SOLITON AND POLARON GENERATION IN POLYACETYLENE

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Abstract The nonradiative decay of an e-h pair into soliton
pair and that of an electron (hole) into polaron as well as
the photoproduction of solitonpairs are considered using the
lattice relaxation theory generalized to include the self-
consistency of multi-electron states with the lattice symmetry
breaking. The branching ratio of the photogenarated neutral
to charged soliton pairs is estimated. The recent related
experiments are discussed.

INTRODUCTION

Since the creation energy of a soliton pair $2E_s = 4\Delta/\pi$ is less
than the energy of an e-h pair, the latter is metastable w.r.t.
the former. Similarly, a single electron (hole) will decay into a
polaron with energy $E_p = 2\sqrt{2}\,\Delta/\pi$. On the other hand, the soliton
pair can be generated directly by absorbing a photon of energy less
than the optical gap with the assistance of the lattice quantum
fluctuation. The nonradiative decay of the e-h pair and that of
the electron have been studied by Su and Schrieffer[1] on a discrete
lattice. The photoproduction of the soliton pairs has been consi-
dered by Sethna and Kivelson[2] using the instanton technique. Both
radiative and nonradiative processes of soliton and polaron gene-
ration as well as the life-time effects on the band-to-band and
kink-to-band absorption have been studied by us[3,4] using the gene-
ralized theory of lattice relaxation[5] In this paper we summarize
our main results and compare them with the recent experiments.

NONRADIATIVE PROCESSES

The standard continuum version of the SSH Hamiltonian can be iden-

tically rewritten as

$$\mathcal{H} = \mathcal{H}_o^e + \mathcal{H}_o^{ph} + \mathcal{H}_{int} ,\tag{1}$$

$$\mathcal{H}_o^e = \int dx \left[\psi^\dagger(x) \left(\frac{\hbar v_F}{i} \frac{d}{dx} \tau_3 + 4\alpha \, u_c(x) \tau_1 \right) \psi(x) + \frac{\rho}{2} \omega_b^2 \, u_c^2(x) \right],\tag{2}$$

$$\mathcal{H}_o^{ph} = \frac{\rho}{2} \int dx \left\{ \dot{u}(x) \dot{u}(x) + \omega_b^2 [u(x) - u_c(x)][u(x) - u_c(x)] \right\},\tag{3}$$

$$\mathcal{H}_{int} = \int dx \left[4\alpha \, \psi^\dagger(x) \tau_1 \psi(x) + \rho \omega_b^2 \, u_c(x) \right][u(x) - u_c(x)] ,\tag{4}$$

where $\psi(x), \psi^\dagger(x)$ are spinor fermion operators, τ_1, τ_3 Pauli matrices, $u(x)$ staggered lattice displacement operator with $u_c(x)$ as its classical counterpart and $\dot{u}(x)$ as the velocity. Here v_F is the Fermi velocity and α the el-ph coupling constant. For simplicity we limit ourselves to the single frequency model ($\omega_b^2 = 4K/M$, K the spring constant, M the (CH) group mass) for the optical phonon. The linear density $\rho = M/a$, where a is the lattice constant. A summation over the spin index is understood where needed, while the x integration is taken over the chain length L.

In the Born-Oppenheimer approximation the state vector can be decomposed as

$$| \ > = |e> \otimes |\tilde{n}>,\tag{5}$$

with $|e>$ diagonalizing the electron Hamiltonian and $|\tilde{n}>$ — the phonon part with shifted origin. Also, the diagonal matrix element of $\mathcal{H}_{int}$ should vanish for both $|e>$ and $|\tilde{n}>$. The nonradiative decay rate is then determined by the Golden rule using $\mathcal{H}_{int}$ as perturbation. It is essential to note, however, that the total $\mathcal{H}$ is split into interacting and noninteracting parts differently in the initial and the final states in accord with their own lattice relaxations $u_c(x)$ and $v_c(x)$. Therefore, they belong to different complete sets. Nevertheless, the result depends only on the transition amplitude but not on the overlap integral.

In the low temperature ($\hbar\omega_b \lesssim k_B T$) and strong coupling ($|5\hbar\omega_b - W_{if}|/5\hbar\omega_b \lesssim 1$) limit the probability of nonradiative

decay is given by

$$W = \frac{\pi \lambda \, v_F}{4} \left(\frac{2\pi}{S}\right)^{1/2} \exp\left\{-\frac{(W_{if} - S\hbar\omega_b)^2}{2S\hbar^2\omega_b^2}\right\} \sum_\nu |\langle e_f| K_\nu |e_i\rangle|^2 \quad (6)$$

with

$$W_{if} = E_i - E_f , \quad (7)$$

$$\lambda \equiv 32\,\alpha^2/\pi\,\rho\,\omega_b^2\,\hbar\,v_F, \quad (8)$$

$$K_\nu \equiv \int dx \, \psi^\dagger(x) \, \tau_i \, \psi(x) \, \zeta_\nu(x) + \rho\,\omega_b^2\,u_\nu^c/4\alpha, \quad (9)$$

$$S \equiv \frac{\rho\omega_b^2}{2\hbar} \int dx \, [\, u_c(x) - v_c(x)\,]^2 \quad (10)$$

with $\zeta_\nu(x)$ as eigenmodes and u_ν^c as the expansion coefficients for the lattice relaxation $u_c(x)$. Here the Huang-Rhys factor S is the average number of phonons needed to bring the initial lattice con-figuration into the final one.

Using the self-consistent solutions of the Bogoliubov-de Gennes equation and assuming the Hartree approximation for the electron states we have estimated the nonradiative decay rate for both po-laron and soliton pair cases to be of order of 10^{13} sec^{-1} in ag-reement with the numerical calculation of Su and Schrieffer[1] with the same set of parameters, namely, $\Delta = 2$ eV, $\hbar\omega_b = 0.1$ eV, $\lambda = 0.62$, $L/\zeta = 10$, where ζ is the coherence length.

It is worthwhile to point out that the nonradiative decay of e-h pair into soliton pair (either neutral or charged) would be forbid-den, if there had been no term proportional to $\rho\omega_b^2 u_c(x)$ in $\mathcal{H}_{int}$ and the many-electron background effects had been ignored, because the term proportional to $\psi^\dagger(x)\tau_i\psi(x)$ in (4) is odd under charge conjugation, whereas the initial as well as the final states are charge conjugation even. As far as the $\rho\omega_b^2 u_c(x)$ term is present, the nonradiative decay is allowed in agreement with the calculation on the discrete model.[1] We would like to mention that this result differs from that of Ref. 6 where the el-ph interaction Hamiltonian does not account for explicitly the lattice symmetry breaking.

RADIATIVE PROCESSES

Within the framework of the lattice relaxation theory the multipho-
non effects are included into radiative processes by calculating
the Franck–Condon overlap integral. In the low temperature, strong
coupling limit the cross section for the direct process of soliton
pair photoproduction is given by[3,4]

$$\sigma^d = \frac{2\pi e^2 v_F^2}{c\,\omega\,\hbar\,\omega_b}\,\sum_{e_f}\,|<e_i|\,\hat{J}\,|e_f>|^2\,[\tfrac{2\pi}{S}]^{1/2} exp\{-\frac{(\hbar\omega-\frac{4}{\pi}\Delta-S\hbar\omega_b)^2}{2\,S\,\hbar^2\,\omega_b^2}\} \quad (11)$$

where

$$\hat{J}\; \equiv \int dx\;\psi^\dagger(x)\,\tau_3\,\psi(x). \tag{12}$$

c the speed of light, ω the photon frequency and S the lattice
relaxation for the s–s̄ pair. Notice that the frequency dependence
of σ^d is Gaussian apart from the pre-exponential factor ω^{-1}.
Such dependence agrees in essential features with what obtained by
Mele[7] for the optical absorption curve of trans – $(CH)_x$ using the
equation of motion method for the discrete lattice. The asymmetric
tail at the high frequency end appearing there is due to the long
time behavior of phonons which we do not consider here. To compare
with the experimental results one needs to include higher excitat-
ions to be discussed later.

We would like to point out the selection rule which forbids the
direct process of photoproducing neutral soliton pairs following
from the symmetry arguments.[3,4] In fact, the current operator (12)
is odd under space inversion whereas the filled valence band state
as well as the neutral s–s̄ pair configuration have even parity, so
the matrix element $<e_f|\hat{J}|e_i>$ vanishes. We should note that this
conclusion is valid up to arbitrary order of multiphonon processes.
This selection rule was also independently obtained by Ball, Su
and Schrieffer using somewhat different arguments.[6]

There are two channels of photogenerating soliton pairs. One is
the direct process we have just considered; the other is an indi-

rect process of first photoexciting the e-h pair and its subsequent
decay into soliton pair via a nonradiative process. The band-to-
band optical absorption with the life-time effects being accounted
for is given by[3,4]

$$\sigma^i = \frac{4\pi^2 e^2 v_F^2}{c\omega} \sum_k \frac{\Delta^2}{\epsilon_k^2} \frac{1}{\pi} \frac{\Gamma_k/2}{(2\epsilon_k - \hbar\omega)^2 + \Gamma_k^2/4},$$

(13)

where $\epsilon_k^2 = \hbar^2 v_F^2 k^2 + \Delta^2$ and Γ_k the line-width due to the nonra-
diative decay. Since the neutral and charged solitons are equally
probable in the nonradiative decay, we can estimate the branching
ratio of neutral to charged solitons in the photogeneration as[3,4]

$$\sigma^i / \sigma^d \simeq 10^{-3}.$$

(14)

To conclude this section we would like to mention that the above
described calculations have been redone by Gu and Wang[8] using the
Slater determinant wave functions for electrons instead of the Har-
tree approximation we have adopted. Although their numbers are
somewhat different from ours, all basic features of the theory
including the selection rules have been confirmed by numerical cal-
culations.

COMPARISON WITH EXPERIMENTS

(i) We have previously compared[3,4] the cross section of soliton
photogeneration given by (11) with earlier data on photoconducti-
vity[9] and the agreement turns out to be good without adjusting pa-
remeters apart from the arbitrariness of the photocurrent units.
Since photoconductivity is a complicated process one might quest-
ion about the legitimacy of such comparison. However, Blanchet et
al.[10] have found recently that the photoinduced (PI) IR absorpt-
ion at 1370 cm^{-1} which should be observed only for charged defect
states, has the same excitation frofile as the photoconductivity.
This confirms the theoretical results in a more convincing way.

(ii) Very recently, Weinberger et al.[11] have shown using the photothermal deflection spectroscopy that the optical absorption has the same frequency dependence as the photocurrent and also that both of them display the typical Urbach tail structure well below the optical gap. These authors intend to interpret their data in terms of disorder effects. We would like to point out that these data are consistent with our theoretical results. First of all, these two curves should coincile with each other because the absorption edge is determined by the direct process of soliton pair generation. Moreover, there is no sharp threshold in the frequency dependence of (11) due to the life-time effects.

(iii) The upper bound for the branching ratio of PI neutral to charged soliton pairs found by Flood et al. [12] from the PI ESR experiments $(2x10^{-3})$ is consistent with our estimate (14). Recently, Orenstein et al.[13] found that the PI ESR signal decreases exactly the same way as the PI IR absorption increases, which means that, probably, the neutral solitons existed before become charged. This observation along with the fact that the nature of the PI absorption at 1.38 eV and 0.45 eV has not yet been fully understood[13,14], shows that the question whether the photocurrent is carried by charged soliton photogenerated directly or indirectly, is still open. In this connection we would like to mention that the neutral solitons are allowed in the indirect process and also that the selection rule which forbids the direct process of neutral pair photoproduction is very sensitive to the parity symmetry. In fact, this rule is strictly obeyed only for a ring consisting of 4N+2 chains but not for rings of 4N chains[8] because the valence band is not strictly parity even for the latter case. The bleaching of 1.38 PI absorption at relatively high temperatures (200K)[14] might be associated with the charging process of the neutral pairs. However, to fully understand the experimental results one needs to include the correlation effects.

REFERENCES

1. W.P. Su and J.R. Schrieffer, Proc. Natl. Acad. Sci. (USA) 77 (1980) 5526.
2. J.P. Sethna and S. Kivelson, Phys. Rev. B26 (1982) 3515.
3. Z.B. Su and L.Yu, Phys. Rev. B27 (1983) 5199; Erratum B29 (1984) 2309.
4. SU Zhao-bin and YU Lu, Commun. in Theor. Phys. (Beijing, China) 2 (1983) 1203, 1323, 1341.
5. See. e.g., HUANG Kun, Progr. in Physics (Nanjing, China) 1 (1981) 31.
6. R. Ball, W.P. Su, and J.R. Schrieffer, J. de Phys. C3 (1983) 429.
7. E.J. Mele, Synth. Metals, 9 (1984) 207.
8. GU Zhong-quan and Wang Yong-liang, Acta Semicon. Sinica (Beijing, China) to be published and private communication.
9. L. Lauchlan, S. Etemad, T.-C. Chung, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. B24 (1981) 3701.
10. G.B. Blanchet, C.R. Fincher, and A.J. Heeger, Phys. Rev. Lett. 51 (1983) 2132.
11. B.R. Weinberg, C.B. Roxlo, S. Etemad, G.L. Baker, and J. Orenstein, Preprint, to appear in Phys. Rev. Lett.
12. J.D. Flood and A.J. Heeger, Phys. Rev. B28 (1983) 2356; A.J. Heeger, These Proceedings.
13. J. Orenstein, These Proceedings.
14. Z. Vardeny, These Proceedings.