

Resonating-valence-bond theory for the square-planar lattice

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The short-range resonating-valence-bond (RVB) wave function with nearest-neighbor (NN) spin pairings only is investigated as a possible description for the Heisenberg model on a square-planar lattice. A type of long-range order associated to this RVB *Ansatz* is identified along with some qualitative consequences involving lattice distortions, excitations, and their coupling.

I. INTRODUCTION

Heisenberg spin Hamiltonians have long provided a relatively simple nontrivial example of electron correlation. For the isotropic spin- $\frac{1}{2}$ case the Hamiltonians have been studied in chemistry¹ under the name of *valence-bond* (or VB) models, and there a “resonance-theoretic” correlated VB approach to the wave functions has traditionally been adopted. The plausibility of the qualitatively different solution techniques of resonating-VB type in chemistry and Néel-state-based solutions in physics has been rationalized² as being relevant for the different coordination numbers to which the models are applied in the two fields. Recently Anderson³ has proposed that the resonating-VB type of solution might be that applicable to perovskite cuprates, such as La_2CuO_4 , which become⁴ high-temperature superconductors when doped. Thence it seems reasonable to explore such descriptions for this purpose too.

Here then we deal with the Heisenberg model for the square-planar lattice. That is

$$H = 2 \sum_{i,j} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j \quad (1.1)$$

with \mathbf{s}_k the spin operator for site k and the $J_{ij} \geq 0$ antiferromagnetically signed exchange-coupling parameters. At least when restricted to nearest neighbor (NN) interactions J , there is⁵ no Néel-state ordering at any positive temperature, but this might occur in the ground state. An alternant type of wave function is built from products of singlet-pair configurations,

$$|C\rangle = \prod_{(i,j)}^C [\alpha(i)\beta(j) - \beta(i)\alpha(j)], \quad (1.2)$$

where the i and j indices may be chosen to range over disjoint A and B sublattices. Simple rules⁶ for the evaluation of matrix elements between such configurations lead to diagonal elements

$$\langle C|H|C\rangle = -\frac{3}{2}J(N/2 - n_C)\langle C|C\rangle, \quad (1.3)$$

where N is the total number of sites (or electrons) and n_C is the number of i,j pairs between other than NN sites. In contrast, the energy for the usual (normalized) Néel states is

$$\langle \text{Néel}|H|\text{Néel}\rangle = -\frac{1}{4}JzN, \quad (1.4)$$

where z is the lattice's coordination number. The lowest-energy singlet spin-pairing configurations $|C\rangle$ correspond to *dimer coverings*, with $n_C=0$, and in the chemical literature¹ are termed *Kekulé structures*. For the present (square-planar) lattice with $z=4$ the Néel state is of lower energy. However, a resonating-valence-bond (RVB) ground-state *Ansatz* constructed from a linear combination of (smaller n_C) configurations $|C\rangle$ would exhibit an enhanced stabilization due to (off-diagonal) configuration mixing. Still the Néel state can also admix with additional higher-energy spin configurations to stabilize. If $J_{ij} > 0$ between next-nearest neighbors (NNN) the problem shifts somewhat: the Néel state is frustrated, while the RVB state is *not*. With $J_{\text{NNN}} = J_{\text{NN}}/4$ the energies of (1.3) and (1.4) are shifted to become equal. In a similar frustrated circumstance for the NN triangular-lattice model Anderson and Fazekas⁷ have argued that the RVB type of picture is preferred. Similar arguments have also been made² in a more general context, but with a focus on benzenoid hydrocarbons, where $2 \leq z \leq 3$ and the case for RVB views is stronger.

To clarify the ideas further it seems worthwhile to investigate the simplest RVB *Ansatz*, namely, solely that with NN spin pairing. Upon understanding such a zeroth-order RVB *Ansatz*, the effect of higher-order corrections and excitations can be better addressed. Here we focus on the role of the type of long-range order discussed in a more general context in an accompanying paper.

II. RVB GROUND STATE AND LONG-RANGE ORDER

The dimer coverings (Kekulé structures) on a square-planar lattice exhibit a novel type of long-range order,⁸

which is distinct from (and likely inconsistent with) the familiar long-range magnetic ordering of a Néel state. The present nonmagnetic ordering is illustrated in Fig. 1 on two width $w=4$ diagonal strips cut from the lattice. In this figure the vertical dashed lines locate cell boundaries where we may count the number of singlet spin pairs on bonds cut by one of these dashed lines. Thence, in Fig. 1(a) one sees these numbers are alternately 3 and $w-3=1$ along the strip. In Fig. 1(b) one finds another sequence of numbers: 2 and $w-2=2$. As proved in the accompanying paper, any such dimer covering, no matter how extended further along the strip, exhibits its own *long-range spin-pairing order*, identified by a number Q_1 of spin pairings crossing a given cell boundary. There is also a perpendicular direction with a long-range ordering identified by the number Q_2 of spin-pairings crossing a horizontal position line. Evidently, Q_1 ranges from 0 to w , and Q_2 ranges from 0 up to the length L of the strip.

Because Q_1 and Q_2 are long-range order parameters, configurations of different Q_1 and Q_2 should not interact. Thence, for each pair Q_1, Q_2 we have a NN RVB *Ansatz*

$$|Q_1 Q_2\rangle \equiv \sum_K^{Q_1, Q_2} |K\rangle, \quad (2.1)$$

where the sum is over those dimer coverings (Kekulé structures) of the given Q 's. The associated energy is

$$E^0(Q_1, Q_2) = \langle Q_1 Q_2 | H | Q_1 Q_2 \rangle / \langle Q_1 Q_2 | Q_1 Q_2 \rangle. \quad (2.2)$$

Now with cyclic boundary conditions a primitive translation carries one position line (of Fig. 1) into an adjacent one, so that it also carries configurations of class Q_1 into those of $w-Q_1$. Likewise, Q_2 can be carried into $L-Q_2$. As a consequence,

$$\begin{aligned} E^0(Q_1, Q_2) &= E^0(w-Q_1, Q_2) \\ &= E^0(Q_1, L-Q_2) \\ &= E^0(w-Q_1, L-Q_2), \end{aligned} \quad (2.3)$$

and the energy per site evidently has an extremum at $Q_1/w = Q_2/L = \frac{1}{2}$. Thence, it is reasonable to introduce

$$\delta_1 \equiv \frac{Q_1}{w} - \frac{1}{2} \quad \text{and} \quad \delta_2 \equiv \frac{Q_2}{L} - \frac{1}{2} \quad (2.4)$$

so that the energy per site is quadratic in δ_1 and δ_2 . There is no cross term $\delta_1 \delta_2$ because δ_1 and δ_2 transform as coordinates along the horizontal and vertical directions, so that $\delta_1 \delta_2$ is of improper symmetry. Next the energy stabilization should tend to be greater, the greater the number of Kekulé structures (or dimer coverings), and this is known⁸ to occur at the present extremum. Thus, we anticipate that this extremum is a minimum.

The energy also varies in an interesting manner with suitable lattice distortions. Let u_1 denote the extent to which every bond in the odd columns of Fig. 1 is contracted and every bond in the even columns is stretched. Let u_2 denote a similar distortion alternating with rows. Now the exchange parameter should vary linearly (to leading order) with u_1 and u_2 ,

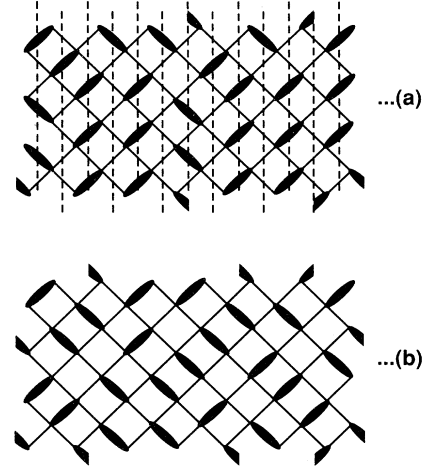


FIG. 1. Two different dimer coverings on square-planar-lattice strips. The top and bottom edges may be imagined to be joined in a cyclic manner; therefore in (a) three and one dimers alternate crossing the dashed "position" lines. In (b) two dimers occur at these (now unmarked) positions.

$$J_{ij} = J_0 + J'(\pm u_1 \pm u_2), \quad (2.5)$$

where $J' > 0$ and the $+$ or $-$ signs apply depending upon the location of bond $i \sim j$. Thus for a class of Kekulé structures the Q_1 double bonds in an odd column and the $w-Q_1$ double bonds in an even column should give stabilizations $\sim +J'u_1 Q_1$ and $\sim -J'u_1(w-Q_1)$, respectively. In addition there should be (say Coulombic) terms giving contributions quadratic in u_1 and in u_2 . The overall energy per site is anticipated to be

$$\epsilon \approx \text{const} + \frac{1}{2}\xi(\delta_1^2 + \delta_2^2) + \zeta(\delta_1 u_1 + \delta_2 u_2) + \frac{1}{2}\kappa(u_1^2 + u_2^2). \quad (2.6)$$

The $\delta_i u_i$ terms here are not forbidden by crystal symmetry. From our preceding arguments, $\kappa > 0$ and $\zeta > 0$.

Within the approximation restricting H to the space of Kekulé structures the electronic and displacive modes couple. If $(\delta_1, \delta_2) \neq (0, 0)$ then Eq. (2.6) implies a distortion to

$$u_i = -\zeta \delta_i / \kappa. \quad (2.7)$$

Moreover if $\zeta^2 > \xi\kappa$, the extremum at $\delta_1 = \delta_2 = u_1 = u_2 = 0$ is a maximum in some skew direction (with no minimum in the regime of our quadratic approximation), so that a large distortion would occur. Evidently then for a square-planar species (such as La_2CuO_4) there is no (ground-state) distortion, and one has $\zeta^2 < \xi\kappa$. Still for excitations with $(\delta_1, \delta_2) \neq (0, 0)$ commensurate distortions should ensue.

III. EXCITATIONS

There are different types of excitations conceivable from the presently studied (maximally spin-paired) ground state. Iske and Caspers⁹ have studied local triplet pair excitations. Also there are excitations involving iso-

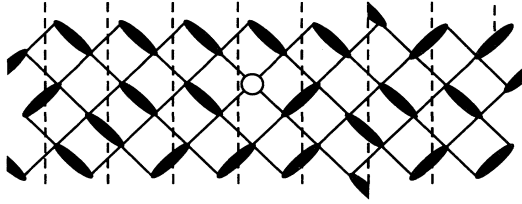


FIG. 2. A dimer covering excepting a single unpaired site. The number of dimers crossing position lines differs by one on the two sides of the unpaired site.

lated sites. A combination of two such isolated sites can lead to triplet pair wave functions, but they presumably exhibit a short-range repulsion, since such a localized NN triplet dimer costs $+J/2$ in energy compared to localization at greater separations. In addition there is a delocalization energy that favors (nearly) independent unpaired sites. Further, the charge-carrying excitations are presumably such isolated sites with an excess or deficit of one electron.

An example of a single-site excitation (configuration) is shown in Fig. 2. Note that on this strip $Q_1=1$ to the left of this singular site and $Q_1=2$ for corresponding columns to the right. In general, there is a shift of the long-range order quantum numbers by $+1$ or -1 in crossing over such an unpaired site. This excitation has features of a *soliton*, which would best be described as a wave packet. There are different *types* of isolated-site configurations depending on whether Q_1 and Q_2 increase or decrease as one proceeds (from left to right and top to bottom) across the unpaired site. Since configurations of each of these different types entail different nonmatching long-range ordering regions (on at least one side), such different types of configurations should not admix, and different types of solitons arise. This type of label is also seen to be uniquely characterized as the two parity labels (say π_1 and π_2) for row and column numbers on which the unpaired site occurs. A pair of types (π_1, π_2) and $(-\pi_1, -\pi_2)$ label soliton and *antisoliton*, since a pair of such excitations near one another entail no overall change in long-range order and so (if they are “neutral” spinons) can annihilate each other. There is only one soliton-antisoliton pair, since there is a correlation between row and column parities, as indicated in Fig. 3. As a consequence, another way to distinguish soliton and antisoliton is by the (*A* or *B*) sublattice of the unpaired site.

On a finite-width w strip, the two phases on either side

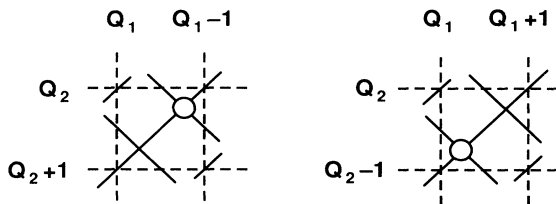


FIG. 3. An illustration to show that Q_1 and Q_2 change by one in opposite directions in crossing past an unpaired site.

of a soliton can be degenerate or nondegenerate. If the phases are nondegenerate then *confinement* of soliton-antisoliton pairs is indicated. If degenerate, as for the strip of Fig. 2, then isolated solitons might occur. On a very large ($w \times L$) lattice the changes in Q_1 and Q_2 in going across a soliton from one phase to another are very small compared to w and L , so that $\delta_1 \sim 1/w$ and $\delta_2 \sim 1/L$, and the two phases are very nearly degenerate. For this case the behavior of these solitons seems to be a more delicate matter.

A fuller characterization of the soliton excitations involves *local* deviations,

$$\delta_i^{\text{local}} = \frac{Q_i^{\text{local}}}{l} - \frac{1}{2}, \quad (3.1)$$

where Q_i^{local} is the number of spin pairings crossing a dashed line (as in Figs. 1 or 2) of orientation i within a local length l . In fact, at a “longitudinal” distance, $\sim l$ past a soliton on the less stabilized side, the defect should also (in order to avoid too long a boundary between different phases) presumably have only spread out a “traverse” distance $\sim l$, so that $\delta_i^{\text{local}} \sim 1/l$, $\epsilon^{\text{local}} \sim 1/l^2$, and the energy contribution from all the sites of the given longitudinal distance past the solution is $\sim l\epsilon^{\text{local}} \sim 1/l$. Summation over all the sites up to a given distance thence gives an energy cost of $\sim \ln l$. Therefore, even for the lattice, two solitons should attract, albeit rather weakly. The local u_1, u_2 lattice distortions would slightly enhance the attraction, while lessening the wave packet dispersion. This applies even if the solitons are charged, although the screened repulsion $\sim e^{-al}/l$ in combination with long flat attraction $\sim \ln l$ could lead to a rather weakly bound pair.

IV. QUALIFICATIONS

The preceding two sections outline a number of qualitative features that arise within the (severe) NN RVB picture. Notably a means for either “spinon” or “holon” pairing emerged.

There remains the question of the adequacy of the NN RVB *Ansatz*. The suggestion of the introduction that the ground state of the NN model is Néel like is supported by accurate computations,¹⁰ but again RVB *Ansätze* should improve with NNN interactions. However, if derived from the Hubbard Hamiltonian, then Kekulé-structure destabilizing terms occur for rings of size 4. This essentially is Hückel’s $4n+2$ rule in chemistry, though for Hückel’s conjugated-hydrocarbon systems the large ratio $t/U \simeq 0.6$ of Hubbard-model parameters destabilizes $4n$ rings even more so. The work of Rokhsar and Kivelson¹¹ with regard to their “hard-dimer” model is relevant for such resonance frustration. A further question remains as to whether the admittance of longer-range spin pairings is sufficiently extensive to destroy the ordering described here. From the accompanying paper it is seen that it is preserved if the additional VB structures have a cutoff in the range of their spin pairings. The key concern is the admixture of VB structures with very-long-range spin pairings.

Another way to stabilize the RVB picture is to dope

the system, as in forming high- T_c superconductors. Even if the dopant sites were immobile the RVB picture should be enhanced, since the mean coordination number z , which appears in (1.4), is reduced. Mobility of the dopant sites gives further kinetic stabilization and is termed "asynchronous resonance" by Pauling.¹² In the

nondilute regime the relevance of the long-range order we have discussed might change.

ACKNOWLEDGMENTS

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