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TUNNELING IN NETWORK MODELS OF MOLECULAR CHAINS*

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ABSTRACT

A network model of electrons as developed by Montroll is used to describe the high anisotropic conductivity of a certain class of molecular crystals. The molecular crystals are modeled as a one-dimensional chain of periodically spaced units of free electron paths separated by potential barriers. Since this anomalously high conductivity in a narrow temperature range seems to result from some subtle interplay between the lattice vibrations of the crystal and certain electron pathways between them, we plot for a model of TTF-TCNQ the energy band edges versus separation distance between benzene units. Our results seem to indicate that there exists critical separation distances between neighboring units in which a free electron tunneling passage way develops so that electron propagation through the chain becomes possible.

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1. INTRODUCTION

A one-electron model of molecules and solids is proposed in which the electrons are restricted to lie only along the bonds of the material. If as a simplification we choose these bonds to be one-dimensional then the electronic properties of our network model of "lines" and "point atoms" are purely topological in origin and are solely characterized by the degree of "bonding."⁽¹⁾

We choose as our one-electron atomic potential the bound "soliton" (fig. 1),

$$V(x) = \frac{-\hbar^2 \gamma^2}{2m} s(s+1) \operatorname{sech}^2 \gamma x \quad (1)$$

In its limiting forms it embodies both the extremely localized Heitler-London and delocalized Bloch models. Thus, as the well-depth parameter $\gamma \rightarrow 0$ $V(x)$ reduces to the Sommerfeld free electron model and as $\gamma \rightarrow \infty$ $V(x)$ approaches a tight binding potential. γ is, therefore, akin to an effective mass and its variation permits description leading from covalency to ionicity. Previous applications involving the use of this potential have been to calculations for

- 1) The density of states of model solid and molecular crystals,⁽²⁻⁴⁾
- 2) The electronic states of interstitial and surface defects and of thin layer films,⁽⁵⁻⁷⁾ and,
- 3) the bulk and surface scattering formulae on networks.⁽⁸⁾

For integral s , the solution to the Schrödinger equation,

$$\psi'' + (k^2 + s(s+1) \gamma^2 \operatorname{sech}^2 \gamma x) \psi = 0 \quad (2)$$

can be expressed in terms of circular and hyperbolic functions. So, with $s = 0, 1, \text{ and } 2$ and $\epsilon = ik/\gamma$

$$\psi(x) = A\{\cosh \epsilon \gamma x + D \sinh \epsilon \gamma x\}, \quad s = 0 \quad (3a)$$

$$\begin{aligned} \psi(x) = A\{ & (\cosh \epsilon \gamma x - \epsilon^{-1} \tanh \gamma x \cosh \epsilon \gamma x) \\ & + D(\sinh \epsilon \gamma x - \epsilon^{-1} \tanh \gamma x \cosh \epsilon \gamma x)\}, \end{aligned} \quad s = 1 \quad (3b)$$

and

$$\begin{aligned} \psi(x) = A\{ & [1 + 3(\epsilon^2 - 1)^{-1} \tanh^2 \gamma x] \cosh \epsilon \gamma x \\ & - 3\epsilon(\epsilon^2 - 1)^{-1} \sinh \epsilon \gamma x \\ & + D\{[1 + 3(\epsilon^2 - 1)^{-1} \tanh^2 \gamma x] \sinh \epsilon \gamma x \\ & - 3\epsilon(\epsilon^2 - 1)^{-1} \cosh \epsilon \gamma x\} \}, \end{aligned} \quad s = 2 \quad (3c)$$

These values of s determine the number of bound states of ψ .

Energy line and band spectra are now derivable in a manner analogous to LCAO⁽⁹⁾ or tight binding computations.⁽⁸⁾ From knowledge of the lattice connectivity and upon application of the appropriate continuity arguments to ψ and to its first derivative at junction points one can easily derive a form factor equation relating the amplitude of the wave function of one atom at

site j to its n_j bonded atoms at sites j_p ,

$$n_j F(k, \gamma) \psi(j) = \sum_{\{j_p\}} \psi(j_p). \quad (4)$$

All the characteristics of the potential $V(x)$ are embedded in $F(k, \gamma)$, which for the three values of s above are,

$$F(k, \gamma) = \cosh 2\epsilon\alpha, \quad s = 0 \quad (5a)$$

$$F(k, \gamma) = (\epsilon^2 - 1)^{-1} \left[(\epsilon^2 - 1 + 2 \tanh^2 \alpha) \right. \\ \left. \times \cosh 2\epsilon\alpha - \epsilon^{-1} (2\epsilon^2 - \operatorname{sech}^2 \alpha) \right. \\ \left. \times \tanh \alpha \sinh 2\epsilon\alpha \right], \quad s = 1 \quad (5b)$$

and

$$F(k, \gamma) = [(\epsilon^2 - 1)(\epsilon^2 - 4)]^{-1} \\ \times \left\{ [\epsilon^4 + \epsilon^2(13 - 18 \operatorname{sech}^2 \alpha) \right. \\ \left. + (4 - 36 \operatorname{sech}^2 \alpha + 36 \operatorname{sech}^4 \alpha)] \cosh 2\epsilon\alpha \right. \\ \left. - 3\epsilon^{-1} \tanh \alpha [2\epsilon^4 + \epsilon^2(4 - 11 \operatorname{sech}^2 \alpha) \right. \\ \left. - (4 \operatorname{sech}^2 \alpha - 6 \operatorname{sech}^4 \alpha)] \sinh 2\epsilon\alpha \right\}, \quad s = 2 \quad (5c)$$

The parameter α in eqs. (5) is related to the value of the potential at the midpoint of a bond of length l , $\alpha = \gamma l/2$. In the next three sections we shall illustrate representative examples to which this model has been applied.

2. DENSITY OF STATES OF PERIODIC CRYSTALS

Band energies of periodic systems are found by substituting the crystal symmetry dependent Bloch functions into the form factor equation (4). A dispersion relation for this symmetry type then results which specifies how the energy states apportion themselves in the Brillouin zone. Specifically, for the nearest neighbor cubic lattices this dispersion relation is

$$3F(k, \gamma) = \lambda(\vec{q}) \quad (6)$$

where $\lambda(\vec{q})$ is a geometrical structure factor defined over the reciprocal lattice vector $\vec{q}$, $-\pi \leq \vec{q} \leq \pi$. For simple cubic, body-centered, and face-centered crystals $\lambda(\vec{q})$ takes the form

$$\text{s.c.} \quad \lambda(\vec{q}) = \cos q_1 + \cos q_2 + \cos q_3 \quad (7a)$$

$$\text{b.c.} \quad \lambda(\vec{q}) = \cos q_1 \cos q_2 \cos q_3 \quad (7b)$$

$$\begin{aligned} \text{f.c.} \quad \lambda(\vec{q}) = & \cos q_1 \cos q_2 + \cos q_1 \cos q_3 \\ & + \cos q_2 \cos q_3 \end{aligned} \quad (7c)$$

The density of energy states function $G(E)$, $mE/\hbar^2 = k^2/2$, can generally be related to the dispersion relation as

$$G(E) = \int_S dS / \left| \nabla_{\vec{q}} E(\vec{q}) \right| \quad (8)$$

$G(E)dE$ represents the number of energy states existing on some surface of constant energy within the energy range E and $E + dE$.

Except for one-dimensional systems where (8) reduces to

$$G(E) = \frac{1}{k\pi\sqrt{1 - F^2}} \left| \frac{dF}{dk} \right| \quad (9)$$

analytic evaluation of (8) is often impossible. There are, however, certain characteristics of this density of states spectrum which are worth noting. At certain points, lines, or planes in the Brillouin zone $G(E)$ has singularities (often referred to as Van Hove singularities). In one-dimension these singularities $\sim E^{-1/2}$, in two dimensions as $\ln E$, and in three dimensions as $E^{1/2}$. The nature of these singularities is due to the periodicity of the lattice and are attributable to the occurrences of maxima, minima, and saddle points in the energy bands, with $\nabla_{\vec{q}} E = 0$ at such points. Figs. (2) depicts $G(E)$ for the simple cubic lattice dispersion relations (6) and (7a) with form factor (5b).⁽²⁾ Note the occurrence of band gaps and how they widen with increasing α .

3. DEFECTS IN CRYSTALS

In our context the notion of a defect is a small perturbation on perfect periodicity. Example are interstitial defects, surface absorption, and localized disorder in an otherwise periodic structure. For a small defect concentration the defect electronic states are conveniently calculated by use of lattice Green's function techniques. I will not go into these procedures here since they have been amply described in refs. 5-8. What I do wish to bring out is that this assumption of perfect periodicity manifests itself in changing the functional form of F wherever these defects are located. Consider fig. 3a, for example. It schematically represents a monolayer of chemically absorbed atoms on the surface of a simple cubic lattice. F , therefore, is modified along the whole of this surface plane and becomes

$$\hat{F} = (2F - F_1) - F_2F_3 \quad (10)$$

where F_1 , F_2 , and F_3 are defined as

$$F_1 = \left\{ \frac{b_1'(b_2' + d_2') - a_1'(a_2' + c_2')}{b_1'(b_1' + d_1') + a_1'(a_1' + c_1')} \right\} \quad (11a)$$

$$F_2 = \left\{ \frac{a_1'(b_2' + d_2') + a_2'(b_1' + d_1')}{b_1'(b_1' + d_1') + a_1'(a_1' + c_1')} \right\} \quad (11b)$$

$$F_3 = b_2''/a_2'' \quad (11c)$$

with

$$a_i' = \sin k \ell_i' + \gamma_i/k \cos k \ell_i' \tanh \gamma_i \ell_i' \quad (12a)$$

$$b_i' = \cos k \ell_i' - \gamma_i/k \sin k \ell_i' \tanh \gamma_i \ell_i' \quad (12b)$$

$$c_i' = \gamma_i^2/k^2 \operatorname{sech}^2 \gamma_i \ell_i' \sin k \ell_i' \quad (12c)$$

$$d_i' = \gamma_i^2/k^2 \operatorname{sech}^2 \gamma_i \ell_i' \cos k \ell_i' \quad (12d)$$

a_2'' and b_2'' are given by (12a,b) but with ℓ_2' substituted with δ_2'' . The localized density of surface states is shown in fig. 3b.⁽⁶⁾

4. TUNNELING IN MOLECULAR CHAINS

The metal-insulator transition in molecular quasi-one-dimensional chains such as TTF-TCNQ and the Pt-complex compounds has been linked to a Fröhlich-Peierls instability which induces an energy gap via lattice

distortions. Although the mechanisms contributing to this phase transition are seemingly different (due to structural differences-see fig. 4-the former compounds have π -like wavefunctions⁽¹⁰⁾ and the latter tightly bound d-orbital wavefunctions⁽¹¹⁾) we present an electron tunneling model with phonon-assist which suggests the plausibility of critical separation distances between neighboring molecular units in which a tunneling passage way develops so that electron propagation through the chain becomes possible.⁽⁴⁾

In our model the molecular chain is divided into alternating regions of free electron paths separated by barriers (fig.5). In an insulating state the units remain isolated from each other while in a conducting state electron tunneling can occur. In correspondence with actual structure we identify the square planar and TTF-TCNQ compounds with figures (6a) and (6b), respectively. If for our one bound state soliton potential (1) we choose as our ground state $V(x) = -\hbar^2 \gamma^2 / m$, then it can readily be shown that the dispersion relations for both the primitive chain and benzene free electron chains are

$$F_{P.C.} = [(F^2 - 1)H_0^{-2} + 2 \cosh(\sqrt{2} \ell_0) F(H_0 H_1)^{-1} - (H_0 H_1)^{-2}] / 2(H_0 H_1)^{-1} = \cos q \quad (13)$$

$$F_{TCNQ} = \left[\{ (F^2 - 1)H_0^{-2} - 4(H_1 H_0)^{-2} \} \{ 3 \cosh^2(\sqrt{2} \ell_0) - H_0^{-2} \} + 4F \cosh(\sqrt{2} \ell_0) (H_0 H_1)^{-1} (\cosh^2 \sqrt{2} \ell_0 - 3(H_0^{-2} H_1)^{-1}) \right] / 4(H_1 H_0)^{-1} = \cos q \quad (14)$$

where

$$H_0 = i \left(\frac{-2}{-2 + k^2/\gamma^2} \right)^{1/2} \operatorname{csech} \sqrt{2} \lambda_0 \quad (15)$$

$$H_1 = \frac{\left[\frac{k^2}{\gamma^2} \left(1 + \left(\frac{\gamma}{k} \right)^2 \right)^2 \cosh^2 \alpha \right]}{\left[\cosh^2 \alpha \left(1 + \left(\frac{k}{\gamma} \right)^2 \right) - 1 \right]} \cdot \frac{\left[1 + \gamma^2/k^2 \tanh^2 \alpha \right]}{\left[\sin k\lambda \left[1 + \gamma^2/k^2 (1 - 2 \tanh^2 \alpha) \right] + \frac{2\gamma}{k} \tanh \alpha \left((2 + \gamma^2/k^2 \operatorname{sech}^2 \alpha) \cos^2 \frac{k\lambda}{2} - 1 \right) \right]} \quad (16)$$

and λ_0 and λ are, respectively, the intra- and inter-molecular electron path lengths.

Density of states graphs for both models for varying intermolecular separation distance λ are shown in figs. 7 and 8. In both cases one clearly notes the occurrence of an insulator-metal transition with decreasing λ . To better understand the nature of this transition we plot in Figs. 9a and 9b the values of the energy band edges as a function of the separation distance between TCNQ-benzene units.

One of the most interesting features of these figures is the existence of a range of $\gamma\lambda$ in which a small decrease in its value yields a large decrease in the band gap between a lower bound or conduction state band and an upper conduction band. When $\gamma\lambda$ is large the band gap is also large so a chain characterized by it should be in an insulating state. When $\gamma\lambda$ is small the band gap is small and the system is in a "metallic" state. The transition from one to another could be accomplished through a small change in γ .

The observed conductivity of TTF-TCNQ complexes is zero at temperatures near 0°K, with the third band only partially filled. A sharp rise in electrical conductivity occurs at $\sim 50^\circ\text{K}$ only to again decline upon a further increase in temperature. Let us suppose that at very low temperatures the easiest (but still difficult) path for electron tunneling is along the dotted line in fig. 8. Furthermore suppose that it corresponds to the γ_2 value identified by point A on the sketched band pattern in fig. 9a.

As the temperature of a TCNQ crystal increases, the amplitude of vibration of the large TCNQ molecules also increases. Since the molecular weight of these molecules is of the order of 200 they oscillate in an almost classical manner. One of the properties of a classical oscillator is that it spends a larger fraction of time within a small distance Δ of the ends of an oscillation (furthest from its equilibrium position) than it does in the same distance Δ in any other part of its trajectory. As the amplitude of our oscillating molecule increases with increasing temperature, a critical temperature T_c is reached such that an optimum path for tunneling is achieved at just the moment that the molecules are at their greatest distance from equilibrium in their oscillation. In this state the optimum path remains intact for the longest possible time.

If it also corresponds to the γ_2 value B in fig. 9a, the band gap between third and fourth excited bands is so small that in the presence of an applied field the crystal would conduct almost as a metal. The observed peak in the experimental conductivity curve would then correspond to this situation. A further temperature increase induces an increased molecular vibration amplitude. Then the point of greatest displacement from equilibrium would

bring the most probable path length for tunneling to that identified by C. The conductivity would be somewhat higher than at an equivalent deviation in temperature from T_c at the low temperature side, since for at least during part of an oscillation the optimum tunneling path is achieved. At still higher temperatures normal scattering processes predominate, causing a further reduction in conductivity. It is hoped that a detailed mathematical discussion of these ideas can soon be presented elsewhere. A future article is in preparation which discusses tunneling as a mechanism for energy transport in such biological molecules as cytochrome C and HIPIP.

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BIBLIOGRAPHY

1. A. B. Budgor, J. Math. Phys. 17, 1538 (1976).
2. E. W. Montroll, J. Math. Phys. 11, 635 (1970).
3. T. Poston and A. B. Budgor, J. Comp. Phys. 19, 1 (1975).
4. A. B. Budgor, in preparation.
5. E. W. Montroll, J. Phys. Chem. Solids 34, 597 (1973).
6. C. H. Wu and E. W. Montroll, J. Nonmetals and Semicond. 2, 153 (1975).
7. F. T. Lee and E. W. Montroll, J. Nonmetals 1, 25 (1972).
8. A. B. Budgor, J. Math. Phys. 16, 2153 (1975).
9. J. R. Platt, "Free Electron Theory of Conjugated Molecules" (Wiley, N.Y., 1964).
10. H. R. Zeller and R. Brüesch, Phys. Stat. Sol. B 65, 537 (1974).
11. A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, Phys. Rev. B 5, 952, (1972).

FIGURE CAPTIONS

- Fig. 1 Sketch of the bound soliton potential (1). Continuity of ψ and its derivative are fixed at the midpoint of a bond connecting two overlapping soliton potentials.
- Fig. 2 a) Form factor F of (5b). The region to the right of origin corresponds to $k/\gamma \geq 0$. The region to the left corresponds to purely imaginary k/γ with $\varepsilon = ik/\gamma$.
- b) Density of states of a simple cubic lattice for several values of $\alpha = 1/2\gamma\ell$. Note that for the lowest energy band of the case $\alpha = 2$, we have plotted $1/4 G(E)$ rather than $G(E)$.
- Fig. 3 a) Configuration for an impurity atom on a surface.
- b) Localized density of states of an absorbed layer characterized by $1/2\gamma_2\ell_2 = 3.0$ on a surface of bulk material with $1/2\gamma_1\ell_1 = 2.5$. The quantity ℓ_1' represents the extension length of the bulk surface connected to the coated surface and ℓ_2'' is the free end length of the coated layer. The solid base line to the left represents the extent of the bulk energy band and that to the right is the band representative of $1/2\gamma_2\ell_2 = 3.0$. The four cases marked A-D are chosen as follows
- A: $\ell_1' = 0.5\ell_1$ and $\ell_2'' = 0.4\ell_2$
- B: $\ell_1' = 0.3\ell_1$ and $\ell_2'' = 0.4\ell_2$
- C: $\ell_1' = 0.5\ell_1$ and $\ell_2'' = 0.6\ell_2$
- D: $\ell_1' = 0.3\ell_1$ and $\ell_2'' = 0.6\ell_2$
- Fig. 4 Schematic sketches of neighboring stacks of Pt-complex and TCNQ molecules. Tunneling is thought to occur most easily along the

dashed lines along stacks and not between stacks. This may account for the anisotropic "one-dimensional" conductivity exhibited by these molecular crystals.

- Fig. 5 Schematic representation of two alternating regions of a molecular chain. Regions of the type delimited by the points A and D are free electron paths, with associated potential $V(x) = -\hbar^2 \gamma^2 / m$, while those regions of the type delimited by the points A and B have associated to them a potential of the form

$$V(x) = \frac{\hbar^2 \gamma^2}{m} \operatorname{sech}^2 \gamma x.$$

The dashed pathway C is a hypothetical tunneling pathway for electrons which tunnel through the potential barrier separating regions of the type AD.

- Fig. 6 Network models for various one-dimensional systems of periodically spaced units with free electron paths separated by potential barriers.

- i) primitive chain-square planar Pt-complex
- ii) benzene free electron paths.

- Fig. 7 Density of electron states from primitive chain model of Pt-complex compounds for various intermolecular chain distances $\gamma \ell$. The Pt-Pt bond distance ℓ_0 is chosen to be 2.8 Å and $\gamma = .13$.

- i) $\gamma \ell = .1$, ii) $\gamma \ell = .5$, iii) $\gamma \ell = 1$, iv) $\gamma \ell = 2$

- Fig. 8 Density of electron states from benzene free electron model of TCNQ compounds for various intermolecular chain distances $\gamma \ell$. The intrabenzene bond length ℓ_0 is fixed at $\ell_0 = 1.4$ Å and $\gamma = .26$.

- i) $\gamma \ell = .0005$, ii) $\gamma \ell = .5$, iii) $\gamma \ell = 1$, iv) $\gamma \ell = 2$.

- Fig. 9 Plots of dimensionless band edge energies $\sqrt{2} \ell_0$ vs. a dimensionless interbenzene separation distance ℓ / ℓ_0 , for various values of the

well-depth parameter γ . The intrabenzene bond length ℓ_0 is fixed at $\ell_0 = 1.4 \text{ \AA}$.

- a) $\gamma = 0.79$, b) $\gamma = 1$.

The points where different bands "kiss" is where free electron propagation from band to band is easiest. At points A, B, and C in Fig. 9a, we relate the magnitude of the conductivity to ease of tunneling. The graph of $\sqrt{2} \ell_0$ vs. ℓ/ℓ_0 in the upper right hand corner of fig. 9b is a blowup of the region where the fourth and fifth bands touch.

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