THEORY OF CONJUGATED POLYMERS AND MOLECULAR CRYSTALS

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I. Introduction: The electronic, spectral and conducting properties of molecular crystals, such as anthracene, naphthalene, and benzene have been studied by modern methods and theories for almost 40 years[1]. In spite of this attention, there are still interesting effects being discovered. The study of the same properties of conjugated polymers, such as polyacetylene and polypyrrole, is only about 10 years old. These systems are surprising and wonderful in many regards, not the least of which is the strong interdisciplinary nature of the scholarship devoted to them.

In this paper, I will review the field from the perspective of a physical chemist who has thought about molecular crystals and conjugated polymers from a theoretical viewpoint always (I hope) with an eye on the experimental details.

II. Molecular Crystals: Molecules in a molecular crystal are only slightly perturbed from their gas phase structure, so that theory always begins with a description of the crystal as a frozen gas of such molecules. The prototypical (for our purposes) system is naphthalene with its planar structure and large number(48) of vibrational modes. Because of its anisotropic shape, the intermolecular forces in the solid are also anisotropic; in addition, they are weak. Because of this, defect structures have low energies, and are important in the description of the properties. The crystal packing is the "herring bone" pattern with two molecules in a unit cell, a structure often seen in planar aromatic systems. The structure is soft: there are low frequency torsional modes as well as
the low frequency acoustic and optical phonons. Because of the anisotropy of the intermolecular forces and their short range, all properties often exhibit strong anisotropies or dimensionalities. All of these lead to the prediction that, in most of these systems, there is no single dominant interaction. On the contrary, many interactions compete, and the final result often depends on small details.

A good example of this is the 20 year struggle to understand the conductivity of electrons and holes in naphthalene crystals[2]. It has taken 20 years of hard work to produce crystals pure and defect-free enough to obtain reliable experimental results over a wide temperature range. The theory of the conduction in naphthalene (and other aromatic crystals) is still not fully worked out, largely, I believe, because a number of phonon and librational modes strongly interact with the charge carriers, making a simple model inadequate.

The hamiltonian for a molecular crystal can be written

$ H = \Sigma h_n + \Sigma V_{nm} $  

where $ h_n $ is the hamiltonian for the single molecule and $ V_{nm} $ is the interaction between molecules $ n $ and $ m $. Even in the simplest cases, we must treat this in an approximate manner, by introducing a basis set which is based on the eigenfunctions of the first term in (1). If we are considering the excited electronic states of the system, we often concentrate on a single band of states arising from one electronic state of the molecule. Then, we find

$ H = \Sigma \epsilon_n a_n^+ a_n + \Sigma t_{nm} a_n^+ a_m + H_{vib} $  

where $ \epsilon_n $ is the energy of the electronic state in the absence of the intermolecular forces while $ t_{nm} $ represents the excitation transfer matrix element between sites $ n $ and $ m $. Finally $ H_{vib} $ represents the phonon and vibrational hamiltonian. In the case of hole or electron conduction, a similar effective hamiltonian would be used, with perhaps the index $ n $ augmented with a spin index, $ \sigma $. If there is electron-phonon or electron vibration interaction, we expand the matrix elements $ \epsilon_n $ and $ t_{nm} $ about the equilibrium positions of the
lattice and keep linear (and sometimes quadratic) terms. The linear electron phonon terms can be written

\[ H_{ep} = \sum g_{n\lambda} a_n^+ a_n (b_{\lambda} + b_{-\lambda}^+) + \sum f_{nm\lambda} a_n^+ a_m (b_{\lambda} + b_{-\lambda}^+), \]

where \( b_{\lambda} (b_{\lambda}^+) \) destroys(creates) a phonon of index \( \lambda \), and \( g \) and \( f \) are coupling constants, describing site diagonal and site off-diagonal interactions. Finally, there is a term in the hamiltonian, important for electron and hole bands, but not for exciton bands, representing the interaction between electrons or excitations:

\[ H_{corr} = \sum U N_n (N_n - 1) + \sum V(n-m) (N_n - 1)(N_m - 1) \]

where \( U \) represents the on-site interaction between electrons, \( V(n-m) \) represents the intersite interaction between electrons, and \( N_n \) represents the number of electrons on site \( n \). In this description of the system, we have neglected static disorder, which can be made small, but never removed from these systems.

In the nearest neighbor approximation, relevant for some of the low lying electronic states (especially the triplet states) of these crystals, the transfer matrix elements, \( t_{nm} \), are replaced by the values to the near neighbors, and all others are set to zero. Since the \( t_{nm} \) are not equal in all directions, the reduced dimensionality of the exciton bands becomes evident at this point, and the bandwidth, \( B \), is equal to \( 2\Sigma t_i \), where the sum is over the nearest neighbor directions, and \( t_i \) is the transfer matrix element in the ith direction. For one-dimensional bands, the bandwidth is \( 4t \), etc. The bandwidth term in the hamiltonian tends to delocalize the wavefunction, while the electron phonon terms, which represent scattering of the electron by the phonons (or vibrations) tend to localize the wavefunction and decrease the effective bandwidth. In addition, in low dimensionality the latter may distort the structure of the lattice (Peierls transition)[3]. The correlation terms add another complication. \( U \) tends to keep electrons apart, spoiling the simple band or molecular orbital picture, and when large, can decrease the effective bandwidth.

This hamiltonian has been discussed by a number of authors for the case of exciton bands in molecular crystals [4,5,6], and has
been applied to study a variety of properties in these systems. As mentioned above, the application to electron and hole conduction in these systems has been less successful (but see ref [7,8]).

III. Polyenes, polyacetylene, and all that: The polyenes, short chains of alternating C-C single and double bonds have been studied by chemists for about 50 years[9,10]. Of particular interest has been the evolution of the optical band gap, or the energy difference between the ground and first dipole allowed excited state. The theoretical description of these molecules has gone from the free electron model, to the Hückel model, through the Pariser Parr Pople (PPP) semi-empirical model, and finally, at least for short chains, to ab-initio quantum chemical calculations. Along the way, it has become dogma, at least to the physical chemists studying these molecules, that the simple description afforded by, for example, Hückel theory, is inadequate. This is so largely because of the inability of the Hückel model to describe the other excited states of these molecules, in particular the triplet or radical states (where the spin densities are given poorly) and the famous second $^1A_1g$ excited state (discussed by Kohler in these proceedings). The latter can be described in a one electron molecular orbital picture only as a double excitation with a large amount of configuration interaction. To treat these correctly, it has become necessary to consider the correlation term carefully.

The Hückel model corresponds to keeping equ(2) as the Hamiltonian for a polyene, where only the $p_z$ ($\pi$) electrons are considered, one per site, and the sigma electrons form part of the core which is unaltered upon excitation of the $\pi$ electrons. The addition of the electron phonon coupling, equ (3), yields the Su-Schrieffer-Heeger (SSH) [11] Hamiltonian for polyacetylene. Addition of equ (4) to equ (2) yields the Hubbard ($V=0$) or extended Hubbard models($V\neq 0$). The sum of equ (2), (3) and (4) for a given geometry (i.e. so the phonon variables are fixed) is the PPP model, recently treated exactly (albeit, numerically) by Soos[12] for chains up to 14 carbon atoms. At the present time, there is no evidence to believe that it is wrong to extrapolate the results of the small molecule calculations (or experiment) to the long chains (presumably in polyacetylene samples). This implies that to understand the properties of polyacetylene, one must treat the correlation terms explicitly and carefully. Thus polyacetylene
becomes a system with three competing interactions: the electron bandwidth $B$, the electron phonon coupling energy $S$, and the correlation energy, $U[13,14]$. This is a hard problem: for example the optical band gap with both correlation effects and Peierls effects (bond alternation) is not known in general, but is known numerically for short chains, and perturbatively for long chains. In addition, the bond alternation as a function of correlation energy is a non-monotonic function of $U$, indicating the complexity of the problem.

IV. Conjugation Lengths and Optical Properties: In studying non-conjugated molecules, it has been possible to treat most properties as bond-additive. That is, the polarizability, for example, of a small molecule can be found by adding (tensorially) the polarizabilities of all the bonds in the molecule. This is not true for conjugated molecules. The strong coupling of the $p$ electrons in an all trans planar polyene leads to a qualitatively different polarizability from the sum of single and double bond polarizabilities found from non-conjugated molecules. In fact, for short polyene chains the polarizability increases non-linearly with the size of the chain, $n$. This can not go on indefinitely as $n$ increases: on some length scale, the $p$ electrons are no longer strongly correlated, and the polarizability increases linearly with the size of the system. This length scale can be associated with the conjugation length. This raises interesting questions: How do we define conjugation length?, What are the physical factors limiting conjugation length?, Is there a different conjugation length for different properties? In this section, we give partial answers to these questions; however, a general formulation of these has still not been worked out.

First, we present a very qualitative argument, due to Ducuing [15], for the length dependence of the polarizabilities, linear and non-linear, for these one dimensional systems. The perturbation formula for the zero frequency polarizability along the chain ($x$) axis is

$$\alpha_{xx}(0) = (2e^2 / \hbar) \sum |\langle 0 | \hat{x} | f \rangle|^2 / \omega_f$$

where $\langle 0 | \hat{x} | f \rangle$ is the matrix element of $\hat{x}$ ($= \Sigma x_i$, the sum being over all electrons) between the ground state and the $f$th excited electronic eigenstate of the molecule in the absence of the field, and
\( \omega_{fo} \) is the frequency (energy) difference between those states. The problem is to find the dependence of \( \alpha_{xx} \) on \( n \), which is both the number of electrons and the length of the chain. Both the matrix element and the frequency are functions of \( n \). A useful approximation is to replace \( \omega_{fo} \) by an "average", \( \bar{\omega} (n) \), and then do the sum, to find

\[
(6) \quad \alpha_{xx}(0) = \left( 2e^2 / \hbar \bar{\omega} (n) \right) \left( <0| \hat{x}^2 |10> - <0| \hat{x} |10>^2 \right)
\]

For small \( n \), the ground state will be extended over the entire chain, so we expect \( <0| \hat{x}^2 |10> \) to be \( O(n^2) \), while for large \( n \), we expect it to be \( O(n) \). In addition, we expect that \( \bar{\omega} (n) = \omega_0 + A/n \), since the band gap scales in this manner. This suggests that \( \alpha_{xx}(0) \sim n^2 - n^3 \) at small \( n \) and \( \sim n \) at large \( n \). If we manipulate the oscillator strength sum rule

\[
(7) \quad \Sigma \langle 0 | \hat{x} | j > |^2 \omega_{fo} = (n\hbar / 2 m) \]

in the same way, we have

\[
(8) \quad \bar{\omega} (n) <0| \hat{x}^2 |10> = (n\hbar / 2 m) \]

Solving (8) for \( <0| \hat{x}^2 |10> \) in terms of \( \bar{\omega} (n) \) and substituting into (6) yields

\[
(9) \quad \alpha_{xx}(0) \approx \left( e^2 / m \right) \left\{ n / [\bar{\omega} (n)]^2 \right\}
\]

which gives \( \alpha_{xx}(0) \sim n^3 \) at small \( n \) and \( \sim n \) at large \( n \) (if \( \omega_0 \neq 0 \)). The length at which it saturates can be called the conjugation length.

A similar argument for \( \gamma_{xxxx} \), the second hyperpolarizability yields

\[
(10) \quad \gamma_{xxxx} \sim \left\{ <0| \hat{x}^4 |10> - 2<0| \hat{x}^2 |10>^2 \right\} / [\bar{\omega} (n)]^3
\]
which is $O(n^4)$ to $O(n^7)$ at small $n$ to $O(n)$ at large $n$. The length scale at which saturation occurs is the conjugation length for $\gamma$. These arguments are very qualitative; however, as a guide to what to expect from the calculation, they are surprisingly sensible.

In the last few years, a number of groups [16,17,18,19] have calculated $\alpha_{xx}$ and $\gamma_{xxxx}$ for all trans polyynes, some using the PPP model (in various approximations[16,17] or exact numerical methods[18]) and some using ab-initio techniques [19]. The results are interesting, and for the most part in agreement. It was found that $\gamma \sim n^\mu$ with $\mu \sim 4$-4.5 in agreement with our qualitative guide above, and in quite good agreement with the experimental values of $\chi$ ($\sim \gamma/n$). These calculations show that saturation sets in for $\alpha$ at about 15 double bonds. However, the calculation of $\gamma$ shows little evidence for saturation up to $n = 20$ (with different authors interpreting these signs slightly differently). So the theoretical situation at present is that perfect all trans chains of polyynes have conjugation lengths larger than about 15 double bonds, but perhaps not much larger.

Another important theoretical issue is the effect of various motions of the chain on these properties. Although this has yet to be addressed directly, recently a calculation appeared[20] of the average angle between $p_z$ orbitals down an all trans chain as a function of $n$, T and torsional potential. The basic physical picture is that the torsional oscillations of the chain will make, on average, the $p_z$ orbitals be less and less conjugated at large separations. Using the available experimental data on torsions, it was found that the angle or a function of this angle, fell off with distance as $\exp(-L/L_C)$. This length scale, $L_C$, was associated with the conjugation length. For polyynes, the prediction is that this length is on the order of 15 double bonds at room temperature, and smaller as T is raised. Note that the coincidence of this conjugation length with the saturation length in the polarizability is fortuitous, as there is no hard connection made between them. For polymers such as polythiophene and polypyrrole, $L_C$ is much smaller, on the order of a few rings at room temperature. Details can be found in ref [20]. If the connection between this length and the saturation length of the polarizability and hyperpolarizability can be made firmly, this suggests a simple way to describe the correlations in these conjugated systems. However, it is clear that the role of torsions
and other motions is important and perhaps limiting. Clearly they should be the focus of more study.

V. The Theoretical Outlook: In my view, the theoretical problems for the study of non-linear optical properties in one-dimensional conjugated polymers in the immediate future are: i) the effects of substitution by electron donating or withdrawing groups, ii) the effects of geometric and electronic defects, including solitons, polaron, and bipolarons, iii) vibronic effects, including a more careful study of torsional motion, and iv) the effect of the solid state (local field effects and chain-chain interactions). Because of the competing interactions and one dimensionality of these systems, all of these must be taken into account before a true understanding of the non-linear properties can be found.

Acknowledgements: This work has been supported in part by a grant from the NSF.

References:


1. Oxidative coupling

1.1 CHEMICAL

In 1961, Konia and Kyriakos described the preparation of polymer films with a low number of constituents from benzene in the presence of AlCl3/C6Cl4(1). This method was expanded in terms of reaction conditions and monomers employed with the result that dehydrogenation of aromatics to be recognized as the general

-C-C- bonds. It begins with oxidative coupling, which at
the start of the 1970s developed through the different
stages of polyaromatic and polyheteroaromatics to
conclude in electrically conducting polymers. Subsequent
chapters embrace vinyl polymers, cycle-condensations and
the formation of aromatic complexes, e.g., of
polyaromatics. Chemical polymerization has been used to
dramatically increase molecular conductivity. Electro-
neutral catalysts and solvents allowed the creation of
metals permit a very wide variety of polymers to be
synthesized. The application of, for example, pseudoperi
reactions has led to variable areoplymers and clearly to
characterized polymers. The article finishes by
considering the synthesis of polymers that have been
oriented by mechanical stretching, the direct preparation
of oriented polymers by matrix polymerization and the
preparation of transparent materials.