

Ground State of *trans*-Polyacetylene and the Peierls Mechanism

J. Ashkenazi,^{(1),(a)} W. E. Pickett,⁽²⁾ H. Krakauer,⁽³⁾ C. S. Wang,⁽⁴⁾ B. M. Klein,⁽²⁾ and S. R. Chubb⁽⁵⁾

⁽¹⁾ *Department of Physics, Technion, Haifa 32000, Israel*

⁽²⁾ *Condensed Matter Physics Branch, Naval Research Laboratory, Washington, D. C. 20375-5000*

⁽³⁾ *Department of Physics, College of William and Mary, Williamsburg, Virginia 23185*

⁽⁴⁾ *Department of Physics, University of Maryland, College Park, Maryland 20742*

⁽⁵⁾ *Sachs/Freeman Associates, Inc., Landover, Maryland 20785-5396*

(Received 15 August 1988)

It is shown formally that the Peierls expression is inadequate for studying the instabilities of a physically realizable one-dimensional chain of atoms, due to the long-range nature of the Coulomb interaction. Detailed total-energy studies of *trans*-polyacetylene, for both suggested crystal structures ($P2_1/n$, $P2_1/a$) and for the one-dimensional chain, establish that no appreciable total-energy minimum occurs for nonzero dimerization amplitude within the local-density approximation. The measured dimerization is discussed within the context of recent models of electron correlation.

PACS numbers: 71.45.Nt, 61.41.+e, 63.20.Kr, 71.30.+h

Polyacetylene, $(\text{CH})_x$, has attracted a great deal of experimental and theoretical attention for several reasons. It is the simplest organic chain polymer, which makes it a prime candidate both as a Peierls system with a broken-symmetry ground state and as a testing ground for models of electronic interactions in one dimension (1D). It can be doped to change its conductivity over many orders of magnitude, and it forms crystals of high enough quality to allow the identification and study of its structure. The 3D crystal structure of *trans*-polyacetylene has been investigated by x-ray^{1,2} and neutron³ diffraction as well as inferred from nutation nuclear-magnetic-resonance spectra.⁴ The structure, from low temperature to above room temperature, consists of two dimerized chains per unit cell and is either the $P2_1/n$ (Ref. 1) or $P2_1/a$ (Ref. 2) space group. The dimerization amplitude, which is the displacement of a C atom projected onto the chain axis, is $u=0.023-0.03$ Å.

Although the literature on $(\text{CH})_x$ is vast, the background for the purposes of this paper can be stated rather directly. It has been widely accepted that the driving force for the dimerization is the Peierls mechanism, that is, a lowering of the electronic energy due to a nonanalytic electron-phonon interaction (EPI) contribution arising from 1D Fermi-surface nesting, and this result is rigorous for noninteracting fermions on a 1D chain. The situation in any physical system must involve effects due to the long-range (LR) Coulomb interaction and to exchange and correlation. A number of sophisticated electronic structure studies, within which the LR interaction is included and screened self-consistently, have been reported. Hartree-Fock studies, which treat exchange exactly but neglect correlation effects, have been carried out for finite models and cyclic rings^{5,6} (which do not contain the Peierls nonanalyticity), and for periodic chains,⁷⁻⁹ and indicate a charge density⁵⁻⁹ (Peierls) [respectively, spin density^{5,6} (spin Peierls)] instability in the restricted [respectively, unrestricted] version. Density-functional studies^{10-12(a)} for *trans*- $(\text{CH})_x$, which include

both exchange and correlation within a local-density approximation, seem finally to conclude^{10,11} that there is no minimum in the energy curve for *trans*- $(\text{CH})_x$, but the energy curve is very flat near the symmetric state (see below).

A wide variety of studies,^{12(b)} both model and *ab initio*, have concluded that, starting from a dimerized configuration (either at the noninteracting or Hartree-Fock levels), zero-point motion decreases the distortion, on-site correlations of the Hubbard-type may increase it somewhat, intersite correlations decrease it, and correlation corrections to the Hartree-Fock approximation decrease it. The near-universal conclusion is that the electron-lattice coupling is dominant and provides the driving force. In this paper we (1) point out crucial limitations on the Peierls picture based on linear response theory, and (2) report and analyze the results of extensive local-density total-energy studies which, based on numerous applications to a wide variety of classes of solids, should describe the EPI contribution realistically. To within our very small uncertainty, no symmetry-breaking state is found, and the analysis of the distortion energy reopens the fundamental question of the mechanism for dimerization in *trans*- $(\text{CH})_x$.

Peierls¹³ separated the system energy into a band-structure term E_{bs} and a strain term E_{str} . For a system with 1D dispersion and a half-filled band, one finds the change due to dimerization (assumed small), that is, due to opening a gap E_g , to be

$$\delta E_{\text{bs}} = -\frac{1}{2} W \left[\left(\frac{1}{2} + \ln 2 \right) \Delta^2 + \frac{1}{8} \Delta^4 - \Delta^2 \ln \Delta + \dots \right], \quad (1)$$

and Peierls *assumed* an elastic form for the (remaining) strain term,

$$\delta E_{\text{str}} = A \Delta^2 + B \Delta^4 + \dots \quad (2)$$

Here W is the occupied bandwidth $W = \hbar v_F (\pi/a)$, where v_F is the Fermi velocity at $u=0$ and a is the lattice constant, and the dimensionless gap $\Delta = E_g/2W$ is proportional to u .

Unlike the Jahn-Teller theorem, for example, which is a rigorous statement about the energy of an interacting many-body system, Peierls's theorem is based on a heuristic decomposition of the total energy which can easily be shown to lack rigor. From linear-response and density-functional (DF) theory (see, for example, Ref. 14) one has, using implicit matrix (real or reciprocal space) notation, a rigorous expression for the change in energy arising from nuclear displacements (giving rise to δV_{ext} and the accompanying density change δn),

$$\delta E_{\text{tot}} = -\frac{1}{2} \delta n \chi^{-1} \delta n = \frac{1}{2} \delta V_{\text{ext}} \epsilon^{-1} v_t^{-1} \delta V_{\text{ext}}. \quad (3)$$

Using the DF eigenvalues¹⁵ and the effective one-electron DF potential V_{eff} , the change in band-structure energy is

$$\begin{aligned} \delta E_{\text{bs}} &= \frac{1}{2} \delta V'_{\text{eff}} \chi_0 \delta V'_{\text{eff}} \\ &= \frac{1}{2} \delta V_{\text{ext}} \epsilon^{-1} v_t^{-1} (\epsilon^{-1} - 1) \delta V_{\text{ext}}. \end{aligned} \quad (4)$$

Here ϵ is the electron dielectric function,¹⁶ and χ (χ_0) is the interacting (noninteracting) susceptibility which satisfies $\epsilon^{-1} = 1 + v_t \chi$ ($\epsilon = 1 - v_t \chi_0$) in terms of the total electron-electron interaction v_t which includes an exchange-correlation part in addition to the direct Coulomb part. The remaining energy, given by the difference between (3) and (4) and corresponding to

Peierls's strain term, is

$$\delta E_{\text{str}} \equiv \delta E_{\text{tot}} - \delta E_{\text{bs}} = \frac{1}{2} \delta V_{\text{ext}} \epsilon^{-1} v_t^{-1} (2 - \epsilon^{-1}) \delta V_{\text{ext}}. \quad (5)$$

The strong Fermi-surface nesting in 1D introduces non-analytic behavior (due to the opening of the Peierls gap) in ϵ , as we show explicitly below for χ_0 . Since ϵ appears in both the band-structure term and the strain term, both contain the $\Delta^2 \ln \Delta$ term, so that obtaining a ground-state distortion is not certain, but depends on their signs and relative magnitudes.¹⁷ Note that the recent "proof" of the 1D Peierls instability by Kennedy and Lieb¹⁸ is restricted to a model system with a quadratic strain term (i.e., without LR electronic screening) and, thus, is not relevant to the present discussion. There are a number of explicit results¹⁹ on model 1D systems with *short-range interactions*, such as the absence of true phase transitions at nonzero temperature and the lack of a Mott transition at zero temperature. *There is very little known rigorously* about structural instabilities in *physically realizable 1D systems* in which the long-range Coulomb interaction may play a crucial role.

It is straightforward, but not simple, to proceed formally from Eqs. (3)–(5) to derive the small-distortion and small-wave-vector (\mathbf{q}) behavior of the various terms (at least within an RPA-like treatment). The spatially homogeneous limit ($\mathbf{G} = \mathbf{G}' = 0$, for reciprocal-lattice vectors \mathbf{G}, \mathbf{G}') of χ_0 in 1D is simple and is given by

$$\chi_0(\mathbf{q}=0, \Delta) = \sum_k \frac{1}{E_k^+ - E_k^-} = (2/W) [\ln(2/\Delta) + \frac{1}{4} \Delta^2 - \frac{3}{32} \Delta^4 + \dots] + \bar{\chi}_0, \quad (6)$$

where $\bar{\chi}_0$ is independent of Δ . The upper and lower bands are given by $E_k^\pm = \pm [v_t^2 (\delta k)^2 + \Delta^2]^{1/2}$, and $\delta k = k - \pi/a$. Equation (6) displays the insulator-to-metal divergence as $\Delta \rightarrow 0$. This establishes that a $\ln \Delta$ singularity of the Peierls type indeed *occurs in the energy rigorously*; however, it arises both in the band-structure term and in the remaining "strain" term, and it is *not necessarily negative* as in Peierls's expression (1). Peierls's expression is incorrect because the strain term that he assumed to be analytic contains the same type of nonanalyticity as the band-energy term.

We have carried out detailed numerical studies of the structural stability of *trans*-(CH)_x within the local-density approximation (LDA) to DF theory. The linearized-augmented-plane-wave (LAPW) method,²⁰ with extensive, highly converged basis sets and general representations of the density and potential, was applied in total-energy studies of both (*P*_{21/n} and *P*_{21/a}) proposed crystal structures as well as a space-filling array of widely spaced *trans*-(CH)_x chains which gives a good representation of an isolated chain. It was found that the region around the zone boundary where the gap opens must be sampled exceedingly carefully in evaluating the total energy; sparse *k*-point meshes which include the zone-boundary point considerably *overestimate* the band energy gain due to dimerization, while crude meshes

which use only points interior to the zone *underestimate* the band energy gain. We have reported¹⁰ earlier that the use of crude *k*-point meshes has led in the past to the incorrect conclusion that LDA predicts the observed distortion in *trans*-(CH)_x, a result confirmed by Mintmire and White¹¹ for an isolated chain, and recently also by Vogl and Campbell^{12(a)} in a 3D self-consistent pseudopotential calculation.

Another complication which must be checked is the effect of the coupling between the dimerization and other distortions, such as bond length and orientation. By carrying out an energy-minimization study for zero dimerization, we found that LDA gives the bond length and angle close to the experimental one. A similar set of calculations for the experimental dimerization ($u = 0.023 \text{ \AA}$) convinced us that coupling between dimerization amplitude and both bond angle and chain length is negligible. Energy differences between the *P*_{21/a} and *P*_{21/n} structures were always within our calculational uncertainty of no more than 0.3 mRy = 50 K per dimer (C₂H₂ unit), implying that these two crystal structures may both be present in the same sample. This conclusion is consistent with the calculations of Vogl and Campbell,^{12(a)} although they believe they can resolve an energy difference of 0.4 mRy/dimer with the *P*_{21/a} structure favored.

The resulting energy versus distortion is shown in Fig. 1 for a single *trans*-(CH)_x chain. Within the relative stability of our calculations (about 0.3 mRy/dimer) there is *no energy minimum for nonzero distortion*. Very similar results were found for both 3D crystal structures, although it is not possible to rule out a minimum of no more than 0.5 mRy for a small distortion of 20%–25% of the experimental value. As a result of the complexity of the 3D band structure¹⁰ near the gap, which arises from the two chains per cell and interchain interactions, the uncertainty about the existence of an energy minimum for the solid was an ambiguous result by itself. Finding no minimum for the 1D chain clarifies the issues. In Fig. 1 we also show the (negative) Peierls band-structure term of Eq. (1), using our calculated value of *W*. *The calculated change in energy is of opposite sign and 2 orders of magnitude smaller than the Peierls term*, reflecting a huge cancellation implicit from the above discussion.

Analysis of the dimerization energy is revealing. A fit by the expression

$$\delta E_{\text{tot}} = \frac{1}{2} W [a_1 + a_2 \Delta^2 + a_3 \Delta^2 \ln \Delta + a_4 \Delta^4 + a_5 \Delta^6], \quad (7)$$

using the calculated value $W = 1.372$ Ry, shows that only $a_3 = -1.76$ and $a_4 = 3.09 \times 10^4$ are non-negligible. Specifically, the $\Delta^2 \ln \Delta$ term is *positive* and there is *no quadratic term*. [We emphasize that these conclusions are *not* artifacts of the fitting procedure. Refitting the points by an analytic form—Eq. (7) without the $\Delta^2 \ln \Delta$ term—leads to a fit where only the Δ^4 term is appreciable and the rms error increases by a factor of 5. Again the quadratic term is absent.] Figure 1 includes both

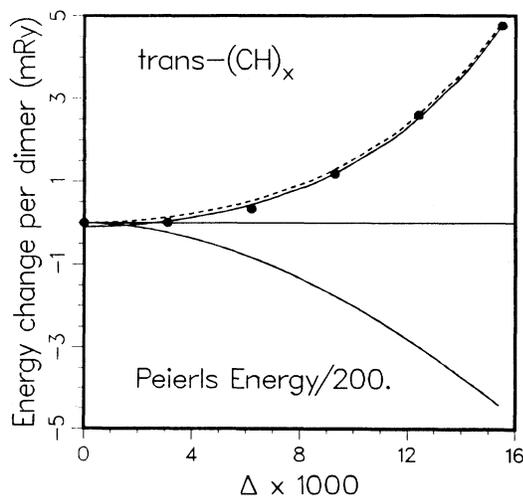


FIG. 1. Calculated energy of distortion (symbols) vs $\Delta = E_g/2W$ for *trans*-(CH)_x. Note that Δ is proportional to the distortion magnitude *u*. Also shown are the five-parameter fit of Eq. (7) (upper solid line), the two-parameter representation (see text, dotted line), and the Peierls band energy scaled down by a factor of 200 (lower solid line).

this five-parameter fit (solid line) and the result from setting $a_1 = a_2 = a_5 = 0$ (dotted line).

To contrast our results with the Peierls form, ΔE_{tot} was separated into the Peierls term of Eq. (1), which arises from the single band bordering the gap, and the remainder δE_r (which is analogous, but not identical, to δE_{str}). The quadratic term in Eq. (1) is *canceled* almost exactly by that in δE_r , while the *negative* $\Delta^2 \ln \Delta$ term in Eq. (1) is more than compensated for by a *positive* contribution from δE_r . In addition, δE_r contributes a *large quartic term* to δE_{tot} , which is equal to the $\Delta^2 \ln \Delta$ term for the largest value of Δ shown in Fig. 1, which is still small.

Our calculations have the following implications. (a) Interchain coupling is unimportant in determining the distortion energy, since the 1D and 3D results are very similar. (b) Since the interaction between the lattice and the electron density should be described well by LDA (see, for example, the reviews in Ref. 21), our results strongly suggest that the *Peierls mechanism is not driving symmetry breaking in trans*-(CH)_x. (c) The screening differences between metallic and insulating states discussed above, which invalidate the Peierls expression, may not be crucial, since the long-range direct Coulomb interaction is handled exactly in the present self-consistent calculations. Item (a) has led to several discussions in the past, and our calculations appear to settle this question. Item (b) is a novel result which, if true, must lead to a reexamination of the picture of *trans*-(CH)_x at the most fundamental level.

Item (c), the implication of the long-range Coulomb interaction (screening), has been addressed in the context of the Pariser-Parr-Pople model by Horsch²² and the Hubbard model by Wu and Kivelson.²³ Both studies conclude that LR (intersite) interactions decrease the distortion relative to that obtained by ignoring them, consistent with the simple physical picture that the direct Coulomb interaction should favor the most uniform state. We have emphasized that the LR interaction leads to a nonanalyticity in what has often been pictured as an analytic strain term.

With respect to the question of “driving mechanism,” there is no clear answer, and clearly electron correlations are involved in a subtle way. From the model Hamiltonian point of view, correlations have been necessary to describe the excitations of *trans*-(CH)_x, but the strength that was inferred led to only a minor effect (albeit an increase) in the ground-state distortion. However, model Hamiltonians are drastic simplifications whose validity must be closely examined in each context, a point emphasized by Wu and Kivelson.²³

Although the LDA has its limitations, its failure for *trans*-(CH)_x is of special interest, since for a wide variety of systems including 3D crystals, 2D surfaces, and molecules it has proven very reliable in predicting ground-state geometries. Since even 3D *trans*-(CH)_x retains a large degree of 1D character, it may be that the

one dimensionality of the virtual scattering processes²⁴ drives its charge-density wave formation. Kondo,²⁵ Kuboki and Fukuyama,²⁶ and others have suggested that symmetry breaking of 1D metals may be of the spin-Peierls type, in which case the present paramagnetic study would not be expected to produce the distortion. However, Bethe²⁷ showed that for a 1D chain of atoms a spin-Peierls state is unstable with respect to a state of "resonating-valence-bond-like"²⁸ correlated pairs. Such a state has no static staggered magnetization, but rather arises from strong spin correlations, and these might also play an important role in *trans*-(CH)_x. A primary implication of the present study is that electronic screening as well as correlations must be included properly to describe the metal-insulator transition accompanying the symmetry-breaking distortion in *trans*-(CH)_x.

We acknowledge helpful discussions with E. Ehrenfreund, C. G. Kuper, and S. Trugman. This work was supported by the Office of Naval Research (W.E.P. and B.M.K.), the Planning and Grant Committee of the Israel Council for Higher Education (J.A.), and National Science Foundation Grants No. DMR-87-19535 (H.K.) and No. DMR-86-01708 (C.S.W.). Computations were carried out under the auspices of the National Science Foundation at the San Diego Supercomputing Center and at the Illinois National Center for Supercomputer Applications.

(a)Present address: Department of Physics, University of Miami, Coral Gables, FL 33124.

¹C. R. Fincher, Jr., C.-E. Chen, A. J. Heeger, A. G. MacDiarmid, and J. B. Hastings, *Phys. Rev. Lett.* **48**, 100 (1982).

²H. Kahlert, O. Leitner, and G. Leising, *Synth. Met.* **17**, 467 (1987).

³P. E. Sokol, G. Tai, C. Gordon, A. J. Epstein, R. Weagly, and J. D. Jorgensen, *Bull. Am. Phys. Soc.* **31**, 330 (1986).

⁴C. S. Yannoni and T. C. Clarke, *Phys. Rev. Lett.* **51**, 1191 (1983).

⁵J. Paldus and E. Chin, *Int. J. Quantum. Chem.* **24**, 373 (1983); J. Paldus, E. Chin, and M. G. Grey, *Int. J. Quantum Chem.* **24**, 395 (1983).

⁶M. H. McAdon and W. A. Goddard, *J. Chem. Phys.* **88**, 277 (1987).

⁷R. Dovesi, *Int. J. Quantum Chem.* **26**, 197 (1984).

⁸S. Suhai, *Chem. Phys. Lett.* **96**, 619 (1983).

⁹H. Teramae, T. Yamabe, and A. Imamura, *J. Chem. Phys.* **81**, 3564 (1984).

¹⁰J. Ashkenazi, W. E. Pickett, C. S. Wang, H. Krakauer, and B. M. Klein, *Bull. Am. Phys. Soc.* **31**, 330 (1986); J. Ashkenazi, W. E. Pickett, B. M. Klein, H. Krakauer, and C. S. Wang, *Synth. Met.* **21**, 301 (1987).

¹¹J. Mintmire and C. W. White, *Phys. Rev. B* **35**, 4180 (1987).

¹²(a) P. Vogl and D. K. Campbell, preceding Letter, *Phys. Rev. Lett.* **62**, 2012 (1989); (b) see, for example, references in S. Kivelson, in *Solitons*, edited by S. E. Trullinger, V. E. Zakharov, and V. L. Pokrovsky (Elsevier, Amsterdam, 1986), p. 30; C.-Q. Wu, X. Sun, and K. Nasu, *Phys. Rev. Lett.* **59**, 831 (1987); D. Baeriswyl and K. Maki, *Phys. Rev. B* **31**, 6633 (1985); S. Kivelson and D. E. Heim, *Phys. Rev. B* **26**, 4278 (1982); S. Kivelson, W.-P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.* **58**, 1899 (1987); Refs. 5-12(a).

¹³R. E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955), p. 108.

¹⁴L. J. Sham, in *Modern Solid State Physics: Phonons and Their Interactions*, edited by H. Enns and R. R. Haering (Gordon and Breach, 1968), Vol. 2, p. 143.

¹⁵W. E. Pickett and B. L. Gyorffy, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglas (Plenum, New York, 1976), p. 251.

¹⁶L. Kleinman, *Phys. Rev.* **160**, 585 (1967); **172**, 383 (1968).

¹⁷This has been noted in another context by R. M. Martin and K. Kunc, in *Ab Initio Calculation of Phonon Spectra*, edited by J. T. Devreese (Plenum, New York, 1983), p. 49. Note that there are several misprints in this paper.

¹⁸T. Kennedy and E. H. Lieb, *Phys. Rev. Lett.* **59**, 1309 (1987).

¹⁹M. Cassandro and E. Olivieri, *Commun. Math. Phys.* **80**, 255 (1981); E. H. Lieb and F. Y. Wu, *Phys. Rev. Lett.* **20**, 1445 (1968); E. H. Lieb and D. C. Mattis, *Phys. Rev.* **125**, 164 (1962).

²⁰S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55**, 1200 (1985); E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **24**, 864 (1981).

²¹*Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter*, edited by J. T. Devreese and P. VanCamp (Plenum, New York, 1985).

²²P. Horsch, *Phys. Rev. B* **24**, 7351 (1981).

²³W.-K. Wu and S. Kivelson, *Phys. Rev. B* **33**, 8546 (1986).

²⁴V. J. Emery, *Phys. Rev. B* **14**, 2989 (1976).

²⁵J. Kondo, *Physica (Amsterdam)* **98B**, 176 (1980).

²⁶K. Kuboki and H. Fukuyama, *J. Phys. Soc. Jpn.* **56**, 3126 (1987).

²⁷H. Bethe, *Z. Phys.* **71**, 205 (1931).

²⁸P. W. Anderson, *Science* **235**, 1196 (1987).