

OPTICAL AND MAGNETIC SIGNATURES OF LOCALIZED EXCITATIONS
IN POLYANILINE

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ABSTRACT

Using a tight-binding Hamiltonian we study the lattice configurations and electronic structures of three forms of polyaniline: leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB). Both bond length and ring rotation angle are considered in the structural relaxation. The dominant elementary excitations of isolated chains are found to be solitons in PNB and bipolarons in EB and in LEB. Optical absorptions of the ground states and of the solitonic and polaronic excitations are calculated and compared with experiments. The spin density profile of a single neutral soliton in PNB is discussed in connection with magnetic measurements.

Polyaniline is an interesting material due to its unusual transport, magnetic, optical and environmental properties. The simultaneous presence of the heteroatoms (the nitrogens) and the phenyl rings makes the theoretical modelling much less straightforward than that for polyacetylene. In this paper we show that it is nonetheless possible to understand much of the optical and magnetic properties from an SSH(Su-Schrieffer-Heeger) type Hamiltonian[1]. This allows a direct identification of the ground state as well as excited state lattice configurations of various forms of polyaniline.

We first discuss PNB. Ignoring the ring rotation for a moment, we can write down the following SSH-like Hamiltonian

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

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Here $c_{i,\sigma}^\dagger$ creates an electron with spin polarization σ in an atomic $2p_z$ orbital on the i -th 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 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 in the last summation sign means a restricted summation over the nitrogen atoms only. $K' = K/\alpha^2 = 1/\text{eV}$ and $V_0 = -2 \text{ eV}$ [2] have been adopted in our calculations.

By minimizing the total energy with respect to $\delta t_{ij} = \alpha\delta r_{ij}$, one finds bond alternation. In addition to that, there is a uniform bond contraction during the relaxation from the $\delta t_{ij} = 0$ initial configuration. A bare value of $t_0 = 1.6 \text{ eV}$ leads to an average renormalized hopping integral around 2.7 eV .

Besides the charged solitonic and polaronic states previously discussed by dos Santos and Brédas[3], we have also studied the relaxed configuration of an electron-hole pair initially photogenerated in a neutral pernigraniline sample. It corresponds to two well-separated kinks. The two gap states associated with the kinks are almost degenerate. Each of them is singly occupied. One can prove that in the adiabatic approximation those neutral spin solitons are directly photogenerated in contrast to polyacetylene wherein only charged solitons are directly photogenerated[4].

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[5]. Hence we must examine the contribution of the ring rotational degree of freedom[2, 6]. Let ϕ_k be the torsional angle of the k -th 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[7], it is more useful to define the staggered order parameter $\psi_k = (-1)^k \phi_k$. Following Ginder and Epstein[2] we adopt the following form of the steric potential

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

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) completes the inclusion of the ring rotation in the Hamiltonian. Henceforth we will refer to this Hamiltonian instead of the one in (1).

For PNB, three parameters V_{11} , V_{20} and V_{40} in (2) are taken to be 0.185 eV , 4.5 eV 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. As in the pure bond order case, there are two degenerate ground states. Each one has a distinct ring rotation dimerization pattern with a uniquely determined bond alternation pattern. 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.

The optical absorbance calculated for a PNB chain in the ground state is displayed as the solid line in Fig. 1. The dashed curve depicts the absorption spectrum of the same PNB chain with a relaxed neutral soliton-antisoliton pair. The energy level diagram is also shown. As in the case of pure bond order soliton, the gap states associated with neutral soliton pairs (S^0, \bar{S}^0) are almost degenerate. The effective charges of these spin 1/2 neutral solitons are vanishingly small. The present model predicts two photoinduced absorption peaks at about 0.9 eV 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 that the subgap absorption to be Coulomb shifted by several tenths of an eV[8]. These neutral soliton predictions are in agreement with the long time component of the photoinduced absorption data obtained by Coplin *et al.*[9], which shows that this shift is about 0.5 eV (to 1.5 eV 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[9]) and electron paramagnetic resonance studies of PNB powders and solutions showing localized spins[10, 11].

To gain more insight into the neutral solitons, we have sketched the chemical structure of a neutral soliton S^0 in Fig. 2. It is noted that neutral solitons that are centered on two adjacent quinoid-like rings are unstable and decay into the benzenoid type soliton described here. That explains why only one type of spin density distribution has been detected in neutral PNB

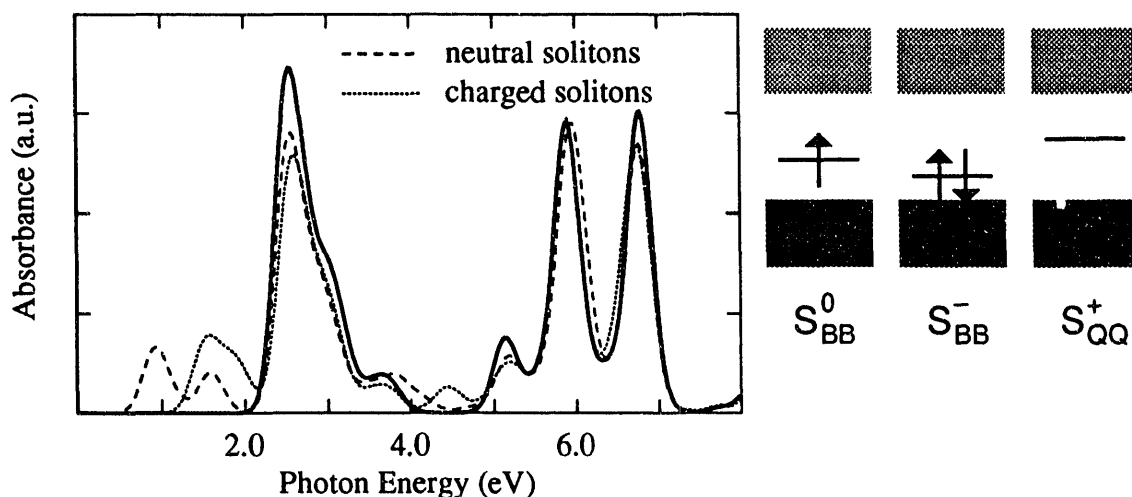


Fig. 1. Calculated optical absorbance of a PNB chain with a pair of solitons.

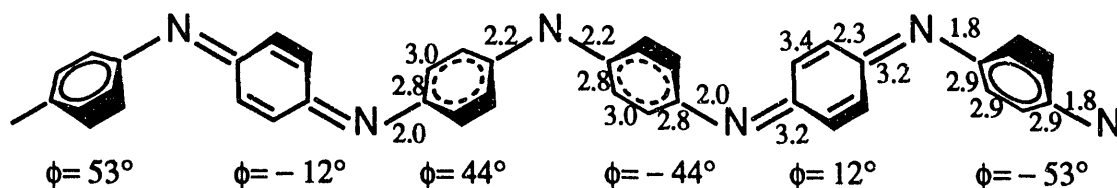


Fig. 2. Bond orders and torsional angles in the vicinity of a neutral soliton in PNB

samples[10, 11]. The probability of finding an unpaired spin at the single central nitrogen site turned out to be 0.45, which is comparable to the value 0.6 deduced from the ESR measurement by Cromack *et al.*[10] and Long *et al.*[11].

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 dotted line in Fig. 1. An S^- consists essentially of two back-to-back benzenoid rings or S_{BB}^- , even more strongly localized than an S_{BB}^0 . On the other hand, an S^+ resembles two adjacent quinoids, or an S_{QQ}^+ . The gap state wave function of an S_{BB}^- is similar to that of an S_{BB}^0 , 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 calculated subgap absorption in Fig. 1 can indeed account for the short time component of the photoinduced absorption measured by Leng *et al.*[12], provided that a Coulomb downshift of 0.5 eV is considered.

Experimentally Leng *et al.*[12] and Coplin *et al.*[9] have recently examined the long time component of the photoinduced absorption in more details and have found two absorption peaks near 1.5 eV and 1.8 eV. It is very tempting to associate them with the double peak feature seen in Fig. 1. The two peaks, however, do seem to have different dynamics which vary with temperature and laser intensity.

Let us now turn to LEB. There is no driving force for dimerization in LEB, but the alternate ring flippings persist because the steric repulsions are still there. The ground states are doubly degenerate as in PNB. In principle ring-torsional kinks can exist as suggested and studied by MacKenzie *et al.*[13]. In practice, however, they are hard to excite. We find, for example, that two band electrons near the conduction band edge relax into a bipolaron and not a

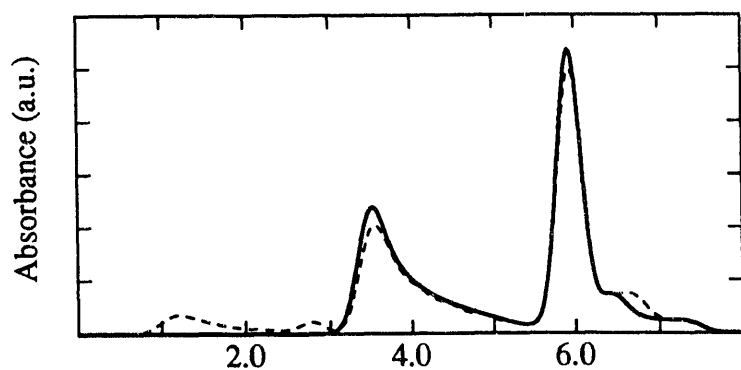


Fig. 3. Calculated absorption of an LEB chain in the ground state (solid line), with a hole bipolaron (dashed line).

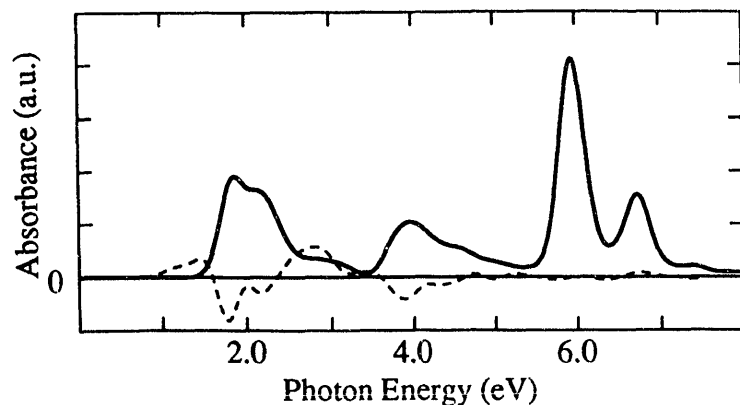


Fig. 4. Calculated absorption of an EB chain in the ground state (solid line), and the photoinduced absorption of a bipolaron pair (dashed line).

kink-antikink pair. As a generic feature of many electron-phonon systems, in the absence of Coulomb repulsion bipolarons here are more stable than polarons. For the model used here the absorption profile of a bipolaron appears to fit the photoinduced absorption of LEB better than those of polarons. Thus we suggest that bipolarons should be considered for the elementary excitations[14] in optical excitations in LEB.

It should be pointed out that we can not inherit all the parameter values in the Hamiltonian from PNB. We have simply adopted a smaller value of $V_{20} = 3.0$ eV, which leads to a uniform $\psi_n = 37^\circ$. The calculated absorbance of the ground state of LEB shown in Fig. 3 compares favorably with existing experimental data[15]. An electron bipolaron gives rise to very small subgap absorption compared to a hole bipolaron as depicted in Fig. 3. This is consistent with the reasoning of McCall *et al.*[15]. Another important feature of the bipolaron absorption is that the lowest absorption peak is more visible than the one at a higher energy. Within this model, the lowest photoinduced absorption peak of McCall *et al.* at about 0.6 eV and part of the 3.0 eV PA peak can be interpreted as intrinsic to LEB. The rest of the spectroscopic features can be ascribed to residual emeraldine base segments contained in LEB. The difference between the calculated peak energy in Fig. 3 of about 1.1 eV and the experimental 0.6 eV can again be regarded as a Coulomb shift.

The last form of polyaniline to be examined is EB. A somewhat different value of $V_{20} = 2.8$ eV is again needed for a good description of the ground state absorption. In addition we have to modify the last on-site term in (1) to reflect a different site energy on the protonated(-2.5 eV) versus unprotonated(-1.5 eV) nitrogen sites[16]. Even with those changes a satisfactory ground state absorption is obtained only if we follow the conventional assumption that the amine groups(-NH-) appear in adjacent pairs regularly. The calculated absorption curve of the ground state of EB does seem to agree with the experimental data[15]. For the model used here the dominant elementary excitations are bipolarons[14] again. The photoinduced absorption and bleaching due to an oppositely charged bipolaron pairs are shown in Fig. 4. That may explain the photoinduced absorption features seen[17] at about 0.9 eV and 3 eV after Coulomb shift. Considering the simplicity of the tight-binding model this is a remarkable fit for a complex material such as EB.

In summary, we have attempted to understand the low-lying excitations of polyaniline 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 particular, we have elucidated the role played by the neutral solitons. As such the theoretical model forms an important basis for further work.

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