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Triplet solitonic excitations in *trans*-polyacetylene

W. P. Su

Department of Physics, University of Houston–University Park, Houston, Texas 77004

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In the Su-Schrieffer-Heeger model of *trans*-polyacetylene, the lowest triplet state consists of a pair of neutral solitons. Absorption of the photogenerated neutral solitons can account for the observed photoinduced high-energy peak in the optical gap, provided electron-electron interactions are properly considered. Consequences of the theory are discussed.

Following a suggestion[1] that solitons can be photogenerated much of the recent experimental effort in polyacetylene has focused on the photospectroscopy of $(CH)_x$. Using laser pulses, Orenstein and Baker[2] were able to generate two photoinduced absorption peaks in the optical gap of pristine $(CH)_x$. It is now generally believed[3-5] that the low-energy peak is due to the absorption of photogenerated *charged* solitons. The high-energy peak has, however, remained mysterious despite many theoretical attempts.

In this connection the abundant existing flash photolysis and pulse radiolysis data on finite-length polyenes[6-11] are very illuminating. Polyenes are molecular analogs of $(CH)_x$. Because of their biological significance they have been extensively studied spectroscopically. It is well known that there exists a photoinduced absorption peak slightly below the optical gap. This peak can be regarded as the counterpart of the high-energy peak seen in $(CH)_x$. It is also widely accepted that this peak is due to a triplet-triplet absorption. Among other reasons this assignment is supported by the fact that the above transient can be sensitized by other triplet states. The polyenes originally pumped into a singlet excited state are believed to make a transition to a triplet state via intersystem crossing.

In Ref. 1, the lattice dynamics following the creation of an electron-hole pair is depicted. Within the Su-Schrieffer-Heeger (SSH) model[12] a pair of solitons is generated in a few picoseconds. The result is identical for both the triplet and the singlet states because they have the same energy. As pointed out in Ref. 13, however, the solitons generated in the singlet channel are charged. We show here that the triplet state relaxes into two neutral solitons.

Consider the lattice configuration of an overlapping pair of a soliton and an antisoliton. In the corresponding electronic energy spectrum there are two gap states ψ_+ and ψ_-, which can be regarded as the bonding and antibonding combinations of ψ_L and ψ_R. ψ_L and ψ_R are the midgap states associated with the left-hand-side soliton S and the right-hand-side antisoliton $\bar{S}$, respectively.

$$\psi_\pm = \frac{1}{\sqrt{2}}(\psi_L \pm \psi_R) \ . \tag{1}$$

In the lowest triplet state ψ_+ and ψ_- are singly occupied. The spatial wave function of the two topmost electrons is antisymmetrical:

$$\frac{1}{\sqrt{2}}[\psi_+(1)\psi_-(2) - \psi_+(2)\psi_-(1)] \ . \tag{2}$$

Combining (1) and (2) we have

$$\frac{1}{\sqrt{2}}[\psi_L(2)\psi_R(1) - \psi_L(1)\psi_R(2)] \ , \tag{3}$$

which shows that both ψ_L and ψ_R are singly occupied. Thus S and $\bar{S}$ are neutral.

Once the neutral solitons are generated they are stable since the effective interaction between them is repulsive.[14] Being the lowest-energy triplet state the neutral solitons are also stable against dipole emission. Hence, they are long lived and can contribute to observable photoinduced properties.

Although in the above analysis electron-electron repulsion was not included, we expect the conclusions to be valid for a certain range of the repulsion strength. The reasons include the following: (a) the triplet ground state is nondegenerate and is separated from some other types of excitations such as polarons by a finite energy difference, (b) the triplet soliton pairs being neutral, there is no effective Coulomb interaction between them, and (c) the kinetic energy available in the dynamic process should enable the system to overcome some possible Coulomb barriers.

Due to the charge-conjugation symmetry there are two lowest degenerate excited states of a neutral soliton. One of them ψ_A is obtained from the ground state by promoting the electron in the midgap state into the conduction band. The other state ψ_B is obtained by exciting an electron in the valence band into the midgap state. Within SSH model these require an energy $E_g/2$. E_g is the optical gap. By treating the interaction repulsion U as a perturbation one can estimate its effect on the absorption by calculating the matrix elements $U_{AA} = (\psi_A | U | \psi_A) = U_{BB}$ and $U_{AB} = (\psi_A | U | \psi_B) = U_{BA}$.

A symmetry operation closely related to the charge-conjugation symmetry is the Pariser pairing operator[15] P. P takes a many-electron state in which certain molecular orbitals are occupied into the charge-conjugated state of its complementing state in which the above orbitals are empty. Using the sign convention in Ref. 15, $P\psi_A = -\psi_B$ and $P\psi_B = -\psi_A$. In a neutral system P commutes with the full Hamiltonian (SSH + U) and anticommutes with the dipole moment operator. Therefore dipole transitions are only allowed between eigenstates of opposite Pariser parity. In the neutral soliton case $\psi_P = (1/\sqrt{2})(\psi_A + \psi_B)$ and $\psi_M = (1/\sqrt{2})(\psi_A - \psi_B)$ are energy eigenstates with energies $U_{AA} + U_{AB}$ and $U_{AA} - U_{AB}$ above $E_g/2$, respectively. ψ_P is odd under P, whereas ψ_M has the same parity as the ground state (even). Therefore all the dipole oscillator strength goes into ψ_P, whereas ψ_M is Raman active.

To estimate U_{AA} and U_{AB} we consider the Hubbard interactions[16,17]

$$U\sum_n [\rho_\uparrow(n)-\tfrac{1}{2}][\rho_\downarrow(n)-\tfrac{1}{2}] \ , \tag{4}$$

where $\rho_\uparrow(n)$ is the up-spin density at the n-th site. Assuming that in the ground state of a neutral soliton the midgap state $\phi_0(n)$ is occupied by a spin-up electron, then we have[12]

$$\rho_\uparrow(n)=\tfrac{1}{2}[1+|\phi_0(n)|^2] \ , \tag{5}$$

$$\rho_\downarrow(n)=\tfrac{1}{2}[1-|\phi_0(n)|^2] \ . \tag{6}$$

Therefore, within the Hartree-Fock approximation the Coulomb energy of the neutral soliton in the ground state is[16,17]

$$-\frac{U}{4}\sum_n |\phi_0(n)|^4 \ . \tag{7}$$

Let $\phi_1(n)$ be the topmost state in the valence band. Then, for the excited state ψ_B,

$$\rho_\uparrow(n)=\tfrac{1}{2}[1+|\phi_0(n)|^2] \ , \tag{8}$$

$$\rho_\downarrow(n)=\tfrac{1}{2}[1+|\phi_0(n)|^2]-|\phi_1(n)|^2 \ . \tag{9}$$

It follows that

$$U_{BB}=\frac{U}{4}\sum_n |\phi_0(n)\Big|^4-\frac{U}{2}\sum_n \Big|\phi_0(n)\phi_1(n)|^2 \ . \tag{10}$$

Since $\phi_1(n)$ is an extended state while $\phi_0(n)$ is a localized state, the overlap between them is negligible. The last term in (10) can be dropped,

$$U_{BB}=\frac{U}{4}\sum_n |\phi_0(n)|^4 \ . \tag{11}$$

The off-diagonal matrix element U_{AB} vanishes in the Hartree-Fock approximation. We have calculated U_{AB} exactly for short chain length $N=3$, 5, and 7. The ratio U_{AB}/U_{BB} is 0.33 for $N=3$, 0.12 for $N=5$, and 0.06 for $N=7$. Thus in our perturbative approach the two excited states ψ_P and ψ_M are almost degenerate in contrast to the numerical result of Soos and Ducasse.[18] They adopted the Pariser-Parr-Pople model and found a large splitting between ψ_P and ψ_M for $N=5$ and $N=7$. Whether ψ_{AB} is vanishingly small for large N in a nonperturbative approach remains to be investigated. Photoinduced Raman absorption can settle the issue experimentally.

By ignoring U_{AB} we find from (7) and (11) that the lowest absorption peak of a neutral soliton should occur at about

$$\frac{E_g}{2}+\frac{U}{2}\sum_n |\phi_0(n)|^4 \ . \tag{12}$$

Through a similar analysis the lowest absorption peak for a charged soliton is located at

$$\frac{E_g}{2}-\frac{U}{2}\sum_n |\phi_0(n)|^4 \ . \tag{13}$$

The results (12) and (13) indicate that the two peaks are symmetrically displaced from the center of the gap. Experimentally the low energy peak in the photoinduced absorption is located at about 0.4 eV and the high-energy peak[2] is at about 1.4 eV. This compares favorably with the above prediction if the size of the gap is taken to be about 1.7 eV.

Previous attempts[19,20] to explain the high-energy peak have invoked charged solitons in the singlet rector. As long as the system is in a singlet excited state it is very likely to cascade down to the ground state. It is very hard to imagine any dynamical hangup that could persist longer than a microsecond. Explanation involving the breather[21] left behind when two photogenerated solitons separate to infinity is also called into question as that would require a very long chain.

It follows from our interpretation that the high-energy peak is not correlated with the photoinduced infrared peaks. They arise from charged solitons only. This is consistent with experiment. The almost free spins associated with the neutral solitons can account for the photoinduced spins[22] recently observed. The origin of the temperature dependence of the intensity of the high-energy peak is not clear in our theory. It might be related to the temperature dependence of the intersystem crossing efficiency.

After the completion of this work we received a copy of unpublished work[23] in which the possibility of photogeneration of a neutral soliton is also discussed.

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