Optical and Magnetic Signatures of Localized Excitations in Pernigraniline: Role of Neutral Solitons

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Using a tight-binding Hamiltonian we study the Peierls distorted form of polyaniline, the pernigraniline base polymer. Both bond order and ring torsional degrees of freedom are considered in the conformational relaxation. The geometrical and electronic structures of the localized excitations are calculated. Comparison with available optical and magnetic measurements is made. Particular emphasis is placed on the spectroscopic and magnetic features of neutral solitons.

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Polyaniline is an interesting material due to its unusual transport, magnetic, optical, and environmental properties [1]. It is the first conducting polymer to be commercialized and now has uses ranging from electrostatic dissipation to batteries [2]. Compared to the prototype conducting polymer polyacetyelene, the physics behind this class of materials has been much less explored. The large unit cell implies a many-band system. The heteroatoms (nitrogens) present a gross violation of the charge conjugation symmetry [3,4], which is an important simplifying feature of polyacetylene. The possibility of the phenyl ring rotation about single bonds in addition to bond length change result in multiple order parameters. Under those circumstances, the multitude and complexity of possible ground states and elementary excitations pose intriguing problems. In this Letter we show that a tight-binding model is capable of describing the basic features of the ground states as well as low-lying excited states as revealed by spectroscopic and magnetic measurements. The results so far constitute a very interesting contrast to those of polyacetylene. The simplicity of our model will certainly encourage and stimulate further work on polyaniline.

In the following we present our results for the pernigraniline base (PNB) polymer, Fig. 1, the form of polyaniline with a Peierls gap and twofold degenerate ground state [5]. Ignoring the ring rotation for a moment, we can write down the following SSH (Su-Schrieffer-Heeger) [6] type Hamiltonian

$$H=\sum_{\langle i,j\rangle}\left\{-(t_0-\alpha\delta r_{ij})\sum_{\sigma}[c_{i,\sigma}^{\dagger}c_{j,\sigma}+\text{H.c.}]+\frac{K}{2}(\delta r_{ij})^2\right\}+V_0\sum_{n,\sigma}{}'c_{n,\sigma}^{\dagger}c_{n,\sigma}\,. \tag{1}$$

Here $c_{i,\sigma}^{\dagger}$ creates an electron with spin polarization σ in an atomic $2p_z$ orbital on the ith backbone atom (carbon or nitrogen), j is a next neighbor of i, and the symbol $\langle i,j\rangle$ denotes summation over bond sites. $\alpha\delta r_{ij}$ is the modulation in the interatomic hopping integral due to a change in bond length δr_{ij} relative to a uniform reference bond length. The spring constant K determines the elastic energy of the sigma bonds. For simplicity we treat a carbon-nitrogen bond like a carbon-carbon bond, but we do add the last term in (1) to reflect a distinct on-site potential V_0 on the nitrogen atoms. The prime there means a summation over the nitrogen atoms only.

By taking $\delta t_{ij}=\alpha\delta r_{ij}$ as the bond variable, only the ratio $K'=K/\alpha^2$ appears in the Hamiltonian as the renormalized elastic constant. For the parameter values used in polyacetylene [7] $\alpha=7$ eV/Å and $K=60$ eV/Å^2, K' is about 1/eV. $K'=1$/eV together with $V_0=-2$ eV [8] have been adopted in our calculations.

Minimizing the total energy with respect to δt_{ij} yields bond alternation. In addition, there is a uniform bond contraction during the relaxation from the $\delta t_{ij}=0$ initial configuration. A bare value of $t_0=1.6$ eV leads to an average renormalized hopping integral of around 2.7 eV. The energy gap thus calculated for PNB turns out to be about 1 eV, too small to account for the observed 2.4 eV energy gap [9]. Hence we must examine the contribution of the ring rotational degree of freedom [8,10].

Let θ_k be the torsional angle of the kth phenyl ring away from the C-N-C plane. Since steric repulsion favors ring twists of opposite signs at neighboring rings, as confirmed by x-ray diffraction experiment [11], it is more useful to define the staggered order parameter $\psi_k=(-1)^k\theta_k$. Following Ginder and Epstein [8] we adopt the following form of the steric potential

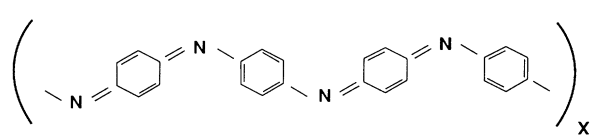

FIG. 1. Chemical structure of the pernigraniline base (PNB) form of polyaniline.

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$$V_s = \sum_k [V_{11}(\sin\psi_k - \sin\psi_{k-1})^2 - V_{20}\sin^2\psi_k + V_{40}\sin^4\psi_k]. \quad (2)$$

The ring rotation decreases the overlap between the two p_z orbitals of the C-N bond. Effectively, the hopping integral of that bond $-(t_0 - \delta t_{ij})$ gets multiplied by $\cos\psi_k$. This together with the addition of the steric potential (2) to (1) complete the inclusion of the ring rotation in the Hamiltonian. Henceforth we will refer to this Hamiltonian instead of the one in (1). The three parameters V_{11}, V_{20}, and V_{40} in (2) are taken to be 0.185, 4.5, and 2.5 eV, respectively. They are chosen to reproduce the correct spin density distribution of the neutral solitons and to yield the proper Peierls gap.

We now discuss the results obtained from the above Hamiltonian. There are two degenerate ground states. Each one has a distinct ring rotation dimerization pattern with a uniquely determined bond alternation pattern; i.e., the phases of the bond length and ring torsion order parameters are coupled. The ring that rotates further (53°) from the C-N-C plane is always benzenoid-like, while the quinoid-like ring twists a little (12°) from the C-N-C plane. This confirms the chemical intuition that it is harder to rotate double bonds than single bonds. For each ground state the energy gap is approximately the experimental value. This implies that the ring rotation dimerization contributes as much to the energy gap as the bond alternation does, consistent with a recent finding by Brédas *et al.* [12].

Each of the two dimerized ground states has identical electronic structure. The optical absorbance calculated for the ground state of PNB is displayed as the solid line in Fig. 2(a). This calculation as well as other calculations to be described later have been done on a 112-site chain (16 C_6N units). A Gaussian broadening of 0.1 eV has been used. Compared to experiment [9], the gap region between 3 and 6 eV is too wide, and the absorption in the lower energy region (2 to 4 eV) is somewhat too large relative to the absorbance above 5 eV. Despite the above discrepancy, there is an overall qualitative agreement between theory and experiment.

Perhaps of greater interest are the absorptions of solitons and polarons. The dashed curve in Fig. 2(a) depicts the absorption spectrum of the PNB chain with a relaxed neutral soliton-antisoliton pair. The energy level diagram is also shown. The ground-state absorption curve is superimposed for each comparison. As in the case of pure bond order soliton, the gap states associated with a neutral soliton pair (S^0,$\bar{S}^0$) are degenerate. The effective charges of these spin-$\frac{1}{2}$ neutral solitons are vanishingly small. The present model predicts two photoinduced absorption peaks at about 0.9 and 1.5 eV since the neutral soliton level is not at midgap due to the absence of charge conjugation symmetry. Just as for the absorption of neutral solitons in polyacetylene we expect the entire subgap absorption to be Coulomb shifted by several tenths of an eV in a perturbative treatment of the Hubbard repulsion [13,14]. The dotted curve in Fig. 2(a) indicates the subgap absorption spectrum for repulsion strength $U=4$ eV. These neutral soliton predictions are in agreement with the long time component of the photoinduced absorption data obtained by Coplin *et al.* [15], which shows that this shift is about 0.5 eV (to 1.5 and 1.8 eV). This identification is strengthened by the near absence of infrared active vibrational mode intensity associated with the S^0 and $\bar{S}^0$ absorptions (reflecting essentially zero charge associated with these defects [15]) and electron

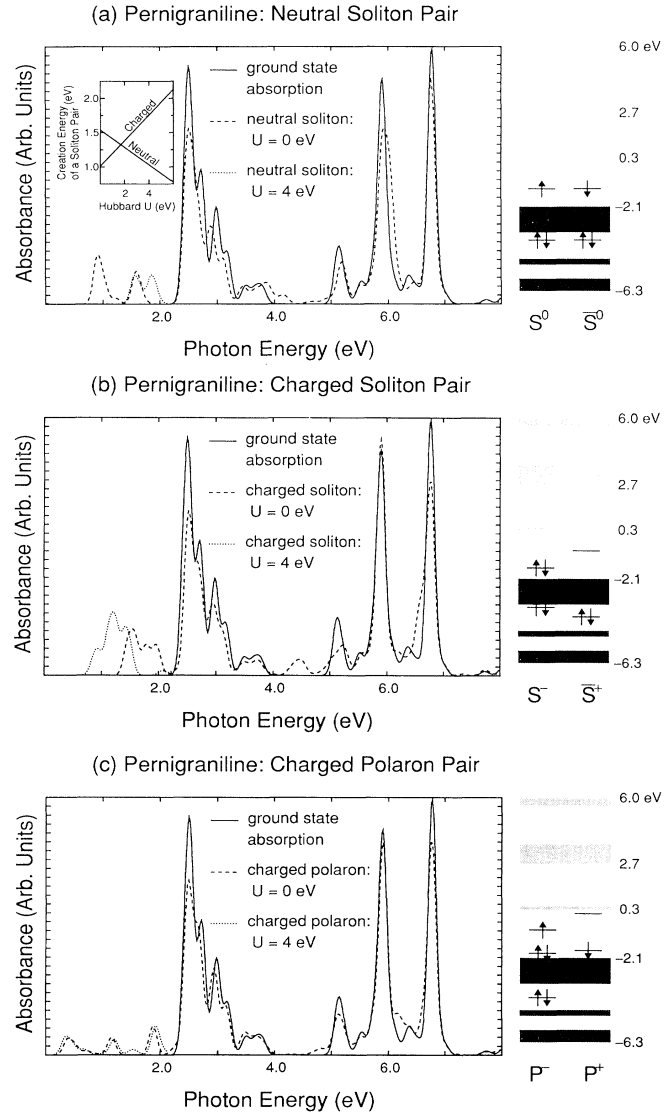

FIG. 2. Calculated absorption spectrum of a PNB chain in the ground state (the solid curves). The dashed and dotted curves show the absorption of the same PNB chain with a neutral soliton pair (a), a charged soliton pair (b), and a polaron pair (c). The energy level diagrams of the solitons and polarons are shown to the right of the absorption curves.

paramagnetic resonance studies of PNB powders and solutions showing localized spins [16,17].

To gain more insight into the neutral solitons, we have sketched the chemical structure of a neutral soliton S^0 in Fig. 3(a). The number next to each bond $\langle i,j \rangle$ is the bond order $(t_0 - \alpha \delta r_{ij})$. It is clear that the kink is essentially confined to two adjacent benzenoid-like rings. The chemical structure of the antisoliton $\bar{S}^0$ is the mirror image of S^0. Thus both neutral solitons have identical electronic structures, in contrast to the result obtained by Baranowski, Büttner, and Voit [18]. That explains why only one type of spin density distribution has been detected in neutral PNB samples [16,17]. The wave function of the gap state is presented in Fig. 3(b). The probability of finding an unpaired spin at the single central nitrogen site is about 0.45, which is comparable to the value of 0.6 deduced from the ESR measurement. As in polyacetylene the Hubbard repulsion is expected to enhance [19] the spin density on the central nitrogen site, bringing it closer to the experimental value. The average probability of finding the unpaired spin on each of the two adjacent benzenoid rings is about 0.1, which is also in reasonable agreement with experiment.

As opposed to neutral solitons, there are two distinct geometrical structures corresponding to the two charged states of charged solitons. The absorption spectrum of the PNB chain with an oppositely charged soliton pair is shown as the dashed line in Fig. 2(b). The torsional angle in the vicinity of an S^- runs like ...53°, −12°, 54°, −54°, 12°, −53°,.... It consists essentially of two back-to-back benzenoid rings or an S^-_{BB}. Compared to a neutral soliton S^0_{BB}, it is even more strongly localized. On the other hand, the ring torsional pattern near an S^+ runs like ...12°, −52°, 16°, −16°, 52°, −12°... reminiscent of two adjacent quinoids, or an S^+_{QQ}. The gap state wave function of an S^-_{BB} is similar to that of an S^0_{BB}, whereas there is a node on the central nitrogen site in the wave function of the gap state of an S^+_{QQ}. As in polyacetylene, both charged solitons are spinless. The Coulomb shifted subgap absorption is shown as the dotted line in Fig. 2(b), it can indeed account for the short time component of the photoinduced absorption measured by Leng *et al.* [20].

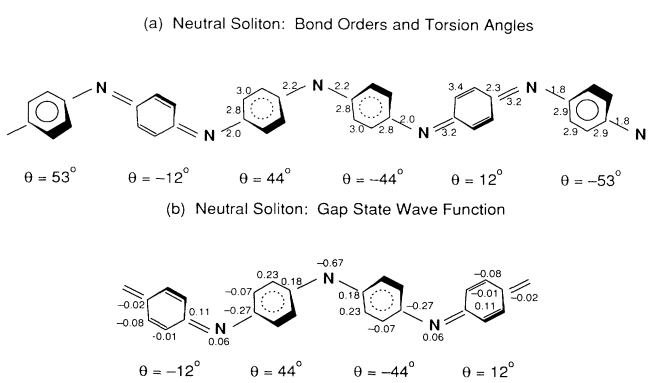

FIG. 3. Bond orders and torsional angles in the vicinity of a neutral soliton (a). (b) The associated gap state wave function.

Another interesting comparison between the charged and neutral solitons is the creation energy. The energy to create a charged soliton pair is 1.0 eV and that of a neutral soliton pair is 1.5 eV. Thus in a pure electron-phonon model, the charged soliton pair is more stable. However, as shown in the inset in Fig. 2(a), the Hubbard repulsion reverses the situation for realistic values of the repulsion strength.

The last type of elementary excitation is the polarons. Their spectroscopic features are depicted in Fig. 2(c). Among the three subgap absorption peaks, the lowest and the highest energy peaks are due to the hole polaron P^+, which is less strongly bound than the electron polaron P^-. The middle subgap absorption peak is due to P^-. The chemical structure and the wave function of the upper gap state of P^- are shown in Fig. 4. The ring torsional pattern near a hole polaron ...12°, −50°, 15°, −41°, 15°, −50°, 12°... is more extended than that of an electron polaron.

Compared to a soliton pair, the creation energy 1.9 eV of an oppositely charged polaron pair is quite high. A polaron pair will therefore decay into a soliton pair unless the polarons happen to be located on different chains or both of them are pinned by some mechanism. As regards the spectroscopic features shown in Fig. 2(c), they are only slightly Coulomb shifted.

Experimentally Coplin *et al.* [15] have recently examined the long time component of the photoinduced absorption in more detail and have found two absorption peaks near 1.5 and 1.8 eV. It is very tempting to associate them with the double peak feature seen in Fig. 2(a). The two peaks, however, do seem to have different dynamics which vary with temperature and laser intensity suggesting a contribution of the P^- to them. This issue remains to be resolved.

In summary, we have attempted to understand the low-lying excitations of PNB within a simple tight binding model. This is a minimum model involving both bond order and ring torsional order parameters. We have demonstrated that with our theoretical results, many of the observed optical and magnetic properties of the localized excitations can be interpreted and correlated. In

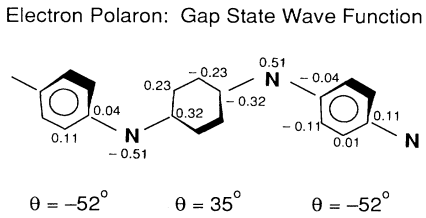

FIG. 4. Structure and the upper gap state wave function of an electron polaron.

particular, we have elucidated the role played by the neutral solitons. As such the theoretical model forms an important basis for further work. We are currently extending the calculation to other forms of polyaniline.

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