Spin Singlet Ordering Suggested by Repulsive Interactions

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ABSTRACT

We consider a correlated wavefunction including particle-hole pairing at half a reciprocal lattice vector for itinerant electrons hopping on a square lattice in two dimensions and subject both to on-site and nearest-neighbor repulsion. We find, within mean field theory, that in a suitable range of parameters there is a tendency toward a novel form of ordering characterized by discrete symmetry breaking and a gap at the magnetic zone boundary, which supports hole-like semiconductor behavior near half filling despite an apparently normal Fermi surface. The effective quasiparticle couplings to phonons includes a significant d-wave piece, which plausibly leads to an especially robust tendency toward superconductivity.
One has become accustomed, especially in connection with the superfluid phases of He$^3$, to the existence of quite intricate pairing correlations between particles. On the other hand, well-known forms of ordering including ferromagnetic, antiferromagnetic, and charge-density wave can be described in terms of particle-hole pairing [1,2]. It is quite natural, then, to consider by analogy the possibility of states of matter characterized by particle-hole pairing of more general types. In this note we shall show that indeed one such ordering is suggested to be favorable in an analysis of the mean-field correlation energy induced by very simple, purely repulsive interactions. This may have significant implications for the Mott insulator problem, as we shall discuss.

1. Analysis

Let us consider electrons on a square lattice in two dimensions with spacing $a$. We suppose that the screened Coulomb interaction can be modelled by an on-site repulsion of magnitude $U$ and nearest-neighbor repulsion of magnitude $V$, that is:

$$H_{\text{int.}} = U \sum_x c^\dagger_\uparrow(x)c_\uparrow(x)c^\dagger_\downarrow(x)c_\downarrow(x) + \frac{1}{2}V \sum_{x,x'} c^\dagger_\alpha(x)c_\alpha(x)c^\dagger_\beta(x')c_\beta(x') , \quad (1.1)$$

where $x'$ runs over the four nearest neighbors of $x$, and $\alpha, \beta = \uparrow, \downarrow$ are summed over. Transforming (1.1) to momentum space, we find the form

$$H_{\text{int.}} = U \sum_{k_i} c_{1\uparrow}(k_1)c_{1\uparrow}(k_2)c_{4\downarrow}(k_3)c_{4\downarrow}(k_4) \delta_L(k_1 + k_3 - k_2 - k_4)$$

$$+ 2V \sum_{k_i} c_{\alpha}(k_1)c_\alpha(k_2)c_{\beta}(k_3)c_{\beta}(k_4) C(k_3 - k_4) \delta_L(k_1 + k_3 - k_2 - k_4) , \quad (1.2)$$

where $\delta_L$ denotes the delta function in the reciprocal lattice, and $C(k_3 - k_4) = \cos(k_3 - k_4)x a + \cos(k_3 - k_4)y a$.

Interesting possibilities for particle-hole correlations, whose energetic consequences can be seen in a mean-field analysis of (1.2), involve ordering at momentum transfer $Q$, where $2Q$ is a reciprocal lattice vector. We shall focus on the case
\( Q = (\pi/a, \pi/a) \). In the spirit of BCS theory, we postulate a wave-function of the form

\[
\Psi = \prod_k (u_{k\uparrow} c_{k\uparrow}^\dagger + v_{k\uparrow} c_{k+Q\uparrow}^\dagger) (u_{k\downarrow} c_{k\downarrow}^\dagger + v_{k\downarrow} c_{k+Q\downarrow}^\dagger) |0> ,
\]

where the product runs over some subset of the interior of the magnetic zone (i.e. the diamond \((k_x \pm k_y)a = \pm \pi\)), and \(|u|^2 + |v|^2 = 1\) for all values of the indices, to preserve normalization, and the number of factors is determined by the density of electrons (see below). The expectation value of \( H_{\text{int.}} \) in the state \( \Psi \) is

\[
\langle \Psi | H_{\text{int.}} | \Psi \rangle = \sum_{k,k'} U (\bar{u}_{k\uparrow} v_{k\uparrow} + u_{k\uparrow} \bar{v}_{k\uparrow}) (\bar{u}_{k'\downarrow} v_{k'\downarrow} + u_{k'\downarrow} \bar{v}_{k'\downarrow}) - 2 V (\bar{u}_{k\uparrow} v_{k\uparrow} + u_{k\uparrow} \bar{v}_{k\uparrow} + \bar{u}_{k\downarrow} v_{k\downarrow} + u_{k\downarrow} \bar{v}_{k\downarrow}) \\
\times (\bar{u}_{k'\uparrow} v_{k'\uparrow} + u_{k'\uparrow} \bar{v}_{k'\uparrow} + \bar{u}_{k'\downarrow} v_{k'\downarrow} + u_{k'\downarrow} \bar{v}_{k'\downarrow}) \\
+ V C(k - k') \left( (\bar{u}_{k\uparrow} v_{k\uparrow} - u_{k\uparrow} \bar{v}_{k\uparrow}) (\bar{u}_{k'\uparrow} v_{k'\uparrow} - u_{k'\uparrow} \bar{v}_{k'\uparrow}) + (\bar{u}_{k\downarrow} v_{k\downarrow} - u_{k\downarrow} \bar{v}_{k\downarrow}) (\bar{u}_{k'\downarrow} v_{k'\downarrow} - u_{k'\downarrow} \bar{v}_{k'\downarrow}) \right),
\]

where the bar denotes complex conjugate.

Without loss of generality we may take the us to be real and non-negative, and write \( v_{k\alpha} \equiv w_{k\alpha} \exp(i \phi_{k\alpha}) \) with the ws real and non-negative. Then (1.4) becomes

\[
\langle \Psi | H_{\text{int.}} | \Psi \rangle = \sum_{k,k'} 4 U (u_{k\uparrow} w_{k\uparrow} u_{k'\downarrow} w_{k'\downarrow}) \cos \phi_{k\uparrow} \cos \phi_{k'\downarrow} \\
- 8 V (u_{k\uparrow} w_{k\uparrow} \cos \phi_{k\uparrow} + u_{k\downarrow} w_{k\downarrow} \cos \phi_{k\downarrow}) (u_{k'\uparrow} w_{k'\uparrow} \cos \phi_{k'\uparrow} + u_{k'\downarrow} w_{k'\downarrow} \cos \phi_{k'\downarrow}) \\
- 4 V C(k - k') \left( (u_{k\uparrow} w_{k\uparrow} \sin \phi_{k\uparrow} u_{k'\uparrow} w_{k'\uparrow} \sin \phi_{k'\uparrow}) + (u_{k\downarrow} w_{k\downarrow} \sin \phi_{k\downarrow} u_{k'\downarrow} w_{k'\downarrow} \sin \phi_{k'\downarrow}) \right).
\]

At this point, it is easy to identify three essentially different ways whereby favorable correlation energy can emerge:

- From the first term, which favors \(| \cos \phi | = 1\) with opposite signs for spin up and spin down – this corresponds to antiferromagnetism (this is the case analyzed in [1]).
• From the second term, which favors $|\cos \phi| = 1$ with the same sign for spin up and spin down – this corresponds to a charge density wave.

• From the third term, which favors $|\sin \phi| = 1$ (that is, $v$ pure imaginary relative to $u$).

The third possibility is in many ways the most interesting, and we shall now discuss it in some detail before returning to compare it with the other two.

To continue the analysis we must minimize the full energy, including both one-particle (hopping) and correlation parts. For the one-particle part, we take the nearest-neighbor form $\epsilon_k = -t(\cos k_x a + \cos k_y a)$. For simplicity let us consider nearly half filling, so that the chemical potential is small and the Fermi surface is near the boundary of the magnetic zone. The equations for the different spin components do not affect one another, so we shall temporarily drop the spin index. By standard methods one then finds the solution of the minimization problem in the form

$$u_k^2 = \frac{1}{2} \left( 1 - \frac{\tilde{\epsilon}_k}{\sqrt{\tilde{\epsilon}_k^2 + \Delta_k^2}} \right)$$

$$w_k^2 = \frac{1}{2} \left( 1 + \frac{\epsilon_k}{\sqrt{\tilde{\epsilon}_k^2 + \Delta_k^2}} \right)$$

(1.6)

where $\tilde{\epsilon}_k \equiv \frac{1}{2}(\epsilon_k - \epsilon_{k+Q})$ and

$$\Delta_k \equiv 4V \sum_{k'} u_{k'} w_{k'} \sin \phi_k \sin \phi_{k'} C(k-k')$$

(1.7)

satisfies the gap equation

$$\Delta_k = 2V \sum \frac{\Delta_{k'}}{\sqrt{\tilde{\epsilon}_k^2 + \Delta_k^2}} \sin \phi_k \sin \phi_{k'} C(k-k')$$

(1.8)

and $C(k-k')$ can be written in the more revealing form

$$C(k-k') = (\cos k_x a \cos k'_x a + \cos k_y a \cos k'_y a + \sin k_x a \sin k'_x a + \sin k_y a \sin k'_y a)$$

(1.9)
The energy will be minimized when $\Delta$ is non-negative; together with the form of the gap equation this determines $\Delta_k$ to be of the form $\Delta_k = A|\sin k_x a|$ (or, what is equivalent energetically, $\Delta_k = B|\sin k_y a|$) which has a $p$-wave-like symmetry on the Fermi surface or $\Delta_k = C|\cos k_x a|$ ($= C|\cos k_y a|$ on the diamond) which is $d$-wave-like. The sign of $\sin \phi_k$ will adjust itself, changing at the zeroes of $\Delta$ so as to enforce these forms. The gap equation is quite complicated in general, but simplifies near half filling. One has in this case

$$1 = 4V \int_0^\pi \frac{d\xi}{\sin \xi} \int d\tilde{\epsilon} \frac{\sin^2 \xi}{\sqrt{\tilde{\epsilon}^2 + A^2 \sin^2 \xi}}$$

(1.10)

for the $A$ form and

$$1 = 8V \int_0^\pi \frac{d\xi}{\sin \xi} \int d\tilde{\epsilon} \frac{\cos^2 \xi}{\sqrt{\tilde{\epsilon}^2 + C^2 \cos^2 \xi}}.$$  

(1.11)

The $\frac{1}{\sin \xi}$ factor, which reflects the van Hove singularity in the density of states exactly at half filling, favors the $C$ form, as does the factor 2 arising from the equality of the first two terms in the final factor of (1.8). Away from half-filling, or in the presence of a next-nearest neighbor hopping term, there will not be a van Hove singularity at the Fermi surface. However, an enhanced density of states will remain if these effects are not too large. At half filling one has occupation up to the edge of the diamond, where $\tilde{\epsilon}$ vanishes, and thus a solution to the gap equation – even apart from the van Hove enhancement – for arbitrarily weak coupling.

To discuss the situation below half filling, we must consider how the condition on electron density is implemented. The operators

$$\gamma^\dagger_{k\alpha} \equiv u_{k\alpha} c^\dagger_{k\alpha} + v_{k\alpha} c^\dagger_{k+Q\alpha}$$

$$\delta^\dagger_{k\alpha} \equiv \bar{v}_{k\alpha} c^\dagger_{k\alpha} - \bar{u}_{k\alpha} c^\dagger_{k+Q\alpha},$$

(1.12)

analogous to the familiar Bogoliubov-Valatin operators in superconductivity theory, are a complete set of fermion creation and annihilation operators with diagonal
anticommutation relations. $\gamma_{k\alpha}^\dagger$ and $\delta_{k\alpha}^\dagger$ create quasiparticles below and above the gap, respectively, or, in semiconductor terminology, in the valence and conduction bands. At half-filling, all of the $\gamma_{k\alpha}^\dagger$, or conduction band, states are filled and the ground state (1.3) can be written $\Psi = \prod_k \gamma_{k\uparrow}^\dagger \gamma_{k\downarrow}^\dagger |0>$, where $\mathbf{k}$ ranges over all momenta in the magnetic zone. In general $\mathbf{k}$ ranges only over momenta within the Fermi surface (actually a curve, in two dimensions), which is determined by the condition $\sqrt{\tilde{\epsilon}_k^2 + \Delta_k^2} = \mu$. The chemical potential, $\mu$, is chosen so that the area enclosed by the Fermi surface is equal to the desired density. Below half-filling the $d\bar{\epsilon}$ integral will be cut off by $\mu$ instead of diverging as $C \to 0$. Thus the gap equation will not have a non-trivial solution at arbitrarily weak coupling, but only starting at a finite value, dependent on the deviation from half-filling, of the coupling.

Nothing in our considerations so far has correlated spin up and spin down, so that spin singlet ($u_{k\uparrow} = u_{k\downarrow}$), spin triplet ($u_{k\uparrow} = -u_{k\downarrow}$), or intermediate possibilities are equally favorable. The degeneracy will be split if we include into our Hamiltonian a nearest-neighbor spin-spin interaction $J \vec{s} \cdot \vec{s}$ where of course $\vec{s}(x) \equiv c_{\alpha}^\dagger(x) \vec{\sigma}_\alpha c_{\beta}(x)$ is the electron spin operator. When such a term is included in the Hamiltonian, contributions sensitive to the pairing correlations arise from the crossed channel. A short calculation shows that for $J > 0$, antiferromagnetic coupling, the spin singlet state is lowered in energy, and the triplet raised. Of course the assumed effective coupling here might have either sign, and it need not be at all the same as the effective $J$ used in a different approximate description of the same material (e.g. in a $t-J$ model). In any case the spin singlet order will be favored by its relative immunity from fluctuations, as we shall presently discuss.

Now let us compare the energies of the competing orders. These are quite complicated and depend on the interplay between the single particle energies and the interaction terms (1.4) (with the $u_{k\alpha}$s and $v_{k\alpha}$s appropriate to these orders substituted). Some qualitative features of the phase diagram may be obtained from the coefficients of the terms in the purely repulsive Hamiltonian $H_{int}$. We find that the terms favoring the three types of states (antiferromagnetic, charge density, “C-type d-density”) are in the ratio $-U : U - 8V : -4V \langle \cos^2 k_x a \rangle$. Here the last factor
arises from the non-trivial angular dependence of the d-density ordering and the pairing interactions that give rise to it. It will be substantially larger than \( \frac{1}{2} \) for the \( C \) form of d-density ordering, because the density of states is largest where the cosine is unity (indeed, to the extent the van Hove singularity dominates, this factor is unity), though its precise value is highly model- and doping-dependent. When this factor is unity, the \( C \) form of d-density ordering is stable only at \( U = 4V \), according to this naive criterion. However, one should also consider that antiferromagnetic ordering, since it breaks a continuous symmetry, is subject to severe fluctuation effects – in principle, for example, a two-dimensional system is rigorously forbidden to exhibit such ordering at any non-zero temperature – which can severely degrade the favorable mean-field energy. In a realistic domain of parameters for CuO\(_2\) planes Schrieffer \textit{et al.} [1] found that the magnetic moment density is renormalized by a factor .6 due to fluctuations, which is also approximately the factor indicated by experiment. One might expect the correlation energy to be renormalized roughly by the square of this factor. The singlet d-density order, as we shall discuss further below, breaks only a discrete symmetry, so it is safer in this regard. Also the d-density order, because it contains nodes, has a more favorable one-particle energy. The one-particle energy for this state, in the presence of a gap of magnitude \( \Delta \), is \( 6.40\Delta^2/t \) while the antiferromagnet or charge-density wave have one-particle energy \( 10.65\Delta^2/t \). (These numerical coefficients were obtained by integrating the one particle energies up to a chemical potential \( \mu = 2\Delta \) which avoids the van Hove singularity. The results are similar for other choices of the chemical potential; the robust point is that the d-density is substantially favored.) Altogether, then, it seems that d-density order, especially in its singlet form, is a serious candidate to describe real states of matter.
2. Comments

1. Since neither the Hamiltonian we analyzed nor the approximation scheme we employed is exact, it behooves us to identify what feature of the proposed state might be expected to have precise validity. As in many cases in physics, a broken symmetry is the heart of the matter. One finds in the spin-singlet d-density state the non-vanishing expectation value

\[ \langle c \alpha^\dagger(k + Q) c \beta(k) \rangle = i \delta_\alpha^\beta f(k), \]

where \( f \) is a real function that changes sign under a \( \pi/2 \) rotation. The \( i \) indicates that time-reversal symmetry \( T \) is violated, and the angular dependence indicates that symmetry under \( \pi/2 \) rotation is violated. Furthermore, the dependence on the momentum offset \( Q = (\pi/a, \pi/a) \) indicates that symmetry under translation through a single lattice spacing is also violated, since this too changes the sign of the order parameter. Let us swiftly add, however, that one can combine any two of these broken symmetry operations to recover a valid symmetry. Thus, in particular, one does not expect to see any simple direct macroscopic manifestation of the symmetry breaking.

Indeed, it is not entirely easy to identify accessible signatures for d-density order even microscopically. There are no extra coherent peaks in elastic x-ray or neutron scattering, since the relevant single-particle expectation values cancel upon integrating over angles. Perhaps the most fundamental signature derives from the existence of low energy particle-hole excitations at momenta connecting points on the Fermi surface repeated after translation through \( Q \). These should reveal themselves in inelastic neutron scattering, as an anomalous extended continuum. Closely related structure would also be expected in photoemission.

Although the model we have analyzed above is two-dimensional, the essential idea of the ordering pattern (2.1) is not intrinsically two-dimensional, and invites generalization to three-dimensional materials.
2. We have already sketched the construction of the quasiparticles. When one replaces the normal electron operators by these quasiparticles, what emerges near half filling can be described to a first approximation using a semiconductor-like picture. A gap has opened up at the boundary of the magnetic zone, so that doping below half-filling it will produce an effective concentration of hole-like charge carriers proportional to the doping. The Fermi surface will have its normal area or volume, though if the nominal Fermi surface passes through the magnetic zone boundary it will be distorted from its nominal band theory form. The critical behavior at the transition will depend crucially on whether or not this occurs [3,4].

Transport in the spin-triplet d-wave state will be anomalous, due to the Nambu-Goldstone mode associated with breaking of the spin rotation symmetry. (More precisely, there will be important fluctuations, but not necessarily a simple Nambu-Goldstone mode, in the appropriate channel.) Transport in the spin-singlet d-wave state will also be anomalous, due to fluctuations associated with transition to this state at a finite coupling and doping. The precise nature of these anomalies is under study.

Because it effectively halves the size of the Brillouin zone without introducing any manifest antiferromagnetic or charge density ordering, the d-density wave ordering appears to be an interesting candidate to describe Mott insulators (or the related doped “semiconductors”) which exhibit neither antiferromagnetic nor charge-density ordering.

3. Because the quasiparticles of the d-density state are composed of d-wave mixtures of fundamental electronic modes, the effective phonon-mediated interaction between these particles will contain a substantial d-wave component. Since it is less sensitive to Coulomb repulsion, effective attraction in this partial wave plausibly leads to a particularly robust instability toward d-wave superconductivity. (Of course, it is still subject to the strong fluctuations associated with two-dimensionality for an isolated layer.) The accumulation of density of states near the magnetic zone, which is close to the Fermi surface for small doping, enhances this tendency.
4. In the states we have considered above, the mean density of spin up and spin down have been supposed equal. Actually the $U$-term energy (though not the single-particle energy) is minimized by a completely polarized, ferromagnetic state. Within the polarized state one can still examine the possibility of d-density ordering, which we find can indeed be energetically favorable. This provides a model for possible ferromagnetic Mott insulator behavior at $\frac{1}{4}$ filling.

**Acknowledgements:** We wish to thank R. Schrieffer and S. Sondhi for valuable comments.
REFERENCES

1. J.R. Schrieffer, X.G. Wen, and S.C. Zhang, Phys. Rev. B 39 (1989) 11663

2. For a nice systematic exposition of this point of view see R. Brout, Phase Transitions, (W.A. Benjamin, New York 1965)

3. A.J. Millis, Phys. Rev. B 48 (1993) 7183

4. S.Sachdev, A.V. Chubukov, and A. Sokol, Crossover and scaling in a nearly antiferromagnetic Fermi liquid in two dimensions, Yale preprint (1994).