Broken Symmetries in a One-Dimensional Half-Filled Band with Arbitrarily Long-Range Coulomb Interactions

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The nature of the ground-state broken symmetry in a one-dimensional half-filled band with arbitrarily long-range Coulomb interactions between electrons is shown to be precisely given by two simple inequalities involving the Coulomb parameters. It is further shown that non-$2k_F$ periodicity may occur if the first of these inequalities is violated.

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Despite considerable recent interest in broken symmetries in quasi-one-dimensional systems with electron-electron interactions, definitive results have been obtained only for *short-range* Coulomb forces.[1-4] Importantly, these investigations[2,3] also indicate that the use of *effective* short-range interactions to approximate long-range forces does not yield the correct ground-state broken symmetry, although it may yield reasonable values for the optical gap or spin density.[5] The few previously available results[5-8] on long-range interactions have been for the Pariser-Parr-Pople models with the *specific* Coulomb interaction parameters thought to be applicable to (the gas phase of) linear polyenes. Here the results of approximate calculations[6-8] for long chains are mutually contradictory, while exact diagonalizations[5] on short chains cannot yield the correct answer if the range of the interactions is greater than half the system size. Thus the accurate calculation of the effects of long-range interactions remains a central issue.

In the present Letter, we report a novel sharp result on broken symmetries in a one-dimensional half-filled band with long-range Coulomb interactions. Our result is valid for *arbitrary range and magnitudes* of positive Coulomb parameters. Thus, in the particular case of polyacetylene, the solid-state screening effects that may reduce the effective range of the Coulomb interactions in going from the gas to the condensed phase do not invalidate our approach. The class of models covered includes both those favored by chemists (e.g., Pariser-Parr-Pople models) and those favored by physicists (extended Peierls-Hubbard models and even the Su-Schrieffer-Heeger limit). Furthermore, our approach provides an intuitive picture of the mechanism for broken symmetry in the presence of correlations. This is significant, for no reasoning analogous to that given by Peierls for the pure electron-phonon coupling limit has previously existed. Explicitly, since there is no single-particle (band) picture for nonzero correlations, and thus no k_F, why should $2k_F$ broken-symmetry states be expected to occur at all? Finally, our result represents an important benchmark against which the predictions of all approximate methods[6-8] can be tested.

The models that we consider are described by the Hamiltonian $H = H_{1\text{-}e} + H_{e\text{-}e}$, where

$$H_{1\text{-}e} = \sum_{i,\sigma} [t_0 + \alpha(y_i - y_{i+1})](c^\dagger_{i\sigma} c_{i+1,\sigma} + c^\dagger_{i+1,\sigma} c_{i\sigma}) + \beta \sum_i q_i n_i, \tag{1a}$$

and

$$H_{e\text{-}e} = U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i,j} V_j n_i n_{i+j}. \tag{1b}$$

Here $c^\dagger_{i\sigma}$ ($c_{i\sigma}$) creates (annihilates) an electron with spin σ ($\uparrow$, $\downarrow$) at site i, $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$, and $n_i = \sum_\sigma n_{i\sigma}$. We work in the half-filled band limit and impose the restriction $U > V_1 > V_2 > \ldots > 0$. We have not included kinetic and potential energy terms corresponding to the *intra* site (q_i) and *inter* site ($y_i - y_{i+1}$) phonons, since we are interested in *unconditional* broken symmetries, i.e., those existing in the limits $\alpha, \beta \to 0^+$. For $H_{e\text{-}e} = 0$, whether the $2k_F$ *intra* site charge-density wave (CDW) or the $2k_F$ *inter* site bond-order wave (BOW) dominates is determined simply by the relative magnitudes[9] of α and β. When $H_{e\text{-}e} \neq 0$, we show here that, for arbitrarily long-range V_j, the ground state is *either* a $2k_F$ CDW *or* a $2k_F$ BOW[10] *provided* that the potential is downward convex, i.e., for all j,

$$V_{j+1} + V_{j-1} \geq 2V_j. \tag{2}$$

Note that models having $V_j = 0$ for $j > j_{max}$ do satisfy (2) and thus our result also applies to short-range (i.e., screened) Coulomb interactions, provided that the nonzero V_j satisfy (2). If (2) does *not* hold, then a CDW with periodicity other than $2k_F$ can be the ground state. The competition between the $2k_F$ CDW and BOW is decided by a second inequality,

$$\sum_j V_{2j+1} \lesssim \tfrac{1}{2} U + \sum_j V_{2j}. \tag{3}$$

For a smaller left-hand side, the $2k_F$ BOW is the dominant broken symmetry, while for a smaller right-hand side, the $2k_F$ CDW dominates. Near the equality, the two broken symmetries can coexist. It is both remark-

able and significant that the inequality (3), which is a sharp result, is consistent with both classical chemical studies[11] (in which electron hopping effects are ignored) and with more recent physical studies focusing on the weakly correlated limit.[12]

Our demonstration of these assertions proceeds in three separate steps. First, we discuss a real-space *mechanism* for broken symmetry and show how the *ground state* of (1) at $H_{1\text{-}e}=0$ determines the dominant broken symmetry when $H_{1\text{-}e}\neq 0$. This argument is heuristic, based on symmetry considerations of real-space configurations. In the second step, we derive the explicit ground-state solution to (1) at $H_{1\text{-}e}=0$. This result represents a significant extension to finite U (for the half-filled band) of results previously[13] obtained for $U=\infty$ (for arbitrary band filling). Finally, we present exact numerical results on finite ($N=10$) chains to illustrate our results.

To describe the real-space mechanism[1,2] of broken symmetry, we note that all many-electron real-space configurations are diagonal or off-diagonal with respect to the discrete symmetry operation (reflection through or between sites) that is lost when the symmetry is broken. Broken symmetry is unconditional only if pairs of configurations which are *off-diagonal* with respect to the symmetry operator, but otherwise equivalent, make *unequal* contributions to the wave function, i.e., resonance (in the chemical sense) is imperfect. The overall barrier to resonance can be determined by inspection of only the extreme pair that favors the broken symmetry most strongly,[1,2] as each member of the pair can be reached by N applications (where N is the system size) of $H_{1\text{-}e}$ on the other, and all other configurations lie along the paths so generated. For $H_{e\text{-}e}=0$, resonance is imperfect in infinite systems because of the infinite lengths of these paths. $H_{e\text{-}e}\neq 0$ enhances (decreases) the barrier to resonance, depending on whether matrix elements of $H_{e\text{-}e}$ of the *intermediate* configurations along *all* paths are higher (lower) in energy than those of the extreme pair. Thus we arrive at our first crucial result: Electron-electron interactions will enhance a given broken symmetry if the appropriate extreme configurations form the ground state of $H_{e\text{-}e}$ (i.e., the ground state of H at $H_{1\text{-}e}=0$). If any other configurations form the ground state of $H_{e\text{-}e}$, the broken symmetry will (for some coupling strength) be destroyed.

Simple inspection (or reference to previous studies[1,2]) shows that the (two) extreme configurations for the $2k_F$ CDW are $L_{\mathrm{CDW}}=c_{1\uparrow}^{\dagger}c_{1\downarrow}^{\dagger}c_{3\uparrow}^{\dagger}c_{3\downarrow}^{\dagger}\cdots|0\rangle$ and R_{CDW}, which has sites 2, 4, . . . doubly occupied. In terms of site occupancies, these configurations are $L_{\mathrm{CDW}}=2020\ldots$ and $R_{\mathrm{CDW}}=0202\ldots$; for $H_{1\text{-}e}=0$, L_{CDW} and R_{CDW} are eigenstates of H and have equal energies. For the $2k_F$ BOW, the two (single-valence bond) extreme configurations are $L_{\mathrm{BOW}}=(c_{1\uparrow}^{\dagger}c_{2\downarrow}^{\dagger}-c_{1\downarrow}^{\dagger}c_{2\uparrow}^{\dagger})(c_{3\uparrow}^{\dagger}c_{4\downarrow}^{\dagger}-c_{3\downarrow}^{\dagger}c_{4\uparrow}^{\dagger})\cdots|0\rangle$ and R_{BOW}, in which perfect spin pairings occur between sites 2 and 3, 4 and 5, etc. Since for $H_{1\text{-}e}=0$ the energies are independent of spins, the energies of both L_{BOW} and R_{BOW} are given by the configuration . . .1111. . ., with all sites singly occupied. The final result of our real-space arguments is thus that the dominant broken symmetry of H is a $2k_F$ CDW (BOW) if the configuration . . .2020. . . (. . .1111. . .) is the ground state for $H_{1\text{-}e}=0$.

Fortunately, we can study this ground-state question precisely and prove the following theorem: If inequality (2) holds, then the ground state of $H_{e\text{-}e}$ is the configuration . . .2020. . . if $\frac{1}{2}U+\sum_j V_{2j}<\sum_j V_{2j+1}$, whereas it is . . .1111. . . if $\frac{1}{2}U+\sum_j V_{2j}>\sum_j V_{2j+1}$.

The detailed proof of this theorem is lengthy and will be presented elsewhere, but a sketch should suffice to motivate its validity. For finite U, we need to consider configurations with all possible numbers of double occupancies N_2, where $0\leq N_2\leq N/2$. As a first step, we consider only the class of configurations with a fixed N_2 and determine the lowest-energy configurations within this class. All configurations are represented by sequences involving only the integers 0, 1, and 2 (denoting site occupancies) and the number of 0's and 2's are equal. Extending a counting technique developed by Hubbard[13] for the $U=\infty$ (so that only 0's and 1's occur) arbitrary-band-filling problem, we prove the following in sequential steps:

(i) For any N_2, configurations with each 2 next to a 0 are lower in energy than those with separated 2's and 0's, provided that Eq. (2) is valid; i.e., in an obvious notation,

$$E(\ldots 112011\ldots)<E(\ldots 12\ldots 1\ldots 0\ldots 1\ldots).$$

(ii) For any N_2, configurations in which the order of the 2-0 alternation is preserved are lower in energy than the others; i.e.,

$$E(\ldots 11\ldots 20\ldots 11\ldots 20\ldots)<E(\ldots 11\ldots 20\ldots 11\ldots 02\ldots),$$

if Eq. (2) is valid.

(iii) Irrespective of N_2 and of the number of 1's intervening between two (2-0) pairs, the energy is always lowered by bringing the pairs closer if Eq. (2) is valid; i.e.,

$$E(\ldots 11202011\ldots)<E(\ldots 112012011\ldots)<E(\ldots 1120112011\ldots)<\ldots.$$

(iv) The last condition remains true even when we consider an arbitrary number of (2-0) pairs, so that the lowest-energy configuration for fixed N_2 is the one in

which *all* 2's and 0's alternate consecutively, as long as V_j's are downward convex.

Since we now know the unique configuration of lowest energy for N_2 double occupancies, let us denote its energy by $E(N_2)$. Our stated result will follow if we can prove that, when $\frac{1}{2}U + \sum V_{2j} > \sum V_{2j+1}$, $E(0) \leq E(N_2)$ for all $0 < N_2 \leq N/2$, whereas when $\frac{1}{2}U + \sum V_{2j} < \sum V_{2j+1}$, $E(N/2) \leq E(N_2)$ for all N_2. We can calculate $E(N_2)$ by inspection:

$$E(N_2) = N_2 U + \sum_{j=1}^{2N_2} [N + (-1)^j (2N_2 - j)] V_j + N \sum_{j=2N_2+1}^{N/2-1} V_j + (N/2) V_{N/2}, \tag{4}$$

for $0 \leq N_2 \leq N/4$, while

$$E(N_2) = N_2 U + \sum_{j=1}^{N-2N_2} [N + (-1)^j (2N_2 - j)] V_j + \sum_{j=N-2N_2+1}^{N/2-1} [N + (-1)^j (4N_2 - N)] V_j + \tfrac{1}{2} V_{N/2} [N + (-1)^{N/2} (4N_2 - N)], \tag{5}$$

for $N/4 \leq N_2 \leq N/2$, where in both (5) and (6) the last terms, which are irrelevant for infinite systems, are indicated in anticipation of our later study of finite rings. Note that (5) and (6) give the correct limit values $E(0) = N(V_1 + V_2 + V_3 + \ldots)$ and $E(N/2) = \frac{1}{2}NU + 2N(V_2 + V_4 + V_6 + \ldots)$, respectively. Simple algebraic manipulations now show that if the left-hand side of Eq. (3) is smaller, so that $E(0) < E(N/2)$, then $E(0) < E(N_2)$ for all N_2 *provided* that Eq. (2) is true. Similarly, if the right-hand side of (3) is smaller, then $E(N/2) < E(N_2)$ follows if Eq. (2) is true. This proves our theorem regarding the exact ground state at $H_{1\text{-}e} = 0$.

To illustrate these results, we next present exact numerical calculations for a periodic ring of $N = 10$ sites. To demonstrate an enhanced $2k_F$ BOW, we study

$$\Delta(\Delta E) = \Delta E(U, V_j) - \Delta E(0), \tag{6}$$

where

$$\Delta E(U, V_j) = E(U, V_j, t_{i,i+1} = t_0[1 + (-1)^i \delta]) - E(U, V_j, t_{i,i+1} = t_0)$$

and $E(U, V_j, t_{i,i+1})$ is the total *electronic* energy. Thus

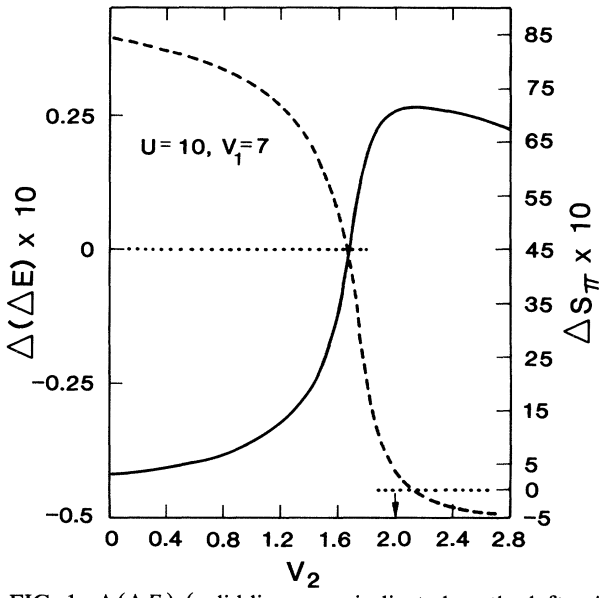

FIG. 1. $\Delta(\Delta E)$ (solid line, zero indicated on the left axis) and ΔS_π (dashed line, zero indicated on the right axis) vs V_2 for $U = 10$ and $V_1 = 7$, in units of t_0. Equation (3) predicts that beyond $V_2 = 2$ (indicated by an arrow on the graph) the CDW should disappear and the BOW should appear. The nonzero intersite electron-phonon coupling causes the BOW to appear slightly before V_2^c, and in the region $1.7 \lesssim V_2 \lesssim 2.1$, both the BOW and CDW coexist. Note that when the plotted quantities fall below zero, there is no tendency toward the corresponding broken symmetry.

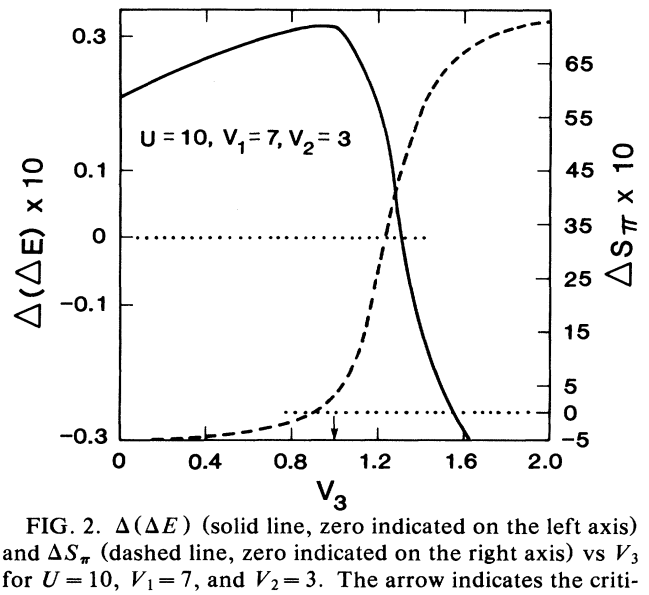

FIG. 2. $\Delta(\Delta E)$ (solid line, zero indicated on the left axis) and ΔS_π (dashed line, zero indicated on the right axis) vs V_3 for $U = 10$, $V_1 = 7$, and $V_2 = 3$. The arrow indicates the critical V_3 $(=1)$ beyond which the CDW should appear and the BOW disappear. The persistence of the BOW beyond V_3^c is in part due to the nonzero electron-phonon coupling used in the measurement of $\Delta(\Delta E)$.

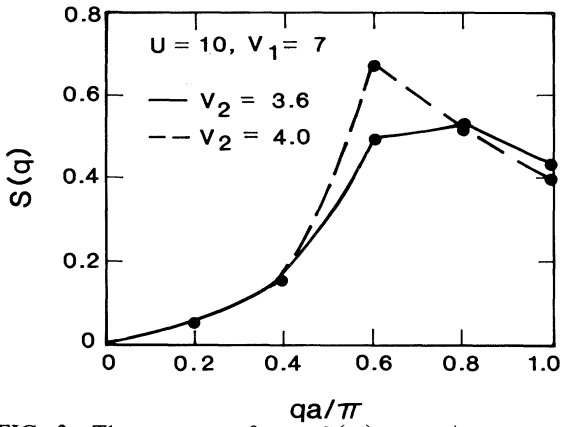

FIG. 3. The structure factor $S(q)$ vs qa/π for $U=10$, $V_1=7$, and $V_2=3.6$ and 4.0. $S(q)$ always peaks at $q=2k_F=\pi/a$ for $0<V_2\lesssim V_2^c=3.5$ but shifts to smaller q as V_2 increases beyond V_2^c.

$\Delta(\Delta E)>0$ implies that the Coulomb interactions enhance the $2k_F$ BOW. To investigate the $2k_F$ CDW, we evaluate the structure factor

$$S(q)=S_q=N^{-1}\sum_{j,l}\langle n_j n_{j+l}\rangle\, e^{iqla} \tag{7}$$

at $q=2k_F=\pi/a$ and study $\Delta S_\pi=S_{\pi/a}(U;V_j)-S_{\pi/a}(0)$, noting that $\Delta S_\pi>0$ implies enhanced $2k_F$ CDW.

The inequalities (2) and (3) are independent of the cutoff in V_j and N, with the only finite-size effect being that the last term on the left-hand side of Eq. (3) must have a coefficient of $\frac{1}{2}$. Altogether we have studied more than fifty different combinations of $U,V_1,\ldots,V_5$ (the maximum physical V_j for the $N=10$ system) and verified our predictions in each case; we focus here on three illustrative examples. First, we take $U<2V_1$, and $V_j=0$ for $j\geq 3$. For $V_2=0$, we have an enhanced $2k_F$ CDW according to Eqs. (2) and (3), while for $V_2^c\gtrsim V_1-\frac{1}{2}U$, we predict an enhanced BOW. We have plotted both $\Delta(\Delta E)$ and ΔS_π for this case—we take $U=10$, $V_1=7$ (where $t_0=1$), so that $V_2^c\cong 2$—in Fig. 1, and we see that numerical results agree with this completely. Second, with $V_j=0$ for $j\geq 4$, we choose values of U, V_1, and V_2 such that we have an enhanced $2k_F$ BOW initially. We now increase V_3 from 0 and expect that for $V_3^c\gtrsim\frac{1}{2}U+V_2-V_1$, the system transforms to an enhanced $2k_F$ CDW. Again, the results in Fig. 2 reflect this behavior. Finally, if we take $U<2V_1$, $V_j=0$ for $j\geq 3$, and increase V_2 until $V_2>\frac{1}{2}V_1$, we violate the downward convexity condition (2) and expect a non-$2k_F$ CDW. In Fig. 3 we plot $S(q)$ from Eq. (7) and show that when (2) is violated it indeed peaks at $q\neq 2k_F=\pi/a$. We have deliberately chosen such large values of U, V_j, etc. to illustrate the validity of our results away from the perturbative regime.[11]

Finally, our results have two immediate and important consequences for attempts to model real quasi-one-dimensional systems. First, we predict bond alternation in the infinite polyene for *both* the Ohno and Mataga-Nishimoto parametrizations of the Pariser-Parr-Pople Hamiltonian, in contradiction to previous approximate theories[6,7] (Ref. 8 investigates only the Mataga-Nishimoto parameters and predicts bond alternation). Second, our inequalities explain why use of effective short-range interactions can lead to incorrect results for ground-state broken symmetry; namely, inclusion of a single additional V_j can cause a switch from CDW to BOW or vice versa. Extensions of our analysis to mixed-stack charge-transfer solids (with V_j's alternating in sign and alternating site energies) and to other band fillings are currently under investigation.

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