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STRUCTURE OF DEFECT STATES IN POLYANILINE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Stephen M. Long, B.S., M.S.

The Ohio State University

1995

Dissertation Committee:
Professor Arthur A. Epstein
Professor Charles H. Pennington
Professor Bruce R. Patton

Approved by
Prof. A. J. Epstein, Advisor
Department of Physics
Dedicated to the memory of my mother, Mary Ruth Long
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VITA

November 1, 1964 ......................................... Born – Dearborn, Michigan

December 1987 ............................................... B.S. Magna Cum Laude
Michigan Technological University
Houghton, Michigan

1988 – 1992 .................................................... Graduate Teaching Assistant,
Department of Physics
The Ohio State University, Columbus Ohio

1992 – Present ................................................ Graduate Research Assistant
Department of Physics
The Ohio State University, Columbus Ohio

June 1992 ........................................................ M.S., Physics
Department of Physics
The Ohio State University, Columbus Ohio

PUBLICATIONS

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Molecule-Based Magnet, S.M. Long, P. Zhou, J.S. Miller, and A.J. Epstein, Molecular


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<td>AO</td>
<td>Atomic Orbitals</td>
</tr>
<tr>
<td>ani</td>
<td>Anisotropic</td>
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<tr>
<td>BNB</td>
<td>Benzenoid-Nitrogen-Benzenoid</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethlyformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfide</td>
</tr>
<tr>
<td>DPPH</td>
<td>2,2 Diphenyl-1-Picrylhydrazyl Hydrate</td>
</tr>
<tr>
<td>EB</td>
<td>Emeraldine Base</td>
</tr>
<tr>
<td>ENDOR</td>
<td>Electron Nuclear Double Resonance</td>
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<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>ESEEM</td>
<td>Electron Spin Echo Envelope Modulation</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>HF</td>
<td>Hyperfine</td>
</tr>
<tr>
<td>HMO</td>
<td>Hückel Molecular Orbital (Model or Theory)</td>
</tr>
<tr>
<td>H.T.</td>
<td>Heat Treatment or Heat Treated</td>
</tr>
<tr>
<td>II</td>
<td>Nuclear Spin - Nuclear Spin Interaction</td>
</tr>
<tr>
<td>iso</td>
<td>isotropic</td>
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<tr>
<td>KBr</td>
<td>Potassium Bromide</td>
</tr>
<tr>
<td>LEB</td>
<td>Leucoemeraldine Base</td>
</tr>
<tr>
<td>LESR</td>
<td>Light-Induced Electron Spin Resonance</td>
</tr>
<tr>
<td>LI</td>
<td>Light-Induced</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-Pyrrolidinone</td>
</tr>
<tr>
<td>p*</td>
<td>Charged Polaron</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PNB</td>
<td>Pernigraniline Base</td>
</tr>
<tr>
<td>QNQ</td>
<td>Quinoid-Nitrogen-Quinoid</td>
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<tr>
<td>S°</td>
<td>Neutral Soliton</td>
</tr>
<tr>
<td>SD</td>
<td>Spin Density</td>
</tr>
<tr>
<td>SS</td>
<td>Spin-Spin Interaction</td>
</tr>
<tr>
<td>Ze</td>
<td>Electronic Zeeman Interaction</td>
</tr>
<tr>
<td>Zn</td>
<td>Nuclear Zeeman Interaction</td>
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I Introduction

The experimental determination of the internal structure of non-linear conformational defects or excitations (solitons, polarons, etc.) in conducting polymers and its comparison to theoretical models is an important area of research which has received little attention in recent years. This neglect has been due in part to the lack of suitable materials to which magnetic resonance techniques, currently the only method capable of directly probing the internal structure of this class of defects, could be applied. During the early 80s EPR (Electron Paramagnetic Resonance) [1-3] and ENDOR (Electron Nuclear Double Resonance) [4-6] were used to probe the soliton conformation predicted to exist in trans-polyacetylene (trans-(CH)x) [7,8], the simplest of the conducting polymers. These observations provided a test of theoretical models, most importantly the Su-Schrieffer-Heeger (SSH) model [8] and lead to the recognition of the importance of Coulomb repulsion effects, neglected in the SSH model. Subbaswamy and Grabowski [9] explored the effects of “on site” Coulomb correlations in an unrestricted Hartree-Fock treatment of the SSH model. Later Soos and Ramasesha [10] calculated the spin density (SD) distribution within the Pariser-Parr-Pople (PPP) model where long range Coulomb correlations were considered and compared this to the ENDOR determined distribution. Now, over a decade later, numerous conducting polymers have been synthesized and conformational defects are known to play a fundamental role in their electronic and magnetic properties. However, despite the importance of these new conducting polymers our understanding of the internal structure of the conformational defects they support is largely based on theoretical models. Validation of these models has come primarily from comparison of predicted band structure and experimental optical
However, in the last few years the internal structure of conformational defects in two conducting polymers have been successfully probed by magnetic resonance techniques. Recently, EPR and ENDOR measurements have been reported by Kuroda et al. [11] identifying polarons in the conducting polymer poly(p-phenylene vinylene), PPV. These measurements have been compared to the structure and SD distribution of the polaron state in PPV calculated by means the Pariser-Parr-Pople model within the unrestricted Hartree-Fock approximation [12]. The second successful study is the subject of this dissertation.

The present work focuses on intrinsic conformational defects which are proposed to be the origin of the paramagnetism in the pernigraniline base (PNB) and emeraldine base (EB) oxidation states of polyaniline. The primary experimental focus is the measurement, using magnetic resonance techniques, of the hyperfine (HF) interactions associated with these conformational defects and the determination of their corresponding internal structure. The primary theoretical focus is on the comparison of the experimentally determined structures to those calculated based on an SSH model modified to include Coulomb repulsion and steric (ring torsion) effects using the unrestricted Hartree-Fock approximation. In chapter II SSH theory is reviewed and the soliton and polaron conformational states are discussed. In chapter III the synthesis and preparation of polyaniline is described and aspects of magnetic resonance theory and techniques are briefly reviewed. In chapter IV EPR and ENDOR spectra of the intrinsic paramagnetic defects in PNB, the degenerate ground state form of polyaniline, are presented from which the hyperfine (HF) coupling constants and associated \( \pi \)-electron spin densities are estimated. These experimentally determined spin densities are compared to the spin density distribution calculated for a neutral soliton in an oligomer of PNB from which an estimate of the structure and Coulomb repulsion strength is made. In chapter V EPR, ENDOR and preliminary ESSEM spectra of EB, the non-degenerate ground state form of polyaniline, are presented from which aspects of the structure and origin of intrinsic paramagnetic defects are determined and shown to arise from
interchain interactions. Finally a “self doping” mechanism based on interchain hydrogen bonding is proposed to explain the origin of these paramagnetic defects.

1.1 Conducting Polymers

The label “conducting polymer” refers to a class of polymers which can be altered by chemical doping or photoexcitation to an electronically conducting state. At first thought the phrase “conducting polymer” or “conducting plastic” seems an oxymoron; plastics are generally known for their insulating properties. However, in 1977 it was discovered that the addition of a chemical dopant, such as iodine, to polyacetylene lead to an electronically conducting state \[\sigma \sim 10^{-5} \text{S}\cdot\text{cm}^{-1}\] for \textit{trans}-(CH), to a conducting or metallic state (conductivities with an order of magnitude approaching that of copper) is not unique to polyacetylene. Since the initial discovery, numerous conducting polymers have been synthesized and the mechanisms which give them their conducting properties also have been found to give rise to a wide variety of other interesting properties. As a result, research in conducting polymers has grown steadily to encompass a broad range of disciplines including not only physics and chemistry, but fields as diverse as welding and biomedical engineering. This broad interest has lead to many proposed technological applications. Some, in fact, have already found their way to the market place. Conducting polymers are currently used in rechargeable lithium-polymer batteries \[15\] and as anti-static coatings. Some potential applications currently being pursued are polymer-based LED’s which promise a broad color range for flat panel displays and microwave absorbers for welding and stealth technologies.

The chemical doping of a conducting polymer is fundamentally different from doping in a conventional semiconductor. In conventional semiconductors the dopant atoms are substituted directly into the host (usually Si or Ga-As) lattice thus adding or removing an \textit{occupied} state. This process leaves the crystal and electronic band structure
relatively unperturbed. So, in the simple picture, electrons (holes) added by the dopant atoms occupy the delocalized Bloch states in the conduction (valence) band thus contributing to the electronic transport. In contrast, conducting polymers are chemically doped by adding the dopant atoms (or molecules) interstitially between the polymer chains. The dopant atom donates an electron (hole) to the polymer but does not change the number of states in the polymer lattice. (Protonic acid doping which is unique to polyaniline is slightly different and is not discussed here.) Thus electrons (holes) are introduced into the conduction (valence) band, however they do not remain there. In response to strong electron-phonon coupling there will be a relaxation of the polymer lattice resulting in a localized state forming in the gap. The would-be conduction electron (hole) drops out of the conduction (valence) band to occupy this lower energy state. It is this state in the gap, referred to as a nonlinear conformational defect or excitation, that is the subject of the present work. These states are commonly termed solitons, polaron and bipolarons to distinguish between the different possible geometries and charge-spin relationships. Photoexcitation of these conformational states is also possible but differs from chemical doping in that electrons are not added or removed from the lattice, but rather moved from one part of the polymer to another (or one polymer chain to another). However the basic relaxation process leading to the conformational state is the same.

When the concentration of doped conformational states is small the polymer will be in its insulating phase. The semiconducting or conducting phases occurs when this concentration becomes large enough that the localized conformational states in the gap have significant overlap or interaction. A number of models have been proposed to explain the conduction mechanisms in conjugated polymers. However, since the conducting phase of these polymers is not the focus of the present work, they will be discussed only briefly. These models generally fall into two categories: variable range hopping (VRH) and band models. In the VRH models an electron (hole) moves through the polymer by hopping from one “localized” conformational state to another. The ease with which an electron (hole) can move between states depends on the overlap (or
exchange) between the states and their relative energies. The energy to hop from a lower energy conformational state to a higher one comes from the thermal energy of the lattice. As a consequence VRH is distinguishable by a conductivity that increases with increasing temperature. In the band models the conformational states are considered to combine to form a partially filled band with delocalized Bloch states. In this model, as in conventional metals, the conductivity decreases with increasing temperature in sharp contrast to the VHR models. This decrease is the result of thermally induced vibration of the lattice which disrupts the delocalized Bloch states.

Figure 1: Repeat units of several conducting polymers.
It is worth mentioning a few words about the terms defect and excitation. The term excitation implies the availability of a relaxation route to the more stable ground state and is certainly appropriate when referring to photoinduced conformational states. However, for states where there is no relaxation route, such as for a single neutral solitons trapped on a polymer chain, the term defect is appropriated. In the present work the intrinsic conformational states are referred to as defects, reflecting their permanence.

Both trans-(CH)$_x$ [1,2] and PNB [16] in their insulating forms have a low concentration of spin detectable by magnetic resonance. The origin of this spin was shown to be consistent with neutral solitons in both trans-(CH)$_x$ [2,4] and PNB [17]. These solitons are likely trapped in the polymer during polymerization by kinks in the backbone or interchain interactions. Or they may originate from the thermal excitation of soliton pairs. Also, because they exist in low concentrations they do not influence the bulk properties of the polymer and thus are not of interest from the perspective of developing materials with practical applications. However precisely because of their low concentration they are of great interest to the physicist. At low concentrations the interactions between these intrinsic defects are negligible. This has two benefits. (1) The magnetic resonance will be affected only by hyperfine interactions (and motional narrowing) making it possible in some cases to infer their internal structure. Dipolar and exchange interactions, which can obscure the HF structure, depend on the distance between defects and can be largely neglected. (2) Theoretical models of these defects are greatly simplified by considering them in isolation. Thus, these intrinsic defects provide
an ideal opportunity to compare the theoretical predictions of their internal structure to experiment observation. In EB the situation is similar except only limited theoretical work has been reported [18] on the type of defects observed. However this is likely to change in light of the results on EB to be discussed in chapter V. These paramagnetic defects have been shown to be directly associated with the interchain interactions responsible for the aggregation effecting the processibility of EB, and thus is of practical interest.

The essential feature of a conducting polymer is a conjugated backbone. A polymer is considered to be conjugated if its structure consists of alternating single and double bonds forming a quasi-one-dimensional array of repeating organic units, \((\text{repeat unit})_x\), some examples are given in Figure 1. To understand this structure it is best to consider \(\text{trans-}(\text{CH})_x\) the simplest of the conjugated polymers, see Figure 2. The \(\text{trans-}(\text{CH})_x\) backbone is commonly described in terms of \(sp^2p_z\) hybridized atomic orbitals (AOs) (see Figure 3) combining to form a network of \(\sigma\) and \(\pi\)-bonds (see Figure 4). Two adjacent \(sp^2\) AO’s pointing towards each other along the line connecting their respective carbon atoms combine to form \(\sigma\) and \(\sigma^*\) molecular orbitals (MOs). The \(\sigma\) MO’s form the \(\sigma\)-bond network which serves to hold the carbon backbone together. The

![Image: sp2 hybridization scheme with labels and notation]

Figure 3: Two views of schematic representations of the \(sp^2p_z\) hybridization scheme.
Figure 4: Schematic representation of the $\sigma$ and $\pi$ MO's and their formation of a conjugated backbone. The cross sections are taken in the plane containing both carbon atoms and the axis of their $p_z$ AO's.

double-single bond structure of the backbone is the result of a Peierls distortion [19] (dimerization) where the carbon atoms pair and their $p_z$ AO's combine to form the $\pi$ and $\pi^*$ MO's. The resulting $\sigma$-$\pi$ bonded structure is shown schematically in Figure 4. In conjugated polymers the $\sigma$ electrons have energies approximately 5 eV below the $\pi$-electrons. As a result, to a good approximation, the $\sigma$-electrons can be treated separately from the $\pi$-electrons. This is the basis for the Hückel molecular orbital (HMO) method [20]. In the models used in this work the $\sigma$-electrons are treated phenomenologically and the electronic structures are estimated considering only the $\pi$-electrons. Within this framework a number of theoretical studies of soliton conformational states in $trans$-$\text{CH}_x$ have been reported [7,8,21,22]. Pople and Walmsley [7] using a simple HMO model
showed that the soliton conformation (although they didn’t call it this) resulted in a localized non-bonding state in the $\pi-\pi^*$ gap with an energy of formation of $2.17$ eV per soliton pair. Su et al. [8] extended this original work to include the delocalization of the bond length distortion associated with the soliton conformation. They found that the soliton conformation delocalized over $\sim 14$ carbons with an energy of formation of $\sim 0.8$ eV per pair. Recognizing that in addition to electron-phonon coupling, electron-electron correlations (Coulomb repulsion) were also important in long-chain polyenes Subbaswamy and Grabowski [9] explored the effects of on-site Coulomb correlations on the energy and SD distribution of solitons in trans-(CH)$_x$ within an unrestricted Hartree-Fock calculation. Similarly a number of other authors also examined the effects of Coulomb correlations [10,23-26]. In addition, polaron conformational defects were theoretically predicted to exist in trans-(CH)$_x$ and other conducting polymers [27-30]. Campbell and Bishop [28] (later Fesser et al. [30]) established the existence, within the continuum electron-phonon-coupled model, of polaron excitations in trans-(CH)$_x$. Also, Brédas et al. [29] (among many others [31]) studied the polaron conformation within the SSH framework.

1.2 Polyaniline

Polyaniline refers to a family of polymers which have been around for more than a century. It is related to a group of dyes, one of which is known as “aniline black”, which were used as far back as the late 1800’s. The first detailed study of the synthesis of polyaniline was reported in 1910 by Green and Woodhead [32]. After the discovery of the doped form of polyacetylene in 1977 by Chaing et al. [14] physicists and chemist began studying other potential conducting polymers including polypyrrole [33-38], polythiophene [39-41], and polyaniline [42-48]. Intense studies, beginning in the mid 1980’s, of polyaniline’s properties found in addition to its conducting properties, a wide variety of other novel properties, including ring torsion effects [49] and long-lived
polarons [50] and solitons [51] generated by photoexcitation. Polyaniline also has the distinction of being the first conducting polymer to be commercialized; it is used in rechargeable lithium-polyaniline batteries [15].

Figure 5: Structure of the three stable oxidation states of polyaniline.
Polyaniline is composed of aniline repeat units (Figure 1) which combine to form a backbone of alternating nitrogen and C₆H₄ rings. The general chemical formula for the insulating form of polyaniline is \([\text{(C₆H₄)NH}]_y\text{[(C₆H₄)N]}_{(1-y)}\) where \(y\) indicates the level of oxidation. There are three stable oxidation states (shown in Figure 5) characterized by \(y = 1, 1/2,\) and 0 and are commonly called leucoemeraldine base (LEB), emeraldine base (EB), and pernigraniline base (PNB), respectively. The chemical structure of these oxidation states are composed of four basic components (shown in Figure 6) and are described in terms of the \(sp^2p_z\) hybridization and \(\sigma-\pi\) molecular orbital schemes as discussed in the previous section. The nitrogens have two possible configurations, -NH- and -N-, which are referred to as amine and imine, respectively. The amine nitrogens have one shared electron in each of the \(\sigma\)-bonds and the remaining two in the \(p_z\) orbital forming a lone pair. The imine nitrogens have one shared electron in its two \(\sigma\)-bonds and one in its \(p_z\) orbital which forms a \(\pi\)-bond with an adjacent carbon; the remaining two electrons form a lone pair in the unbonded \(sp^3\) orbital. In addition to the two different
nitrogen sites, there are also two types of $C_6H_4$ rings referred to as benzenoid and quinoid rings. In a benzenoid ring the carbon $p_z$ electrons are shared equally among themselves which results in all the C–C bonds of equal length. In the chemical structure drawings throughout this work, benzenoid rings are designated by a hexagon (the carbon symbol “C” is customarily omitted) where the $\pi$-electrons are represented by a circle. In a quinoid ring two of the six carbon $p_z$ electrons are shared with the adjacent nitrogens forming double bonds; the other four electrons form two C=C double bonds between the meta and ortho carbons.

The physics of polyaniline is considerably more complex than of $trans$-(CH)$_x$, which has made it an especially interesting system to study. This added complexity can be attributed to three factors. (1) The presence of three stable oxidation states; $trans$-(CH)$_x$ has only one. Polyaniline in its PNB oxidation state has a degenerate Peierls ground state similar to $trans$-(CH)$_x$ but also a non-degenerate ground state when in its EB and LEB forms. This leads to additional conformational defects and a wider variety of physics. (2) Steric repulsion between hydrogens on the $C_6H_4$ rings causes them to rotate out of the molecular plane defined perpendicular to the nitrogen $p_z$ axis. This ring torsion gives rise to additional interesting physics because of the competition between $\pi$-electron delocalization energetics which favor rings in the molecular plane and steric repulsion favoring rings out of the plane. (3) The nitrogen-carbon heteroatomic backbone which gives rise to charge conjugation asymmetry affecting the energy and distribution of the gap state associated with localized conformational defects.
II Theoretical Background

This chapter summarizes the theoretical background necessary for describing the quantum calculations of the ground state and defect states of polyaniline. To facilitate an understanding of these states in polyaniline the corresponding features in trans-(CH)$_x$ are reviewed [52]. The theory that was developed in the late 70s and early 80s to describe the electronic, magnetic, and structural states of trans-polyacetylene, based on the Su-Schrieffer-Heeger (SSH) Hamiltonian [8], involved concepts that formed the foundation for theoretical studies of conducting polymers, including polyaniline. This chapter begins with a brief outline of the SSH theory and its description of trans-(CH)$_x$ followed with a description of the soliton and polaron conformational state.

2.1 Su-Schrieffer-Heeger Theory

Pople and Walmsley [7] in a paper published in 1962 proposed that bond alternation defects (solitons) in long polyene molecules would give rise to localized non-bonding molecular orbitals. Further they calculated the electronic properties of such defects in a chain of trans-(CH)$_x$ using HMO theory. For a pair of defects they found that the energy of formation for two soliton defects was in fact relatively small, 2.17 eV. The most significant drawback to their treatment of the soliton conformation was their assumption that the bond alternation defect was localized to a single carbon atom. They recognized that the soliton bond length alternation should be delocalize over some number of carbon atoms and that this would lead to an energy of formation considerably
less than their estimate. After the discovery of the conducting form of \textit{trans-}(\textit{CH})\textsubscript{x}, more than a decade later Su, Schrieffer and Heeger \cite{8} independently reexamined the soliton conformation addressing the problem of delocalization.

The Su-Schrieffer-Heeger (SSH) model \cite{8} was first developed in the late 70s to describe the ground state and low-lying excited states in \textit{trans-}(\textit{CH})\textsubscript{x}. Its popularity stems from its ability to account for the delocalization of the bond alternation associated with the soliton defect through a bond order parameter. It is based on the tight-binding approximation where the polymer states are described in terms of carbon \textit{sp}\textsubscript{2} \textit{p}\textsubscript{z} AOs. The simplicity of the SSH theory stems from the assumption that the \textit{sp}\textsubscript{2}-electrons forming the \textsigma-bond network can be considered phenomenologically through an effective lattice potential energy which is modeled as simple springs (see Figure 7). Further, the kinetic energy (first term in Eq. (1)) is neglected in the adiabatic approximation (i.e. electrons respond instantaneously to changes in the atomic positions in the lattice). Also neglected are the coulomb interactions between electrons, the interactions between chains, and the differences in atomic site potentials (important in heteroatom polymers like polyaniline). Despite these assumptions the SSH model provides a surprisingly good description of the phenomena observed in \textit{trans-}(\textit{CH})\textsubscript{x} and in many other conducting polymers. However, as more complicated polymeric systems are studied these neglected interactions become important. In particular electron-electron or Coulomb interactions will be found to be important in explaining the \pi-electron SD distribution, discussed in chapter IV, of paramagnetic defects (neutral solitons) in PNB as well as \textit{trans-}(\textit{CH})\textsubscript{x}. Also interchain interactions (hydrogen bonding) will be shown, chapter V, to be linked to the origin of the paramagnetic defects observed in EB.
The Su-Schrieffer-Heeger (SSH) Hamiltonian is written as follows:

\[ H_{SSH} = \frac{1}{2} \sum_n \left( \frac{\partial^2}{\partial u_n^2} \right)^2 + \frac{1}{2} \sum_n K(u_{n+1} - u_n)^2 - \sum_{n \sigma} t_{n+1, n} \left( c_{n+1, \sigma}^\dagger c_{n, \sigma}^\dagger + c_{n, \sigma}^\dagger c_{n+1, \sigma} \right) + \varepsilon_0 \sum_{n \sigma} c_{n+1, \sigma}^\dagger c_{n, \sigma} \]  

where \(<n, \sigma>\) denotes the sum over nearest neighbor carbons. The first term represents the lattice kinetic energy where \(M\) is the mass of one CH unit and \(u_n\) is the displacement of the \(n^{th}\) carbon atom from its equilibrium position. The second term is the lattice potential energy where \(K\) is the effective spring constant which includes contributions from the \(\sigma\)-bond network. The last two terms are the tight-binding \(\pi\)-electron energy where \(t_{n+1, n}\) is the transfer integral between adjacent carbon atoms and \(\varepsilon_0\) is the carbon site energy usually taken to be zero. The operator \(c_{n, \sigma}^\dagger (c_{n, \sigma})\) creates (annihilates) a \(\pi\)-electron with spin \(\sigma\) on site \(n\). The electron-phonon coupling enters the Hamiltonian through the functional dependence of the transfer integral on the displacement \(u_n\). This dependence is approximated to first order by,

\[ t_{n+1, n} = t_0 - \alpha(u_{n+1} - u_n) \]  

where \(t_0\) is the "bare" transfer integral for the undimerized carbon-carbon bond and \(\alpha\) is the electron-phonon coupling constant.
The SSH Hamiltonian can easily be solved in the case where electron-phonon interactions are neglected ($\alpha = 0$). In this case the energy dispersion relation for the $\pi$-electrons is given by

$$\varepsilon(k) = \varepsilon_0 - 2t_0 \cos(ka)$$  \hspace{1cm} (3)

where $k$ is the wave number, $a$ is the lattice constant, and $\varepsilon_0$ is the carbon $p_z$ site energy. The $p_z$ energy states are broadened due to orbital overlap and form a band of width $4t_0$, see Figure 8. In this case the $\pi$-band is half filled and indicates the $\text{trans-}(\text{CH})_x$ should be metallic. However, nature does not neglect electron-phonon interactions.

The Peierls theorem states that a one dimensional metallic state is unstable and will undergo dimerization [19] caused by the competition between the lattice potential energy and $\pi$-electron energy. The lattice potential favors a uniform carbon chain where the carbon-carbon bond lengths are equal to $a$, the equilibrium length. The electronic energy favors constriction of the lattice which maximizes the $p_z$ orbital overlap or $t_{n+1,n}$. The result of the tug-of-war between these effects is the Peierls distortion or dimerization of the lattice. In $\text{trans-}(\text{CH})_x$ a uniform dimerization occurs with displacement of the $n^{th}$ atom from equilibrium given by the order parameter $u_n = (-1)^n u$. This distortion doubles the size of the unit cell to $2a$ and moves the Brillouin zone edge in to $k = 1/(2a)$. The energy dispersion relation in this case is given by

$$\varepsilon(k) = \sqrt{4t_0 \sin^2(ak) + \Delta^2(k)}$$  \hspace{1cm} (4)

where

$$\Delta(k) = 4ausin(ka).$$  \hspace{1cm} (5)

This dispersion relation and the corresponding density of states are shown in Figure 9. The gap between the valence and conduction bands ($\pi-\pi^*$) is proportional to the strength of the electron-phonon coupling and dimerization, $E_\pi = 2\Delta_0 = 8au$. For $\text{trans-}(\text{CH})_x$ $E_\pi$ is calculated [8,52] to be $\sim 1.4$ eV and the accepted experimental value [53] is
$E_x \approx 1.8$ eV based on the observed $\pi-\pi^*$ absorption edge. In the LEB and EB forms of polyaniline the maximum in the $\pi-\pi^*$ band-gap absorption is observed to be $\sim 3.8$ eV [50], much larger than in $\text{trans-}(\text{CH})_x$. This larger band gap is predominantly attributed to effects involving the overlap of molecular orbitals of neighboring phenyl rings and nitrogen [54]. In EB there is an additional absorption near $\sim 2.0$ eV which is attributed to an exciton absorption [50] (benzenoid to quinoid transition). In the PNB form of polyaniline the $\pi-\pi^*$ absorption near $\sim 2.4$ eV [51,55] is attributed to a Peierls ground state similar to $\text{trans-}(\text{CH})_x$. However unlike $\text{trans-}(\text{CH})_x$, PNB in addition to bond-length dimerization characterized by an alternating benzenoid quinoid geometry it also undergoes ring-torsion dimerization [49]. This additional dimerization, due to rotation of the C$_6$H$_4$ rings out of the polymer plane, is shown to give a substantial contribution to the Peierls gap.

The presence of localized electronic states of energies less than the band gap arising from changes in local bond order, including the formation of solitons, polarons, and bipolarons have lead to the novel charge conduction mechanisms in $\text{trans-}(\text{CH})_x$ and other conducting polymers [13,56-58]. As a function of the degree of $p$- or $n$-type doping the room temperature conductivity of $\text{trans-}(\text{CH})_x$ can be varied from $10^{-13}$ S/cm to $\sim 10^5$ S/cm [59-61]. Conducting forms of $\text{trans-}(\text{CH})_x$, with conductivities of $\sim 10^5$ S/cm, are achieved with the use of a catalyst with additional reducing agents via doping with iodine [59,60]. Similar to $\text{trans-}(\text{CH})_x$ the EB form of polyaniline can be converted from an insulating (conductivities of $\sim 10^{-10}$ S/cm) to a “metallic” state (conductivities of $\sim 5$ S/cm) if protons are added to the $-\text{N}=\text{sites}$ while the number of electrons in the chain is held constant [62-65].
Figure 8: The energy dispersion (a) and density of states (b) for undimerized \textit{trans-} \textit{(CH)}\textsubscript{x} based on the SSH model where $\alpha = 0$. (Adapted from Reference [8].)

Figure 9: The energy dispersion (a) and density of states (b) for dimerized \textit{trans-} \textit{(CH)}\textsubscript{x} based on the SSH model where $\alpha \neq 0$. (Adapted from Reference [8].)
2.2 Conformational Defects: Soliton and Polarons

For trans-(CH)$_x$, the total energy per repeat unit (CH) calculated from the SSH Hamiltonian as a function of the dimerization has two equal minima (see Figure 10). These minima, $u_0 = \pm 0.04\,\text{Å}$ [8], correspond to two Peierls degenerate ground states and are referred to as A phase and B phase. Although its repeat unit is more complicated, PNB also has a two-fold Peierls degenerate ground state. Trans-(CH)$_x$ [8], PNB [66], and poly(1,6-heptadiyne) [67] are some of the few known conjugated polymers with degenerate ground states. In this section the soliton and polaron states are described and for clarity as is customary, trans-(CH)$_x$ is used as a model system.

![Figure 10: Schematic plot of the Born-Oppenheimer energy per CH unit (based on the SSH model) as a function of the dimerization amplitude. (adapted from Reference [8])](image-url)
The similarity between trans-(CH)\textsubscript{x} and PNB can be understood if in PNB the benzenoid and quinoid rings connecting the nitrogens is viewed as alternating single and double bonds, respectively (see chemical structures in Figure 10). However there is an important difference. The conformational structure of trans-(CH)\textsubscript{x} can be described using only one order parameter for its bond length alternation. PNB requires two order parameters corresponding to bond length and ring angle alternation to adequately describe its conformational structure. However, it should be pointed out that the bond length and ring angle alternation are not independent effects, but are coupled through the transfer integral. Phenomenologically the transfer integral for polyaniline is written:

$$t_{C,N} = \left( t_0 - \alpha (u_c - u_n) \right) \cos \theta_{C,N}, \text{ where } \theta_{C,N} \text{ is the ring torsion angle [49,68].}$$

Rotation of a phenyl ring will decrease the overlap between the nitrogen and para carbon \( p \) orbital reducing the strength of the corresponding \( \pi \)-bond changing its bond length. Thus the bond length and ring torsion order parameters are not fully independent.

*Trans*-polyacetylene in its ground state can contain only one phase. If it contains both phases it is said to be in an excited state resulting from conformational distortion at the required A-B interface. This distortion results in one state being pulled into the band gap symmetrically from the valence and conduction bands (the states in the valence and conduction bands will under go a phase adjustment as a result of the distortion). This localized state at the center of the band gap and is commonly referred to as a soliton. The soliton is not localized to a single carbon site, as indicated by the chemical structure diagrams shown in Figure 11, but is delocalized over a number of carbon sites. To quantify this spreading out of the soliton conformation (also shown in Figure 11) it is common to introduce the order parameter, \( \Psi_n = (-1)^n u_n \), to represent the lattice distortion. Su, Schrieffer, and Heeger [8] estimated the soliton size by assuming an order parameter of the form \( \Psi_n = u_0 \tanh(na/\xi) \) and minimizing the \( H_{SSH} \) energy (variational principle) with respect to \( \xi \). They found that the soliton decay length to be \( \xi \approx 7a \).
There are two possible configurations for the neutral soliton one where there are two single bonds at the interface and the other where there are two partially occupied double bonds at the interface. The conventional chemically structures corresponding to these two configurations are shown in Figure 11 where the soliton is assumed to be localized on one repeat unit (i.e. the lattice has not been allowed to relax). The first configuration, Figure 11 (a), has the unpaired electron located on the central carbon $p_z$ orbital. Upon relaxation of the lattice the soliton will delocalize giving the probability density shown in Figure 11 (a). This corresponds to the gap state or soliton wavefunction with an antinode on the central carbon. In the second configuration, Figure 11 (b), the unpaired electron is shared between two partially occupied π-bonds. If the lattice is relaxed without shifting its center the soliton will delocalized to give a probability density similar to Figure 11 (b) with a node in the soliton wavefunction on the central carbon. In other words the probability density has shifted by one carbon, to $n = 1$ for instance, while maintaining its symmetry about the center resulting in a node on the central carbon.

In trans-(CH)$_x$ the distinction between these two configurations has not been important because the soliton is delocalized over ~14 carbons and results in very little difference between their respective HF structures. Magnetic resonance measurements are not capable of distinguishing these two configurations due to the high mobility of the soliton. Most of the EPR and ENDOR HF structure is averaged out. The end result has been that the distinction between these two types of solitons has been largely ignored. However it will be seen, chapter IV, that this distinction cannot be ignored in pernigraniline base.

dos Santos and Brédas [66] proposed that PNB can support two types of charged solitonic distortions, both centered on nitrogen atoms, one having an aromatic (benzenoid) ring geometry and the other a quinoid ring structure; these have been experimentally observed via millisecond photoinduced absorption spectroscopy [69].
Figure 11: Gap state probability density schematically represented for (a) antinode centered and (b) node centered soliton in \textit{trans}-polyacetylene.
Theoretical studies by Su and Epstein [68] and Baranowski et al. [70] have focused on the stability and dynamics of the Peierls state in PNB. Using a tight-binding model, Su and Epstein found the structure of neutral solitons ($S = 1/2$) to be of the benzenoid-nitrogen-benzenoid (BNB) form with the wave function centered symmetrically on a nitrogen site and primarily localized to the two adjacent rings. This is in contrast to solitons in $trans$-(CH)$_x$ where the wave function extends over $\sim$ 14 repeat units. Recently neutral solitons were detected in PNB via photoinduced absorption and light induced EPR measurements [51]. Also intrinsic neutral solitons in PNB have been identified and their internal structure determined via solution EPR [17].

In the present work defects which are intrinsic to conducting polymers are of interest. In $trans$-polyacetylene there are two processes which could lead to intrinsic solitons. The first is thermal excitation which should lead to some equilibrium density of
soliton pairs. However, the energy to create a soliton has been estimated [8] to be ~ 0.4 eV or ~ 4600 K and the thermal equilibrium density of soliton pairs will be much too small to account for the concentration of paramagnetic defects observed in trans-(CH)x. Instead, solitons are likely created during the polymerization and/or annealing process and subsequently trapped. A polymer segment with a single soliton excitation cannot decay back to the ground state. If solitons are created in sufficient numbers during the polymerization process then it is expected that approximately 50% of the polymer segments will have a trapped soliton. Segments with an odd number of solitons created during polymerization will relax to a single trapped excitation and those with an even number will relax back to the ground state. Further, Gibson et al. [71] found that there is always a residual 740 cm⁻¹ optical absorption normally assigned to cis linkages indicating a remnant cis content of ~ 5% in trans-(CH)x. These remnant cis linkages within the trans crystal structure experience considerable strain. They argued that at sufficiently high temperatures cis-transoid linkages might open up to form a diradical followed by electronic rearrangement leading to the formation of two neutral solitons separated by a twisted trans-cisoid linkage. This process would result in a concentration of neutral solitons related to the concentration of cis linkages and annealing temperature that is much higher than can be accounted for by simple thermal excitations. A similar process maybe responsible for the intrinsic defects observed in PNB.

Unlike trans-(CH)x and PNB, the EB form of polyaniline does not have a degenerate Peierls ground state and therefore can not support the soliton conformation. However, an electron (hole) added to the polymer through doping or some other mechanism will be accompanied by a relaxation of the lattice and can be described by a dip in the order parameter, see Figure 13. This paramagnetic conformation is called a polaron and results in two states being pulled into the π-π* gap. Similarly if two electrons (holes) are added to the polymer there will be a stronger distortion of the lattice as illustrated schematically in Figure 13. This conformation is non-paramagnetic and is therefore EPR silent; it is commonly referred to as a bipolaron.
Figure 13: Schematic representation for the bond length order parameter and energy level diagrams for the polaron (left) and bipolaron (right) conformations. (Adapted from reference [52].)
III Experimental Techniques

3.1 Sample Synthesis and Preparation

The synthesis routes of emeraldine base [72,73] (EB) and pernigraniline base (PNB) [74-77] are described in detail elsewhere. A brief description of some of these routes is given here. Also, sample handling and preparation techniques are described for powder, oriented films, and solutions as they are applied to the EPR studies of EB and PNB.

The most common synthesis route for EB is through oxidative chemical polymerization of aniline. An aqueous solution of (NH₄)₂S₂O₈ is added to a solution of aniline dissolved in 1.0 M aqueous HCl [73]. After ~ 1 hour the precipitate formed is removed by filtration, washed with 1 M HCl and dried under dynamic vacuum. This material is emeraldine hydrochloride which is then converted to emeraldine base by stirring in a dilute NH₄OH solution followed by washing with a water-methanol solution and drying under dynamic vacuum. The resulting product is amorphous emeraldine base, sometimes noted as EB-I [78-80]. In general, the EB-I material is formed when the polymer is obtained from solution in the protonated form, as described. Characterization of this material has found that the oxidation level differs from the ideal \((1 - \gamma) = 0.5\) depending on the conditions under which it is synthesized [81]. EB prepared in air has an oxidation state of \((1 - \gamma) \sim 0.4\) whereas when prepared under an inert atmosphere, \((1 - \gamma) = 0.5\). There is a second class of emeraldine base, EB-II, which exhibits a partially crystalline structure [78,79]. In general, the EB-II materials are formed when
the polymer is obtained from solution in the nonprotonated form or through treatment of EB-I with tetrahydrofuran (THF) and/or N-methyl-2-pyrrolidone (NMP).

There are two synthesis routes to obtain PNB which are described here. The first method involves the conversion of EB directly to PNB [75]. EB is dissolved in a solution of N-methyl-1-pyrrolidinone (NMP) mixed with glacial acetic acid. The solution is then oxidized by adding a solution of \( m \)-chloroperbenzoic acid in glacial acetic acid. Triethylamine is then added, resulting in a dark purple precipitate which is then filtered and washed with acetone and diethyl ether. The end product is a powder, brownish/purple in color, with an oxidation level shown to be \( (1 - y) \sim 0.97 \pm 0.2 \) [76].

The second synthesis route to PNB involves the oxidative chemical polymerization of aniline directly to PNB. This route begins identically with the synthesis of EB, ammonium peroxydisulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) is added to a solution of aniline in aqueous 1.0 M HCl. It is found that the initial polymerization occurring in the presence of excess aniline results in PNB and, if allowed to go to completion, EB [77]. To isolate the PNB, the mixture is added to aqueous NaOH (~5°C) at the time during the polymerization when the oxidative potential first begins to decrease, ~15 minutes. The PNB obtained has an oxidation state of \( (1 - y) \sim 0.97 \pm 0.2 \). The electronic and infrared spectra were found to be identical to PNB obtained from emeraldine base [77].

The PNB samples studied here were made via the conversion of EB directly to PNB. These samples were prepared by Y. Sun and the University of Pennsylvania. The EB samples studied were all of the EB-I type prepared by G. Min at the University of Pennsylvania and M. Angelopoulos at the IBM T. J. Watson Research Center.

3.1.1 Powder Samples

Powder samples of PNB and EB were used either as a loose powder or as a powder suspended in a KBr pressed pellet. The preparation of KBr pellets has been described elsewhere [82]. The EB/KBr pellet samples were used for the LESR studies to reduce the effects of heating due to exposure to (laser) light. The loose powder samples
were just the “as is” powder synthesized as described above. These samples were loaded into 3 mm I.D. EPR tubes, pumped on for at least 30 minutes using an Alcatel diffusion pump and sealed using an acetylene torch. Samples used in low temperature measurements had helium added as a thermal exchange gas.

3.1.2 Oriented Samples

Oriented samples of emeraldine base were free-standing stretched films. The procedure used to make these films is described as follows. EB powder, synthesized via the oxidative chemical polymerization of aniline described above, was dissolved in \( n \)-methyl-2-pyrrolidinone (NMP). The resultant EB/NMP solution was then cast into films on glass substrates. Once dry, they were washed with a 0.1 M \( \text{NH}_2\text{OH} \) solution dried a second time and peeled from the glass substrate. These free standing films were then cut and stretched at \( \sim 150^\circ \text{C} \) under a constant force [83]. Stretch ratios \( L/L_0 \) ranged from zero (unstretched) to a maximum of \( \sim 5 \).

For the orientation-dependent EPR studies it was necessary to maximize the amount of sample in the active region of the EPR spectrometer while maintaining its uniform orientation. This was done by cutting the sample films into small rectangular pieces approximately 2 mm \( \times \) 5 mm (see Figure 14 (a)) and then loading these pieces length-wise into a small Teflon holder as shown in Figure 14 (b). These holders were made from Teflon cylinders machined to fit into a 3 mm EPR tube and had a notch \( \sim 1.5 \) mm wide and \( \sim 5 \) mm deep cut in one end. The sample mounted in the holder was dropped into an EPR tube followed by a cylindrical Teflon cap and some Teflon cotton to hold everything in place. The EPR tube with the sample was then pumped on with a mechanical pump for roughly an hour and sealed with a torch. With the sample mounted in this way, orientations with the sample’s stretch axis both parallel and perpendicular to the EPR static magnetic field can be obtained simply by rotating the EPR tube about its axis while in the Bruker ESP300 spectrometer. EPR scans of the Teflon holder found no significant signal.
Figure 14: (a) Diagram showing how EB stretch oriented films were cut prior to loading into sample holder (---- cut lines). (b) Schematic diagram of oriented films sample holder.

### 3.1.3 Solution Samples

Polyaniline is soluble in a variety of solvents such as N-methyl-1-pyrrolidinone (NMP), N,N-dimethyformamide (DMF), 2,2-diphenyl-1-picylhydrazyl hydrate (DMSO), and dioxane (see Table 1 for details). In this study NMP and dioxane were used. NMP is the better solvent for polyaniline. However, because of dioxane's low dielectric loss and the larger effective sample volume obtainable the highest resolution
spectra were obtained with this solvent. Here the procedure used to prepare solutions of PNB is described. The procedure used to prepare EB solution is identical and the only relevant difference in regard to solubilities and concentration is addressed.

Table 1: List of common solvents and some of their properties.

<table>
<thead>
<tr>
<th>Solvent Name</th>
<th>abbr.</th>
<th>Structure</th>
<th>M.P.</th>
<th>B.P.</th>
<th>dielectric const. (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>H₂O</td>
<td>0 °C</td>
<td>100 °C</td>
<td>~100</td>
<td>81</td>
</tr>
<tr>
<td>dioxane</td>
<td>dioxane</td>
<td>O(CH₃)₂O(CH₃)₂</td>
<td>11.8</td>
<td>~100</td>
<td>2.29</td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>DMF</td>
<td>HCO(CH₃)₂</td>
<td>-61</td>
<td>153</td>
<td>36.7</td>
</tr>
<tr>
<td>N-methyl-1-pyrrolidinone</td>
<td>NMP</td>
<td>CH₃N(CH₃)₂CO</td>
<td>-24</td>
<td>202</td>
<td>32</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>THF</td>
<td></td>
<td>-106</td>
<td>~65</td>
<td>32</td>
</tr>
<tr>
<td>2,2-diphenyl-1-pierylhydrazyl hydrate</td>
<td>DMSO</td>
<td>CH₃(SO)</td>
<td>18.4</td>
<td>189</td>
<td>46.6</td>
</tr>
</tbody>
</table>

The starting material for solutions of PNB in NMP and dioxane was PNB powder oxidized from emeraldine base. The PNB powder was ground for ~30 seconds (three 10 second bursts to prevent heating) using a Wiggle Bug in an Argon filled glove box free of oxygen and water. Approximately 50 to 150 mg of the finely ground powder was then sealed in a small 20 ml sample jar and removed from the glovebox. The PNB powder was then placed in a nitrogen filled glove bag along with the solvent and a pipette. The solvents used were all 0.005% anhydrous and delivered and stored under nitrogen. Using the pipette ~15 ml of solvent was added to the PNB powder along with a magnetic stirring bar and sealed. The sealed solution was removed from the glove bag and magnetically stirred vigorously for 1 to 2 hours. The solution was then returned to the glove bag and double filtered using a 0.45 µm Teflon filter to remove any undissolved particulates. The double filtration was done by first drawing the solution through a filter into a glass syringe. The used filter was then replaced with a new filter and the solution pushed through and into a clean sample jar. At this point the solution could be loaded into a round quartz tube or a quartz flat cell (Figure 15) depending on the solvent used.

Only a small percentage, approximately 1 to 3 percent, of PNB was found to dissolve in either solvent. The low percentage of soluble PNB may be a result of a
distribution in the molecular weight and/or crystallinity of the PNB sample similar to emeraldine base [84]. Starting with 50 to 150 mg resulted in a few milligrams of PNB dissolved in roughly 15 ml of solution or \( \sim 0.2 \text{ g/l} \). The solution was transparent with a light purple color.

It was necessary to degas all solutions to remove dissolved oxygen. Oxygen is paramagnetic with a triplet ground state. Although oxygen does not have an observable resonance it does dramatically broaden the linewidths of other radical species effectively accelerating their spin-lattice relaxation. A 3-step method for degassing a solution is the freeze/pump/thaw method [85].

1. An EPR tube containing the solution to be degassed was attached to a mechanical pump using 0.25 inch Tygon tubing. Then it was quickly frozen by submersion in liquid nitrogen. If the solution is frozen slowly (especially from the bottom up) there is a greater chance that the tube will break while thawing.

2. Next, the EPR tube was pumped out with the mechanical pump and the Tygon tube clamped closed.

3. Last, the solution was allowed to thaw and dissolved gas was released to fill the vacuum. Solution at the bottom of the EPR tube tended to thaw more rapidly than the rest and it was sometimes necessary to refreeze it to prevent this. If the solution at the base of the tube was allowed to thaw before the rest, the tube would often break. It was necessary to repeat the cycle once or twice to fully degas the solutions.

For some solutions the concentration could be increased by a factor of \( \sim 5 \) by applying dynamic vacuum using a mechanical pump to draw off solvent. To do this the solution was loaded into an EPR tube and connected to a mechanical pump using 0.25 inch Tygon tubing. To begin pumping on the solution it was important that the valve to the mechanical pump be opened very slowly. Initially the solution will bubble as it degasses. If the valve is opened too quickly to vacuum, rapid degassing/bubbling will draw solution into the pump. Also, after the degassing was complete, care had to be taken not to pump so quickly that vaporization would cause solvent at the solution/vacuum interface to freeze.
Figure 15: Diagram of the Wilmad Glass Co. WG-808 variable temperature quartz flat cell. [From the Wilmad Glass Co. Catalog No. 852]
There are two forms of emeraldine base corresponding to amorphous structure (EB-I) and crystalline structure (EB-II). EB-I was found to be more soluble than EB-II and was used to make all the solutions. The preparation of the EB solutions followed the same procedure as described above for PNB. The starting material was between 5 and 15 mg of EB-I powder which was mixed with 15 ml of solvent. Close to 100% of the powder dissolved, giving concentrations between 0.3 and 1 g/l and resulting in dark blue transparent solutions.

The PNB in solutions stored at room temperature would slowly precipitate out of solutions over the course of a few months. If the solutions were heated above ~ 320 K they would degrade rapidly. This made it impossible to take high temperature spectra of these solutions where higher hyperfine resolution is expected. The solutions could be stored indefinitely at dry ice temperatures, < 30° C.

3.2 Aspects of Magnetic Resonance Theory

Electron spin resonance (ESR) was discovered by Zavoisky in 1945 [86]. Today it is one of the most powerful techniques used to study magnetic phenomena at the atomic level. The technique of ESR is based on inducing and observing transitions among magnetic moment (spin) energy states. In a typical experiment a static magnetic field is applied to a sample, inducing splitting of the energy states. This splitting is then determined by measuring the absorption of electromagnetic (microwave) radiation due to transitions between these energy states. ESR is a form of spectroscopy in which a spectrum can be obtained by either the magnetic field sweep or frequency field sweep methods. Due to the experimental constraint of a fixed cavity resonance the former method of magnetic field sweep is almost always adopted.

The theory of magnetic resonance is commonly described in two equivalent but phenomenologically different pictures, the classical and quantum. Each of these provides a different perspective and yields its own particular insights into the magnetic resonance phenomenon.
3.2.1 Classical Picture of Magnetic Resonance

The classical approach is based on the work of Bloch [87] where the spins are treated in terms of a bulk magnetic moment. The starting point is the equation of motion for a magnetic moment in the presence of a magnetic field $\mathbf{H}$ given by the vector equation [88]

$$\frac{d\mathbf{J}}{dt} = \mathbf{M} \times \mathbf{H},$$  \hspace{1cm} (6)

where $J$ is the angular momentum and $M$ is the magnetic moment. To simplify our discussion one can assume the classic magnetic resonance experiment composed of a large static field $H_0$, taken to lie along the $z$-axis, and a perpendicular perturbing microwave field, $H_1(t)$. Substituting $M = \gamma J$ into (6) and adding damping terms give the well known Bloch equations,

$$\frac{dM_z}{dt} = \gamma (M \times H)_z + \frac{M_0 - M_z}{T_1}$$  \hspace{1cm} (7a)

$$\frac{dM_x}{dt} = \gamma (M \times H)_x - \frac{M_x}{T_2}$$ \hspace{1cm} (7b)

$$\frac{dM_y}{dt} = \gamma (M \times H)_y - \frac{M_y}{T_2},$$  \hspace{1cm} (7c)

where $T_1$ is the longitudinal (spin-lattice) relaxation time, viewed in this picture as the characteristic time required for $M_z$ to relax to its thermal equilibrium value $M_0$, and $T_2$ is the transverse (spin-spin) relaxation time characterizing the relaxation of $M_x$ and $M_y$ towards zero.

The steady state solution of the Bloch equations, given in terms of the magnetic susceptibility ($\chi = \chi' + i\chi''$) and the frequency ($\omega_0$) of the perturbing magnetic field, is
The imaginary part of the susceptibility is proportional to the absorption of energy by the magnetic system. The magnetic resonance experiments used throughout this work measure only the absorptive component of the susceptibility. The real part of the susceptibility is proportional to the phase lag between the transverse component of the magnetization and the microwave field.

The classical approach is useful in relaxation studies where the effects of spin-lattice relaxation $T_1$ are important and the details of spin-spin interactions can be neglected. All effects of spin-spin interactions are lumped into the parameter, $T_2$, and details of the resonance lineshape are lost. At low microwave powers where $\gamma^2 H_1^2 T_1 T_2 \ll 1$, the susceptibility given by (9) and (10) approximate a Lorentzian lineshape where $\Delta \omega = 1/T_2$. At higher microwave powers where $\gamma^2 H_1^2 T_1 T_2 \approx 1$, the resonance is said to be in a regime of partial saturation and the susceptibility deviates from a Lorentzian and is a function of $T_1$. By measuring the deviation of the resonance lineshape from Lorentzian as a function of microwave power, $T_1$ can be estimated. At very high microwave powers, $\gamma^2 H_1^2 T_1 T_2 >> 1$, the resonance is said to be saturated and corresponds to the magnetization, $M$, pressing at 90° to the static field.

3.2.2 Quantum Mechanical Picture of Magnetic Resonance.

The quantum mechanical approach differs from the classical approach in that it takes into account the details of individual spin-spin interactions. One of the big advantages of magnetic resonance spectroscopy is that it can probe the microscopic or local environment of individual quantum magnetic moments (electrons, nucleons, and
muons). In order to describe and interpret the result of these experiments one must look at individual moments. This requires a quantum mechanical approach.

A typical magnetic resonance experiment employs magnetic fields on the order of $10^3$ to $10^4$ Gauss. For magnetic moments originating from electrons this corresponds to energies on the order of 0.1 to 1 Kelvin lying in the microwave range. For magnetic moments originating from protons, energies are about 0.0001 to 0.001 K corresponding to radiowave frequencies. The quantum mechanical description of these magnetic moments requires that interactions on the order of roughly $10^{-4}$ to 1 K be considered. The typical starting point for magnetic resonance theory is the spin Hamiltonian operator:

$$H = H_{Ze} + H_{SS} + H_{HF} + H_{Ze} + H_{NN} + O(B S^3, S^4, S^3 I, S^2 I, S I^3, I^4, \ldots)$$ (11)

where, $H_{Ze}$ is the electronic Zeeman energy, $H_{SS}$ is the spin-spin interaction, $H_{HF}$ is the hyperfine interaction, $H_{Ze}$ is the nuclear Zeeman energy, $H_{NN}$ is the spin-spin nuclear interaction, and the last term represents all other spin-field or spin-spin interactions of order 4 and higher. For the ESR and ENDOR experiments only the first three terms in (11) need be considered.

To solve the secular equation corresponding to (11), one writes the Hamiltonian matrix and diagonalizes it to obtain the energy levels and eigenfunction. The matrix form of the spin Hamiltonian operator is

$$H = \beta_e S^I \cdot g \cdot B + S^I \cdot D \cdot S + \sum_{a=1}^{NI} \left( S^I \cdot A_{a} \cdot I_a - \beta_a I^I \cdot \mathbf{g}_a \cdot B \right) +$$

$$\sum_{a=1}^{NI} \left( I_a^I \cdot P_a \cdot I_a + \sum_{a' a}^{NI} \left( I_a^I \cdot J_{aa'} \cdot I_{a'} + I_{a'}^I \cdot J_{aa'} \cdot I_a \right) \right) +$$ (12)

$$O(B S^3, S^4, S^3 I, S^2 I, S I^3, I^4, \ldots),$$

where $\beta_e$ and $\beta_a$ are the Bohr and nuclear magnetons and $NI$ is the number of nuclear spins. The parameters $g, D, A_a, \mathbf{g}_a$, and $P_a$ are second-order tensors, representing the g-tensor, electronic spin-spin interaction, hyperfine interaction, nuclear g-tensor, nuclear
spin-spin interaction, respectively. The terms in (12) correspond respectively to the terms in (11). The matrix form (12) has a dimensionality

$$N = (2S + 1) \prod_{a=1}^{N_I} (2I_a + 1)$$

(13)

The spin operators $S$ and $I_a$ are vectors in 3D-space with $N^2$ matrix components given by the Kronecker products

$$^N S_j = S_j \otimes E_{i,j} \otimes \cdots \otimes E_{a,j} \otimes \cdots \otimes E_{N_I,j}$$

(14)

and

$$^N I_{a,j} = E_{0,j} \otimes E_{i,j} \otimes \cdots \otimes E_{a-1,j} \otimes I_{a,j} \otimes E_{a+1,j} \otimes \cdots \otimes E_{N_I,j},$$

(15)

where $S_j$ and $I_{a,j}$ are the appropriate “single spin” matrices and $i = x, y, z$. (Example: for $S = 1/2$ the single spin matrices are just one half the Pauli spin matrices.) The magnetic field vector is given by

$$B = \begin{bmatrix} B_0 \sin \theta \cos \phi \\ B_0 \sin \theta \sin \phi \\ B_0 \cos \theta \end{bmatrix}$$

(16)

where the standard polar coordinates are used.

Once the energy levels of the spin Hamiltonian are found, the magnetic resonance transitions, $\omega_j$, appropriate to a given experiments section rules can be determined. For EPR the selection rules are $\Delta m_S = \pm 1$ and $\Delta m_I = 0$. For ENDOR and NMR they are $\Delta m_S = 0$ and $\Delta m_I = \pm 1$. To construct a simulated spectrum, a stick spectrum consisting of delta functions $\delta(\omega - \omega_j)$ to each transition is convoluted with a lineshape function. A Lorentzian function is usually chosen because every transition is subject to lifetime broadening. Because the excited state has a finite lifetime $T_1$, its energy is smeared out according to the Heisenberg uncertainty principle and this translates to Lorentzian broadening with a linewidth $\Delta \omega_E \propto 1/T_1$. In some cases it may be appropriate to use a
lineshape other than a Lorentzian. The most common case is where small unresolved hyperfine or dipole-dipole interactions are present but neglected in the spin Hamiltonian. The effects of these weak interactions can in many cases be accounted for through a Gaussian broadening function. Simulations of the EPR spectra of PNB in chapter 4 make use of a Gaussian broadening function to account for unresolved hyperfine splitting. Later ENDOR measurements were able to resolve this hyperfine splitting.

In most instances it is adequate to assume that all EPR transitions have equal probability and therefore equal intensity, as was assumed in the previous paragraph. However, when the assumption is not justified, transition intensities must be calculated. An EPR transition is induced through a Zeeman interaction between the electronic spin and microwave field given by

\[ H_{\text{oc}} = \beta S \cdot g \cdot H \cos(\omega t) \]  

(17)

where \( H \) is the microwave field strength. The intensity is given by

\[ I \propto \left| \langle f | H_{\text{oc}} | i \rangle \right|^2 \cdot \frac{g \beta H_0}{(2S+1)kT} \]  

(18)

where \( \langle f | \) and \( | i \rangle \) are the final and initial states. The second factor comes from the Boltzmann population of the \( f \) and \( i \) states where it is assumed \( g \beta H_0 \gg kT \).

### 3.2.3 Zeeman Interaction

The high-energy electronic \( (H_a) \), crystal field \( (H_{CF}) \), and spin-lattice \( (H_{LS}) \) interactions are much greater in energy than the Zeeman term and are handled separately from the spin Hamiltonian. However, they do influence the form of the spin Hamiltonian and it is more accurate to refer to (11) as the effective spin Hamiltonian. In the case where crystal field energies are negligible compared to the spin-orbit coupling, such as for free transition series and rare earth elements, \( J \) is a good quantum number. The Zeeman term then takes the form...
or

\[ \beta_s g S \cdot B \]  

3.2.4 Hyperfine Interactions

There are two types of hyperfine interactions, isotropic and anisotropic. Both of these interactions are accounted for in \( H_{HH} \) through the hyperfine tensor:

\[ A = A_{iso} I + A_{ani} \]  

where \( A_{iso} \) is the isotropic hyperfine coupling constant, \( I \) is the identity matrix and \( A_{ani} \) is the anisotropic hyperfine coupling tensor. One of the experimental goals of the present work is the determination of \( A_{iso} \) for the various hyperfine couplings in polyaniline’s defect states.

The anisotropic hyperfine interaction originates from the dipolar interaction between the electronic spin and a nuclear spin. Because of the nature of the dipolar interaction \( A_{ani} \) is traceless and

\[ \frac{1}{3} Tr(A) = \frac{1}{3} Tr(A_{iso} I + A_{ani}) = A_{iso} . \]  

The consequence of this is that in a solution or gas where a radical is rotating rapidly, the anisotropic interaction will be averaged out. The spin Hamiltonian can be greatly simplified.
The isotropic hyperfine interaction was shown by Fermi to be proportional to the probability that an unpaired electron and a nuclear spin are in contact. This is given approximately by

\[ A_{\text{iso}} = \frac{8\pi}{3} g \beta g_n B_n |\Psi(0)|^2, \]

where \( \Psi(0) \) is the unpaired electron wavefunction evaluated at the nucleus. (In radicals, knowledge of \( \Psi(0) \) does not readily give insight to the structure of a radical.) For instance, in conjugated polymers it is more interesting to determine the spin densities corresponding to different nuclear centers in the \( \pi \)-structure. From \( \Psi(0) \) it is nontrivial to estimate spin densities due to spin polarization effects. To solve this problem a parametric approach must be used. McConnell showed that there is a linear relationship between the isotropic hyperfine coupling constant and the unpaired \( p_z \)-electron densities in \( \pi \)-type organic radicals, \( A_i = Q_i \rho_i \), where \( \rho_i \) is the \( \pi \)-electron spin density and \( Q_i \) an empirically-determined spin polarization constant at the \( i \) nuclear site. The general form is

\[ A_i = Q_i \rho_i + \sum_{j \neq i} Q_{i,j} \rho_j, \]

where \( Q_{i,j} \) is the spin polarization at site \( i \) due to spin density on site \( j \).

### 3.2.5 Spin-Spin Interactions

Spins can interact through both dipolar and exchange interactions. For interacting electronic spin, however, there are three different situations which are commonly treated in magnetic resonance theory. Two originate from the dipolar interaction and are referred to as the dipolar broadening interaction and the zero-field splitting. The third is the exchange interaction, which will be addressed in the next section.

A magnetic sample is composed of a distribution of interacting magnetic dipoles (electronic and/or nuclear spins) which can interact through the classical dipolar interaction given by
41

\[ H_{\text{dp}} = \sum_{i,j} g_1 g_2 \beta_i \beta_j \left[ \mathbf{S}_i \cdot \mathbf{S}_j \frac{3(\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{S}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3} - \frac{3}{r_{ij}^5} \right], \quad (25) \]

where \( \mathbf{r}_{ij} \) is a vector from dipole \( \mathbf{S}_i \) to dipole \( \mathbf{S}_j \). The strength of this interaction goes as \( 1/r^3 \), falling off more slowly than the exchange interaction. In general, a system is composed of many dipoles and equation (25) is far too complex to solve exactly. In this situation the effects of the dipolar interaction is not treated within the spin Hamiltonian framework but instead enter spectral simulations through the broadening function. For a system, such as a crystal, where the dipoles form a regular lattice it is possible to solve (25) exactly and is found, in most cases, that the dipolar interaction can be reasonably approximated by a Gaussian lineshape (i.e. a random distribution of resonance fields).

When two (or more) electronic spins occupy the same atomic site (or nearby site), such as in a triplet system, the dipolar interaction between these nearby spins can be treated within the spin Hamiltonian framework. In this situation the dipolar interaction is referred to as the zero-field splitting. For this case Eq. (25) is more conveniently expressed in terms of the total spin operator \( \mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 \) in the form

\[ H_{\text{dp}} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (26) \]

where

\[
\mathbf{D} = \frac{g_1 g_2 \beta_i \beta_j}{2} \begin{bmatrix}
\left\langle \frac{r^2 - 3x^2}{r^5} \right\rangle & \left\langle -3xy \right\rangle & \left\langle -3zx \right\rangle \\
\left\langle -3xy \right\rangle & \left\langle \frac{r^2 - 3y^2}{r^5} \right\rangle & \left\langle -3yz \right\rangle \\
\left\langle -3zx \right\rangle & \left\langle -3yz \right\rangle & \left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle
\end{bmatrix}
\]

and \( \left\langle \right\rangle \) denotes an average over the electronic wavefunction. For a detailed discussion of zero-field splitting see Wertz [89] chapter 10.

When an electronic and nuclear spin are involved the dipolar interaction (26) enters the spin Hamiltonian through the hyperfine tensor \( \mathbf{A} \) and gives rise to the hyperfine
anisotropy. For the present work it is important to note that since the dipolar interaction tensor $\mathbf{D}$ is traceless it will not contribute to measurements of the isotropic hyperfine interaction.

3.2.6 Stochastic Theory of Lineshapes: Exchange and Motional Narrowing

There are three basic types of narrowing mechanisms: exchange interaction, spin diffusion, and molecular motion. All of these mechanisms operate on the same basic principle. The effect of the narrowing mechanism is to cause line broadening fluctuations, $\omega_1$, experienced by a spin to change with time. This time dependence given by the fluctuation is the basis for line narrowing. The change in the fluctuation with time is referred to as the modulation and the mechanism causing it the modulation process. In the case of radicals in dilute solutions the modulation is due to the anisotropic hyperfine interaction and the modulation process is the kinetic motion of the radical. The effect is that the spins respond to only the isotropic hyperfine interaction. Thus, solution EPR is a powerful technique for determining $A_{iso}$ and, hence, the spin distribution, as shown in the case of solitons in PNB [17]. In the case of dilute solitons or polarons in a conjugated polymer the modulation arises from both the isotropic and anisotropic hyperfine interactions. As the spin moves or diffuses along the polymer it will encounter different spin states among the various nuclear sites. Since the nuclear Zeeman splitting among these state is much less than $kT$, the spin will encounter, on average, equal numbers of spin-up and spin-down state. As a result, the electronic spin will respond to an averaged nuclear spin for each site. This is the modulation process. In chapter 4 the absence of this type of narrowing is used to place an upper limit on the diffusion rate of solitons in PNB.

Lineshape theory of narrowed resonances was initially developed by Van Vleck [90], and subsequently by Anderson [91], and Kubo and Tomita [92,93]. Here, a brief overview of the theory is discussed as described by Kubo. The treatment is general to all modulation processes and gives needed insight into narrowed resonances. It begins with
the assumption that a system of spins can be described by the equations of motion of a randomly modulated oscillator:

$$\frac{dM_s}{dt} = i\omega(t)M_s$$  \hspace{1cm} (28)

where

$$\omega(t) = \omega_0 + \omega_f(t).$$  \hspace{1cm} (29)

The time dependent part, $\omega_f(t)$, is called the fluctuation and is assumed to have a time average of zero. In statistical physics, fluctuations are characterized by a probability distribution $P(\omega)$ and a correlation function $\langle \omega(t)\omega( t + \tau) \rangle$. It is assumed that the process $\omega_f(t)$ is ergodic and stationary in time. This implies that $P(\omega)$ is Gaussian and $\langle \omega(t)\omega(t + \tau) \rangle$ does not depend explicitly on time. Under these assumptions the solution to equation (28) is

$$M_s(t) = M_s(0)\exp \left( i\omega_0 t + i\int_0^t \omega_f(t')dt' \right).$$  \hspace{1cm} (30)

In an actual experiment it is the correlation function of the expectation value $\langle M_s(t) \rangle$ that is of interest. Performing an ensemble average over the random process and multiplying by $M_s(0)$ gives the correlation function,

$$\langle M_s(t)M_s(0) \rangle = |M_s(0)|^2 e^{i\omega_0 t} \exp \left( i\int_0^t \omega_f(t')dt' \right).$$  \hspace{1cm} (31)

The ensemble average on the right is defined as the relaxation function

$$\Phi(t) = \exp \left( i\int_0^t \omega_f(t')dt' \right).$$  \hspace{1cm} (32)

Using the fluctuation-dissipation theorem, the relaxation function is related to the absorption spectrum through a Fourier transform so,
where \( I(\omega - \omega_0) \) is the intensity of the absorption spectrum and is normalized to unity.

A narrowed resonance can be characterized by two parameters: the modulation amplitude and the correlation time. The modulation amplitude is defined as

\[
\Delta^2 = \langle \omega^2 \rangle = \frac{1}{2} \int_{-\infty}^{\infty} e^{i(\omega - \omega_0)t} \Phi(t) dt,
\]

(33)

where \( I(\omega - \omega_0) \) is the intensity of the absorption spectrum and is normalized to unity.

For an un-narrowed Gaussian resonance, \( M_2 = 0.180 \left( \frac{\Delta H_{1/2}}{J} \right)^2 \). The correlation time represents the effectiveness of the modulation process and is defined as

\[
\tau_c = \frac{1}{\Delta^2} \int_0^\infty \psi(t) dt,
\]

(34)

where \( \psi(t) \) is the correlation function \( \psi(t) = \langle \omega(t)\omega(t+\tau) \rangle \). \( \tau_c \) corresponds to the time after which the correlation function is reduced to half its initial value. Depending on the narrowing mechanism, the correlation time can be related to various macroscopic quantities. For exchange-coupled spins, \( \tau_c \approx \hbar/J \), where \( J \) is the exchange. For isotropic tumbling in a solution the correlation time is given by \( \tau_c \approx 4\pi \eta a^3 / 3kT \), where \( \eta \) is the viscosity and \( a \) is the radius of the solute molecules. For a spins moving along a 1-dimensional polymer, \( \tau_c \approx a_0^2 / 2D \), where the constant \( D \) is the diffusion coefficient.

For a Gaussian modulation process Kubo showed that the relaxation function can be written as

\[
\Phi(t) = \exp \left( -\int_0^t (t - \tau) \psi(t) d\tau \right),
\]

(36)
This can easily be solved for the following two limiting cases of slow and fast modulation:

**Slow modulation limit, \( \tau_c \Delta \gg 1 \):** When \( t << \tau_c \), the correlation function can be approximated as \( \psi(t) \approx \psi(0) = \Delta^2 \). Equation (36) then yields

\[
\Phi(t) = \exp\left(-\frac{\Delta^2 t^2}{2}\right) \tag{37}
\]

Applying Equation (33), the resonance absorption spectrum at \( \omega \) is found to be

\[
I(\omega - \omega_0) = \frac{1}{(2\pi)^{1/2}} \frac{1}{\Delta} \exp\left(-\frac{1}{2\Delta^2} (\omega - \omega_0)^2\right) \tag{38}
\]

Thus the relaxation function yields a Gaussian lineshape.

**Fast modulation limit, \( \tau_c \Delta \ll 1 \):** When \( t >> \tau_c \), the spins will be uncorrelated, \( \psi(t) \approx 0 \), and the upper limit in equation (36) can be replaced by infinity. Therefore, equation (37) simplifies to

\[
\Phi(t) = \exp\left(-\Delta^2 \tau_c t\right) \tag{39}
\]

Again applying equation (33), the resonance absorption spectrum at \( \omega \) is found to be

\[
I(\omega - \omega_0) = \frac{\Delta^2 \tau_c}{\pi} \left(\frac{1}{(\omega - \omega_0)^2 + \Delta^2 \tau_c^2}\right) \tag{40}
\]

Thus, in this limit, the relaxation function yields a Lorentzian lineshape with \( \Delta \omega_{\nu_2} = \Delta^2 \tau_c \).

**Extension to one dimension:** For systems where the narrowing mechanism operates in low dimensions, the effectiveness of the modulation process is reduced. This manifests itself in the correlation function as an extended tail for long-times. In one dimension the correlation function can be redefined as
Now, equation (22) yields

$$
\psi(t) = \psi(0)\left(\frac{\tau_c}{t}\right)^{1/2}.
$$  \hfill (41)

The corresponding lineshape will have a linewidth of $\Delta \omega \sim \Delta^{4/3}\tau_c^{1/3}$.

### 3.3 Electron Paramagnetic Resonance

![Figure 16: A Block diagram of the Bruker ESP300 Spectrometer.](image)

**3.3.1 EPR Spectrometer**

The experimental EPR spectra presented in the following chapters were obtained with a Bruker Instruments ESP300 X-Band spectrometer operating in the continuous
wave field sweep mode. A block diagram of this spectrometer is shown in Figure 16. Not shown in this figure is the Oxford Instruments ER900 continuous helium flow cryostat which allowed the sample temperature to be varied from 3 to 300 K. In the following sections the components of the Bruker spectrometer and cryostat are described. Also a short section is devoted to the particularities of solution EPR.

The Bruker ESP300 spectrometer measures an EPR spectrum in the follow manner. The magnetic samples are placed in a fixed frequency microwave resonant cavity and a spectrum is scanned by sweeping the field through the EPR transition. The microwave energy absorbed by these transitions near resonance is not detected directly. Rather, changes in the microwave power reflected from the resonant cavity are measured. In normal operation at a field off resonance, the cavity is critically coupled to the microwave bridge. This means that the impedance of the microwave bridge and cavity are exactly matched and the signal amplitude is independent of the incident power. Now, as a transition nears resonance, the samples susceptibility, \( \chi'' \), changes and causes a change in the Q-value of the cavity given by

\[
Q = \frac{2\pi(\text{energy stored in cavity})}{(\text{energy dissipated per cycle})},
\]

and hence in the reflected power. The resonance is detected by lock-in amplification of changes in the reflected microwave power induced by modulation the magnetic field at the sample. This results in measurement of the derivative of the absorption as opposed to the direct absorption. In addition to change in the absorption of energy, there is a shift in the cavity’s resonant frequency proportional to the discursive component of the susceptibility, \( \chi' \). The samples dispersion can be measured by detection of this frequency shift. However, the Bruker ESP300 spectrometer uses an automatic frequency control circuit which locks on to the cavity’s resonant frequency. Thus, the spectrometer’s operating frequency follows shifts in the cavities resonant frequency and
the dispersion cannot be observed. For details on the operation of the ESP300 spectrometer see the Bruker manuals.

### 3.3.2 Cryogenics

In the ESP300 spectrometer, sample temperature was controlled using an Oxford Instruments ESR-900 continuous flow helium cryostat, GFS-650 helium transfer tube, and an ITC-503 (similar to the ITC-4) temperature controller. Figure 17 shows a diagram of these cryogenic components and how they are interconnected. Shown in Figure 18 is a detailed diagram of the ESR-900 cryostat. This cryogenic arrangement allowed the temperature to be varied from ~ 3 to 300 K.

![Figure 17: Schematic diagram showing the interconnections between the various temperature control components. [From the Oxford Instruments ESR-900 manual.]]
Figure 18: A diagram of the Oxford ESR-900 continuous flow helium cryostat. [From Oxford ESR-900 manual.]
Monitoring the temperature of the sample was done using a thermocouple mounted in the helium flow about ~ 15 mm below the EPR tube. This separation between the thermocouple and the sample results in a difference between the monitored thermocouple temperature and the actual sample temperature. The error ranged from ~ 1 to and much as 10 K depending of the helium pressure and flow, heater current, temperature set point, integrity of the vacuum insulating jackets, and ambient temperature. The largest error consistently was near ~ 90 to 120 K. To correct for this, the system was calibrate by using a second thermocouple mounted in the bottom of an EPR tube at the sample position and recording the two temperatures during a normal temperature run.

3.3.3 Solution EPR

The EPR of solutions offers the advantage of increased resolution over solids and simplified hyperfine structure. Specifically, the rapid tumbling motion of dilute radicals in solution averages out all spin-spin interactions except the isotropic hyperfine interaction. This phenomena was described in the section covering motional narrowing effects. The result is spectra where the resolution is limited only by the natural linewidth \( \left( \frac{1}{T_1} \right) \). However, these advantages do not come without cost --- there are several experimental complications which accompany solutions.

The electromagnetic field in the resonant cavity of an EPR experiment is damped through its interaction with electric dipoles induced in a solvent. This loss of electromagnetic energy results because the motion of the solvent molecules induced by the electromagnetic field is damped due to the finite viscosity of the solvent. This loss mechanism is referred to as dielectric loss. The strength of this loss is a function of a solvents dielectric constant \( \varepsilon \) and viscosity. For water, where \( \varepsilon = 80 \), the dielectric loss can reduce Q by more than an order of magnitude thereby wiping out the cavity resonance. In a frozen solution, where the viscosity is extremely large, this dielectric loss is virtually eliminated; unfortunately, so are the effects of motional narrowing.
Figure 19: Electromagnetic field configurations in a TE_{102} mode rectangular resonant cavity. (From reference [85].)

Experimentally, the problem of dielectric loss can be reduced while still maintaining the advantages of solutions. In EPR it is the alternating magnetic field which induces the Zeeman transitions. The electric field has no effect on these transitions, it only introduces dielectric loss. Shown in Figure 19 are the electric and magnetic field lines for a TE_{102} resonant cavity. For an EPR experiment the sample is positioned on the planar antinode in the $H$-field along the axis parallel to the $x$-axis and passing through the center of the cavity. This axis also lies on a planar node of the electric field where the dielectric loss will be zero. The EPR signal can be maximized by maximizing the amount of sample lying on the planar node in the electric field. This is commonly done using a quartz flat cell, Figure 15.

3.4 Electron Nuclear Double Resonance

It was mentioned that the resolution of an EPR spectrum is fundamentally limited by the natural linewidth $(1/T_1)$. For $T_1$'s common to conjugated polymers, hyperfine splitting of less than ~ 1 G will be obscured. ENDOR (Electron Nuclear Double Resonance) is a technique which can be simply described as EPR detected NMR. It was first demonstrated by Feher [94] in 1956. The advantage is that the resolution is limited
by the nuclear spin-lattice relaxation time which is generally slower than its electron counterpart.

The basic principles of the ENDOR technique can be understood by examination of a simple system involving a single electron of $S = 1/2$ and a single nucleus of $I = 1/2$. The energy level diagram for this situation is shown in Figure 20. These levels are obtained from the spin Hamiltonian (12) where only the electron Zeeman, nuclear Zeeman, and hyperfine terms are included. The first step in an ENDOR experiment is to scan the ESR spectrum to optimize the spectrometer parameters and determine the ESR resonance field values, e.g. $(\omega_e \pm A/2)\hbar/g_\beta$. Next, the applied $H$-field is set to one of these values, for instance $(\omega_e \pm A/2)\hbar/g_\beta$ corresponding to transition $2 \rightarrow 3$, and the power increased to saturate the ESR transition. The ENDOR spectrum is obtained by monitoring the ESR signal as a radio frequency magnetic field is swept through the ENDOR transitions. When ENDOR transition $1 \rightarrow 2$ is excited there will be an increase in the population of level 2 resulting in an increase in the ESR signal. Similarly, when ENDOR transition $3 \rightarrow 4$ is excited there will be a decrease in the population of level 3 again resulting in an increase in the ESR signal. The ENDOR spectrum acquired will look similar to Figure 21 (b).

An important phenomenon that must be recognized is that for $\omega_N > A/2$ the ENDOR spectra will be centered about $\omega_N$ and the separation between hyperfine peaks pairs will be equal to the hyperfine splitting constant $A$. If $\omega_N < A/2$, the low frequency line will be reflected through zero as shown in Figure 21 (b). For proton hyperfine splitting, $\omega_N = 14.9$ MHz at 3.5 kG. Therefore most splitting in conjugated polymers will fall under the case where $\omega_N > A/2$. For nitrogen hyperfine splitting, $\omega_N = 1.1$ MHz at 3.5 kG, thus $\omega_N < A/2$ will hold in most cases (see Figure 21 (a)).
3.4.1 ENDOR Spectrometer

The spectrometer used to acquire the ENDOR spectra presented in this thesis was a Bruker Instruments ESP300 with the ENDOR accessory. The main components required for ENDOR were a specially designed TE$_{102}$ cavity with a coil tuned for radio frequencies embedded in the walls of the cavity and a radio frequency generator.

\[
\begin{align*}
M_e &= + \frac{1}{2} \\
M_e &= - \frac{1}{2} \\
M_s &= + \frac{1}{2} \\
M_s &= - \frac{1}{2} \\
M_1 &= - \frac{1}{2} \\
M_1 &= + \frac{1}{2} \\
\frac{\Delta}{2} &+ \frac{\Delta}{2} + \alpha_N \\
\frac{\Delta}{2} &- \alpha_N \\
\end{align*}
\]

Figure 20: Energy level diagram showing the electron Zeeman (left), hyperfine (center), and nuclear Zeeman (right) splitting for single electron and nucleon of spin \( S = 1/2 \) and \( I = 1/2 \), respectively. The EPR and ENDOR transitions are indicated. (From reference [98])
Figure 21: ENDOR spectra for an $S = 1/2$ and $I = 1/2$ system (a) when $\omega_N < A/2$ and (b) when $\omega_N > A/2$. (c) Dependence of the ENDOR frequency $\omega_{\text{ENDOR}}$ on the NMR frequency $\omega_N$. (From reference [95])
IV Pernigraniline Base: Neutral Solitons

4.1 Experimental Determination of Hyperfine Splitting constants

In this section the solid and solution state EPR spectra and ENDOR spectra of PNB are presented. It will be shown that the spins in PNB are consistent with the presence of neutral soliton excitations or defects. With the neutral soliton in mind the main emphasis will on the determination of its associated hyperfine structure.

Figure 22: Diagram of the PNB-$S^0$ spin site where the nitrogen reference frame is denoted by $x$, $y$ and $z$ and the hydrogen reference frame by $x'$, $y'$ and $z'$. The angles $\alpha$, $\theta$ and $\phi$ denote rotations about $z$, about the N-C bond, and in the plane of the phenyl rings.

Before proceeding it is helpful to first define the postulated spin system and the various coordinate frames in which the hyperfine tensors will be described (see Figure 22). The primary reference frame is defined by the solitons central nitrogen where the
principle axes $x$, $y$ and $z$ lie along the nitrogen’s $sp^3$ orbital containing the lone pair, the polymer axis, and the nitrogen’s $p_z$ orbital, respectively. Another reference frame which will be referred to is that of the hydrogens where the principle axes $x'$, $z'$ and $y'$ lie along the C–H bond, the $p_z$ orbital, and direction perpendicular to $x'$ and $z'$, respectively. The notation used to describe the hyperfine coupling constants is $A_{\text{site component}}$, where the superscript denotes the hyperfine site or nucleus and the subscript denotes the tensor component or it’s isotropic value.

4.1.1 Powder EPR

The cw-EPR spectra of PNB powder are characterized by three partially resolved peaks spanning ~ 60 G and are virtually unchanged over the range 10 to 300 K. The PNB powder spectrum obtained at 10 and 300 K are shown in Figure 23 and Figure 24. The three partially resolved peaks are characteristic of a paramagnetic spin interacting strongly with a single spin one nuclei, nitrogen. In PNB $^{14}N$ is the only source of a spin one nuclei. The asymmetry of the spectra is due to an anisotropic g-tensor and nitrogen hyperfine tensor. The integrated intensity of the 10 K spectrum is roughly 30 time that of the 300 K spectrum and is consistent with non-interacting Curie spins. The spin concentration, calibrated against DPPH, was measured four 4 different preparations of PNB. Assuming $S = 1/2$ the spin concentrations were ~ 70, 200, 440, and 3,100 rings per spin.

To accurately determine the nitrogen hyperfine splitting the PNB powder spectra were simulated using a modified version [96] of the Quantum Chemistry Program Exchange (QCPE), Program No. 265. This program uses a Downhill Simplex search algorithm to optimize the fully anisotropic g and hyperfine tensors, and the parallel ($z$) and perpendicular ($x,y$) broadening function linewidths to an experimental spectrum. The program allows the user to choose either a Gaussian or Lorentzian broadening function. The simulated powder spectra for a paramagnetic $S = 1/2$ interacting with a
single nuclear spin of $I = 1$ optimized to fit the 10 and 300 K experimental spectra are shown in Figure 23 and Figure 24 as the dotted lines. The corresponding optimized spectrum parameters are shown in Table 2 where a Gaussian broadening function was chosen. Simulations using a Lorentzian broadening function did not give as good fits. The Lorentzian broadening produced too much spectral density in the wings of the spectrum where as Gaussian broadening did not. The need for a Gaussian broadening function is typically an indication of unresolved weaker hyperfine interactions. The isotropic hyperfine splitting constants, from which the $\pi$-electron spin densities can be calculated, are equal to $1/3$ of the trace of the hyperfine tensor,

$$A_{iso}^N = \frac{1}{3} \text{Tr}(A^N) = \frac{1}{3} (A_{xx}^N + A_{yy}^N + A_{zz}^N).$$ (44)

Table 2: Optimized parameters for PNB powder pattern simulations using a Gaussian broadening function. All hyperfine constants and linewidths are given in Gauss.

<table>
<thead>
<tr>
<th>PNB Powder Simulation Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNB sample</td>
</tr>
<tr>
<td>&quot;as made&quot; powder, 10K</td>
</tr>
<tr>
<td>&quot;as made&quot; powder, 300K</td>
</tr>
<tr>
<td>insoluble powder, 300K</td>
</tr>
<tr>
<td>in KBr, dark, 20K</td>
</tr>
<tr>
<td>in KBr, illuminated, 20K</td>
</tr>
<tr>
<td>in KBr, light-induced, 20K</td>
</tr>
</tbody>
</table>

The g-value can also give an indication of the local environment of the paramagnetic spin. Calculating the isotropic g-value from the data in Table 2 for "as made" PNB powder gives

$$g = \frac{1}{3} \text{Tr}(\bar{g}) = \frac{1}{3} (g_z + g_y + g_x) = 2.0055$$ (45)

for the 300 K spectrum. G-values for organic molecules containing nitrogen typically range from $g \approx 2.0036$ for 2,2 diphenyl-1-pierylhedrahydrade (DPPH) [97] to $g \approx 2.0060$ for nitroxyl radicals [98,99]. The g-value observed for the spins in PNB is
slightly, but significantly, less than that of typical nitroxyl radicals. Nitroxyl radicals containing the structure

\[
\begin{array}{c}
\text{C} \\
\cdot \text{N} \\
\text{C} \\
\text{O}
\end{array}
\]

are expected to have a g-tensor of the form \( g_x \approx 2.0089, \ g_y \approx 2.0061 \) and \( g_z \approx 2.0021 \), where \( g_{\text{iso}} \approx 2.0059 \). This g-tensor form is similar that for PNB in Table 2. The magnitude of the \( g \) anisotropy is \( g_x - g_z \approx 0.0062 \) for nitroxyl radicals and for PNB \( g_x - g_z \approx 0.0048 \). This similarity leads to the question of whether or not the nitrogen spin center has an oxygen bonded to it. Nitroxyl radicals have nitrogen splitting constants of ~15 G indicating more spin density on the central nitrogen relative to the spins in PNB. It is conceivable that the slightly lower isotropic g-value and g-anisotropy in PNB is due to delocalization of the spin density off of the nitrogen center and on to the adjacent phenyl ring. This would move the g-tensor toward a form more like an aromatic hydrocarbon system (i.e. more symmetric and closer to two).

A strong argument against the presence of an oxygen bonded to the PNB nitrogen spin center lies in the similarity between the intrinsic spins and observed long lived photoinduced spins [51]. A light-induced ESR (LESR) spectrum of PNB taken at 20 K, shown in Figure 25, has the same characteristic partially resolved peaks as the intrinsic spectrum. The only difference is in relative peak heights. This similarity indicates that the intrinsic spins and light-induced (LI) spins are similar in structure. Thus either both the intrinsic and LI spins have a bonded oxygen or neither do. It is unlikely that the LI spins are the result of a photochemical reaction involving oxygen. The spin center in PNB is either an amine or imine nitrogen, any other configuration would not be consistent with the known structure. In principle the ideal PNB structure has only imine nitrogens, amine nitrogens would be present only if it is partly reduced. In the next section it will be shown based the hyperfine structure observed in the solution phase that of these two choices imine nitrogen is the only possibility.
Figure 23: Experimental EPR spectrum of PNB powder (solid line) at 10 K obtained with a modulation amplitude of 0.991 and microwave power of 0.02 mW. Simulated powder spectrum (dashed line) is based on a single anisotropic $N^{14}$ hyperfine interaction and anisotropic g-value where $A_{xx}^N = 2.29$ G, $A_{yy}^N = 2.39$ G, $A_{zz}^N = 22.16$ G, $g_x = 2.0081$, $g_y = 2.0053$ and $g_z = 2.0033$. 
Figure 24: Experimental EPR spectrum of PNB powder (solid line) at 300 K obtained with a modulation amplitude of 0.951 and microwave power of 0.1 mW. Simulated powder spectrum (dashed line) is based on a single anisotropic N\(^{14}\) hyperfine interaction and anisotropic g-value where \( A_{xx}^{N} = 2.41 \text{G}, \ A_{yy}^{N} = 2.37 \text{G}, \ A_{zz}^{N} = 22.55 \text{G}, \ g_x = 2.0077, \ g_y = 2.0059 \) and \( g_z = 2.0030 \).
Figure 25: ESR spectra of PNB powder in KBr taken before and after photoexcitation. The spectrum after subtraction of the spectrum after photoexcitation is the light-induced ESR (LESR) spectrum. The pump energy was 2.54 eV, pump intensity 100 mW·cm\(^2\), sample temperature 20 K, and exposure time 20 seconds.
Figure 26: ESR spectra of a sample of "as made" PNB powder and the insoluble component of the same sample.
The most significant difference between the dark and light-induced spectra of PNB is the relative heights of the three peaks. The origin of this difference likely do to variations in the local morphology surrounding the spin sites. As discussed in the section on Solution Samples pernigraniline base is only partially soluble which is reminiscent of emeraldine’s EB-I (soluble/amorphous form) and EB-II (insoluble/crystalline form) phases. In Figure 26 the room temperature spectra of “as made” PNB and the insoluble component from the same sample batch are shown. The relative peak heights are significantly different showing that the spins local environment does play a significant role in the EPR line shape. We are primarily interested in the isotropic hyperfine interactions and from Table 2 we see that $A^N_{iso}$ does not vary significantly, even with temperature. In fact, in four different preparations of PNB powder is was found that $A^N_{iso} = 9.0 \pm 0.15$ a variation of less than $\pm 2\%$. Also the hyperfine splitting $A^N_{iso}$ is based on a simulation taking into account only a single N$^{14}$ interaction. The broadening function linewidth of $\sim 8$ G indicates significant unresolved hyperfine structure which could systematically effect the estimated values of $A^N_{iso}$.

4.1.2 Solution EPR

The solution EPR was the key experiment which made it possible to resolve sufficient detail of the hyperfine structure in PNB to identify the intrinsic spins as neutral solitons. The first attempts at solution EPR used a solution of PNB in NMP. NMP is one of the best known solvents for PNB unfortunately it has a very high dielectric loss, $\varepsilon = 32$. In fact all the best solvents, DMSP, DMF, NMP, etc. have high dielectric loss, $\varepsilon \sim 30$ to 50. To limit the effects of dielectric loss a quartz flat cell was used. Unfortunately the flat cell has a very small active sample volume, approximately $0.5 \text{ mm} \times 4.75 \text{ mm} \times 25 \text{ mm} = 59 \mu\text{l}$. All of these factors resulted in a tremendous loss in instrument sensitivity. Shown in Figure 27 is a spectrum of PNB in NMP at room temperature representing the highest resolution that was obtained using NMP. The experimental parameters were pushed to their limit to maximize the sensitivity. For
example a microwave power of 200 mW was used which is the instrument maximum. Also, a modulation amplitude of 9.51 G was used which in itself will limit the resolvable hyperfine structure to splitting of ~10 G or more. The spectrum, Figure 27, shows only the same nitrogen splitting identified in the PNB powder spectra where \[ |A_{iso}^N| \sim 10 \text{ G} \] and \[ \Delta H_{pp} \sim 7 \text{ G} \].

The discovery that PNB dissolved in dioxane made it possible to get much higher resolution spectra. Dioxane is not as good a solvent as NMP but this is more than compensated for by its very low dielectric loss, \( \varepsilon = 2.29 \). The experimental spectrum shown in Figure 28 is of a saturated solution of PNB in dioxane. The sample was degassed and loaded into a non-standard 4 mm I.D. quartz tube sporting an active sample volume of \( \pi \times (2 \text{ mm})^2 \times 25 = 314 \mu\text{l} \). To achieve the best signal to noise ratio while maintaining adequate hyperfine resolution a modulation amplitude of 0.951 G and microwave power of 5.0 mW was used. 5 mW was the maximum power that could be used with out appreciable saturation effects. In addition the spectrum was time averaged over approximately 8 ½ hours. Measurement of the g-value calibrated against DPPH was found to be 2.0057 in good agreement with the PNB powder spectra simulations where \( g_{iso} = 2.0055 \).
Figure 27: EPR solution spectrum of PNB in NMP at 300 K obtained with a modulation amplitude of 9.51 G and microwave power of 200 mW. The sample was degassed and loaded in a quartz flat cell.
Figure 28: EPR solution spectrum (solid line) of PNB in dioxane at 300 K obtained with a modulation amplitude of 0.951 G and microwave power of 5.0 mW. The sample was degassed and loaded in a non-standard 4mm I.D. quartz tube. The simulated hyperfine spectrum (dotted line) is of one $^{14}$N nuclei with $|A_{iso}^N| = 9.8$ G and four equivalent $^1$H nuclei with $|A_{iso}^H| = 3.0$ G. The broadening function was Gaussian with $\Delta H_{pp} = 3.0$ G.
The experimental spectrum in Figure 28 is readily modeled in the rapid motional narrowing limit in terms of hyperfine splitting due to a single $N_{1s}$ ($I = 1$) and four equivalent $H^{1}$ ($I = 1/2$) hyperfine interactions. The simulated spectrum is shown in Figure 28 as the dotted line where the absolute value of the isotropic hyperfine splitting constants giving the best fit were $|A_{iso}'| = 9.8$ G in agreement with the PNB powder spectra and $|A_{iso}''| = 3.0$ G. The simulated spectrum show excellent agreement for all the peak positions and the peak intensities in the $M_{s} = +1$ and $-1$ lobes. However, the peak intensities in the center of the spectrum ($M_{s} = 0$ lobe) deviate form the experimental spectrum substantially. This difference indicates the possibility of an additional weaker signal underlining the center region of the spectra.

The four equivalent spin $1/2$ hyperfine interactions indicated that the spin density is distributed symmetrically about the nitrogen center. A Gaussian broadening function, $\Delta H_{pp} = 3.0$ G, was found to give a much better fit than the usual Lorentzian indicating the presence of still more unresolved hyperfine structure. Based on symmetry and the structure of PNB it is reasonable to assume the broadening results from additional interactions with four equivalent hydrogens and possible two nitrogens. Assuming the Gaussian broadening function is associated with four roughly equivalent hydrogens (line intensity pattern shown in Figure 29 (a)) a splitting constant of $\sim 1.4$ G is indicated. If the broadening is due instead to two roughly equivalent nitrogens (line intensity pattern shown in Figure 29 (b)) a splitting constant of $\sim 1.2$ G is indicated. Thus $|A_{iso}'| \leq 1.4$ G is an upper limit for all unresolved hyperfine interactions. In the next section ENDOR spectra will be shown where this hyperfine structure has been resolved and $|A_{iso}'|$ determined.
Figure 29: (a) Hyperfine intensity pattern for four equivalent hydrogen \((I = 1/2)\) interactions compared to a Gaussian function \((\Delta H_{pp} = 3.0)\) and a Lorentzian function \((\Delta H_{pp} = 1.8)\). (b) Hyperfine intensity pattern for two equivalent nitrogen \((I = 1)\) interactions compared to a Gaussian function \((\Delta H_{pp} = 3.0)\) and a Lorentzian function \((\Delta H_{pp} = 2.0)\). This figure illustrates the arbitrary nature of choosing a broadening function when there are relatively strong unresolved hyperfine interactions involved.
4.1.3 Powder ENDOR

The ENDOR measurements were done on samples of PNB powder to further resolve the hyperfine structure which could not be seen in the solution ESR. The EPR spectrum shown in Figure 23 was obtained just prior to making the ENDOR measurements to determine suitable static H-field settings. Shown in Figure 30 are two ENDOR absorption spectra obtained at static H-fields of 3466.2 and 3484.1 G (denoted by the arrows in Figure 23) and for convenience are referred to as the low and mid field ENDOR spectra, respectively. The high field ENDOR spectrum, had it been obtained, would have had a static H-field of ~ 3510 G near the high field minima. Unfortunately ESR intensity at this field was too weak for ENDOR measurements. This was disappointing because it would have isolated the z-oriented spin more effectively than the low field spectrum.

From the plot of the ENDOR absorption spectra, Figure 30, three distinct hyperfine couplings, 6.6, 2.1 and ~ 0.7 MHz, are observed. The corresponding derivative ENDOR spectra are shown in Figure 31 showing a complex powder pattern resulting form hyperfine anisotropy. In principle from this pattern the hyperfine coupling tensors for the 6.6 and 2.1 MHz coupling groups can be determined. Also, the orientation of the coupling tensors and hence the ring torsion angles should be obtainable. Unfortunately because of the weak signal in PNB, the ENDOR spectra at the high H-field maxima could not be obtained and the spectra at 3466.2 and 3484.1 G contain substantial baseline distortion and unresolved structure. However despite these problems it is still possible to determine the coupling constants along the z-axis and estimate the isotropic coupling constants. Also it can be shown that the spectra are consistent with the first adjacent rings rotated out of the x-y plane.
Figure 30: The ENDOR absorption spectra of PNB powder at 10 K for static H-fields of 3466.28 and 3484.19 G corresponding the first maximum and zero crossing in the EPR derivative spectrum shown in Figure 23.
Figure 31: The ENDOR derivative spectra of PNB powder at 10 K for static H-fields of 3466.28 and 3484.19 G corresponding the first maximum and zero crossing in the EPR derivative spectrum shown in Figure 23.
Figure 32: Idealized ENDOR powder pattern for a single proton coupling with $A_{xx}'' = 3$ MHz, $A_{zz}'' = 6$ MHz and $A_{yy}'' = 9$ MHz.
The difference between the two ENDOR spectra, shown in Figure 30 and Figure 31 as the solid and dashed lines, arises because only a subset of the spins in PNB will be resonant at any particular static H-field. Referring to the EPR PNB powder spectrum, Figure 23, an applied field of 3484.1 G corresponds roughly to the zero crossing point. At this field there will be roughly equal contributions to the resonant spins from the x and y orientations. However z-oriented spins will be shifted off resonance by the central nitrogens large hyperfine coupling, $A^z$, for nitrogens in the $M_z = \pm 1$ quantum states. Since the $M_z$ states are equally populated the contribution from the z-oriented spins to the resonance will be reduced by 2/3. In other words the mid field powder pattern will be composed of contributions from the x, y and z orientations in the proportion 3:3:1. For the low field spectrum the static field, $H_{stat} = 3466.2$ G, corresponds to the first maximum in the PNB EPR powder pattern. Referring to Figure 23 it is apparent that the large majority of resonant spins will be orientated along the z-axis with the central nitrogen in the $M_z = -1$ state. Thus to a reasonable approximation the low field powder pattern will be composed of contributions from the x, y and z orientations in the proportion 0:0:1.

The hyperfine coupling tensor for a proton bonded to a carbon with $sp^3$ symmetry has the form [89,100]

$$
A_{ij} = A_{is} \begin{bmatrix}
(1 - \alpha) & 0 & 0 \\
0 & (1 + \alpha) & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

(46)

where $\alpha \approx 0.5$ and the principle axes are defined as in Figure 22. The isotropic ENDOR powder pattern for a single proton with coupling given by (46) is shown in Figure 32. The maxima in the spectral density occurs at points $\nu_p \pm A_{iso}/2$. In the general case where a subset of the spin are resonating the maxima will occur at

$$
\nu_p \pm A_{eff} / 2
$$

(47)
where $A_{\text{eff}}$ is the average coupling constant weighted by the relative contributions from various spin orientations. With this in mind it should be apparent that for the mid and low field ENDOR spectra the maxima in the spectral density will be determined by

$$A_{\text{eff}} = 3\left(A^{(xx)}_{HH} + A^{(yy)}_{HH} + \frac{1}{3} A^{(zz)}_{HH}\right)/7$$

and

$$A_{\text{eff}} = A^{(zz)}_{HH},$$

respectively. It should be apparent that if ring torsion is neglected $A_{\text{eff}} = A_{iso}$ for both cases. Thus the effective coupling constants of 6.6 and 2.1 MHz identified in Figure 30 can be assume to be roughly the isotopic values.

The low field ENDOR spectrum, Figure 30, has four resolved maxima at 11.482, 14.333, 15.318, and 17.535 and the mid field spectrum has two at 14.333 and 15.459. The very sharp peak at 14.333 is called the matrix line and is due to the very weakly coupled protons. This line is centered exactly at the proton frequency, $\nu_p$, and is most easily seen in the derivative spectra, Figure 31. Only the peak near 15.5 MHz, aside from the matrix line, is fully resolved in both spectra and corresponds to the 2.3 MHz coupling. If there were no ring rotations then these two peaks should lie at exactly the same frequency as explained in the preceding paragraph.

The shift in the 15.459 MHz peak in the mid field spectrum to 15.318 in the low field spectrum can be quantified using equations (47), (48) and (49) where the proton hyperfine coupling tensor is rotated into the nitrogen reference frame. This rotation is given by

$$A_{\mu}^{\nu} = R(\alpha)R(\theta)R(\phi)A_{\mu}^{\nu}R^{-1}(\phi)R^{-1}(\theta)R^{-1}(\alpha)$$

where $D$ denotes the central nitrogen reference frame and $D'$ the protons reference frame. The rotation matrices are given by
$R(\phi) = \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$R(\phi) = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$$

(51)

(52)

and

$R(\alpha) = \begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}$

(53)

where $\phi$, $\theta$, and $\alpha$ are described in Figure 22. $R(\alpha)$ rotates the x-axis about z aligning it with the C–N bond, $\alpha = \pm 30^\circ$. $R(\theta)$ rotates the rings out of the nitrogen x-y plane by the ring torsion angle $\theta$. Last, $R(\phi)$ rotates x by $\phi = \pm 30^\circ$ and $\pm 150^\circ$ depending on the proton such that it is aligned with the C–N bonds. After some algebra we find

$$\langle A_h^{(xx)} + A_h^{(yy)} \rangle_{\text{arg}} = A_{\text{iso}} \left[ 1 + \frac{\alpha}{4} \left( 1 - \cos^2 \theta \right) \right]$$

(54)

and

$$A_h^{(xx)} = A_{\text{iso}} \left( 1 - \frac{\alpha}{2} \sin^2 \theta \right).$$

(55)

Substituting equations (54) and (56) into equations (48) and (49) gives the effective coupling constant as a function of the ring torsion angle. For the low field case

$$A_{\text{eff}} = A_{\text{iso}} \left( 1 - \frac{\alpha}{2} \sin^2 \theta \right)$$

(56)

and for the mid field case

$$A_{\text{eff}} = A_{\text{iso}} \left[ 1 + \frac{\alpha}{4} \left( 1 - \cos^2 \theta \right) \right].$$

(57)
Figure 32 shows a plot of these equations as a function of $\theta$ for $\alpha = 0.5$. The shift in the peak position from $15.459$ to $14.318$ MHz amounts to a downward fractional shift of $0.141/(15.459 - 14.333) = 0.125$. Referring to Figure 32 this fractional shift corresponds to a ring torsion angle of $\sim 45^\circ$. In light of the approximate nature of the analysis and experimental error this should not be considered an accurate estimate of the PNB–$S^0$ ring torsion angle. Instead one should take this as evidence that ring torsion is important in PNB. And most importantly this analysis demonstrates the feasibility of directly measuring the ring torsion angles of defect states in polyaniline via magnetic resonance techniques.

Figure 33: Plot of the hydrogen hyperfine splitting along the $z$-axis defined by the nitrogen $p_z$ orbital in PNB as a function of the ring torsion angle. The splitting constant is given as a percentage of the $A_{iso}$ or the isotropic value.
The isotropic proton hyperfine splitting associated with peak near 15.5 MHz can be accurately estimated from the mid field spectrum because for ring torsion angles of less than 60° the effective splitting constant never deviate from the isotropic value by more than 2% percent. Thus \( |A'_{uu}| \) is assigned a value of \( 2(15.459 - 14.333) = 2.25 \) MHz with an assumed error of \( \pm 0.141 \) MHz equal to the peak shift. From the 17.535 MHz peak in the low field spectrum \( |A''_{uu}| \) is estimate to be \( 2(17.535 - 14.333) = 7.319 \) MHz with an assumed error of \( \pm 0.80 \) MHz based on the difference between the low and high frequency peak positions. Last the unresolved hyperfine splitting resulting in the relatively broad peak centered about the matrix line can be used to estimate \( |A''_{uu}| \). Looking at the derivative spectra in Figure 31 it is that a reasonable assignment would be \( |A''_{uu}| = 0.50 \pm 0.25 \) MHz.

4.2 Spin Density Distribution

McConnell [101] described a linear relationship between the hyperfine coupling constant and the unpaired \( p_z \)-electron densities for \( \pi \)-type organic radicals, \( A'_{uu} = Q' \rho' \), where \( \rho' \) is the \( \pi \)-electron spin density, \( Q' \) an empirically found spin polarization constant, and \( A'_{uu} \) is the measured hyperfine splitting constant for the \( i^{th} \) atomic site. Later, Karplus and Fraenkel [102] developed a more detailed theory for the hyperfine splitting from the nuclei of atoms such as carbon or nitrogen that is applicable when the atoms have \( sp^2 \) hybridized orbitals. According to their formulation, the coupling constant \( A^X \) arising from the nucleus of atom \( X \) is given by

\[
A^X = \left( S^X + \sum_{i=1}^{3} Q^X_{yi} \right) \rho^X + \sum_{i=1}^{3} O^X_{yi} \rho^Y
\]

where \( \rho^X \) and \( \rho^Y \) are the \( \pi \)-electron spin densities on atoms \( X \) and \( Y \), respectively; \( S^X \) represents the contribution to the splitting from the \( 1s \) electrons of atom \( X \). The
predominant notation for the spin polarization constants $Q_{XY}^Z$ represents the sigma-pi interaction for the nucleus of atom $Z$ resulting the interaction between the $X-Y$ and the $\pi$-electron spin density on atom $Y$. The sigma-pi interaction (spin polarization) parameters are usually found empirically by comparing calculated $\pi$ spin densities to measured coupling constants in model systems.

Radical nitrogen heterocyclic anions such as pyridine provide a good model system for the nitrogen center in PNB. Talcott and Myers [103] found in anions of pyridine and related molecules that $Q_N^N = S_N^N + 2Q_{NN}^N = 27.3 \text{ G}$ and $Q_{NN} = -1.7 \text{ G}$. In PNB it is known that the rings adjacent to the central nitrogen are rotated out of the $x-y$ plane. This will reduce the strength of the $N-C$ bonds increasing the $N-C$ distance. Hence, the effectiveness of the spin polarization on the nitrogen due to spin density on the adjacent carbons will be reduced. Thus it is reasonable to assume $Q_{NN} = 0$. It has been shown that the $Q$ values depend on the charge state of the radical. The above $Q$ values were determined for anion radicals and the spin site in PNB is assumed to be charge neutral. Fortunately, in even the extreme cases $Q$ varies by only $\pm 15$ percent [89]. Since nitrogen heterocyclics are not an extreme case this effect can be ignored. In general $Q_N^N$ have values ranging from 23 to 30 G [89]. Using this as a gauge of accuracy an assigned error of half this range is reasonable, thus $Q_N^N = 27.3 \pm 1.8 \text{ G}$.

For the hydrogens bonded to the rings in PNB the $Q$ values can be estimated from benzene anion and cation numbers. Bolton [104] reported for the benzene anion $Q_{CH}^H = -22.5 \text{ G}$ and Carter and Vincow [105] $Q_{CH}^H = -25.7 \text{ G}$ for the cation. Since both the anion and cation $Q$ value are available the neutral benzene radical value can be estimated by a simple average [106,107], $Q_{CH}^H = -24.1 \text{ G}$. Using half of the difference between the anion and cation value as the assigned error gives $Q_{CH}^H = -24.1 \pm 0.8$.

Using equation (58) the $\pi$-electron spin densities corresponding to each of the isotropic coupling constants found in the previous section can be determined. The
calculations are straight forward and are summarized in Table 3 and Table 4 for the solution and solid states of PNB, respectively. In the solid state all the coupling constants are consistently smaller by roughly 10% than their corresponding values in the solution state. Otherwise they are in good agreement. This difference is consistent with the defect state being more delocalized in the solid state, which could be caused if rings are less free to rotate out of the polymer plane in the solid state due to interchain effects. The reduced ring angle increases the transfer integrals between the nitrogens and rings, allowing for paramagnetic spins to delocalize more relative to the solution state. Alternatively thermal kinetics might explain the differences in the ring angles between the solid and solution state measurements. If one assumes that the steric potential between rings is due entirely to proton-proton repulsion it is easy to see that the steric potential will be larger for $\theta = 0^\circ$ than at $\theta = 90^\circ$. This suggests an asymmetric potential favoring a larger angle at higher temperatures. Thus the solution measurements at 300 K will reflect a slightly larger ring angle than the solid state measurements done at 10 K. This is consistent with the thermochromism studies reported by Masters et al.[108] where the temperature-dependent optical spectra of insulating PNB (from 295 K to 383 K) showed that the 3.8 eV optical absorption peak, assigned to a transition from the VB to the CB, shifted to higher energy and weaken with increasing temperature. This thermochromatic behavior was attributed largely to an increase in the ring torsion angle with increasing temperature.

The hyperfine site assignments for N and H1-H3, are shown in Figure 34. These assignments are base on the assumption that the spin defect is centered symmetrically on a nitrogen. Further the sites are assigned in decreasing order moving out away from the central nitrogen.

dos Santos and Brédas [66] proposed that PNB could support two types of soliton distortion, one a benzinoid-nitrogen-benzenoid (BNB) geometry, a quinoid-nitrogen-quinoid (QNO) geometry, with an antinode and node in the gap state wavefunction on the central nitrogen, respectively. For an isolated neutral soliton the BNB geometry is energetically most stable. These two configurations, shown in Figure 34 are analogous to
the two types of solitons in polyacetylene, Figure 11. It was explained in chapter 2 that in polyacetylene these two types of solitons could not be distinguished due to the large extent of delocalization. This is not the case in PNB because ring torsion results in a much more localized soliton state. Clearly the experimental hyperfine splitting shows a large spin density for a single nitrogen consistent with the BN-B-S\textsuperscript{0} geometry. However, the differences between our experimental and simulated solution spectra indicated the possibility of an additional weaker signal underlining the center region of the spectra.

Table 3: Summary of solution state EPR determined hyperfine coupling constants and corresponding $\pi$-electron spin densities for PNB. $Q_N^N = S_N^N + 2Q_{NN}^N = 27.3$ G and $Q_{NN}^{\prime \prime} = -24.1$ are assumed.

| nuclei | site degeneracy | hyperfine constant, $|A_{NN}|$ | $\pi$-electron spin density, $|\rho|$ |
|--------|----------------|-------------------------------|---------------------------------|
| N      | 1              | 9.8 G                         | 0.359                           |
| H1     | 4              | 3.0 G                         | 0.124                           |
| H2     | unknown$^\dagger$ | $\leq 1.4$ G       | $\leq 0.058$                     |
| N2     | unknown$^\dagger$ | $\leq 1.4$ G       | $\leq 0.051$                     |

$^\dagger$ Could not be determined from the ENDOR spectra.

Table 4: Summary of solid state EPR and ENDOR determined hyperfine coupling constants and corresponding $\pi$-electron spin densities for PNB. $Q_N^N = 27.3 \pm 1.8$ G and $Q_{NN}^{\prime \prime} = -24.1 \pm 0.8$ are assumed.

| nuclei | site degeneracy | hyperfine constant, $|A_{NN}|$ | $\pi$-electron spin density$^\ast$, $|\rho|$ |
|--------|----------------|-------------------------------|---------------------------------|
| N      | 1              | 9.00 ± 0.15 G                 | 0.330 ± 0.027                   |
| H1     | unknown$^\dagger$ | 2.61 ± 0.15 G       | 0.108 ± 0.010                   |
| H2     | unknown$^\dagger$ | 0.803 ± 0.025 G   | 0.0333 ± 0.0021                  |
| H3     | unknown$^\dagger$ | 0.18 ± 0.05 G     | 0.0075 ± 0.0023                  |

$^\dagger$ Could not be determined from the ENDOR spectra.

$^\ast$ errors calculated using $\delta \rho = \frac{1}{Q} \delta Q_{NN}$.
Figure 34: Structure of the benzenoid-nitrogen-benzenoid (BNB) and quinoid-nitrogen-quinoid neutral soliton. Indices -9 to 9 denote atomic site where 0, ±2, ±3, and ±7 correspond to N, H1, H2, and H3 respectively. To the left of the central nitrogen are the $\pi$-electron spin densities corresponding to the solid state PNB and to the right solution state PNB.

4.3 Effects of Coulomb Repulsion

Based on the tight-binding (Su-Schrieffer-Heeger) Hamiltonian, Su and Epstein calculated [68] the gap state wavefunction for a BNB type neutral soliton. If the effects of coulomb repulsion or spin polarization are ignored then the gap state wavefunction is a good measure of the spin density distribution associated with the neutral soliton. Su and Epstein found that the probability density of the gap state is primarily localized to a central nitrogen and immediate adjacent rings. The probability of finding an unpaired electron at the single central nitrogen was found to be 0.45 in fair agreement with our experimentally determined values.

The spectral width can be used to quantitatively compare the theoretical spin density distribution to the experimental spectrum. The spectral width of a motionally
narrowed resonance, such as the solution spectrum of PNB, depends only on hyperfine interactions and can be expressed as

\[ \Delta H_{sw} = 2 \sum_{<i>} I_i |Q_i| \rho_i \]  

(59)

where \( <i> \) represents the sum over all hyperfine sites, \( I_i \) is the nuclear spin quantum number, \( Q_i \) the spin polarization parameter and \( \rho_i \) the \( \pi \)-electron spin density. Assuming the \( S^0 \) gap state wavefunction reported by Su and Epstein is equal to the \( \pi \)-electron spin density distribution, \( \rho_i = |\Phi_i|^2 \), the spectral width given by (59) is calculated to be \( \Delta H_{sw} = 31.3 \text{ G} \), significantly smaller than \( \Delta H_{sw} \sim 41 \text{ G} \) for the experimental solution spectrum. As \( \Delta H_{sw} \propto \sum_{<i>} |\rho_i| \) where the sum is over all hyperfine sites this difference in the spectral width can be accounted for by Coulomb repulsion resulting in negative spin densities at some sites and compensating positive spin densities at other sites.

A sum of all \( \pi \)-electron spin densities should equal one corresponding to a total spin of \( 1/2 \). Summing the experimental spin densities in Table 3 assuming only positive values gives \( |0.36| + 4|0.125| + 4|0.04| \approx 1.02 \) for the PNB in solution. This sum is only a partial sum of the total spin density despite its coincidental value of \( \approx 1 \). This sum does not include the four carbons at sites \( \pm 1 \) and \( \pm 4 \) where a sizable spin density is expected as well as other non-hyperfine sites beyond the first adjacent rings. It is unreasonable to expect all these non-hyperfine sites to have a zero or even a small fraction of the total spin density. Based on the Su’s \( S^0 \) gap state wavefunction it is expected that \( \approx 30\% \) of the total spin density lies on sites with no hyperfine interaction. Thus sites with negative spin densities must be present in the BNB-\( S^0 \) density distribution in order to account for the total spin density to sum to one.
4.3.1 Estimate of Coulomb Repulsion and Ring Torsion in PNB Solutions

Using the Su and Epstein geometry [68] for the BNB-S\(^{0}\) the effects of “on site” Coulomb repulsion in the \(\pi\)-electron spin density can be estimated. The Hamiltonian used was

\[ H = \sum_{n,\sigma} V_n c_n^\dagger c_n^\sigma + \sum_{i,j,o} t_{i,j}(c_{i,o}^\dagger c_{j,o}^\sigma + c_{j,o}^\dagger c_{i,o}^\sigma) + \sum_{i} U_{i,i} n_{i,\uparrow} n_{i,\downarrow} \]

where the last term is the “on site” Coulomb repulsion (Hubbard “\(U\)”). Using the bond orders, \(t_{i,j}\), and site energies \(V_n\) utilized by Su and Epstein (optimization of the bond orders included ring torsion but no Coulomb repulsion effects) for the BNB-S\(^{0}\) the self-consistent \(\pi\)-electron spin densities for values of \(U\) up to 5 eV were calculated. Using these results \(\Delta H_{sw}\) has been calculated as a function of \(U\) and is shown in Figure 35. The best fit to the experimental spectral width, \(\sim 41\) G, corresponds to \(U = 2.5\) eV. In Figure 36 the calculated \(\pi\)-electron spin densities for \(U = 0\) and 2.5 eV are shown. The result of the Coulomb repulsion is to increase the densities on even numbered sites and compensate with negative densities on odd sites. This is precisely the same behavior calculated [9] for S\(^{0}\) with \(U = 3\) eV in trans-(CH)\(_{x}\) and observed by ENDOR [4-6]. Though \(U_{(CH)_{x}}\) and \(U_{PNB}\) are approximately equal, the smaller bandwidth for PNB implies the greater importance for the latter system. The calculated densities of the central nitrogen and meta carbons (sites \(\pm 2\)) are somewhat larger and smaller, respectively, than observed. A decrease in the torsion angle of the adjacent rings of \(\sim 15\)% from that of the assumed Su and Epstein geometry (form a torsion angle of 44° to \(\sim 30°\)) would result in a decrease in spin density (\(\sim 25\)% on the central nitrogen and an increase in that of the rings while decreasing \(\Delta H_{sw}\) by only \(\sim 5\)%.
Figure 35: Plot of the spectral width, $\Delta H_{\pi}$, as a function of the Coulomb repulsion strength $U$. The dotted lines correspond to the experimentally determined spectral width of the PNB solution spectrum.

Figure 36: Plot of the $\pi$-electron spin density distribution for $U = 0$ and 2.5 eV. Spin density are the sum of all equivalent atoms for a given site, i.e. the density on site 2 is $0.08 + 0.08 = 0.16$ including both equivalent meta carbon sites.
4.4 Hubbard Model

In this section the EPR and ENDOR determined π-electron spin density distribution in PNB powder is compared to an unrestricted Hartree-Fock treatment of the Su-Schrieffer-Heeger Hamiltonian with added Hubbard and steric potentials. The Hamiltonian used was

\[ H = \sum_{i,o} V_i c_{i,o} c_{i,o} - \sum_{\alpha,\beta,\gamma} (t_0 - \alpha \delta r_{i,j})(c_{\alpha,\sigma}^i c_{\alpha,\sigma}^j + c_{\beta,\sigma}^i c_{\gamma,\sigma}^j) + \frac{K}{2} \sum_{\alpha,\beta,\gamma} (\delta r_{i,j})^2 + \sum U_i n_{i,1} n_{i,4} + \sum_{\alpha,\beta,\gamma,\eta} \left[ V_{1,1}(\sin \theta_\alpha + \sin \theta_\eta)^2 - \frac{V_{2,0}}{2}(\sin^2 \theta_\alpha + \sin^2 \theta_\eta) + \frac{V_{4,0}}{2}(\sin^4 \theta_\alpha + \sin^4 \theta_\eta) \right]. \] (60)

The first term in (60) is the site energy where \( V_c = 0 \) and \( V_n = -2 \text{eV} \) [49]. In the second and third terms the bare transfer integral, electron-lattice coupling constant and effective spring constant are those used for polyacetylene [109], \( t_0 = 1.6 \text{eV}, \alpha = 7 \text{eV/Å} \) and \( K = 49 \text{eV/Å}^2 \) respectively. The transfer integral, \( t_0 - \alpha \delta r_{i,j} \), between the para carbons and the nitrogens is multiplied by \( \cos \theta \) to account for ring rotation effects, however it is not explicitly shown in (60). The third term is the “on site” Coulomb repulsion where \( U \) is Hubbard parameter. The last term is the steric potential where \( V_{1,1} = 0.185 \text{eV} \) and \( V_{4,0} = 2.5 \text{eV} \) are the values utilized by Su and Epstein [68]. The Hamiltonian, Eq. (60), was optimized to yield spin densities in agreement with the experimental value by varying \( U \) and \( V_{2,0} \). In the previous section it was seen that the ring torsion angles used by Su and Epstein could in part account for the disagreement between the calculated and experimental spin densities. In this section the parameters \( U \) and the ring torsion angles are optimized for best agreement between the calculated and experimental spin density distributions. However, instead of arbitrarily adjusting the ring torsion angles the steric potential parameter \( V_{2,0} \) is varied. \( V_{2,0} \) is the strength with which the rings are forced out of the plane. Thus the semiempirical model described by (60) is optimized with respect to \( U \) and \( V_{2,0} \).
Finding the BNB-S\(^0\) \(\pi\)-electron spin density distribution for a given set of model parameters, \(U, V_{2,0}, \text{ etc.}\), involved a two step process. First, the PNB geometry was optimized by minimizing the energy given by (60) for a sixteen unit aniline chain with circular boundary conditions where the structure (optimized) variables were the bond lengths \(\delta r_{i,j}\) and ring torsion angles \(\theta\). To reduce the number of variables in the minimization, a repeat unit consisting of 4 aniline units was assumed where the aniline geometry was considered to be symmetric. Thus, each aniline units was described by three \(\delta r_{i,j}\) corresponding to the C–N, C\(_{\text{para}}\)–C\(_{\text{meta}}\), and C\(_{\text{meta}}\)–C\(_{\text{ortho}}\) bond lengths and the ring torsion angle \(\theta\); a total of 16 structure variables were optimized. Next, the BNB-S\(^0\) geometry was optimized an eight unit aniline chain where the first two and last two anilines were fixed to the A phase and B phase PNB geometry found in the first step. The energy given by (60) was minimized with respect to the geometry of the four center aniline units connecting A and B phases. In the model an extra nitrogen was added to the end of the eight unit chain to introduce the odd electron. Thus the model has the form 

\[ \text{N=Q=N=B-N=S'=N-S-N=S=N=B-N=Q=N} \]

where \(S\) represents aniline units assumed to have the soliton geometry. Again, to reduce the number of structure variables symmetry about the central nitrogen was assumed. The two unique aniline units \(S\) and \(S'\) are each described by four \(\delta r_{i,j}\) corresponding to the C–N, C\(_{\text{para}}\)–C\(_{\text{meta}}\), C\(_{\text{meta}}\)–C\(_{\text{ortho}}\) and C–N bond lengths and the ring torsion angle \(\theta\); thus a total of eight structure (optimized) variables were used.

In the Hamiltonian given by (60) the Hubbard term involves both spin up and down operators. To solve the eigenvalue problem it is standard practice to break (60) into two coupled Hamiltonians corresponding to spin up and spin down electrons. To do this the following mean field approximation is used:
\[ n_{i,\uparrow} n_{i,\downarrow} = \left( \langle n_{i,\uparrow} \rangle + \langle n_{i,\downarrow} \rangle \right) \left( \langle n_{i,\uparrow} \rangle - \langle n_{i,\downarrow} \rangle \right) \]
\[ = \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle + \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle - \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle \]
\[ + \langle n_{i,\downarrow} \rangle \langle n_{i,\uparrow} \rangle - \langle n_{i,\downarrow} \rangle \langle n_{i,\downarrow} \rangle \]
\[ \approx \langle n_{i,\uparrow} \rangle n_{i,\downarrow} + \langle n_{i,\downarrow} \rangle n_{i,\uparrow} - \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle \]

where

\[ \langle n_{i,\sigma} \rangle = \sum_{\sigma} |\varphi_{i,\sigma,n}|^2 \]

is the sum of the eigenfunction coefficients for site \( i \) over all occupied states of spin \( \sigma \) and

\[ \langle n_{i,\sigma} + \langle n_{i,\sigma} \rangle \rangle \ll 1. \]

Substituting Eq. (2) into Eq. (1) gives

\[ H_{\sigma} = \sum_{i} (V_{i} + U \langle n_{i,\sigma} \rangle) c_{i,\sigma}^\dagger c_{i,\sigma} - \sum_{j,\sigma} \left( \epsilon_{0} - \alpha \delta_{ij} \right) c_{j,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{j,\sigma} + \sum_{j} U_{i} \langle n_{j,\sigma} \rangle \langle n_{j,\sigma} \rangle \]

for the spin up and down Hamiltonian where \( \sigma = -\sigma \). In this approximation the Hubbard term acts to modify the site energy. Next a self-consistent solution is found by iterative substitution. For each iteration \( \langle n_{i,\sigma} \rangle \) is calculated based on the results of the previous iteration (the first iteration \( \langle n_{i,\sigma} \rangle \) is calculated based on the \( U = 0 \) solution). A problem which occurred was that iterative substitution did not always converge but instead oscillated. To prevent this \( \langle n_{i,\sigma} \rangle \) was calculated from a mixture of the previous two iterations results, usually 90% and 10% of the \( n-1 \) and \( n-2 \) iterations. Once the eigenfunctions are found the \( \pi \)-electron spin densities for each site is given by

\[ \rho_i = [\varphi_{i,\uparrow,\text{Hubbard}}]^2 + \sum_{n=1}^{\text{Hubbard}-1} \left( [\varphi_{i,\uparrow,n}]^2 - [\varphi_{i,\downarrow,n}]^2 \right). \]
Figure 37: Contour plot of the $\chi^2$ deviation between the predicted and experimental spin densities as a function of the Hubbard constant $U$ and steric potential parameter $V_{2,0}$. The minimum occurs at $U \approx 3.0$ eV and $V_{2,0} \approx 3.1$ eV.
The goodness of fit between the calculated and experimental \( \pi \)-electron spin densities distribution is estimated using

\[
\chi^2 = \left( \frac{\rho - \rho_N}{\sigma_N} \right)^2 + 4 \left( \frac{\rho - \rho_{\text{III}}}{\sigma_{\text{III}}} \right)^2 + 4 \left( \frac{\rho - \rho_{\text{H2}}}{\sigma_{\text{H2}}} \right)^2
\]

(66)

where \( \rho \) and \( \sigma \) with subscripts N, H1 and H2 denote the experimental values. Shown in Figure 37 is contour plot of the \( \chi^2 \) as a function of \( U \) and \( V_{2,0} \). The best fit (minimum \( \chi^2 \)) corresponds to \( U \approx 3.0 \text{ eV} \) and \( V_{2,0} \approx 3.1 \text{ eV} \). This value of \( U \) is in almost perfect agreement with the value found for trans-polyacetylene [9]. The optimized bond orders, torsion angles, and \( \pi \)-electron spin densities are shown in Figure 38 for \( U \approx 3.0 \text{ eV} \) and \( V_{2,0} \approx 3.0 \text{ eV} \).

An alternative method for estimating the Hubbard would be to consider only the ratio of the spin density on the first adjacent meta to ortho carbons. The experimental ratio is \( \rho_{\text{III}} / \rho_{\text{H2}} = 3.24 \). Comparing to the theoretical ratios one finds that \( U \) ranges from 2.5 eV to 3.7 eV for \( V_{2,0} \) equaling 2.0 to 4.5 eV respectively. For \( V_{2,0} \approx 3.0 \) the estimated Hubbard constant is 3.0 eV, the same as found in the previous analysis.

One of the problems with this model becomes apparent if one examines the spin density distribution behavior in the wings of the soliton, see Figure 39. There is a discontinuity in the spin distribution at sites \( \pm 11 \) and is a consequence of fixing the first two and last two aniline units to the PNB geometry, A and B phases. In effect as the spin density relaxes away from the soliton center it has the tendency to pile up at the assumed interface between the soliton units (aniline units 3-6) which are allowed to relax and the A and B phase aniline units (units 1,2,7, and 8). The result is that the spin densities on the rings 3 and 6 will be artificially inflated. As a consequence the experimentally determined spin density, \( \rho_{\text{H3}} = 0.0075 \), is much smaller than what is predicated for the meta and ortho carbons on rings 3 and 6. However upon examination of the predicted densities hyperfine site H3 can reliably be assigned to the ortho carbons (site numbers \( \pm 8 \)) on the second adjacent rings (rings 3 and 6) to the soliton center. In addition this
discontinuity together with the experimental spin density for H3 indicate that there is still significant solitonic distortion extending out to the second nearest neighbor phenyl rings to the central nitrogen.

Figure 38: (a) The Bond orders and torsion angles for the BNB-S^0 geometry. The first two aniline units on the left correspond the PNB optimized quinoid and benzenoid units. (b) The π-electron spin densities for the BNB-S^0.
Figure 39: Plot of the $\pi$-electron spin density distribution for $U \approx 3.0$ eV and $V_{2.0} \approx 3.0$ eV. The horizontal dotted lines denote the experimentally determined spin densities. The spin densities shown are weighted by the site degeneracy, i.e. spin densities corresponding to the meta and ortho carbons are multiplied by 2.
4.5 Soliton Mobility

In trans-(CH)\textsubscript{\textalpha}, solitonic defects are highly mobile having an intrachain hopping rate of \( \tau_{c}^{-1} \sim 10^{11} \text{sec}^{-1} \) (diffusion coefficient \( D_{c} \sim 10^{-4} \text{cm}^{2} \cdot \text{sec}^{-1} \)) at room temperature [2]. This mobility gives rise to motional narrowing or averaging of the hyperfine interactions and results in a very narrow linewidth, \( \Delta H_{1/2} < 1 \text{G} \) [1-3]. In PNB there is no evidence of any motional narrowing of the hyperfine interactions in either the powder or solution spectra. Thus the solitonic defects (experimentally 1 per 100 to 1 per 3000 rings depending on the preparation) must be immobile or at least slow moving. Based on the narrowing condition and the linewidth \( \Delta H \approx 20 \text{G} \), the intrachain hopping rate must be \( \tau_{c}^{-1} < \left( \frac{\hbar}{g\beta\Delta H} \right)^{-1} \sim 10^{8} \text{sec}^{-1} \) (diffusion coefficient along the chain of \( D_{c} < 10^{-8} \text{cm}^{2} \cdot \text{sec}^{-1} \)).

The lower mobility of \( S^{0} \) in PNB is attributed to the short localization length of \( S^{0} \) and the role of ring torsion angle changes. A soliton must skip one nitrogen during a move from one site to the next; the geometry requires the interchange of a benzenoid and quinoid (i.e., BQB-BQBQ to BQBQB-BQ) with concomitant ring-angle and bond length changes. This required structural reordering introduces a substantial barrier to motion. In contrast for polyacetylene the solitonic distortion is spread out over 14 carbon atoms [8], i.e., much larger than the distance that it moves in a hop, two carbons, and its motion involves only translation of carbon atoms. The delocalized solitonic distortion results in a lower energy barrier to motion in the \textit{trans-}-(CH)\textsubscript{\textalpha} case. This view is supported by the absence of fine structure in the EPR of polarons in nondegenerate emeraldine (EB) in solution (solution linewidth \( \approx 1.7 \text{G} \), \( \tau_{c}^{-1} \sim 10^{11} \text{sec}^{-1} \), and \( D_{c} \sim 10^{-3} \text{cm}^{2} \cdot \text{sec}^{-1} \)) where polaron motion involves smaller ring torsion angle changes.
V Emeraldine Base: Interchain “Self-Doping”

It was discovered early in the study of polyaniline that emeraldine base (EB) in its solid form (powder and films) is paramagnetic. Javadi et al. measured the EPR spectra of EB and found that the spectral lineshape could be deconvoluted into a Lorentzian and Gaussian component [16]. He attributed the Lorentzian component to mobile spins, presumably due to residual doping left over from the synthesis, and the Gaussian component to paramagnetic defects, such as chain ends. In this chapter EPR, ENDOR, and ESEEM measurements on EB powders, solution, and stretch oriented films are discussed. It will be shown that the paramagnetic defects in the solid forms of EB are due to interchain interactions. Further it will be argued that two paramagnetic spin species are present in EB perhaps accounting for Javadi’s observations. One has a relatively broad featureless resonance and the other narrower but with partially resolved hyperfine structure in the wings. From resolved hyperfine coupling in the EB oriented films, aspects of the structure and spin density distribution of the latter spin defect is determined. It is argued that interchain self-doping is the origin of the paramagnetic defects. Two doping mechanisms involving the destabilization of quinoid rings via interchain hydrogen bonding of amine and imine nitrogens are proposed.

5.1 EPR of Powder and Solution forms of EB

The room temperature EPR spectrum of EB powder (shown in Figure 40), synthesized by the oxidative chemical polymerization of aniline using standard 0.25 ratio of persulfate to aniline with subsequent treatment with an aqueous solution of 0.1 M
NH₄OH to dedope (amorphous form, EB-I), is featureless with a linewidth of $\Delta H_{pp} = 11.3$ G ($\Delta H_{FWHM} = 17.1$ G). Similar to the analysis of Javadi et al., this spectrum can be fit by the combination of a Lorentzian (77%) and Gaussian (23%) function offset by 1.3 G with $\Delta H_{FWHM} = 16.9$ G and 15.9 G, respectively. However, this lineshape does not necessarily indicate the presence of two spin species. Resonances broadened by unresolved HF coupling can often be fit in this manner (as an example see Figure 29). Alone this spectrum gives little information about the nature of the paramagnetic defects in EB. However, the $g$-value calibrated against a DPPH standard was found to be 2.0035 consistent with a delocalized paramagnetic spin in an organic heteroatomic system of carbon and nitrogen. Also, rough estimates of the spin concentrations, based on the EPR integrated intensities, of this and other EB powder samples ranged from 1 spin per few 100 to 1 spin per few 1000 rings depending on the particular preparation. Cromack using a Faraday Balance measured similar spin concentrations in EB, ~ 1 spin per 1000 rings [110].

The room temperature EPR spectrum of EB (from the same preparation used to obtain the powder spectrum of Figure 40) in dioxane is shown Figure 41. This spectrum is roughly Lorentzian (93%) with $\Delta H_{pp} = 1.62$ G ($\Delta H_{FWHM} = 2.68$ G), indicating a motionally narrow resonance with no resolved HF structure. A similar spectrum was observed in solutions of EB in NMP. This is disappointing considering the success of solution EPR in the PNB system. A possible explanation for this lack of HF structure in the solution spectrum is that through solvation spins trapped or slowed in the solid are free to move rapidly along the polymer chain. From the linewidths it is possible to estimated limits for the spin mobility in solid and solution EB. Assuming the second moment of the resonance is on the order of the linewidth the intrachain hopping rate at the motional narrowing limit is given by $\tau_c^{-1} \ll \left(\frac{\hbar}{g\beta\Delta H}\right)^{-1}$ sec$^{-1}$ (see section 3.2.6). Thus from the width of the solution spectrum, Figure 41, the interchain hopping rate of EB in dioxane must be $>10^8$ sec$^{-1}$ (diffusion coefficient $D < 10^{-6}$ cm$^2$·sec$^{-1}$). Similarly
Figure 40: Room temperature EPR spectrum of EB-0.25 powder.
EPR Spectrum of EB in Dioxane

$T = 300 \text{ K}$

$\Delta H_{pp} = 1.62 \text{ G}$

$\Delta H_{FWHM} = 2.68 \text{ G}$

$g = 2.0039$

Figure 41: Room temperature EPR solution spectrum of EB-0.25 in dioxane.
in the EB powders the hopping rate must be \( \ll 10^8 \text{ sec}^{-1} \). This difference in the intrachain diffusion rate could be readily explained by interchain interactions or aggregation trapping or reducing the mobility of the spin in the solid state. In solution the interchain interactions and/or aggregation would be reduced by the solvating effect of the solvent. If the paramagnetic spin were due to polaron like defects induced by interchain self-doping, partial solvation of the aggregated regions would lead to a more open conformation and increased motility. In addition screening provided by the dipolar nature of the solvents might reduce the Coulomb interaction between the effective dopant and the charge polaron also leading to an increased mobility.

An alternative explanation is that the paramagnetic defects in the solid and solution states of EB are not the same. It has been suggested that the dipolar nature of NMP (due to the double bonded oxygen) may act as a weak dopant for polyaniline. Dioxane with its two oxygens might also act as a weak dopant. Hence, the narrow resonance in the solution state may be due to polarons induced by the solvent itself. The spins observed in the solid if due to interchain self-doping would be substantially reduced in solution where the interchain interactions are expected to be smaller.

### 5.2 Effects of Aggregation and Heat Treatment in solid EB

In this section it will be shown that there is a direct correlation between the degree of aggregation in EB and the concentration of paramagnetic spins. The EB samples used in the EPR studies were synthesized via the oxidative chemical polymerization of aniline in an aqueous solution of HCl with a 1: \( x \) ratio of aniline to oxidant (persulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\)) as described in chapter 3. In the standard “MacDiarmid” route a ratio \( x = 0.25 \) is used. Through out this section the following labeling is adopted for the emeraldine base samples: EB- \( x \), where \( x \) was the persulfate oxidant level relative to aniline used in the synthesis.
5.2.1 Gel Permeability Chromatography

Gel permeation chromatography (GPC) measurements on EB by Angelopoulos et al. are reviewed [111]. GPC is a type of liquid-solid elution chromatography that separates polydisperse polymers into fractions by means of the sieving action of a cross-linked polystyrene or other sieve like packing [112]. Since the smaller molecules permeate the gel particles preferentially, the highest molecular weight fractions are eluted first. Thus, the polymer fractions are separated on the basis of size. For the following measurements the elution of polyaniline from the gel is detected by monitoring the UV/VIS response at 640 nm.

The GPC curve for a solution of EB in NMP (Figure 42) has two peaks corresponding to molecular weights (MW) of ~25,825 and ~554,015 g/Mol. The second curve in Figure 42 for EB in NMP with 0.5% LiCl shows only a single peak at a MW of ~31,636. The addition of the LiCl to the solution removes the high MW peak. Since it is not possible for LiCl to cleave the EB polymer the high MW peak must be due to physically entangled or aggregated chains. It has been proposed by Angelopoulos et al. [111] that EB chains aggregate or cluster as a result of intermolecular interactions (i.e. H-bonding, see Figure 44 (a)) to form physically entangled structures. The effect of the LiCl is to break these hydrogen bonds allowing the polymer chains to separate.

Angelopoulos et al. [111] also performed GPC measurements on samples of solid EB heat treated for 1 hour at 100, 125, and 150° C, see Figure 43. The aggregation peak in these samples were observed to increase with increasing heat treatment temperature. Also it was observed that for heat treatment temperatures above 250° C EB was no longer soluble in NMP. Angelopoulos has attributed this behavior to the formation of physical cross-links (Figure 44 (a)) at the lower heat treatment temperatures and chemical cross-links [113,114] (Figure (b)) at the higher temperatures. Since chemical cross-links involve covalent bonding between polymer chains they cannot be broken by solvation. On the other hand the physical cross-links involving hydrogen bonding are much weaker and can be broken by the solvation process.
Figure 42: Gel permeation chromatography curves showing the elimination of the aggregation peak by the addition of LiCl to EB/NMP. (Figure provided by Angelopoulos et al. [111].)
Figure 43: Gel permeation chromatography curves of solid EB after 1 hour of heat treatment at 100, 125 and 150°C. The fractional area (in percent) for the aggregation peak relative to the total area is given. (Figure provided by Angelopoulos et al. [111].)
Figure 44: (a) Physical cross-linking scheme based on hydrogen bonding proposed by Angelopoulos et al. [111] for emeraldine base. (b) Chemical cross-linking scheme observed in emeraldine base heat treated at 300°C for 4 hours [112,113].
Although no GPC curves are shown here Angelopoulos et al. observed that the degree of aggregation in EB increases with the oxidant (persulfate) level. This is attributed to the more rapid precipitation of the polymer from the aqueous HCl solution at the higher oxidant levels.

### 5.2.2 EPR Linewidths and Spin Concentrations

The room temperature EPR measurements on three syntheses of emeraldine base (EB-0.25, EB-0.50 and EB-0.75) in their “as made” powder forms have been performed. The measurements were done on ~ 5 mg of sample loaded in to 3mm I.D. quartz tubes and seal under vacuum after ~ 30 minutes of pumping. Prior to loading, the samples were handled in air. The relative spin concentrations have been estimated from their EPR integrated intensities and are listed in Table 5. The room temperature EPR spectra of the three EB samples normalized to their relative spin concentrations is also shown in Figure 45. (Although the spin concentrations were not calibrated against a standard, from similar forms of EB the number of rings per spin ranges from a ~ 100 to several thousand.) EB-0.25 shows the lowest spin concentration while EB-0.75 the highest. The trend that is apparent is that the spin concentration increases with the increasing ratio of persulfate (oxidant) to aniline used in the synthesis and correlates with the increased aggregation observed the GPC measurements. Thus interchain interactions are in some way associated with the presence of paramagnetic defects and is consistent interchain self-doping of EB.

<table>
<thead>
<tr>
<th>Synthesis Route</th>
<th>EB-0.25</th>
<th>EB-0.50</th>
<th>EB-0.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Spin Concentration</td>
<td>3.71</td>
<td>8.42</td>
<td>14.54</td>
</tr>
<tr>
<td>FWHM Linewidth (G)</td>
<td>18.5</td>
<td>17.5</td>
<td>17.3</td>
</tr>
</tbody>
</table>

**Table 5: Room temperature EPR determined relative spin concentrations and linewidths for three EB-x powders.**

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Increasing Aggregation

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The EPR FWHM linewidths for the EB-x samples (shown in Table 5) show a small but significant decrease with increasing oxidant level. As a conservative estimate, the experimental linewidths can be determined to within ±0.1 G.

Room temperature EPR measurements have been performed on heat treated EB-x powder samples sealed under vacuum in 3 mm I.D. quartz tubes. The samples were allowed to bake (in vacuum) in a box furnace for 1 hour at the heat treatment temperature. Upon completion of the heat treatment the samples were removed from the furnace and allowed to cool rapidly to room temperature, usually taking ~ 3 minutes. While the samples were cooling they were loaded into the Bruker spectrometer and after ~ 10 minutes a room temperature EPR spectrum was scanned. Subsequent scans were also made at approximately 1, 24, and 96 hours after heat treatment. A summary of the relative spin concentrations and linewidths for these measurements in Table 6 and Table 7, respectively. Clearly, as the samples approach equilibrium after ~ 96 hours there was an overall increase in the spin concentrations with increasing heat treatment temperature relative to the original concentrations. This increase in the spin concentration range from ~ 0% in the EB-0.75 for the 100°C treatment to ~ 175% in the EB-0.25 for the 200°C treatment. However, during the first ~ 96 hours there was a complex relaxation observed in the EPR spectra. Approximately 10 minutes after cooling the spin concentration was 10% to 80% larger than its original value. Then after ~ 24 hours the spin concentration reached a minimum of ~ 15% to 35% less than the original value where upon it began to increase to its equilibrium value. The $\Delta H_{FWHM}$ values reported in Table 7, taken to be the width in Gauss between the half maximum points, are not sensitive to the details of the lineshape and can be easily determined to within ±0.1 G. The $\Delta H_{FWHM}$ values of samples heat treated at 100°C decreases slightly from their values in the untreated samples. At the 200°C H.T. temperature $\Delta H_{FWHM}$ decreases by ~ 15% to 30% from ~ 18 G to ~ 14 G and remained roughly constant with time. Also, at both heat treatment temperatures a small but significant maxima in $\Delta H_{FWHM}$ was observed after ~24 hours corresponding the minima in the spin concentration. Last, shown in Figure 46 and Figure 47 are the EPR
spectrum of EB-0.5 (intermediate aggregation) before and ~ 96 hours after heat treatments at 100° and 200° C, respectively. In the 200°C heat treated samples the lineshape shows definite HF structure emerging in the wings with a splitting constant of ~ 8 G. This HF structure is resolved in the EPR spectra of stretched oriented EB films and is discussed in the next section.

The complex relaxation after heat treatment is puzzling. The observed minima in the relaxation of the spin concentration precludes the simple explanation that heat treatment induces interchain interactions (spins) which relax after the sample is cooled back to room temperature. Instead, to explain this minima at least two relaxation processes are required, one involving a relatively rapidly decay of spins and the other a slow increase. Further the changes observed in the linewidth are not easily explained.

Plotted in Figure 48 is $\Delta H_{\text{FWHM}}$ as a function of the spin concentration for all the EB-x samples before and after heat treatment. The linewidth in the untreated and 100° C treated EB-x samples decreases roughly linearly with increasing spin concentration. A possible explanation of this decrease might be exchange narrowing. If it is assumed that the spins are uniformly dispersed in the sample then the strength of the exchange interaction should increase with increasing concentration resulting in a smoothly decreasing linewidth. However the EB-x samples treated at 200° C do not follow this trend. It maybe that the even though the total number of spins decreases aggregation results in regions of high spin concentration hence stronger exchange leading to the narrower linewidths. However, if exchange narrowing were responsible for the narrow linewidth in the 200° C treated samples then the hyperfine structure in the spectral wings should show signs of be washed out rather than better resolved as is observed (see figure 47). Clearly this behavior is not consistent with exchange narrowing. Either the internal structure (i.e. spin distribution) is changing as the result of heat treatment or their are at least two distinct species of paramagnetic spin.
Table 6: Room temperature EPR determined spin concentrations of three EB-x powders before and after heat treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H.T. Temp.</th>
<th>Before H.T.</th>
<th>~ 10 min.</th>
<th>~ 1 hr.</th>
<th>~24 hr.</th>
<th>~96 hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB-0.25</td>
<td>100 °C</td>
<td>3.7</td>
<td>4.0</td>
<td>3.8</td>
<td>~</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3.7</td>
<td>5.3</td>
<td>5.2</td>
<td>~</td>
<td>10.2</td>
</tr>
<tr>
<td>EB-0.50</td>
<td>100</td>
<td>8.7</td>
<td>11.0</td>
<td>10.5</td>
<td>5.8</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>8.2</td>
<td>13.2</td>
<td>12.1</td>
<td>5.4</td>
<td>11.2</td>
</tr>
<tr>
<td>EB-0.75</td>
<td>100</td>
<td>14.5</td>
<td>18.6</td>
<td>17.6</td>
<td>10.3</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>14.6</td>
<td>26.4</td>
<td>25.3</td>
<td>12.2</td>
<td>23.2</td>
</tr>
</tbody>
</table>

Table 7: Room temperature EPR linewidths of three EB-x powders before and after heat treatment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H.T. Temp.</th>
<th>Before H.T.</th>
<th>~ 10 min.</th>
<th>~ 1 hr.</th>
<th>~24 hr.</th>
<th>~96 hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EB-0.25</td>
<td>100 °C</td>
<td>18.4 G</td>
<td>18.1 G</td>
<td>18.1 G</td>
<td>~</td>
<td>17.7 G</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>18.5</td>
<td>13.8</td>
<td>13.7</td>
<td>~</td>
<td>13.5</td>
</tr>
<tr>
<td>EB-0.50</td>
<td>100</td>
<td>17.5</td>
<td>17.4</td>
<td>17.4</td>
<td>17.8 G</td>
<td>17.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>17.5</td>
<td>14.1</td>
<td>14.0</td>
<td>14.1</td>
<td>13.9</td>
</tr>
<tr>
<td>EB-0.75</td>
<td>100</td>
<td>17.3</td>
<td>16.7</td>
<td>16.8</td>
<td>17.2</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>17.2</td>
<td>14.7</td>
<td>14.8</td>
<td>15.4</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Figure 45: Room temperature EPR spectra of three EB-x powders. EB-0.25, EB-0.50 and EB-0.75 are reported to have increasing aggregation, respectively [111].
Figure 46: Room temperature EPR spectra of EB-0.5 powder before and after heat treatment for 1 hour at 100° C. An ~15% increase in the integrated intensity is observed in the spectrum after heat treatment.
Figure 47: Room temperature EPR spectra of EB-0.75 powder before and after heat treatment for 1 hour at 200° C. An ~ 37 % increase in the integrated intensity is observed in the spectrum after heat treatment. The spectrum after heat treatment is narrower overall and shows hyperfine structure emerging in the wings.
Linewidth Versus Spin Concentration for EB-x Powder Samples

Figure 48: Plot showing the roughly linear relationship between the linewidth and relative spin concentration for EB-x before and after heat treatment at 100° C. The 200° C heat treated samples do not follow this trend.
5.3 EB Stretch Oriented Films

The process of stretching a polyaniline [83] film results in the polymer chain having a preferred orientation along the stretch axis, see Figure 22. By measuring the EPR spectrum with the polymer chains oriented parallel and perpendicular to the applied H-field it is possible, at least in part, to isolate components of any hyperfine couplings occurring in the polymer. This will be especially effective for highly anisotropic interaction as is the case for the imine nitrogens of polyaniline. Recalling the EPR powder spectra for the neutral soliton in PNB, where $A_i^N \approx 2.4$ G and $A_i^N \approx 22.4$ G, the imine nitrogen in polyaniline is found to be highly anisotropic with $A_i^N/A_i^N \approx 0.107$ (Note: the parallel direction is defined by the nitrogen $p_z$ axis, not the polymer axis).

The EPR of EB stretch films does show a strong orientation dependence and in fact much of the hyperfine coupling has been resolved from these spectra. Combining oriented EPR with ENDOR and ESEEM results, much information on the structure and spin density distribution of at least one defect state in EB has been determined. These results are discussed below.

The films used in this study were all made at the University of Pennsylvania by Dr. G. Min with EB-0.25 powder (the standard persulfate level) as the starting material. The process of making and stretching the EB films is described in chapter 3. However it should be mentioned that during the process the films are heated to 150°C, in effect heat treating them similar to the EB-x samples of the previous section. The only chemical difference between these stretched films and the powder is the presence of some residual NMP left over from casting the initial film.

5.3.1 EPR Results

The room temperature EPR spectrum of an EB film stretched to 5 times its original length is shown in Figure 49 for orientations of the stretch axis parallel and perpendicular to the applied H-field. The linewidths are $\Delta H_{\text{FWHM}} \sim 11.6$ G and 14.5 G for
the parallel and perpendicular orientation, respectively. The spectrum shows strong spectral anisotropy. There are two expected sources of this anisotropy, nitrogen and hydrogen hyperfine coupling. In the parallel orientation the polymer chains lie preferentially along the applied H-field and thus for all EB nitrogens $A^N_{xx}$ will be the primary hyperfine coupling component, see Figure 22. Similarly in the perpendicular orientation $A^N_{xx}$ and $A^N_{zz}$ hyperfine components will be equally weighted in the EPR spectrum. For the hydrogens protonating the EB phenyl rings the situation is a bit more complicated. As stated in chapter 4 the proton hyperfine coupling components are given by $A^H_{xx} = (1 - \alpha)A^H_{xx}$, $A^H_{zz} = A^H_{xx}$, and $A^H_{sy} = (1 + \alpha)A^H_{xx}$ where $\alpha \sim 0.5$. Again referring to Figure 22, it is easily seen that in the parallel orientation all three of the principle hyperfine coupling components of $A^H$ will have some projection along the applied field with a slight preference for the larger $A^H_{xx}$ component. Similarly in the perpendicular orientation there is a slight preference for the $A^H_{yy}$ component. Thus nitrogen hyperfine coupling can be expected to cause a dramatic orientation dependence in the EPR spectrum of these films and result in a narrow line in the parallel orientation. Hydrogen hyperfine coupling can not be expected to significantly effect the anisotropy of the EPR spectrum. Thus we can conclude that the coupling in the spectra of the EB stretched films is primarily due to nitrogen.

The EPR of the stretched EB films show a striking similarity with that of the 200° C heat treated EB-x powders. A simple way to demonstrate this similarity is to compare linewidths. The isotropic linewidth of the EB 5X stretched film can be estimated by the weighted average of the parallel and perpendicular spectra:

$$\Delta H_{FWHM} \sim \frac{11.6}{3} + 2\left(\frac{14.5}{3}\right) = 13.5 \text{ G}$$. This is comparable to the linewidth in the EB-x powder after the 200° C heat treatment. In fact in EB-025 sample where the largest increase (175%) in the equilibrium spin concentration after heat treatment was observed the linewidth was measured to be 13.5 G. This also was the smallest linewidth observed in the EB-x samples.
Figure 49: Room temperature EPR spectrum of an EB film stretched to 5 times its original length showing strong anisotropy in the spectral lineshape, where the applied H-field was parallel and perpendicular to the stretch axis.
Scaled Difference EPR Spectrum between Perp. and Parallel Orientations of EB 5X Str. Film

Figure 50: Perpendicular EPR spectrum of EB 5X stretched film with 0.5 time the corresponding parallel spectrum subtracted out. The small H-shift was also added to account for a slight g-shift.
Simulated EPR Spectra for Parallel Orientation of EB 5X Stretched Film

Figure 51: Simulated EPR spectrum of the parallel orientation of EB 5X stretched film using four equivalent nitrogens with an assumed isotropic hyperfine coupling, $A^N = 0.84$ G, and a Lorentzian broadening function of $\Delta H_{\text{FWHM}} = 11.0$ G.
Simulated EPR Spectrum for Perpendicular Orientation of EB 5X Stretched Film

Figure 52: Simulated EPR spectrum of the perpendicular orientation of EB 5X stretched film based on the superposition of the simulated spectrum for the parallel orientation, Figure , and simulated spectrum for four equivalent nitrogens with an assumed isotropic hyperfine coupling of $A_{iso}^N = 7.35$ G and a Lorentzian broadening function of $\Delta H_{FWHM} = 7.9$ G.
The partially resolved hyperfine structure due to $A_{zz}^N$ in the perpendicular spectrum can be better isolated by subtracting the portion of the spectrum corresponding to the field along $x$. Since $A_{xx}^N$ and $A_{yy}^N$ are roughly equal and the hydrogen coupling does not contribute significantly to the spectral anisotropy a weighted subtraction (perpendicular minus 0.5 time parallel) should achieve this reasonably well. The result of this subtraction is shown in Figure 49 where a small positive H-field shift was also added to account for differences in the $g$ between the $x$ and $y$ orientations. This spectrum clearly shows nine roughly equally spaced hyperfine line. The splitting constant is estimated to be $\sim 8.4$ G, the distance from the first to the last line ($\sim 67$ G) by 8. In light of the high anisotropy in the spectrum the most likely origin of these nine lines are 4 nearly equivalent imine nitrogens. For this situation the hyperfine pattern will involve $4 \cdot (2I_n) + 1 = 9$ lines with a 1:4:10:16:19:16:10:4:1 intensity pattern. Thus the predominant hyperfine splitting is assigned as $A_{zz}^N \sim 8.4$ G. It should be mentioned that there are two other hyperfine configurations involving nitrogen and hydrogens which can give rise to a nine line pattern. Eight equivalent hydrogens will have $8 \cdot (2I_n) + 1 = 9$ lines with a 1:8:28:56:70:56:28:8:1 intensity pattern. Also two nitrogen and four hydrogen interactions with a coincidental equivalent coupling will give $2 \cdot (2I_n) + 4 \cdot (2I_n) + 1 = 9$ lines with a 1:6:17:30:36:30:17:6:1 intensity pattern. However it will be shown in the following section that these last two configurations are not consistent with the observed ENDOR.

Using the form of the nitrogen coupling tensors estimated form the PNB powder spectra in Table 2 the isotropic coupling can be estimated from $A_{zz}^N$ as follows

$$A_{iso}^N = A_{zz}^N \sum_{i=x,y,z} \frac{A_{ij}^N_{obs}}{3A_{zz}^N_{obs}} = 3.4 \text{ G.}$$

Finally, the corresponding spin density can be calculated,
\[ \rho_N \sim Q_N^N A_{iso}^N = 0.125 \]  
(68)

where \( Q_N^N = 27.3 \) G. Thus the spin density for the predominant paramagnetic defect in the EB films and 200° C heat treated samples is determined to be partially distributed (0.125) in four nitrogen (imine nitrogenous based on the ENDOR results).

### 5.3.2 ENDOR Results

The ENDOR spectrum at 10 K, shown in Figure 53, shows a single value of the hydrogen hyperfine coupling, \( A''_N = 1.2 \) MHz or 0.43 G, in addition to the matrix line centered at 14.5 MHz. For this weak proton coupling the corresponding spin density is

\[ \rho_H \sim Q_H^N A_{iso}^N = 0.050, \]  
(68)

where \( Q_H^N = 24.1 \) G as described in chapter 4. Further there is no evidence of stronger hydrogen coupling up to 10 MHz (3.6 G), the width of the ENDOR scan. Based on the expected form of the HF coupling tensor for protonated carbons in EB if the 8.4 G coupling observed in the EPR were due to protons it would have to correspond to the \( A''_N = (1 + \alpha) A_{iso}^N \) component of the HF tensor. The accompanying \( x \) component of the hyperfine interaction would be given by

\[ A''_{iso} = (1 - \alpha) A_{iso}^N = A_{iso}^N \left( \frac{1 - \alpha}{1 + \alpha} \right) \sim 2.8 \text{ G.} \]  
(69)

This coupling lies well within the ENDOR scan range and is not observed. Thus, confirming that no strong proton HF coupling is present.
Figure 53: ENDOR spectra of EB 5X stretched film showing a proton coupling of 1.2 MHz or 0.43 G. Inset is the full scan showing no signs of proton coupling up to 10 MHz or 3.6 G.
ESEEM Spectrum of EB 5X Stretched Film

Microwave Freq. = 11.6549 GHz
Static H-Field = 4170.00 G
Tau = 250 ns

Figure 54: Representative ESEEM spectra of EB 5X stretched film for the parallel orientation at 4.2 K.
5.3.3 ESEEM Results

The ESEEM spectrum of the EB 5X stretched film is shown in Figure 54. This spectrum shows strong hyperfine couplings centered near 1.2 MHz corresponding to the nuclear g-value of nitrogen. The peaks at 6.8 and 9.2 MHz correspond roughly to the hyperfine coupling \( A^N_{zz} = 16 \) MHz (5.7 G). The peaks at \( \sim 0.8 \) and 3.2 MHz correspond roughly to the nitrogen \( x \) and \( y \) hyperfine coupling components, where \( A^N_{xx} \sim A^N_{yy} \sim 4 \) MHz (1.4 G). The peak at 17.7 MHz corresponds to proton coupling and is resolved in the ENDOR spectra. Clearly this spectrum is consistent with the defect state involving four roughly equivalent nitrogen coupling and no strong hydrogen couplings.

5.4 Interpretation of the Experimental Results

It is proposed that the observed time dependent behavior in EPR of the heat treated EB samples and the hyperfine structure resolved in EB stretched films can be attributed to interchain self-doping. In this section two self-doping mechanisms involving interchain hydrogen bonding are postulated.

Angelopoulos et al. [111] suggested that hydrogen bonding from two adjacent amine nitrogens on an EB chain to two imine nitrogens of a single quinoid unit on an adjacent EB chain could give rise to paramagnetic spin, Figure 56. In this scheme the hydrogen atoms of the two amine nitrogens approach the imine nitrogen on the second EB chain destabilizing the quinoid ring unit and leading to spin density on the two imine nitrogen. This structure is similar to the ring centered positive polaron calculated by Libert and Bredas [18]. The expected hyperfine interactions would involve two equivalent nitrogen couplings and four relatively weak proton couplings. Clearly this is not what is observed in the EB 200°C heat treated EB powders and EB stretched films. However it is suggested that paramagnetic defects of similar form are present in the EB powder before heat treatment and to a lesser degree after heat treatment. And that they give rise to a broad featureless resonance with \( \Delta H_{HFHM} \sim 19 \) G. This bonding scheme
will be referred to as a “quinoidal” hydrogen bond and the paramagnetic defect it induces as a trapped polaron.

A second paramagnetic defect I propose as a preliminary explanation of the four equivalent nitrogens involves interchain hydrogen bonding from an EB chain to an over oxidized, PNB like, region on a second chain. It is known that EB synthesized in air will be slightly over oxidized resulting in \( \approx 60\% \) imine nitrogens as opposed to 50\% in pristine EB. These over oxidized, PNB like regions are more favorable to the formation of hydrogen bonds. In Figure 56 the proposed bonding scheme is shown. The hydrogen atoms of the two amine nitrogens approach the imine nitrogens of two different quinoid units in an over oxidized region of the second chain destabilizing two quinoid ring unit. This leads to spin density on four nitrogens as opposed to two in the previous scheme. For convenience this bonding scheme will be referred to as the “biquinoidal” hydrogen bond and the paramagnetic defect state it induces the “dipolaron”.

There is no clear explanation of the observed time dependent behavior of the spin concentrations and linewidths in the heat treated EB powder samples. However, as a bare minimum two spin species are needed as was pointed previously. The observed changes in the lineshape suggests that one species is relatively broad, \( \Delta H_{FWHM} \approx 18 \text{ G} \), with little or no discernible HF structure. The second species is narrower, \( \Delta H_{FWHM} \approx 13.5 \text{ G} \), with HF structure partially resolved in the wings, see Figure 47. In the “as made” EB prior to any treatment the interchain interaction (possible the “quinoidal” hydrogen bonding scheme) is predominant and contributes to the broader linewidth. However this interaction is less favorable than the “biquinoidal” HB interaction and after heat treatment at temperatures in the vicinity of the glass transition. It was reported by Wei et al. that in films of EB with a 15\% NMP content the glass transition occurred at 140\° C and for films with no NMP content at 220\° C [115]. The EB-x powders, although not a film, have no NMP content and thus likely a \( T_g \) in the neighborhood of 220\° C. The oriented EB films on the other hand where stretched from films cast form an EB/NMP solution an
thus are expected to have a high NMP content and thus a $T_g$ near 150° C at which the films were processed. Thus the samples of EB that were heat treated at temperatures near their glass transition show a predominance of the “dipolaron” defects.

A possible explanation of the time dependent behavior in the EB-x powders after heat treatment involving the two postulated spin defects is now described. Prior to heat treatment the trapped polaron like defects are predominant giving a FWHM linewidth of $\sim 18$ G. Upon heat treatment the hydrogen bonds inducing them are broken and the concentration of these defects decreases. For H.T. temperatures near the glass transition virtually all of these bonds are broken and replaced by the more stable “biquinoidal” HBs resulting in an immediate decrease in the linewidth. The complex relaxation observed in the spin concentration is the result of two relaxation processes involving the “biquinoidal” HBs. Shown in Figure 57 is a plot of the combined effect of all of these (proposed) processes on the spin concentration and linewidth where the “quinoidal” and “biquinoidal” HBs are assumed to have characteristic EPR linewidths of 18.5 and 13.5 G. The most striking feature is the minimum in the spin concentration at $\sim 24$ hours after H.T. which is below the initial spin concentration before H.T.. Another feature is the abrupt decrease in the linewidths immediately after H.T. and the maximum in the linewidth corresponding to the minimum in the spin concentration. The simple model where the “quinoidal” HBs relax slowly ($\sim 96$ hr.) to a more stable “biquinoidal” hydrogen bonded conformation cannot account for the linewidth behavior.

The time dependence observed in the spin concentration and linewidth is likely the result of a slow relaxation EB’s conformation after the stress of H.T.. It is well known that the viscoelastic properties of polymers arise from a combination of solid and fluid like properties and in amorphous polymers give rise to superslow relaxation processes [116,117]. It is possible for entangled polymers to creep or reptate [118] on long time scales. A widely studied amorphous high polymer is polyisobutylene where fluid like properties are observed on time scales of $\sim 24$ hours and greater [119,120].
Figure 55: Possible "quinoidal" hydrogen bonding scheme in EB leading to the creation of a paramagnetic defect through the destabilization of a signal quinoid units. The spin distribution is similar to the positive ring centered polaron proposed by Libet et al..
Figure 56: Possible "diquinoidal" hydrogen bonding scheme for EB leading to the creation of a paramagnetic defect through the destabilization of two quinoid units. The spin is distributed roughly on four equivalent nitrogens.
Figure 57: Proposed relative concentrations of “quinoidal” and “biquinoidal” hydrogen bonding in EB as a function of time after heat treatment ends at $t = 0$. 13.5 and 18.5 G linewidths are assumed.
5.5 Future Directions

The interchain "self doping" mechanisms proposed in the previous section are preliminary and much further work is needed. In this section several obvious experiments are suggested aimed toward better understanding the nature of interchain interactions in EB.

The "quinoidal" and "diquinoidal" hydrogen bonding schemes both involve hydrogen bonding between an amine and imine nitrogen. Thus it should be expected that the degree of aggregation and spin concentration should depend on the oxidation state of polyaniline. This should be especially evident in EB samples heat treated near \( T_c \) where "diquinoidal" HB, Figure 55, is proposed to dominate. This HB mechanism requires a region of one of the EB chains to be slightly over oxidized, i.e. a section of form BNQNBQNB. Thus EB samples with a slightly high average oxidation state should have a larger spin concentration. EB prepared in air is known to be slightly over oxidized (\( y \sim 0.6 \)) and if prepared under an inert atmosphere slightly under oxidized (\( y \sim 0.4 \)) [81]. Thus the EB prepared in air should have a higher spin concentration than EB prepared under an inert atmosphere.

Another more involved study would be to measure the spin concentration and aggregation in polyaniline as a function of the oxidation level. Because both the proposed interchain interactions involve hydrogen bonding between amine and imine nitrogen it should be expected that both the LEB and PNB forms of polyaniline should have no spin concentration (due to interchain "self-doping") nor aggregation. This is certainly the case in PNB where the paramagnetic spin has been identified as neutral solitons; there is no evidence of any other contribution to the spin concentration. The dependence of the spin concentration on oxidation level could provide important insight into the nature of the interchain interactions in polyaniline.
Also a study of the temperature and time dynamics of the spin concentration after heat treatment could prove very insightful. Such a study might yield the energies associated with the relaxation mechanisms. In addition, a comparison to the results of dynamically mechanical measurements could prove useful.
BIBLIOGRAPHY


