin excitations. Which side of the muon is favoured depends on where it was introduced relative to the bonding pattern of the unperturbed chain; if the muon ends up at a carbon site on the left-hand end of a double bond then the spin is bound to it on the right, and vice versa. Figure 3 shows the corresponding results when the muon is introduced
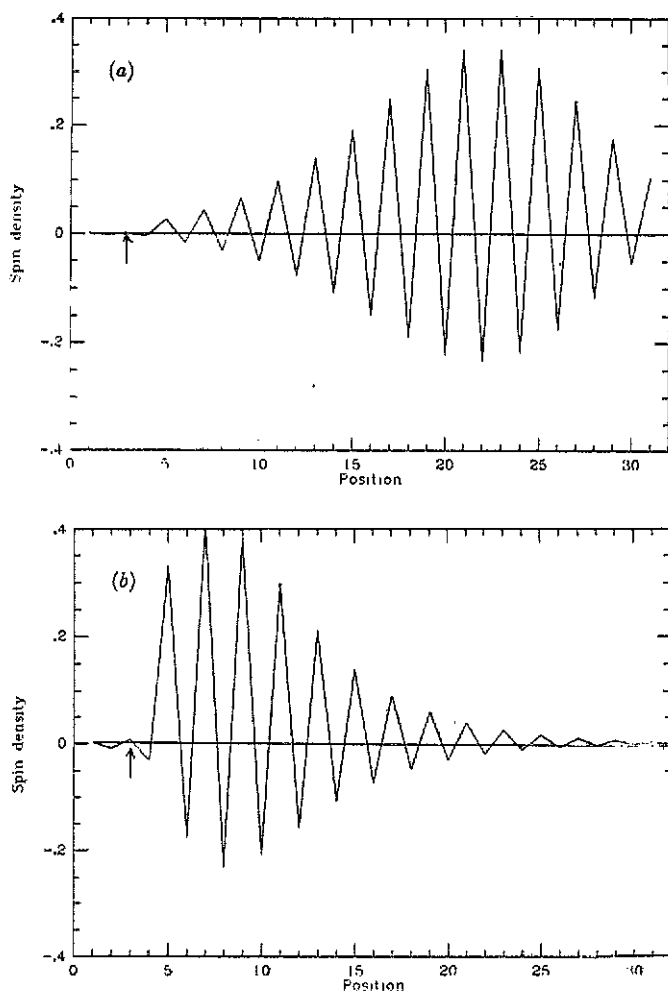
Figure 3. Spin density as a function of position for a muon introduced near the end of a chain of (*a*) *trans*-polyacetylene; (*b*) *cis*-polyacetylene. The arrow shows the muon site.

near one end of the chain, with the unpaired spin always residing in the longer part of the chain. In the case of the degenerate polymer *trans*-polyacetylene, the spin density is attracted to the opposite end of the chain; in the case of the non-degenerate polymer *cis*-polyacetylene however, it remains bound near the muon site. The reason for this is clear from the corresponding plots of dimerization as a function of chain length exhibited in figure 4. The separation of the spin density from the muon in *trans*-polyacetylene involves a change of sign of the dimerization over a long stretch of the chain. This would be highly unfavourable energetically in *cis*-polyacetylene, so in these materials the spin density remains bound near the muon.

We now compare the results of these calculations with previous experiments. A series of muon studies of polyacetylene have been reported by Nagamine and co-workers, who compared μSR in the *trans*- and *cis*-isomers of polyacetylene (Nagamine *et al* 1984). They reported that at low fields, significant muon polarization was observed for *trans*-polyacetylene, corresponding to more than half of the implanted
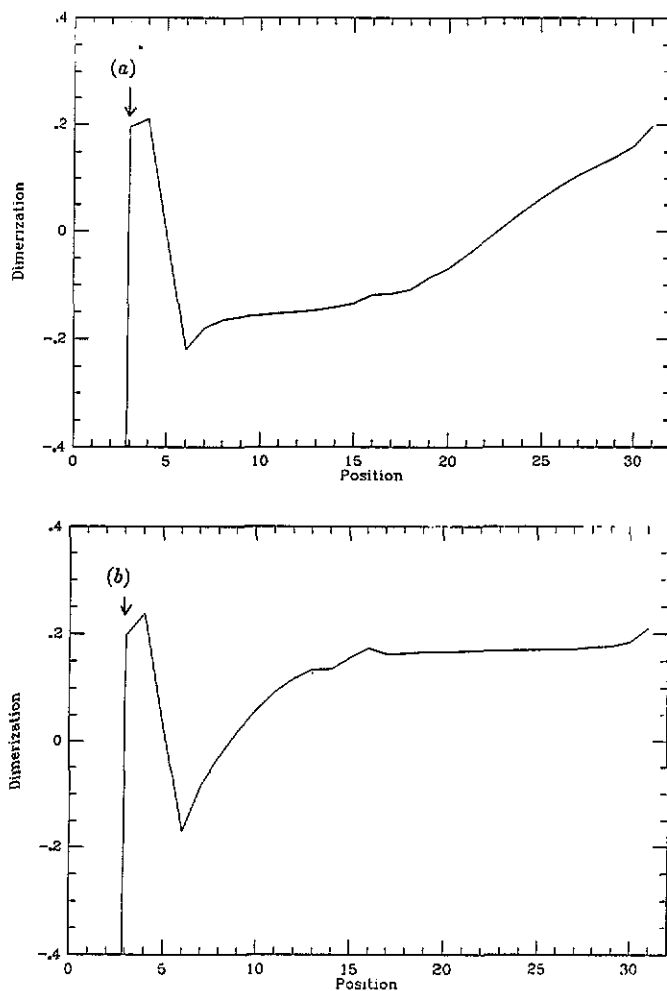
Figure 4. Dimerization as a function of position for a muon introduced near the end of a chain of (*a*) *trans*-polyacetylene; (*b*) *cis*-polyacetylene. The arrow shows the muon site.

muons. The retention of substantial polarization of these diamagnetic muons in *trans*-polyacetylene at short times was interpreted in terms of soliton diffusion (Ishida *et al* 1985). On the other hand, the muon spin polarization was almost completely lost in *cis*-polyacetylene after the shortest times that could be resolved, and this loss of polarization was interpreted in terms of the formation of a paramagnetic muonium-substituted radical state. Muon spin rotation experiments in *cis*-polyacetylene in a 16.6 kG transverse field give a hyperfine coupling constant of 91 MHz (Nishiyama *et al* 1986), which is of approximately the right size for a radical state.

It is straightforward to calculate the hyperfine coupling in the paramagnetic state of the muon expected in *cis*-polyacetylene on the basis of these calculations, as it is dominated by the contact interaction with the electron spin density in the hydrogenic s-state associated with the muon (Stoneham 1985). (Note that this quantity is not displayed in figures 2 and 3, which display the spin density along the carbon backbone only.) On this basis we estimate $A_\mu \approx 170$ MHz in *cis*-polyacetylene, larger than
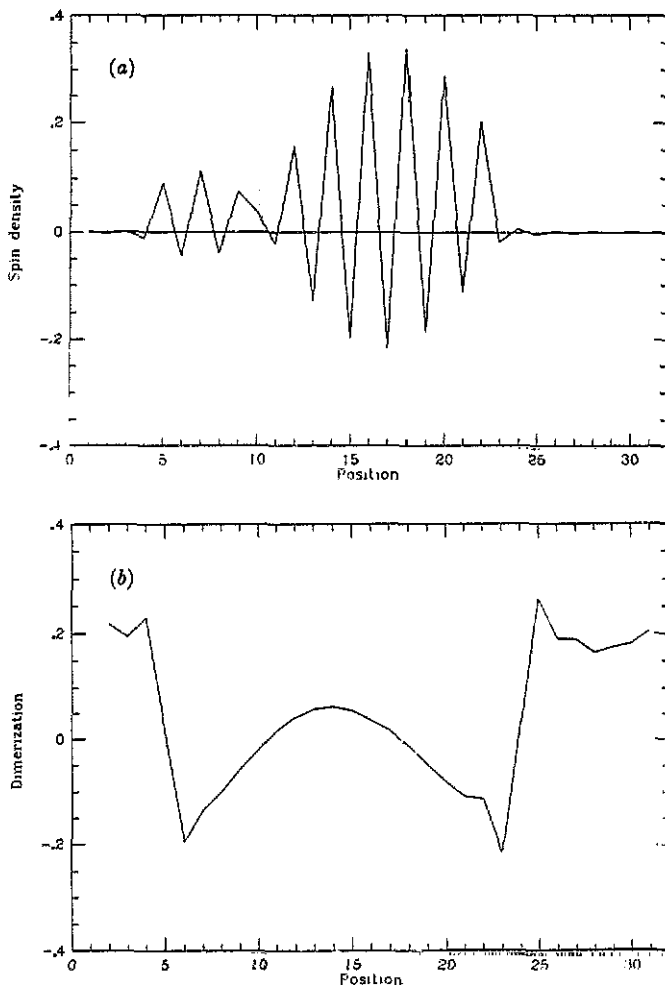
Figure 5. (*a*) Spin density and (*b*) dimerization for a chain of *cis*-polyacetylene containing both an implanted muon and an oxygen defect. The muon is on the left of the chain, the oxygen on the right.

the observed value. This leads us to conjecture that a typical electron state in *cis*-polyacetylene associated with the muon may not be well modelled by a perfect chain plus an implanted muon. If, instead, additional defects are present which themselves produce a change of sign in the dimerization (i.e., a reversal in the sense of bond alternation), the unpaired spin will be bound approximately equally to the muon and to the other defect. Effectively, it can tunnel back and forth between two nearly degenerate mid-gap states. This model leads to a reduction in the expected hyperfine coupling, improving the agreement with experiment. The dimerization and spin patterns induced when such an additional defect (in this case a hypothetical oxygen radical; see Helmie *et al* (1985)) is added to the chain at another point are shown in figure 5. The unpaired spin is shared betwen soliton-like distortions associated with the muon and with the oxygen defect, and the hyperfine interaction with the muon in the arrangement of figure 5 is $A_\mu \approx 60$ MHz. Our suggestion

that other defects may play a rôle is also supported by experimental work on other non-degenerate polymers, polypyrrole and polyaniline (Pratt *et al* 1990 and to be published), where the relaxation rate for the muon spin is relatively slow and indeed resembles the reported results for *trans*-polyacetylene more closely than it does *cis*-polyacetylene (see Nagamine *et al* 1984).

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