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The excitonic ground state of the half-filled Peierls insulator

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Abstract

We point out that the half-filled Peierls insulator, celebrated for its soliton excitations and its application to *trans*(polyacetylene), is an excitonic insulator in which collectively bound electron–hole pair excitations (excitons) are mixed into the ground state. Unlike the bound electron pairs of the Bardeen–Cooper–Schrieffer (BCS) superconductor, however, the excitonic pairs can be photoionized leading to the direct observation of the excitonic energy gap 2Δ in the optical conductivity. A deeper understanding is provided of the discovery of Kuper in 1955 of a BCS-like gap equation describing the thermodynamic properties of the Fröhlich (1954) one-dimensional charge-density-wave state.

1. Introduction and synopsis

It is interesting that the mean-field gap equations describing the thermodynamic evolution of the BCS superconductor [1] and the Peierls distortion of a 1D or suitably nested higher dimensional metal [2] are mathematically identical. Their familiar forms are

$$\Delta_k = N^{-1} \sum_{k'} V(k,k')(\Delta_{k'}/2E_{k'})(1-2f(E_{k'})), \tag{1}$$

where $V(k,k')$ is the pairing potential for the case of the superconductor while it is the electron–lattice interaction potential for the Peierls insulator. Here, k denotes the electronic wavevector. In both cases $E_k = \sqrt{\epsilon_k^2 + |\Delta_k|^2}$ is the electron quasi-particle (QP) energy, while ϵ_k is the band energy in the normal state measured relative to the chemical potential μ. $f(E)$ is the Fermi function $1/(\exp(E/k_BT)+1)$. The BCS relation [1] was derived in 1957 while the Peierls form was obtained by Kuper [3] in 1955 following the original work of Fröhlich in 1954 on the charge-density-wave (CDW) state of the 1D metal. Peierls [2] independently noted the latter for the 1D and suitably nested higher dimensional metals in 1955. Today, the system in the joint Fröhlich–Peierls work is generally referred to as the Peierls insulator (PI). The

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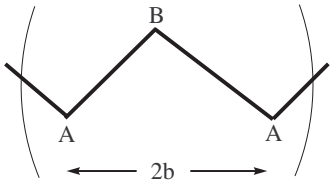

Figure 1. Schematic diagrams of a zigzag dimerized Peierls insulator. There are two atoms, A and B, in the unit cell of extent $2b$. The bond AB is shorter than the bond BA. There is one electron per atom.

detailed tight-binding theory of the PI was worked out in 1973 by Rice and Strässler [4] with the inorganic 1D metal $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KPC) [5] in mind, while the same calculation was repeated in 1980 by Su, Schrieffer and Heeger [6] (SSH) with the conjugated polymer *trans*(polyacetylene) [7] (PA) in mind. At this time, Brazovskii [8], Rice [9] and SSH [10] had independently suggested the possibility of (nonlinear) soliton excitations in PA when doped away from half-filling. The electrodynamic properties of the PI were investigated by Lee *et al* [11] in 1974.

In this paper we point out that the half-filled PI is actually an excitonic insulator [12] in which collectively bound electron–hole pair excitations (i.e., excitons) are mixed into the ground state. This is not unlike the situation in a BCS superconductor in which pairs of electrons are mixed into the ground state [1]. However, the excitonic pairs, unlike the electron pairs in the clean superconductor, can be directly *photoionized* with light with energy $\hbar\omega \geqslant 2\Delta$ (where 2Δ is the average excitonic energy gap), leading to the appearance of a gap in the optical conductivity of the undoped chain. A deeper understanding of the PI is thus achieved. The somewhat remarkable discovery of Kuper in 1955 of a BCS-like gap equation can be easily understood.

The layout of our paper is as follows. The standard mean-field treatment of the half-filled Peierls problem is considered. The effect of the lattice is eliminated leading to a lattice-mediated electron–hole attraction. This leads to the excitonic ground state. The number of bound electron–hole pairs in the ground state N_p is calculated, as is also the optical conductivity $\sigma_1(\omega)$ of the chain in the excitonic state. Finally, our conclusions are discussed.

2. The standard Peierls problem and elimination of the lattice distortion

The Hamiltonian describing the dimerized half-filled PI may be written in the form

$$H = KN\delta r^2/2 - \sum_{j\sigma}[(t_0 B^\dagger_{j\sigma}(A_{j-1,\sigma} + A_{j+1,\sigma}) + \text{h.c.}) + (\gamma\delta r B^\dagger_{j\sigma}(A_{j-1,\sigma} - A_{j+1,\sigma}) + \text{h.c.})]. \tag{2}$$

We have defined the PI to be a dimerized linear chain with one electron per atom with *no* direct electron–electron interactions. For convenience, we have taken a zigzag linear chain. Figure 1 shows the choice of the labelling of the A and B atoms of the PI unit cell. In equation (2) $B^\dagger_{j\sigma}$ and $A^\dagger_{j\sigma}$ are fermion operators which create electrons with spin polarization σ at the B and A sites respectively. The quantity t_0 is the hopping integral for the undimerized chain and δr is the bond alternation amplitude in the dimerized chain. The hopping integral for the shorter bond is $t_0 + \gamma\delta r$ while it is $t_0 - \gamma\delta r$ for the longer bond. $\gamma = -\partial t/\partial r$, which we refer to as the electron–lattice coupling constant. K is the sigma bond linear spring constant and N the

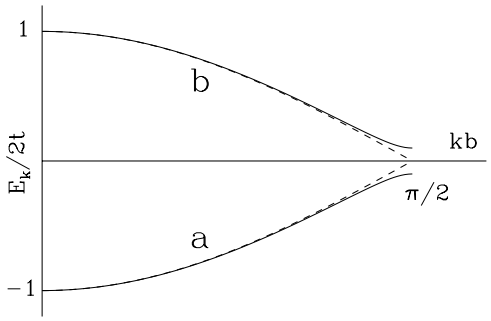

Figure 2. The band structure of the undimerized (broken line) and dimerized (solid line) zigzag chain. With one electron per atom, the lower band a is completely filled at $T = 0$.

total number of atoms in the chain ($N \to \infty$). The sum in equation (2) over j runs over the $N/2$ B sites. The length of the unit cell of the dimerized chain is $2b$ (see figure 1).

The standard solution [4] of (2) leads to the energy bands $E_k = \pm\sqrt{\epsilon_k^2 + \Delta^2 \sin^2 kb}$, where $\epsilon_k = 2t_0 \cos kb$ is the conduction band energy of the undimerized chain and $2\Delta = 2\gamma\delta r$ is the energy gap at the X point of the dimerized chain and determined by the familiar gap equation

$$1 = (4\gamma^2/KN) \sum_{k\sigma} \sin^2 kb/E_k. \tag{3}$$

The wavevectors k lie in the range $-\pi/2 < kb \leqslant \pi/2$. Ostensibly, the dimerized chain is a simple band insulator.

By means of the simple transformations $A_{k\sigma} = (a_{k\sigma} + b_{k\sigma})/\sqrt{2}$ and $B_{k\sigma} = (-a_{k\sigma} + b_{k\sigma})/\sqrt{2}$, the Hamiltonian (2) may be rewritten in the 'ab' form

$$H = K\Delta^2/8\gamma^2 + \sum_{k\sigma}[\epsilon_k(b_{k\sigma}^\dagger b_{k\sigma} - a_{k\sigma}^\dagger a_{k\sigma}) - \mathrm{i}\Delta \sin kb(b_{k\sigma}^\dagger a_{k\sigma} - a_{k\sigma}^\dagger b_{k\sigma})]. \tag{4}$$

For $\Delta = 0$, it corresponds to the metallic band structure of the undimerized chain with the finite density of states at the X point ($k = \pi/2b$) as shown in figure 2. The lower band a is filled while the upper band b is empty at $T = 0$. If the direct Coulomb interaction is allowed for, it is easy to see that this Fermi surface is unstable. An electron excited from the lower to the upper band will bind to the hole in the lower band via the attractive Coulomb interaction. The situation is quite analogous to the Cooper instability [13] in superconductivity.

Since Δ, or the lattice displacement $\gamma\delta r$, is a classical quantity we may formally differentiate H with respect to Δ and express Δ in terms of the electronic parameters:

$$\Delta = (4\mathrm{i}\gamma^2/K) \sum_{k\sigma} \sin kb(b_{k\sigma}^\dagger a_{k\sigma} - a_{k\sigma}^\dagger b_{k\sigma}). \tag{5}$$

This value may be substituted back into the Hamiltonian (4), thus eliminating the lattice distortion from the Hamiltonian: we obtain

$$H = \sum_{k\sigma} \epsilon_k(b_{k\sigma}^\dagger b_{k\sigma} - a_{k\sigma}^\dagger a_{k\sigma}) + (2\gamma^2/KN)L^2, \tag{6}$$

where

$$L = \sum_{k\sigma} \sin kb(b_{k\sigma}^\dagger a_{k\sigma} - a_{k\sigma}^\dagger b_{k\sigma}). \tag{7}$$

Inspection of the term L^2 in equation (6) shows that it describes an *attractive* electron–hole interaction, as well as, interestingly, the simultaneous creation and destruction of electron–hole pairs. Within mean-field theory, the presence of L^2 will lead to an excitonic ground state.

Finally, we express the Hamiltonian in terms of hole operators $a^\dagger_{k\sigma h}$ which create holes in the filled valence band. They are defined as $a^\dagger_{k\sigma h} = a_{-k,-\sigma}$. The final Hamiltonian that we wish to work with is thus

$$H = -\sum_{k\sigma} \epsilon_k + \sum_{k\sigma} (b^\dagger_{k\sigma} b_{k\sigma} + a^\dagger_{k\sigma h} a_{k\sigma h}) + (2\gamma^2/KN) \sum_{k\sigma} \sum_{k'\sigma'} W_{kk'} P_{k\sigma} P_{k'\sigma'}, \tag{8}$$

where

$$W_{kk'} = \sin kb \sin k'b \tag{9}$$

and

$$P_{k\sigma} = b^\dagger_{k\sigma} a^\dagger_{-k,-\sigma,h} - a_{-k,-\sigma,h} b_{k\sigma}. \tag{10}$$

3. The excitonic ground state

The excitonic ground state of (8) is easily demonstrated in the mean-field form and we need not go into detail [12]. We take as the order parameter

$$\Delta_k = (4\gamma^2/KN) \sum_{k'\sigma'} W_{kk'} \langle P_{k'\sigma'} \rangle, \tag{11}$$

where $\langle A \rangle$ denotes the thermodynamic average of the operator A. On linearizing the Hamiltonian (8) in the usual manner the resulting H is diagonalized by the transformation to the new electron and hole QP operators $\beta_{k\sigma}$ and $\alpha_{k\sigma}$:

$$\begin{aligned} b_{k\sigma} &= u_k \beta_{k\sigma} + v_k^* \alpha^\dagger_{-k,-\sigma}, \\ a^\dagger_{-k,\sigma,h} &= -v_k \beta_{k\sigma} + u_k^* \alpha^\dagger_{-k,-\sigma}. \end{aligned} \tag{12}$$

Here the complex coefficients are $u_k = |u_k| \exp(\mathrm{i}S/2)$ and $v_k = |v_k| \exp(-\mathrm{i}S/2)$, provided that we have defined $\Delta_k = |\Delta_k| \exp(\mathrm{i}S)$. The moduli are

$$\begin{aligned} |u_k|^2 &= (1 + \epsilon_k/E_k)/2, \\ |u_k|^2 &= (1 - \epsilon_k/E_k)/2. \end{aligned} \tag{13}$$

These equations lead to the gap equation for Δ:

$$1 = (4\gamma^2/KN) \sum_{k\sigma} (\sin^2 kb/E_k)(1 - 2f(E_k)), \tag{14}$$

which is identical to the standard result, equation (3).

The number of pairs N_p mixed into the ground state is easily calculated from $N_\mathrm{p} = \sum_{k\sigma} \langle b^\dagger_{k\sigma} b_{k\sigma} \rangle$. With the use of (12), we find the result

$$N_\mathrm{p} = \sum_{k\sigma} [(1 - \epsilon_k/E_k)/2 + f(E_k)\epsilon_k/E_k]. \tag{15}$$

When $\Delta = 0$, above the mean-field transition temperature, $N_\mathrm{p} = \sum_{k\sigma} f(\epsilon_k)$ is just the number of thermally excited electron–hole pairs. At the absolute zero, $N_\mathrm{p} = \sum_{k\sigma} (1 - \epsilon_k/E_k)/2$. Thus $N_\mathrm{p} \neq 0$ if $\Delta \neq 0$. The latter is the hallmark of the excitonic insulator.

4. The optical conductivity

The optical conductivity $\sigma_1(\omega)$ is given by the Kubo formula [14]

$$\sigma_1(\omega) = \lim_{q \to 0} \frac{1 - \mathrm{e}^{-\omega/k_\mathrm{B}T}}{\omega} \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} \langle J(q,t) J(q,0) \rangle, \tag{16}$$

where the time-independent wavevector-q-dependent current is

$$J(q) = e\sum_{k\sigma} w_0 e^{iqb/2} \sin kb(b^{\dagger}_{k+q/2,\sigma} b_{k-q/2,\sigma} - a^{\dagger}_{k+q/2,\sigma,h} a_{k-q/2,\sigma,h}), \tag{17}$$

where the velocity $w_0 = 2t_0 b/\hbar$. At $T = 0$, equation (16) may be evaluated with (17) and (12), with the result that the optical conductivity of the excitonic insulator is

$$\sigma_1(\omega) = (\pi e^2/\hbar N b d^2 \omega) \sum_{k\sigma} w_k^2 |\Delta_k|^2 \delta(\omega - 2E_k/\hbar)/E_k^2. \tag{18}$$

Here d is the interchain spacing perpendicular to the chain axis, while $w_k = w_0 \sin kb$. For weak coupling, the source of the oscillator strength of (18) may be seen to reside in the Drude conductivity above the mean-field transition temperature; with $\Delta \neq 0$, the Drude conductivity vanishes at the absolute zero. Equation (18) is strictly derived for the half-filled band case. For the incommensurate PI the 'sliding' conductivity of the CDW enters the conductivity sum rule [11]. In their celebrated 1966 paper on the excitonic insulator, Jérome *et al* [15] did not consider the frequency regime $\omega \gtrsim 2\Delta$. Consequently, to our knowledge, the photoexcitation of excitonic pairs in the excitonic insulator has been ignored up to now.

The minus sign in equation (17) reflects, of course, the difference in sign of the electron and hole charges. In the excitonic phase each pair carries an electric dipole moment. Therefore, light of frequency ω can directly photoionize a pair into an electron and hole QP according to the relation $\hbar\omega = E_{k+q/2} + E_{k-q/2}$, where $q \simeq 0$ is the wavevector of the light. This is precisely expressed by the result (18). For the clean superconductor, the Cooper pair has no internal transition dipole moment and consequently there can be no light absorption for any finite ω [14].

5. Conclusions

We have shown that the half-filled Peierls insulator within the framework of mean-field theory is an excitonic insulator. In this state, there are collectively bound electron–hole pairs (excitons) mixed into the ground state. At zero temperature the number of such bound pairs is

$$N_p = \sum_k (1 - \epsilon_k/E_k), \tag{19}$$

where $E_k = \sqrt{\epsilon_k^2 + \Delta^2 \sin^2 kb}$ is the excitonic QP energy and 2Δ is the excitonic energy gap at the X point of the chain. It is determined self-consistently by the BCS-like equation

$$1 = (8\gamma^2/KN) \sum_k \sin^2 kb/E_k. \tag{20}$$

This equation is identical to the usual gap equation for the Peierls gap. A non-vanishing Δ guarantees a non-vanishing N_p.

Since the bound electron–hole pairs possess a dipole moment, they may be *photoionized* by light leading to the absorption of light at the energies $\hbar\omega \gtrsim 2\Delta$, where 2Δ is the mean excitonic energy gap of the insulator. The absorption is polarized along the chain axis and the insulator is rendered a photoconductor.

A deeper understanding of the Peierls insulator is thus achieved. As an excitonic insulator it is, like the BCS state, a two-fermion collective state phenomenon involving an attractive interaction between *pairs* of fermions. And, again like for the BCS state, the attractive pair interactions are lattice mediated. The somewhat remarkable discovery of Kuper in 1955 of a BCS-like gap equation for the Fröhlich CDW state can now be understood.

That polyacetylene itself is probably an excitonic insulator is implied by the impressive body [16] of work on the effects of electron–electron interactions on the insulating state of

the polymer. In particular, the work of Baeriswyl and his co-workers [17, 18] has stressed the importance of the attractive electron–hole interaction that arises from the nearest neighbour electron–electron interaction V in the polymer. Typically, V is found to be a much larger effect than the electron–lattice interaction. If the latter is neglected, one is in fact dealing with the problem of the regular excitonic insulator [12]. This point was made already in 1979 by Giuliani *et al* [19].

The prospect of quasi-1D polymeric excitonic insulators is, we believe, a particularly interesting one.

Acknowledgments

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