

High Temperature Superconductivity

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With 125 Illustrations



Springer-Verlag 1990
New York Berlin Heidelberg
London Paris Tokyo Hong Kong

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Library of Congress Cataloging-in-Publication Data
High temperature superconductivity / Jeffrey W. Lynn, editor.
p. cm. — (Graduate texts in contemporary physics)
Includes bibliographical references.
ISBN 0-387-96770-2 (alk. paper)
I. High temperature superconductivity. I. Lynn, Jeffrey W.
II. Series.
QC611.98.H54H5433 1990
537.6'23—dc20 90-9436

Printed on acid-free paper.

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Camera-ready text provided by the editor.
Printed and bound by R.R. Donnelley & Sons, Harrisonburg, Virginia.
Printed in the United States of America.

9 8 7 6 5 4 3 2 1

ISBN 0-387-96770-2 Springer-Verlag New York Berlin Heidelberg
New York, NY 10010, USA

Electron Pairing: How and Why?

Philip B. Allen

9.1. Introduction

As this chapter is being written, a year has elapsed since high T_c superconductors became an accepted reality. The mechanism for the high T_c is still mysterious. It is not even certain that the superconducting state is BCS-like. This ripe situation is forcing theorists to rethink.

It is beyond my ability to summarize fairly all serious theoretical papers of the last 12 months; instead of trying, my aim will be to explain in my own way as many aspects of the problem as I can. Alternate views can be found in several review papers [1-3] or by scanning conference proceedings such as the June 1987 Berkeley conference [4a] and the March 1988 Interlaken meeting [4b].

This chapter tries to emphasize the basics - Cooper pairing (Sec. 2), Bose Condensation (Sec. 3), and BCS Theory (Secs. 4,5,6). Yang's conjecture that off-diagonal long-range order (ODLRO) is the minimal essence of superconductivity is described in Sec. 7. In Secs. 8,9,10 the popular mechanisms which fit into conventional BCS theory are mentioned. The alternative possibility of superconductivity arising from something other than a conventional Fermi liquid is discussed in Sec. 11, where the terms "weak" and "strong" are introduced for conventional and unconventional theories. Two "strong" theories, bipolarons and resonating valence bonds (RVB), are the subject of Secs. 12 and 14. In Sec. 13 a short explanation is given of the Mott insulator phase of the Hubbard model in the large U , half-filled band case. This is intended to motivate and clarify the notions of RVB theory which are attracting attention from many theorists. In Sec. 15 several models are described in which BCS superconductivity arises via magnetic interactions in a

doped Mott insulator.

One can roughly distinguish four classes of superconductors. (1) Ordinary metallic superconductors, such as Pb, Al, Nb, NbN, V_3Si , Nb_3Sn , etc. These all appear to be based on BCS singlet pairing, caused by the electron-phonon interaction. T_c ranges up to 23 K (so far) [5]. (2) "Organic" superconductors such as $(BEDT-TTF)_2I_3$. T_c is mostly low, but increasing [6]. (3) "Heavy Fermion" superconductors. Here $T_c < 1$ K is usual [7]. (4) High T_c copper oxide-based superconductors, with T_c up to 125 K and possibly higher.

The last three categories share some surprising similarities: (a) the mechanism of superconductivity is not clear; (b) the nature of the pairing scheme is also not clear - BCS triplet or d-wave has not been ruled out; (c) all show a proximity between superconductivity and antiferromagnetic order. In addition, the organics and the CuO superconductors show metal-insulator transitions (no doubt related to antiferromagnetism). A fifth category could be added: (5) 3He . This is definitely established to be a BCS triplet state, with proximity to ferromagnetic spin ordering, and a low T_c , $\sim 10^{-3}$ K, driven at least partly by spin fluctuations.

It is logical to believe two things about the CuO-based superconductors. First, their behavior should be closely related to that of $Ba(Pb_{1-x}Bi_x)O_3$, a structurally related system showing a similar interplay of superconductivity and a metal/insulator transition [8]. Second, their superconductivity should be closely related to their antiferromagnetic properties. This would help explain the high T_c , because the magnetic energy scale appears to be $\sim 10^3$ K [9]. It is well understood how antiferromagnetism arises from strong Coulomb repulsion (Sec. 13) but is as yet a matter of conjecture and controversy how superconductivity, especially with high T_c , can arise from repulsive interactions. This may require an unconventional, highly-correlated metallic state (such as RVB) rather than the normal state of BCS theory which is a Fermi liquid. A possible phase diagram for $La_{2-x}Sr_xCuO_4$ is shown in Fig. 1. It illustrates the interplay of antiferromagnetism and superconductivity.

Interestingly, the two logical beliefs mentioned above are in apparent conflict. There is no evidence yet for antiferromagnetism in $Ba(Pb_{1-x}Bi_x)O_3$, and the strong correlations which create its insulating state may originate more from electron-phonon than from Coulomb interactions [11]. Therefore it is premature to rule out anything.

Before commencing, a few preliminary remarks. The reader who knows BCS theory can skip to Sec. 8. However, I give in Sec. 4 a derivation of T_c in BCS theory using perturbation theory to find the divergence of the pair susceptibility, and this may be worth reading because it is used later on. I assume the structure of CuO superconductors is familiar (see Chapter 4) and that the electronic states near ϵ_F are located in the square-planar sheets and on the chains, as is explained in Chapter 5.

Finally I want to clarify what I mean by "BCS theory" [12]. Some take this to mean the electron-phonon interaction, which causes a pairing instability. In this sense the CuO superconductors are probably *not* BCS. However, to others (including myself) the central core of BCS theory is the pairing instability of the Fermi liquid in the presence of an attractive interaction, with the source of this interaction a peripheral aspect. In this sense the new materials may be BCS-like. If future experiments should confirm this, then the remaining issue is to identify the source of attraction.

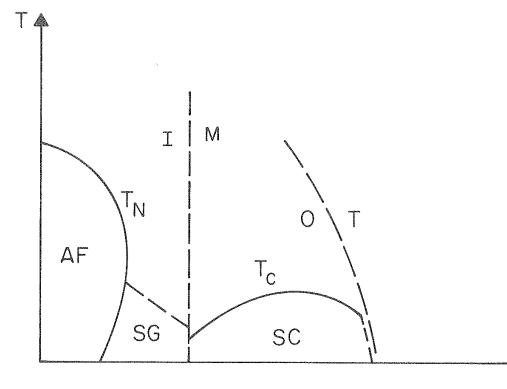


Fig. 9.1. A possible (T, x) phase diagram for $La_{2-x}Sr_xCuO_4$, after Aharony *et al.* [10]. The solid curves are the Neel (T_N) and superconducting (T_c) temperatures separating antiferromagnetic (AF) from non-magnetic insulating (I) and superconducting (SC) from normal metallic (M) regions. Also shown is a possible spin glass (SG) phase and the orthorhombic (O) to tetragonal (T) phase boundary which occurs near $x = 0.2$.

9.2. Cooper Pairs

Cooper [13] discovered that if two electrons, in an otherwise non-interacting gas of electrons, are allowed to interact via an attractive force, they always bind together, with a binding energy

$$E_B = 2\Theta e^{-2/\lambda} . \quad (9.1)$$

A derivation of this formula will be sketched below; λ is $N(\epsilon_F)V$ where V is the interaction strength and $N(\epsilon_F)$ is the density of states at the Fermi energy. Generalizing to the case where all electrons attract each other, one should expect an instability of the normal Fermi liquid, and this is the essence of BCS theory. The cause of the instability is the Pauli principle and the sharpness of the Fermi surface. At higher temperatures the Fermi surface is fuzzy over a range $k_B T$ and the instability goes away when $k_B T \approx E_B$.

To derive Eq. (9.1), let the wavefunction for the interacting electron pair be

$$\psi(r_1, r_2) = \sum_{\mathbf{k}} g(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}_1} e^{-i\mathbf{k} \cdot \mathbf{r}_2} . \quad (9.2)$$

To satisfy the Pauli principle, we choose $g(-\mathbf{k}) = g(\mathbf{k})$ and a singlet spin arrangement, and we restrict the sum in (9.2) to wave vectors \mathbf{k} outside the occupied Fermi sea, $\epsilon_F < \epsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$, which is the meaning of the prime on the sum. Translation symmetry makes the center of mass momentum $\mathbf{Q} = \mathbf{k}_1 + \mathbf{k}_2$ a constant of the motion, and we have chosen $\mathbf{Q} = 0$ or $\mathbf{k}_1 = -\mathbf{k}_2 = \mathbf{k}$ because this gives the lowest energy.

We now operate on $\psi(r_1, r_2)$ with the Hamiltonian $p_1^2/2m + p_2^2/2m + V(r_1, r_2)$ and seek the lowest eigenvalue E which will be written as $2\epsilon_F - E_B$, so that E_B is the binding energy. This gives an equation

$$[2(\epsilon_{\mathbf{k}} - \epsilon_F) + E_B]g(\mathbf{k}) = \sum_{\mathbf{k}'} |V(\mathbf{k}, \mathbf{k}')| g(\mathbf{k}') . \quad (9.3)$$

Here we are assuming that $V(\mathbf{k}, \mathbf{k}')$, the Fourier transform of $V(r_1, r_2)$, is negative, or attractive.

Now it helps to consider one specific type of attractive interaction, the Bardeen-Pines [14] form of the phonon-induced interaction.

$$V_{BP}(\mathbf{k}, \mathbf{k}') = \frac{2\hbar\omega_q |M_{\mathbf{k}, \mathbf{k}'}|^2}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}')^2 - (\hbar\omega_q)^2} . \quad (9.4)$$

Here $q = k - k'$, ω_q is a phonon frequency, and $M_{\mathbf{k}, \mathbf{k}'}$ is an electron-phonon matrix element. This equation is derived by making

a canonical transformation to eliminate the electron-phonon interaction in lowest order. It is not exact, and is replaced in the more sophisticated Eliashberg [15] version of BCS theory by a time-dependent interaction. After Fourier transforming time to frequency the Eliashberg interaction looks like (9.4) with $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}$, replaced by $\hbar\omega$. The interaction (9.4) is attractive if $|\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'}|$ is less than $\hbar\omega_q$. A reasonable caricature of Eq. (9.4), which is convenient for use in Eq. (9.3), is

$$V_{BP}(\mathbf{k}, \mathbf{k}') \approx -V\theta[k_B\Theta - |\epsilon_{\mathbf{k}} - \epsilon_F|] \theta[k_B\Theta - |\epsilon_{\mathbf{k}'} - \epsilon_F|] , \quad (9.5)$$

where $k_B\Theta \approx \hbar\omega_D$, and θ is the unit step function. Notice that V is a positive number and denotes an attractive interaction. With a reinterpretation of V and Θ , Eq. (9.5) might be used for other types of interactions, such as excitons, plasmons, etc.

Now insert Eq. (9.5) into Eq. (9.3). Then $g(\mathbf{k})$ will depend only on $\epsilon_{\mathbf{k}} = \epsilon$, and vanish unless $\epsilon_F < \epsilon < \epsilon_F + k_B\Theta$. In this interval, $g(\epsilon)$ obeys

$$[2(\epsilon - \epsilon_F) + E_B]g(\epsilon) = V \int_{\epsilon_F}^{\epsilon_F + k_B\Theta} d\epsilon' N(\epsilon') g(\epsilon') . \quad (9.6)$$

This equation has a solution, $g(\epsilon) = c/[2(\epsilon - \epsilon_F) + E_B]$, provided E_B obeys the consistency equation

$$1 = V \int_{\epsilon_F}^{\epsilon_F + k_B\Theta} d\epsilon' N(\epsilon') / [2(\epsilon' - \epsilon_F) + E_B] . \quad (9.7)$$

Cooper's answer for E_B , Eq. (9.1), follows immediately from (9.7) upon two further approximations: (1) $k_B\Theta \ll \epsilon_F$ so that variations of $N(\epsilon')$ can be neglected and $N(\epsilon')$ can be replaced by $N(\epsilon_F)$; (2) $E_B \ll k_B\Theta$, as is justified by Eq. (9.1) in the weak coupling limit $\lambda < 1$. These are reasonable approximations in most metals. A formula for λ also emerges from Eqs. (9.4, 9.5), namely

$$\lambda = N(\epsilon_F) \langle 2 |M_{\mathbf{k}, \mathbf{k}'}|^2 / \hbar\omega_Q \rangle \quad (9.8)$$

where the bracket in Eq. (9.8) denotes averaging \mathbf{k} and \mathbf{k}' over the Fermi surface. The same parameter λ appears in Eliashberg theory for T_c .

It is interesting to examine Eq. (9.7) in a different regime, namely the very dilute limit where $\epsilon_F \rightarrow 0$ and electron pairs are

bottom of the band and cannot be replaced by a constant value. The result depends sensitively on the dimensionality d of the electronic system. For the non-interacting electron gas,

$$N(\varepsilon) = N(c_d/\varepsilon_0)(\varepsilon/\varepsilon_0)^{(d-2)/2} \quad (9.9)$$

where in $d = 1, 2, 3$, we have $c_1 = 1/2\pi$, $c_2 = 1/4\pi$, and $c_3 = 1/4\pi^2$. The energy scale ε_0 is $\hbar^2/2ma^2$, where a is a microscopic length defined by $Na^d = \Omega$, where N = number of atoms and Ω = d -dimensional sample volume. Then, setting $\varepsilon_F = 0$, Eq. (9.7) becomes

$$\frac{1}{\lambda} = \int_0^\theta \frac{dx \, x^{(d-2)/2}}{x + \delta} \quad (9.10)$$

where the dimensionless variables are $x = \varepsilon/\varepsilon_0$, $\delta = E_B/2\varepsilon_0$, $\theta = k_B\Theta/\varepsilon_0$, and $\lambda = c_d V/2\varepsilon_0$. If we further assume weak binding ($\delta \ll \theta$), the binding energies found from Eq. (9.10) are

$$\delta = (\pi\lambda)^2 \quad (d=1) \quad (9.11a)$$

$$\delta = \theta e^{-1/\lambda} \quad (d=2) \quad (9.11b)$$

$$\delta = (4\theta/\pi^2)(1-\lambda_c/\lambda)^2 \quad (d=3) \quad [\text{provided } \lambda > \lambda_c = 1/2\theta^{3/2}] \quad (9.11c)$$

In $1d$, there is always a bound state with binding scaling as V^2 and independent of the cutoff energy Θ . In $2d$, there is also always a bound state, but for small V , E_B is exponentially small, with a scale set by Θ . In $3d$, no binding occurs until V exceeds a critical strength $V_c = 4\pi^2\varepsilon_0 \sqrt{\varepsilon_0/k_B\Theta}$.

The results for the dimension-dependence of binding are essentially the same as the well-known single-particle quantum results for particles in wells. These results contrast sharply with Cooper's result (9.1), which is independent of dimension and reminiscent of the $2d$ result (9.11b). Because of the Pauli principle, the electrons in Cooper's problem explore a section of k -space with a density of states analogous to Eq. (9.9) with $d=2$.

The role of the sharpness of the Fermi surface is to cause a logarithmic divergence of the integral in Eq. (9.7) as E_B goes to zero. This is what permits a bound state $E_B > 0$ no matter how small V is. Suppose the background Fermi sea had a non-zero temperature. This could be modeled by using in Eq. (9.3) a factor $1 - f(\varepsilon_k')$ instead of a sharp cutoff $\theta(\varepsilon_k' - \varepsilon_F)$ in the sum on the right. The logarithmic divergence in Eq. (9.7) would cut off at $k_B T$ and there would be no binding for $k_B T$ greater than the zero temperature binding energy. For the same reason the superconducting instability goes away as T increases.

As a final note, one can imagine solutions of Eq. (9.3) with other symmetries; for example, a triplet state with $g(-k) = -g(k)$. For an interaction like Eq. (9.4) one expects to find E_B largest for the most symmetric state, namely the singlet. Other bound states of smaller E_B are irrelevant to superconductivity. For special kinds of potentials $V(k, k')$, a triplet state (or any other state of different symmetry) might become the most strongly bound, leading to a more exotic BCS-like state. The superfluid phase of ^3He at millikelvin temperatures is the only proven example, having triplet spin pairing and $\ell = 1$ orbital symmetry. The $\ell = 0$ channel presumably has a repulsive interaction because of the hard core. It is speculated that certain "organic" superconductors and "heavy Fermion" superconductors may also involve triplet pairs or possibly singlet $\ell = 2$ ("d-wave") pairs. These all have low T_c 's, and it seems to me unlikely that exotic pairing could lead to a high T_c .

9.3. Bose Condensation

If we could regard a Cooper pair as a good composite particle (as we can a ^4He atom, for example, when probed at energies of a few eV or less) then a Cooper pair would be a Boson, having spin 0 in the singlet $\ell = 0$ case and spin $J = L + S$ with $J = 0, 1$, or 2 in the $\ell = 1$ triplet case. In ordinary metallic superconductors, Cooper pairs actually have a large radius $\xi \sim 10^2\text{--}10^4 \text{ \AA}$, and are therefore strongly overlapping, and poorly defined composite particles. Nevertheless there is a sense in which the BCS ground state is a Bose condensate of Cooper pairs. Therefore it is appropriate to review Bose condensation here. It should be born in mind that unlike the ideal gas Bose condensate, in the BCS case the Boson pairs *do not exist except when condensed*. However, it is possible to imagine an alternate scenario where a non-BCS (or at least non-conventional BCS) superconductor is formed out of preexisting pairs. Consider for example, ^4He atoms, which are good Bose particles up to $T > 10^4 \text{ K}$. The superfluid transition occurs at $T_\lambda = 2.18 \text{ K}$ which is quite close to the condensation temperature 3.2 K of the corresponding gas of non-interacting He atoms. If these particles were endowed with a special charge which enabled them to couple to external fields without altering their interaction with each other, then the superfluid phase of ^4He would be superconducting. Each ^4He atom is made of two electrons and an alpha particle (two Fermions and a Boson). Thus this imaginary charged gas of ^4He atoms would be a non-BCS superconductor in which Bosons based on electron pairing would be formed at very high temperatures (almost 10^5 K) but would condense only at low temperatures (2.18 K).

The idea of Bose condensation was put forward by Einstein, who realized that the formula which fixes the chemical potential μ_b for Bosons,

$$N = \sum_k [\exp(\beta(\epsilon_k - \mu_b)) - 1]^{-1} \quad (9.12)$$

is not necessarily correctly expressed by the corresponding integral

$$N = \int_0^\infty d\epsilon N(\epsilon) [\exp(\beta(\epsilon - \mu_b)) - 1]^{-1} \quad (9.13)$$

Let us assume that the Bosons are free particles of mass m . Equation (9.9) for $N(\epsilon)$ applies to Bosons as well as Fermions. Then Eq. (9.13) becomes

$$(\beta\epsilon_0)^{d/2} = c_d \int_0^\infty dx x^{d/2-1} [\exp(x - \beta\mu_b) - 1]^{-1} \quad (9.14)$$

The quantity $\beta\mu_b$ must be negative in order for the Bose-Einstein occupation function to be positive. The difficulty is that for $d > 2$, Eq. (9.14) has no solution for $\beta\mu_b$ if $\beta\epsilon_0$ is too large, because the integral in (9.14) is bounded above by the value it attains when $\mu_b = 0$,

$$c_d \int_0^\infty \frac{dx x^{d/2-1}}{e^x - 1} = q(d) \quad (9.15)$$

For $d = 1$ or 2 , $q(d)$ is infinite which means that a solution $\beta\mu_b < 0$ can be found for any value of $\beta\epsilon_0$. However, $q(3)$ is ~ 0.0586 , so that there is a minimum value of $\beta\epsilon_0$, corresponding to $1/\beta_c = k_B T_c \equiv 6.62 \epsilon_0$, and for lower T , no positive value of $-\beta\mu_b$ exists which satisfies Eq. (9.14). Einstein resolved the dilemma by observing that the process of converting (9.13) to (9.14) does not do justice to the discrete nature of the sum at small k . In particular, the minimum energy state, $k = 0$, must be treated separately, and can develop a macroscopic occupancy below T_c . Anderson [16] has discussed how this macroscopic occupancy requires phase coherence, and Yang [17] has shown how this state exhibits what he calls "off-diagonal long range order" (ODLRO), a property which would lead to flux quantization, the Meissner effect, and superconductivity if the particles had charge.

It is interesting to notice that dimensionality plays a large role in Bose condensation, in a fashion closely related but reciprocal to the role of dimensionality discussed in Sec. 2 for pair binding. In low dimensions, there are proportionately many states near $\epsilon = 0$ to accommodate the Bosons (because $N(\epsilon)$ is large) whereas for $d > 2$ there are fewer states near $\epsilon = 0$ which forces

condensation into the $\epsilon = 0$ state. In the jargon of phase transitions (of which this is the simplest example) "enhanced quantum fluctuations" in low dimensionality destroy the condensed or ordered state. But exactly this availability of low energy states in low d is what promotes pair binding. This creates a dilemma for Boson scenarios of superconductivity: If d is low, Fermions can more easily bind to form Bosons but can't Bose condense, whereas if d is high, condensation is permitted but binding of Fermions into Bosons is suppressed (except in degenerate Fermi systems where the Fermi surface promotes binding).

9.4. BCS Theory for T_c

At high T , the thermal broadening of the Fermi surface eliminates the binding of Cooper pairs. As T is lowered to T_c , a collective rearrangement occurs in which all electrons near ϵ_F bind into a pair condensate. Below $T = T_c$, energy 2Δ is required to unbind a pair of electrons from this condensate. This "gap" Δ is temperature dependent, and goes to zero as T increases to T_c . This is analogous to a ferromagnet, where the energy required to flip a spin goes to 0 as T approaches the Curie temperature T_c from below. In fact, the BCS theory is completely analogous to a mean field theory of a magnetic transition, so it is appropriate to review the simplest such theory, the Curie-Weiss theory of ferromagnetism.

Consider \mathcal{N} permanent moments μ_i which experience an external field \mathbf{B} but not each other.

$$H_{ext} = - \sum_i \mu_i \cdot \mathbf{B} \quad (9.16)$$

Elementary statistical mechanics shows that the susceptibility $\chi = \partial M / \partial B$ is

$$\chi_0 = \frac{\mathcal{N} \mu^2}{k_B T} \quad (9.17)$$

(this is for $s = \frac{1}{2}$; classical spins have an extra factor $1/3$). Now suppose there is an interaction between moments

$$H_{int} = - J \sum_{\langle ij \rangle} \mu_i \cdot \mu_j \quad (9.18)$$

where the sum runs over nearest-neighbor pairs. Mean field theory replaces μ_i by $\langle \mu \rangle + \delta_i$ where the fluctuation δ_i is $\mu_i - \langle \mu \rangle$ and is regarded as small. Omitting quadratic terms $\delta_i \delta_j$, (9.16) and (9.18) can be combined

$$H_{MF} = - \sum_i \mu_i \cdot (\mathbf{B} + z\mathbf{J} \langle \mu \rangle) \quad (9.19)$$

where $\langle \mu \rangle = M/\mathcal{N}$ and z is the coordination number. The magnetization of the system described by (9.19) obeys

$$M = \chi_o(\mathbf{B} + z\mathbf{J}M/\mathcal{N}) = \chi \mathbf{B} \quad (9.20)$$

$$\chi = \chi_o / (1 - z\mathbf{J}\chi_o/\mathcal{N}) \quad (9.21)$$

Using Eq. (9.17) for χ_o , the mean field susceptibility χ diverges as $c/(T-T_c)$ where T_c is the solution of $z\mathbf{J}\chi_o/\mathcal{N} = 1$, or $T_c = z\mathbf{J}\mu^2/k_B$.

In the case of superconductivity, there is also a susceptibility which diverges as T_c is approached from above, but it does not couple to any readily available field and thus is hidden from measurement. The key question is, what plays the role of the "order parameter", analogous to $M = \sum_i \langle \mu_i \rangle$ for the magnet. The BCS answer is that a nonclassical quantity, the "pair amplitude", plays this role. Playing the roles of the moment operators μ_i are the pair creation and destruction operators

$$\begin{aligned} b_k &= c_{k\uparrow} c_{-k\downarrow} \\ b_k^\dagger &= c_{-k\downarrow}^\dagger c_{k\uparrow}^\dagger \end{aligned} \quad (9.22)$$

Suppose we imagine a field F which coupled to such an operator

$$H_{ext} = - \sum_k b_k^\dagger F e^{-i\omega t} + hc \quad (9.23)$$

where hc means the Hermitian conjugate term. Then in response there would be a pair field

$$\phi = \sum_k \langle b_k \rangle \quad (9.24)$$

and the pair susceptibility would be

$$\chi_p \equiv \frac{\partial \phi}{\partial F} \quad (9.25)$$

To compute χ_p , we can use a Kubo-type formula

$$\chi_p(\omega) = - (i/\hbar) \sum_{kk'} \int_0^\infty dt e^{+i\omega t} \langle [b_k^\dagger(0), b_{k'}^\dagger(t)] \rangle \quad (9.26)$$

completely analogous to a well known Kubo formula for the magnetic case [18]. For non-interacting electrons it is easy to evaluate Eq.

(9.26) becomes

$$\chi_p^o(\omega) = \sum_k \frac{1-2f_k}{2(\epsilon_k - \mu) - \hbar\omega} = \int d\epsilon N(\epsilon) \frac{\tanh \beta(\epsilon - \mu)/2}{2(\epsilon - \mu) - \hbar\omega} \quad (9.27)$$

At $T = 0$, this integral has a logarithmic divergence arising from the sharpness of the Fermi surface. It is convenient to introduce a cutoff $\theta(k_B\Theta - |\epsilon_k - \mu|)$ into the k -sum in (9.23), to avoid an uninteresting ultraviolet divergence in Eq. (9.27). The susceptibility then becomes

$$\begin{aligned} \chi_p^o(0) &= \frac{1}{2} N(\epsilon_F) \int_{-k_B\Theta}^{k_B\Theta} d\epsilon \frac{\tanh \beta\epsilon/2}{\epsilon} \\ &= N(\epsilon_F) \log \frac{1.13\Theta}{T} \end{aligned} \quad (9.28)$$

The last step above is a familiar manipulation in BCS theory and is explained, for example, by Rickayzen [19].

Notice that both the Curie susceptibility χ_o for free spins, and the pair susceptibility, χ_p for free electrons, diverge as $T \rightarrow 0$. These systems become infinitely polarizable and an arbitrarily weak interaction favoring alignment will induce a spontaneous polarization at low T . The analog for superconductivity of the magnetic interaction (9.18) would be a term of the form

$$H_{red} = - V \sum_{kk'}^{c.o.} b_k^\dagger b_{k'}^\dagger \quad (9.29)$$

where c.o. denotes that a cutoff is used as in Eq. (9.5). The subscript "red" stands for "reduced" as will be explained below. Mean field theory now replaces b_k by $\langle b_k \rangle$ plus the fluctuation $\delta_k = b_k - \langle b_k \rangle$. The same is done for $b_{k'}$, and the term $\delta_k \delta_{k'}$ is dropped. Then the external field in (9.23) and the mean field version of (9.29) combine to give

$$H_{MF} = - \sum_k b_k^\dagger (\text{Fe}^{-i\omega t} + V\phi) \quad (9.30)$$

where Eq. (9.24) is used for ϕ . This equation is the analog of (9.19). Finally the pair field ϕ is computed.

$$\phi = \chi_p^o (\text{Fe}^{-i\omega t} + V\phi) = \chi_p \text{Fe}^{-i\omega t} \quad (9.31)$$

$$\chi_p = \frac{\chi_p^o}{1 - V\chi_p^o} \quad (9.32)$$

pair susceptibility in mean field approximation. It diverges at $\omega = 0$ when $T = T_c$, where T_c is the solution of $1 = V\chi_p(T_c)$. Using Eq. (9.28), we find the famous BCS result,

$$T_c = 1.13 \Theta \exp(-1/N(\epsilon_F)V) \quad (9.33)$$

This is the analog of the magnetic result $T_c = zJ\mu^2/k_B$. The exponential dependence of T_c on $1/V$ tends to make T_c small, and is a consequence of the logarithmic divergence (9.28) of the non-interacting pair susceptibility.

In the case of magnetic systems, mean field theory is not usually a very good approximation; especially in lower dimensions $d < 3$, the neglected fluctuations qualitatively change the behavior of the system. For superconductivity this is usually not true. Unlike Eq. (9.18) where only z nearest neighbor spins j interact with spin i , in Eq. (9.29) the number of wave vectors k' interacting with k grows as the size of the system, making fluctuations relatively unimportant. The BCS solution is exact in the thermodynamic limit for the interaction (9.29). However, unlike the magnetic case, the interaction (9.29) contains only a small piece of the complete interaction. If a pairwise interaction $V(r_1, r_2)$ exists between electrons, then, expressed in a Bloch-state basis, the interaction is

$$H_{int} = \sum_{kk'q\sigma\sigma'} V(k, k', q) c_{k+q\sigma}^+ c_{k'\sigma'}^+ c_{k'\sigma} c_{k\sigma} \quad (9.34)$$

The interaction (9.29) has taken only a small subset of the terms of Eq. (9.34), namely those with $\sigma' = -\sigma$ and $k' = -k$, and is called the BCS "reduced" Hamiltonian. The coupling constant $V(-k, k, q)$ is then relabeled as $-V(k, k+q)$; the sign change is a peculiar BCS convention which allows attractive V 's to be positive. The final replacement of $V(k, k+q)$ by V in Eq. (9.29) is only a convenience which permits a closed form solution.

There is no proof that the terms omitted from Eq. (9.34) are innocuous and cause no further new phenomena, but the success of BCS theory provides empirical proof for many materials. BCS theory is built on Landau theory which asserts that all terms of (9.34) are absorbed in building a ground state and quasiparticle excitations which interact weakly. BCS theory adds to Landau theory the hypothesis that a small subset of terms of (9.34), namely (9.29), have an important additional effect in altering the ground state and excitation spectrum. All remaining terms are believed to define the parameters of the Landau theory, but not to alter it qualitatively or destroy it.

9.5. The Interaction in BCS Theory

A rigorous procedure for locating T_c within the philosophy of BCS theory is to find the divergence of the pair susceptibility, Eq. (9.26). The mean field theory of Sec. 9.4 is exact (in the thermodynamic limit) for the special "reduced" Hamiltonian (9.29), but for a more general interaction, such as (9.34), or if electron-phonon interactions are present, a more powerful scheme for evaluating Eq. (9.26) is needed. This is provided by graphical (Feynman-Dyson) perturbation theory. In order to use this theory, a related correlation function is needed [20],

$$\chi_p(i\omega_\lambda) = \frac{1}{2} \sum_{k, k'} \int_{-\beta}^{\beta} d\sigma e^{i\omega_\lambda \sigma} \langle T_\sigma [b_k(\sigma) b_k^\dagger(0)] \rangle \quad (9.35)$$

Here σ is an imaginary time, ω_λ is a Matsubara frequency, and T_σ is a "time-ordering" operator. From the function (9.35) the susceptibility (9.26) can be retrieved, but (9.35) is better suited to the development of a systematic perturbation theory.

First consider the case where the only interaction is the reduced interaction (9.29). Then we should be able to recover the BCS results (9.32, 9.33) from perturbation theory. The terms in the perturbation theory for χ_p correspond to diagrams:

$$\chi_p = \begin{array}{c} \text{---} \xrightarrow{k \uparrow} \text{---} \\ \text{---} \xrightarrow{-k \downarrow} \text{---} \end{array} + \begin{array}{c} \text{---} \xrightarrow{k \uparrow} \text{---} \text{---} \xrightarrow{k' \uparrow} \text{---} \\ \text{---} \xrightarrow{-k \downarrow} \text{---} \text{---} \xrightarrow{-k' \downarrow} \text{---} \end{array} + \dots \quad (9.36)$$

After integrating over k and k' , a simple infinite series results: $\chi_p = \chi_p^0 + \chi_p^0 V \chi_p^0 + \dots$. The n^{th} order term is just $\chi_p^0 (V \chi_p^0)^n$ and the sum of the resulting geometric series is just Eq. (9.32). Notice that because of the form of H_{red} , there can be no terms corresponding to graphs like

$$(a) \begin{array}{c} \text{---} \xrightarrow{k \uparrow} \text{---} \text{---} \xrightarrow{k \uparrow} \text{---} \\ \text{---} \xrightarrow{-k \downarrow} \text{---} \end{array} \quad (b) \begin{array}{c} \text{---} \xrightarrow{k \uparrow} \text{---} \text{---} \xrightarrow{k+q \uparrow} \text{---} \\ \text{---} \xrightarrow{-k \downarrow} \text{---} \text{---} \xrightarrow{-k-q \downarrow} \text{---} \end{array} \quad (9.37)$$

although any physical interaction, such as (9.34), permits them. These graphs are important in a complete theory. Graph (a) renormalizes the one particle properties and graph (b) screens the

Next consider the case where there is only an electron-phonon interaction

$$H_{int} = \sum_{kQ\sigma} M_{k,k+Q} c_{k+Q\sigma}^+ c_{k\sigma} (a_Q + a_Q^+) \quad (9.38)$$

$$H_0 = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} + \sum_Q \hbar\omega_Q a_Q^+ a_Q \quad (9.39)$$

It should be understood that both phonons and electrons have band indices and the symbols k , Q can be considered short for (k,n) and (Q,j) . Many new kinds of graphs are possible. Fortunately, only a simple subset is important:

$$\chi_p = \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \text{---} \text{---} \text{---} + \dots \quad (9.40)$$

This looks exactly like Eq. (9.36), but it is actually more complicated. The double lines are shorthand for other infinite series:

$$\text{---} \text{---} = \text{---} \text{---} + \text{---} \text{---} \text{---} \text{---} \quad (9.41)$$

$$\text{---} \text{---} = \text{---} \text{---} + \text{---} \text{---} \text{---} \text{---} \quad (9.42)$$

Equation (9.42) renormalizes the phonon frequencies. Fortunately, if the frequencies are known from experiment, these are already renormalized so we can bypass this step. Unfortunately, if the frequencies have not been measured, then evaluating (9.42) properly (including Coulomb effects not shown in (9.42)) is very difficult. Weber [21] and Weber and Mattheiss [22] have made a good preliminary attempt on oxide superconductors, but their work has adjustable constants and is not quantitatively predictive. Equation (9.41) contains the "mass renormalization" of the electronic states which causes a significant correction to T_c .

When the terms of Eq. (9.40) are summed, an integral equation results which is different from the original BCS equation using the Bardeen-Pines interaction. The reason for the difference is that there is a time-delay in phonon propagation. This results in an ω -dependence of the gap $\Delta(k,\omega)$ and of the integral equation. Thus Eq. (9.40) corresponds to a time-dependent generalization of BCS theory. It is called Eliashberg theory, and has been thoroughly

metallic superconductors. The explicit construction of Eliashberg theory by this route was done by Allen [20] including Coulomb and impurity effects.

Besides the graphs shown in Eq. (9.40-9.42), it is appropriate to consider graphs like

$$(a) \quad (b) \quad (c) \quad (9.43)$$

These have phonon lines crossing each other. Migdal [23] has shown that each graph of this kind is negligible in comparison to a similar but uncrossed graph which is already contained in Eqs. (9.40-9.42). This situation, known as Migdal's "theorem", is special to the electron-phonon problem, and is related to the smallness of a parameter sometimes denoted $(m/M)^{1/2}$, but more properly denoted as $N(\varepsilon_F)\hbar\omega_D$.

Next consider the case of an ordinary pairwise Coulomb interaction as in Eq. (9.34). There is an important set of terms which is the analog of Eqs. (9.40-9.42).

$$\chi_p = \text{---} \text{---} + \text{---} \text{---} + \text{---} \text{---} + \dots \quad (9.44)$$

$$\text{---} \text{---} = \text{---} \text{---} + \text{---} \text{---} \quad (9.45)$$

$$\text{---} \text{---} = \text{---} \text{---} + \text{---} \text{---} \quad (9.46)$$

Equation (9.46) is the Coulomb interaction screened in random phase approximation (RPA), and Eq. (9.45) represents the "screened exchange" approximation to the electron quasiparticle states. Formal answers can be written for the theory at this level, but evaluation of these formal expressions for real materials is very difficult. To make matters worse, none of the graphs analogous to Eq. (9.43) are *a priori* negligible. Formally one includes many of these by inserting "vertex functions" into Eqs. (9.45) and (9.46), making them "formally exact". Like Eq. (9.42), Eq. (9.46) and to some extent Eq. (9.45), correspond to measurable spectral properties, but such measurements are normally done only in limited

spectral ranges. Thus we often must guess at the appropriate screening function and quasiparticle energies, using LDA (local density approximation) band theory as an imperfect guide.

Finally, consider a generalization of the graphs like (9.43a), that is, "maximally-crossed" graphs.

$$(9.47)$$

If we redraw the graphs, they simplify as in

$$(9.48)$$

There is a piece of this graph which is very closely akin to the transverse magnetic susceptibility χ_{+-} ,

$$\chi_{+-}(Q, \omega) = -i \sum_{k, k'} \int_0^{\infty} dt e^{i\omega t} \langle [c_{k+Q\uparrow}^{\dagger}(t) c_{k\downarrow}(t), c_{k'\downarrow}^{\dagger} - Q\downarrow(0) c_{k'+Q\downarrow}(0)] \rangle \quad (9.49)$$

$$\chi_{+-} = \text{[Diagram 1]} + \text{[Diagram 2]} + \dots \quad (9.50)$$

In the paramagnetic state, χ_{+-} is equivalent to the longitudinal susceptibility χ_{zz} , which for $Q \rightarrow 0$, $\omega \rightarrow 0$ is the measured $\chi = \partial M / \partial B$. Experiment shows that some metals such as Pd have large values of χ corresponding to incipient ferromagnetism. The ladder series (9.50) contains a mechanism for the enhancement, but it is not possible to prove that other graphs are insignificant. In simple models [24] this series (9.50) can be evaluated, and $\text{Im}\chi_{+-}(Q, \omega)$ shows peaks which are well-enough defined to be given a name, "paramagnons". These "particles" have not been easy to find by neutron scattering experiments. If we bend the graph (9.48) yet again, it looks like

$$(9.51)$$

This graph is interpreted physically as a pair of electrons exchanging a paramagnon and flipping their spins. This is a well-defined event in metallic ordered magnets such as rare earth elements where itinerant nonmagnetic electrons interact with the ordered spin array of the localized f electron system, but it is a fairly fuzzy event in a paramagnet. Nevertheless, paramagnons provide a potentially useful physical concept. Unfortunately there are many other high-order terms in perturbation series related to (9.51) but not easily summable. Paramagnon theory is not especially well-defined. At some point we are forced to stop looking for more graphs, sum up what we have, and hope to explain T_c . Spin fluctuation graphs of the type in Eq. (9.51) are harmful to singlet superconductivity, and this explains the absence of superconductivity in Pd. The basis for phonon mechanisms as well as plasmon, exciton, and weak-coupling spin-fluctuation mechanisms are all in Eq. (9.35) and its graphical expansion. Only for the phonon part does the perturbation series converge rapidly enough to be treated rigorously.

9.6. The BCS ground state

A collective pair condensate should have a wave function of the kind

$$\Psi_0 = \mathcal{A} \{ \psi(r_1, r_2) \psi(r_3, r_4) \dots \psi(r_{N-1}, r_N) \} \quad (9.52)$$

where ψ is a pair function like Eq. (9.2) and \mathcal{A} denotes antisymmetrization. In fact, the BCS wavefunction has this form [25] but it is usually written in a very different way. Notice that the electronic wavefunction for $N/2$ ^4He atoms would have the same form. Equation (9.52) is even under exchange of pairs of indices such as $(1,2) \leftrightarrow (3,4)$. Thus Eq. (9.52) can describe composite Bosons, but in the BCS case, different ψ 's so strongly overlap that such an interpretation is not very appropriate.

By analogy with Eq. (9.2), (9.52) can be rewritten as

$$|\Psi_0\rangle = \left(\sum_k g(k) c_{k\uparrow}^{\dagger} c_{-k\downarrow}^{\dagger} \right)^{N/2} |0\rangle \quad (9.53)$$

where $|0\rangle$ is the vacuum. Because of the anticommutation relations

of the c_k^+ 's, this state is fully antisymmetric, but unfortunately very awkward for calculations. Therefore a trick is used:

$$|\Psi_{BCS}\rangle = \exp\left(\sum_k g(k) c_{k\uparrow}^+ c_{-k\downarrow}^+\right) |0\rangle \quad (9.54)$$

The series expansion of the exponential in (9.54) contains the term (9.53) and many others with all possible exponents n . Only if Eq. (9.54) is dominated by terms with $n \approx N/2$ does it make a sensible approximation to Eq. (9.53).

The next trick is to rearrange (9.54)

$$\begin{aligned} |\Psi_{BCS}\rangle &= \prod_k \exp(g(k) c_{k\uparrow}^+ c_{-k\downarrow}^+) |0\rangle \\ &= \prod_k (1 + g(k) c_{k\uparrow}^+ c_{-k\downarrow}^+) |0\rangle \end{aligned} \quad (9.55)$$

where the last line of (9.55) is an exact consequence of the fact that $(c_{k\uparrow}^+ c_{-k\downarrow}^+)^2 = 0$. To normalize Eq. (9.55), each factor $(1 + g(k) c_{k\uparrow}^+ c_{-k\downarrow}^+)$ should be divided by $(1 + |g(k)|^2)^{1/2}$. To retrieve the ground state of a normal metal, choose $g(k) \rightarrow \infty$ for $\epsilon_k < \epsilon_F$ and $g(k) = 0$ for $\epsilon_k > \epsilon_F$. The probability that a state k is occupied is $n_k = |g_k|^2 / (1 + |g_k|^2)$, the mean number of electrons is $2\sum_k n_k = \langle N \rangle$ and the rms fluctuation $[\langle N^2 \rangle - \langle N \rangle^2]^{1/2}$ is $2[\sum_k n_k(1 - n_k)]^{1/2}$ which is less than $\sqrt{2N}$, i.e. small enough to justify using (9.54) in place of (9.53).

Equation (9.55) is the standard form of the BCS wavefunction. It is very convenient for calculations. The $g(k)$'s are treated as variational parameters, and turn out all to have the same phase, $g(k) = |g(k)|e^{i\phi}$. The amplitude for having exactly $2n$ electrons has phase $n\phi$. The phase difference between the component of Ψ with n pairs and the component with $n + 1$ is always ϕ . This phase coherence is an essential property, leading directly to the possibility of supercurrents $\mathbf{j}_s \propto \nabla\phi$.

Further details on the ground state and excited states are available in many texts, e.g., Rickayzen [19].

9.7. Off-Diagonal Long Range Order (ODLRO)

The essence of BCS theory is the pairing instability and the formation of a coherent pair condensate. Yang [17] attempted to answer a deeper version of this question: What is the essence of superconductivity which has somehow been correctly captured by BCS theory? His answer is that it is ODLRO, a property of the reduced density matrix. The functions are defined

$$f_1(r, r') = \text{tr}[\hat{\rho} \hat{\psi}^+(r) \hat{\psi}(r')] \quad (9.56)$$

$$f_2(r, r') = \text{tr}[\hat{\rho} \hat{\psi}_\downarrow^+(r) \hat{\psi}_\uparrow^+(r) \hat{\psi}_\uparrow(r') \hat{\psi}_\downarrow(r')] \quad (9.57)$$

where $\hat{\rho}$ is the density matrix, equal to $e^{-\beta H}/Z$ in equilibrium, where $Z = \text{tr} e^{-\beta H}$. The operator $\hat{\psi}_\sigma(r)$ creates a particle of spin σ at position r . By way of contrast, consider a correlation function

$$g(r, r') = \text{tr}[\hat{\rho} \delta \hat{n}(r) \delta \hat{n}(r')] \quad (9.58)$$

where $\delta \hat{n}$ is the deviation of the particle density from its average value

$$\delta \hat{n} = \sum_\sigma \hat{\psi}_\sigma^+(r) \hat{\psi}_\sigma(r) - \bar{n} \quad (9.59)$$

In a liquid, $g(r, r') \rightarrow 0$ as $|r - r'|$ gets large, but in a solid, $g(r, r') \rightarrow \langle \delta n(r) \rangle \langle \delta n(r') \rangle$ which remains non-zero for large $|r - r'|$. This is an example of long-range order. If f_1 or f_2 [Eqs. (9.56), (9.57)] should remain finite as $|r - r'|$ gets large, this would be an expression of ODLRO, a purely quantum effect involving off-diagonal elements of the density operator which have no classical analog. Yang showed that $f_1(r, r')$ cannot remain finite at large $|r - r'|$ in a system of Fermions, but in a Bose condensate, f_1 becomes $\langle \psi^+(r) \rangle \langle \psi(r') \rangle$ which is nonzero at large separations. Similarly for a normal metal, f_2 goes to zero at large $|r - r'|$ whereas in a BCS superconductor, f_2 becomes $\langle \psi_\downarrow(r) \psi_\uparrow(r) \rangle \langle \psi_\downarrow(r') \psi_\uparrow(r') \rangle$ which is not zero. To be specific, since

$$\psi_\uparrow(r) = \sum_k \psi_k(r) c_{k\uparrow} \quad (9.60)$$

the pair amplitude has expectation value

$$\langle \psi_\uparrow(r) \psi_\downarrow(r) \rangle = \sum_k |\psi_k(r)|^2 g(k) / (1 + |g(k)|^2) \quad (9.61)$$

This has phase ϕ , and vanishes in the normal state.

Yang made the following statements based on either proofs or plausible conjectures: (a) There is only one route by which f_1 or f_2 exhibit ODLRO and this route is chosen by the ideal Bose gas (for f_1) and by the BCS superconductor (for f_2). (b) The existence of ODLRO is a sufficient condition for quantization of magnetic flux, the quantum being hc/e or $hc/2e$ depending on whether f_1 or f_2 exhibits ODLRO. (c) From flux quantization, the Meissner effect and superconductivity are almost certainly derivable.

statements it is expected that ODLRO will be a property not only of BCS superconductors, but of any alternate type of superconductivity which may be found. In the "RVB" picture to be described later, Anderson conjectures a ground state with ODLRO. As a counter-example, Fröhlich [26] made a very interesting theory of a one-dimensional "superconductor" based on an incommensurate charge-density-wave (CDW) distortion which introduced a gap at the Fermi surface. Because of incommensurability, the CDW is free to slide in a perfect crystal, carrying current in a collective way. The effect is realized in such materials as NbSe₃. Unfortunately, perfect conductivity is destroyed by even a small number of impurities (as it is also in a pure non-superconducting metal at $T = 0$). In fact the impurities pin the CDW giving zero conductivity unless the field is big enough to de-pin the CDW. The missing ingredient in Fröhlich's theory (and also in a perfect normal metal at $T = 0$) is ODLRO.

9.8. Eliashberg Theory of Electron-Phonon Superconductors

This is a much studied subject with a recent review [5] so this section will be a series of comments.

(a) The basic equations can be derived from Eqs. (9.40-9.42) and (9.44-9.46). The interaction is both r and ω dependent. The Coulomb interaction in first approximation is

$$V_c = \langle k' \uparrow, -k' \downarrow | \int d\mathbf{r}'' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}'', \omega) e^2 / |\mathbf{r}'' - \mathbf{r}'| | k \uparrow, -k \downarrow \rangle \quad (9.62)$$

and is repulsive over a large fraction of (r, r', ω) -space. The electron-phonon interaction is

$$V_{ph} = 2 |M_{kk'}|^2 \hbar \omega_{k-k'} / \hbar^2 [\omega^2 - \omega_{k-k'}^2] \quad (9.63)$$

and is attractive when $\omega^2 < \omega_{k-k'}^2$. The dimensionless parameters λ and μ are defined by Fermi surface averages

$$-\lambda = N(\varepsilon_F) \langle V_{ph}(k, k', \omega=0) \rangle, \quad (9.64)$$

$$\mu = N(\varepsilon_F) \langle V_c(k, k', \omega=0) \rangle. \quad (9.65)$$

Note that (9.64) is identical to Eq. (9.8).

(b) In a naive BCS approach one would expect

$$T_c(\text{BCS}) = \Theta \exp(-1/(\lambda - \mu)) \quad (9.66)$$

In an approximate treatment of Eliashberg theory [27] one gets

$$T_c(\text{McMillan}) = \Theta \exp \left[-1 / \left(\frac{\lambda}{1 + \lambda} - \mu^* \right) \right], \quad (9.67)$$

$$\mu^* = \mu / (1 + \mu \log(\varepsilon_F / \hbar \omega_D)) \quad (9.68)$$

The parameter λ is "renormalized" by the factor $(1 + \lambda)^{-1}$ which enters via Eq. (9.41). The parameter $\mu \approx 1$ is "renormalized" to $\mu^* \approx 0.1$ by an entirely different effect: The slow propagation of phonons (retardation) allows electrons to interact without being close at the same time, thus reducing the Coulomb repulsion.

(c) The parameter λ ranges from 0.1 (Cu, Na) to 1.5 (Pb) or even larger (≥ 2 in amorphous Pb/Bi alloys). When $\lambda \geq 1.2$, the form of Eq. (9.67) starts to fail; after a wide crossover region, the asymptotic regime with $T_c \propto \sqrt{\lambda}$ occurs (with $\lambda \geq 10$, an apparently unrealistic case) [28].

(d) Detailed, first principles calculations of T_c are still quite unreliable because of the difficulty of calculating ω_Q . If ω_Q is known from experiment, the reliability of theory is not bad.

(e) T_c is bounded above by $0.18 \sqrt{\lambda \langle \omega^2 \rangle}$. This can also be expressed as $0.18 \sqrt{\Sigma_a \eta_a / M_a}$, where a runs over atoms of mass M_a and η_a is the "McMillan-Hopfield parameter". Although values of T_c as large as 100 K are allowed, this would require fairly extreme choices of η_a and M_a .

(f) A practical limit to T_c is apparently set by problems of structural stability [29]. As Eq. (9.42) suggests, strong electron-phonon coupling drives phonon frequencies down, risking a second order instability. First order instabilities are probably more serious, but very difficult to anticipate theoretically.

(g) Although most high T_c superconductors are quite anharmonic for reasons given in (f), there is little evidence to suggest that anharmonicity *per se* affects T_c beneficially or adversely relative to a corresponding harmonic solid with equivalent vibrational frequencies. Anharmonic effects to a large degree are absorbed into the structure of Eliashberg theory with no experimentally detectable change [30].

(h) The new oxide superconductors probably can not be explained on the basis of electron-phonon theory. This is suggested by isotope effect measurements, attempts to calculate T_c , and past experience on the difficulty of getting high T_c by this mechanism.

(i) On the other hand, a very small isotope shift by no means proves anything. A nice analysis is by Pines and Coleman [31].

PdD has a higher T_c than PdH (reverse isotope effect) and yet is believed to be electron-phonon induced with a healthy $T_c \sim 12$ K.

9.9. Excitons and Plasmons

Given that known electron-phonon superconductors all have $T_c < 23$ K, it is logical to look for new mechanisms if higher T_c 's are wanted. It is also logical to blame low T_c 's on the low energy $\hbar\omega_D$ of the phonon. This immediately suggests that a higher-energy Boson might act in place of (or in addition to) phonons, yielding a higher T_c . The subject has been nurtured by Little [32] and Ginzburg [33]; recent reviews are by Ginzburg and Kirzhnits [34], Ruvalds [35], and Little [36]. Since they have been the target of some ridicule (Matthias [37]), it is appropriate to acknowledge that their optimism (although not yet their specific mechanisms) has now been validated.

When a test charge is inserted into a solid, three kinds of distortion occur: The lattice distorts (virtual phonons), the electrons can repopulate any partly filled band (virtual plasmons), or they can mix in components from higher unfilled bands (virtual excitons). The words "plasmon" and "exciton" are used quite loosely here. To a spectroscopist, an exciton is a narrow resonance in $\text{Im}\epsilon$, and a plasmon is a narrow peak in $-\text{Im}\epsilon^{-1}$. Most of the spectral weight is not in narrow peaks, but broadly distributed in ω . It is necessary to use all this broad structure to get a significant interaction, and the usage of the terms "exciton" and "plasmon" is correspondingly broadened. If the test charge is time-dependent (for example, moving) then these distortions follow in time, with a lag which is larger for a lattice distortion than electronic distortions. A second test charge will feel both the direct instantaneous repulsion of the first test charge and a time-dependent attraction from these dynamical distortions. The usual Eliashberg picture assumes that electronic polarization serves only to cancel part of the direct Coulomb repulsion, and that only phonon polarization is sufficiently strong and retarded to contribute to pair binding. Thus a reasonable question is whether, in the absence of phonons, the other polarization mechanisms can (in principle) cause superconductivity.

9.9.a. Plasmons

Rietschel and Sham [38] have answered this question affirmatively for the free electron gas using the RPA (Lindhard) version of ϵ ; i.e. for the plasmon mechanism. Their numerical calculations use

the full (\mathbf{k} and ω -dependent) Eliashberg equations with no other interaction besides $\epsilon^{-1}(Q, \omega)v(Q)$. This is always repulsive (positive) for $\omega = 0$, but has an attractive region for $\omega_{\min} < \omega < \omega_p$ and Q/k_F not too large. Their results depended sensitively on the density of the electrons, expressed by the parameter $r_s = 1.92/a_B k_F$. For $r_s < 3$, superconductivity does not occur; at $r_s = 4$, T_c is ~ 0.3 mK, and at $r_s \approx 5$, T_c is ~ 0.22 K. This result is surprising for two reasons. First, ω_p is so large ($\hbar\omega_p/\epsilon_F = 0.94\sqrt{r_s}$) that no simple scenario based on retardation can make this seem intuitively necessary. It is a source of optimism that electronic pairing is sufficiently versatile to take successful advantage of the limited attractive part of (\mathbf{q}, ω) space. Second, alkali metals and noble metals are not superconducting. It is difficult to see how the less dense alkalis with $4 < r_s < 6$ could fail to superconduct given both plasmon and phonon attraction, unless something else occurs to cancel the plasmon attraction.

This question has been further addressed by Grabowski and Sham [39], who approximately include the effects of the lowest order vertex corrections and the graph with crossed Coulomb interactions. The solution of Rietschel and Sham is totally altered by these corrections, and the net effective interaction becomes again repulsive. One lesson to be drawn from this is that superconductivity induced by high energy Bosons is difficult to predict because results are very model-sensitive. We are unable to calculate interactions to the necessary accuracy. Grabowski and Sham conclude with the remark, "One or two tens of degrees Kelvin in the increase of T_c above that due to phonon attraction appears possible, but a T_c higher than the liquid nitrogen temperature appears impossible by purely raising the Boson energies." Of course, now that T_c exceeds 100 K, it might be appropriate to rethink this conclusion.

For metals more complicated than alkalis, band effects become significant and the free-electron model becomes less relevant and possibly misleading. One measure of this is the f -sum rule, an exact relation for any system:

$$\frac{2}{\pi} \int_0^\infty d\omega \omega \epsilon_2(\omega) = \frac{4\pi n e^2}{m} \quad (9.69)$$

On the right of (9.69) n is the total number of electrons (including core electrons) and m is the free electron mass. In many cases it is reasonable to integrate the left hand side up to an energy less than the minimum for core electron excitation, and to use for n on the right the valence electron density. In band theory, $\epsilon_2(\omega)$ has two distinct parts, a Drude region representing acceleration of electrons within partially filled bands ($\hbar k = -eF$) and an interband

term. These can be separately calculated; results are given in Table 9.1 for representative cases. In the first column, Ω_p^2 is the contribution to the integral (9.69) from the Drude part of ϵ_2 . The last column gives the fraction of the spectral weight which is in the intraband (Drude) channel. As materials become more complicated there are more bands at a given k and less room for Drude-like behavior. The result for La_2CuO_4 is not pathological, but typical of a complicated metal; the calculation assumes La_2CuO_4 is metallic rather than semiconducting and that \mathbf{E} is polarized in the metallic a - b plane. Table I shows that most of the electronic polarizability of complicated materials is in "exciton" (interband) rather than "plasmon" (intraband) form.

There have been proposals that the nearly $2d$ plasmons of quasi- $2d$ metals like La_2CuO_4 are especially beneficial for superconductivity, but so far there is no convincing calculation of this, even for an electron gas, let alone a real material with interband dominance.

9.9.b. Excitons

Crudely speaking, two versions of this idea exist. Allender, Bray, and Bardeen (ABB, [43]) proposed getting a metal into such intimate contact with a polarizable, narrow gap semiconductor that the metallic electrons would be able to interact strongly with interband excitations of the semiconductor. Pairing would then occur by exchange of these virtual excitations. It was not proposed that the electron-hole pairs should be required to bind to each other to form Wannier excitons. Instead the word "exciton" is used loosely to describe the sort of virtual excitation involved in the polarization of a valence band.

The exciton mechanism, like the plasmon mechanism, surely

Table I. The Drude plasma frequency Ω_p for Al and Nb [40], Nb_3Ge [41], and La_2CuO_4 [42]. The free electron values ω_p are based on the assigned valences: $\text{Al}(3)$, $\text{Nb}(5)$, $\text{Ge}(4)$, $\text{La}(3)$, $\text{Cu}(11)$, and $\text{O}(6)$.

	$\hbar\Omega_p(\text{eV})$	$\hbar\omega_p(\text{eV})$	$(\Omega_p/\omega_p)^2$
Al	12.4	15.8	0.62
Nb	9.1	19.6	0.22
Nb_3Ge	3.7	19.5	0.04
La_2CuO_4	3.0	17.2	0.03

exists, and helps in the sense that it weakens the direct Coulomb repulsion of electrons. Unlike the plasmon in the free electron gas studied by Sham *et al.*, there is no obvious simple model system which should be subjected to rigorous theoretical investigation. The merit of the ABB paper was that it proposed a testable mechanism involving thin metal layers on semiconductor surfaces. Careful experiments by Miller *et al.* [44] did not see the effect. Inkson and Anderson [45] thought the ABB estimates for T_c were much too high, and that no significant improvement of T_c ought to occur by this scheme.

The other version of this idea is in the original paper by Little [32]. It is almost the same as the ABB mechanism except it is presumed that it is better *not* to have intimate contact between the electrons involved in pairing and the entity undergoing electronic polarization. Spatial separation should reduce the interaction strength, but even at 14 \AA , e^2/r is 1 eV if unscreened. Separation eliminates exchange interactions between Cooper pairs and polarizing electrons, which otherwise would reduce the attraction. Little also proposed looking in $1d$ organic systems with polarizable side chains. In recent years superconductivity has been found in $1d$ "organic" metals [6] but these do not look much like Little's proposal. Two dimensions is probably more favorable, and Little [36] proposes that the out-of-plane oxygen-copper bonds may be the polarizing entity.

9.9.c. Excitonic Insulator

If a semiconductor has a very narrow indirect gap, then in principle electrons could be promoted across this gap, motivated by the possibility that they could gain more energy by binding to the holes left behind than they lost in promotion energy. This is called the "excitonic insulator" phase [46]. Lo and Wong [47] proposed that additional carriers in such a system might be superconducting. Abrikosov [48] pointed out that a phase related to the excitonic insulator could be a candidate for a high T_c superconductor, namely one where instead of an exciton condensate, the heavy holes crystallized and the light electrons paired by exchanging "phonons" of the hole lattice.

9.10. Spin Fluctuations

In a magnetic medium, a free electron can scatter off the spin system, emitting a spin wave. Superconducting systems are generally not magnetically ordered, except perhaps at low temperatures.

T_c as in rare-earth-substituted $\text{YBa}_2\text{Cu}_3\text{O}_7$ (see Chapter 8). An exception is URu_2Si_2 [49,50], and superconductivity in this heavy Fermion metal may be caused by exchange of antiferromagnetic spin fluctuations. A more common situation is for a metal to be close to magnetic ordering when becoming superconducting. In this situation one expects to have relatively long-lived local spin fluctuations, for example, locally ferromagnetic regions in a ferromagnet above its Curie temperature, or in a metal like Pd which is an incipient ferromagnet. The scattering of electrons from these fluctuations will alter the tendency to form pairs. Usually this alteration has been assumed to be harmful. Pd is not superconducting even though the value of λ is probably $\sim 0.3 - 0.5$. The reason almost certainly is that a spin up electron will attract other electrons of up spin, creating a locally ferromagnetic region, and repelling the down spin electron needed for singlet Cooper pairing. This is shown diagrammatically in Eq. (9.51). Clearly this same process should be helpful to triplet pairing, and is believed to be an important source of triplet pairing in liquid ^3He . So far there is no proof that any metal has a triplet pairing state, although UPt_3 and other heavy Fermion systems, as well as some "organic" superconductors, are possible candidates. These candidates all have a low T_c .

Antiferromagnetic spin fluctuations are a more complicated situation [51-53]. It is not so obvious whether an up spin electron will create or destroy local antiferromagnetic polarization, or whether this will attract or repel other electrons of opposite (or parallel) spin. Different answers seem to emerge in different regions of k -space and r -space. These questions were first raised because of the experimental discovery of closely related antiferromagnetic and superconducting states in organic metals, and then in heavy Fermion metals. Recently they have acquired a new urgency because of the discovery of antiferromagnetism in $\text{La}_2\text{CuO}_{4-y}$ [54] and $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ [55] (see Chapter 8).

An interesting simple scenario has been proposed by Schrieffer et al. [56]. The idea is that free carriers in a material wanting commensurate antiferromagnetism will weaken the tendency to order (for example, by changing the Fermi surface "nesting" property in $\chi(Q)$). Thus an up-spin electron repels local spin order. Other free carriers, with either spin orientation, will be attracted to the region of depleted spin, (called a "spin bag") giving a net attractive interaction.

9.11. Weak versus Strong Coupling

All mechanisms discussed so far are derivable by perturbation theory starting from a normal

Fermi liquid reference state; in other words, they are in the "weak" regime. It is conventional to call Pb a "strong coupling" superconductor because with $\lambda \sim 1.5$ it exhibits deviations from "normal" BCS-like behavior ($2\Delta/k_B T_c > 3.52$, etc.). But in the sense used in this section, Pb is "weak". An example of "strong" would be ^3He viewed as a collection of electrons and nuclei. At $T \sim 10^6$ K, one would have a plasma of electrons and ^3He nuclei; at high enough densities this would give two interpenetrating quantum Fermi liquids. This would be the wrong Fermi liquid starting point for a perturbative theory of superfluidity in liquid ^3He at 10^{-3} K.

By analogy, exotic forms of superconductivity could emerge in solids from highly correlated electronic states which are not describable as ordinary Fermi liquids. Bipolaronic and RVB superconductors are such proposals, and will be described in subsequent sections. Neither of these yet constitutes a full theory in the way that BCS is for Fermi liquids. One can imagine scenarios in which the final superconducting state looks BCS-like, and others in which it doesn't. For example, the ^3He case just described starts at very high T and P as a Fermi liquid, and ends at very low T and P looking BCS like, with a low T Fermi liquid in between, and two crossover regions, one between plasma and ^3He vapor, and one between ^3He vapor and normal Fermi liquid ^3He (at $T \lesssim 1$ K). But ^4He presents an alternate scenario, ending with a Bose condensate which would be superconducting if endowed with an extra hidden charge to couple it to external E-fields. This superconductor would not look BCS like, and at T_c the superconducting state would evolve into a normal Bose liquid.

Presumably all states share the property of ODLRO, and show flux quantization, the Meissner effect, and supercurrents. Even if the oxide superconductors turn out to be in the weak regime, they have enlarged our vision, and a search for strong superconductors will endure.

9.12. Bipolarons

In Sec. 9.2 the Cooper problem was addressed and solved in two limits: The usual Cooper limit [$\epsilon_F \gg E_B$, $\epsilon_F \gg \Theta$] and the dilute limit [$\epsilon_F \ll E_B$, $\epsilon_F \ll \Theta$]. In the latter case electrons form mobile bound pairs provided the attractive interaction is strong enough to support a bound state (which requires a critical strength in three dimensions). The "bipolaron" is just such a mobile bound pair of electrons, bound by electron-phonon interactions. There is no unambiguous evidence that bipolarons exist in any known solid, but a plausible case has been made [57] that the metal-insulator transitions seen in TiO_2 at 140 K and 150 K could be described as

bipolaronic. Specifically it is assumed that as T is reduced, Ti atoms form dimers of Ti^{3+} (one dimer, on average, per cell, with two undimerized Ti^{4+} atoms per cell). At 150 K the dimers form in a disorganized, liquid form, and at 140 K these pre-formed dimers crystallize into a relatively normal insulating phase. In the "liquid" phase between 140 and 150 K one has pairs of electrons bound to pairs of Ti^{3+} ions and free to move by breaking bonds and forming new ones neighboring undimerized Ti^{4+} atoms which then form new dimer bonds. Later Chakraverty [58] proposed that in the liquid state the bipolarons could Bose condense to form a new kind of superconductor.

Actually this kind of superconductivity is not a new idea. Ogg [59] mistakenly believed that he had seen high T_c superconductivity in metal-ammonia solutions. His explanation was that free electrons might prefer to pair in cavities in NH_3 , and could then Bose-condense. The idea is identical to more modern proposals. Another precursor of BCS theory [60] involved Bose-condensed electron pairs and subsequently it has been shown that much of BCS theory can be re-cast in this form. Leggett [61] worked out a model showing the crossover from BCS condensation to Bose condensation of molecular pairs. Other oxides besides Ti_4O_7 have provoked theoretical speculation about bipolarons. SrTiO_3 supports superconductivity when doped n -type with n as low as $10^{19}/\text{cm}^3$, possibly the most dilute superconductor known, and thus a natural suspect for bipolaronic effects.

A case closely related both to Ti_4O_7 and to CuO-based superconductors is $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ which is insulating when $x > 0.35$ and superconducting for $x < 0.35$, with a surprisingly high $T_c \sim 15$ K occurring close to the phase boundary. Rice and Sneddon [11] proposed that the superconducting phase was normal BCS and electron-phonon driven, but with increasing x and increasing electron-phonon coupling, "real-space pairing" took over and created an insulator. The real-space pairs are hypothesized to consist of pairs of electrons bound to pairs of Bi atoms making Bi^{3+} - Bi^{5+} frozen dimers, i.e. another kind of bipolaronic crystal.

It is possibly accidental but nevertheless interesting that the idea of bipolaronic superconductivity, specifically in Jahn-Teller distorted systems, is part of what motivated Bednorz and Müller [62] to search for superconductivity in CuO-based systems. Scalapino *et al.* [63] argue that CuO-based superconductivity may be electron-phonon driven, and on the border between bipolaronic and BCS-like.

Finally, a related notion is the Anderson "negative- U " center, an isolated but immobile bipolaron. An example is a vacancy in crystalline Si, which has a stable neutral configuration; when a

atomic rearrangement occurs which makes it energetically favorable for a second electron (of opposite spin; a singlet pair) to bind to the same site. The lattice relaxation overcomes the Coulomb repulsion, as if there were a negative value for the on-site "Hubbard" Coulomb repulsion U . This idea was originally proposed by Anderson [64]. It was suggested [65,66] that if such sites occurred in a superconducting metal, T_c would be enhanced by the additional binding available if Cooper pairs temporarily fell into negative- U centers. This creates a difficult theoretical problem, being a hybrid of a perturbative BCS problem and a local non-perturbative problem with an internal dynamical degree of freedom (the lattice distortion). Schüttler *et al.* [67] claim to have made some progress by numerical methods and to verify that the enhancement is significant.

9.13. The Hubbard Model in Strong Coupling

The best evidence that superconductivity in CuO-based superconductors has something to do with the Hubbard model comes from diffraction experiments showing ordered antiferromagnetism in La_2CuO_4 [54] and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [55] (see Chapter 8). In this section the Hubbard model will be discussed for large U and nearly half-filling. In particular, the relation to a Heisenberg antiferromagnet will be explained. Anderson [1] has recently reviewed this subject.

The Hubbard model is defined by three specifications: (1) a Hamiltonian

$$H = t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (9.70)$$

(2) a lattice which defines the pattern of bonds $\langle ij \rangle$ on which the electrons can hop with matrix element t , and (3) a filling factor x , which I define such that $x = 0$ is the half-filled case (a standard reference point) and x counts the number of holes as in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The Coulomb energy U inhibits double occupancy. I now state what can be called the "Hubbard" hypothesis:

"Hubbard" Hypothesis: The fundamental physics of the oxide superconductors is contained in the Hamiltonian (9.70) on a 2-d square lattice for small numbers of holes $0 \leq x \leq 0.2$.

Since the properties of the Hubbard model in this limit are not yet under good theoretical control, there is no proof or disproof, and testing the hypothesis is regarded as a low issue. Many people

suspect that it is wrong, but that a modified Hubbard hypothesis (with added features such as electron-phonon effects, two bands, or next neighbor interactions) is right, with superconductivity still driven by the Coulomb U term. This does not diminish the urgency of testing the simple hypothesis because it may be impossible to work out the consequences of modifications without first having a better understanding of the unmodified model.

There are various versions of the Hubbard Hypothesis, some of which claim ultimately to give "weak" superconductivity via spin fluctuations. In this section and the next I will focus on versions which hope to generate "strong" superconductivity, by first condensing into a new state (claimed by Anderson [68] to be a "resonating valence-bond" (RVB) state). This new state is not a conventional Fermi liquid, so the low T superconducting condensate is not conventional BCS.

One approach to understanding the strong-coupling Hubbard model is exact diagonalization of finite-size systems. Let us consider the $x = 0$ case. With one site and one electron there are two states, \uparrow and \downarrow , both having zero energy. With two sites and two electrons there are six states, each described by a Slater determinant: $|1\rangle = (1\uparrow, 1\downarrow)$, $|2\rangle = (2\uparrow, 2\downarrow)$, $|3\rangle = (1\uparrow, 2\downarrow)$, $|4\rangle = (1\downarrow, 2\uparrow)$, $|5\rangle = (1\uparrow, 2\uparrow)$, and $|6\rangle = (1\downarrow, 2\downarrow)$. If t is neglected compared to U , H is diagonal in this basis. States 1 and 2 have energy U , and 3-6 have energy 0. After t is turned on, a triplet of states of energy 0 remains, $(|5\rangle, |6\rangle, \text{and } 2^{-1/2}(|3\rangle + |4\rangle))$ and one state, $2^{-1/2}(|1\rangle - |2\rangle)$, has energy U . The singlet state plays a special role:

$$|\text{VB}\rangle = 2^{-\frac{1}{2}}(1\uparrow 2\downarrow - 1\downarrow 2\uparrow) = 2^{-\frac{1}{2}}(|3\rangle - |4\rangle) \quad (9.71)$$

It is a Heitler-London "valence bond" state. Two eigenstates are mixtures of $|\text{VB}\rangle$ and ionized states $2^{-1/2}(1\uparrow 1\downarrow + 2\uparrow 2\downarrow)$, with eigenvalues $U/2 \pm \sqrt{(U/2)^2 + 4t^2}$. For $t \ll U$, the ground state is the $|\text{VB}\rangle$ state with a weak admixture of ionized states, and the energy is $-4t^2/U$.

As the number of "atoms" N increases, the size of the space grows rapidly, as $(2N)/(N!)^2 \sim 4^N$. Of these, exactly 2^N correspond to states with only one electron per site, giving a 2^N -fold degenerate ground state of energy 0 when $t = 0$. These states (denoted $|\Sigma\rangle$) are characterized by the spin orientation on each site. It is this very large ground state degeneracy which makes the problem so interesting and difficult.

For even a modest nine atom (3×3) $2d$ array, direct diagonalization of the 48,620-order matrix is not easy. A considerable simplification occurs if t is small, and the problem is truncated to the 2^N -order space (512 for $N = 3 \times 3$) of singly occupied

states. This truncated problem has spins at each site but no "charge" degrees of freedom. Hence it describes an insulator, as is reasonable for small enough t/U . The H -matrix is 0 in this truncated basis, and it is necessary to do first order degenerate perturbation theory in the parameter t/U . This introduces matrix elements

$$\langle \Sigma' | H_{\text{eff}} | \Sigma \rangle = \sum_n \frac{\langle \Sigma' | H | n \rangle \langle n | H | \Sigma \rangle}{E_0 - E_n} \quad (9.72)$$

between the states $|\Sigma\rangle, |\Sigma'\rangle$ of the singly occupied subspace $E(\Sigma) = E_0 = 0$. The intermediate states $|n\rangle$ always have one site doubly occupied ($E_n = U$). The resulting matrix (9.72) turns out to be the same as the matrix of

$$H_{\text{eff}} = J \sum_{\langle ij \rangle} (\sigma_i \cdot \sigma_j - \frac{1}{4}) \quad (9.73)$$

where $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices. When applied to the two-site problem, (9.73) has eigenvalues 0 (triply degenerate) and $-J$ (singly degenerate) leading to the identification $J = 4t^2/U$. The additive constant $-J/4$ per bond is then dropped from (9.73), which is the antiferromagnetic Heisenberg Hamiltonian. In a three-dimensional simple cubic lattice, (9.73) has an antiferromagnetically ordered low temperature phase (the "Neel" state), a phase transition at $T_N \sim J$, and a high temperature paramagnetic phase with disordered local moments. This is believed to provide a correct qualitative description for systems such as NiO and CuO which are antiferromagnetic insulators at low T and remain insulating even above T_N irrespective of whether the number of electrons per unit cell is even or odd. (Alternative descriptions also exist for NiO, etc; spin-density-functional band theory captures at least some of the physics correctly (see [69])).

In one dimension, the Heisenberg antiferromagnet has no long range spin order, even at $T = 0$. The ground state is given by the famous "Bethe ansatz" [70,71], and is very complicated. It is easy to see why ordered spins are not favored, by making variational estimates of ground state energies using simple trial wavefunctions. The simple antiferromagnetic state $|\text{Neel}\rangle$ is $|1\uparrow, 2\downarrow, 3\uparrow, 4\downarrow, \dots\rangle$ and has energy per site $-J/4$, which is also the energy per bond, and comes entirely from the $s_{iz}s_{jz}$ part of (9.73). A "valence bond" state $|\text{VB}\rangle$ of the form $|\text{VB}(1,2), \text{VB}(3,4), \dots\rangle$ does better. Each valence bond has energy $-3J/4$, with equal contributions from the three Cartesian components $s_{iz}s_{j\alpha}$. Since there are two sites per bond, the energy per site is $-(3/8)J$, 50% lower than the Neel state. The "quantum fluctuations" carried by the operators

$$\frac{1}{2}(s_i^+ s_j^- + s_i^- s_j^+) = s_{ix}s_{iy} + s_{jx}s_{jy} \quad (9.74)$$

are responsible for destroying the ordered state for small spin ($s = \frac{1}{2}$) and low dimensionality. In a two dimensional square lattice, the ground state of Eq. (9.73) is not known. It may be ordered antiferromagnetically, but it is quite certain that no long-range magnetic order persists above $T = 0$.

For a $2d$ triangular lattice, the best "Neel" state has three spin sublattices oriented at 120° . It is not likely that much long range magnetic order occurs in the ground state. The triangular geometry causes "frustration". Anderson [72,73] argued that in this case the ground state would be a "resonating valence bond" (RVB) state

$$|\text{RVB}\rangle = \sum_P c(P) |\text{VB}, (1,2), \text{VB}(3,4), \dots\rangle \quad (9.75)$$

where the sum runs over all permutations P of bond arrangements. It is possible that such a state is also the ground state of the $2d$ square lattice. Even if this is not true, still when second-neighbor exchange coupling is introduced or else a finite hole-concentration x , these sources of frustration could stabilize an RVB state. Anderson [68] has proposed that an RVB state with finite x would be a novel kind of superconductor. The scale of T_c would be related to $J \sim 1000$ K rather than $\omega_D \sim 200$ K.

9.14. RVB Theory

This theory starts with the hypothesis that for insulating La_2CuO_4 , the ground state is of the RVB form (9.75). Next it is necessary to add holes, or remove electrons. With a single hole, the wavefunction becomes

$$|\text{RVB}, 1 \text{ hole}\rangle = \sum_P c'(P) |H(1)N_\alpha(2) \text{VB}(3,4) \text{VB}(5,6) \dots\rangle \quad (9.76)$$

Note that the missing electron alters two sites: $H(1)$ means a missing electron on site 1, $N_\alpha(2)$ means that site 2 is neutral but not valence-bonded and thus has a free spin $\alpha = \pm \frac{1}{2}$. The sum runs over all permutations of sites, and $c'(P)$ are variational.

Actually, the starting hypothesis has been overstated and can be weakened. In the pure undoped case, La_2CuO_4 may have a Neel ground state (strongly assisted by weak $3d$ interplanar spin coupling). Beyond a critical doping level (e.g. a few percent Sr, Ba, or Ca atoms in place of La) the Neel state disappears. The

hypothesis says that states like (9.76) take over. It has not been proved that such a state occurs in the large U , small x Hubbard model. It may be necessary to admit some next-neighbor interactions or some electron-phonon effects to stabilize the state (9.76).

It was pointed out by Kivelson, Rokhsar, and Sethna (KRS, [74]) that the state (9.76) can be thought of as embodying two "topological defects" (or solitons): A site of charge $+|e|$ which behaves like a Boson, and a neutral site of unpaired spin which behaves like a Fermion. Although necessarily created together, these two "particles" wander separately through the crystal. Their statistical (Fermi/Bose) properties were explicitly verified by checking the sign of wavefunctions like (9.76) with two identical defects present, as the locations of defects were moved adiabatically until they switched places.

At this point the scenario of Anderson *et al.* [75,76] and of KRS diverge from each other. In the latter picture the neutral Fermions ("spinons") have a finite creation energy (of order J or t^2/U) and thus are not present except as virtual pairs in the ground state; a second hole added to the state (9.76) will bind to the "spinon" creating a second charged Boson and leaving no Fermion degrees of freedom. Superconductivity is then expected as a Bose condensation of the charged Bosons.

The picture of Anderson involves a gapless spinon spectrum with a ground state of N occupied spinon states and a spinon Fermi surface. The nesting property of this "pseudo-Fermi surface" accounts for the antiferromagnetism. Doping destroys the antiferromagnetism but does not shrink the pseudo Fermi surface; charged Bosons are added which Bose condense. The superconducting transition is supposed to be a pairing transition at still lower temperature within the Bose condensate [77].

These scenarios are changing rapidly, as is the experimental situation, so it is too early to perceive the shape into which the final picture may evolve.

9.15. Oxygen Holes and Copper Spins

Various experiments suggest that carriers in Cu-O superconductors are located primarily on oxygen atoms, rather than in hybridized Cu(3d) Oxygen (2p) antibonding bands as suggested by band theory. For example, Cu-K edge X-ray absorption ($1s \rightarrow 4p$ transitions) seems to give a clear fingerprint of the valence state of Cu. Tranquada [78] find that pure La_2CuO_4 has the fingerprint of the Cu^{2+} ($3d^9$) ion, and does *not* evolve toward Cu^{3+} as carriers are introduced by Sr doping ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $0 \leq x \leq 0.2$). The oxygen $1s$ to $2p$ transitions have been explored by Nücker *et al.* [79] using electron

spectra seem to show a filled O(2p)-shell for values of x, y in the insulating region, but holes in this shell, roughly proportional to x and y , for conducting samples. This leads to the view that the Cu sublattice remains insulating with $s = \frac{1}{2}$ Cu(d^9) correlations even in samples which are metallic. Long range antiferromagnetic (AF) order is lost, short range spin order of some kind is presumed to remain.

Two interesting models have been proposed which treat the oxygen holes as a conventional Fermi liquid and achieve BCS pairing by an attractive interaction caused by Cu spins. Both models, like the "spin-bag" model mentioned in Sec. 9.10, derive the attraction from the fact that the oxygen hole alters the magnetic energy of the Cu sublattice in such a way that it is preferable to bunch the carriers spatially. The specific mechanisms, however, are quite different.

Birgeneau, Kastner, and Aharony (BKA, [80]) require that superconducting samples should exhibit fluctuating AF order with a correlation length of several planar Cu-Cu spacings; this is quite different in principle from the RVB spin organization, but available neutron scattering data [81] do not seem to distinguish these pictures unambiguously. The BKA model says that the oxygen hole (carrying $s = \frac{1}{2}$) tends strongly to orient its two neighboring Cu spins into a $S = 3/2$ ferromagnetic cluster. (See Fig. 2a). A second such cluster of opposite S will then prefer to be close because the pair of clusters is less disruptive to fluctuating AF order than either one individually. The source of the ferromagnetic alignment energy of Fig. 2a is Hund's rule energy (from ordinary

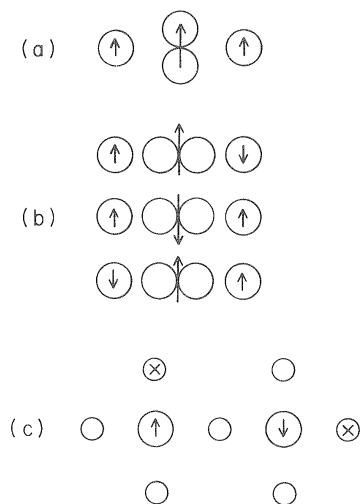


Fig. 9.2. A Cu-O-Cu group in the CuO_2 plane, showing possible arrangements of the spin of a hole on oxygen coupling to its two Cu neighbor spins. (a) model of Birgeneau, Kastner and Aharony (1988); (b) model of Emery and Reiter (1988); (c) possible sites of oxygen holes denoted by x which experience attraction due to enhanced superexchange.

Coulomb exchange energy) which dominates over AF exchange (t^2/U effects) because the oxygen hole is assumed to lie in a p_y -orbital (where x is the Cu-O-Cu bond axis and $x-y$ is the CuO_2 plane). This orbital is orthogonal to Cu ($d_{x^2-y^2}$) and the hopping matrix element t vanishes by symmetry. The p_y -orbital is assigned the highest energy based on an electrostatic calculation. (See also Guo *et al.*, [82]).

Emery and Reiter (ER, [83]) assign the oxygen hole to the p_x -orbital (see Fig. 2b) which is favored by antibonding covalency as in band theory. Then one expects an antiferromagnetic interaction J' between Cu spins and O spins, which should be larger than the previous Cu-Cu coupling J . Spin configurations shown in Fig. 2b are expected for a Cu-O-Cu complex, dominated by the $\uparrow\uparrow$ state where Cu atoms are ferromagnetically arranged. Just as in the BKA model, this complex disrupts local AF order. A second such complex, dominantly $\downarrow\downarrow$, would be attracted in order to minimize the disruption to AF energy. However, ER identify a separate mechanism which causes attraction and makes no specific demand on the nature of the fluctuating magnetic order. The $2d$ $s = \frac{1}{2}$ Heisenberg antiferromagnet is apparently a marginal case, so theory provides little guidance as to the type of magnetic order expected in doped weakly $3d$ systems, and the ER theory is safer for making fewer assumptions. Their new mechanism is "enhanced superexchange". The Cu-Cu exchange J is only partly given by t^2/U , because the hopping parameter t to go from Cu to Cu is small. Instead, the principal route is to hop indirectly via the intervening oxygen ion using a larger matrix element t' . But then the process is fourth order, and complicated expressions result, such as

$$J' \sim \frac{t'^4}{(\epsilon_p + V)^2} \left[\frac{2}{U_d} + \frac{4}{U_p + 2\epsilon_p} \right] \quad (9.77)$$

where ϵ_p is the O(2p) upper valence orbital energy, relative to the copper ϵ_d orbital energy chosen to be zero; U_p and U_d are onsite (Hubbard) Coulomb repulsions on O and Cu respectively, and V is a first neighbor Coulomb repulsion ("extended" Hubbard model). Now suppose that there is an oxygen 2p hole on one of the six oxygens adjacent to one (but not both) of the copper atoms in question (see Fig. 2c). Then by the nearest neighbor repulsion V , this raises the energy ϵ_d of a Cu-hole and correspondingly diminishes some of the denominators in Eq. (9.77). If a second O(2p) hole occurs in another of the six atoms (see Fig. 2c), this will further diminish denominators in (9.76). The effect is bigger than the additive energy changes of two single oxygen satellite holes, and causes attraction of oxygen holes located at second neighbor sites. For reasons mentioned before, this interaction is more effective for

9.16. Postscript

In the last few months there has been an interesting controversy concerning the statistics (i.e. the behavior under interchange) of charge-carrying and spin-carrying excitations of the RVB state. The situation is summarized in table II.

Authors	Ref	h o l o n	s p i n o n
KRS	74	+	-
KL	84	$\pm i$	$\pm i$
HL; RC	86,87	-	+
K	88	+	?

Table II. Phase change $e^{i\phi}$ of the RVB wavefunction after interchange of two identical quasiparticles.

As mentioned in sec. 9.14, Kivelson, Rokhsar, and Sethna (KRS [74]) were the first to notice that spin and charge degrees of freedom were likely to decouple in an RVB state. Their assignment of Bose statistics to $S = 0$, $q = |e|$ "holons" and Fermi statistics to $S = \frac{1}{2}$, $q = 0$ "spinons" agrees with naive expectations, but has been challenged. Kalmeyer and Laughlin (KL [84]) have proposed "fractional" statistics, which can be constructed in two dimensions [85]. Haldane and Levine (HL) [86] and Read and Chakraborty (RC) [87] have argued for Bose and Fermi, but in reverse order to KRS. Finally, Kivelson (K) [88] has reexamined these arguments. He agrees with HL and RC when the hole hopping term is ignored, but finds that the holon turns back into a boson once it is given a reasonable hopping matrix element. The spinon can go either way. This controversy seems to have sharpened the understanding of the meaning of statistics in two dimensions. Three dimensions apparently is different and lacks the rich possibilities found in $d = 2$. Kivelson's [88] argument also clarifies the subtle issue of flux quantization in units of $h/2e$ even when the object condensing is a charge $|e|$ boson rather than charge $-2e$ Cooper pair. Experiments clearly indicates $h/2e$.

An experimental discovery [89] worth noting is superconductivity at $T_c \sim 30K$ in the system $Ba_{0.6}K_{0.4}BiO_3$. Like the $Ba(Ph, Bi)O_3$ system, this is an approximately cubic perovskite

with a metal-insulator transition but no sign of local magnetic moments. The lack of a unifying theory for these diverse but evidently related high T_c systems is an embarrassment. It is safe to say that the discovery of high T_c superconductors has already altered our view of physics, and that this process will continue.

Acknowledgements

I thank V. Emery, S. Kivelson, W. E. Pickett, J. Serene and C. N. Yang for helpful discussions. This work was supported in part by NSF grant no. DMR 84-20308.

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