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Electronic and Optical Properties of Conjugated Polymers

SECOND EDITION

WILLIAM BARFORD



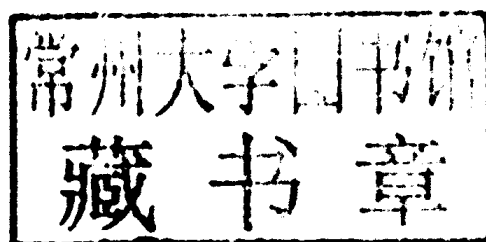
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Electronic and Optical Properties of Conjugated Polymers

Second Edition

WILLIAM BARFORD

*Physical and Theoretical Chemistry Laboratory
Department of Chemistry
University of Oxford
United Kingdom*



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Preface

Since the discovery of the light emitting properties of the phenyl-based organic semiconductors in 1990 there has been a huge growth of interest in conjugated polymers. The potential device applications are enormous, ranging from optical switching to solar cells and light emitting devices. These new developments are a direct consequence of the active research in the 1980s on conjugated nonelectroluminescent polymers, such as *trans*-polyacetylene. Polyacetylene has particularly interesting and unusual low-lying electronic excitations, and has attracted much experimental and theoretical interest, culminating in the award of the Nobel prize for chemistry in 2000 for research in this field.

The progress in our understanding of the fundamental physics of conjugated polymers, which provides a crucial underpinning to the technological applications, has also been large. This progress has been driven by experimental, theoretical, and computational developments. A number of very careful and elegant linear and nonlinear optical spectroscopies over the last two decades have established the energies and symmetries of the excited states. Meanwhile, computational advances have been driven by the development of sophisticated numerical techniques, coupled with cheaper and more powerful computers. One of these numerical techniques is the density matrix renormalization group (DMRG) method. This method is highly suited for solving correlated one-dimensional problems.

Conjugated polymers behave as quasi-one-dimensional systems owing to their strong intramolecular interactions and rather weak intermolecular interactions. As a consequence, electron-electron interactions are weakly screened, and thus both electron-electron interactions and electron-nuclear coupling are fundamentally important in determining the electronic behaviour. Electronic interactions play a crucial role in determining the nature of electronic excitations as they completely change the noninteracting electronic description. Moreover, the coupling of these correlated electronic states to the nuclei is also a delicate and complicated problem. Together, electronic interactions and electron-nuclear coupling determine the relative energetic ordering of the electronic states, and this, in turn, largely determines the optical properties of conjugated polymers. This understanding of the origin and nature of the electronic states helps us to explain why some conjugated polymers, for example poly(*para*-phenylene), are electroluminescent, while others, for example *trans*-polyacetylene, are not.

One of the key aims of this book is to explain how electron-electron interactions and electron-nuclear coupling determine the types and character of the low-lying electronic states. Since these effects are complicated, our strategy will be to start with the simplest approximation of noninteracting electrons and gradually develop the full description. At each step care will be taken to explain how electron-electron interactions and electron-nuclear coupling modify the predictions of the simpler approximations.

We will see that one of the reasons why understanding the electronic properties of conjugated polymers is such a challenge is because the electronic potential energy is comparable to the electronic kinetic energy. In other words, the relevant parameter regime is intermediate between the weak and strong electron-electron interaction limits. A useful strategy is therefore to tackle these systems from both the weak and strong coupling extremes. In fact, light emitting polymers lie on the weak-coupling side of the intermediate regime, whereas nonelectroluminescent polymers (such as *trans*-polyacetylene) lie on the strong-coupling side.

We focus on semiempirical models of π -conjugated systems. There are two advantages to this strategy over studying *ab initio* models. First, reduced basis models in one dimension can be solved essentially exactly via the DMRG method for very large systems. Thus, there is no need to make approximations in the method which might obscure or prejudice an understanding of the physics. Second, being approximate, reduced basis models retain some symmetries not present in the *ab initio* models. In particular, electron-hole symmetry is particularly useful in characterizing neutral excited states. We also remark that although they are semiempirical, π -electron models are carefully parametrized so that they also provide accurate predictions of excited state energies.

Solving very large systems by the DMRG method reveals the physics of conjugated polymers not present in conjugated molecules, namely that when the size of the chain (or more precisely, the conjugation length) exceeds the spatial extent of the internal structure of the excited states a quasi-particle description becomes appropriate. Conjugated polymers exhibit a wealth of different quasi-particles: solitons, excitons, magnons, polarons, etc. It is an aim of this book to explain the origin and physical consequences of these quasi-particles. In particular, the description of an exciton as two independent quasi-particles will prove to be a very useful concept.

Having established how two key effects in conjugated polymers (electronic interactions and electron-nuclear coupling) affect their electronic properties, the third key effect will be discussed, namely, disorder. Most conjugated polymer systems are subject to conformational and environmental disorder. Disorder localizes charges and excitons, and determines their energetic and spatial distributions. An understanding of the role of disorder is a necessary prerequisite for the development of theories of charge and energy transport.

Nonlinear optical measurements provide the most direct probe of the electronic states. Conversely, the nonlinear susceptibilities can be calculated if there exists a theoretical understanding of the excited states. We describe the theory of linear and nonlinear optical processes, and recast the so-called essential states model in terms of the primary excitons.

We demonstrate how our theoretical understanding of excited states enables us to make a consistent interpretation of experimental results. Two chapters draw these themes together in discussing *trans*-polyacetylene, and the technologically important phenyl-based light emitting polymers.

Once an understanding of these intramolecular processes is established, a final aim of this book will be to explain electronic processes arising from intermolecular interactions. Thus, energy transfer and migration, and excited state complexes involving two

or more polymer chains are described. Another important consequence of interchain interactions is dispersion interactions, which significantly modify the energy of some intrachain excitations. An understanding of this effect is crucial to the interpretation of optical experiments.

Throughout we apply models to, and develop theories for, conjugated polymers with relatively simple chemical structures, e.g., *trans*-polyacetylene and poly(*para*-phenylene). These polymers serve as model systems to understand the generic electronic properties of most classes of conjugated polymers.

The book is therefore organized as follows. Chapter 1 gives a brief overview of the electronic properties of conjugated polymers. Our basic models for describing these properties are semiempirical π -electron models. So, Chapter 2 introduces and motivates these models. Next, we consider the solution of these models in various limits: noninteracting electrons with fixed geometry in Chapter 3, noninteracting electrons with electron-nuclear coupling in Chapter 4, and interacting electrons with fixed geometry in Chapter 5. Chapter 6 is devoted to a discussion of excitons, as these are so important in determining the photophysical properties of conjugated polymers. The electronic states of interacting electrons with electron-nuclear coupling are described Chapter 7. The next two chapters illustrate the applicability of the concepts thus developed via a discussion of the experimental and theoretical investigations of *trans*-polyacetylene and light emitting polymers in Chapters 8 and 9, respectively. The roles of disorder and electron-nuclear coupling in localizing excitons are then described in Chapter 10, where the fundamental concept of a chromophore is given a quantitative definition. Chapter 11 introduces the nonlinear optical spectroscopies that are used to identify the excited states of conjugated polymers discussed in Chapters 8 and 9. Finally, Chapter 12 describes excitonic processes in conjugated polymers.

This book was written with two kinds of readers in mind, the first being experimentalists who wish to understand and interpret their experimental data in terms of the fundamental electronic and optical properties of conjugated polymers. The other type of readers are theoretical and computational chemists and physicists who want both to understand the fundamental properties of conjugated polymers and to develop models and perform calculations of their own. For these readers there are a number of appendices containing material too technical for the main chapters.

Acknowledgements

My interest in conjugated polymers began in 1995 when Donal Bradley established a polymer optoelectronics research group in the Department of Physics and Astronomy at the University of Sheffield. At the same time three theorists then at Sheffield, Robert Bursill, Gillian Gehring, and Tao Xiang, were using Steve White's highly-accurate density matrix renormalization group (DMRG) method to solve one-dimensional correlated electron problems. The opportunity to apply the DMRG method to models of conjugated polymers at the same time as developing a collaboration with the experimental group was too great to miss.

Since then I have learnt a great deal about conjugated polymers from a large number of people. Donal Bradley, Paul Lane (both then in Sheffield) and Simon Martin are three experimentalists who patiently answered many questions on the optoelectronic properties of conjugated polymers.

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This book is dedicated to my mother and father.

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Introduction to conjugated polymers

Research into the electronic, optical, and magnetic properties of conjugated polymers began in the 1970s after a number of seminal experimental achievements. First, the synthesis of polyacetylene thin films (Itô *et al.* 1974) and the subsequent success in doping these polymers to create conducting polymers (Chiang *et al.* 1977) established the field of synthetic metals. Second, the synthesis of the phenyl-based polymers and the discovery of electroluminescence under low voltages in these systems (Burroughes *et al.* 1990) established the field of polymer optoelectronics.

The electronic and optical properties of conjugated polymers, coupled with their mechanical properties and intrinsic processing advantages, means that they are particularly attractive materials for the electronics industry. There are many potential applications including, light emitting devices, nonlinear optical devices, photovoltaic devices, plastic field-effect transistors, and electromagnetic shielding. The discovery and development of conductive polymers was recognized by the award of the Nobel prize for chemistry in 2000 to Heeger (2000), MacDiarmid (2000), and Shirakawa (2000).

A conjugated polymer is a carbon-based macromolecule through which the valence π -electrons are delocalized.¹ *Trans*-polyacetylene, illustrated in Fig. 1.1, is a linear polyene, whose ground state structure is composed of alternating long and short bonds. Also shown in Fig. 1.1 are two other linear polyenes, *cis*-polyacetylene and polydiacetylene. The light emitting polymers, for example, poly(*para*-phenylene) (or PPP) and poly(*para*-phenylene vinylene) (or PPV), are characterized by containing a phenyl ring in their repeat units. PPP and PPV are illustrated in Fig. 1.2.

As well as their many important technological applications, conjugated polymers are also active components in many biological photophysical processes, for example, as light collectors in photosynthesis, and in the vision mechanism via photoisomerization. Charge transport in organic molecules is also an important component of cellular function. Many of the concepts developed in this book are therefore applicable to these biological systems.

Conjugated polymers exhibit electronic properties that are quite different from those observed in the corresponding inorganic metals or semiconductors. These unusual electronic properties may essentially be attributed to fact that conjugated polymers behave as quasi-one-dimensional systems owing to their strong intramolecular electronic interactions and relatively weak intermolecular electronic interactions. Weak intermolecular electronic interactions (arising from poor electronic wavefunction over-

¹Conjugate from the Latin *conjugatus*, meaning to join or unite.

trans-polyacetylene*cis*-polyacetylene

polydiacetylene



Fig. 1.1 The carbon backbone of some linear polyenes. The hydrogen atoms are not shown. More detailed chemical structures are illustrated in Chapter 2.

lap) coupled to strong dissipation (or dephasing) mechanisms means that quantum mechanical coherence is generally confined to a single chain, or at most a few other chains. Electronic wavefunctions are therefore typically localized on single chains, or to pairs of chains in the case of excited state complexes. This quasi-one-dimensionality also means that electron-electron interactions are weakly screened. Thus, electronic correlations are important in determining the character of the electronic states. Another important factor in determining the character of the electronic states is that the electrons and nuclei are strongly coupled. As for electronic interactions, the effects of electron-nuclear coupling are enhanced in low dimensions.

Much early theoretical work on conjugated oligomers and polymers treated electron-electron and electron-nuclear interactions independently. In the 1950s the focus was on the role of electron-nuclear interactions in causing a metal-semiconductor transition in one-dimensional metals (Fröhlich 1954; Peierls 1955), and in determining the bond alternation in linear polyenes (Ooshika 1957, 1959; Longuet-Higgins and Salem 1959). It was also realized that a broken-symmetry ground state of bond alternation implies bond defects between different domains of bond alternation (Ooshika 1957; Longuet-Higgins and Salem 1959), and to associated mid-gap electronic states (Pople and Walmsley 1962). Theoretical and experimental investigations into excited states and their associated bond defects (or solitons) grew rapidly after the introduction of a simplified model of electron-nuclear interactions in *trans*-polyacetylene by Su, Schrieffer, and Heeger (Su *et al.* 1979). These developments are reviewed in (Heeger *et al.* 1988).

An alternative point of view, namely that electron-electron interactions are important in determining the electronic properties in conjugated polymers, was advocated by Ovchinnikov and coworkers (Ovchinnikov *et al.* 1973), who argued that electronic

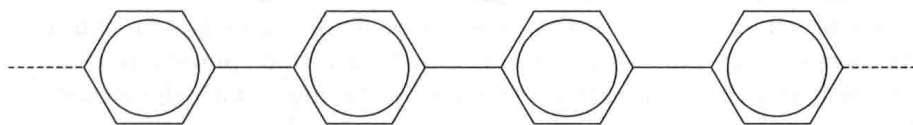
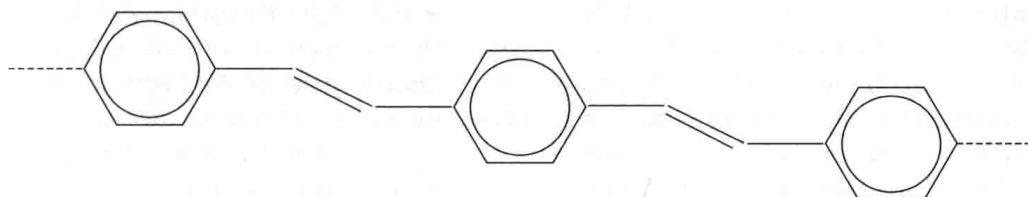
poly(*para*-phenylene)poly(*para*-phenylene-vinylene)

Fig. 1.2 The carbon backbone of some phenyl-based light emitting polymers.

correlations are principally responsible for the optical gap in linear polyenes. Likewise, the lack of electroluminescence in linear polyenes was attributed to a dipole-forbidden strongly correlated singlet state lying below the dipole-allowed singlet (Hudson and Kohler 1972; Schulten and Karplus 1972). Another indication of the importance of electronic interactions is that electroluminescence from light emitting polymers occurs from exciton (or bound electron-hole states), and not from a direct band to band transition.

In fact, as we emphasize in this book, both electron-electron and electron-nuclear interactions must be treated together in order to achieve a coherent description of the excited states of conjugated polymers. It is the interplay of these two processes that leads to the rich variety and relative energetic ordering of the electronic states in conjugated polymers, and ultimately to their electronic and optical properties. For example, strong electronic interactions *and* electron-nuclear coupling in *trans*-polyacetylene reverses the energy of the dipole allowed and forbidden singlet states, rendering it non-electroluminescent.

As a consequence of their size, conjugated polymers exhibit some physical properties more associated with solid state physics than molecular physics. One of these concepts is broken symmetry ground states. Another is the quasi-particle description of excited states, widely used in solid physics, which is also appropriate in conjugated polymers provided that the conjugation length is longer than the internal spatial extent of the excited state. Since the conjugation length is typically 10–40 repeat units (much longer than a conjugated molecule) while the typical size of the internal structure of an excited state is 2–10 Å, conjugated polymers do indeed exhibit a wealth of quasi-particles, including solitons, excitons, magnons, and polarons. It is an aim of this book to explain the origin and physical consequences of these quasi-particles.