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REAL TIME DYNAMICS IN POLYACETYLENE

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Dynamical solutions to a one-dimensional coupled electron-phonon model of polyacetylene are explored numerically. The results indicate that interesting objects in polyacetylene such as neutral spin-carrying solitons, charged spinless solitons, polarons and breathers can be dynamically generated by single electron and electron pair tunneling, photoabsorption, and chain breaking

I. INTRODUCTION

We now have a good understanding of the ground state properties of both pristine and doped trans-polyacetylene based on the Peierls distortion and domain walls (kinks) separating two senses of dimerization (the A phase and B phase in Fig. 1.). Thus, neutral kinks can account for the ESR observed in pure samples, while charged spinless kink formation upon doping explains the anomaly in Curie susceptibility.[1] Theoretical effort has so far been mostly limited to static properties. It is the purpose of this paper to introduce a simple method[2] to study dynamical phenomena and illustrate the results with a few interesting examples.

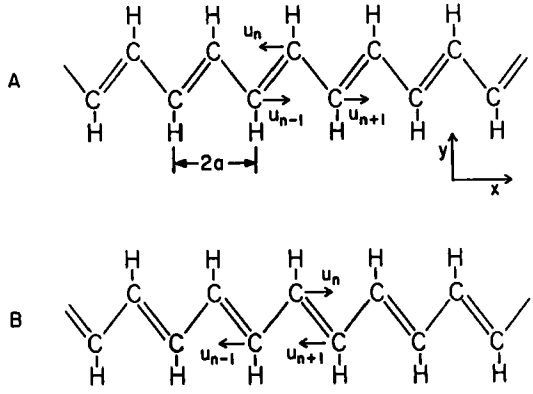

FIGURE 1 Structure of the $(CH)_x$ chain, illustrating the pattern of displacement coordinates $\{u_n\}$ in the A (Upper) and B (Lower) phases.

II. METHOD

A simplified model of trans-polyacetylene consists of a harmonic lattice (CH groups of mass M connected by springs of stiffness constant K) with π electrons that hop from one site to its nearest neighbors, with an amplitude depending linearly on the intersite spacing. If we denote by u_n the displacement of the n-th group from its equilibrium position then the Hamiltonian is

$$H = \frac{M}{2}\sum_n \dot{u}_n^2 + \frac{K}{2}\sum_n (u_n - u_{n+1})^2 + A\sum_n (u_n - u_{n+1}) - \sum_{n,s}[t_o + \alpha(u_n - u_{n+1})](c^+_{n+1,s}c_{n,s} + c^+_{n,s}c_{n+1,s}) \quad (1)$$

where $c_{n,s}$ annihilates an electron on site n with spin s. The linear term in the elastic energy is needed to keep the chain stable with respect to a uniform compression.[3]

By treating the phonon field u classically, the electron hopping matrix $\hat{T}$, where $T_{n,n+1} = T_{n+1,n} = -[t_o+\alpha(u_n-u_{n+1})]$ can be diagonalized numerically to get the electronic levels $\epsilon_{\nu,s}$ for any nuclear configuration $\{u_n\}$. In the Born-Oppenheimer approximation, the occupation numbers $n_{\nu,s}$ remain constant during a dynamical process, excluding interactions with external fields, such as the electromagnetic field. Spontaneous emission of a photon will induce transitions between levels in a time of order of 10^{-8} sec, a rather long time in comparison to the interesting times for changes of the phonon field $\simeq 10^{-13}$ sec, as we shall see later. Within this approximation, the total energy of the system can be written as

$$H_{eff} = \frac{M}{2} \sum_n \dot{u}_n^2 + V(\{u_n\}) \tag{2}$$

where the effective potential energy is

$$V = \frac{K}{2} \sum (u_n-u_{n+1})^2 + A\sum_n (u_n-u_{n+1}) + \sum_{\nu,s} n_{\nu,s}\epsilon_{\nu,s} \tag{3}$$

H_{eff} depends only on u_n and $\dot{u}_n$ so we can immediately write down the equations of motion

$$M\ddot{u}_n = -\frac{\delta V}{\delta u_n} \tag{4}$$

There is no simple analytical expression of V in terms of u_n, but $\frac{\delta V}{\delta u_n}$ can be evaluated numerically. Given any initial conditions $u_n(o)$, $\dot{u}_n(o)$ and the occupation numbers $n_{\nu,s}$, equation (4) can be integrated by finite difference methods.

In order to facilitate the calculation, we treat a finite chain of 30 $\sim$ 40 sites. The coupling constant α in (1) is chosen so that the coherence length is 2.7a, compared to 7a in actual polyacetylene. This implies a uniform dimerization amplitude u = 0.1 $\mathring{A}$ in an infinite chain and

an energy gap $2\Delta = 4.0$ eV in the electronic spectrum. With the wisdom of hindsight let us also introduce the normalized staggered order parameter

$$\bar{\psi}_n = (-1)^n \frac{u_n}{u} \tag{5}$$

III. RESULTS

We will illustrate the richness of the nonlinear dynamics by a few examples corresponding to distinct initial conditions.

Example 1: End-Kink Generation. The initial conditions are $\bar{\psi}_n(0) = 1$, $\dot{\bar{\psi}}_n(0) = 0$, $n = 0,1, \ldots 30$. A total of 31 electrons fill doubly occupy the lowest possible states with the highest energy filled state being occupied by one electron. The evolution of the system is shown in Figure 2 (left). A neutral kink is generated from the right end in less than 10^{-13} sec, sweeping across the chain until it bounces back from the left end. The center of the kink moves with an almost uniform velocity 1.3×10^6 cm/sec [Fig. 2 (Right)]. The fact that the kink cannot travel faster than the speed of sound implies that the fast neutral spin carriers in polyacetylene should move about 10^2 times slower than electrons in metals. The spin diffusion constant obtained by Nechschein et al.[4] 10^{14} cm^2/sec in a pristine sample is consistently smaller than the 10^{17} cm^2/sec obtained in a heavily doped sample where the spin carrier is probably the conventional electron or hole.

By removing the kinetic energy of the ions we can gradually bring the system into its ground state configuration, which was found to be well represented by the following tanh wall except near both ends,

$$\bar{\psi}_n = \tanh\left(\frac{15-n}{2.7}\right) \tag{6}$$

In the chemist's language, this means that an odd polyacetylene chain has double bonds on both ends and a "misfit" in the middle.[3]

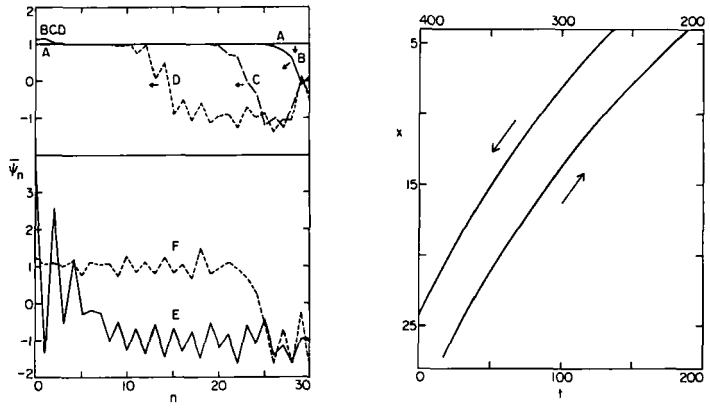

FIGURE 2 (Left) Time evolution of $\bar{\psi}_n$, illustrating an end-generated soliton for time t=0, 10, 40, 100, 226 and 400 in units of $\tau = 1.25 \times 10^{-15}$ sec. (Right) Position of center of soliton in units of lattice spacing vs. time in units of $\tau = 1.25 \times 10^{-15}$ sec. The graph is folded in the time axis and illustrates the uniformity of the velocity.

Example 2: Electron Pair Tunneling. Suppose at time t=0 we place two extra electrons on the conduction band of an even chain of 40 sites initially at rest, $\bar{\psi}_n(0) = 1$, $\dot{\bar{\psi}}_n(0) = 0$, n=0, 1, ...,39. The electrons fill up the lowest 21 states [Fig. 3(a)]. The evolution depicted in Fig. 4 shows that a pair of kinks is born in $\simeq 10^{-13}$ sec. Both kinks are charged and therefore spinless. The departing kinks thus generated eventually will bounce back from the chain ends and collide with each other again. Fig. 5 is an example of such collisions. The final velocity is only about 2/3 of the initial velocity. This is because phonons are generated during the collision. If we cool down the system, the two kinks will be found separated from each other and from both ends corresponding to soliton doping.

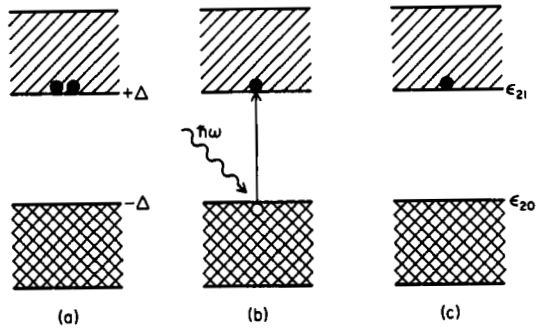

FIGURE 3 Initial electronic configurations corresponding to (a) electron pair tunneling, (b) photogeneration of kinks and (c) electron injection.

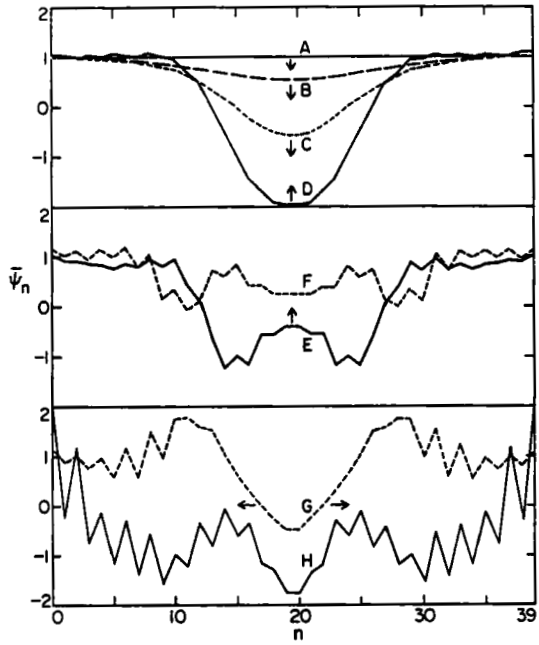

FIGURE 4 $\bar{\psi}_n$ vs. n for t = 0, 6, 12, 20, 30, 50, 60 and 130 in units of $\tau = 1.25 \times 10^{-15}$ sec, describing the generation of a soliton-antisoliton pair from a pair of electrons created at t = 0 at the band edge.

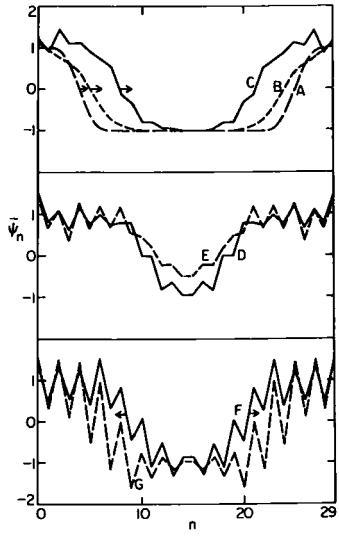

FIGURE 5 $\bar{\psi}_n$ vs. n for t = 0, 10, 30, 50, 76, 100 and 130 in units of $\tau = 1.25 \times 10^{-15}$ sec, describing the collision of a charged soliton-antisoliton pair.

Fig. 4 actually allows another interpretation[5] if we consider a spinless version of (1). There is one spinless charged particle (called S particle) for every two sites. By halving the M and K and dropping the spin index s in (2) (3) we are essentially multiplying H_{eff} by a factor of $\frac{1}{2}$. Therefore the equation of motion (4) has the same form and we conclude that injection of an S particle leads to its breaking up into two fractionally charged (-e/2) particles in 10^{-13} sec. This should be contrasted with the single particle injection in polyacetylene, where as will be seen in Example 4, only a polaron is formed.

Example 3: Photogeneration of Kinks. Instead of injecting two electrons at t=0, we could excite our electron-hole pair by a photon of energy 2Δ [Fig. (3(b)]. The initial evolution is the same as in Example 2 (Fig. 4) because $\epsilon_{20} = -\epsilon_{21}$, $2\epsilon_{20} + 2\epsilon_{21} = 0 = \epsilon_{20} + \epsilon_{21}$. The two levels ϵ_{20}, ϵ_{21} move towards the gap center as the kink pair start to separate. They are the bonding and antibonding states formed from the two localized midgap states associated with the two kinks. From this it follows that the kink pair generated is a superposition of different charge eigenstates. It is equally probable to find both kinks charged as well as neutral. The rapid change in $\bar{\psi}_n$ and accordingly in ϵ_{21} means that there is a significant broadening of the absorption edge due to nonadiabatic effects.

The above result opens up a very efficient way of generating solitons. Many properties of the system peculiar to the kink could therefore be photoinduced. Photoinduced midgap absorption would be a good example. That we can create midgap states by photons seems to be an attractive idea with possible future applications.

After a certain period of time the excited electron hole pair will eventually recombine either through radiative decay or breakdown of the adiabatic approximation. Once this happens the dynamics start to differ from that of the previous example. Fig. 6 shows the collision of two fast incoming kinks with all the electrons in the ground state. Unlike the repulsive inter-

action between two charged kinks, the kink pair here are trapped and the system undergoes a quasi periodic oscillation (with a frequency close to $\sqrt{\frac{K}{M}}$) slowly loses its energy by shaking off soft phonons. This is very similar to the breather mode found in a numerical study of φ^4 theory.[6]

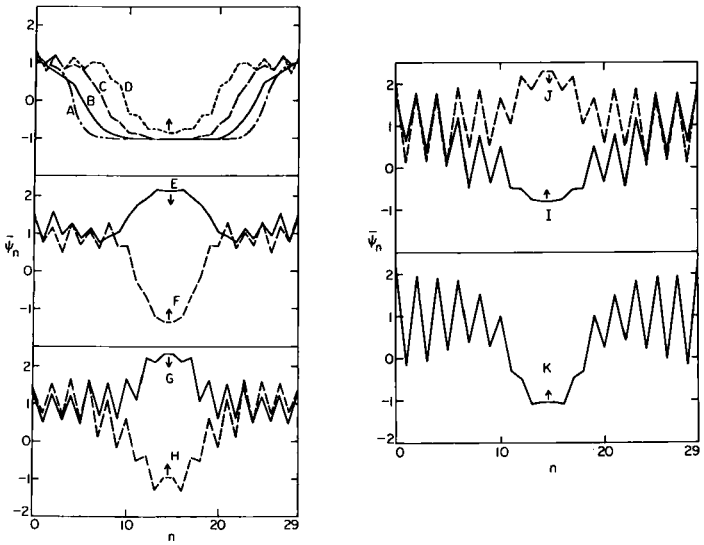

FIGURE 6 $\bar{\psi}_n$ vs. n for t=0, 10, 24, 38, 58, 79, 99, 119, 145, 165 and 185 in units of $\tau=1.25\times10^{-14}$ sec, describing the formation of a breather from a soliton-antisoliton collision.

By inspecting the average kinetic energy of the outgoing phonons, we get a rough estimate of the lifetime of the breather, to be $\simeq 10^3$ oscillations. This mode might be detected in Raman scattering.

Example 4: Electron Injection. The initial condition is the same as in Example 2, except we put one instead of two electrons in the conduction band [Fig. 3(c)]. Fig. 7 shows how the electron self-consistently distorts the lattice and localizes

itself in a split-off state, forming a strong polaron. There is not enough energy to generate a kink pair. Fig. 8 shows the ground state configuration of the polaron. The two split-off states are located at about 0.6Δ away from the gap center. The binding energy is about 0.3 eV, a small number compared to $\Delta = 2.0$ eV.

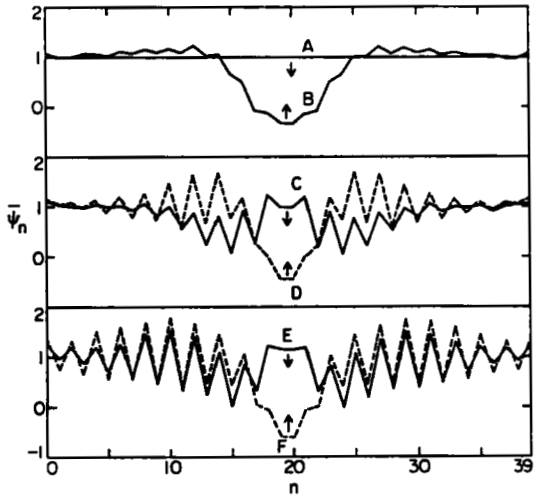

FIGURE 7 $\bar{\psi}_n$ vs. n for t=0, 26, 50, 74, 96 and 116 in units of $\tau = 1.25 \times 10^{-15}$ sec for an electron injected at the conduction band edge.

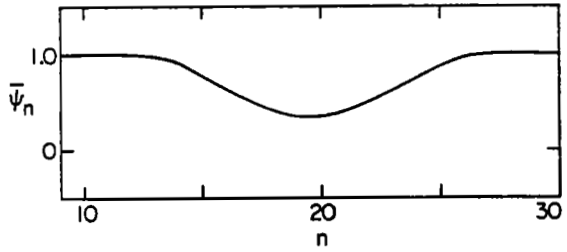

FIGURE 8 $\bar{\psi}_n$ vs. n for the ground state of one electron added to the conduction band.

The list of examples could be extended indefinitely. Other ways of adding energy into the system might generate other interesting objects.

IV. CONCLUSION

The real time dynamics in polyacetylene is a promising field. Easy and interesting numerical calculations can be performed, and later, no doubt, some of the results will find their analytic expressions. The results presented here should describe the properties of fairly short chains, quite independent of the complex morphology of the actual polyacetylene. They should constitute good topics for experimentalists to pursue.

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REFERENCES

1. W. P. Su, J. R. Schrieffer and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979); Phys. Rev. B 22, 2099 (1980); M. J. Rice, Phys. Lett. 71A, 152 (1979).
2. W. P. Su and J. R. Schrieffer, Proc. Nat. Aca. Sci. U.S.A. 77, 5626 (1980).
3. W. P. Su, Solid State Commun. 35, 899 (1980); D. Vanderbilt and E. J. Mele, Phys. Rev. B 22, 3939 (1980).
4. M. Nechschein, F. Devreux, R. L. Greene, T. C. Clarke and G. B. Street, Phys. Rev. Lett. 44, 356 (1980).
5. W. P. Su, Ph.D. Thesis, University of Pennsylvania.
6. C. A. Wingate, Los Alamos preprint.