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OPTICAL CONDUCTIVITY OF SOLITONS IN POLYACETYLENE

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The soliton lattice solution of the continuum model for polyacetylene is used to derive the frequency dependent conductivity of charged solitons. The limit of low soliton density is explicitly evaluated and shown to be free of singularities. The conductivity sum rule is proven for the model Hamiltonian, and is shown to be satisfied by the explicit solution. Implications for polyacetylene and for TTF–TCNQ are discussed.

THE PROPOSAL that the doping process of polyacetylene is accomplished by forming charged solitons has received considerable experimental support [1]. In particular Suzuki *et al.* [2] have measured an additional absorption within the semiconducting gap, which may correspond to transitions to the mid-gap state of a charged soliton [3]. They have also calculated the frequency dependent absorption by using the continuum model for polyacetylene [4].

However, this calculation seems to give divergent results for the interband transitions. As noted by Tinka Gammel and Krumhansl [5] the difficulty is removed by imposing appropriate boundary conditions. Another way of removing the divergence, as suggested by Maki and Nakahara [6], is to consider the system with a small but finite density of solitons. These calculations consider a system of uncorrelated solitons and show that there is a finite reduction of the interband transitions, proportional to the soliton density.

The neglect of correlations between solitons implies that these calculations are not exact; in particular the conductivity sum rule is not exactly satisfied in any of the previous calculations [2, 5, 6].

Here I use the exact solution for the soliton lattice [7] to calculate the frequency dependent conductivity in the limit of low soliton density. The result is qualitatively as in the previous calculations [5, 6], however the detailed frequency dependence is different. This may be significant for extracting the soliton density from the experimental data. I also consider a long-standing puzzle in the optical conductivity of TTF–TCNQ [8], which may be explained by the existence of two gaps in the electron spectrum.

I first derive the conductivity sum-rule for the continuum model. Since the electron spectrum is linearized, the conventional derivation [9] does not apply. The Hamiltonian is [4]

$$H = \sum_s \int \mathrm{d}x \left\{ -iv_F \left[u_s^+(x) \frac{\partial}{\partial x} u_s(x) - v_s^+(x) \frac{\partial}{\partial x} v_s(x) \right] + \Delta(x)[u_s^+(x)v_s(x) + v_s^+(x)u_s(x)] \right\} + (2\pi\lambda v_F)^{-1} \int \mathrm{d}x\, \Delta^2(x), \tag{1}$$

where $u_s(x)$, $v_s(x)$ are fermion fields representing right and left moving electrons. The phonon field $\Delta(x)$ is time independent in the adiabatic limit considered here, v_F is the Fermi velocity and λ is the dimensionless electron–phonon coupling constant.

The kinetic part of the Hamiltonian [first term in equation (1)] has the spectrum $\pm v_F k$ where k is the electron momentum. This spectrum is unbounded and therefore the ground state contains an infinite density of fermions. This also results in unusual commutation rules for the density operators $\rho_{\pm,q}$ with momentum q of the right (+) and left (−) moving fermions as shown by Mattis and Lieb [10]:

$$[\rho_{\pm,q}, \rho_{\pm,-q'}] = \mp \frac{qL}{2\pi} \eta_s \delta_{q,q'} \tag{2}$$

where L is the length of the system and η_s is the number of spin states ($\eta_s = 2$ for electrons). If H_0 is the kinetic part of H, it was also shown that [10]

$$[H_0, \rho_{\pm,q}] = \pm v_F q \rho_{\pm,q}. \tag{3}$$

Therefore I obtain for $\rho_q = \rho_{+,q} + \rho_{-,q}$

$$[[H_0, \rho_q], \rho_{-q}] = -v_F q^2 L \eta_s / \pi. \tag{4}$$

This commutator for the interaction terms in equation (1) vanishes, so that one can replace H_0 by H in equation (4). In the usual derivation [9] of the sum rule, the commutator (4) is given by $-nLq^2/m$ where n is the fermion density and m its mass. Here the density n is infinite, but the mass m is infinite too – spectrum linear in k. The ratio n/m corresponds however to a

finite quantity, which from equation (4) is $v_F\eta_s/\pi$. One can also define formally a Fermi wavevector k_F so that $n = \eta_s k_F/\pi$ and then the correspondence in the commutator (4) is $v_F \leftrightarrow k_F/m$. The derivation of the sum rule proceeds now as in the usual case [9] with the plasma frequency given by $\omega_p^2 = 4e^2 v_F \eta_s$ and the results for electrons with spin 1/2 is

$$\int_0^\infty \mathrm{Re}\,\sigma(\omega)\,\mathrm{d}\omega = e^2 v_F. \tag{5}$$

The continuum model seems to have lost the dependence on the number of electrons. Note however, that changing k_F while m is fixed means that we have to change v_F in the linearized model. Thus the sum rule depends on the number of electrons through the choice of the parameter v_F.

Consider now the conductivity of the soliton lattice solution [7]. The electron eigenfunctions $u_q(x), v_q(x)$ satisfy

$$\left[-v_F^2\frac{\partial^2}{\partial x^2} + \Delta^2(x) - v_F\Delta'(x)\right] f_q(x) = \epsilon_q^2 f_q(x),$$

$$\left[-v_F^2\frac{\partial^2}{\partial x^2} + \Delta^2(x) + v_F\Delta'(x)\right] g_q(x) = \epsilon_q^2 g_q(x), \tag{6}$$

where $f_q(x) = u_q(x) + iv_q(x)$, $g_q(x) = u_q(x) - iv_q(x)$. The solution for $\Delta(x)$ is [7]

$$\Delta(x) = \Delta_1 k\,\mathrm{sn}\,(x/k\xi, k)\,\mathrm{cd}\,(x/k\xi, k), \tag{7}$$

where $2\Delta_1$ is the gap in the commensurate case (if $\lambda \ll 1$), $\xi = v_F/\Delta_1$ and sn, cd are Jacobian elliptic integrals with parameter k. This parameter determines the soliton density $\rho = 2/l$ with $l = 2\xi k K(k)$ and K is the complete elliptic integral. The eigenvalues ϵ_q form 3 bands as shown in Fig. 1; the solution corresponds to the valence band ($q < -\pi/l$) being full, the mid-band ($|q| < \pi/l$) being either empty or full (with two spin states) and the conduction band ($q > \pi/l$) is empty.

The current operator is $ev_F(|u(x)|^2 - |v(x)|^2)$ and leads to the conductivity [5, 6]

$$\mathrm{Re}\,\sigma(\omega) = \frac{2\pi e^2 v_F^2}{\omega L}\sum_{q'}{}'\sum_{q}{}''|M_{q,q'}|^2\,\delta(\omega + \epsilon_{q'} - \epsilon_q), \tag{8}$$

where $\Sigma'(\Sigma'')$ is summation on occupied (empty) states and

$$M_{qq'} = \frac{1}{2}\int \mathrm{d}x\,[f_q(x)g_{q'}^*(x) + f_{q'}^*(x)g_q(x)]. \tag{9}$$

For low soliton density the valence to midband transitions are easily evaluated (for empty midband; if full consider midband to conduction transitions). The result is the same as for the single soliton calculation [2, 5, 6]

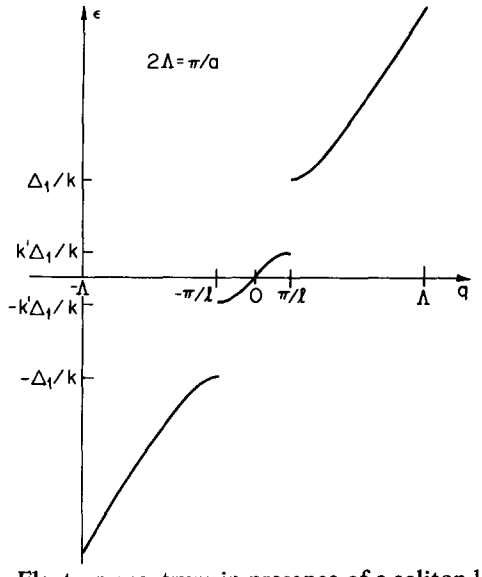

Fig. 1. Electron spectrum in presence of a soliton lattice with periodicity l. The extended zone scheme is used and the spectrum appears symmetrically to the left of the point $-\Lambda$.

$$\mathrm{Re}\,\sigma_1(\omega) = \frac{1}{2}v_F\xi\rho e^2\pi^2\frac{\mathrm{sech}^2\left[\frac{\pi}{2}\sqrt{\left(\frac{\omega}{\Delta_1}\right)^2 - 1}\right]}{\sqrt{\omega^2 - \Delta_1^2}} \times\theta(\omega - \Delta_1). \tag{10}$$

For the valence to conduction band transitions equation (9) can be written as

$$M_{qq'} = \frac{i}{2}\int \mathrm{d}x\left\{-v_F g_q'(x)g_{q'}^*(x)\left(\frac{1}{|\epsilon_q|} - \frac{1}{|\epsilon_{q'}|}\right) + g_q(x)\Delta(x)g_{q'}^*(x)\left(\frac{1}{|\epsilon_q|} + \frac{1}{|\epsilon_{q'}|}\right)\right\}. \tag{11}$$

When $k' \to 0$ ($\rho \sim \ln^{-1} 4/k' \to 0$) $\Delta^2(x) + v_F\Delta'(x) \to \Delta_1^2 + 0(k'^2)$ except at the minimum points of dn $(x/k\xi, k)$. Thus $g_q(x) = e^{iqx}/\sqrt{L} + \delta g_q(x)$ and $\delta g_q(x)$ can be shown to yield corrections of order ρ^2 which are neglected. Thus the first term of equation (11) vanishes while the second term with a Fourier expansion of $\Delta(x)$ yields for the interband transition

$$\mathrm{Re}\,\sigma_2(\omega) = \frac{\pi^2 e^2 v_F^2}{2\omega}\rho^2\sum_Q \frac{1}{\mathrm{sh}^2(\pi Q\xi/2)}\int_{\pi/l}^\infty \mathrm{d}q\left(\frac{1}{|\epsilon_q|} + \frac{1}{|\epsilon_{q+Q}|}\right)^2\delta(\omega - |\epsilon_q| - |\epsilon_{q+Q}|), \tag{12}$$

where $Q = (2n+1)\cdot 2\pi/l$ and n is an integer. (Note that the Fourier components of $\Delta(x)$ are only odd multiples of $2\pi/l$.)

To first order in ρ the spectrum is [7]

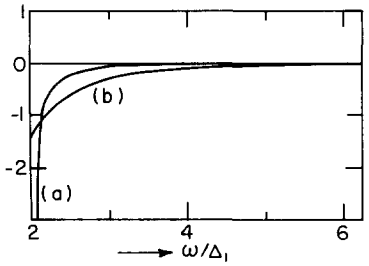

Fig. 2. The contributions to the correction of the interband transition: (a) Re $\sigma_2^{(1)}(\omega)$ [equation (15)]; (b) Re $\sigma_2^{(2)}(\omega)$ [equation (16)] in units of $e^2\xi^2\rho$.

$$\epsilon_q = (1+\bar{q}^2)^{1/2} + \rho\bar{q}(1+\bar{q}^2)^{-1/2}\tan^{-1}\bar{q}, \tag{13}$$

where $\bar{q} = q - \pi/l$. To obtain the correction due to the second term of equation (13) use the leading term of $\mathrm{sh}^2(\pi Q/2)$ as $Q \to 0$ and $Q \to 0$ in the integral with the result Re $\sigma_0(\omega)$ + Re$\sigma_2^{(1)}(\omega)$ where

$$\mathrm{Re}\,\sigma_0(\omega) = e^2 v_F \left(\frac{2\Delta_1}{\omega}\right)^2 (\omega^2 - 4\Delta_1^2)^{-1/2}\theta(\omega - 2\Delta_1), \tag{14}$$

$$\mathrm{Re}\,\sigma_2^{(1)}(\omega) = -4\Delta_1 v_F \rho\,\omega^{-2}\,\mathrm{Re}\,\sigma_0(\omega). \tag{15}$$

$\sigma_0(\omega)$ is the conductivity in the absence of solitons, while equation (15) gives the leading order correction due to the spectrum correction equation (13). This correction is dominated by interband transitions $q' \to q$ where $|q|$ and $|q'|$ are almost equal. This limit was also assumed in the previous calculations [5, 6]. Here however it is strictly an expansion in ρ and in fact there is an additional correction which is not dominated by the $Q \to 0$ terms. To see this use $\epsilon_q = (1+q^2)^{1/2}$ in equation (10) and then the q integration can be done. Next choose $N_0 \gg 1$ but $Q_0 = (2N_0+1)\cdot 2\pi/l \ll 1$. For $n \leqslant N_0$ expand $\mathrm{sh}^2(\pi Q/2)$ as before and the sum can be done. For $n > N_0$ change the sum to an integral and integrate by parts the terms which are singular at $Q = 0$ and $\omega^2 = v_F^2 Q^2 + 4\Delta_1^2$. This leads to equation (14) with an additional correction (here $v_F = \Delta_1 = 1$)

$$\mathrm{Re}\,\sigma_2^{(2)}(\omega) = 8e^2\rho\omega \int_0^{\sqrt{\omega^2-4}} \frac{\sqrt{\omega^2-Q^2-4}}{\mathrm{th}(\pi Q/2)} \times \frac{\partial}{\partial Q}\left[\frac{\sqrt{\omega^2-Q^2}}{(\omega^2-Q^2)^2+4Q^2} \times \frac{1}{\omega^2-Q^2-4+\frac{2Q}{\pi}\,\mathrm{sh}\frac{\pi Q}{2}\,\mathrm{ch}\frac{\pi Q}{2}}\right] \mathrm{d}Q. \tag{16}$$

This correction is compared with equation (15) in Fig. 2; its effect is to moderate the sharpness of the peak of equation (15). The total correction to interband intensity Re $\sigma_2(\omega)$ = Re $\sigma_2^{(1)}(\omega)$ + Re $\sigma_2^{(2)}(\omega)$ is shown

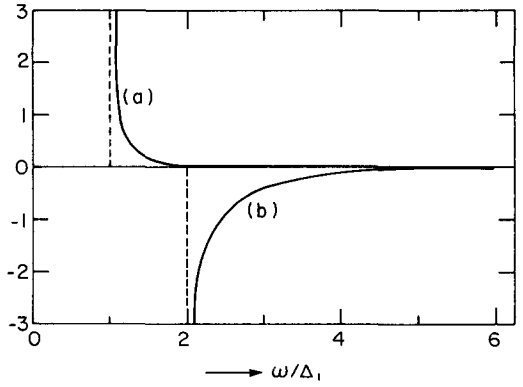

Fig. 3. The corrections to the optical absorption due to solitons with low density ρ. (a) Re $\sigma_1(\omega)$ – transition to (or from) the mid-gap states; (b) Re $\sigma_2(\omega)$ – valence to conduction band transitions (in units of $e^2\xi^2\rho$).

in Fig. 3 together with the mid-band contribution equation (10). The corrections to the interband transition is singular at $\omega = 2\Delta_1$ and decreases as ω^{-3} at high frequencies, approaching $-2\rho\xi$ Re $\sigma_0(\omega)$.

The contribution of equation (10) to the sum rule is

$$\int_0^\infty \mathrm{Re}\,\sigma_1(\omega)\,\mathrm{d}\omega = v_F e^2 \cdot \rho\xi \cdot (2.82 \pm 0.005). \tag{17}$$

The contribution of the interband transitions to the sum rule can be found by first integrating equation (12) and then following the previous procedure. For $\rho = 0$ the sum rule is satisfied since

$$\int_0^\infty \mathrm{Re}\,\sigma_0(\omega)\,\mathrm{d}\omega = e^2 v_F \tag{18}$$

while the contribution of $\sigma_2(\omega)$ to the sum rule is found to cancel exactly equation (17). [The cancellation is analytic, i.e. it does not use the numerical results in equation (17).] Thus the sum rule is obeyed also to first order in ρ, which is a useful check on the validity of the calculation.

Consider next the experimental data on polyacetylene [2]. It was noted by Maki and Nakahara [6] that comparisons of the ratio of equation (17) in the sum rule with the experimental data yields soliton densities which are larger than the doping level, e.g. by a factor ~ 2 at 0.5% doping level. If so, this supports the possibility that for very low doping levels the added charge forms a bound state of a charged soliton and neutral one [11]. This state, which does not change the topology of the chain, has spin $\frac{1}{2}$ and charge $\pm e$, i.e. it is a polaron. The optical spectrum of a neutral soliton is identical to that of a charged one – the transition from the valence band to the singly occupied mid-gap state adds up with the transition from the mid-gap state to the conduction band to give equation (10). Thus the optical

intensity of a polaron should be roughly twice that of a soliton.

Conserving the topology at the ends of a chain means that an even number of charges will form solitons, while an odd number will form one polaron and solitons. Thus upon doping beyond 0.5% the ratio of solitons/polarons on each chain should increase and (for $\rho\xi \ll 1$) the agreement with equation (15) should improve.

Finally, consider the optical conductivity data of TTF–TCNQ [2]. This system has 0.59 electrons per TCNQ molecule, and is therefore highly incommensurate. However, the effects of the second order unklapp process should still be there, i.e. the gap appears at the Fermi surface *and* symmetrically above the band center at higher energies (see Fig. 1). The absorption peak associated with the additional gap appears at the frequency of $4t \cos k_F b + \Delta \simeq 2.4t$ assuming a tight binding band with transfer integral t, and a gap $\Delta \ll t$.

Experimentally [8] there is indeed a broad minimum at $\sim 1400\ \text{cm}^{-1}$ followed by a maximum at $\sim 1900\ \text{cm}^{-1}$. A possible explanation of this feature is intramolecular phonon modes [12]. However, the required electron–phonon coupling seems to be too large. If the maximum is due to the additional gap then $t \simeq 0.1$ eV in good agreement with other estimates [8]. This interpretation implies that the band structure in TTF–TCNQ is highly one-dimensional.

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NOTE ADDED IN PROOF

After submitting this paper I received a preprint by Kivelson *et al.* [13] in which the boundary conditions in presence of a single soliton are carefully studied. These authors show that the correct procedure yields an optical absorption which indeed satisfies the optical sum rule in the continuum limit. The soliton lattice solutions used here, have the correct boundary conditions built in them. The results of Kivelson *et al.* coincide with mine in the limit of low soliton density, confirming the validity of both calculations.

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