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Valence-bond approach to two-dimensional broken symmetries: Application to La_2CuO_4

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We use a real-space approach to geometric broken symmetries to show that the on-site electron correlation destroys the bond alternation in a square lattice, even though this interaction enhances the one-dimensional bond alternation. Boundary lines between charge- and spin-density waves are derived for nonzero short-range intersite Coulomb correlations. Implications for systems like La_2CuO_4 are briefly discussed.

In spite of initial controversies, it is now generally accepted that mean-field and perturbative theories of Coulomb effects on one-dimensional (1D) broken symmetries predict erroneous results. Thus, in contradiction to Hartree-Fock predictions it is found that the bond alternation and the associated $2k_F$ bond order wave (BOW) in a half-filled 1D band is enhanced by moderate on-site electron repulsion (Hubbard U), and that the BOW and the $2k_F$ spin-density wave (SDW) coexist for all correlation parameters.[1-4] The BOW gets destroyed only at the onset of the $2k_F$ intrasite charge-density wave (CDW), in which the on-site atomic charge, rather than the bond order or spin density, is modulated. The boundary between the 1D BOW-CDW has now been precisely defined, even for arbitrarily long-range Coulomb correlations.[4] All these have raised anew the questions regarding corresponding broken symmetries in two-dimensional (2D) correlated systems.[5-7] While the problem is of fundamental interest in its own right, more recent excitement is largely due to the high-temperature superconductivity found in oxide materials.[8-11] Various mechanisms for destroying *specific* geometric broken symmetries while leading to singlet pairing have been postulated by investigators who have emphasized the role of electron correlation in the above materials.[12-15] It is relevant even in this context to determine correlation effects on 2D broken symmetries, especially since one of the above mechanisms[13] for superconductivity requires enhancement of the 2D BOW by U and its coexistence with SDW, just as in 1D.

We are interested in the Hamiltonian,

$$H = H_{1e} + H_{ee} \ , \tag{1a}$$

$$H_{1e} = \sum_{\langle ij \rangle, s} [t_0 - \alpha(y_i - y_j)] \times [c_{is}^{\dagger} c_{js} + c_{js}^{\dagger} c_{is}] + \sum_i \epsilon_i n_i \ , \tag{1b}$$

$$H_{ee} = U \sum_i n_{i\uparrow} n_{i\downarrow} + V_1 \sum_{\langle ij \rangle} n_i n_j + V_{\mathrm{NNN}} \sum_{[kl]} n_k n_l \ . \tag{1c}$$

Here, all interactions are for a square lattice H_{1e} and H_{ee} are the one-electron and many-electron parts of H, $\langle ij \rangle$ imply nearest neighbors, while $[kl]$ are next nearest neighbors; y_i is the displacement of the ith atomic unit from its equilibrium position, α is the intersite electron-phonon coupling constant, and ϵ_i can be *any interaction* that promotes a $2k_F$ CDW: site energy, a molecular crystal kind of electron-vibration coupling, or even the breathing-mode displacements of the oxygen atoms surrounding the copper atoms in the oxide materials. The exact nature of ϵ_i does not matter for the general problem, since we are interested in *unconditional* broken symmetries that occur for, $\alpha, \epsilon_i \rightarrow 0^+$. Therefore, we have not explicitly included the elastic energy contributions. Finally, $n_{is} = c_{is}^{\dagger} c_{is}$, $n_i = \sum_s n_{is}$, where s is the spin. We have retained both V_1 and V_{NNN} and are interested in determining the effect of each term on the BOW, CDW, and SDW.

The approach we use is the valence bond (VB) approach to broken symmetry.[1,4] This method has not only been highly successful with controversial 1D problems,[1] but has also been used to predict unanticipated results elsewhere.[16] Indeed, it was claimed very early[1] that the chief utility of the VB approach would be its application to broken-symmetry problems that cannot be solved by either analytic or numerical methods. Recent solution of the 1D broken-symmetry problem even in the presence of *arbitrarily long-range Coulomb interactions*[4] is the clearest example of the above. VB ideas have recently been postulated even to explain the high-T_c superconductivity,[12] while in the past they were used to postulate a theory of metals that is quite different from band theory.[17] There is of course a good reason why the VB method can in principle be used to predict qualitative results for *all* geometric broken symmetries: the definition of broken symmetry as imperfect resonance (in the VB sense, see below) is a *natural* definition. In the same context, Pauling's theory of metals[17] requires perfect resonance. In general, there are only two caveats to the application of the VB ideas. Firstly, the approach requires that the free-fermion results are precisely known since the VB approach can only predict the effects of H_{ee} on broken symmetries that already exist within H_{1e}. Usually, this is not a problem. Secondly, it requires judicious choice of what we have called *extreme configurations*[4] (see below), since it is the barrier to resonance between these extreme configurations that leads to broken symmetry. Often, determining the extreme configurations is the difficult step, since they can depend on geometries and dimensionalities (see below).

We briefly present here the VB ideas for the sake of

completeness. We shall illustrate our ideas with the example of the $2k_F$ broken symmetry in the 1D half-filled band; the implications for 2D will be obvious. Within VB theory the wave function is a linear combination of all possible many-electron real-space configurations. To understand broken symmetry we start by classifying all configurations into L, R, and S, where L and R favor the "left" and "right" phase of the broken symmetry in question, while S stands for "symmetric." In the two-site CDW case for example, $|L\rangle = |20\rangle$, $R = |02\rangle$, and $S = |11\rangle$ where the numbers denote the number of electrons on a given site. Within each class for the infinite chain, configurations are then further classified according to the *extent* to which they favor broken symmetry; e.g., L_1 would favor the left phase most strongly, L_2 slightly less strongly, and so on. The following are then true in general: (i) $|L_i\rangle = \sigma |R_i\rangle$, where σ is the symmetry operator in question (mirror plane passing through a site for BOW, passing through a bond center for CDW and SDW), (ii) L_i and $L_{i\pm1}$ (and similarly R_i and $R_{i\pm1}$) are related by a single application of H_{1e}, i.e., $H_{1e}|L_i\rangle = |L_{i\pm1}\rangle$, and (iii) only L_1 and R_1 are unique; L_2, for example, is the full set that can be obtained from L_1 from one application of H_{1e} *anywhere* along the infinite chain. Resonance is the process of repeated application of H_{1e} on L_1 to reach R_1 along an infinite number of paths[1] each of which looks as follows:

$$L_1 \rightarrow L_2 \dashrightarrow S \dashrightarrow R_2 \rightarrow R_1 \ . \tag{2}$$

Here the solid and broken arrows represent one and $(N/2-1)$ applications of H_{1e}, respectively. Broken symmetry is an unequal contribution to the wave function by L_i and R_i and arises within H_{1e} due only to the infinite length of the paths. It can be both enhanced or destroyed by H_{ee}. If L_1 and R_1 are such that $H_{ee}^{(1)} < H_{ee}^{(2)} < \ldots H_{ee}^{(S)}$, where $H_{ee}^{(i)} = \langle Li_i | H_{ee} | L_i \rangle = \langle R_i | H_{ee} | R_i \rangle$, Coulomb effects enhance the broken symmetry in question. If the reverse is true, resonance is enhanced and broken symmetry disappears at some critical H_{ee}. Thus, the ground state of H_{ee} gives the dominating broken symmetry of H.[4]

Therefore, we see that correct results can always be predicted *provided* L_1 and R_1 have been chosen judiciously. In 1D, $L_1^{\rm CDW}$ ($R_1^{\rm CDW}$) and $L_1^{\rm SDW}$ ($R_1^{\rm SDW}$) can be chosen from inspection alone: $L_1^{\rm CDW} = \ldots 2020 \ldots$ and $L_1^{\rm SDW} = \ldots 1\bar{1}1\bar{1} \ldots$, where the numbers 0, 1, and 2 denote site occupancies by electrons and $\bar{1}$ denotes a spin opposite to that of 1. Determining $L_1^{\rm BOW}$ is more complicated, because charge transfer depends both on occupancy as well as spin. Since an extreme configuration must have a short repeat unit which favors the maximum difference in local bond orders, we see[1] that there are two candidates for $L_1^{\rm BOW}$, $\ldots 2200 \ldots$, and $\ldots (1\bar{1}-\bar{1}1)(1\bar{1}-\bar{1}1) \ldots$, where it should be obvious that $(1\bar{1}-\bar{1}1)$ denotes a pair of nearest neighbors linked by a singlet coupled *bond*.[1,4] This particular linear combination is a Kekulé structure in the chemistry language. Within the repeat unit $\ldots 2200 \ldots$, maximum charge transfer is favored between atoms with occupancies 2 and 0, while minimum charge transfer is favored between nearest neighbors with occupancies (2,2) or (0,0). The Kekulé structure with single occupancies similarly favors strong charge transfer between nearest-neighbor bonded sites, and much weaker charge transfer between a nonbonded pair, since in the latter case spins are parallel or opposite with equal probability.[1] By explicitly writing down *all* possible electron occupancy and spin arrangements over three consecutive sites, it is easily ascertained that there are no other contenders for extreme BOW configurations. In order to choose between these two possibilities we now have to decide on proper boundary conditions. In 1D we had argued in detail why the infinite chain behaves more like a $4n+2$ membered periodic ring rather than a $4n$ ring, where n is an integer (a Jahn-Teller, rather than Peierls, distortion occurs in the latter). Based on this argument we had discarded the configurations $\ldots 2200 \ldots$ and its translated version, and chosen the two Kekulé structures as $L_1^{\rm BOW}$ and $R_1^{\rm BOW}$, since the former pair cannot occur in a $4n+2$ ring. On the other hand, *because* the former pair does occur in a $4n$ ring, and because the on-site correlation destroys double occupancies, for the $4n$ ring $H_{ee}^{(1)} > H_{ee}^{(2)} > \ldots$ in (2), so that Hubbard U reduces bond alternation in $4n$ rings even while it enhances it in finite $4n+2$ rings and the infinite chain. All of the above predictions, as well as those corresponding to V_1, etc., are completely borne out by exact numerical calculations.[1,4]

Coming back to the 2D problem, we first note that none of the basic VB principles on imperfect resonance can be different, except that $2K_F$ is now $(\pi/a, \pi/a)$, where a is the lattice spacing. The bond alternation pattern for this case is shown in Fig. 1(a). The difference can occur only in the choice of extreme configurations (as for instance in the case of $4n$ vs $4n+2$ periodic rings). Inspection again shows that the extreme configurations that promote either the 2D CDW or the SDW most strongly are simply the 2D counterparts of $\ldots 2020 \ldots$ and $\ldots 1\bar{1}\ 1\bar{1} \ldots$, where now these units are repeated along both the x and y axes. It is when we come to the BOW that we see a major difference: there is *no* Kekulé structure which promotes the $2K_F$ BOW here. Note that now from each lattice point there originate *two,* and not one, strong bonds (which are mutually orthogonal), and there can be no covalent structure (at least within the nondegenerate Hubbard models) in which a neutral atom with only one electron is bonded to two nearest neighbors. It is further significant that there are now virtually an infinite number of VB structures with nearest neighbors bonded (instead of just two in 1D, where all other covalent structures have long bonds between nonnearest neighbors), thus further

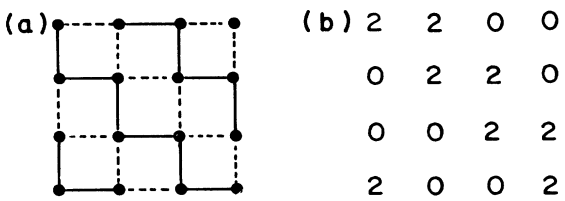

FIG. 1. (a) Bond-alternation pattern in a square lattice and (b) the extreme VB configuration that favors it most strongly (see text). Here solid and dashed lines represent strong and weak bonds and the square is distorted in reality.

indicating that the $2K_F$ BOW is not promoted by these. On the other hand, the 2D equivalent of the configuration with the repeat unit ...2200... is entirely possible, as shown in Fig. 1(b). Again, strong charge transfer is favored between nearest neighbors with occupancies 2 and 0, and much weaker charge transfer between the other sites. The configuration in Fig. 1(b) thus strongly favors the $2K_F$ BOW, with two strong bonds and two weak bonds originating from each lattice point. Exactly as in 1D, one can now construct paths as in (2).

Having determined the extreme configurations that promote the $2K_F$ BOW, CDW, and SDW in 2D, it is now easy to predict all the effects of the Coulomb correlations in Eq. (1). From Fig. 1, U destroys the BOW in 2D, in contrast to the enhancement effect in 1D. From the natures of the CDW and the SDW extreme configurations, U destroys the CDW, but enhances the SDW, exactly as in 1D. Since each broken symmetry is favored by a distinct extreme configuration, two different broken symmetries will coexist only if the ground state *simultaneously* can contain both the corresponding extreme configurations. In 1D, the BOW structure $\ldots(1\bar{1}-\bar{1}1)(1\bar{1}-\bar{1}1)\ldots$ contains $\ldots1\bar{1}1\bar{1}\ldots$, so that a BOW *must* coexist with SDW. In 2D, L_1^{BOW} (and R_1^{BOW}) contain double occupancies and empty sites, so that BOW-SDW coexistence is not possible. An additional twist is that while the 1D Kekulé structure contains the SDW configurations, *the converse is not true,* so that once long-range antiferromagnetic order sets in even in 1D, BOW vanishes. Another way of looking at it is to consider the definition of bond order as the expectation value of charge transfer: in the Néel configuration charge transfers to the left and to the right are equally probable. This explains why the appearance of long-range antiferromagnetic order and disappearance of BOW coincide[18] in the Ising-Heisenberg model. Long-range antiferromagnetic order has been postulated to exist in 2D for all U by Hirsch,[5] and while we are not able to confirm this for arbitrary U it should be clear from what we have said that the BOW disappears as the antiferromagnetic order sets in.

In the absence of V_1, V_{NNN} the magnitude of U_c depends on α and cannot be determined from VB arguments alone. The boundaries between the various phases are easier to determine for nonzero intersite interactions. This again is similar to the 1D case, where just from the nature of the extreme configurations the line $V_1=U/2$ was predicted[1] to be the CDW-BOW and the CDW-SDW boundaries. Here also we predict V_1 to enhance the SDW first, by examining paths such as (2): initial charge transfer in L_1^{SDW} produces a neighboring double occupancy and an empty site which are excitonically bound[1] for $V_1>0$, i.e., an energy V_1 is required to separate them. However, here the extreme configuration for the CDW has a lower energy for $V_1>U/4$. Therefore $V_1>U/4$ enhances the $2K_F$ CDW and destroys the $2K_F$ SDW.

For both V_1 and $V_{\mathrm{NNN}}\neq0$, V_{NNN} destabilizes the CDW much more strongly than the SDW. From the extreme configurations the CDW-SDW boundary is given by $V_1\gtrless U/4+V_{\mathrm{NNN}}$, where for a smaller left-hand side we have enhanced SDW, while for a smaller right-hand side we have enhanced CDW. We assume $U>V_1>V_{\mathrm{NNN}}$ and therefore do not worry about the BOW.

For convenience, the theoretical discussion has focused on the square lattice, but all the above arguments are valid for the rectangular planes that occur in orthorhombic systems like La_2CuO_4. The completely general case in the $U=0$ limit has been discussed by Horovitz *et al.*[19] For the half-filled band with hopping limited to nearest neighbors on a bipartite lattice nesting always occurs, and therefore bond alternation is again unconditional for $U=0$, although the mean bond lengths as well as the distortions along the two axes are different. For large U, bond alternation disappears and antiferromagnetism appears as before, with two different exchange integrals. The only difference between the square and the rectangular lattices is that in the inequality discussed above V_1 should strictly speaking be replaced by the average of the two nearest-neighbor interactions in the latter case. In La_2CuO_4 itself, antiferromagnetism has recently been found.[20]

To sum up then, we have determined the effect of short-range Coulomb correlations on the three geometric broken symmetries in a square lattice. Our most important result is that the U destroys the $2K_F$ BOW in 2D. The spin-Peierls state is therefore a unique feature of 1D. Based on the hypothesis that the spin-Peierls state persists in 2D, Hirsch[13] has argued against the resonating valence bond (RVB) theory of superconductivity[12] for systems slightly away from the half-filled band limit. Rather, it has been proposed, that the tendency to the spin-Peierls state persists even when weakly doped, and pairing involves the electrons on a short bond in the presence of high-frequency phonons. Present work shows that both the objection to the RVB theory as well as the alternate theory of superconductivity are based on an incorrect hypothesis. It is emphasized that this does not necessarily imply that the RVB approach to superconductivity is correct. We finally note that most of the present results, in particular the noncoexistence of the BOW and the SDW, can be carried over to 3D, in contrast to the 1D results.

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