Proof of the Peierls Instability in One Dimension

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Fröhlich and Peierls showed that a one-dimensional system with a half-filled band can lower its ground-state energy by a dimerization from period 1 to period 2. It was an open question whether or not this dimerization was exact, i.e., whether additional symmetry breaking would further lower the energy. We prove that the dimerization is exact for a periodic chain of infinitely massive, harmonically bound atoms with nearest-neighbor electron hopping matrix elements that vary linearly with the nearest-neighbor distance.

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A quarter of a century ago Frölich[1] and Peierls[2] discovered an instability in one-dimensional electron systems that has come to be called the Peierls instability. Earlier, Jones[3] used such a mechanism to explain the high diamagnetism and low conductivity of bismuth. He also used the mechanism to explain the Hume-Rothery alloys. Peierls's observation was that this dimerization always occurs in one dimension.

In a word, Frölich and Peierls note that a long chain of $2N$ atoms of total length L and $2N$ electrons (half-filled band) will not have a ground state with the "obvious" periodicity $L/2N$. They show this by constructing a trial wave function of period L/N (a dimerized state) having lower energy than the period $L/2N$ function. With $L/2N$ as one unit, we have symmetry breaking from period 1 to period 2.

Given this fact, the question arises whether the energy can be lowered further by more symmetry breaking, say to period 4 or perhaps to no periodicity at all. In this paper we prove that at least for one well-known choice of the Hamiltonian the answer is no. We prove, for all N, that the dimerized states with the lowest energy are exact ground states and are the only ground states. (The amount of dimerization is unique, although for small, odd N the dimerization can vanish, in which case the ground state is unique and has period 1.) We also show that the chemical potential is discontinuous at the half-filled band, as expected. These results were announced by Lieb.[4,5] Physical intuition notwithstanding, these results are not at all obvious, for they are true for all coupling constants and do not require the infinite-N limit. In fact, as we remark later, they are not true for certain choices of the Hamiltonian and N.

The precise formulation of the electron system we shall consider is as follows. Consider a linear chain of $2N$ atoms (with periodic boundary conditions) and let w_i $(i=1,\ldots,2N)$ denote the distance from atom i to atom $i+1$ (with $2N+1\equiv 1$). If $d>0$ is the equilibrium distance and $\kappa>0$ is a measure of the stiffness, the distortion energy associated with the w_i is taken to be

$$U(\{w\})=\frac{1}{2}\kappa\sum_{i=1}^{2N}(w_i-d)^2. \tag{1}$$

Now suppose there are $2N$ (spin $\frac{1}{2}$) electrons (half-filled band) which can hop between nearest-neighbor atoms, with an amplitude $t_i=t(w_i)$ to hop from atom i to $i+1$ and from $i+1$ to i. *In this paper we consider the half-filled band.* The function $t(w)$ will be explained shortly. The ground-state energy of these $2N$ electrons is

$$K(\{w\})=2\sum_{j=1}^{N}\lambda_j(T), \tag{2}$$

where $\lambda_1\le\lambda_2\le\ldots\le\lambda_{2N}$ are the eigenvalues of the $2N\times 2N$ matrix T having matrix elements $T_{i,i+1}=T_{i+1,i}=t_i=t(w_i)$ and $T_{ij}=0$ otherwise.

The total Hamiltonian is $H(\{w\})=K(\{w\})+U(\{w\})$ and the problem is to determine the ground-state energy $E_0(2N)=\min_{\{w\}}H(\{w\})$ and the configurations $\{w\}$ that attain it.

The function $t(w)$ should be something like ae^{-cw}, but we shall adopt the linear function of Su, Schrieffer, and Heeger[6]: $t(w)=b-c(w-d)$ with $b,c>0$. (We emphasize, however, that the w_i are treated as dynamical, quantum variables in Ref. 6, whereas here they are static.)

It is well known that our problem is identical to the so-called "spin-Peierls" instability for XY interacting spin-$\frac{1}{2}$ particles. Namely, let

$$h(\{w\})\equiv 4\sum_{i=1}^{2N}\{S_i^xS_{i+1}^x+S_i^yS_{i+x}^y\}t(w_i).$$

Then the ground-state energy $e(\{w\})$ of $h(\{w\})$ is obtained by a Jordan-Wigner transformation to free fermions[7] and one finds $e(\{w\})=K(\{w\})$.

If the definition of $t(w)$ and $U(\{w\})$ are suitably changed, an "integrable system" is obtained.[8,9] However, the solution in Ref. 8 covers all electron numbers *except* the half-filled band which is the most interesting case from our point of view since it is only here that one might expect only a *partial breaking* of the symmetry from period 1 to period 2.

To state our main result we must distinguish two cases. The minimum can either be taken over all choices of $\{w_i\}$, or we can add the restriction that $\sum_{i=1}^{2N}w_i=2Nl$, where l is a constant. We will refer to these two cases as

the variable- and fixed-length cases, respectively. For the variable-length case, which is the physical case, our results hold for all values of the parameters N, κ, b, c, and d. In the fixed-length case, N is arbitrary, but we require a restriction on the other parameters. The fixed-length constraint may be relevant for certain statistical mechanical systems in which one conventionally fixes the total "volume."

One might expect that with another $t(w)$ or another $U(\{w\})$, a similar theorem would hold, at least when κ is large enough. We were unable to prove such a theorem, and wish to point out that some restriction on the parameters is essential in general, e.g., κ being large. A simple example of $N=2$ for which the ground state does not have period 2 is to let $t(w)=1-w$ and

$$U(\{w\})=\sum_{i=1}^{4}\left(\tfrac{1}{2}\kappa w_i^2+4w_i^4\right),$$

with $\kappa>0$ and small. One finds that the best dimerized configuration is $w_1=w_3=W$, $w_2=w_4=0$, where W is the solution of $8W^3+\frac{1}{2}\kappa W+1=0$. For small κ, $W\approx-\frac{1}{2}$. Let $H(\epsilon)$ denote the total energy of the configuration $w_1=w_3=W$, $w_2=\epsilon$, $w_4=0$. Then $H'(0)=0$, $H''(0)=-(1-W)^{-1}+\kappa$. If κ is small, then $H''(0)<0$, and so there is a configuration whose total energy is less than that of the best dimerized configuration. This example does not prove anything about large N or large κ, but it does show that one should not try to prove too much. It is conceivable that for certain $t(w)$ and $U(\{w\})$ and large N there could be a phase transition as a function of κ from period 2 (large κ) to period 4 or no periodicity (small κ).

We define the chemical potential $\mu(m)$ to be the energy required to add the mth electron to the ground state, i.e., $\mu(m)=E_0(m)-E_0(m-1)$. Here $E_0(m)$ is defined as before except that K is replaced by $2\sum_{j=1}^{m/2}\lambda_j(T)$ for even m and by

$$2\sum_{j=1}^{(m-1)/2}\lambda_j(T)+\lambda_{(m+1)/2}(T)$$

for odd m.

Theorem.—In the variable-length case for all b, c, d, κ, and N, the only configurations that minimize H are

$$w_i=W+(-1)^i\delta \quad \text{or} \quad w_i=W-(-1)^i\delta, \tag{3}$$

with W and δ being uniquely determined by b, c, d, κ, and N. Moreover, there is a gap, i.e., there is a positive constant ϵ which depends on b, c, d, and κ, but not on N, such that for all N, $\mu(2N+1)-\mu(2N)\geq\epsilon$. In the fixed-length case the same conclusions hold provided that b, c, d, and κ satisfy

$$\kappa[b-c(l-d)]\geq c^2. \tag{4}$$

Remark: Kivelson and Heim[10] argued that $\delta>0$ for all even N, while δ can be zero for N odd. However, δ is always positive for large enough N. There is no difficulty proving these statements rigorously.

Proof: Since T is unitarily equivalent to $-T$ [the unitary operator is $(-1)^i\delta_{ij}$], we see that the sum in Eq. (2) is identical to the sum of the negative eigenvalues of T. This implies that $K=\mathrm{Tr}|T|$ since $\mathrm{Tr}T=0$. From now on we shall use $\{t_i\}$ to specify the positions of the atoms rather than $\{w_i\}$. Hence,

$$H=\frac{1}{2}g\sum_{i=1}^{2N}(t_i-b)^2-\mathrm{Tr}|T|, \tag{5}$$

with $g=\kappa/c^2$.

Let Θ_κ be the unitary operator associated with translation by k sites. Then the concavity of the square-root function implies that

$$\mathrm{Tr}|T|=\mathrm{Tr}(T^2)^{1/2}\leq\mathrm{Tr}(\langle T^2\rangle)^{1/2}, \tag{6}$$

where $\langle T^2\rangle\equiv\sum_k\Theta_k T^2\Theta_k^{-1}/2N$. It is important to note here that for a configuration satisfying (3), $\Theta_k T^2\Theta_k^{-1}=T^2$, and so the above inequality is an equality.

The nonzero matrix elements of T^2 are $(T^2)_{i,i}=t_i^2+t_{i-1}^2$ and $(T^2)_{i,i+2}=(T^2)_{i+2,i}=t_it_{i+1}$. Thus, the nonzero matrix elements of $\langle T^2\rangle$ are $(\langle T^2\rangle)_{i,i}=2y^2$ and $(\langle T^2\rangle)_{i,i+2}=(\langle T^2\rangle)_{i+2,i}=z$, where $y^2=\sum_{i=1}^{2N}t_i^2/2N$ and $z=\sum_{i=1}^{2N}t_it_{i+1}/2N$. Let Ω be the matrix whose only nonzero elements are $\Omega_{i,i+2}=\Omega_{i+2,i}=1$. Then $\langle T^2\rangle=2y^2+z\Omega$.

The distortion energy is trivially expressed in terms of y and $x=\sum_{i=1}^{2N}t_i/2N$. Combining all our results we have shown

$$H\geq\tfrac{1}{2}g2N(y^2-2bx+b^2)-\mathrm{Tr}(2y^2+z\Omega)^{1/2}. \tag{7}$$

Let $s_i=x-t_i$. Then $y^2=x^2+\sum_i s_i^2/2N$, so $y^2\geq x^2$. With use of Cauchy's inequality,

$$z=x^2+\sum_i s_is_{i+1}/2N\geq x^2-\sum_i s_i^2/2N=2x^2-y^2. \tag{8}$$

We now consider two cases depending on whether this lower bound on z is positive or negative.

Case 1 $(2x^2-y^2\geq0)$.—Consider $\mathrm{Tr}(2y^2+z\Omega)^{1/2}$ as function of z. This function is clearly concave. Since T is unitarily equivalent to $-T$, it is also even in z. Thus, it is a decreasing function of $|z|$, so that in (7) we can replace z by $2x^2-y^2$. The resulting inequality is an equality for the dimerized configuration with $\bar{t}_i=x+(-1)^i(y^2-x^2)^{1/2}$. Furthermore, since $\sum_i\bar{t}_i=2Nx=\sum_i t_i$, the total length of the configuration corresponding to $\{t_i\}$ is the same as the total length of the configuration corresponding to $\{\bar{t}_i\}$. Thus, we have shown that for any choice of $\{t_i\}$ satisfying $2x^2-y^2\geq0$, there is a configuration satisfying (3), with the same total length, whose energy is at least as low. This energy is

$$H=gN(y^2-2bx+b^2)-\mathrm{Tr}[2y^2+(2x^2-y^2)\Omega]^{1/2}. \tag{9}$$

Case 2 $(2x^2-y^2<0)$.—Since $\mathrm{Tr}(2y^2+z\Omega)^{1/2}$ is de-

creasing in $|z|$, we can bound it from above by replacing z with 0. This yields

$$H/2N \geq \tfrac{1}{2} g(y^2 - 2bx + b^2) - \sqrt{2}y. \quad (10)$$

In the variable-length case we use $x^2 < y^2/2$ to obtain

$$H/2N > \tfrac{1}{2} g(y^2 - \sqrt{2}by + b^2) - \sqrt{2}y. \quad (11)$$

A little calculation shows that this lower bound on H is attained by the dimerized configuration $\bar{t}_i$ which alternates between 0 and $\sqrt{2}y$.

The total length of the configuration corresponding to $\{\bar{t}_i\}$ need not be the same as that corresponding to $\{t_i\}$, and so we need a separate argument for the fixed-length case. Fixing the length of the chain to be $2Nl$ is equivalent to fixing x to be $b - c(l-d)$. Recalling that $g = \kappa/c^2$, the restriction (4) is equivalent to $gx \geq 1$. This inequality and $y > \sqrt{2}x$ implies $\frac{1}{2} gy^2 - \sqrt{2}y > gx^2 - 2x$. From (10) we then obtain

$$H/2N > gx^2 - gbx + \tfrac{1}{2} gb^2 - 2x.$$

For the dimerized configuration $\bar{t}_i$ which alternates between 0 and $2x$ this lower bound is attained. Furthermore, the configuration corresponding to $\{\bar{t}_i\}$ has the same total length as the configuration corresponding to $\{t_i\}$. This analysis shows that for any configuration belonging to case 2, there is a configuration belonging to case 1 whose energy is lower. Hence, under the hypotheses of the theorem the minimizing configurations always belong to case 1.

We have shown that for any configuration with energy E there is a configuration satisfying (3) whose energy is at least as low as E. Thus H attains its minimum at such a configuration. It remains to be shown that H attains its minimum *only* at such configurations, that W and δ are unqiue, and that there is a gap. The following lemma, which is an improvement of inequality (6), will be used.

Lemma.—As before, let $\langle T^2 \rangle$ be the average of T^2 over translations. Then

$$\mathrm{Tr}(T^2)^{1/2} \leq \mathrm{Tr}(\langle T \rangle)^{1/2} - \tfrac{1}{8} \|T\|^{-3} \mathrm{Tr}(T^2 - \langle T^2 \rangle)^2. \quad (12)$$

Proof: By replacing T by $T/\|T\|$, we may assume $\|T\| = 1$. We claim that the function $A \to \mathrm{Tr}A^{1/2} + \frac{1}{8}\mathrm{Tr}A^2$ is concave on the set of operators A with $0 \leq A \leq 1$. To prove the claim, it suffices to show that $f(x) = x^{1/2} + \frac{1}{8}x^2$ is concave on [0,1], which is trivial. The argument is now the same as in (6) with the additional remark that $\mathrm{Tr}(T^2 - \langle T^2 \rangle)^2 = \mathrm{Tr}(T^4 - \langle T^2 \rangle^2)$. Q.E.D.

By using the lemma in place of inequality (6), we see that for any configuration at which H attains its minimum we have $\mathrm{Tr}(T^2 - \langle T^2 \rangle)^2 = 0$. This implies that $T^2 = \langle T^2 \rangle$, which implies that the configuration satisfies (3).

We must show that W and δ are unique. For such configurations H equals the right-hand side of (9), which we think of as a function of $X = x^2$ and $Y = y^2$. It is *strictly* jointly convex in X, Y, and so has a *unique* minimum over the convex region $0 \leq X \leq Y$ (variable-length case) and over the region $Y \geq X$, X fixed (fixed-length case). There are two configurations corresponding to this unique minimum unless $x^2 = y^2$, in which case there is only one configuration and $\delta = 0$.

To complete the proof of the theorem we must show that there is a gap. For a configuration satisfying (3) the spectrum of T may be explicitly computed. One finds that it has a gap between the $(2N)$th and $(2N+1)$th eigenvalues. However, this does not by itself imply that the system has a gap because the configuration that minimizes H for $2N-1$ or $2N+1$ electrons need not be the configuration that minimizes H for $2N$ electrons.

Recall that $E_0(2N-1)$, $E_0(2N)$, and $E_0(2N+1)$ are the ground-state energies with $2N-1$, $2N$, and $2N+1$ electrons, respectively. Let $\{t_i^-\}$, $\{t_i\}$, and $\{t_i^+\}$ be configurations which attain these minima. Let T^-, T, and T^+ be the associated T's and λ_i^-, λ_i, and λ_i^+ their eigenvalues. Then

$$\mu(2N+1) - \mu(2N) = \Delta^+ + \Delta^- + \lambda_{N+1}^+ - \lambda_N^-, \quad (13)$$

where

$$\Delta^{\pm} U(\{t_i^{\pm}\}) + 2\sum_1^N \lambda_i^{\pm} - U(\{t_i\}) - 2\sum_1^N \lambda_i. \quad (14)$$

The energy E for $2N$ electrons with the atoms in configuration $\{t_i^+\}$ is at least as large as the energy for $2N$ electrons with the atoms in configuration $\{t_i\}$, so that Δ^+ is nonnegative. The same reasoning shows that Δ^- is also nonnegative. Recall that T is unitarily equivalent to $-T$. This implies that the spectrum of T is symmetric about 0. Hence, $\lambda_{N+1}^+ \geq 0$ and $\lambda_N^- \leq 0$. Thus, Eq. (13) implies that $\mu(2N+1) - \mu(2N) \geq \Delta^+ + \lambda_{N+1}^+$.

We now consider three cases: (i)

$$\|(T^+)^2 - T^2\| \leq (\lambda_{N+1})^2/2,$$

(ii)

$$\|(T^+)^2 - \langle (T^+)^2 \rangle\| \geq (\lambda_{N+1})^2/4,$$

and (iii)

$$\|\langle (T^+)^2 \rangle T^2\| \geq (\lambda_{N+1})^2/4.$$

By the triangle inequality, at least one of these cases must hold. We claim that λ_{N+1} is bounded away from zero, uniformly in N, for the following reason. When N is even or when N is odd and $N \geq$ some N_0, we have $\delta > 0$. Also, δ does not go to zero as $N \to \infty$. This implies the claim in the two cases just cited. If N is odd and $N < N_0$ then $\lambda_{N=1} > 0$ since 0 is not an eigenvalue of T in this case, even if $\delta = 0$. (It is precisely for this reason that δ can be zero in the odd-N case.) Since N_0

is finite, this implies a positive lower bound to λ_{N+1} when $N < N_0$, which proves the claim.

In case (i), note that $(\lambda_{N+1})^2$ and $(\lambda^+_{N+1})^2$ are the smallest eigenvalues of T^2 and $(T^+)^2$. Then,

$$(T^+)^2 = T^2 + [(T^+)^2 - T^2] \geq T^2 - \|(T^+)^2 - T^2\| \geq T^2 - (\lambda_{N+1})^2/2 \geq (\lambda_{N+1})^2/2,$$

and thus $(\lambda^+_{N+1})^2 \geq (\lambda_{N+1})^2/2$ which implies there is a gap. In case (ii) we bound Δ^+ as before except that we use the lemma in place of (6). This yields

$$\Delta^+ \geq \|T^+\|^{-3} \mathrm{Tr}[(T^+)^2 - \langle (T^+)^2 \rangle]^2. \tag{15}$$

Combining this with (ii), and the fact that $\mathrm{Tr}A^2 \geq \|A\|^2$ for Hermitean A, shows that Δ^+ is bounded away from zero. (The norm of T^+ is easily bounded from above.)

To handle case (iii) consider the dimerized configuration with the same y and x as $\langle (T^+)^2 \rangle$. Call these parameters y^+, x^+ [and $z^+ = 2(x^+)^2 - (y^+)^2$]. Since $\|\Omega\| \leq 2$, the triangle inequality and (iii) imply $|y^2 - (y^+)^2| + |z - z^+| \geq (\lambda_{N+1})^2/8$. Since λ_{N+1} is bounded away from zero, at least one of $|y - y^+|$ and $|x - x^+|$ must be bounded away from zero. A simple calculation using (9) then shows that $\Delta^+ = O(N)$, which more than suffices.

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