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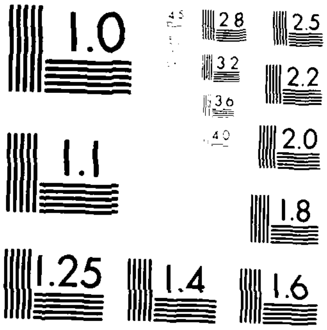

MICROCOPY RESOLUTION TEST CHART

Polymer Engineering:

Polymeric and Molecular Electronic, Dielectric and Optical Properties for Device Applications

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Introduction

The technology of using polymers and molecules for device purposes is an emerging technology. There is no body of knowledge which can provide a manufacturer with a complete guide to that use at the present time. Despite this lack, which exists with every emerging technology, there is certainly a large body of knowledge providing background to the main thrust of the field. That body of knowledge is provided by the theoretical physics and chemistry of polymers and molecules. Successful engineering applications will result from the judicial use of that theoretical knowledge.

There is certainly a great deal of activity in the technology field (see (C1)). However, there do not seem to be distinctive "lead horses" which have broken away from the main pack. For example, in a recent conference on optical processing (see (C2)), there seemed to be as many optical processor "hobby horses", or approaches to optical processing architecture, as there were participants. Yet there remains a conviction that optical processing, which will rely on polymer engineering for its actualization, is an important discipline. The young field is extremely robust but has just not thinned out yet. Nor may it ever. Each device architecture may be specific to each application.

There is also the issue of whether materials with nonlinear susceptibility of organic *or* inorganic origin are preferable for use in optical devices. In the same university or company one can find champions of both types of materials. A decision concerning this issue will be decided case-by-case on the basis of performance and economics. Optical phase conjugation using the third-order nonlinear susceptibility of organics/inorganics offers phase conjugate mirrors for "time-reversed" signal clean-up, for optical amplification and optical fiber busses which do not deplete the energy of the signal carrying wave. Without deciding exactly *which* class of *materials* will provide the nonlinear optical properties required, one can nevertheless see an important use for the *devices* which rely on those properties.

There are a number of thrusts in polymer science which, if not yet "lead horses", do show a great deal of potential. One example is the pyrolized or ekaconjugated polymers which show promise for applications to dielectrics, high-frequency capacitors and remanent magnetism (Pohl and Pollak, 1977; Vijayakumar & Pohl, 1984). Another is the charge-transfer salts which show promise for applications to light-addressed memories and analog-digital processing (Potember and Poehler, 1983). It is expected that both of these programs will be readily transferable to applications.

In the field of information processors, polymers will have a major impact just as soon as it is realized that an enormous versatility can be obtained in information processing architectures if those architectural designs are an emergent from a match of polymeric material capabilities and the task to be performed. The physics of polymer and molecular dynamical function offers textbook design mechanisms for non-von-Neumann processing, information fusion and content-addressable resonance interaction. The enormous variety of polymer and molecular dynamics offers an even greater variety of architectural designs once the mind-set is discarded of the classical digital-switch as the only building block for architectures. New polymer-based architectures offer more efficient analog transformations and simpler, more robust architectures dedicated to function. Optical (boson) processing, unlike electronic (Fermion) processing, [illegible] also resistant to electromagnetic interference.

The use of laser-induced chemistry, chemical synthesis techniques, Langmuir-Blodgett monolayer self-ordering and precision chemical reaction doping, offer chemical device fabrication and lithographic techniques with advantages over current etch lithography. Precision in the achievement of electron mobilities and Fermi-levels can be obtained with chemical synthesis of donor-acceptor compounds. Multiple-quantum-well structures can also be achieved with monolayer techniques and electrodeposition.

The fields of polymer and molecular physics and chemistry offer an enormous variety of material properties usable in polymer engineering. Presently, there is a requirement for fundamental studies of (a) barriers made from thin films and (b) methods to achieve molecular order. The use of electric and magnetic fields in polymer processing for ordered materials is a subject under study.

In the first five chapters the theoretical physics and chemistry which underpin device function is introduced. Chapters six to nine address the problems of material organization. Chapters ten to fifteen address applications. An attempt has been made in these chapters to indicate the possibilities and opportunities in this emerging field, but, at the same time, to indicate the difficulties. There are roses to be picked in this field, but they are surrounded by thorns. Guarding against scratches, however, does not seem impossible.

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(C1) **Basic Properties of Optical Materials**, National Bureau of Standards, Gaithersburg, Maryland, 7-9 May 1985.

(C2) **Topical Meeting on Optical Computing**, March 18-20, 1985, Incline Village, Nevada, sponsored by the Optical Society of America, the Computer Society of the Institute of Electrical and Electronics Engineers and the Society of Photo-Optical Instrumentation Engineers.

(C3) **The 3rd International Conference on Solid-State Sensors and Actuators (Transducers '85)**, sponsored by the IEEE Electron Devices Society and the Electrochemical Society, Philadelphia, 11-14 June 1985

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I Polymer Semiconductors

In 1964 Little suggested the possibility of synthesizing a polymeric, organic conductor of high transition temperature. The mechanism suggested for achieving this superconductivity at room temperature was an electron-electron coupling or one involving the exchange of molecular excitations instead of phonons. The suggestion was thus named an "exciton" mechanism (Ginzburg, 1968) and can be contrasted with the BCS theory involving electron pairs coupled to phonons. If not at room temperature (but at 0.9^0 Kelvin), the first organic superconductors have at least appeared. They consist primarily of stacks of tetramethyltetraselenafulvalene (TMTSF), the molecules of which are said to be donors in that they tend to give up their valence electrons. Crystals are grown in which the TMTSF molecules are adjacent to acceptor ions, and they have paths of easy electrical conduction which are essentially molecular corridors. Along the favored direction, an electron is scattered approximately once every 1000 molecules, which is ten to twenty times less frequently than in a typical metal. These materials are now known as Bechgaard salts.

The search for the true room temperature superconductor continues (Little, 1983), but in the meantime, polymeric organic semiconductors and metals and even organic superconductors of moderately low transition temperature (Jerome et al., 1980; Chaikin et al, 1983) have come along. The first organic compound shown to display metallic conductivity is also now intensively studied (tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)).

It has been known for many years that organic molecules can be semiconductors (Kallmann & Silver, 1960; Gutman & Lyons, 1967; Katon, 1968; Meier, 1974; Kao & Hwang, 1981; Pope & Swenberg, 1982; Seanor, 1982) but sustained interest began with the experimental studies of dark conductivity in phthalocyanines by Eley (1948) in England and Vartanyan (1948) in the Soviet Union. The phthalocyanines (Moser & Thomas, 1983) and the porphyrins (Lever & Gray, 1983) continue to be of interest and so does photoconductivity (Bube, 1960). The organic conducting field in general has attracted numerous investigators and some of the important results have been summarized in recent reviews (Wegner, 1981; Baughman et al, 1982; Simionescu and Perec, 1982; Duke & Gibson, 1982; Etemad & Heeger, 1982).

There will continue to be theoretical difficulties in the treatment of polymer semiconductors. This is because the conductance is dependent upon delocalized pi-orbitals, which are treated by many approximation methods with varying degrees of success, e.g., valence band theory, molecular orbital theory, free electron theory, etc. It is instructive, therefore, to trace the development of free electron theory and note the problems still to be solved.

In the 1920s the band theory of crystals was developed resulting in the Bloch scheme describing independent motion of charge carrying electrons and holes. In 1931 the concept of exciton arose (Frenkel, 1931; Peierls, 1932), which is an electronic excitation wave which does not carry electric current - but does carry energy - and involves correlated motion of electrons and holes. Excitons have been found in all basic types of nonmetallic crystals, as well as certain rare earths and intermetallics. There are three basic types of excitons: (1) the **Frenkel type**, which have no energy levels; (2) the **charge-transfer type**, where an electron exists on a different atom to a hole; and (3) the **Wannier type** (Wannier, 1937), where there are energy levels of charge transfer in analogy to the energy levels of the hydrogen atom. Excitons can be associated with any critical point in the band structure, the criterion for existence being that the electron and hole have equal velocity.

A related concept is that of **polaron**, which had an initial meaning of an electron interacting with long-wave optic vibrations. The wider meaning is now of a self-trapped electron or exciton and it is this meaning which is used in descriptions of conduction in organics with nondegenerate ground states. Another concept is that of **polariton**, which arises when an e.m. field interacts with an exciton in a very specific way. The conditions for this interaction come about because the exciton has a polarization which can be either longitudinal or transverse and only the transverse exciton can interact with the e.m. field. The polariton is created by an exciting photon and the transverse exciton mix in a crossover region, both losing their identity in a combined particle of the polariton.

If one wishes to study polymeric semiconduction, one should be aware at the start that there is even a difficulty in knowing, theoretically, what is meant by **semiconduction**. For the delocalized states of the pi-electrons there are a number of theories of carrier transport, all of which have advantages and disadvantages (Kao & Hwang, 1981). For example, there is the **energy band model** - which is only appropriate for high mobilities. Then there is the **tunneling model** - which has failed to explain negative temperature dependence of mobility and the difference between electron and hole mobilities. Or the **hopping model** - which only succeeds if the electron-phonon interaction is strong. Or the **polaron theory** - the validity of which is in doubt for the cases in which the interaction between electron and surroundings depends on electron velocity. There is also a fundamental difference between semiconduction in inorganics and organics. It is known that the basic mechanism of charge transport depends on the nature of the electron exchange interactions and the electron phonon interactions. Whereas, on the one hand, in inorganic semiconductors the electron interactions are much larger than the electron-phonon interactions, so that the electrons behave as quasi-free particles occasionally scattered by phonons causing the charge transport to be coherent, in organic semiconductors, on the other hand, the electron exchange interactions are much smaller, while the electron-phonon interactions may be the same, so that electron-phonon interactions may dominate. There are further difficulties.

For example, in order to describe the dielectric susceptibilities of these organics there are a variety of models, e.g., the resonance oscillator model and the self-consistent solution model. Unfortunately, there is no single unique form for the **spatially dispersive dielectric function**. In 1957 Pekar, in the Soviet Union, pointed out the wave-vector dependence of the dielectric response function. This means that the constitutive relation between induced polarization and inducing electric field is **not spatially local**. The determination of the correct linear combination of exciton-field can be reduced to a boundary value problem, which is known as the problem of **a**dditional **b**oundary **c**onditions or the "**abc problem**". The origin of this problem (of nonlocality) is due to the propagation of the excited state.

So the desired characteristic of excitation propagation due to delocalized electrons brings with it theoretical intransigence. There are theoretical attempts on the abc problem, e.g., the "semimacroscopic solution" of Pekar and the Hopfield and Thomas (1963) solution, but each is based on unverifiable assumptions and is also macroscopic, so a complete solution must await the development of **combined Maxwell-Schrödinger equations**. Attempts in this direction include Zeyher et al (1974) and Hyzhnyakov *et al* (1975), both having found limited success (Birman, 1982).

There are two types of conducting polymers (Wynne & Street, 1982). The first category is a category of one - $(SN)_x$, which is an **intrinsically conducting polymer**, and the only one. $(SN)_x$ has open shell electronic structure and has metallic conductivity. The more numerous second class includes those in which the pi-bonding system, (not the closed valence shells), have been modified by oxidation or reduction. Oxidation leads to a partial emptying of previously filled bands, while reduction leads to partial filling of previously empty bands giving rise to p- and n-type conductivity, respectively. The conducting polymers include: poly(sulfur nitride), polyacetylene, poly(1,6-heptadiyne), polypyrrole, polythiophene, poly(p-phenylene), poly(p-phenylene sulfide), poly(p-phenylene vinylene, poly(pyrrole tetrafluoroborate) and bridge-stacked phthalocyanines.

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II Physical Bases of Excitons

A half a century ago the concept of exciton was conceived and since then there have been many attempts to refine the concept with work still in progress (Rashba & Sturge, 1982). However, there are few unambiguous experiments which demonstrate the most important property of the exciton, namely its ability to transport energy over large distances (large in comparison with atomic dimensions). We shall commence then with some definitions of what an exciton is. It is:

(1) a quantum of electronic excitation energy traveling in a periodic structure, (nearly impossible to achieve empirically), whose motion is characterized by a wave vector (Dexter & Knox, 1965).

(2) a particle able to transfer energy, but not charge, in "wave packets" of excitation. Concerning this latter one may observe that although there are experiments to show that an exciton moves, there are none to show how far it moves. Given these definitions, and comments, the reader will realise immediately that the concept of exciton is an idealised theoretical one. However, if the exciton concept is not actually an observable one, then there are, at least, many experiments requiring interpretation which urgently need to invoke its explanatory power.

Probes of excitons in semiconductors include resonant Raman and Brillouin spectroscopy (Yu, 1979), and the nonparamagnetic nature of electrical conduction in most polymers indicates the existence of charged Bose particles which may be excitons or polarons or bipolarons (Brazovskii & Kirova, 1981). From the theorist's point of view, the field is a unique meeting place of transport theory from a non-equilibrium statistical mechanics orientation, which addresses the movement of the excitons, as well as the interaction of light with matter and the creation and radiative decay of excitons (Kenkre & Reineker, 1982). A current major theme of exciton theory is the development of an account of the absorption of light in materials (Davydov, 1962; Knox, 1963, 1983).

More recently, a new field has been created for the study of excitons at high density in semiconductors (Haken & Nikitine, 1975). These consist of hydrogen-like excitons which are made up of an electron in the conduction band and a hole in the valence band coupled together by Coulomb interaction and perhaps modified by polarization effects. The creation of high concentrations of excitons (by shining laser light on insulating crystals) has resulted in the study of different species of excitons. There are excitonic molecules ("biexcitons"); possibly Bose condensation of excitons; possibly such condensation of biexcitons; electron-hole droplets which are bound mainly by Coulomb exchange interaction between electrons and holes; possibly polyexcitons and even "crystal-type" excitons in which a quantum crystal is formed within a crystal. All of such species are possible, because the mass ratio between the exciton and hole may vary over a wide range.

Returning now to the theoretical underpinning for the concept, and assuming purely electronic states in perfectly periodic systems, the two major images of a solid, namely, the "tight-binding approximation" and the "Bloch description" both lead to the conclusion that there must exist low-energy, excited states of insulating crystals. The "tight-binding approximation" picture is of a periodic array of atoms or molecules. The "Bloch description" emphasizes electrons traveling around in a periodic potential provided by the positive nuclei. In biological structures, only chlorophyll arrays have shown clear-cut evidence of delocalization of electronic energy, perhaps some nucleic acids, and perhaps also, the purple membrane of some salt-loving bacteria (Perlstein, 1982). Excitons confined to a single molecule without charge-transfer and without energy levels are Frenkel excitons, and intramolecular vibrational excitations may be considered as vibrational Frenkel excitations (Belousov, 1982). Such excitons may also be of importance in conduction in organics.

For example, associated with the charge-density wave in organics is a localized electronic state or states within the bandgap. Before doping, the organic polymer is sometimes paramagnetic, indicating the existence of spin. The rationale is that if the localized state contains one electron, a soliton (or charge-density wave) is neutral, with spin 1/2, and therefore is paramagnetic. On the other hand, if the localized state is empty (doubly occupied) the soliton is positively (negatively) charged, with spin 0 and nonmagnetic. Therefore: doping results in conductivity or the ability to transfer charge, an absence of spin (the socalled charge-spin exchange), and effectively a "hole" or "holes" created in the bandgap. If these "holes" are paired with electrons of the dopant, then one has a type of exciton. This would necessarily stretch the definition, as in the past the concept of exciton has been associated with energy transfer but not charge.

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III Soliton Physics and Quantum Engineering

In 1977 Shirakawa et al demonstrated that the conductivity of polyacetylene can be increased thirteenfold on doping with either electron-accepting or electron-donating substances (Shirakawa et al 1977; Chiang et al 1977). Previously, organic polymers were largely considered to be insulators. The demonstration of electrical conductivity in organics is especially noteworthy for two reasons. The first is that a whole new class of conducting compounds is becoming available which can be tailored to specific requirements, have the potential for being the basis for electronic device miniaturization, and also the potential for conductivity for minimum heat generation. The second, which is the main topic of this section, is that the way these organics conduct has been described using a new **nonlinear analytical mechanics** itself only developed to any degree in the last twenty years. The development of this new nonlinear mechanics is itself an extensive topic with impact on many diverse fields quite apart from electrical conduction in organics. In fact, acquiring a familiarity with this mechanics, a mathematical development, is not trivial. The situation is further complicated by the fact that the new mechanics has found application in **two distinctly different examples of conduction** in organics: charge conduction, e.g., in doped trans polyacetylene (for energies above 0.45 e.v.; Chen, 1984a), but also in the postulated vibrational energies (0.2 e.v.) conduction-without-decrement in proteins and perhaps DNA. As the vibrational soliton, also known as the **Davydov soliton** (Davydov, 1977-80; Scott, 1981) is concerned with the transfer and conservation of energies presently not usable in microelectronics, this development will not be considered further here, even although the topic is important in other contexts.

In order to consider the current theories of charge density wave conduction in organics which should find application in future microelectronic designs and which implicate the nonlinear wave mechanics aforementioned, it is necessary to digress into mathematical considerations for a while. This digression is intended to quickly define what a soliton is, but with the caution that the implications of the concept are very extensive and still being drawn. A quick definition might be that a soliton is a normal mode of a nonlinear system and may be compared and contrasted with cisoidal functions (sines and cosines), which are normal modes of linear systems. A comparison may also be drawn between the **inverse scattering transform** (and its turn-of-the-century predecessor, the **Bäcklund transform**) and the Fourier transform. The former commences with a system describable by a **Pfaffian form** of a partial differential equation and derives soliton solutions, the latter commences with a non-Pfaffian form of a partial differential equation and derives cisoidal solutions. In fact, the

[illegible]

[illegible] *nonlinear case* [illegible] the [illegible] **Korteweg de Vries equation** [illegible] sine Gordon equation [illegible] the nonlinear **Schrodinger equation** [illegible] *linear case* [illegible] the [illegible] Schrodinger equation [illegible] the equation [illegible] really [illegible] **the (intensity dependent) nonlinearities of the system are in balance with the frequency dispersion.** A further interesting property [illegible] each other and yet preserve their [illegible] This property is related to the [illegible] integrability.

[illegible] solitons, a term coined by Zabusky and Kruskal [illegible] if they exist in a system, have a special property of interest to anyone designing small circuits with conducting elements of minimum heat loss. This property is that energy is conserved in the balance of nonlinearity and dispersion and energy is only lost to the system in [illegible] which are purely dispersive and cause radiation. Thus an ideal soliton-type conducting mechanism conducts decrementlessly. Even although the soliton is a generic concept, any conducting mechanism which only approximates its description will suffer radiation loss in inverse proportion to that approximation.

We are not through with this mathematical digression. One of the partial differential equations mentioned above which describe systems amenable to soliton solutions was the sine-Gordon equation. This equation can represent **topologically invariant quantities** in a system, for example, in polymers which may change bonding arrangements but which remain, under left-right transformation, the same. Such polymers have degenerate ground states. Another invariant property would be **a moving domain wall** or a dislocation in a crystal. Solutions of the sine-Gordon of this type are solitons which are sometimes called **"kinks"**.

After that digression we may pick up again the polymer physics. Undoped trans-polyacetylene was described by Su et al (1979, 1980) by an harmonic approximation Hamiltonian of the simple Huckel type. A neutral or uncharged perturbation was introduced to the Hamiltonian system description to describe the mechanism for carrying charge when charge is introduced. Then, as a trial function (Ansatz) for the order parameter, Su et al proposed a kink and anti-kink pair. Here, then, is where the new method is applied to the new empirical observations of conduction in organics. One may also observe that the terms conduction band and valence band, well known and well used in describing conduction in, for example, metals, take on a different, if analogous meaning in (for trans-polyacetylene) they refer to the two degenerate ground states. There is thus an analogy, but the physical mechanisms of conduction in metals and organics and semiconductors are different.

When one reads, therefore, that trans-polyacetylene at certaint dopant levels "conducts like a semi-conductor", or, at other dopant levels "conducts like a metal" one should keep in mind that, whereas analogies can be made on the basis of a band structure model, for example, between metals, semiconductors on the one hand and organics on the other, at the physical mechanism level, on the other hand, all three are different. And again: whereas it makes sense, when the temperature-dependence of the conductivity of highly doped trans-polyacetylene is considered, to call such an organic a "synthetic metal", at the level of the physical mechanism, (dependent upon degenerate states in the case of trans-polyacetylene and energy differences between filled and unfilled electronic levels in the case of the metal), the physical mechanism is nonetheless different. Nor should degenerate ground states be considered the defining attribute of organic conductors, as examples will be noted below of organic conductors without degenerate ground states. Furthermore, the soliton mechanism itself is currently **not** considered to be the ***sine qua non*** of organic conduction at **all** dopant levels and in **all** organics (see Chien, 1984b). And finally: the term soliton, which can be defined so rigorously as a **moving, dynamic mathematical entity**, is sometimes used in the literature to refer to a **stationary dislocation**. The reader may, at least, remain assured that organics do, indeed, conduct (even with conductivities as high as 103 (ohm cm)$^{-1}$), and await a completed theory of conduction so necessary to crafting of polymer to function.

Now, the Hamiltonian derived by Su et al (1979,1980) which was written in terms of creation and annihilation operators and is now known as the **SSH Hamiltonian**, can be rewritten in the partial differential equation form to obtain the continuum limit (Brazovskii, 1978, 1980; Takayama et al, 1980). From this Hamiltonian one obtains a pair of **Bogoliubov-de Gennes equations** (kinetic equations) the solution of which is the total mean field energy. Campbell and Bishop (1981; 1982a,b; Bishop, 1980) observed that these Bogoliubov-de Gennes equations demonstrate that the conduction mechanism is **polaron-like**. Using the analogy of the relativistic-field-theory of Gross and Neveu (Gross & Neveu, 1974; Dashen et al, 1974, 1975a,b, Andrei & Lowenstein, 1979), they further demonstrated that the Su et al (soliton) kink-anti-kink pair has a single electron spectrum with two states symmetrically placed at the band-gap. These states only exist when there is a single unpaired electron occupying the localized "electron or negative" state, or when there is a single unpaired electron occupying the other localized "hole or positive" state. As the electron (or the hole) is trapped in the lattice and coupled to phonons, the excitation is polaron-like. The polaron is a much studied entity in physics and hence the novel conduction mechanism was given a familiar description.

The soliton mechanism for conduction is unidirectional and hence, for oriented polymers, conduction anisotropy is to be expected and has been observed. However, other conduction mechanisms are involved and Kivelson (1981a,b, 1982) proposed an "intersoliton" conduction mechanism, (or, for the rigorous-minded: an "inter-stationary-domain-wall" conduction mechanism). The theory requires the presence of both a charged soliton and a neutral soliton (i.e., stationary dislocation) being situated near a dopant ion or "impurity site".

So far we have considered electrical conduction in trans polyacetylene, an organic which has two degenerate ground states. Electrical conduction can also occur in organics with nondegenerate ground states. The mechanism is due to charge transfer taking place between the organic polymer and the dopant. As a result the polymer becomes ionized and the equilibrium geometry in the ionized state is different from that in the ground state creating a **Franck-Condon-like ionized state**. If no lattice distortion or geometry relaxation occurs, then a hole is created in the valence band, or, in other words, an electron is created in the conduction band (Brédas, 1984). If it is energetically favorable to localize the charge on the polymer chain then a local distortion of the lattice occurs, resulting in the appearance of localized electronic states in the bandgap which appear as polarons or radical-ions (spin 1/2). The polaron binding energy is 0.05 e.v. in trans polyacetylene (Brédas et al, 1982), 0.03 e.v. in polyparaphenylene (Brédas et al, 1982) and 0.12 e.v. in polypyrrole (Bredas et al, 1984a). When two charges are present on a polymer chain with nondegenerate ground states, the formation of a bipolaron is energetically favored. (A bipolaron is defined as a pair of like charges (diion) associated with a strong lattice distortion). However, because trans polyacetylene has a degenerate ground state, two charges can separate to lower the electrostatic repulsion and form two isolated charged solitons rather than a bipolaron (Su et al 1979, Rice, 1979). Thus, trans polyacetylene has been considered to be **a special case** of a conducting polymer rather than a prototype (Brédas, 1984). There are theoretical predictions of a new class soliton-supporting polymers, polyarenemethides, which also possess degenerate ground state bonding patterns (Boudreaux et al, 1985).

This view clearly distinguishes between the mechanism of the creation of states in organic and inorganic material. Whereas in the organic polymer the localized electronic states in the bandgap are created by charge-transfer-induced modifications of the pi electronic system of the polymer, and are thus intrinsic to the organic polymer. In doped inorganic semiconductors, on the other hand, the states in the bandgap are dopant levels (Brédas et al, 1984b). In the case of p-type doping of organics, the bipolaron levels in the gap are empty. Conversely, in the case of n-type doping of organics, the bipolaron levels in the gap are fully occupied. The bipolarons are thus spinless.

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IV Photon Molecular Switching

IV.I. Bistable Molecules and Photon Switching

Optical bistability requires some combination of microscopic nonlinearity with some microscopic feedback. We shall first consider nonlinearity in polymeric materials and then address how the feedback may be achieved.

Recent developments in the field of nonlinear optics hold promise for applications in optical information processing. This field has emerged from solid-state physics and has become of great interest since the realization that organic and polymeric materials with very large delocalized pi-electron systems can exhibit extremely large nonlinear responses ($chi_{(3)}$, for example) - larger, in some instances, than those of most inorganic materials. It is now recognized that thin films of organic materials with even second-order nonlinearities offer the possibility of novel phenomena and devices for laser modulation, frequency conversion, deflection, power limiting and information control in optical circuitry. When large third-order nonlinearities are available, then **degenerate four-wave mixing** (DFWM) is possible for use in integrated circuits with for a variety of purposes. The physical mechanisms underlying the large responses of organics are different from those underlying the responses of inorganics (Williams, 1983). The origin of the nonlinear effects in organics is the polarization of the **pi-electron cloud** as opposed to displacement or rearrangement of nuclear coordinates found in inorganic materials. An additional benefit of this circumstance is that there is a potential use of organics in **very high frequency applications** (due to the relative fast response time of the electron cloud) versus the relatively slower response time of nuclear rearrangements (Franck-Condon principle).

The theoretical prediction that a particular polymer in bulk will possess large nonlinear character is difficult. This is because a theoretical analysis at the single polymer level is difficult to extrapolate to the macroscopic or bulk material. For example, the second order molecular hyperpolarizability is zero in centrosymmetric media and is related to the bulk material second order susceptibility through summations over the number of contributing atoms or molecules per unit volume corrected for contributions from neighboring molecular fields. Therefore, a molecule which is asymmetric and possessing a second order hyperpolarizability may still exist in a centrosymmetric crystal or a molecular environment in which orientations are averaged (liquid or amorphous polymer). The bulk material, in this instance, will exhibit a small second order susceptibility despite the large single molecular or polymer hyperpolarizability.

Despite this theoretical difficulty, the organics offer an empirical opportunity to tailor charge asymmetry and provide the polymeric conditions for radiation induced nonlinear effects in one part of the radiation spectrum but transparency in another.

Examples of optically nonlinear single crystal polymers possessing three-dimensional long range order include diacetylene (Garito & Singer, 1982), 1,6-bis(2,4-dinitro-phenoxy)-2,4-hexadiyne or DNP (McGhie et al, 1981) and 2-methyl-4-nitroaniline or MNA substituted diacetylenes known as NTDA and MNADA (Garito & Singer, 1982). Flytzanis (1983) has observed that in polyacenes and polydiacetylenes Pople-Walmsley (1962) defects can occur which are the conditions for soliton-type motion. The electron delocalization length determines the optical third order susceptibility of polydiacetylene and its dynamical behavior is dictated by soliton mechanics. These defects (optical solitons) can be created by excitation near the main visible absorption peak.

Such organics are, however, essentially one-dimensional and their unique properties arise from this one-dimensionality. The nonlinear response requires response times longer than 1-4 psec. which are the diffusion times of conjugation defects along the constraints of the polymer chain. In three-dimensional semiconductors, on the other hand, the response is almost instantaneous.

An interesting technique for the investigation of the third-order nonlinear susceptibility of multilayers of polydiacetylene has been reported by Carter *et al* (1983). This measurement technique has possible device applications. Polydiacetylene was deposited to a thickness of 5000 Å one monolayer at a time using the Langmuir-Blodgett technique on a silver overcoated grating etched on a silicon wafer. The third order effect was measured indirectly by its effect on the refractive index. The grating permitted coupling of a freely propagating laser beam into the planar waveguide structure formed by the polydiacetylene on the metal. The third order susceptibility is intensity dependent, so changing the intensity of the laser beam permitted the observation of a change in coupling angle to the waveguide mode. From this an estimate of the nonlinear index of refraction of the polydiacetylene near the absorption edge was obtained.

We turn now to the use of these organic nonlinearities in optical switches based on the principle of **optical bistability**. Optical bistability requires a combination of microscopic (material) nonlinearity, which we have already discussed, with some macroscopic feedback, so that a device's transmission depends upon the output intensity. This occurs when a nonlinear optical medium interacting with a coherent driving field has more than one stable steady state. Now, the nonlinearities discussed above are intensity dependent, thus it should come as no surprise that the current problems with optically bistable switches involve the difficulty of obtaining adequately fast switching times at sufficiently low powers or switching energy to make useful devices. Attempts to minimize switching energy have involved the use of Fabry-Perot resonant cavities (Agrawal & Carmichael, 1979; Gibbs et al, 1980; Agrawal & Flytzanis, 1981), but, of course, this increases the difficulty of fabrication.

The **quantum theory of optical bistability** has undergone some recent development (Drummond & Walls, 1981; Carmichael et al, 1983). The observation of bistability can occur either in the absorptive operation, or in dispersive operation with detuning of the laser and interferometer from the atomic transition. Cooperative effects in resonance fluorescence are also possible (Bonifacio & Lugiato, 1978; Bonifacio et al, 1979). Radiative and collisional damping of atoms and losses at cavity mirrors are modeled by coupling the atoms and cavity mode to thermal reservoirs resulting in a **Fokker-Planck equation** or **quantum-statistical treatment**. The theory remains, however, without empirical confirmation.

Recently, however, a new type of optical bistability has been discovered which requires only on a material whose absorption increases as the material becomes excited (Miller et al, 1984a). No mirrors or other external feedback are required, as the feedback is internal and positive. Furthermore, new electroabsorptive processes, larger than those in conventional semiconductors, are seen in room-temperature GaAs/GaAlAs **multiple quantum well (MQW)** material (Chemla et al, 1983; Wood et al, 1984). These new developments have been combined to make a hybrid version of optical bistability in which a micron-thick piece of MQW is used as both detector and electroabsorptive modulator (Miller et al, 1984b). With only a series resistor and a constant voltage bias added to a p-i-n diode (where i refers to the MQW material) the resulting device is referred to as a **self-electro-optic effect device (SEED)**. The switch is activated by incident light at a wavelength near the exciton resonance position for zero voltage across the diode.

With low optical power, nearly all the supply voltage of the SEED is dropped across the diode as there is little photocurrent. This voltage shifts the excitation absorption to longer wavelengths, i.e., lower energies, and there the optical absorption is relatively low. Increasing the optical power increases the photocurrent, reducing the voltage across the diode. This reduced voltage, however, gives increased absorption as the exciton resonances move back, resulting in further increased photocurrent. This can lead to regenerative feedback and switching. Switching time has been demonstrated in the nanosecond range.

There is a large family of organo-metallic compound semiconductors which possess threshold and memory switching. The electron acceptor molecules 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 11,11,12,12-tetracyano-2,6-napthoquinodimethane (TNAP) have been shown to produce electrically conducting solids with aromatic heterocyclics, as well as with alkali, and divalent transition metal counterions. The electrical conductivities of TCNQ and TNAP complexed with electron donors such as tetrathiofulvalene (TTF) have also been intensively investigated. Sharp changes have been reported in electrical conductivity due to phase transitions in both TCNQ and TNAP complexes induced by varying the temperature of the material. More remarkably, a ***reversible*** electric field (light or e.m. field) induced phase transition has been observed in films of either copper or silver complexed with the electron acceptors TCNQ, TNAP or other TCNQ derivatives (Potember et al, 1979-83; Poehler et al, 1984; Benson et al, 1983). This remarkable transition is accompanied by an abrupt increase in the electrical conductivity of the organic semiconductor when the applied field surpasses a threshold value. The highly conductive state remains intact as long as the field is present. On removal of the field, the system can either return to the high impedance state, or, if a voltage significantly higher than the threshold voltage was used to induce the highly conductive state, the material will remain in the low-impedance state after the applied field is removed.

For intermediate field strengths,. it is possible to operate a device using, e.g., Cu-TCNQ, as either a memory switch or a threshold switch by varying the strength or duration of the applied field in the low-impedance state. Although the limiting speed of response is not presently known, a Cu-TNAP sample was able to switch and follow the rise time of a 4 nanosec. pulse (Potember & Poehler, 1982). It has also been demonstrated that optical switching in such semiconducting organometallic films can be erased using the heat from CO_2 laser radiation (Benson et al, 1983). Of special interest is the possibility that below threshold a device using these films might add inputs algebraically, a capability offering the possibility of the fabrication of **analog-digital hybrid computer elements**.

IV.II. Switches Activated by Polarized Light

Refraction is one consequence of the scattering of light by the electrons and nuclei in the constituent molecules of the medium, and can be accompanied by **Rayleigh** and **Raman scattering** in all directions. Raman activity is dependent upon an induced polarizability due, almost always, to an **induced electric dipole moment**. An **induced magnetic dipole moment** also can occur, but usually at a magnitude 10^6 less than the induced electric dipole (Chiu, 1970). An exception to this magnitude differential occurs if the incident light is (a) in resonance with a magnetic substate split in zero field, and (b) an effective magnetic field able to interact with magnetic states, i.e., the light is circularly polarized. When conditions (a) and (b) apply, the ratio of induced electric to magnetic dipole is 1:1 (Barrett, 1981, 1982).

If the interaction of light and magnetic substate is of the kind in which the substate is filled by an electron from a donating molecule, then a special interaction occurs in which the substate, populated by circularly polarized light photon energy, is "otherwise occupied", and cannot play the role of electron acceptor. If the electron donating molecule, now prevented from donating, becomes a p-semiconductor when it is able to donate, the molecule now becomes less of a conductor.

This situation was reported to occur in the phthalocyanines (Pc), which are the electron donating species, and oxygen, which was the electron accepting species, and the magnetic substates of which were filled by incident circularly polarized radiation (Barrett, 1983; Barrett, Wohltjen & Snow, 1983).

Light interaction with the Pcs in an oxygen or electron-accepting atmosphere is possible from two points of view. On the one hand, magnetic circular dichroism studies of the metal Pcs indicate resonance interaction with the central metal in the red (long wavelength) end of the visible spectrum. On the other hand, light interaction with O_2 adsorbed to the Pc ring occurs over most of the visible spectrum. However, the two effects were dissociated by studying both metal substituted and metal-free Pcs. The demonstrated ability to modulate, with circularly polarized (versus linearly polarized) light, the electrical conductance of Pc films sublimed onto an interdigital electrode surface is due to light interaction with the electron acceptor, O_2, rather than with metal d electrons. The effect offers the possibility of fast light-induced switching in electron- donating/electron-accepting sandwiches. More investigation is required with monolayer sandwiches and other semiconducting organics.

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V. Properties of Bioconductors

The term "bioconductor" can be used with two different meanings. The first meaning refers to the presently undecided issue of whether a biopolymer can function like a semiconductor. The second meaning refers to the use of biopolymers either as resists or as deposits for electrodeposition for materials which themselves do conduct. The first meaning also has two corollary meanings, depending on whether conduction *in vivo* and conduction *in vitro* is intended, for it is clear that whatever happens in the natural system, a biopolymer, considered as just another organic polymer, might be doped to conduct and function quite otherwise than in its naturally occurring state.

We shall begin by considering the first meaning and the first corollary meaning of the *in vivo* condition, because this is the hardest to demonstrate. In 1938 Jordan suggested that giant biopolymer molecules have the properties of solids and in 1941 Szent-Gyorgyi postulated that proteins may behave like semiconductors (Szent-Gyorgyi, 1941a,b), i.e., possess conduction bands. Another suggestion was made that electronic excitation energy migrates between aromatic amino acid residues or between nonprotein chromophore groups by nonradiative resonance transfer (Förster, 1948).

Szent-Gyorgyi's semiconduction idea was criticised on the grounds that bandgap in such systems as protein macromolecules is of the order of 3 e.v., so that under normal temperature conditions, there would be no migration of electrons across the bandgap, and hence no conduction. Furthermore, the absence of low-lying levels of electronic neutral excitations of peptide bonds is known spectroscopically, hence there would appear to be little interaction between them. In semiconductors the distance between electronically occupied and unoccupied bands should be of the order of thermal energy, kT. Furthermore, pi-electrons are partly delocalized only in single peptide groups which are separated by insulating groups.

However, the argument over whether proteins semiconduct really addressed the special case of ***intrinsic*** semiconduction. Actually, real proteins contain many "impurity" centers such as prosthetic groups, ionized side groups, etc. If these side groups were doped in vitro, then the question of semiconduction might be answered quite differently. So the argument appears still open. Yet again, some feel that the multitude of electron and hole traps located close to a protein's conduction bands might preclude the motion of charge carriers over large distances (Blumenfeld, 1981).

Certainly, the primary light process in **photosynthetic systems** demonstrates ***signs*** of semiconduction. Furthermore, in higher plant chloroplasts and bacterial chromatophores, the excitation may migrate through an ensemble of dye-packed molecules by an exciton mechanism

However, the question is still open on ***definite*** proof of semiconduction mechanism involvement in the primary stages of photoinduced charge separation in photosynthetic systems.

Turning now to the sense of "bioconductor" as exemplified in biopolymer resists and substrates, it is clear in this regard that biopolymers have an important rôle. The ordering of proteins in regular arrays and with a periodicity of a superlattice (Uzgiris & Kornberg, 1983), together with deposition techniques and antibody-antigen deposition, promise the advantage of chemical crafting of electronic materials - an advantage which is unavailable to conventional or etch lithography. An additional advantage is that computer architectures, as an emergent of a material's physical properties, will be possible, rather than the rigid architectures related to materials only superficially in their requirement for the usual building blocks of capacitors, resistors and inductances. Novel (bio)materials will thus offer versatility and assist in achieving non-von Neumann processing. Furthermore, analog-digital hybrid element computation may be superior in context-dependent data processing tasks which require complex weighting and recognition functions and integration of information and computations from different sources.

At the supramolecular molecular level there is the nerve impulse of the excitable membrane, which is the working element of nervous systems. However, this type of bioconduction is unlikely to be used in computer design, as the conduction, which is based on ionic concentration gradient breakdown or release mechanisms, is far too slow, and requires metabolic energy to reestablish the conditions for another impulse. It would seem that in the foreseeable future, computers will not use metabolic mechanisms for a reconstition mechanism.

There are, however, more near-term problems to be tackled. If, for example, conducting elements are formed from polymer resists in two-dimensional arrays, the task of understanding how many such arrays can be stacked must be undertaken. A simple union of two types of semiconductor material with different Fermi levels is known as a Schottky barrier. If the two different materials are of monolayer thickness, then it is likely that no Schottky barrier will exist, but rather a composite material due to tunneling and electronic interaction. It makes sense, therefore, to ask questions concerning how many monolayers must be laid down in order for two different semiconducting materials to coexist in a Schottky barrier arrangement. This is another way of asking: **how small (i.e., in this case, how thick) can one make materials so that the diverse individual physical characteristics are retained.** ***Only when diversity is retained are devices possible.*** In other words: if there is no retention of material diversity, then there can be no subelement control and no device is possible. ***And by diversity is meant functional*** *diversity. Just because structural independence is present does not mean that functional independence of elements exists.*

A cautious first step in understanding bioconduction will be to undertake the investigation of **the solid state physics of the contact junction of thin materials**. The first milestone in this study will be the achievement of material-dependent, **minimum thickness Schottky barriers**. The overwhelming advantage of the molecular approach over present (etch) lithography lies in the ***versatility*** offered by the diversity of molecular/material properties in control of electron mobilities, in new architectural designs predicated on the material's properties, and in ***analog-digital hybrid microelements***. There is also the question of whether devices could be made smaller than those presently possible. Yet making devices smaller with molecular lithography, than those presently achieved by etch lithography, has yet to be determined to be theoretically feasible, but if it is, it would still be icing-on-the-cake of the above mentioned advantages.

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VI Langmuir Blodgett Films for Oriented Mono- & Multilayers

[illegible] that have a degree [illegible] end groups can be spread at the air-water interface [illegible] a single layer [illegible] molecules. Further developments were made by Blodgett (1934, 1935; Blodgett & Langmuir 1937) and the technique of fabrication of ultrathin films by the Langmuir-Blodgett method has been found applicable to [illegible] members of [illegible] including fatty acids, [illegible] esters, [illegible] stearate, acrylates, methacrylates and certain polymers [illegible] Gaines 1966; Kuhn et al 1972 [illegible] the spreading of a chemical on a clean water surface to form a film of only molecular thickness and then transferring the film under controlled conditions of pressure, temperature and e.m. field application to a solid substrate by dipping the solid into and out of the water. The solid may be dipped repetitively into the same film or into different films alternatively. Technical difficulties involve the choice of solid substrate to which the particular monolayer will adhere, as well as achieving monolayers which are mechanically stable.

Typical procedures involve preparation of dilute solutions of polymer samples in a volatile solvent such as benzene or chloroform, application of small volumes to the water surface and, after evaporation of the solvent, advancing a surface barrier to compress the spread film. The area of the film and the surface pressure are recorded simultaneously. When the surface pressure either reaches a plateau or an arbitrary high value, the barrier motion is stopped and then reversed so that the film area increases again. The obtained hysteresis loop provides information on the stability of the polymer film and indicates the surface pressure regime in which the film may have sufficient integrity to attempt L-B film buildup.

Film deposition can be assessed by maintaining a desired constant surface pressure. The area reduction (barrier motion) can then be compared with the area of the solid immersed and withdrawn in each cycle. The deposition ratio, which is the area of film removed from liquid divided by the area of solid substrate immersed, provides a measure of transfer efficiency. Besides surface pressure, other variables which may be adjusted are speed of immersion, temperature and solution properties of the aqueous subphase such as ionic strength and pH. Protonation by the aqueous subphase of monolayer films has sometimes resulted in better mechanical stability. It is to be expected that in the future deposition under the influence of an e.m. field will be attempted.

The principles of two-dimensional order in protein arrays can be investigated using the L-B technique. Such arrays would have the **periodicity** of **superlattices** and when electrodeposited with conducting materials would have the **behavior** of superlattices. Alternatively, such arrays could be transferred to the gate region of an FET device for the detection of antigen binding by electrical signals. Repetitive insertions of a solid surface through a spread monolayer can, in some cases, lead to the generation of multilayer films on the surface. Each monolayer can be of alternating orientation in the final film to provide mechanical stability. The natural membrane, a bilayer lipid film, can also be simulated and proteins introduced. Such structures could be used in the development of molecular specific detectors in microbial fermentation and other biologically based material production.

There are many other potential applications for thin organic films made of monolayers. For example, insulators on semiconductors, high-energy-density capacitors, optoelectronic devices, microlithography, optical coatings, two-dimensional magnets, besides the very many applications in the biomedical area. In the case of semiconductor insulators, it is relevant that many semiconductors (e.g., indium phosphide, gallium arsenide, gallium phosphide, indium antimonide, and mercury cadmium telluride) do not form simple oxides, and the vapor-deposited insulators used have drawbacks such as shifts in flat-band voltage, high density of surface states, and hysteresis effects. On the other hand, polymer films offer the potential for extremely passive insulating layers.

It is possible to envisage the creation of **entirely new classes of materials** by L-B technology. These materials would include ordered, layered structures for the field of photography, electron-beam or X-ray lithographic resists for the microcircuitry field, specific membrane structures for gas separation or water separation, and adhesives ([illegible]).

The microscopic details of the L-B process, which presently consist of, in effect, recipes for multilayer fabrication, as well as any generalizations and predictive rules, have yet to be studied in any rigorous fashion. Future thrusts in the area are expected to [illegible] the [illegible] of higher molecular weight than are presently [illegible] the fabrication of [illegible]

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VII Organization of Polymeric Conductors

In recent years numerous polymeric materials have been synthesized which, on ionization yield ***complexes*** with conductivities in the semiconductor-to-metal range. The ionization of these conjugated backbone polymers is achieved by addition of electron donor or acceptors to polymer precursors, e.g. polyacetylene, polyparaphenylene, polypyrrole, poly(paraphenylene sulfide) and polythiophene. The similarity of the electrical properties of these materials resulted in a search for a unifying underlying model to correlate their electronic properties. The concept of conduction by spinless charge defects was introduced by Su, Schrieffer and Heeger (1980) and applied to trans polyacetylene. This model was extended to apply to polparaphenylene (Brédas et al, 1982), to polyparaphenylene (Brédas et al, 1984a, 1984b) and polythiophene (Brédas et al, 1984a, 1984b). The mathematical consequences of the model have also been explored (Takayama et al, 1980; Maki, 1982a,b,c; Baeriswyl and Maki, 1983).

It appears that transpolyacetylene (and also the as yet unsynthesized polyarenemethides (Boudreaux et al, 1985)) are quite different from other conjugated polymers in that the ground-state bonding geometry is degenerate. One consequence of this uniqueness is that in the doped transpolyacetylene **complex** the possibility exists for intrachain transport by isolated charged solitons. However, the lack of similar degenerate ground states in other doped polymers leads to a description of mobile defects as coupled pairs of solitonlike defects referred to as polarons or bipolarons.

The explanation of electrical conduction in organics is even more confused in that not all the empirical evidence related to conduction in these organics is in agreement with the soliton model (Chien, 1984). In fact, the most that can be said for now is that conduction by soliton-like mechanisms may occur at some dopant levels, but probably not all. At the time of writing, however, these organic complexes, which supposedly conduct using soliton mechanisms, fall into the first category of conductors described above.

Despite the present lack of a finished ***theoretical*** picture of conduction, these organics complexes are known ***empirically*** to conduct. Their organization in devices can procede by the usual lithographic techniques. A possible difficulty is that the conducting material is a **complex**, that is, the nonconducting organic precursor requires ionization and this has meant doping. Doping by conventional methods would preclude any chemical synthesis for achieving device fabrication. Attempts in this direction would be greatly advanced if the organic complex could be synthesized *in toto*. Even if the organic complex could be synthesized, the complexed molecule will be one of many such, which together form a conducting element of a device. Inter-complex electron hopping must always occur therefore.

The organization of different organic complexes in one device must encounter the difficulties of **interfacing materials of different lattice constants**. The great advantage of superlattices is that lattice constants do not have to be matched, but their method of conduction is not solitonlike. It is clear, therefore, that the organization of soliton conductors requires further research.

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VIII Devices: Materials Considerations

A broad classification of organic solids with enhanced electrical properties into two types has been attempted (Vijayakumar and Pohl, 1984). The first type consists of the **charge-transfer complexes** and would include the charge-transfer salts and also those organics with soliton properties whose conductivity also depends upon spin-charge exchange, e.g., trans-polyacetylene, polythiophene, polypyrrole, polyphenylene, poly(phenylene sulfide). Correlated electron-hole states that have a spatial extent of one or two lattice constants were termed ionic states by Lyons (1967) and are now called charge-transfer excitons (Pope and Swenberg, 1982). These intermediate excitons can be thought of as distorted Wannier-like excitons due to the anistropic nature of the molecular crystals. The second type consists of those polymers with **inherent long-range delocalization** and these include the polyphthalocyanines and the polyacene quinone radical (PAQR) polymers (Pohl and Pollak, 1977). The giant polarization observed in this second type is due to long-ranging travel of freed charges or "nomadic polarization" or the response of highly delocalized carriers as they travel, usually as polarons, over the long molecular domains provided by the associated pi orbitals of properly conjugated polymers.

Now, although polaron-type conduction is postulated for some cases of the first type - in particular, for those with soliton-like mechanisms - the polaron mechanism, in this instance, involves degeneracies in ground states or Franck-Condon-like states, both in short-ranging orbitals coupled by phonons. It seems reasonable, therefore, to assume the aforementioned broad two part classification, and it is the second type, or those with highly delocalized carriers which will be considered here.

A case can be made that this second type is much more stable than the first. The first type includes many which are thermally instable, and are sensitive to atmospheric attack. The second type are highly stable down to 77° K and highly conductive. It includes nickel-doped pyropolymers (Wyhof and Pohl, 1970) and other pyrolized polymers. The term "**ekaconjugation**" (as opposed to "**rubiconjugation**") was proposed for these polymeric systems (Pohl, 1968). An ekaconjugated structure is one in which, as the degree of polymerization increases, the energy difference between the ground state and the first excited electronic ionized state approaches zero. On the other hand, in rubiconjugated structures, the difference in such energy states remains nonzero as the molecular size is increased. To obtain enhanced electroactive character, materials must possess conjugated spines with stabilized orbital delocalization permitting continuous intramolecular overlap of pi orbitals extending over long domains. According to the nomadic polarization theory of Pollak and Pohl (1975) the dielectric constant should vary with the intensity of the applied field, with the square of the chain length of the polymer, and with applied frequency. This prediction has been confirmed for PAQR polymers (Vijayakumar and Pohl, 1984).

These highly aromatized structures are prepared by a pyrolization technique and fine grounding to a powder. They are thus in an "almost graphite"-like state. However, they retain enough of their "base stock" properties, that dielectric constants (of up to 60-300,000) and conductivities can be "tailor made".

As the pyrolization produces an increase in the size of the polymer, there is a hint as to the mechanism of conduction. For example, the hopping of an electron-hole pair (exciton) from molecule to molecule is the migration of the exciton. When the electron and the hole jump together from molecule to molecule as they migrate, we have the tight-binding case, and the migrating excitation is a Frenkel exciton. It is also possible for the electron and hole to be on different molecules, but in each others vicinity; this is the weak-binding case and the migrating excitation, now spread over several molecules (or ions) is a Wannier exciton. As, increase in conduction results from increased polymerization (with pyrolization), it is likely that some type of Frenkel excitations are involved. It is best to realize, nonetheless, that the Wannier-type and Frenkel-type excitons are probably extremes of a continuum.

These ekaconjugated polymers clearly offer advantages in stability, high conductivity and high dielectric constants. Their preparation by a pyrolization process precludes them, however, from any chemical lithography of building from small upwards in analogy to the Merrifield synthesis technique. They could be used in a hybrid "etch-down-then-synthesize-up" technique. Clearly, the type-one-polymers do not possess the speed of conduction nor, presently, the environmental stability of these type-two (except, perhaps, in the case of polypyrrole, and also polyacetylene according to recent unverified claims from a Japanese company). It is likely, therefore, that the ekaconjugates have advantages too great to ignore, and will never be superceded by the type-one. Nonetheless, the two types of materials each have their advantages and disadvantages.

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IX Polymer Interfaces

A distinction was made above between conduction in (1) charge-transfer complexes which include those to which soliton-like properties have been attributed and which possess distorted Wannier-like excitonic states, and (2) those polymers with inherent long-range delocalization for which the conductivity is attributed to the response of highly delocalized carriers and which possess Frenkel-like excitons traveling usually as polarons. Type (1) was identified with advanced device conduction, and Type (2), with intermediate-stage device conduction. The interfacing of intermediate-stage devices with advanced devices is equivalent to the interfacing of Frenkel-like excitons with Wannier-like excitons, i.e., of strong-binding excitons with weak-binding excitons (Knox, 1963). We now consider the problems associated with this interfacing.

We can commence by examining the range of validity of the Frenkel and Wannier models. The Frenkel exciton problem obtains a quick solution because an assumption is made that the excited electron shares a unit cell with the hole. Physically, a single exciton is a good eigenstate of the molecular Hamiltonian if it can be correctly argued that it lies well below all higher excitations and does not interact strongly with them. This is true only of molecular excitons. Formally, it is possible to solve ***any*** exciton problem with Frenkel states, but a very large radius exciton would then be an enormously complicated mixture of highly interacting, high-energy atomic states. Thus, large radius excitons are usually treated in terms of the Wannier model.

The Wannier model, on the other hand, is not appropriate for small radius excitons nor is it appropriate for orbits which attain the dimensions comparable with the "crystal". The excitons will then interact with the surface of the material. Thus, whereas the strict-sense Frenkel model is based on excited states of individual atoms, the strict-sense Wannier model requires large Bohr radii for the excitons treated. It should be realized then, that strict-sense Wannier and Frenkel excitons are hard to find! In fact, the type (1) and (2) conductors exhibit intermediate-type Frenkel and Wannier excitons.

Given, however, two distinctively different types of excitons, even if both are rare in the strictest sense, any interface will involve barriers. We may try an energy band picture of this interface. When a type 1 semiconductor is making contact with a type 2 semiconductor, the Fermi levels in the two materials must be coincident at thermal equilibrium. On contact, the Fermi level of the lesser conductor is lowered by an amount equal to the difference between the two work functions, the work function being the energy difference between the vacuum level and the Fermi level. The contact potential will be the difference between electron affinities and band gaps.

The barrier height between the two materials is simply, according to this picture, the difference between the work function of one material less the electron affinity of the other.

This energy band model provides an answer, but has a flaw, probably fatal. The model assumes no differences in binding of the electrons between the two semiconducting materials. Thus, extrapolation to materials in which tight-binding and weak-binding applies is, at best, a mere approximation. Far better, would be to attempt to bridge the gap between the Frenkel and Wannier limits rigorously. This attempt was made by Takeuti (1957) using a Green's function approach with limited success. However, Knox (1963), although critical of the ***petitio principii*** inherent in the assumptions used by Takeuti, has provided hints as to how the Green's function approach might effectively bridge the Frenkel and Wannier limits.

In conclusion, the two main types of polymeric material probably can be interfaced for electrical conduction, but this interface lacks a complete theoretical structure at the present time. New theoretical attempts are required, together with experimental tests of type 1 and 2 semiconductor junctions.

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X Applications

In considering applications of organic ((bio)polymeric and (bio)molecular) chemistry, the materials consideration and the device consideration will be treated together, as it is difficult to dissociate the one from the other. The applications include the following:

(1) Sensitive Piezoelectric Materials.

Piezoelectricity in organics is something of a theoretical misnomer as organic polymers contain no rigid lattice structure to be displaced. However, some organics do transduce pressure into electrical potential differences (e.g., PVF_2), so the point is academic. There are two criteria, which may not be sufficient, to keep in mind when considering piezoelectric materials. firstly, there should be a large dipole moment, and secondly, the processing of the material should obtain a high degree of ordering. Polymers such as the low-odd nylons, and some ureas offer high dipole moments. These may also be exceeded by materials in which light induces a large dipole moment. In the latter, the material would be used in a device which would be light interrogated.

Piezoelectric organic material has the advantages of good processability into large arrays, flexibility, good impedance match to the interfaced medium, high sensitivity, low-cost and, most important, high sensitivity. The uses are many, and include impact and strain sensors, accelerometers, fuses, detonators and anti-fouling coatings for ships.

(2) Organic polymer and molecule organization for device/material purposes:

Inorganic superlattices can possess conductivity or semiconductivity (Döhler, 1983). Superlattices are artificial one-dimensional periodic structures of at least two different semiconductors, in which the relatively long period of alternation (about 100 Å) results in the subdivision of the Brillouin zones into a series of minizones (Esaki and Tsu, 1969). The realization of superlattices has revealed powerful new technologies by which new classes of semiconductors based on thin films can be tailored. Some of these include: multiple quantum wells, modulation doped superlattices, superlattice avalanche structures, laser diodes, strained superlattices, field-effect transistors, photodetectors, etc. An example of practical use is to take a very high impurity concentration in one of the sandwich materials, resulting in low mobility, and then select the other material to be of high purity. If there are charge carriers in the sandwich, the mobility is then very high. This high mobility is due to the very small dimensions permitting wavefunction overlap of the electrons.

If the period of the superlattice, 100 Å, which is generally 20 times as long as the lattice constant of the host material, but **shorter than the electron mean free path**, is examined, a series of narrow allowed and forbidden bands may be expected due to the **subdivision of the Brillouin zone into a series of minizones**. When the same semiconducting material is doped into p and n types, **the lattice constants of the two types of material need not be matched**. This, the most crucial property of superlattices, promises simultaneous processing of information at different frequencies in the same structure, miniaturization, as well as speed.

The width of each miniband in the superlattice can be designed. This width is determined by the strength of interaction between neighboring potential wells, and increases with decreasing width of the layers of that semiconductor in the superlattice whose bandgap is greater. Bloch oscillations occur due to the slope in the bands, the inclination of which is due to the application of an electric field. In a conventional semiconductor, the electrons in the conduction band are driven toward the upper edge of the tilted band. However, due to the relatively large width of the band, they never reach the end and lose energy by emitting thermal vibrations in the crystal. In the superlattice, on the other hand, the minibands are narrow, and the probability of an excited electron reaching the edge of the band is high. At the upper edge, the electrons are reflected (Bragg reflection) and return to the bottom edge of the band for possible repeated reflection. As the band is tilted more (with increasing applied voltage), the curious effect is obtained of **negative resistance** (Esaki and Tsu, 1970), due to an increased Bragg reflection but with decreasing energy loss or resistance.

In ordinary semiconductors, doping results in a decrease in mobility. In superlattices, the reverse is the case. This is because a doping of donors is confined to the layers of the semiconductor with the largest bandgap. As each donor contributes a free electron to the crystal, and as the electrons seek the available states that have the lowest energy, the electron mobility increases. The increase itself is due to the states of lowest energy residing in the bands of the other semiconductor in the sandwich, and separation will be achieved between the donor layer and the electrons donated.

The superlattice architecture lends itself to tuning by (i) organics with large molecular orbital overlap matched to obtained the desired superlattice characteristics, and (ii) organics controlled by incident light, so that the tunability of the characteristics mentioned in (i) is obtained. A periodic array of n and p doped layers separated by undoped layers is known as **a nipi superstructure** (Döhler, 1972a,b), where i means intrinsic. This intrinsic layer of the nipi structure can be organic material, which, as the properties of organic materials are limited only by the extent of the synthetic chemist's art, promises a great variety of designed superlattice materials.

The results of this application will include multiple and tunable lasing lines from diode lasers giving parallel processing capabilities, simpler fabrication, megabyte chips and denser electronic arrays.

(3) Computers dedicated to task with information integration capabilities

There are many situations taken from the military combat scenario and from the situations encountered by the airline pilot, the automobile driver and the subway and surface train driver, in which accurate information processing is required, but if it arrives after a set time, then a catastrophe occurs, and the information processing, no matter how accurate the outcome, need not have taken place. In other words, some situations require computations to be accurate, but have the overriding requirement that they be accomplished within a finite time span. Of what good is accuracy if it arrives too late for it to be acted on?

It is for such computational requirements that the analog-digital hybrid elements of molecular devices offer advantages. The informational funneling and fusion from different sensors and devices can, by analog methods, be summated for a final judgment within a specified time span. This time-limited informational compression can proceed in parallel with the retainment of source of input. The organic components offer the greatest versatility in dedication to task in the most compact form.

(4) The Molecular Transistor and Molecular Amplification

Molecular and polymeric dynamics are quite different from electrical and transistor circuit dynamics. However, in one regard there is a similarity between them, namely, in the phenomenon of amplification in which a small change in one input variable results in a large change in an output variable.

Transistor amplification is well-known. A similar effect could be realized in the many polymer and molecular systems which function far from chemical equilibrium (Kondepudi, 1982, Kondepudi and Prigogine, 1981, Kondepudi and Nelson, 1983). When a chemical system is far from equilibrium, the dissipative processes of diffusion and chemical reaction act concertedly to produce a variety of dissipative structures. Mathematically, the transition to these dissipative structures, from the homogeneous thermodynamic state, is the bifurcation of new solutions to the equations that describe the spatio-temporal variations of the concentrations of the reactants. In other words, if there is an order parameter, be it solution ionic strength, solution pH, electric field strength, or magnetic field strength, then when it is less than a critical value the system is in a homogeneous state, but when it exceeds that critical value, the system undergoes a transition to another state. Such behavior is well-known for molecules in solution in the case of the helix-to-coil transition. It is also apparent in the case of the electric-field induced changes in Cu-TCNQ, and the polarized-light-induced paramagnetic changes in porphyrins and phthalocyanines. In all these cases if the molecule is designed to be near a symmetry-breaking threshold, then a small influence will result in a large change. Such an effect is an amplification, or switching, which can have all the uses of present-day transistors plus the additional ones of chemical detection. Degenerate four-wave mixing (see Appendix) permitted by a material nonlinear susceptibility is also a mechanism for optical transistor-like amplification.

(5) Use of Organics as Resists for Electrodeposition and Etching.

The patents of McAlear and Wehrung (1978a,b) address this application.

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XI Application of Advanced Devices

Advanced devices will include organic [illegible] properties. The organic material [illegible] attendant advantages already discussed. Such devices will [illegible] application in future high-speed general purpose [illegible] computers [illegible] compact, lightweight dedicated computers. The applications [illegible] determined by material characteristics and properties [illegible] be likewise a function of material considerations.

This clearly places the solid state physics of materials [illegible] is warranted by the revolutionary advances in the understanding [illegible] materials in the last fifteen years. Even more new [illegible] which the devices made of organic and organic materials [illegible] fabricated. Rather than being just more materials to be used in [illegible] to those ways in which present inorganics are used, the new [illegible] the possibility of new versatile lithographies based on self-[illegible] the precise control and crafting of electronic properties by chemical [illegible] and binding. Unlike the present technology which [illegible] ***materials-in-sandwich*** with etching creating the required [illegible] the synthesis approach creates the diversity [illegible] "self **organization"** [illegible] from chemical reactions unlike those [illegible] charge repulsion, entropy considerations and adoption of [illegible] state. This means that whereas the designer of a device of today [illegible] by the material properties and lithographic processes of today, the [illegible] of the future, on the other hand, will have available material properties [illegible] extensive as the organic chemist's imagination and the physicist's ability to determine molecular properties, as well as lithographic techniques [illegible] as known molecular dynamics.

We pass, then, from an age in which one group of scientists produces [illegible] materials and a second separate group of scientists do what they [illegible] the materials to fabricate devices, to an age in which one group [illegible] **interdisciplinary scientists** can relate application requirements [illegible] material properties and the device becomes ***an emergent from both the application and those properties***. We foresee [illegible] time of crafting molecular dynamic [illegible] to application [illegible] requirement of interdisciplinary training [illegible] that the [illegible] will be a natural extension of the molecular properties.

There will be **two major results** of the new molecular electronics [illegible] increase in computer power both in terms of speed [illegible] and [illegible] miniaturization, but also (2) an increase in the ability to measure [illegible] and detect any chemical or physical variable. Indeed, [illegible] advances be in terms of the information gathering capabilities [illegible]

[illegible] retain [illegible] other [illegible] span [illegible] layers has [illegible] doped [illegible] level, [illegible] clay and [illegible]

[illegible] alpha- [illegible] resolution an [illegible] Fariss Lando [illegible] resolution of 200-350 [illegible] rather than film thickness. Electron lithography permits resolutions as small as 10 nm and these investigators demonstrated results with beam widths of 25 nm.

Monolayers of poly(vinyl stearate) are reported to be usable as barrier layers in Josephson tunnel junctions for Josephson diodes (Larkins et al, [illegible]). The estimated switching time is 16 ps.

There is a wide potential application of thin films in transducer technology (Roberts, 1983, Table 1).

Table 1, From Roberts (1983)
Potential Applications of L-B Films

*(1) **Electron Beam Microlithography** (Peterson et al, 1983; Barraud et al, 1980a,b, 1983; Fariss et al, 1983; Broers and Pomerantz, 1983).*

<u>Comments:</u> Good sensitivity and contrast; acceptable plasma etching resistance; less scattering of electrons from substrate and therefore better resolution; negative and positive resists possible.

*(2) **Integrated Optics** (Pitt and Walpita, 1976, 1977; Grunfeld and Pitt, 1983; Bogner et al, 1983).*

<u>Comments:</u> Film thickness plus refractive index of film and hence guided wave velocity can be controlled with great precision; acceptable attenuation loss. Possible uses in conventional optics and optical data storage.

*(3) **Electro-optics** (Garito and Singer, 1980).*

<u>Comments:</u> Control of molecular architecture so as to produce asymmetrical structures with high nonlinear coefficients; orientation of molecules over acceptable area may require assistance of external forces during dipping, e.g., electric fields.

*(4) **Dilute Radioactive Source** (Mori et al, 1980).*

<u>Comments:</u> Radioactive nuclide incorporated in conventional L-B films; used to measure the ranges of low-energy electrons.

*(5) **Electronic Displays** (Batey et al, 1983; Daniel et al, 1983; Roberts et al, 1979, 1980).*

<u>Comments:</u> Large area capability of L-B films is an advantage; the monolayers can either be the active electroluminescent layer or used to enhance efficiency of inorganic diode; passive application to align liquid crystal display. Deposition of liquid-crystal type molecules also possible.

*(6) **Photovoltaic Cells** (Roberts et al, 1981; Tredgold and Jones, 1981).*

<u>Comments:</u> Used as a tunnelling layer in an MIS solar cell or as an active layer in p-n junction diode, perhaps involving an inorganic/organic junction. Dye sensitization possible to match

photoconductor surface to spectrum of incoming radiation.

(7) ***Two-dimensional Magnetic Arrays*** *(Pomerantz et al, 1978; Asaolu et al, 1983).*

Comments: Magnetic atoms, e.g., Mn, periodically spaced in L-B film; possible applications include magnetic control of superconducting junctions and bubble and magneto-optical devices.

(8) ***Field Effect Devices*** *(Roberts et al, 1978; Petty and Roberts 1980; Kan et al, 1980, 1983; Lloyd et al, 1980, 1983; Sykes et al, 1980)*

Comments: Accumulation, depletion and inversion regions possible with a variety of semiconductors; can therefore also form basis of other devices, e.g., CCD; coating process disturbs semiconductor surface very little compared to conventional deposition techniques. Can form the basis of gas detector or pyro/piezo FET if suitable LB films are used.

(9) ***Biological Membranes*** *(Flanagan, 1983; Heckman et al, 1983).*

Comments: Reverse osmosis/solar powered desalination membranes. Attractive supporting membranes for commercial exploitation of biological material, e.g., immobilization of membrane bound enzymes in solid state sensors; ISFET type structures.

(10) ***Supermolecular Structures*** *(Vincett and Roberts, 1980).*

Comments: Speculative work aimed at superconductors, organic metals, Esaki superlattices, 3D memory storage, etc.

It is clear, therefore, there are many potential applications of advanced devices, even if restricted to the case of two-dimensional structures of the L-B film type. More research into the synthesis of suitable materials is required and the L-B deposition technique itself. The way is also open to integration of L-B sensors with standard electronics.

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XII Architectures

The ENIAC, the UNIVAC and today's pocket calculators are based on a single central processor performing operations sequentially to produce the desired result, which is the traditional view of computer design as put forward by Charles Babbage, Alan Turing and John von Neumann. Such designs, which are referred to as von Neumann computers, are constrained to perform one task at a time in real time. If they are programmed to perform more than one task, then they do not perform the additional tasks in parallel real times but switch between tasks rapidly, so that the central processor is "time shared" with a concomitant loss in speed for each task time. This observation is not absolute, because every computer has a word of eight bits or more, which enables it to address eight questions, but relatively speaking, most present computers are serial processors, with some notable exceptions (such as COLOSSUS, ILLIAC-IV, PARALLEL ELEMENT PROCESSING ENSEMBLE, DISTRIBUTED ARRAY PROCESSOR and HETEROGENEOUS ELEMENT PROCESSOR (HEP) among others).

Multiprogramming enables some of today's computers to perform operations in parallel and vector architectures permit a single operation to be performed on several components of a vector simultaneously (Browne, 1984). Knowing in advance the sequence of operations permits the some programs to order some data, while the central processing unit is working on other data, an operation known as pipelining. However, there is still a single central processing unit. Thus, among digital architectures one can distinguish three basic types: (a) The computer applies a single stream of instructions to a single stream of data; (b) The computer applies a single stream of instructions to multiple streams of data; and (c) The computer applies multiple streams of instructions to multiple streams of data. The analog-digital hybrid, based on molecular components, is yet another approach which we consider later.

Further advances being considered are: use of gallium arsenide for higher speeds, further use of parallelism in the software, such as that described above, and other non-von Neumann architectures using standard components. Yet another influence on computer performance, quite apart from the individual processors, is their **organization into a network**. A current theory now being considered is that by Hopfield (1982,1984). This is a content addressable memory, admittedly difficult to construct in standard digital hardware, but which is a collective property of a set of devices conceived in analogy to biological nerve cells. Particular memories are stored nonlocally in many interconnections with recall a collective decision made by the network as a whole in a single settling time, with the decision about the memory to reconstruct made in the analog domain and with the memory developing its full digital representation. At the present time small matrix memories are being tried. If the difficult scale-up to large dimensional memories is to be achieved, then the use of molecular components, such as the Cu-TCNQ charge-transfer salt, will be unavoidable.

Here, then, is an abstract idea inspired by a biological metaphor, which must reach out for molecular components if it is to become of competitive size. Also seen, here, is the demand for analog elements. In the future, one foresees (i) the task to be performed by a particular computer being matched by (ii) the capabilities of a particular molecular material, so that the architecture is dependent on (i) and (ii). Thus, the traditional method of saddling the architecture designer with (i) the task and (iii) traditional digital transistor computer components will be obviated, permitting far greater versatility in design.

Architectures are also influenced by the complexity of electronics available, i.e., the complexity of the chips available. MOS (field-effect transistor) technology may be able to create a future computer technology with element dimensions of 0.25 um, and even 0.1 um elements may be possible. However, the scale down will encounter (a) switching energies of too small a multiple of kT, (b) tunneling through thin gate oxide layers, (c) statistical fluctuations in threshold voltages across many devices due to impurity ions, (d) at submicron size the resistance of a few mm of metal wire being so large that the wire cannot be treated as an equipotential, so that diffusive propagation of signals occurs (Seitz & Matisoo). A subsidiary problem is that of interconnection wiring. Bipolar transistor circuits have an advantage over MOS circuits in speed but chip integration is poorer due to problems in interconnection wiring.

The use of molecular elements instead of inorganic elements will also run into these difficulties, if the same transistor/Schottky barrier element designs are followed. However, due to the analog nature of the charge-transfer dependent switching of, for example, Cu-TCNQ and the possibilities of light-control of superlattices from organic elements, both resulting in multiple inputs to a single element, ***the same designs need not be followed***. The opportunities for simultaneous information integration and preservation are available in molecular elements and such designs **do not even obey the same logic truth tables as the digital transistor switch**. Thus, it is inappropriate to assume the same limiting constraints, and due to the opportunity for analog interaction between switching elements, as well as the great versatility offered in molecular control and material fabrication, those limiting constraints are not the same. Only an inveterate stone-thrower would require the same yardstick for the two physically distinct device technologies.

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XIII Other Applications Including Advanced Sensors

The applications of molecular transducers for information gathering purposes are many and include those to biomedical diagnostics, sensory prosthetic devices, sensory systems in robotics, chemical sensing in fermentation systems, and sensing in airframes and engines. In many instances, the molecular transducer technology will be integrated with optical fiber and wave guide technology and in the biomedical field will include patch clamping techniques.

Already optical fibers are being used in aircraft structures to determine the orientation of composite fibers and to assess excessive strain on aircraft parts. In the future, even jet engine temperatures will be monitored by optical fiber sensors. In a day not too distant, one can foresee an aircraft's systems and airframe being routinely tested by a computer controlled interrogation of an optical fiber bus which links to all the aircraft sensing components.

The sensing of molecules for diagnostic purposes in the medical diagnostics field will depend a great deal on coating technology and the ability to miniaturize. Hirschfeld (1983) has pointed out that as the scale of engineering grows smaller, so does the importance of phenomena which vary as a high power of size. For example, gravity, inertia and magnetism, vary in increasing importance as the third power of size; flow phenomena as the fourth power; and thermal emission as the second to the fourth power. Electrostatics and surface tension vary directly with size; diffusion as the square root and Van der Waals forces as the negative fourth power. The latter, unimportant for bulk material dynamics, may become predominant at small size. Quantum effects, a minor consideration at bulk size, become preeminent [illegible] small scales causing tunneling and nonlinear behavior. Hirschfeld's point is summed up in the observation that "you don't get a workable ant by scaling down an elephant."

His other point is, however, that by scaling down an elephant you obtain unelephant-like dynamics which you may be able to use for quite different devices than ants, i.e., scaling laws sometimes produce different functions. **This other point should always be kept in mind together with the first.**

Fiber optic sensors are devices that provide optical signals in response to physical, chemical or other stimuli. In a typical sensor of this type, light from a solid state optical source is coupled into an optical fiber which then transmits it to the sensing region. In the sensing region, some property of the light (intensity, phase, polarization or spectral content) is modulated by the phenomenon of interest. The modulated optical signal is then returned via the optical fiber to a processing location, where it is converted to an electrical signal by a solid state detector.

There are two generic classes of fiber optic sensors: "**intrinsic**" **sensors** in which the parameter under measurement modulates a property of the optical fiber itself, and "**extrinsic**" **sensors** in which the optical fiber is merely used to transmit light to and from the sensing region. The devices can be potentially as small as the fibers themselves (i.e., less than 0.1 mm) and can be configured either as distributed sensors or point sensing elements. All of the publicized advantages of fiber optic technology apply to fiber optic sensors as well. These include: relative freedom from electromagnetic interference and pulse effects, large intrinsic bandwidth, and the ability to perform in hostile environments. In addition, a number of methods exist for multiplexing such sensors onto a single optical fiber, thereby providing a potential system capability.

Among the many kinds of microsensors are: microdielectrometry for vapor sensors applications, ion-sensitive field effective transistors, ion-controlled diodes, pyroelectric devices for flow monitoring (air, liquid, heat), pressure transducers and thermal IR detector arrays, microaccelerometers, surface acoustic-wave vapor sensors, sensors for pH and pCO_2, thermal history sensors, chemical pump diodes, piezoelectric vapor sensors.

The field of microsensors is allied with the field of microlithography (Wohltjen, 1984). CHEMFETS, ion-controlled diodes, Schottky diodes, thin-film tin oxide gas sensors, chemiresistors and microdielectrometers, surface acoustic wave devices, potentiometric gas sensors and pyroelectric enthalpimetric sensors all can, and are, fabricated by microlithographic techniques of the etch-down variety. The extension of the molecular "build-up" variety of lithography to these devices is to be expected. The dependence of microsensor technology on coating technology also gives the molecular build-up technology another opportunity for contributions.

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XIV Defense and Aerospace Applications

The defense and aerospace applications range from cryptic message decoding using supercomputers to small dedicated computers in small arms. In airplanes, missiles and small arms, there is a requirement of compactness, speed and the additional requirement of a finite computation time already mentioned above. All the applications implicate the utilization of the molecular attributes of analog addition of charge with digital readout and resonance interaction with energy levels **split in zero field** to achieve parallel processing, as well as informational integration for fast detection, lateral inhibition for contrast enhancement, and chemical amplification by methods mentioned above. Using Langmuir-Blodgett technology, it is possible to fabricate thin films of great purity (preventing dielectric breakdown), which can have great charge storage capacity, but yet have **extremely high frequency response**. We shall describe in more detail, here, as one example of chemical switching among many, the possibility of resonance interaction with phthalocyanines and porphyrins to provide **paramagnetic switching**.

The use of molecular resonances offers opportunities for the achievement of **content addressable systems**. The ability to rotate incident linearly and horizontally polarized light, which is induced in a material by an **effective magnetic field such as circularly polarized light**, is proportional to the **Verdet constant** (Atkins and Miller, 1968a,b). The Verdet constant for iron is 195 (at wavelength 5890 Å), whereas for water it is 0.013 and for the oxygen molecule it is 0.0559 (Partington, 1953, p. 596). As magnetic optical activity originates in interference between waves scattered because of the symmetrical polarizability and the antisymmetric polarization, its appearance implies antisymmetric scattering of light. ***Therefore, the induction of magnetic optical activity results from the incident circularly polarized light being of a frequency near an electronic absorption band that is rigorously symmetry-forbidden to lower-order multipoles, i.e., the d-d transitions of transition metal compounds and rare earths. In this case, the next higher multipoles (the magnetic and the quadrupole) account for any optical activity (Chiu, 1969).***

Using magnetic circular dichroism (Stephens, 1970; Stephens, Suetaak and Schatz, 1966) as a probe, magnetic resonances have been demonstrated for metal-free Pc, CoPc, NiPc and CuPc (Hollebone and Stillman, 1978). Changing the metal in the phthalocyanine has a noticeable effect. For example, whereas changing the metal iron from cobalt(II) to zinc(II) results in a slight increase in angular momentum, changing the axial ligand on iron(II) phthalocyanine from dimethyl sulphoxide to cyanide produces a large change in magnetic moment from 3.24 to 4.58 Bohr magnetons (Stillman and Thomson, 1974). Magnetic absorption resonances have also been reported in porphyrins using the **normal Faraday effect** as a probe (Volkenstein, Sharonov and Shemelin, 1966, 1967). The dispersion is a sharp Macaluso-Corbino curve (Macaluso and Corbino, 1898) which indicates the direction of the circular current producing the effect.

Thus, circularly polarized light at an energy equal to the zero field splitting energy can result in a coupling to a d-d magnetic dipole transition, due to the radiation magnetic field. For zero field splitting energy to be as large as the energy of incident visible radiation is due to the following considerations.

The **crystal field influences** (Van Vleck, 1932; Bethe, 1929; Abragam and Bleaney, 1970, p. 595) are larger in porphyrins and phthalocyanines than the intramolecular spin-dependent interactions (Chan, van Dorp, Schaafsma and Van der Waals, 1971). The orbital momentum of the metal d electrons are "quenched" due to the presence of asymmetrical intramolecular fields (Van Vleck, 1932, p. 287). However, although there is also no longer an axis of symmetry about which angular momentum is conserved, tetragonal symmetry will not remove all the degeneracy of the d electrons (Bethe, 1929, 1930).

For this circumstance, special considerations apply. For example, Bethe (1930) demonstrated that when an average magnetic moment persists despite the absence of an axis of symmetry, then there can be no first-order Zeeman effect, but unusually large changes are permitted in the spatial quantum number which do not have the usual significance of being proportional to a component of the angular momentum (Van Vleck, 1932, p. 292). Of first importance is that the **Zeeman energy**, which is the zero field splitting energy, is greatly increased. (Bethe's theory was confirmed in Becquerel's observation (1929) of abnormally large Zeeman effects in certain rare earth crystals; and Van Vleck (1932, p. 292) assumes that crystals involving iron ions have fields of the same symmetry, but of much greater magnitude than Becquerel's rare earth compounds. In fact, if these large fields producing large Zeeman energies were not present, the susceptibilities of the iron group would not be dependent upon spin states, which they are).

Thus, the removal of angular momentum requires a large asymmetrical crystal field resulting in a large Zeeman. The existence of this asymmetry in phthalocyanines and porphyrins can be established by the following considerations. Metalloporphyrins have a fourfold axis of symmetry with the lower excited states, triplets as well as singlets, doubly degenerate. The triplets have a threefold spin degeneracy, and the lowest triplet state of the free molecule is a manifold of six levels. The spin independent perturbations of tetragonal symmetry such as crystal field effects, although electrostatic in nature, operate in conjunction with **Jahn-Teller coupling**, which cannot by itself remove the degeneracy of the vibronic levels of a tetrapyrrole system (Van Vleck, 1939; Ham, 1965, 1968, 1969; Abragam & Bleaney, 1970, p 791).

Van der Waals, van Dorp and Schaafsma (1979) have demonstrated that when a porphyrin is subjected to electrical fields not of tetragonal symmetry, one of two orbital components will be favored energywise over the other, resulting in the splitting of the two states. The authors envisage a similar effect occurring in the case of ligand binding, leading to a difference in shape relative to the environment of the two nuclear conformations near the minima of the two wells. Thus, the evidence is that porphyrins do not possess a fourfold axis in the excited state, and the lowest vibronic level of a Jahn-Teller unstable triplet or singlet state has a degeneracy removable by an anisotropic crystal field (Chan, van Dorp, Schaafsma and Van der Waals, 1971a,b; Canters, van Egmond, van Dorp and Van der Waals, 1973). It is also known that in the case of quantum mechanical treatment of **the Jahn-Teller effect**, the molecular Hamiltonian contains a term describing interaction of the molecule with its environment by means of oscillating electric fields set up by vibrations of the lattice (Williams, Krupka and Breen, 1969; Hoffman and Ratner, 1978). The crystal field asymmetry producing a large zero field energy is thus present. Tanabe and Sugano (1954) calculated that the cubic field splitting parameter is 37,000 cm^{-1} and the critical cubic field splitting parameter is 18,500 cm^{-1}. This value is close to that of yellow light and demonstrates that magnetic substates, split in zero field, can be populated by interaction with ***visible***, circularly polarized, light.

In summary, in porphyrins and phthalocyanines, a Jahn-Teller instability and a large crystal field quench spin angular momentum so that a zero field energy is large. This large zero field energy permits removal of the d electronic degeneracy creating two levels, one diamagnetic, the other paramagnetic. If, then, incident light is at a wavelength giving an energy equal to the zero field potential energy, i.e., the light is at **the Larmor precession frequency** (Larmor, 1897, 1899, 1900), and if the light is also circularly polarized, permitting magnetic field coupling to the metal electronic transitions, then magnetic resonance occurs and the paramagnetic state is assumed. The result is **an inverse Faraday effect** (Barrett, 1981, 1982, 1985).

The class of porphyrins and phthalocyanines is large and there are opportunities to tailor many different resonances. However, this is just one example of the many ways to obtain chemical switching and tailor a chemical device to the application.

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XV Defense and Aerospace Market Considerations:

The days when a strong right arm would win the day are long gone. They were gone by the time of the Battle of Culloden in 1746. Even the believers in ***élan vital*** were dismayed by the efficiency of the water-cooled machine gun of the First World War. There is a school of thought which believes that it is not the side with the best equipment or the best generals which wins, but the side with the greatest production capability. As evidence, it cites the Civil War, and the Second World War. There are exceptions to this rule of the greatest gains to the greatest producer of war material. For example, the Messerschmidt 262 Schwalbe, if it had not been burdened by the opinions of an amateur commander-in-chief, might have had a significant effect on the outcome of daylight bombing. Hopefully, this is not an isolated example, because if he who has, or is willing to have, the greatest military production wins, then the west is surely in trouble. Perhaps, then, that argument is dated, or, at least, in some cases it may not apply. In those cases, perhaps we are in a new age, in which the better technology has the edge. In other words, a high technology "machine gun" can confront and beat a whole company of charging troops with the highest ***élan*** in the world; or, put another way, an aircraft, with sensing capability which exceeds in range that of its adversary, might outfight its adversary even with a disadvantage of three to one.

If one had to state succinctly what that high technology advantage might be, which offsets a numerical disadvantage, then there is no doubt that one would settle on the broad definition of information. All things being equal in offensive capability, and even with numerical disadvantage, he who has more information and at the right time, might make up for that disadvantage. Defining a defense market, therefore, is relatively simple. Molecular electronics will permit a greater integration of information, from a larger sensor capability , and in a faster operational time scale, than present technology is able to provide. It will also permit the human operator greater freedom from the chores of equipment management, so that he may concentrate on the higher strategies of combat. Taken to its logical conclusion, the ultimate defense impact of high technology is to remove the human operator and heroics entirely, so that war becomes an emotionless and rational chess game.

We are not yet at that stage, and it is not the present purpose to persuade that such a stage ***should be*** reached, but there are significant ways in which miniaturization and dedication-to-task of electronics capability and the monitoring of multiple sensors can provide equalizing capability. After a national expenditure on the construction of the Maginot line which left the French army insufficient funds for an adequate amount of field artillery pieces, the adversary chose not to fight in the way or in the direction it was considered he would. Similarly, matching tank-for-tank and bomber-for-bomber may not be cost-effective nor a winning strategy. Furthermore, a large expensive piece of offensive weaponry is only effective in as much as it can detect (and, of course, destroy, which we take for granted) the countermeasures against it.

The miniaturization and dedication of electronics in defense will bring an economic and also military payoff. When great computing capability becomes inexpensive, a large number of small, cheap and "smart" or "brilliant" weapons can be sacrificed in pursuit of a small number, perhaps only one, of large and expensive pieces of military equipment. Only if the large equipment has sensing and information processing capabilities of the type we are discussing would it survive such a deluge.

APPENDIX

Degenerate Four-Wave Mixing (DFWM).

Degenerate Four-Wave Mixing (DFWM) can be viewed as a real-time holographic exposure and readout process. In fact, phase conjugation and aberration correction of waves with a transient holographic material used in a degenerate four-wave mixing geometry was first demonstrated by Stepanov et al (1971). DFWM is part of the larger field of phase conjugate optics, which involves the use of nonlinear optical techniques for real-time processing of electromagnetic fields. The name, phase conjugate optics, refers to the phase reversal of an incoming electromagnetic field (Yariv (1978), Fisher (1983)).

This is different from the reflection from a conventional mirror, as is apparent when one considers what happens if a plane wave passes through an optically distorting piece of glass, is reflected from a conventional mirror, and then passes again through the glass. What happens is that the double pass through the distorting glass results in a doubling of the wavefront distortion. If, however, the conventional mirror is replaced by a "conjugate mirror" then the reflected wave is the phase conjugate of the incident (and distorted) wave (which is equivalent to time reversal). In the case of the conventional mirror, the incident and reflected wavefronts are related by reflection, but not so in a "conjugate mirror" which reflects wavefronts which are identical to those of the incident ones. Hence, on the second pass through the distorting glass, the wave's distortion will undergo compensation and restoration of the initial wave before the first pass through the glass, (i.e., there is "healing" of spatial distortion). Phase conjugation has many applications, e.g., in optical waveguides, optical fibers, in three-wave mixing, and in DFWM, in which two pump incoming waves are phase conjugated. Yariv and Pepper (1977) have also demonstrated that DFWM is also capable of amplifying an incoming wave, as well as providing its complex conjugate.

Phase conjugation is really "time reversal". In its use in DFWM we commence with a nonlinear medium characterized by a third-order nonlinear polarization:

$$P^{(NL)}(\omega_3=\omega_1+\omega_2-\omega_3) = \chi^{(3)}A_1(\omega_1)A_2(\omega_2)A_4{}^*(-\omega_4) \tag{1}$$

and nonlinear susceptibility, $\chi^{(3)}$, which mixes the input waves A_1, A_2 and A_4 defined by:

$$(2) \qquad E_i(r,t) = 1/2\, A_i(r_i) \exp i\, (\omega_i t - k_i r) + c.c.$$

Waves 1 and 2 travel in exact opposition to each other and are phase conjugate, so that

$$(3) \qquad k_1 + k_2 = 0.$$

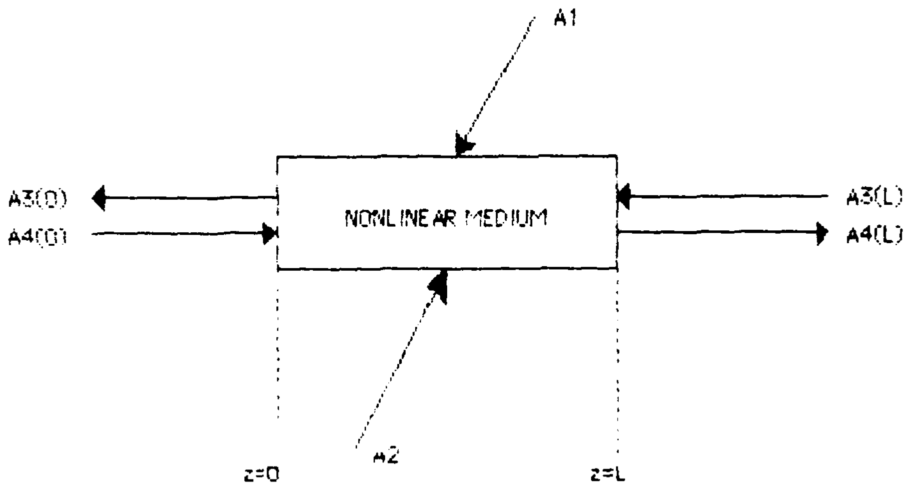

Fig. 1

Wave 4 in Fig. 1 is incident along an arbitrary z direction, and the induced polarization is

$$(4) \qquad P^{(NL)}(\omega_3 = \omega_1 + \omega_2 - \omega_4) = 1/2\, \chi^{(3)} A_1 A_2 A_4^* \exp i\, [(\omega_1 + \omega_2 - \omega_4)t - (k_1 + k_2)r + kz] + c.c.$$
$$= 1/2\, \chi^{(3)} A_1 A_2 A_4^* \exp i\, (\omega t + kz) + c.c.$$

which gives the physical reason why a fourth wave, A_3, is generated traveling in the -z direction.

In the case of phase conjugation, $A_3(L) = 0$, and the situation is as shown in Fig. 2:

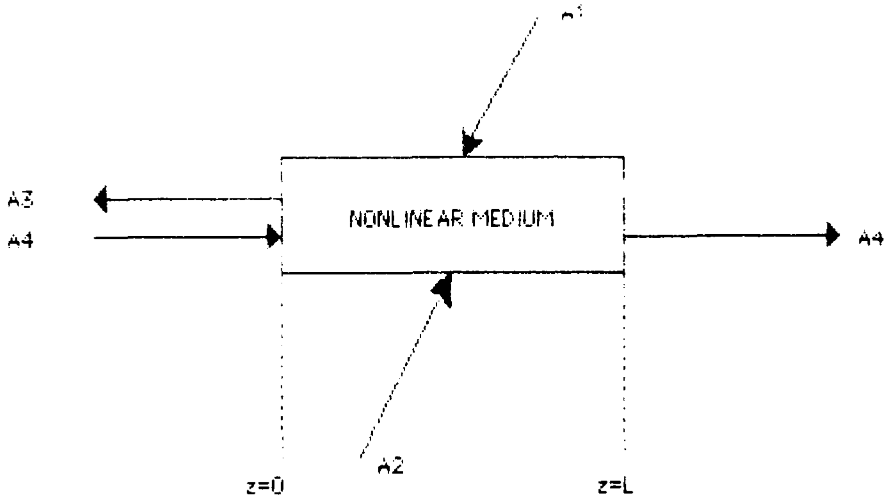

Fig. 2

and:

(5) $A_3(0) = -i\,[\,(\mathbf{K}^*/|\mathbf{K}|)L]\,A_4^*(0)$,

where:

(6) $\mathbf{K}^* = (2\pi\omega/cn)\,\chi^{(3)}A_1A_2$.

Equ. (5) shows that at z=0 the reflected field, $A_3(0)$, is proportional to the complex conjugate of the incident field, $A_4(0)$ multiplied by a factor.

The field distribution inside the interaction region is shown for a value of **K**L satisfying: $(\pi/4) < |\mathbf{K}|\,L < (3\pi/4)$ (Fig. 3).

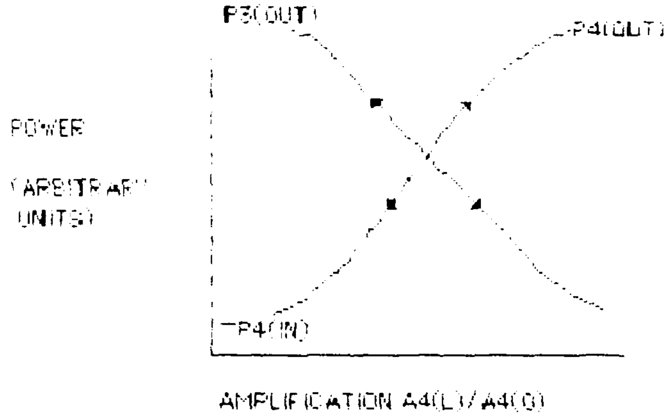

Fig. 3

in this regime, the reflected wave intensity exceeds that of the input wave and the device functions as both a phase-conjugate-reflection and transmission amplifier.

Semiconductors are excellent materials for phase conjugation when the optical wavelength is near or above bandgap. In such cases, mobile particles such as free electrons or holes may be created (Jain and Klein, 1979; Jain, 1982), and DFWM measurements have also been made in a resonant homogeneously broadened gas (Steel et al, 1981, 1982; Steel and Lam, 1979, 1981; Lam et al, 1981; Bloom et al, 1978), in the liquid fluoralcohol, hexafluoroisopropanol (HI) (Giuliani, 1972), in a CS2-filled waveguide (Jensen and Hellwarth, 1978), and in multimode fibers or optical waveguides (Yariv et al, 1978; Hellwarth, 1979; AuYeung et al, 1979), in HgCdTe (Jain and Steel, 1980, 1982). Theoretical treatment of resonantly enhanced DFWM has progressed (Lam and Abrams, 1982; Lind et al, 1982) and also for transient DFWM (Marburger and Lam, 1979; Lam, 1982). DFWM has been related to the detection of two-photon coherent states (Yuen and Shapiro, 1979) and to the temporal processing of information in general (O'Meara and Yariv, 1982) with applications in signal processing, radar and communications systems.

In optical fiber systems, the A_4 wave is the information carrying wave. When that wave is tapped or read in an optical fiber buss, then energy is lost. If it is read too many times, then the signal energy is severely depleted. DFWM provides a means of reading the signal as often as one wishes, because the energy for the readout is provided by the two pump waves, A_1 and A_2.

There remains the obtainment of high $\chi^{(3)}$ materials. We have already described above the competition between proponents of organic and inorganic materials. An obstacle remains in that for many such materials there will be a trade-off between a high nonlinearity and the speed of response. Future research will address this problem.

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GLOSSARY

Bipolaron: Analogous to the Cooper pair in the BCS theory of superconductivity, which consists of two electrons coupled through a lattice vibration or phonon. In the case of a bipolaron, there are two **polarons** coupled. Charged **soliton-antisoliton pairs**. A **diion**.

Electron Affinity: That energy required to remove an electron from the bottom of the conduction band to a position just outside the material (vacuum level).

Exciton: If we think of an excitation in a crystal or polymer as being caused by the removal of an electron from one orbital of a molecule (or atom or ion) and its elevation to a higher orbital, then the excited state of the molecule can be envisaged as the coexistence of an **electron and a hole**. The hopping or movement of an electron-hole pair from molecule to molecule is the migration of the exciton. When the electron and the hole jump together from molecule to molecule as they migrate we have the **tight-binding case,** and the migrating exciton is a **Frenkel exciton**. If, on the other hand, the electron and hole are one different molecules, the **weak-binding case** applies, and the migrating excitation, spread over several molecules and ions, is a **Wannier exciton**.

Because the wavelength of incident light is so **long in comparison with molecular spacing**, its electric field has **the same phase over a large number of molecules**. Therefore, it stimulates a whole domain of transition dipoles to move in phase, and in the presence of exciton coupling results in: (1) a shift in the absorption band to **higher energy** (if all dipoles are parallel), or (2) a shift in the absorption band to **lower energy** (if all dipoles are head-to-tail). The splitting between absorption bands is called **Davydov splitting**.

Heterojunction: A junction between two dissimilar semiconductors. When the two semiconductors have the same type of conductivity, the junction is called an **isotype heterojunction**. When the conductivity types differ, the junction is called an **anisotype heterojunction**.

Multiple Quantum Wells (MQW): A superlattice constructed of two semiconductors with different electrical and optical properties but with

crystal structures having nearly identical lattice spacings ensuring a continuous crystal with few defects. The minimum energy for free electrons is lower in one of the semiconductors so electrons congregate in the lower energy material whose layers form the wells. The picture is much like the textbook picture of electrons in potential wells. Because the layers are so thin, the energy levels available to electrons moving perpendicular to the boundary between layers no longer make one nearly continuous band, but split into a few discrete bands, giving the material qualitatively different properties.

N-i-p-i Structure: A **doped superlattice** consisting of a periodic array of n and p doped semiconductor layers separated by layers of the same intrinsic semiconductor. The **same bulk semiconductor** is used for the three layers. The result is a periodic electrostatic potential which modulates the conduction and valence bands much as it does in a **compositional superlattice**. The great advantage of the doped superlattice is that any semiconductor can be the host material, provided only that n and p doping are possible. In contrast, the compositional superlattice requires a choice of two semiconductors **so that the interatomic distance in one of them matches at least approximately the distances in the other**. A doped superlattice can be **tuned** or modulated within wide limits by, e.g., light excitation. This is because **electron-hole recombination by tunneling** can occur in doped superlattices. Furthermore, doped superlattices can be tailored so that free electrons and holes can have lifetimes ranging from a few nanoseconds up to several hours. The concentrations of electrons and holes are tunable quantities. In fact, the electrical conductivity, optical absorption, light emission, or **anything at all about the electrical and optical properties of a doped superlattice, can be tuned.**

Polaron: A polaron is a defect in an ionic crystal or charged-polymer complex which is formed when an excess of charge at a particular point polarizes the lattice in its vicinity. Thus, if an electron is captured on a polymeric lattice it may be surrounded by other negative ions which move a distance away. As the electron moves through the lattice it is accompanied by this distortion, which makes the electron a more **massive particle**. A **radical ion**.

SEED: A **s**elf **e**lectro-optic **e**ffect **d**evice using MQW material properties.

Due to the quantum well properties which confine excitons, application of an electric field does not dissociate the excitons but creates a large shift in the excitonic absorption. Using the MQW material in a diode arrangement, a bistable switch is possible. With the SEED reverse biased, the voltage is across the MQW material and the resulting electric field shifts the MQW exciton lines to longer wavelengths, so that laser light whose wavelength is near the zero-field exciton line is only weakly absorbed. As the laser intensity increases, the free electrons and holes from dissociating excitons lower the resistance of the SEED, so that less of the voltage is across it and more is across a resistor. The lower voltage releases the exciton line back toward its normal position, resulting in increased absorption by positive feedback, until the exciton line and the laser wavelength match. Then the SEED switches from high transmitting to low transmitting because of the greatly increased absorption.

Unlike optical bistable devices using other materials and arrangements, the switching time in a SEED is fast. A speed of 10 nanoseconds is thought reachable and perhaps 1 nanosecond as well.

Soliton: A normal mode of a nonlinear system. A <u>mathematical entity</u>, although it can have a physical representation. A good cross comparison can be made with cisoidal functions (sines and cosines). A cisoidal function can be defined with respect to the Fourier transform of an arbitrary (linear) function and, analogously, a soliton can be defined with respect to the Backlund transform or the inverse scattering transform of a nonlinear function. The nonlinear function must be one which can be placed in a [illegible] form and have complete analyticity and integrability, resulting in a [illegible] of nonlinearity to dispersion. Thus, not every function can have soliton solutions, only those which satisfy these requirements. Those functions satisfying these requirements include: (1) The **nonlinear Schrodinger equation** (whose derivation has nothing to do with quantum mechanics) which is generic to systems which are weakly nonlinear but strongly dispersive; (2) The **Korteweg-de Vries equation** or **Toda lattice**, which describe water waves; and (3) The whimsically named **sine-Gordon equation**, which expresses topologically invariant quantities in a system, e.g., a domain wall or a dislocation in a magnetic crystal or a shift in the bond-alternation pattern in a polymer.

Solitons in one spatial dimension and with a small number of degrees of freedom at each "site" of a notational lattice occur in only three forms: **kinks, pulses** and **envelopes**. The kink is a solution to the sine-Gordon equation, and the pulse is a solution to the Korteweg-de Vries or Toda lattice equation. Both propagate without change in shape and the kink interpolates between two degenerate ground states. (It is invoked to describe conduction in trans-CH_x, which possesses degenerate ground states.) Envelope solitons (which may be called **breathers** or **biions**) probably represent the most widespread class (in polymer conduction). The envelope describes the localized soliton structure, which may be moving or not, and there is an additional periodic oscillation of the envelope amplitude or internal carrier wave. In this instance, **four (not two) canonical variables** are needed to specify the soliton's state. Breathers can **interpolate** between linear modes and extremely nonlinear structures such as kinks. Breathers are obtainable from both the sine-Gordon equation and the nonlinear Schrödinger equation.

Of course, whether or not a physical phenomenon describable as a soliton actually exists in a polymer depends on whether it can be demonstrated experimentally that the match between an intensity dependent nonlinearity and dispersion occurs. Until then, the use of solitons to describe the demonstrated conduction in organics must remain an Ansatz or a hypothesis. Furthermore, solitons are generic. That is, they will rarely be seen in nature in the precise from required by mathematicians. Nevertheless, the nonlinearity-dispersion balance mentioned above is approximated in nature, hence the dynamics of empirical systems are in many cases "soliton-like".

Superlattice Structure: Periodic layered **heterojunctions** with layer thickness of the order of 100 Å. This means that both of the semiconductor layers are only several of molecules thick. The semiconductors are chosen so that their bandgaps are different. The narrowness of the conduction band (or minibands) in a superlattice results in **Bloch oscillations** with **Bragg reflection**. Confining doping to the semiconductor with the largest bandgap results in high electron mobilities, (whereas doping in conventional semiconductors results in reduced mobilities).

Work Function: That energy required to remove an electron from the Fermi level to a position just outside the material, i.e., to the vacuum level.