

# Ground State Properties and Soliton Excitations in Polyacetylene

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(Dated: November 23, 2005)

A tight-binding model including phonon coupling is used to describe the quasi-one-dimensional polymer *trans*-polyacetylene. The eigenenergies and eigenstates are found for both the undimerized and perfectly dimerized cases. It is shown that the dimerization due to phonon coupling gives rise to the Peierl's instability found in *trans*-polyacetylene. The twofold degeneracy of the ground state gives rise to peculiar excitations known as solitons. A few basic properties of these topological excitations are discussed.

## I. INTRODUCTION

The study of polymers and solitons has been a large area of research over the last several decades. In the last three decades there have been thousands of papers on polyacetylene alone!<sup>1</sup> This project will focus on two aspects of polyacetylene. First, a model for quasi-one-dimensional *trans*-polyacetylene arrangement will be presented and solved in some detail. The alternating bond lengths in the chain and inclusion of phonon coupling will be shown to account for the Peierl's instability found in *trans*-polyacetylene. Second, the excitations found in *trans*-polyacetylene will be studied. It will be shown that due to the twofold degenerate ground state of *trans*-polyacetylene, peculiar excitation known as solitons can arise in the chain. The activation energy, various charge states, spin, effective mass, and width of these solitons will be discussed.

The model for *trans*-polyacetylene presented here was first developed by Su, Schrieffer, and Heeger in 1979 to describe soliton excitations.<sup>2</sup> Further details on the Su-Schrieffer-Heeger (SSH) model for polyacetylene and soliton excitations can be found in Refs. 1-3 and references therein.

## II. POLYACETYLENE AND THE MODEL HAMILTONIAN

Polyacetylene is the simplest linear conjugated polymer. It consists of weakly coupled chains of CH units forming a quasi-one-dimensional lattice and is denoted  $(\text{CH})_x$ . Three of the four valence electrons for a particular carbon atom in the chain are used in bonding with the nearest carbon atoms and hydrogen atom. The fourth creates a double bond between a pair of carbon atoms as shown in Fig. 1. The optimal bond angle of  $120^\circ$  between the bonds can be obtained with two possible arrangements of the carbon atoms. These configurations are known as *trans*-polyacetylene and *cis*-polyacetylene. In this project, only the thermodynamically stable form of *trans*-polyacetylene shown in Fig. 1 will be discussed due to its interesting ground state properties and peculiar excitations.<sup>1</sup> The arrangement *trans*-polyacetylene will be referred to as simply polyacetylene from hereafter.

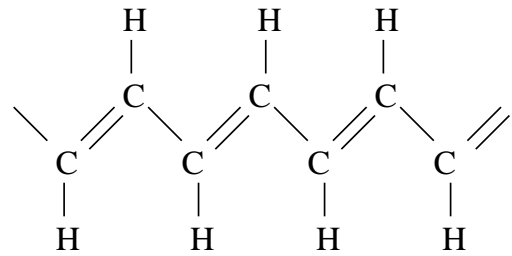


FIG. 1: Polyacetylene in its *trans* configuration. This configuration of polyacetylene is thermodynamically stable and has interesting ground state properties and topological excitations that will be discussed later in this paper.

The alternating single and double bonds (these are  $\sigma$  and  $\sigma$  plus  $\pi$  bonds, respectively) will be treated in one dimension along the symmetry axis of the chain using a tight-binding approximation including phonon coupling. To proceed, first define a configuration coordinate  $u_n$  for the  $n^{\text{th}}$  CH group as shown in Fig. 2. For a group  $n$

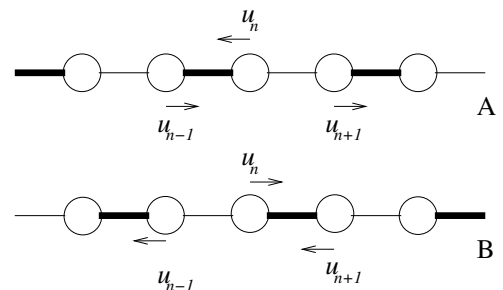


FIG. 2: Model of polyacetylene using a quasi-one-dimensional axis along the symmetry axis of the chain. The alternating single and double bonds are described using the coordination coordinate  $u_n$ . The two degenerate ground states will be referred to as the A phase and the B phase.

having a double bond to the left and a single bond to the right one has  $u_n < 0$  and  $u_{n-1}, u_{n+1} > 0$ . For the other degenerate ground state the signs are reversed. By assuming that the displacements due to the alternating single and double bonds are small, one can approximate the bonding energy of the  $\sigma$  bonds as

$$E_\sigma = \frac{1}{2} \sum_n K (u_{n+1} - u_n)^2, \quad (1)$$

where  $K$  is the effective spring constant for the  $\sigma$  bonds. The “extra” electron that is responsible for forming the  $\pi$  bond will be treated in a tight-binding approximation. Since the probability of hopping between sites will depend on the distance between sites, one can expand the hopping integral  $t_{n+1,n}$  to first order as

$$t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n), \quad (2)$$

where  $t_0$  is the hopping integral for a polyacetylene chain with equal bond lengths and  $\alpha$  is the phonon coupling constant. Finally, to take into account the motion of the CH groups, one includes the following kinetic energy term given simply by

$$E_k = \frac{1}{2} \sum_n M \dot{u}_n^2, \quad (3)$$

where  $M$  is the mass of the CH group. The model SSH Hamiltonian is then

$$H = - \sum_{ns} t_{n+1,n} \left( c_{n+1,s}^\dagger c_{ns} + c_{ns}^\dagger c_{n+1,s} \right) + \frac{1}{2} \sum_n K (u_{n+1} - u_n)^2 + \frac{1}{2} \sum_n M \dot{u}_n^2, \quad (4)$$

where  $c_{ns}^\dagger$  and  $c_{ns}$  are the creation and annihilation operators for an electron with spin  $s = \pm 1/2$  on the  $n^{\text{th}}$  CH site. The chain is assumed to have  $N$  sites with periodic boundary conditions. The length of the chain is given by  $L = Na$ , where  $a$  is the separation between CH groups when the configuration coordinate  $u$  is identically zero, i.e. the chain is undimerized.

Several approximations and assumptions have been made in writing out this Hamiltonian. In addition to the approximations mentioned above for writing out the individual terms of the Hamiltonian, it should be pointed out that this model also has the shortcoming that it neglects Coulomb interactions between the  $\pi$  electrons. These effects can be partially included by using screened values for  $t_0$  and  $\alpha$ , however, for large Coulomb interactions between  $\pi$  electrons this model is no longer valid.<sup>3</sup>

### III. THE PERFECTLY DIMERIZED CHAIN

One proceeds in the Born-Oppenheimer approximation by taking the CH group positions as fixed. By assuming that the chain is perfectly dimerized, i.e.  $u_n = (-1)^n u$ , one can write the model Hamiltonian as

$$H_d(u) = - \sum_{ns} [t_0 + (-1)^n \delta] \times c_{n+1,s}^\dagger c_{ns} + c_{ns}^\dagger c_{n+1,s} + 2NKu^2, \quad (5)$$

where  $\delta = 2\alpha u$ . The goal is to calculate the ground state energy as a function of  $u$  and then minimize this energy to find the most stable ground state for polyacetylene.

It is clear from the form of (5) that our model now consists of a one-dimensional tight-binding chain with alternating hopping constants  $t_> \equiv t_0 + \delta$  and  $t_< \equiv t_0 - \delta$  as shown in Fig. 3. It is therefore convenient to treat the  $N$

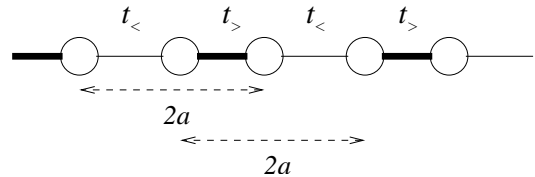


FIG. 3: Model of the  $N$  site polyacetylene chain as two  $N_d = N/2$  site systems of even and odd sites, respectively, with lattice constants  $2a$ . The alternating hopping constants are given by  $t_> \equiv t_0 + \delta$  and  $t_< \equiv t_0 - \delta$ .

site system as two  $N_d = N/2$  site systems, corresponding to even and odd sites, respectively. The Hamiltonian can then be written as

$$H_d(u) = - \sum_{ns} \left[ (t_0 + \delta) \left( c_{2n,s}^\dagger c_{2n+1,s} + h.c. \right) + (t_0 - \delta) \left( c_{2n+1,s}^\dagger c_{2n,s} + h.c. \right) \right] + 2NKu^2, \quad (6)$$

where  $h.c.$  denotes the Hermitian conjugate of the preceding term.

To proceed further, one transforms to  $k$ -space for the even and odd site annihilation operators, respectively:

$$c_{2n,s} = \frac{1}{\sqrt{N_d}} \sum_k e^{ik(2n)a} c_{ks}^{(e)}, \quad (7)$$

$$c_{2n+1,s} = \frac{1}{\sqrt{N_d}} \sum_k e^{ik(2n+1)a} c_{ks}^{(o)}. \quad (8)$$

The creation operators  $c_{2n,s}^\dagger$  and  $c_{2n+1,s}^\dagger$  are given by the Hermitian conjugates of the above equations, respectively. The allowed  $k$  are determined by imposing cyclic boundary conditions over  $N_d$  sites:

$$e^{2ik(n+N_d)a} = 1. \quad (9)$$

It follows that there are  $N_d$  allowed  $k$  values over the first Brillouin zone

$$k \in \left( -\frac{\pi}{2a}, \frac{\pi}{2a} \right]. \quad (10)$$

This is precisely the Brillouin zone for an ordinary lattice with twice the lattice constant, as expected.

Inverting (7) and (8) one obtains

$$c_{ks}^{(e)} = \frac{1}{\sqrt{N_d}} \sum_n e^{-ik(2n)a} c_{2n,s}, \quad (11)$$

$$c_{ks}^{(o)} = \frac{1}{\sqrt{N_d}} \sum_n e^{-ik(2n+1)a} c_{2n+1,s}. \quad (12)$$

The Hamiltonian can now be rewritten as

$$H_d(u) = - \sum_{ks} \left\{ [-2t_0 \cos(ka) + 2i\delta \sin(ka)] c_{ks}^{\dagger(e)} c_{ks}^{(o)} + [-2t_0 \cos(ka) - 2i\delta \sin(ka)] c_{ks}^{\dagger(o)} c_{ks}^{(e)} \right\} + 2NKu^2. \quad (13)$$

Diagonalizing, one can show that the Hamiltonian can be written as

$$H_d(u) = - \sum_{ks} E_k \left( \psi_{ks}^{\dagger(v)} \psi_{ks}^{(v)} - \psi_{ks}^{\dagger(c)} \psi_{ks}^{(c)} \right) + 2NKu^2, \quad (14)$$

where the eigenenergies  $E_k$  are given by

$$E_k = \pm (\varepsilon_k^2 + \Delta_k^2)^{1/2}, \quad (15)$$

in terms of  $\varepsilon_k = -2t_0 \cos(ka)$  and  $\Delta_k = 2\delta \sin(ka)$ . It can be shown that the eigenstates are given by

$$\psi_{ks}^{(v)} = \frac{1}{\sqrt{2}} \left( c_{ks}^{(e)} + \frac{\varepsilon_k + i\Delta_k}{E_k} c_{ks}^{(o)} \right), \quad (16)$$

and

$$\psi_{ks}^{(c)} = \frac{1}{\sqrt{2}} \left( c_{ks}^{(e)} - \frac{\varepsilon_k + i\Delta_k}{E_k} c_{ks}^{(o)} \right), \quad (17)$$

where superscript  $v$  denotes the valence band, corresponding to  $-E_k$ , and  $c$  denotes the conduction band, corresponding to  $+E_k$ .

### A. Undimerized Polyacetylene

For the undimerized case, i.e.  $\delta = 0$ , the energies are simply  $\varepsilon_k = \mp 2t_0 \cos(ka)$ . The dispersion is plotted in Fig. 4. The eigenstates also take the much simpler form

$$\psi_{ks}^{(v)} = \frac{1}{\sqrt{2}} \left( c_{ks}^{(e)} + c_{ks}^{(o)} \right), \quad (18)$$

and

$$\psi_{ks}^{(c)} = \frac{1}{\sqrt{2}} \left( c_{ks}^{(e)} - c_{ks}^{(o)} \right). \quad (19)$$

On closer inspection one sees that these solutions are simply the regular tight-binding chain solutions mapped to a reduced-zone scheme from  $-\pi/(2a)$  to  $\pi/(2a)$ . This was expected since in the  $\delta \rightarrow 0$  limit one expects that the even and odd sites would contribute to the solution with equal weights giving the regular tight-binding solution.

### B. Dimerized Polyacetylene

For dimerized polyacetylene a gap opens up in the dispersion due to the non-zero  $\Delta_k$  term in (15). For a realistic choice of parameters the ratio of the phonon coupling constant and the hopping integral is  $\delta/t_0 \sim 0.1$ .<sup>3</sup>

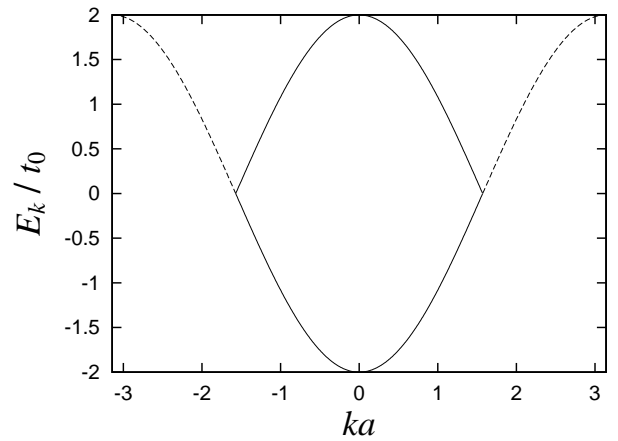


FIG. 4: The dispersion energy  $E_k/t_0$  versus wave vector  $ka$  for undimerized polyacetylene inside the first Brillouin zone from  $-\pi/(2a)$  to  $\pi/(2a)$  (shown with the solid lines). The extended range from  $-\pi/a$  to  $\pi/a$  is shown for comparison to the regular tight-binding solution with no phonon coupling. For the undimerized case polyacetylene would behave as a metal, with the levels above and below  $E_k/t_0 = 0$  filled and empty, respectively.

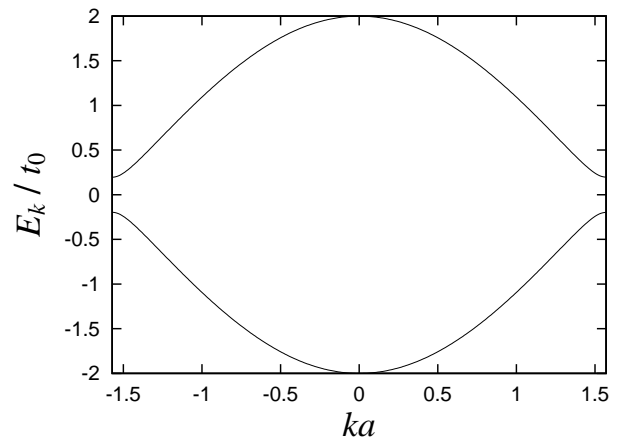


FIG. 5: The dispersion energy  $E_k/t_0$  versus wave vector  $ka$  for dimerized polyacetylene inside the first Brillouin zone from  $-\pi/(2a)$  to  $\pi/(2a)$ . Here, the ratio of the phonon coupling constant and the hopping integral is  $\delta/t_0 = 0.13$ . For the dimerized case a gap opens in the dispersion, rendering polyacetylene a semiconductor.

A plot of the dispersion is shown in Fig. 5 for the value  $\delta/t_0 = 0.13$ . It turns out that for these parameters, the gap is sufficiently small such that polyacetylene behaves as a semiconductor.<sup>1</sup> In the next section it will be shown that dimerized polyacetylene has a lower ground state energy and is therefore closer to the true ground state for polyacetylene.

#### IV. THE GROUND STATE ENERGY

The ground state energy can now be calculated. Recognizing that the operators in (14) are just the number operators for the valence and conduction bands and that for the ground state the valence band is filled and the conduction band is empty, one can write (14) as

$$E_0(u) = -\sum_{ks} E_k = -2 \sum_k E_k. \quad (20)$$

To convert this sum to an integral use  $\Delta k = 2\pi/L$  and integrate over the first Brillouin zone:

$$\begin{aligned} E_0(u) &= -2 \frac{L}{2\pi} \int_{-\pi/2a}^{\pi/2a} dk E_k + 2NKu^2 \\ &= -\frac{4Nt_0}{\pi} \mathcal{E}(\sqrt{1-z^2}) + \frac{Nkt_0^2 z^2}{2\alpha^2}, \end{aligned} \quad (21)$$

where

$$\mathcal{E}(\sqrt{1-z^2}) = \int_0^{\pi/2} [1 - (1-z^2)\sin^2\theta]^{1/2} d\theta \quad (22)$$

denotes the complete elliptical integral of the second kind.<sup>4</sup> The parameter  $z \equiv \delta/t_0 = 2\alpha u/t_0$  has also been defined. For small values of  $z$ , i.e. small phonon couplings, the elliptical integral can be expanded as

$$\mathcal{E}(\sqrt{1-z^2}) \simeq 1 + \frac{1}{2} \left( \ln \left( \frac{4}{|z|} \right) - \frac{1}{2} \right) z^2 + \dots \quad (23)$$

This shows that even for arbitrarily small couplings, the dimerized state is always at lower energy than the undimerized state. Hence, the dimerized state is closer to the true ground state of polyacetylene, as expected. The astute reader may have expected this to occur on the onset due to Peierl's instability in one-dimensional metals. This will be discussed in the next section.

It is useful to look at the ground state energy per site as a function of the configuration coordinate  $u$ . The following realistic parameters for polyacetylene will be used:<sup>3</sup>  $a = 1.22 \text{ \AA}$ ,  $K = 21 \text{ eV/\AA}^2$ ,  $t_0 = 2.5 \text{ eV}$ , and  $\alpha = 4.1 \text{ eV/\AA}$ . Converting (21) to dimensionless form the plot shown in Fig. 6 is obtained. There are two local minima at  $u = \pm u_0 \simeq \pm 0.04 \text{ \AA}$ , corresponding to the two degenerate A and B phases of the ground state of polyacetylene. This dimerization corresponds to a small shift of about 3% in the bonds lengths of the chain.

#### V. PEIERL'S INSTABILITY

It is interesting to note that the lowering of the ground state energy due to dimerization is not unique to the study of polyacetylene presented here. The effect arose by simply having slightly different values for the hopping integrals in the chain, namely  $t_0 + \delta$  and  $t_0 - \delta$ . Therefore,

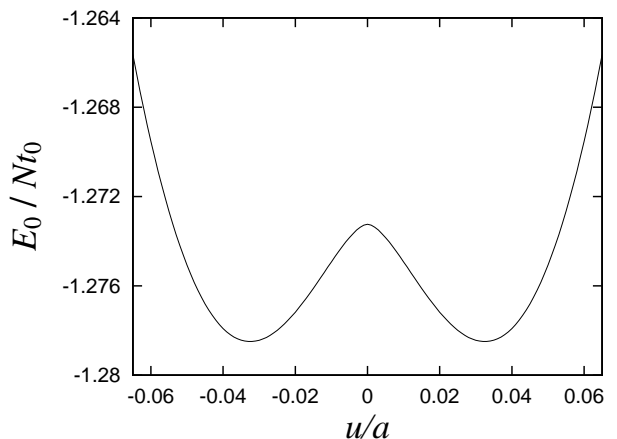


FIG. 6: The ground state energy per site  $E_0/Nt_0$  as a function of the configuration coordinate  $u/a$  for the set of parameters given in the text. The minimum energies occur for  $u = \pm u_0 \simeq \pm 0.04 \text{ \AA}$ , corresponding to the A and B phases of the twofold degenerate ground state of polyacetylene.

one would expect all one-dimensional metals to spontaneously distort to effectively double their lattice spacing, alter the hopping integrals by a small amount, and therefore lower their ground state energies. This is indeed the case and was first proposed by Peierl's in 1955.<sup>5</sup> This spontaneous distortion always forms a gap at the Fermi level and lowers the energy of the one-dimensional metal by suppressing the energy states near the Fermi level. The case of polyacetylene is of special interest because the physical reasoning by which the chain distorts to double its effective lattice length is much more clear than in other systems.<sup>5</sup>

#### VI. SOLITON EXCITATIONS

The twofold degeneracy of the ground state gives rise to peculiar excitation known as solitons. These excitations appear in the following form. Consider a chain of polyacetylene in the A phase to the far "left" and in the B phase to the far "right", as shown in Fig. 7. The soliton



FIG. 7: A soliton excitation in polyacetylene. To the far "left" the chain is in the A phase of its ground state, and to the far "right" the chain is in the B phase of its ground state. The soliton is localized in the region in between these two phases.

is localized in the region between the two phases of the ground state. These excitations are truly unique in the sense that to move from one phase of the ground state to the other, all alternating single and double bonds must be interchanged. The term soliton is defined as a self-

reinforcing solitary wave caused by non-linear effects in a medium with the properties that they represent waves of permanent form and are localizable, that is, they decay or approach a constant at infinity.<sup>6</sup> The excitations in polyacetylene described above fit this definition.<sup>7</sup>

It turns out the energy to create such a soliton excitation is less than the energy cost to create a usual electron-hole pair across the band gap, and therefore soliton excitations are of particular interest.<sup>3</sup> The details of soliton excitations are extensive and only a summary of a few main features will be discussed here, namely the activation energy, spatial extent, charge, spin, and effective mass of the soliton excitations.

### A. Energy of a Soliton

To calculate the energy of a soliton one first defines an order parameter  $\chi_n$  which is equal to  $-u_0$  for the A phase of polyacetylene,  $+u_0$  for the B phase of polyacetylene, and some superposition of these phases in the region centered around the site  $n = 0$  where the soliton is assumed to be localized. The Hamiltonian for the system is then rewritten as  $H = H_0 + V$ , where  $H_0$  is the Hamiltonian for the perfectly dimerized chain from before with the hopping integral set to zero over the finite range where the soliton is assumed to be localized and  $V$  is the hopping term in the range where the soliton is localized. This perturbation  $V$  will depend on the superposition of the A and B phases in the soliton regime. A variational method on  $\chi_n$  can then be applied to minimize the total energy of the system and determine the energy of the soliton. A trial wave function that possesses the desired limiting behaviour (i.e. approaches  $\pm u_0$  for the A and B phases, respectively) is given by

$$\chi_n = \begin{cases} -u_0, & n \leq -m, \\ +u_0 \tanh(na/\ell), & -m < n < m, \\ +u_0, & n > m, \end{cases} \quad (24)$$

where the index  $m$  has been introduced to give the range of sites over which the soliton is localized and  $\ell$  is the half-width of the soliton. The form of (24) is reasonable as we expect the order parameter to vary from the A phase to the B phase in some smooth fashion over the regime of the soliton.

The detailed variational analysis was carried out by Su, Schrieffer, and Heeger and it was found that for a energy gap of 1.4 eV in polyacetylene (this is consistent with the choice of parameters given earlier in this paper), the soliton energy is  $E_s = 0.42$  eV.<sup>3</sup> Therefore, the cost of a soliton excitation is less than the cost of creating an electron-hole pair across the energy gap and is the lowest lying type of excitation in polyacetylene. It can also be shown that for an energy gap of 1.4 eV the spatial extent of the soliton excitation is over approximately 14 lattice sites, with an effective length of about 17 Å.<sup>3</sup>

### B. Charge and Spin of a Soliton

For the perfectly dimerized Hamiltonian studied earlier the density of states  $\rho(E)$  can be easily calculated from (15) using  $\rho(E) = (L/\pi)|dk/dE_k|$ . It is clear that the result would simply show that there are allowed states in the valence band and allowed states in the conduction band, and no allowed states in between. It turns out that the perturbed Hamiltonian  $H = H_0 + V$  gives rise to a state centered in the middle of the gap, corresponding to the existence of soliton excitations. The details of the analysis of this change in the density of states are beyond the scope of this paper, but it is noted that three types of solitons are found: neutral solitons of charge  $Q_0 = 0$  and spin  $s_0 = 1/2$  and charged solitons of charge  $Q_{\pm} = \pm e$  with spin  $s = 0$ . Further details on the interesting electronic properties of soliton excitations in polyacetylene can be found elsewhere.<sup>1,3</sup>

### C. Effective Mass of a Soliton

The effective mass of a soliton excitation can be found by calculating the energy of a slowly moving domain wall. This is achieved by writing the soliton regime of the trial wave function from (24) in the following time-dependent fashion:

$$\chi_n(t) = u_0 \tanh [(na - v_s t/a)/\ell], \quad (25)$$

where  $v_s$  is the velocity of the soliton. The effective mass can then be found using

$$\frac{1}{2}M_s v_s^2 = \frac{1}{2}M \sum_n \dot{\chi}_n^2, \quad (26)$$

where  $M_s$  is the effective mass of the soliton and  $M$  is the mass of the CH group. For the choice of parameters used in this project it can be shown that the effective mass is approximately six times that of an electron mass. This low mass suggests that soliton excitations are highly mobile and truly quantum particles.<sup>3</sup>

## VII. SUMMARY

Several interesting features of polyacetylene have been discussed. The SSH model has been presented and solved for the polyacetylene ground state in some detail. The understanding of this model paved the way for studies of the peculiar topological excitations known as solitons in polyacetylene. The key results of this project are as follows. First, the SSH model showed that the dimerization due to phonon coupling accounts for the Peierl's instability in polyacetylene. This was done by looking at the ground state energy per site and noticing that there were two stable minima for a non-zero bond shift corresponding to the two degenerate ground states of polyacetylene.

Second, the excitations of polyacetylene were discussed. The energies, electronic properties, effective length, and effective mass for these peculiar solitons were discussed.

There are several other interesting properties of solitons, including the spatial distribution of the soliton's spin and charge density, its interactions with impuri-

ties, and its internal vibrations.<sup>3</sup> For a more detailed account of polyacetylene and soliton excitations, including comparison of these results to experiment, the interested reader is encouraged to read the review by Heeger *et al* and references therein.<sup>1</sup>

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<sup>1</sup> A.J. Heeger, S. Kivelson, J.R. Schrieffer, W.P. Su, *Rev. Mod. Phys.* **60** (3), 2099 (1988).

<sup>2</sup> W.P. Su, J.R. Schrieffer, A.J. Heeger, *Phys. Rev. Lett.* **42** (25), 1698 (1979).

<sup>3</sup> W.P. Su, J.R. Schrieffer, A.J. Heeger, *Phys. Rev. B* **22** (4), 2099 (1980).

<sup>4</sup> M.R.S Spiegel and J. Liu, *Mathematical Handbook of Formulas and Tables*, 2nd ed. (McGraw Hill, New York, 1999).

<sup>5</sup> R.E. Peierls, *Quantum Theory of Solids*, (Oxford University Press, London, 1955).

<sup>6</sup> P.G. Drazin and R.S. Johnson *Solitons: An Introduction*, (Cambridge University Press, Cambridge, 1989).

<sup>7</sup> Most definitions of a soliton also require that solitons pass through one another unchanged (up to a phase factor) in the event of a collision. The excitations in polyacetylene do not satisfy this last requirement, however, they are still referred to as solitons.<sup>3</sup>