PHYSICAL REVIEW B VOLUME 28, NUMBER 8 15 OCTOBER 1983

Competing electron-phonon interactions and the Peierls instability

S. Kivelson
Physics Department, University of California, Santa Barbara, California 93106
and Physics Department, State University of New York at Stony Brook, Stony Brook, New York 11794[*]

Daniel Hone
Physics Department, University of California, Santa Barbara, California 93106

(Received 1 July 1983)

We consider a general one-dimensional tight-binding model of interacting phonons and electrons. From this model, we derive the adiabatic potential-energy functional for a system which is not commensurability 2. Terms that have been neglected in previous studies of the Peierls state are found to result in a competition between two types of electron-phonon interaction. This competition can eliminate the Peierls instability or lead to a first-order commensurate-to-commensurate structural phase transition.

In this paper we report on the results of a careful study of the zero-temperature properties of a linear-chain system of interacting phonons and electrons. To simplify the problem, we will consider only systems in which the direct electron-electron interactions are sufficiently small that they can be ignored, and we assume that the ions are sufficiently massive that the problem can be treated in the Born-Oppenheimer approximation. Thus, we can "integrate out" the electrons and obtain an effective Hamiltonian $H^{\text{eff}}(\vec{u})$ involving only lattice degrees of freedom, in which the total electronic ground-state energy plus the purely elastic potential energy, $E_T(\vec{u})$, for each lattice configuration $\vec{u}$ plays the role of the effective (adiabatic) potential energy in H^{eff}. Such a procedure was first adopted by Lee, Rice, and Anderson[1] and later extended by Rice *et al.*[2] However, we consider a more general model than previous authors[3] which includes the possibility of a competition between different types of electron-lattice interactions. In order to obtain an analytically tractable expression, we restrict ourselves to considering only lattice configurations which differ from the ground-state (Peierls-distorted) configuration by at most the presence of a long-wavelength distortion. Nonetheless, we find some new features of the adiabatic potential which can have important physical consequences for ground-state and low-energy excited-state properties of the Peierls system.

We consider a nearest-neighbor tight-binding model with one electronic orbital per site,

$$H=\sum_n\sum_s[-t_n(\vec{u})(c^\dagger_{ns}c_{n+1s}+\text{H.c.})+\epsilon_n(\vec{u})c^\dagger_{ns}c_{ns}]+H_{\text{lat}}(\vec{u}) \ , \tag{1}$$

where $c^\dagger_{ns}$ creates an electron of spin s on site n, $\vec{u}$ represents schematically all the lattice degrees of freedom, and $H_{\text{lat}}(\vec{u})$ is the lattice (elastic) part of the Hamiltonian. As indicated, the hopping matrix elements $t_n(\vec{u})$ and the site energies $\epsilon_n(\vec{u})$ are functions of the lattice configuration $\vec{u}$.

Our results are applicable generally to systems of the form of Eq. (1). However, it is instructive also to consider as a concrete example a specific simple case, the "linear model": Here there is only a single important lattice degree of freedom per site, u_n. Furthermore, with lattice displacements assumed small compared to a lattice constant, we expand t_n and ϵ_n about the undistorted state to first order in u_n:

$$\begin{aligned} t_n(\vec{u})&=t_0+\alpha(u_n-u_{n+1}) \ , \\ \epsilon_n(\vec{u})&=\epsilon_0+\beta(u_{n-1}-u_{n+1}) \ , \end{aligned} \tag{2}$$

where we have kept explicitly the only linear terms coupling nearest-neighbor sites which are consistent with the translational symmetry of the molecule. The term proportional to α reflects the fact that the hopping matrix between sites n and $n+1$ decreases as they move apart; β measures the change in site energy if the neighboring atoms compress around that site (most probably it increases, $\beta>0$).

Our first step in constructing the adiabatic potential is to compute the energy of the uniformly Peierls-distorted state. Thus, we consider a configuration in which the lattice distortion produces a new periodicity $a/Q=(2k_F)^{-1}$. We characterize the magnitude of this distortion, and hence of the spatial modulation of the tight-binding matrix elements by a dimensionless amplitude z, and by an angle θ, which determines the phase of the electronic charge density wave (CDW) which adiabatically follows the lattice distortion relative to the underlying lattice. Hence, to first order in z,

$$\begin{aligned} (\epsilon_n/\bar{t})&=z\cos(\phi_0)\cos(Qn+\theta+\phi_1/2) \ , \\ (t_n/\bar{t})&=1+z\sin(\phi_0)\cos(Qn+\theta-\phi_1/2) \ , \end{aligned} \tag{3}$$

where $Q=2k_Fa$, as above, and $\bar{t}$ is the average value of the hopping matrix element (the average value of ϵ_n can be absorbed into the chemical potential). The two phases ϕ_0 and ϕ_1 are, in general, determined by the form and relative magnitudes of the various electron-lattice couplings. ϕ_0 determines the relative magnitude and ϕ_1 the relative phase of the spatially modulated on-site and hopping energies. For instance, in the linear model, if we let

$$u_n=u\sin(Qn+\theta-Q/4) \ ,$$

where

$$z=2u[\beta^2\sin^2(Q)+\alpha^2\sin^2(Q/2)]^{1/2} \ , \tag{4}$$

then

$$\phi_0=\tan^{-1}[(\alpha/\beta)\sin(Q/2)/\sin(Q)] \ ,$$

and $\phi_1 = -Q/2$. Notice that for this model, ϕ_1 is independent of the magnitudes of the coupling constants α and β. In more complicated models, this need not be so.

The sinusoidal dependence on position of ϵ_n and t_n in Eq. (3) *is* the correct leading behavior for small z; larger z first brings in more general periodic behavior and can ultimately lead[4] to such interesting and qualitatively new effects as pinning of an incommensurate CDW and aperiodic spatial dependence. Here we confine ourselves to the more usual case $|z| \ll 1$. We also exclude the special case of a nearly half-filled band, $k_F \simeq \pi/2a$, which must be treated separately.

From the calculated self-consistently determined electronic dispersion relation $\epsilon(k)$, we can find the total ground-state energy, or effective potential energy, V^{eff}:

$$V^{\text{eff}}(z,\theta) = 2 \sum_{|k| \le k_F} \epsilon(k) + E_{\text{lat}}(z,\theta) \ , \tag{5}$$

where E_{lat} is the lattice (elastic) energy. The θ dependence of these energies is largely determined by the general form of Eq. (3). If the system has commensurability m, that is if $k_F a = \pi(n/m)$, where n and m are relative prime integers, then the system is invariant under $\theta \rightarrow \theta + (2\pi/m)$, and hence all the energies must be periodic functions of θ. In particular, V^{eff} can be expanded in a Fourier series,

$$[V^{\text{eff}}(z,\theta) - V^{\text{eff}}(z=0)]/\bar{t} = z^2 F_0(z) + \sum_{n=1}^{\infty} z^{nm} F_n(z) \sin[nm\theta + \theta_n(z)] \ , \tag{6}$$

where we have included explicit powers of z for later convenience. To obtain the z dependence of the single-particle energies and of the total energy we will exploit the fact that $|z| \ll 1$ and evaluate the terms in perturbation theory.

Since the perturbation introduced by the lattice distortion $H' \propto z\cos(Qn+\alpha)$ connects degenerate states across the Fermi surface, we use self-consistent (Brillouin-Wigner) perturbation theory for the calculation of the distorted electronic band structure $\epsilon(k)$. As is well known, the Peierls distortion opens an energy gap at the Fermi surface, of magnitude $2\Delta_0$, with

$$\Delta_0/\bar{t} = |z| \, |\tfrac{1}{2}\cos\phi_0 + e^{i(2\phi_1+Q)/2} \sin\phi_0| + O(z^3) \ , \tag{7}$$

where only terms through second order in z have been written explicitly.

We note that the second-order expression for the energy is independent of θ. This is because the θ dependence of the matrix element that carries us from the initial to the intermediate state, $\langle k \pm Q | H' | k \rangle$, exactly cancels the dependence of the matrix element which carries us back, $\langle k | H' | k \pm Q \rangle$. Indeed, it is clear that aside from umklapp terms, no θ dependence occurs in any order of perturbation theory, since each term contains as many matrix elements between states which differ by $+Q$ as by $-Q$. The physics behind this is clear; it is precisely the umklapp terms which depend on the underlying lattice periodicity. The first umklapp term occurs in mth order, with the $(m-1)$ intermediate states at $k \pm Q, k \pm 2Q, \ldots, k \pm (m-1)Q$. By definition of m, the commensurability, mQ is a reciprocal lattice vector, and the states $|k+mQ\rangle$ and $|k\rangle$ are identical. Because this process occurs in mth order, it depends on $e^{im\theta}$, and hence has the required periodicity in θ. Also notice that it is not possible to continue the same reasoning to $2m$th order, since $|k+mQ\rangle \equiv |k\rangle$ and hence cannot appear as an intermediate state. The higher harmonics [such as $\cos(2m\theta)$] which appear in the Fourier series for the energy [e.g., Eq. (6)] are generated by the self-consistency conditions with the mth-order expression for the energy put into the energy denominator. Note that for k near $\pm Q/2$, one of the energy denominators in the mth-order term involves the state on the other side of the Fermi surface, and is therefore vanishingly small. Thus, for k within z of k_F, the θ-dependent term has magnitude of order z^{m-1}.

We can use these results to calculate the total energy, V^{eff}, according to Eq. (6). The contribution from the lattice (elastic) energy is, in general, an analytic function of the lattice displacement (and hence of z), whose leading term is of order z^2 and contributes a constant part to $F_0(z)$ in Eq. (6); it is necessarily positive. The other contribution to V^{eff} is the sum of electronic energies. The largest part of this contribution comes from second-order perturbation theory. As is true of all second-order corrections to the ground-state energy of a system, this term is necessarily negative.

Near $k \simeq \pm Q/2$ the energy spectrum is $\epsilon(k) \simeq -(x^2+\Delta^2)^{1/2}$, where $x = v_F(k-k_F)$ and v_F is the Fermi velocity. Then from the integral over k near the Fermi surface at $\pm Q/2$ we pick up a logarithmic contribution of the form $\Delta_0^2 \ln \Delta_0$, or $z^2 \ln z$, to the total energy. Overall, then, we find that the coefficient of z^2 in Eq. (6) is

$$F_0(z) = -A_0(\phi_0,\phi_1)\ln(1/z) + B_0(\phi_0,\phi_1) + O(z^2) \ , \tag{8}$$

where $A_0 > 0$ is determined solely by the electronic part of $\mathcal{H}$:

$$A_0(\phi_0,\phi_1) = \frac{|\tfrac{1}{2}\cos\phi_0 + (\sin\phi_0)e^{i(2\phi_1+Q)/2}|^2}{2\pi\sin(Q/2)} \ , \tag{9}$$

and B_0 contains a contribution from the sum over electronic energies and a contribution from the elastic energy. (A detailed derivation of this and the following results, as well as the explicit evaluation of the rather complicated expression for B_0, will be contained in a forthcoming communication.[5]) For small values of z the logarithmic term dominates the energy. Thus, it is always energetically favorable for the system to develop a lattice distortion of magnitude $z_0 \simeq \exp[-(B_0/A_0) - \tfrac{1}{2}]$ in its ground state. This is, of course, just the familiar Peierls instability. The mean-field transition temperature is, in similar fashion, of order $kT_c/\bar{t} \sim z_0$.

The first θ-dependent term in Eq. (6) is mth order in z $[z^m F_1(z)]$ and so is small compared to the second-order term. However, since it is the leading-order term in the pinning of the charge density wave, it is nonetheless important. The elastic energy contributes a constant term to F_1. The same considerations that applied to F_0 lead to the conclusion that the electronic contribution to F_1 consists of a logarithmic term and a constant term in addition to higher-order terms in z. Hence

$$F_1(z) = -A_1(\phi_0,\phi_1)\ln(1/z) + B_1(\phi_0,\phi_1) + O(z^2) \ , \tag{10}$$

where again A_1 is determined solely by the electronic contribution and B_1 depends on both the electronic and lattice energies. The full expression for A_1 is easily obtained (see Ref. 5). It is a rather complicated polynomial of degree $2m$ in $e^{i\phi_0}$ and degree m in $e^{i\phi_1}$. For example, for the linear model with $m = 3$,

$$A_1 = \frac{1}{6\sqrt{3}\pi}\left(\tfrac{1}{2}\cos\phi_0 + \sin\phi_0\right)(\cos\phi_0 - \sin\phi_0)^2 \ . \tag{11}$$

The phase $\theta_1(z)$ which appears in Eq. (6) is also complicated but can be determined in a straightforward way. In the linear model, $\theta_1(z) = 0$ for all z and ϕ_i. Note that, unlike the case of the second-order term F_0, there is no constraint on the sign of either A_1 or F_1; in general, the sign of F_1 depends on the values of ϕ_0 and ϕ_1.

To complete our discussion of the adiabatic potential, we imagine that z and θ are slowly varying functions of position and calculate the first terms in the gradient expansion of V^{eff}. If we assume that the pure lattice potential is relatively short ranged, then the characteristic length which enters the gradient expansion is the electronic correlation length, $\xi_0 = a(2\bar{t}\sin(Q/2)/\Delta_0)$. The gradient expansion is useful so long as the characteristic wavelength l over which z or θ vary, is much less than ξ_0. The energies involved in varying the amplitude of the CDW (z) are much larger than those involved in varying θ.

Thus, for the purposes of the present communication we will ignore amplitude excitations (such as the amplitude soliton in Ref. 6) and consider only the variation of the phase. The resulting effective Hamiltonian is

$$\mathscr{H}^{\text{eff}} = \int \frac{dx}{a}\left\{\frac{m^{\text{eff}}}{2}\dot{\theta}^2(x,t) + V^{\text{eff}}(z, \theta(x,t)) + \frac{\bar{t}}{2}\left(\frac{a\,\partial\theta}{\partial x}\right)^2\left[1 + O\left(\xi_0\frac{\partial\theta}{\partial x}\right)^2\right]\right\} \ . \tag{12}$$

This expression for the adiabatic potential is our principal new result. From it, it is possible to deduce several new and interesting effects. First we notice that it is possible for A_0 to vanish for suitable choice of parameters. For instance, this occurs in the linear model when $\alpha = \beta$. At this point the Peierls instability, per se, disappears. More importantly, there is a finite (indeed large) region of parameter space over which the competition between the two types of interaction produces a substantial reduction of the magnitude of A_0. Since the ground-state magnitude of z and the Peierls transition temperature depend exponentially on A_0, this results in an enormous suppression of the Peierls transition. This is possibly a partial explanation of the observed lack of a Peierls transition in the organic superconductors such as $(\text{TMTSF})_2X$ (di-tetramethyltetraselenafulvalene-X). Secondly, if we consider a commensurate system and confine ourselves to a region of parameter space where the system does develop a Peierls distortion $(A_0 \neq 0)$, we can explore the consequences of F_1 changing sign. If $F_1 > 0$ the energy is minimized when $\theta - \theta_1(z) = \pi/2 + nQ$ while for $F_1 < 0$, the energy is minimized when $\theta - \theta_1(z) = -\pi/2 + nQ$. If one can change the relative strengths of the various coupling constants, say by applying pressure to the system (for instance, in the linear model we expect α to be more strongly pressure dependent than β), then one can drive the system from the region of parameter space where $F_1 > 0$ to the region $F_1 < 0$. The result is an abrupt, first-order transition between two inequivalent commensurate ground states. At the point at which the transition takes place, the pinning energy is of order z^{2m} rather than the usual z^m when $F_1 \neq 0$. This has important consequences for the excitation spectrum. For instance, Rice *et al.* have shown[2] that the lowest-energy (fractionally) charged excitations of a commensurate Peierls system are sine-Gordon phase solitons with creation energy E_s of order $(E_s/\bar{t}) \sim z^m$, and width of order $(l/a) \sim z^{-m/2}$. From Eq. (12) it follows that in the vicinity of the point $F_1 = 0$, the solitons have a slightly more complicated structure, a much smaller creation energy, $(E_s/\bar{t}) \sim z^{2m}$, and a correspondingly much greater width, $(l/a) \sim z^{-m}$. As far as we know, a commensurate-to-commensurate transition of this sort has never been observed. Finally, it can be shown[5] that the inclusion of weak electron-electron interactions does not affect any of the present conclusions.

ACKNOWLEDGMENT

This work was supported in part by National Science Foundation Grant No. 80-08004.

---

*Permanent address.

[1] P. Lee, M. Rice, and P. W. Anderson, Solid State Commun. 14, 703 (1974).

[2] M. J. Rice, A. J. Bishop, J. A. Krumhansl, and S. E. Trullinger, Phys. Rev. Lett. 36, 432 (1976).

[3] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979); Phys. Rev. B 22, 2099 (1980).

[4] See, e.g., S. Aubry, in *Physics of Defects*, Proceedings of the Les Houches Summer School, Session XXXV, edited by R. Balian *et al.* (North-Holland, Amsterdam, 1981), p. 431.

[5] D. Hone and S. Kivelson (unpublished).

[6] W. P. Su and J. R. Schrieffer, Phys. Rev. Lett. 46, 738 (1981).