Superconductivity and the Quantum Hard-Core Dimer Gas

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We discuss the short-range resonating-valence-bond system as realized by a quantum hard-core dimer gas of arbitrary density on a two-dimensional square lattice. When the dimers completely cover the lattice, we argue that there is a first-order transition from a dimer crystal to an insulating quantum liquid state which possesses low-energy, neutral, spinless excitations which we call "resonons." For less than close-packed densities, the ground state is a superfluid. In addition to the usual Goldstone mode, there are low-energy, spinless zone-boundary excitations.

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We discuss the properties of a system with a short-range resonating-valence-bond (RVB) ground state. In a "valence-bond" state, electrons on nearby sites of a lattice are spin paired to form singlet bonds, thereby lowering their energy. A "resonating" valence-bond state[1] is a coherent superposition of such singlet-bond states; its energy is further lowered as a result of the matrix elements connecting the different valence-bond configurations. Heuristically, valence bonds can be viewed as real-space Cooper pairs which repel one another, a joint effect of the Pauli principle and the Coulomb interaction. When there is one electron (i.e., half a valence bond) per site, charge fluctuations are suppressed, leading to an insulating state. As electrons are removed by doping, current can flow; the system becomes superconducting as the valence bonds Bose condense.[2] A complementary but equivalent picture emerges if one focuses instead on the sites not participating in a valence bond,[3] dubbed "holons." We have argued[3] that holons are spinless, charge-e bosons, and that the superconducting RVB state can be understood as a peculiar Bose condensate of them.[4,5]

Two qualitatively different sorts of RVB states have been proposed: the Princeton RVB state[2] which has important contributions from valence bonds of all lengths and consequently gapless spin excitations, and the "short-range" RVB state,[3] in which states with long valence bonds have exponentially small amplitudes. This state is believed to have a spin gap, based on its exponentially decaying spin-spin correlations.[7,8] We consider here a prototype for the short-range RVB state in the limit where the spin gap is large, so that the manifold of low-energy states is spanned by the linearly independent set of nearest-neighbor valence-bond states. (Indeed, it has recently been shown[8] that this set spans the ground-state manifold of a frustrated spin-$\frac{1}{2}$ Heisenberg model.)

Restricting the physical Hamiltonian to the nearest-neighbor valence-bond subspace defines an effective Hamiltonian for a quantum hard-core gas of charge-$(-2e)$ dimers. The usefulness of this interpretation depends upon the assumption that this effective dimer Hamiltonian is short ranged. We argue that this is in fact the case despite the nonorthogonality of the valence-bond states, as follows.

Let $|\Psi_C\rangle$ be the valence-bond state associated with dimer configuration C. We can formally define an orthonormal basis set $|C\rangle=\sum_{C'}(S_{CC'})^{-1/2}|\Psi_{C'}\rangle$, where $S_{CC'}=\langle\Psi_C|\Psi_{C'}\rangle$ is the overlap matrix. If H is the physical Hamiltonian, the effective dimer Hamiltonian $\mathcal{H}$ is given by

$$\mathcal{H}_{CC'}=\sum_{DD'}(S^{-1/2})_{CD}H_{DD'}(S^{-1/2})_{D'C'}, \tag{1}$$

where $H_{DD'}$ is $\langle\Psi_D|H|\Psi_{D'}\rangle$. The overlap matrix is easily computed[7]: $S_{CC'}=2^{n(CC')}x^{-L(CC')}$, where $x=1/\sqrt{2}$, and $n(CC')$ and $L(CC')$ are the number of nontrivial loops and the net length of loop, respectively, in the "transition graph" between C and C'. [The transition graph, Fig. 1(c), is constructed by drawing configurations C and C' on the same lattice. On a bipartite lattice, the dimers from configuration C can be drawn as arrows pointing from one sublattice (which we will call "red") to the other ("black"); those of configuration C' can be drawn in the opposite sense. The transition graph then consists of closed, nonintersecting, directed loops. When a dimer is in the same position in both configurations, a trivial loop is obtained.]

Kohmoto and Shapir[7] have argued that S can be interpreted as the Boltzmann weight of a loop gas which is deep in its high-temperature (small x) phase; we have carried out an expansion[9] of the effective dimer Hamiltonian in powers of x which appears to converge rapidly even for $x=1/\sqrt{2}$. We conclude that orthogonality is *not* an essential issue, and are led to consider the simplest short-range model for dimers on a two-dimensional square lattice. More generally, we consider this to be a model of highly correlated real-space Cooper pairs.

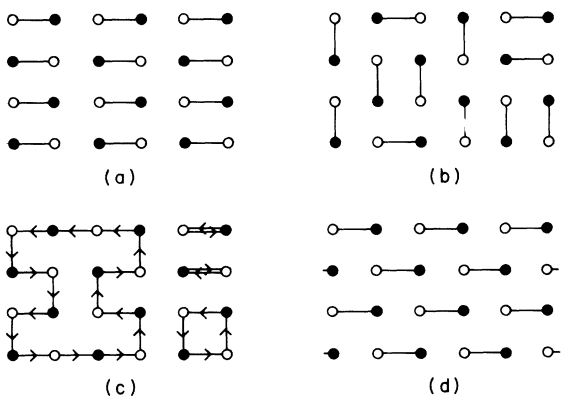

FIG. 1. (a) The "column state," C_0; (b) a state C in the same topological sector as C_0 (the readers are encouraged to convince themselves of this by explicitly determining a sequence of flips which take C into C_0); (c) the transition graph of the dimer configurations C and C_0, obtained by drawing them both on the same lattice with dimers in C directed from the "red" sublattice (open circles) to the "black" sublattice (filled circles), and dimers in C_0 directed oppositely; (d) a valence-bond crystal (VBC) state.

There are natural generalizations to other lattices and dimensions.

Summary of results and relation to oxide superconductors.— In this paper, we establish the following properties of the zero-temperature quantum dimer gas. As the balance between dimer kinetic and potential energies is varied, the close-packed dimer gas undergoes a first-order transition from a dimer crystal [a spin-Peiels or valence-bond crystal (VBC) phase] to a state we have identified as a quantum dimer liquid (corresponding to a short-range RVB state). This state has a branch of neutral, low-energy excitations of the orientational degrees of freedom of the system, which we call "resonons." At the transition, the resonons are gapless,[10] although in the liquid phase they may develop a gap. Away from the close-packed density we show that the ground state is a Bose condensate of dimers. At nonzero doping, low-energy excitations (which are not accompanied by long-wavelength charge fluctuations) are found, with momenta near (π,π).

We believe this model may be relevant to the layered perovskite superconductors. The presence of a spin gap in the superconducting phase is suggested by tunneling and infrared-absorption gap measurements, and by the exponential temperature dependence observed in nuclear magnetic relaxation; furthermore, the superconducting state appears to exhibit very short-range magnetic correlations. The mapping to the dimer problem requires only short-range valence bonds or Cooper pairs, which are implied by the observed short superconducting correlation length. Our calculations apply only at temperatures less than the spin gap; we speculate that this gap collapses at T_c in a manner qualitatively but not necessarily quantitatively similar to that predicted by BCS theory.

The close-packed dimer gas: ground states.— Let us consider quantum hard-core dimers on a square lattice. The Hilbert space is spanned by the *orthonormal* states $\{|C\rangle\}$, where C specifies a dimer configuration. For simplicity, we study a model dimer Hamiltonian with only the most local terms. We first address the close-packed case:

$$\mathcal{H}_{\text{dimer}} = \sum_{\text{plaquettes}} [-J(|\,\|\rangle\langle =|+\text{H.c.})+V(|\,=\rangle\langle =|+|\,\|\rangle\langle\|\,|)]\,. \tag{2}$$

The first term is a pure dimer kinetic energy which flips pairs of parallel nearest-neighbor dimers; the second is a repulsion between such nearest-neighbor pairs. The coupling constants J and V are to be regarded as phenomenological parameters; making contact with the large-U Hubbard model, we expect both J and V to be comparable to the exchange energy J_{exch}: The lowest-order terms in the expansion in x yield $J\sim 2x^4 J_{\text{exch}} = J_{\text{exch}}/2$, and $V\sim 4x^8 J_{\text{exch}} = J_{\text{exch}}/4$. [Note that in the close-packed case the sign of J is a matter of convection: In particular, the sign of J can be changed by multiplying each state in our basis set by a factor of $i^{v(C)}$, where $v(C)$ is the number of horizontal bonds in configuration C. With the "fermionic" convention that a bond is created by $c_i^\dagger c_j^\dagger + c_j^\dagger c_i^\dagger$, J is negative.]

The analysis of $\mathcal{H}_{\text{dimer}}$ is facilitated by classifying each dimer configuration C according to the winding number of its transition graph relative to a reference configuration C_0 [which we take to be the "column state," Fig. 1(a)]. On a two-torus there are two winding numbers Ω_x and Ω_y which are given by the net number of loops (clockwise minus counterclockwise) encircling the torus in the x and y directions, respectively. Any two dimer configurations with the same winding numbers can be obtained from each other by repeated application of the Hamiltonian; no local operator has matrix elements between states of different winding number. The winding numbers therefore label the disconnected sectors of Hilbert space.

For close-packed dimers, there exist individual configurations which comprise their own topologically distinct subspaces. These VBC configurations [Fig. 1(d)] contain no parallel nearest-neighbor dimers, and are zero-energy eigenstates of $\mathcal{H}_{\text{dimer}}$ for arbitrary J and V. For $V \geq J \geq 0$, $\mathcal{H}_{\text{dimer}}$ is positive semidefinite, and these VBC's are the only ground states; the other topological sectors all have positive energies.

At $V=J$, each topological sector possesses a unique zero-energy ground state $|\Omega\rangle$, namely, the equal-amplitude superposition $\sum_{C\in\Omega}|C\rangle$ of all configurations in that sector. It is easy to verify that these states are

zero-energy eigenstates of $\mathcal{H}_{\text{dimer}}$. Since all off-diagonal matrix elements of the Hamiltonian $\mathcal{H}_{\text{dimer}}$ are nonpositive, the ground state must be nodeless, i.e., a state vector with all positive amplitudes. The equal-amplitude states are therefore the unique ground states in their respective topological sectors. These coherent superpositions are the precise analogs of the RVB originally discussed by Anderson[1] in 1973; the resonance energy is simply the dimer kinetic energy. An important feature of the equal-amplitude states discussed above is that any dimer correlation function can be computed exactly from the results of Fisher and Stephenson[11] for the classical dimer problem. (This does not, however, imply that the quantum problem is related to a two-dimensional classical problem, in the sense that if we perturb the quantum Hamiltonian slightly the ground-state correlation functions need not be derivable from any simple classical statistical mechanics problem.)

For $V<J$, we can use the equal-amplitude state as a variational wave function, and obtain an upper bound to the ground-state energy of $E\leq -\frac{1}{4}(J-V)$ per site. Since E is identically zero for $V\geq J$, the energy has a discontinuous first derivative at $V=J$, implying a first-order transition from a VBC to a quantum liquid (RVB) state. When V is negative, we expect[9] another transition to a different crystalline ground state, the "column phase," dominated by configurations like C_0 [Fig. 1(a)]. While we have no proof that the RVB phase persists for a nonzero range of V/J, we consider it likely.[9]

The doped dimer gas: ground states.—Upon doping (i.e., removing dimers), additional processes contribute to the Hamiltonian:

$$\mathcal{H}=\mathcal{H}_{\text{dimer}}-t\sum_{\langle ijk\rangle}(|-\cdot\rangle\langle\cdot-|+\text{H.c.})+V_h\sum_{\langle ij\rangle}|\cdot\cdot\rangle\langle\cdot\cdot|\,. \tag{3}$$

The first sum, over triples of sites such that the first and third are nearest neighbors of the second, is a "hole kinetic energy" which moves a dimer to an adjacent unoccupied position. Note that a "red" hole remains on the red sublattice and a "black" hole remains on the black sublattice. The second sum, over nearest-neighbor sites, is a "hole-hole repulsion," which can be rewritten as a local dimer-dimer interaction.

If we imagine obtaining $\mathcal{H}$ from an underlying electronic model, t would be comparable to the electron bandwidth, and V_h would be roughly the nearest-neighbor Coulomb repulsion. Away from close packing, if we choose a phase convention to make t positive, the naive J due to exchange will be negative. In this paper we consider the simple case of t and J positive.

The ground state of the dimer Hamiltonian (3) can be determined exactly when $J=V$ and $V_h=-2t$, for t and J positive. For these parameters, the equal-amplitude superposition $\sum|C\rangle$ of all dimer configurations can be shown to be a nodeless eigenstate of $\mathcal{H}$, and hence the unique ground state. The energy of the equal-amplitude superposition is $-4t(N_r+N_b)$, where N_r and N_b are the numbers of red and black holes, respectively. Note that away from close packing there is only a single, topologically trivial sector, since any two configurations can be connected by repeated application of the Hamiltonian.

The equal-amplitude states are similar to the ground states of two interpenetrating free Bose gases. Their phonon excitations have k^2 dispersion, as described below. At $J=V$, $V_h>-2t$, additional repulsive interactions lead to a Bose condensate with linearly dispersing Goldstone modes, as for an interacting Bose gas. If V_h is less than $-2t$ (attractive interactions between holes) the system phase separates. Away from close packing, the equal-amplitude states possess off-diagonal long-range order, i.e., $\langle d^\dagger_{R\tau}d_{R'\tau'}\rangle$ for $|R-R'|\to\infty$ is bounded[9] from below by $\frac{1}{4}x^2(1-x)^2$ ($d^\dagger_{R\tau}$ creates a dimer on the link connecting sites R and $R+\tau$). When $|V|\gg J$, it seems plausible[9] that the ground state will be a "supersolid," with both broken translational (i.e., VBC) and broken gauge symmetry. In such a state, the vacant sites would be spatially paired.

Excitations of the dimer gas.—We discuss the excitations about the RVB state by considering the excitations of the equal-amplitude states in the single-mode approximation.[12] This approximation describes excitations about a ground state $|G\rangle$ in terms of variational wave functions of the form

$$|\mathbf{k}\rangle=\Psi_{\mathbf{k}}|G\rangle=\textstyle\sum_{\mathbf{R}}e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{R})|G\rangle\,, \tag{4}$$

where $\psi(\mathbf{R})$ is a local operator. [For example, if $\psi(\mathbf{R})$ is the density operator at $\mathbf{R}$, $|\mathbf{k}\rangle$ is a phonon.] The variational energy of such a state (measured from the ground state) can be succinctly expressed as $\omega_{\mathbf{k}}=f(\mathbf{k})/s(\mathbf{k})$, where $f(\mathbf{k})$ is the oscillator strength $\frac{1}{2}\langle[\Psi_{-\mathbf{k}},[\mathcal{H},\Psi_{\mathbf{k}}]]\rangle$, and $s(\mathbf{k})$ is the static structure factor, i.e., the Fourier transform of the ground-state correlation function $\langle\psi(\mathbf{R})\psi(\mathbf{0})\rangle$. If these quantities are evaluated in the exact ground state, they provide a rigorous upper bound on the lowest excitations at momentum $\mathbf{k}$.

In general, when ψ describes a conserved quantity and the Hamiltonian is local and inversion symmetric, the oscillator strength varies as k^2 for small momenta. This property can be used, in conjunction with the single-mode approximation to the bulk modulus $\partial^2E/\partial\Psi_0^2=\lim_{\mathbf{k}\to 0}f(\mathbf{k})/2s^2(\mathbf{k})$, to determine the small-momentum behavior of $s(\mathbf{k})$ and therefore the excitation energy of the corresponding long-wavelength mode. For example, a vanishing bulk modulus (e.g., for a free Bose gas) implies a dispersion which vanishes faster than k, while a finite, nonzero bulk modulus yields a linear dispersion (e.g., for an interacting Bose gas).

These principles can be used to demonstrate gapless excitations in the equal-amplitude doped dimer gas. Away from close packing, we note that the Hamiltonian (3) conserves both total hole number (since dimers are neither created nor destroyed), and the total "topological

charge," the difference between the number of red and black holes (since each dimer covers one red and one black site). When the ground states are the equal-amplitude states, the corresponding moduli $\partial^2 E/\partial(N_r+N_b)^2$ and $\partial^2 E/\partial(N_r-N_b)^2$ vanish. We conclude that there exist two gapless modes, one a phonon and the other an oscillation involving the out-of-phase motion of red and black holes, with momentum near $\mathbf{Q}=(\pi,\pi)$. If $s(\mathbf{Q}+\mathbf{k})$ is analytic in k^2, these excitations have dispersions $\omega_{\mathbf{k}}\sim tk^2$. Introducing additional repulsions between holes leads to a linear dispersion for small momenta, as in the interacting Bose gas. While the phonon mode is expected to be shifted to the plasma frequency in the presence of Coulomb interactions, no long-wavelength charge fluctuations should accompany the red-black mode, which would remain gapless at $J=V$. For $|V|>J$, i.e., in the hypothesized supersolid phase, it seems likely that this mode will develop a gap. We speculate that a gap also develops for $|J|<|V|$; the resulting state is then qualitatively similar to a BCS state.

At close packing, the bulk modulus diverges and the system becomes incompressible, indicating the transition to an insulating state; the zone-center phonon mode described above acquires a gap in its spectrum. Surprisingly, at $V=J$, there remains a gapless branch of excitations at (π,π); we suspect[9] that for $V<J$ this mode develops a gap. We call these modes "resonons," since they involve the dephasing of dimer configurations which differ by large loops in their transition graphs. The conserved quantity in this case is the topological winding number Ω, described above. The local operator $\psi(\mathbf{R})$ used in (4) to create such an excitation is given by $\mathbf{p}_\tau(\mathbf{R})=e^{i\mathbf{Q}\cdot\mathbf{R}}n_\tau(\mathbf{R})$, where $n_\tau(\mathbf{R})$ is the dimer density operator on site $\mathbf{R}$ for dimers pointing in the τ direction. (There are the two "polarizations," for resonons, corresponding to τ along either the $\hat{\mathbf{x}}$ or $\hat{\mathbf{y}}$ axes.)

It is easy to verify that the oscillator strength for the resonon is $f(\mathbf{k})\sim J(\mathbf{k}\times\tau)^2$. At $V=J$, the resonon structure factor $\mathbf{s}(\mathbf{k})$ approaches a constant as $k\to 0$, corresponding to the algebraic decay of dimer-dimer correlations in the classical problem.[11] The resulting disperison is $\sim Jk^2$. Resonons correspond to the Goldstone modes of the gauge symmetry which allows the phases of different topological sectors to be varied without changing the energy when $J=V$. Away from $J=V$, the structure factor cannot be computed from the classical case, and the presence or absence of a resonon gap is unclear.

The dense dimer gas as a dilute holon gas.— While it is always possible to describe a dimer gas with dimer coordinates, it is clearly preferable to have a quasiparticle description in terms of holons for the nearly close-packed regime. We have argued elsewhere[3] that holons are bosonic. In terms of dimers this is trivail, since exchanging holons moves the (bosonic) dimers around and can lead to no sign change. (The dimers themselves consist of pairs of electrons, and can be thought of as Cooper pairs of spinons.[3])

We believe that the holes behave as locally interacting bosons except for the topological constraint that they can only be created or destroyed in pairs. This constraint prevents the appearance of an anomalous expectation value for the creation of a single holon. Such an order parameter for the creation of two holons can develop, however, even if they are far apart. A spatially unpaired distribution of holons is preferred, since it minimizes the effect of the Coulomb interaction on the condensate.

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[1]P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973); P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 432 (1974).

[2]P. W. Anderson, Science **235**, 1196 (1987); G. Baskaran, Z. Zhou, and P. W. Anderson, Solid State Commun. **63**, 973 (1987).

[3]S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987); S. A. Kivelson, Phys. Rev. B **36**, 7237 (1987).

[4]S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, Europhys. Lett. **6**, 353 (1988).

[5]D. Thouless, Phys. Rev. B **36**, 7187 (1987).

[6]V. Kalmeyer and R. B. Laughlin, Phys. Rev. Lett. **59**, 2095 (1987); R. B. Laughlin, Phys. Rev. Lett. **60**, 2677 (1988), and **61**, 379, (E) (1988); S. A. Kivelson and D. S. Rokhsar, to be published.

[7]W. Sutherland, Phys. Rev. B **37**, 3786 (1988); M. Kohmoto and Y. Shapir, Phys. Rev. B **37**, 9439 (1988); D. H. Lee and S. A. Kivelson, unpublished; S.-D. Liang, B. Doucot, and P. W. Anderson, Phys. Rev. Lett. **61**, 365 (1988).

[8]D. Klein, J. Phys. A **15**, 661 (1982); J. Chayes, L. Chayes, and S. A. Kivelson, to be published.

[9]D. S. Rokhsar and S. A. Kivelson, to be published; E. Fradkin and S. A. Kivelson, to be published.

[10]These excitations may be related to the gapless excitations (of undetermined spin) which Affleck [(I. Affleck, Phys. Rev. B **37**, 5186 (1988)] argued should be present in any half-integer-spin antiferromagnet with a disordered ground state. His argument presumes, however, that an odd-width strip ground-state degeneracy implies a broken symmetry. The dimer liquid ground state on an odd-width strip is twofold degenerate, although there is no local order parameter.

[11]M. E. Fisher and J. Stephenson, Phys. Rev. **132**, 1411 (1963).

[12]R. P. Feyman, *Statistical Mechanics: A Set of Lectures* (Addison-Wesley, Reading, MA, 1972). See also S. Girvin in *The Quantum Hall Effect*, edited by R. Prange and S. Girvin (Springer-Verlag, New York, 1987).