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by

Richard P. Messmer and Robert B. Murphy

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# Valence Bond Theory and Superconductivity

Richard P. Messmer[+‡] and Robert B. Murphy[‡]

[+] General Electric Corporate Research and Development
Schenectady, New York 12301

[‡] Department of Physics, University of Pennsylvania
Philadelphia, Pennsylvania 19104

Two necessary criteria for a theory of superconductivity are a phase coherence of the wave function and an attractive electron-electron interaction. We review how the BCS theory achieves these criteria and then show how a valence bond wave function can also meet these conditions. The energy scale of the latter approach has a larger range in principle than that possible *via* the electron-phonon interaction.

## Introduction

The recent discovery of ceramic high-$T_c$ superconductors has forced a re-examination of the basic concepts and physical assumptions employed in current theoretical approaches. In re-examining basic concepts, it is well to remember that the true N-electron wave function may be expanded in terms of components each of which is made up of N single particle functions and that this expansion can be made in (at least) two different ways:

$$\Psi = \sum_\nu c_\nu \, \Phi_\nu \tag{1}$$

(*molecular orbitals / Bloch orbitals / delocalized basis*)

$$\Psi = \sum_\nu d_\nu \, \Phi_\nu^\ddagger \tag{2}$$

(*valence bond orbitals / localized basis*).

The former expansion is the one typically assumed both in molecular and solid state work. The ease with which the single particle basis can be obtained in this case is certainly a significant advantage. Furthermore, it might be argued that either approach is equivalent *in the end*, and hence it makes sense to choose the mathematically more straightforward approach. In fact, one *always* considers only a small fraction of the terms in either expansion and the more relevant question is which is more rapidly convergent and/or more physically

motivated. The concepts derived by the two approaches may be quite different. This has been illustrated recently in a series of molecules and clusters, (1-5) for which calculations using Equation (2) were carried out. For metal clusters it was found (1,2) that electrons became localized into interstitial regions. And for double (3), triple (4) and conjugated bonds ($C_6H_6$) (5), it has been found that bent-bonds made up of essentially tetrahedral hybrids describe the bonding. These conclusions are quite different than those based on MO theory.

A key factor in superconductivity is the presence of an energy gap which separates the ground state (superconducting state) from the continuous single particle spectrum characteristic of the normal state of a metal. Let us write the many electron wave function as

$$\Psi = \sum_\nu a_\nu \, \Phi_\nu^{'}$$ (3)

without specifying the representation. Assume $\Phi_\nu^{'}$ are solutions of $H_0$ ($H_0 \Phi_\nu^{'} = E_\nu \Phi_\nu^{'}$) and the full Hamiltanian is $H = H_0 + U$. The question is what forms do $U$ and $\Psi$ need to have in order to produce a significant energy lowering of the ground state with respect to the $E_\nu$? That is, how can an energy gap be produced? The total energy is

$$W = \sum_\nu E_\nu \, |a_\nu^2| \; + \; \sum_{\mu\nu} U_{\mu\nu} a_\mu^{*} a_\nu$$ (4)

A significant lowering in energy can be achieved, as is well known (6), if the $E_\nu$ are all nearly equal and the $U_{\mu\nu}$ are all nearly equal. In this case, if the $E_\nu \simeq \bar{E}_o$ and the $U_{\mu\nu} \simeq -V$, the energy is

$$W = E_o \; -V \sum_{\mu\nu} a_\mu^{*} \; a_\nu$$ (5)

with the lowest energy obtained when all the $a_\nu$ are the same. If there are m terms contributing in the expansion of the wave function, the result is

$$W = E_o \; - \; mV$$ (6)

with the energy gap

$$\Delta = (E_o - W) = V \sum_{\mu\nu} a_\mu^{*} a_\nu = mV.$$ (7)

Hence to produce a gap, one has to devise a physically meaningful wave function that has phase coherence and equal amplitudes for the $\Phi_\nu^{'}$ and a potential U which is attractive (i.e., leads to matrix elements $U_{\mu\nu} = -V$). In the next section, we review how Bardeen, Cooper and Schrieffer (7) (BCS) met this challenge.

## Review of the BCS Theory of Superconductivity

Here we present a brief review of the essential aspects of the BCS theory of superconductivity which was introduced in 1957 and is still the most successful and complete theory of superconductivity which exists. The purpose of this section is to stress the unique features of the superconducting wave function which should be preserved in any new theory which involves a different mechanism for obtaining the ground state wave function.

In the BCS theory, the normal (non-superconducting) state of the metal is described by Bloch single particle eigenstates (8) $|k>$ labelled by a wavevector $k$,

$$\mathbf{h} \mid k> = \epsilon_k \mid k>, \tag{8}$$

where h is the single electron Hamiltonian and $\epsilon_k$ is the single particle energy of state $|k>$. The wave function of the metal is described by the occupation of single particle states $|k>$ and in the ground state all single particle levels are filled up to the Fermi energy $E_F$ with states above $E_F$ being unoccupied. This Bloch model does not include correlations between electrons due to Coulomb forces nor the interaction of the electrons with the lattice vibrations (phonons). In the superconducting state the phonon interaction is accounted for, but the electronic correlation is neglected except for effects produced by the electron-phonon coupling. The argument for ignoring other electronic correlation effects is that they are characteristic of both the normal and superconducting phases and therefore cannot be responsible for producing a gap.

The BCS superconducting state is characterized by an attractive potential between electrons arising from an electron-phonon interaction. We will now review how this interaction is derived (9). The direct electron-phonon interaction is a result of the potential between the electrons and the nuclear charges when the nuclei vibrate about their equilibrium positions. The electron-ion (e-i) interaction is expanded in terms of displacements $Q_j$ of the nuclear coordinates from their equilibrium positions $R_j$,

$$V_{e\text{-}i} (\mathbf{r}_\gamma - \mathbf{R}_j - \mathbf{Q}_j) = V_{e\text{-}i} (\mathbf{r}_\gamma - \mathbf{R}_j) + \mathbf{Q}_j \cdot \nabla V_{e\text{-}i} (\mathbf{r}_\gamma - \mathbf{R}_j) + \cdots \tag{9}$$

$$\mathbf{r}_\gamma = \gamma^{th} \text{ electron coordinate}; \quad V_{e\text{-}i} (\mathbf{r}_\gamma - \mathbf{R}_j) = \frac{-Z}{|\mathbf{r}_\gamma - \mathbf{R}_j|}.$$

By making a Fourier transformation of $V_{e\text{-}i}$ and using a plane wave basis $|k>$ for the electrons, we can consider the electron-ion interaction in the usual scattering terms in which we consider the amplitude $M_q$ to transfer momentum $q$ to the electron state $|k>$ "scattering" it into state $|k + q>$. The corresponding diagram for this process in Figure 1.

Fröhlich (10) showed how second order perturbation theory could be applied to derive an effective interaction between electrons from the direct electron-ion interactions. The physical idea is that as one electron scatters from a nuclear center it distorts the lattice, this distortion is felt by another electron, and thus the electrons experience an indirect interaction. The result is that we can think of the electrons as exchanging phonon momentum q in an electron-electron scattering process shown in Figure 2. The effective potential of interaction between the electrons for a scattering involving a change in momentum $q$ is (11),

$$V_{e\text{-}ph} = \frac{|M_q|^2}{(\epsilon_k - \epsilon_{k+q})^2 - (\hbar\omega_q)^2} \tag{10}$$

where $M_q$ is the amplitude for the electron to directly absorb a phonon of momentum q; $\epsilon_k$ and $\epsilon_{k+q}$ are the single particle energies before and after scattering, and $\hbar \omega_q$ is the energy of the phonon. The important point is that for $|\epsilon_k - \epsilon_{k+q}| < \hbar \omega_q$, the potential is attractive and it is this attractive interaction which leads to the superconducting state. Counterbalancing this attractive interaction is the repulsive Coulomb interaction which in momentum space is

$$V_C = \frac{4\pi e^2}{|k_1 - k_2|^2} \tag{11}$$

creating the potential for the scattering of an electron from $|k_1>$ to $|k_2>$ in the Coulomb field of another electron.

The object of the BCS theory was to maximize this attractive electron-phonon (e-ph) interaction since it could possibly lead to a physically different state, lower in energy than the normal metal. To maximize the interaction BCS considered only electron-phonon interactions for which $V_{e-ph}$ is negative which requires scattering of electrons from states $|k>$ to $|k'>$ such that $|\epsilon_k - \epsilon_{k'}| < \frac{1}{2} \omega_c$ where $\frac{1}{2} \omega_c$ is some average phonon frequency of the order of a Debye frequency. In other words only $|k>$ states within a region $\pm \frac{1}{2} \omega_c$ of the Fermi energy can contribute to the scattering process. To simplify matters further an average constant attractive potential -V was defined as $-V = <V_{e-ph} + V_c>$ which is an average of the electron phonon potential and the Coulomb potential over the k region defined for attractive $V_{e-ph}$.

The next crucial step in the theory was the development of a superconducting wave function that both optimizes the attractive phonon interaction and minimizes the Coulomb repulsion. This means specifying a particular occupation of $|k>$ states. Considering the matrix elements of the attractive potential, BCS showed that the optimal wave function involved an occupation of k states such that if state $|k\sigma>$ with momentum k and spin $\sigma$ is occupied then the state with opposite momentum and spin, $|-k-\sigma>$ is also occupied. This condition is referred to as electron pairing and is responsible for the coherence of the wave function. The scattering from $V_{e-ph}$ only occurs from the pair state $|k,-k>$ to another pair state $|k',-k'>$ where $k' = k+q$ as shown in Figure 2 and again k and $k'$ are in the restricted region near the Fermi level. The paired wave function is written as,

$$\Psi_{BCS} = \prod_k (v_k + u_k b_k^\dagger) | 0 >$$ (12)

where $u_k$ is the amplitude to have pair state $|k,-k>$ occupied, $u_k^2$ is the probability to occupy pair state $|k,-k>$, $v_k$ is the amplitude to have pair state $|k,-k>$ unoccupied, $b_k^\dagger = c_{k\sigma}^\dagger c_{-k-\sigma}^\dagger$ is the pair creation operator in second quantized form, and $|0>$ is the vacuum.

In the ground state at 0°K of the normal metal $u_k^2$, the probability to occupy pair state $|k,-k>$, is unity up to the Fermi energy after which it is zero. In the superconducting state $u_k^2$ differs from the Fermi distribution by the excitation of some pair states above the Fermi level. These pairs interact via the attractive potential which more than compensates for the excitation energy above the Fermi level. Thus a rounded Fermi distribution is obtained (Figure 3).

The Hamiltonian which describes these interactions is simply,

$$H_{BCS} = \sum_{k,\sigma} \epsilon_k \, c_{k\sigma}^\dagger c_{k\sigma} - \sum_{k,k'} V_{k,k'} b_{k'}^\dagger \, b_k$$ (13)

$V_{k,k'}$ is the potential obtained for each scattering of pair state $|k,-k>$ to $|k',-k'>$ for $k,k'$ in the region near the Fermi level. The energy is simply

$$E_{BCS} = 2 \sum_k u_k^2 \, \epsilon_k - \sum_{k,k'} V_{k,k'} \, u_k \, v_k \, u_{k'} \, v_{k'}.$$ (14)

The coefficients $u_k$ and $v_k$ are determined variationally giving (see Figure 3),

$$u_k^2 = 1/2 \, (1 - \epsilon_k/E_k), \quad v_k^2 = 1/2 \, (1 + \epsilon_k/E_k).$$ (15)

It is assumed that the matrix element $V_{k,k'} \simeq V$ (i.e., are independent of k and are non-zero only in the vicinity of $\epsilon_F$). This leads to a gap parameter

$$\Delta = V \sum_{k'} u_{k'} \, v_{k'}$$ (16)

which may be compared to Equation (7) and a new quasiparticle energy given by $E_k = \sqrt{\epsilon_k^2 + \Delta^2}$ (12).

That a set of nonzero $u_k$ has been obtained for $k > k_F$ means that a new many-electron state has formed with a lower energy than the normal state. The key feature of the new state is its stability to single particle excitations. In the normal metal, single particle excitations above the Fermi level can be made with vanishingly small energies. In the superconducting state there is not only an energy lowering of the whole system relative to the normal metal but there is also a finite energy gap to single particle-like excitations of the order of the gap parameter $\Delta$. This gap to single particle excitations is responsible for most of the physically observable properties of a superconductor including a specific heat which grows as $\exp(-\Delta/kT)$ and perfect diamagnetism to be discussed below.

When a magnetic field is applied to a superconductor, a current is induced in the material which creates a new field opposed to the applied field such that $B = 0$ in the material (Meissner effect). The quantum mechanical current density $j$ in the material is given by,

$$ j = - \frac{-ie\hbar}{2mc} \, [\Psi^* \nabla \Psi - (\nabla \Psi)^* \Psi] - \frac{e^2}{mc} A \Psi^* \Psi \tag{17} $$

where A is the vector potential defined by $B = \nabla \times A$. The first term is the paramagnetic contribution to the current and the second is the diamagnetic term. $\Psi$ is the wave function in the presence of the field A which differs from the ground state superconducting function $\Psi_0$ to first order in A by,

$$ \Psi = \Psi_0 + \sum_{n \neq 0} \frac{<n \mid A \cdot p \mid 0>}{(E_n - E_0)} \mid n > \tag{18} $$

where $\mid n >$ are excited states above $\Psi_0$. $E_n - E_o$ is at least as large as the gap parameter $\Delta$ which makes the perturbation to $\Psi$ relatively small; thus we can use $\Psi = \Psi_0$ in the calculation of $j$. In the ground state $\Psi_0$, the paramagnetic term in the current is zero, hence the only response of the system is purely diamagnetic, $j = -(e^2/mc) A \Psi^* \Psi$. Since $\nabla^2 A = -(4\pi n/c) j$, $A = A_0 \exp(- \sqrt{(4\pi n e^2/mc^2)} \cdot z)$, which shows, in the one-dimensional case, the exponential drop of the field as z increases into the material from the surface. This shows that diamagnetism is a direct consequence of the stability of the superconducting state to single particle like excitations.

Finite temperature effects are easily included in the theory by modifying all the matrix elements by including Fermi-Dirac factors, $1/(\exp(-\beta E_k) + 1)$. Variationally minimizing the free energy $G = U - TS$ shows the gap function decreasing as a function of temperature until it reaches zero at the critical temperature $T_c$, at which the transition to the normal state occurs. The expression for $T_c$ is, $kT_c \sim \hbar\omega_c \exp(-1 / N(0)V)$, for $N(0)V < 1$. $N(0)$ is the density of states of the normal metal at the Fermi level.

To summarize, the BCS theory of superconductivity provides an energy gap and a physical mechanism to achieve: (1) phase coherence in the wave function and (2) an attractive interaction. Both of these are required to produce a gap as seen in the discussion of the Introduction. The BCS mechanism of pairing electrons with k and -k momenta is the key to accomplishing these goals.

· Why, then, are there so many discussions of new mechanisms to explain the high $T_c$ superconductors? First, there is a limitation to the magnitude of V if it arises from the electron-phonon interactions; second, the density of states for these oxide materials is quite low. Taken together, these observations make it difficult to understand a transition temperature of 90°K. Recently, the band structure of the tetragonal $La_2CuO_4$ compound has been calculated (13,14). The results indicate a partially filled band at the Fermi level which can be well described in a tight binding model as Cu $d_{x^2-y^2}$ and O p orbitals in the plane hybridizing to form the four Cu-O bonds in the plane. The Fermi surface of the undistorted tetragonal

lattice in 2-D is just a square. The lattice vibrations associated with a transition from the tetragonal phase to an orthorhombic structure have wave vectors that exactly span the Fermi square and hence can cause a Peierls distortion (15) to the orthorhombic phase and opens a gap at the Fermi level, creating a semiconductor. The Ba substituents are believed to change the Fermi level thus changing the shape of the Fermi surface and destroying the Peierls instability, bringing the symmetric structure back without the semiconducting band gap. Unfortunately, new experiments (16) seem to indicate that the lattice distortion can occur in the superconducting state.

Calculations of the phonon modes and BCS electron phonon coupling constants (17) suggest that a high $T_c$ is the result of the high frequency of a Cu-O(1) in-plane bond-stretching mode ($\omega_c$) rather than a strong electron phonon coupling parameter. The highest $T_c$ calculated was 40K, limited by the highest Cu-O frequency. Unfortunately replacement of $^{16}O$ with $^{18}O$ in this system (18) shows no change in $T_c$ casting doubts on this mechanism.

The first conclusion to be drawn from this work is that calculations based on the BCS model cannot presently explain the $T_c$'s of order 90°K given the phonon frequencies and band structures calculated. This points out that perhaps a mechanism other than an electron-phonon mechanism is involved, which depends on parameters with larger energy scales. A possibility is an electronic mechanism, many of which have been proposed. We will discuss one of these in the next section.

The second point is that the oxide electronic structure is discussed in a real space local bonding framework although traditionally band structure/k-space methods have been used. The simple picture of the k,-k pairing in BCS seems to be lost in these complicated band structure calculations. It should be noted also that there have been serious difficulties associated with applying traditional band structure *concepts* for predicting the *normal* behavior of metallic oxides. As a typical example, simple band filling models for MnO cannot avoid attaining a partially filled band indicating that it should be a conductor (19,20); however, MnO is one of the best insulators known in nature. Such difficulties led to the use of the Hubbard model (21) of metals, which includes strong atomic-like correlation effects in a model Hamiltonian form to rationalize some of these band problems. More of the history of the importance of correlation effects in the oxides can be found in References 19,20,22. The point is that correlation effects have been known to be very important for predicting the properties of oxides, and this should be kept in mind when using the results or concepts of mean field theories which neglect these very important effects.

## Valence Bonds and Superconductivity

One of the authors (22), has proposed a model of superconductivity which is based on a highly correlated description of metals, closer to the Wigner lattice limit of electron localization (23) than to the free electron limit usually assumed. For small metal clusters of Li atoms McAdon and Goddard (1,2) have shown using correlated *ab-initio* methods that electron pairs localize in tetrahedral interstices of the lattice. It also has been shown (24) that one can obtain a very good approximation to the experimental charge density of Be using this description. Furthermore, studies on molecular systems (3-5) have shown an energetic preference in sp valence atoms for bent bonds formed from *tetrahedral hybrids* rather than the traditional $\sigma,\pi$ bonds based on MO theory. The use of tetrahedral hybrids for Be metal suggests that the electron/pairs can localize into tetrahedra in two separate ways, as shown in Figure 4. The fully symmetric wave function is a coherent superposition of the two structures. However, each of these structures is only a shorthand way of describing a large number of valence bond structures with alternative hybrids forming bonds. But, what does this have to do with superconductivity?

Let us return to the discussion in the Introduction and recall that to obtain a theory of superconductivity it is necessary (see Equations 4-7) to have an attractive potential, -V, and to have the $a_v$ of Equation (3) be equal. In the BCS theory, Equation (1) was used as the basis of the model. Here, we use Equation (2) as our starting point. The question, as it was above in the discussion of BCS theory, is how do we obtain a physically meaningful wave function and potential to satisfy these criteria?

Returning, then, to the expansion of Equation (2), we note that the terms represent different valence bond structures. Why should they all have the same amplitude and phase? This situation is very similar to the problem of determining the "resonance energy" of benzenoid molecules (25,26,27). In that case, of all the possible valence bond structures which might contribute, *only* the Kekule´ structures are used. For large benzenoid systems this is only a small fraction of the total number of *structures*. *Furthermore*, it is assumed that they all enter with equal expansion coefficients (*i.e.,* equal amplitude and phase). In addition, the matrix elements which convert one structure into another are set equal to a common value, determined empirically. Thus, the energy lowering associated with "resonance" in benzenoid molecules has a mathematical structure which maps onto the discussion in the Introduction. However, there are some important differences.

A necessary, but not sufficient, condition for producing a superconducting ground state is that the number of available orbitals exceeds the number of electrons. In order to describe a superconducting metal, the lowering of the ground state produces a gap with respect to a continuum of single particle excitations. From a valence bond viewpoint such a continuum is easily achieved when the number of orbitals (hybrids) is significantly larger than the number of electrons (e.g., the ratio $\dfrac{\# \; of \; orbitals}{\# \; of \; electrons}$ may be in the range ~1.1 - 4.0). For the oxide materials it is the ratio of orbitals to holes which is important. *However,* for the benzenoid molecules this ratio is unity and the ground state is an insulator; the lowest lying excited states will have significant excitonic and polaronic effects. Thus, in spite of the coherent superposition of alternative bonding structures ("spatial resonance") in these molecules, which is one of the necessary conditions for superconductivity, there are insufficient orbitals for the number of electrons, therefore failing another of the requirements.

For superconducting metals, the non-Kekule´ valence bond structures (analogs of Dewar and "long-bond" structures) provide the basis for constructing the continuum of single particle excitations. Raising the temperature in this model will eventually destroy the stability gained from the resonance because the entropic term, -ST in the free energy will increase when the electron pairs take on the many other possible configurations that are available to them than just those which maximize the resonance energy. A more quantitative *discussion* will be given elsewhere (28).

In order to discuss the new superconductors with this model, it must be shown that such a coherent spatial resonance can occur in these materials as a consequence of their local bonding. As a first step, we have calculated the electronic structure of the $SF_6$ molecule to gain some insight into the bonding occurring in octahedral complexes which are an important part of the environment in the new superconductors.

## Bonding in a Octahedral Environment

The molecule sulfur hexafluoride ($SF_6$) has recently challenged both molecular spectroscopy with its unexpected rotational spectra (29) and electronic structure theories with novel correlation effects (30,31,5). The electronic structure must explain the molecule's high stability, octahedral symmetry, and, most importantly, provide a simple picture of the bonding. At first glance, the traditional chemical models do not appear to be appropriate because sulfur seemingly forms six bonds to fluorines, yet the sulfur $s^2p^4$ valence configuration allows for at most two covalent bonds.

In this section we report on some preliminary results which suggest a novel interpretation of the electronic structure of $SF_6$ by considering the wave function as a coherent superposition of low symmetry generalized valence bond structures involving ionic bonding and little sulfur d-orbital character. This coherent superposition provides a significant fraction of the correlation energy by including both intra- and inter-pair correlation while retaining a local picture of the bonding.

At the lowest level, $SF_6$ is described by the molecular orbital Hartree-Fock wave function with doubly occupied orbitals $\phi_i$ which are determined self consistently in the mean field of the other pairs,

$$\Psi_{HF} = \det [\phi_1 \alpha \, \phi_1 \, \beta \, \phi_2 \alpha \, \phi_2 \, \beta \, .....]. \qquad (19)$$

The Hartree-Fock calculations were performed at the experimental (32) octahedral geometry with a S-F bond length of 1.564Å. A standard double zeta basis was used for the fluorine atoms (33), while the sulfur was described by an effective potential (34) with a valence double zeta s-p basis. In a separate calculation a single d polarization function with exponent .532 was added to the sulfur basis to assess the importance of d functions.

The most striking feature of the results is that $SF_6$ is not bound with respect to the separated atoms when d functions are not included in the sulfur basis while the introduction of the d function on sulfur lowers the energy by 10.5 eV making $SF_6$ bound by 5.6 eV. Similar results were obtained by Reed (30). Without further evidence this result would suggest that sulfur has a large $sp^3d^2$ component from which six equivalent S-F bonds can be made.

From the Hartree-Fock calculation, the zeroth order description of $SF_6$ is of fluorine forming partially ionic bonds to sulfur, with a small population of the sulfur d function energetically very important for bonding. Reed has concluded that the d orbital occupation is small because the d orbitals are high in energy. The Hartree-Fock binding energy falls far short of the experimental value of 20.1 eV indicating that there are major correlation effects neglected, which we will discuss below.

In order to gain both a more local and a more accurate description of the bonding in $SF_6$ we introduced intra-pair correlations *via* the perfect pairing generalized valence bond method (GVB-PP) (35). The valence electrons are described by generalized Heitler-London pairs,

$$(\phi_a \, \phi_b + \phi_b \, \phi_a) \; (\alpha\beta - \beta\alpha) \qquad (20)$$

where the singlet coupled overlapping spatial orbitals $\phi_a$, $\phi_b$ forming a local valence bond are variationally determined. The GVB-PP wave function is the antisymmetrized product of the pair functions and perfect pairing refers to the orthogonality of the pair functions and the nature of the spin coupling:

$$\Phi_{GVB\text{-}PP} = \det [\phi_a(1) \, \phi_b(2) \, \phi_c(3) \, \phi_d(4) \; \cdots \; \Theta_{PP}] \qquad (21)$$

with

$$\Theta_{PP} = (\alpha(1)\beta(2) - \beta(1)\alpha(2)) \; (\alpha(3)\beta(4) - \beta(3)\alpha(4)) \; \cdots \qquad (22)$$

Six pairs of electrons were described as correlated pairs (Equation 20) while the other pairs were treated at the Hartree-Fock level. No symmetry restraints were placed on the wave function for reasons that are explained below. The basis set included the sulfur d functions. The correlation energy obtained relative to Hartree-Fock is 3.0 eV indicating the extent of intra-pair correlation.

These GVB results suggest that we may think of $SF_6$ forming in a hypothetical sequence in which the axial fluorines first form largely ionic bonds to sulfur, thus promoting an effective $sp^3$ valence configuration of sulfur. The four sulfur electrons are left in a tetrahedral orientation on sulfur available for the bonds with the equatorial fluorines.

The equatorial bonds have small z components on the sulfur in the GVB results. The lack of z character in the orbitals is a result of the high electronegativity of the fluorines, causing highly polarized bonds, the lack of inter-pair correlations in the perfect pairing method, stemming from the orthogonality constraints between the pairs, and the neglect of the correlation effects described next.

Inter-pair correlations introduced by the tetrahedral $sp^3$ orbitals bonding to the equatorial fluorines can be seen in Figure 5, where we have shown schematically what the equatorial bonds would look like with more sulfur $p_z$ character in the bonds. This figure shows the inter-pair correlation occurring by pulling two pairs above the equatorial plane and two below, thus reducing the Pauli repulsion relative to having all pairs in the plane. The choice of the axial direction for the ionic components is not unique. To restore the symmetry in this scheme we must also include the degenerate configuration in which this $sp^3$ state is reflected about the equatorial plane and consider the four other orientations obtained from the other equivalent "axial" positions. Thus we suggest that the $SF_6$ wave function is described by a coherent superposition of these six structures,

$$\Psi_{SF_6} = C(\Phi_1 + \Phi_2 + \ldots + \Phi_6).$$ (23)

Such a coherent superposition of degenerate states leads to the well known "resonance" energy defined as the difference in energy between the energy of $\Phi_1$ alone and $\Psi_{SF_6}$ (33,5). This bonding scheme for introducing inter-pair correlations beyond the GVB-PP method using a superposition of resonance structures emphasizing the atomic hybridization has been shown to be successful for benzene (5).

Much remains to be done to implement the ideas outlined here about valence bond wave functions, in order to address the many questions about new high-$T_c$ materials. However the fact that it is formulated in *real space* and is based on chemical bonds, should allow much more direct contact with the *chemical aspects* than has been previously possible.

Acknowledgement

Literature Cited

[1]   McAdon, M.H.; Goddard, III, W.A. *Phys. Rev. Lett.* 1985, 55 2563.

[2]   McAdon, M.H.; Goddard, III, W.A. *J. Phys. Chem.* 1987, 91 2607.

[3]   Messmer, R.P.; Schultz, P.A.; Tatar, R.C.; Freund, H.-J. *Chem. Phys. Lett.* 1986, 126 176.

[4]   Messmer, R.P.; Schultz, P.A. *Phys. Rev. Lett.* 1986, 57, 2653.

[5]   Schultz, P.A.; Messmer, R.P. *Phys. Rev. Lett.* 1987, 58, 2416.

[6]   Kittel, C. "Introduction to Solid State Physics", Third Edition, p. 624, Willey, 1966, See Reference 11, also.

[7]   Bardeen, J.; Cooper, L.N.; Schrieffer, J.R. *Phys. Rev.* 1957, 108, 1175.

[8]   Bloch, F. *Z. Phys.* 1928. 52, 555.

[9]   Mahan, G.D. " Many Particle Physics", Plenum, 1981.

[10]  Fröhlich, H. *Phys. Rev.* 1950, 79, 845.

[11]  Feynman, R.P. "Statistical Mechanics, A Set of Lectures", Ch. 10, Benjamin Press, 1972.

[12]  Reference [7] and an alternative derivation by Bogoliubov, N.N.; Nuovo cimento, 1958, 7, 794.

[13]  Mattheiss, L.F. *Phys. Rev. Lett.* 1987, 58, 1028.

[14] Yu, J.; Freeman, A.J.; Xu, J.H. *Phys. Rev. Lett.* 1987, *58*, 1035.

[15] Peierls, R. "Quantum Theory of Solids", Clarendon, 1956.

[16] Fleming, R.M.; Batlogg, B.; Cava, R.J.; Rietman, E.A. to be published.

[17] Weber, W. *Phys. Rev. Lett.* 1987, *58*, 1371.

[18] Batlogg, B;, Cava, R.J.; *et al. Phys. Rev. Lett.* 1987, *58*, 2333.

[19] Adler, D. *Solid State Physics*, 1968, *21*.

[20] Adler, D.; Feinleib, J. *Phys. Rev. B* 1970, *2*, 3112.

[21] Hubbard, J. *Proc. Royal Soc., A276* 238 (1968); *ibid. A277* 237 (1964); *ibid. A281* 401 (1964); *ibid. A285* 542 (1965); *ibid. 296* 82 (1966); *ibid. A296* 100 (1966).

[22] Messmer, R.P. *Solid State Commun.* 1987, *63*, 405.

[23] Wigner, E. *Faraday Discussions* 1934, *34*, 678.

[24] Tatar, R.C.; Messmer, R.P. to be submitted for publication.

[25] Pauling, L. "The Nature of the Chemical Bond", Third Edition, Chapter 6, Cornell University Press, 1960.

[26] Wheland, G.W. "Resonance in Organic Chemistry", Wiley, 1955.

[27] For recent work, see for example: Gutman, I.; Cyvin, S.J. *Chem. Phys. Lett.* 1987, *136*, 137.

[28] Murphy, R.B.; Messmer, R.P. to be published.

[29] "Physics Today", July 1984, 17.

[30] Reed, A.E.; Weinhold, F. *J. Amer. Chem. Soc.* 1986, *108*, 3587.

[31] Hay, P.J. *J. Amer. Chem. Soc.* 1977, *99*, 1003.

[32] Herzberg, G. "Molecular Spectra and Molecular Structure", Vol. III, Polyatomic Molecules, Van Nostrand, NY 1966.

[33] Dunning, Jr., T.H.; Hay, P.J. "Methods of Electronic Structure Theory" Vol. 3 of Modern Theoretical Chemistry, edited by H.F. Schaefer III, (Plenum, New York, 1977), p. 1.

[34] Wadt, W.R.; Hay, P.J. *J. Chem. Phys.* 1984, *82*, 284.

[35] Hunt, W.J.; Hay, P.J.; Goddard, III, W.A. *J. Chem. Phys.* 1972, *57*, 738; Goddard, III, W.A.; Dunning, Jr., T.H.; Hunt, W.J.; Hay, P.J. *Acc. Chem. Res.* 1973, 6, 368; Bobrowicz, F.W.; Goddard, III, W.A. "Methods in Electronic Structure Theory", Vol. 3 of "Modern Theoretical Chemistry", edited by H.F. Schaefer III (Plenum, New York, 1977), p. 79.

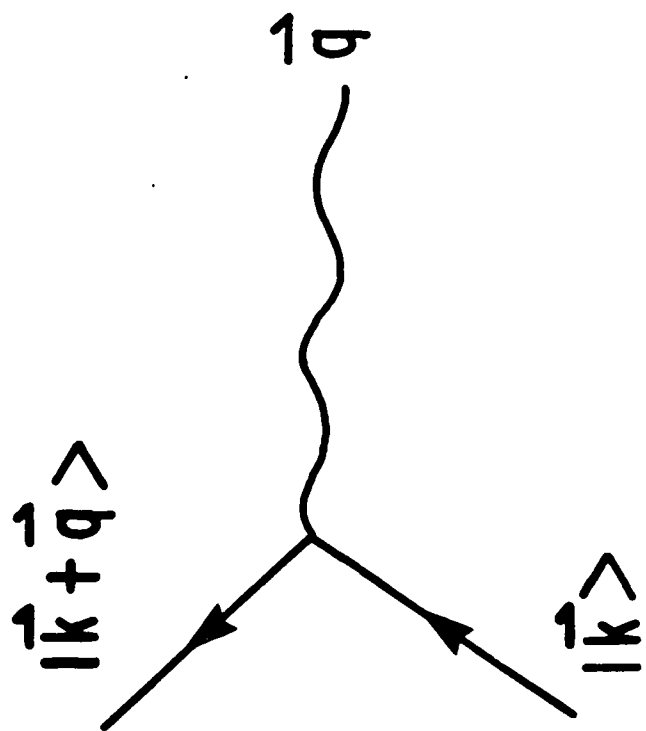[36] Voter, A.F.; Goddard, III, W.A. *Chem. Phys.* 1982, *57*, 253.

Figure 1. Electron of momentum **k** being scattered by phonon into state with momentum **k** + **q**.
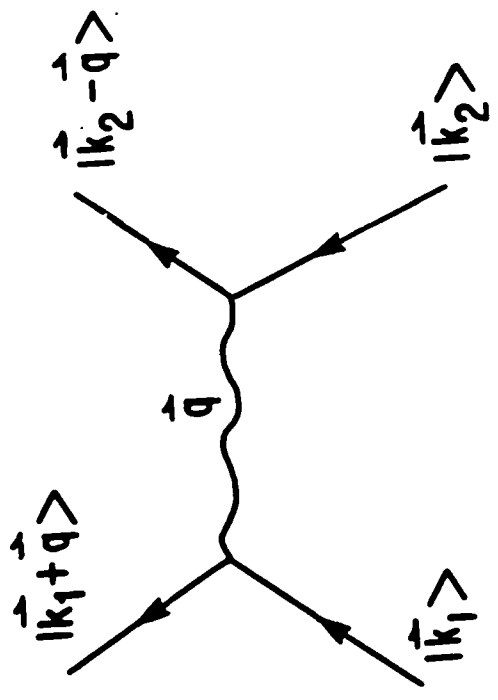
Figure 2. Two electrons with momenta $k_1$ and $k_2$ exchanging a phonon of momentum q in an electron-electron scattering process.
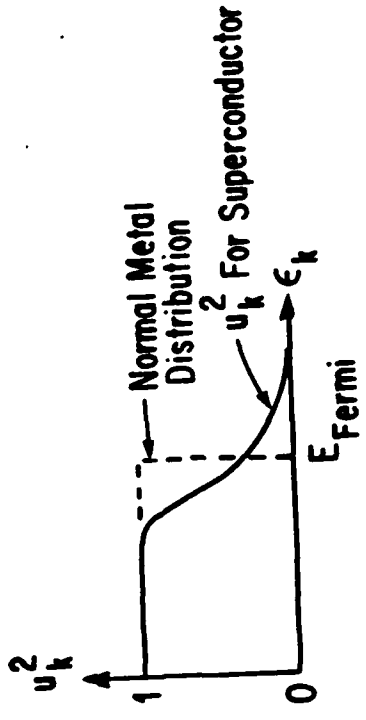
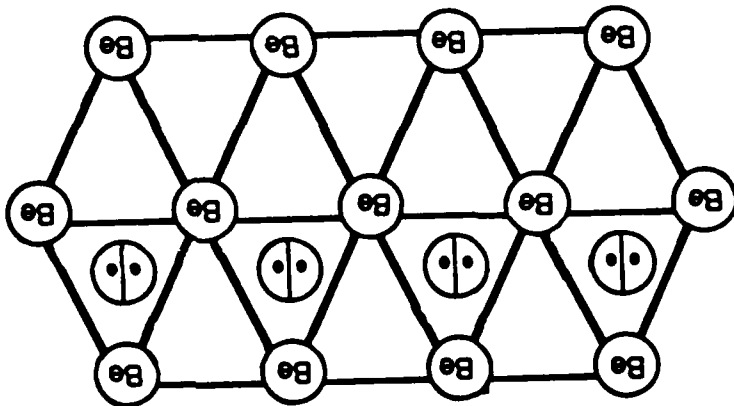Figure 3. Occupancy of k-states for the normal metal and in the superconducting state.
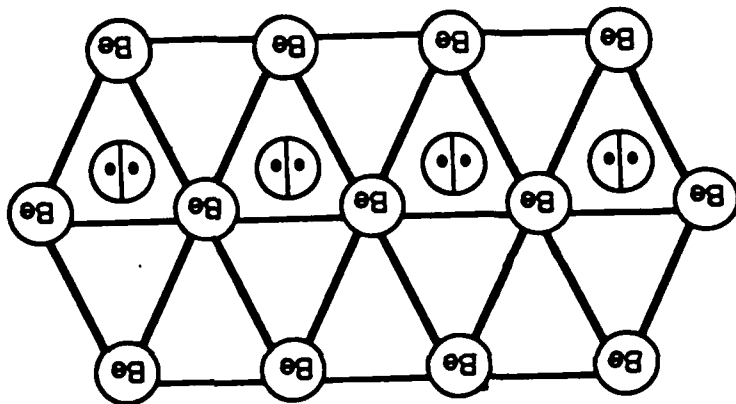
Figure 4. Schematic representation of electrons localized in tetrahedral interstices of hcp Be metal. The electron pairs are distributed among four hybrids at each site. Only a representative number of electron pairs are shown.
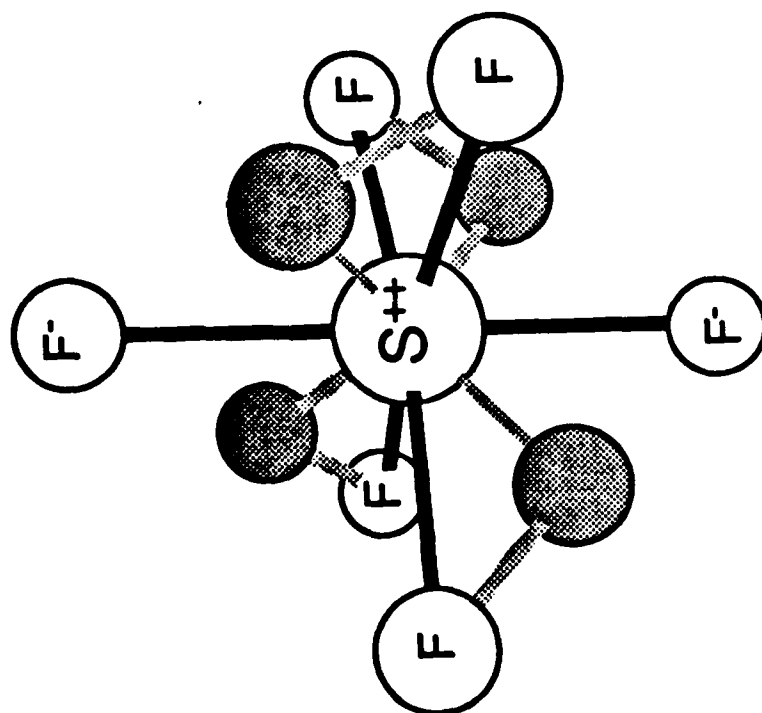
Figure 5. Schematic representation of bonding in $SF_6$ for one of the *spatial resonance* structures. There are six equivalent structures, each has two "ionic" bonds and four "covalent" bonds. The shaded spheres represent the positions of electron pairs; the light connecting lines represent approximate tetrahedral hybrid orbitals. The dark connecting lines merely show the octahedral geometry.

$$|\vec{k_2}-\vec{q}\rangle \qquad |\vec{k_2}\rangle$$

$$\vec{q}$$

$$|\vec{k_1}+\vec{q}\rangle \qquad |\vec{k_1}\rangle$$

END

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