

Photoinduced soliton pair production in polyacetylene: An instanton approach

James P. Sethna and S. Kivelson

Institute for Theoretical Physics, University of California, Santa Barbara, California 93106

(Received 3 May 1982; revised manuscript received 6 July 1982)

Optical absorption at photon energies less than the Peierls gap can occur via the direct production of a soliton-antisoliton pair. This involves a standard dipole electronic transition which is accompanied by a highly nonlinear lattice motion. We study the transition as a tunneling problem, using an extension of the instanton bounce methods of Coleman and Callan. We present the major results in simple physical terms. Comparison is made with recent measurements of the photoconductivity in polyacetylene.

Polyacetylene is highly anisotropic; and so it is usually modeled as a one-dimensional system consisting of a half-filled band of electrons coupled to phonons. The electron-phonon coupling leads to a Peierls instability which produces a "dimerized" ground state in which long and short bonds alternate along the carbon backbone, and an energy gap $2\Delta_0$ opens at the Fermi surface. If the atomic masses were infinite, the threshold for electronic transitions would be $2\Delta_0$.

The solitons in polyacetylene are domain walls between regions of the two possible senses of the ground-state dimerization. A soliton distorts the electronic spectrum, and introduces a localized electronic state at midgap. In a soliton pair, the gap states hybridize to form a bonding and an antibonding state (Fig. 1). Since the soliton creation energy, E_s , is smaller than Δ_0 ($E_s = 2\Delta_0/\pi$ in the standard models^{1,2}), the threshold for electronic transitions is $2E_s$.

The absorption process involves a transition from the ground state (in which soliton pairs exist as fluctuations) to a final state which consists of a widely separated soliton pair with an electron in the antibonding state and a hole in the bonding state. The electronic transition is simple and has nonexponential frequency dependence; the matrix element is asymptotically proportional to the soliton separation ($D \approx eER$ as $R \rightarrow \infty$). The overlap between the lattice wave functions in the initial and final states is more subtle since the soliton fluctuations in both states are highly anharmonic and occur with equal probability at all positions along the $(\text{CH})_x$ chain. It is here that instanton methods are useful.

We shall calculate the transition rate within the continuum version of the model of Su, Schrieffer, and Heeger,¹ studied first by Takayama, Lin-Liu, and Maki.² The Hamiltonian is

$$H_0 = \sum_s \int dx \left[\psi_s^\dagger(x) \left(i2t_0 a \sigma_z \frac{\partial}{\partial x} + \Delta(x) \sigma_x \right) \psi_s(x) + \frac{1}{2} M \frac{\dot{\Delta}^2(x)}{(4\alpha)^2 a} + \frac{1}{2} k \frac{\Delta^2(x)}{(2\alpha)^2} \right]. \quad (1)$$

Here Δ is the gap order parameter, and ψ_s is a spinor with two components representing right and left moving electrons; t_0 is the hopping integral, a is the lattice spacing, α is the electron-phonon coupling, M is the (CH) mass, and k is the lattice spring constant.

We are interested in transitions between the instantaneous electronic ground state and the first excited state. (In terms of the simple model studied here, this involves promoting an electron from the bonding to the antibonding state; in the presence of electron-electron interactions these states will be suitably dressed.) Transitions involving higher-lying electronic states require larger energies $\sim 2\Delta_0$. Using the Born-Oppenheimer approximation, we can integrate out the valence band, leaving us formally with a two-electronic-state Hamiltonian coupled to the pho-

non field:

$$H_0 = \begin{pmatrix} V_0(\Delta) & 0 \\ 0 & V_1(\Delta) \end{pmatrix} + \int dx \frac{1}{2} M \frac{\dot{\Delta}^2(x)}{(4\alpha)^2 a}, \quad (2)$$

where $V_0(\Delta)$ [$V_1(\Delta)$] is the total potential energy as a function of Δ in the bonding [antibonding] state [Fig. 1(b)].

We wish to calculate the transition rate per unit length of chain due to the presence of an external electromagnetic field:

$$H_{\text{int}}(t) = \begin{pmatrix} 0 & D e^{i\omega t} \\ D e^{-i\omega t} & 0 \end{pmatrix}. \quad (3)$$

Now, consider calculating the time evolution operator $U(t) = e^{-iHt/\hbar}$ of the perturbed system, by doing a

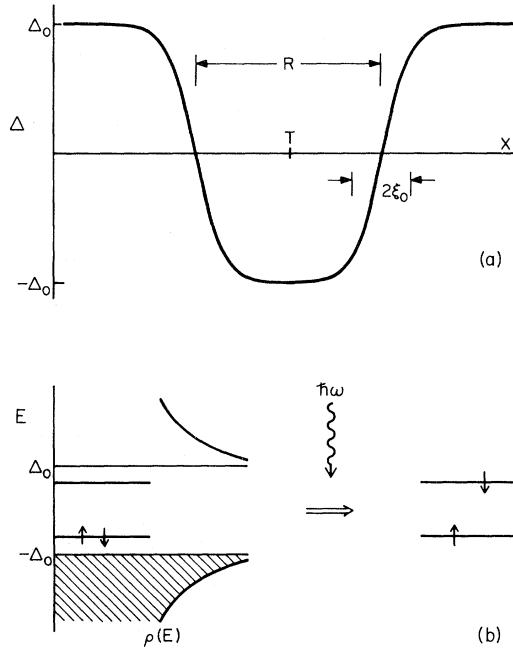


FIG. 1. (a) Soliton pair: schematic representation of a soliton antisoliton pair. $2\xi_0$ is the soliton width, R is the separation between solitons, and T is the pair center of mass. (b) Electronic transition: Density of electronic states in the presence of a soliton pair, with a schematic representation of the electronic transition.

path integral in the two-state electron space

$$U(t) = \int D(\Delta) D\epsilon e^{-iS/\hbar},$$

where $\epsilon(t) = 0, 1$ is a discrete variable which specifies the electronic state at time t , and S is the action. A flip at time t_s from zero to one will multiply the path's contribution to U by $(iD dt_s/\hbar) e^{-i\omega t_s}$; the return flip at t_f will multiply it by $(-iD dt_f/\hbar) e^{+i\omega t_f}$. The net effect of the time dependence of the external field is to multiply the contribution by $\exp[i\omega(t_f - t_i)]$. Since $t_f - t_i$ is the time spent in state one, the potential energy V_1 is effectively lowered by $\hbar\omega$. The time evolution of $H_0 + H_{\text{int}}(t)$ forced at frequency ω is precisely that of the static Hamiltonian

$$H = \begin{pmatrix} V_0(\Delta) & D \\ D & V_1(\Delta) - \hbar\omega \end{pmatrix} + \int dx \frac{1}{2} M \frac{\dot{\Delta}^2(x)}{(4\alpha)^2 a}. \quad (4)$$

It is worth noting here that this transformation is of quite general utility. We have taken a complicated transition rate problem involving a two-level system coupled to a highly anharmonic phonon field, and have turned it into a tunneling problem (see Fig. 2). Because of the highly nonlinear nature of the phonon

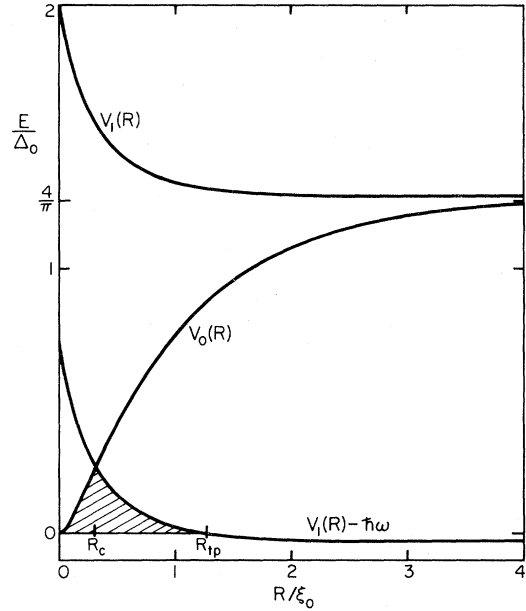


FIG. 2. Transition as a tunneling problem: Adiabatic potential surfaces as a function of soliton separation R . Also shown is the upper surface shifted by a photon energy $\hbar\omega$. The shaded region is the tunneling barrier.

field, standard multiphonon techniques such as are used to calculate Frank-Condon phonon overlap factors are not of practical utility.

However, in this form, the instanton bounce method of Coleman and Callan³ can be used to reduce the many-body decay problem to a one-coordinate WKB calculation. This is possible because the decay rate is dominated by the vicinity of the "instanton bounce" path. The instanton path is an extremum of the Euclidean action, S_E , and hence is a solution to the classical equations of motion in the inverted potential, $-V$. In our problem, this path starts with the formation of a soliton pair which then separates. At a critical separation, R_c , which can easily be seen⁴ to be the point at which $V_0 = V_1 - \hbar\omega$, the electron flips from the ground state to the excited state, and the potential abruptly shifts from V_0 to $V_1 - \hbar\omega$. The pair continues to separate until the turning point, R_{tp} , is reached (where $V_1 - \hbar\omega = 0$) and then bounces back.

We can parametrize the instanton path by the soliton separation R ; $\Delta_I(x, \tau) = \Delta^{R(\tau)}(x)$. The Euclidean action for the instanton path is given by a slightly modified WKB exponent

$$S_I = 2 \int^{R_{TP}} [2M^*(R) V_\omega(R)]^{1/2} dR, \quad (5)$$

where the potential energy is

$$V_\omega(R) = \min[V_0(\Delta^R), V_1(\Delta^R) - \hbar\omega], \quad (6)$$

and the effective mass

$$M^*(R) = M \int \frac{dx}{(4\alpha)^2 a} \left(\frac{d\Delta^R(x)}{dR} \right)^2 \quad (7)$$

is a function of R because other coordinates move with R .⁵

We cannot find the exact instanton path; integrating out the valence-band electrons for an arbitrary $\Delta(x)$ is certainly not feasible. However, the particular soliton pair configurations

$$\begin{aligned} \Delta^R(x) &= \Delta_0 - V_F K [\tanh K(x + R/2) \\ &\quad - \tanh K(x - R/2)] , \\ \tanh(KR) &= V_F K / \Delta_0 , \end{aligned} \quad (8)$$

happen to be reflectionless potentials. For these configurations, the total potential energies $V_l(R)$ are known⁶ (Fig. 2):

$$\begin{aligned} V_0(R) &= 4/\pi \Delta_0 \{ \tanh(KR) \\ &\quad - \tanh[\sinh(KR)] \operatorname{sech}(KR) \} , \\ V_1(R) &= V_0(R) + 2\Delta_0 \operatorname{sech}(KR) . \end{aligned} \quad (9)$$

This is not precisely the instanton path; however it is certainly close.⁷ The instanton action we compute with it will be an upper bound to S_I , with errors quadratic in the path error, and will suffice for our purposes.

To complete the calculation of the decay rate, one must include quadratic fluctuations about the instanton bounce path. We discuss this calculation in an institute report.⁸ There are two effects of these fluctuations. First, the shift in the phonon zero-point energies reduces the soliton creation energy⁹ by $\sim 0.6\hbar\omega_0$. Secondly, the fluctuations determine the prefactor of the decay rate. The resulting optical-absorption constant is

$$\alpha_{\text{opt}} = \alpha_0 \left(\frac{\hbar\omega}{2\Delta_0} \right) S(\omega) \exp[-S_0 S(\omega)] , \quad (10)$$

where $S(\omega)$ is the dimensionless WKB exponent, and $S_0 = (\Delta_0/2\alpha\hbar)(2t_0 M)^{1/2}$ can be computed from experimental numbers. We adopt a reasonable¹⁰ set of parameters: $2\Delta_0 = 1.65$ eV, $\alpha = 4$ eV/Å, and $t_0 = 2.5$ eV, giving $S_0 = 13$. Using the aforementioned prefactor estimates, $\alpha_0 \sim 2 \times 10^7$ cm⁻¹. This fact alone indicates that soliton pair creation should be a very significant component of the optical absorption; α_0 is two orders of magnitude larger than the experimental value of $\alpha(\omega)$ for $\hbar\omega \rightarrow 2\Delta_0$. (The prefactor of course is valid only asymptotically as $\hbar\omega \rightarrow 2E_s$, and in fact is zero at $2\Delta_0$. Also, prefactor calculations are notoriously inaccurate, and we attach no great significance to this one.)

The experimental situation in polyacetylene is complicated. In the data of Ref. 11, we believe that the intrinsic optical absorption (which emerges from the

background at 1.45 eV) is largely due to soliton pair creation. The background which masks the low-energy intrinsic absorption is presumably due to localized states (e.g., at impurities, cross links, etc.). Solitons are probably dominant¹² to the transport properties of real polyacetylene. Photoconductivity should thus be sensitive to the intrinsic optical absorption; we have compared our results to the photoconductivity data of Sethna and Kivelson and Lauchlan *et al.*¹¹ (see Fig. 3).

There are three clear indications that their data represent photoassisted soliton pair creation. First, the photoconductivity has an apparent threshold well within the gap, at roughly the expected soliton pair creation energy. Above this threshold, the photoconductivity rises exponentially. Note that this is unusual behavior; the photoconductive threshold usually lies at or above the optical band gap. Secondly, the effect disappears in the *cis*-isomer where free solitons do not exist. Thirdly, the conductivity does not change abruptly at the band gap. The (roughly frequency-independent) photoconductivity above the band gap is presumably due to direct band-band transitions. These transitions are the analytic continuation of the soliton pair formations we have studied.

Our theory is asymptotically exact near threshold. We have corrected the threshold $2E_s$ both for the phonon zero-point energy mentioned above, and for electron-electron interactions. These latter interactions lower the neutral soliton pair creation energy by

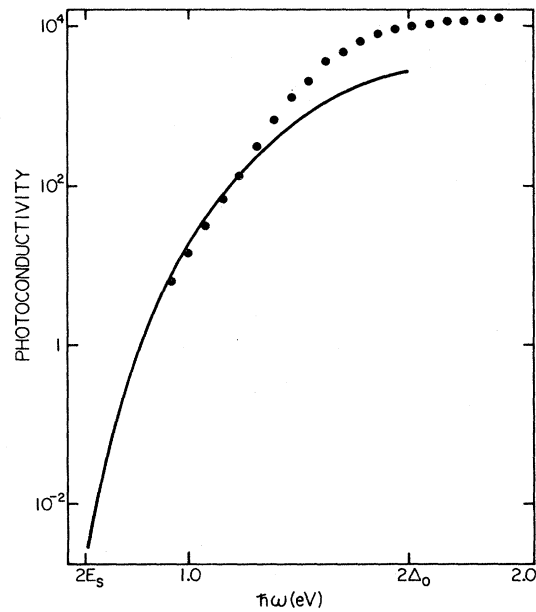


FIG. 3. Theory vs experiment: optical absorption (theoretical curve) and photoconductivity [experimental crosses, see Lauchlan *et al.* (Ref. 11)] vs frequency of the incident light. The experimental data are in arbitrary units.

$(U/2)(a/\xi_0) \approx 0.2$ eV (Ref. 13), where U is the Hubbard on-site repulsion. Therefore $2E_S \approx 0.7$ eV. Since the experimental data are expressed in arbitrary units, we have fitted the magnitude of the prefactor to the tail of the photoconductivity data.

As shown in Fig. 3, the connection to experiment near threshold is very good. For clarity in Fig. 3, we have dropped the factor $S(\omega)$ in the prefactor (it is constant near threshold, but unphysically goes to zero at $2\Delta_0$). At the point $\hbar\omega \sim 1.2$ eV where the two curves separate, $S(\omega) \approx 2$ and WKB is expected to break down. Moreover, near $2\Delta_0$ disorder and three-dimensional band-structure effects should affect the photoconductivity. Nonetheless, our rough calculation fits the experimental data (which span

three orders of magnitude of photoconductivity) within a factor of 3 over the entire range $2E_S < \hbar\omega < 2\Delta_0$.

There are indications that related effects involving polaron creation may occur in conjugated polymers with nondegenerate ground states. More generally, we believe that our application of instanton methods to a complicated transition rate problem heralds an expansion of the utility of these asymptotic methods.

ACKNOWLEDGMENT

The authors would like to acknowledge support from the National Science Foundation, under Grant No. PHY 77-27084.

-
- ¹W. P. Su, J. R. Schrieffer and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).
²H. Takayama, Y. R. Lin-Liu, and K. Maki, Phys. Rev. B **21**, 2388 (1980).
³S. Coleman, Phys. Rev. D **15**, 2929 (1977); C. G. Callan, Jr., and S. Coleman, Phys. Rev. D **16**, 1762 (1977); S. Coleman, in *The Whys of Subnuclear Physics*, edited by A. Zichichi (Plenum, New York, 1979).
⁴J. P. Sethna, Phys. Rev. B **25**, 5050 (1982).
⁵J. P. Sethna, Phys. Rev. B **24**, 698 (1981).
⁶A. Bishop and D. Campbell, Nucl. Phys. **B200**, 297 (1982); D. Campbell (private communication).
⁷Systematic improvements on this path can be made. Given our approximate path (8), one can do perturbation theory about it in the spirit of the instanton methods (by including linear and quadratic terms). Work on this is in progress, and will be published if the available experimental data warrants.
⁸J. P. Sethna and S. Kivelson (unpublished).

- ⁹M. Nakahara and K. Maki, Phys. Rev. B **25**, 7789 (1982).
¹⁰We have adopted the values of α and t_0 quoted in Ref. 1. Reference 8 quotes the somewhat higher values $\alpha = 6.9$ eV/Å and $t_0 = 3$ eV. The value of $\Delta = 1.65$ eV is a current best guess [S. Etemad (private communication)] although the actual value may be somewhat larger. As a result, S_0 may be as much as 20% smaller than the value quoted in the text. This makes no qualitative change in the fit to experiment in Fig. 3.
¹¹L. Lauchlan, S. Etemad, T. -C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **24**, 3701 (1981).
¹²S. Kivelson, Phys. Rev. Lett. **46**, 1344 (1981); Phys. Rev. B **25**, 3798 (1982).
¹³W. P. Su, S. Kivelson, and J. R. Schrieffer, in *Physics in One Dimension*, Springer Series in Solid State Sciences, edited by J. Bernasconi and T. Schneider (Springer, Berlin, 1980), Vol. 26; S. Kivelson and D. E. Heim, Phys. Rev. B (in press).