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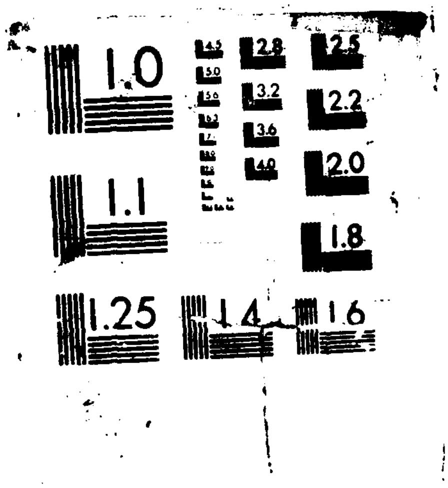

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The Chemical Bond and Superconductivity

by

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THE CHEMICAL BOND and SUPERCONDUCTIVITY

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1. INTRODUCTION

The search for understanding of the physical mechanisms operating in the recently discovered high T_c superconductors[1] forces a re-examination of the basic concepts and physical assumptions of current theoretical approaches. Is it possible to generalize the Bardeen-Cooper-Schrieffer[2] pairing mechanism and obtain an alternative attractive interaction while preserving the basic structure of the theory? Surely, the answer must be in the affirmative. The BCS theory has been so highly successful in describing the physical properties of previous superconductors that the structure must be fundamentally correct. Thus the focus is on alternative pairing mechanisms.

The attractive interaction of a more general theory may be rather more complicated than the electron-phonon interaction usually assumed. In fact, it probably contains the critical *chemical* parameters of the material. This is the motivation for the present work in which the focus is two-fold: first, to call attention to some recent developments in our understanding of the chemical bond, and second, to propose that this new understanding is not only germane to the electronic structure of solids but also provides a new perspective on the relationship between the chemical bond and superconductivity.

Studying the connection between chemical bonding and superconductivity would seem to be a rather academic exercise if it were not for the high temperature superconductors. These new materials have brought to our attention in a dramatic fashion the ignorance which exists in relating chemistry to the important physical parameters of a superconductor. Although this point was raised in numerous contributions by Matthias,[3] its full import was never so apparent when the superconductors were "traditional" metals and alloys.

The new materials are certainly rather more complicated chemically and structurally than the physicists' favorite model of a metal - the free electron gas! Typically the structure and bonding in these ceramic oxides has been rationalized by chemists in terms of ionic concepts introduced by Pauling and others many years ago.[4] Thus, there is a serious dichotomy between the two starting points which one might employ to describe the metallic oxides. Suggesting that our understanding of the electronic structure of these materials is rather primitive can be accepted readily. However, finding agreement on the appropriate theoretical approach and the choice of models which should be adopted is difficult. This is one reason why these materials are such an exciting area for theoretical activity at present.

In re-examining basic concepts, it is useful 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:

$$\Psi = \sum_{v} c_v \Phi_v \tag{1}$$

{ molecular orbitals / Bloch orbitals / delocalized basis }

or

$$\Psi = \sum_{v} d_v \Phi_v^{\ddagger} \tag{2}$$

{ 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, hence it makes more sense to choose the mathematically more straightfoward 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 is illustrated in Section 2 for a series of molecules and clusters.

In order to motivate the discussion on molecules and clusters, which involves the use of Eq. (2), it is important to realize that the concepts derived from these small systems can be transferred to the solid. This will be elaborated upon below. Further, in order to appreciate the connection that a valence bond description has to superconductivity, it is instructive to consider those aspects of the BCS theory which are essential to any model of superconductivity. Therefore the electronic structure problem is best set up in its most general context.

The many-electron wave function is written as:

$$\Psi = \sum_{v} a_v \, \Phi_v'. \tag{3}$$

The Φ_v' are solutions of H_0 ($H_0 \Phi_v' = E_v \Phi_v'$) and the full Hamiltonian is $H = H_0 + U$. The question is what forms do U and Ψ need to have in order to produce a significant energy lowering of the ground state with respect to the E_v? That is, how can an energy gap be produced? The total energy is:

$$W = \sum_{v} E_v \, |a_v|^2 + \sum_{\mu v} U_{\mu v} \, a_\mu^{*} a_v \tag{4}$$

A significant lowering in energy can be achieved, as is well known,[5] if the E_v are all nearly equal and the $U_{\mu v}$ are all nearly equal. In this case, if the $E_v \cong E_0$ and the $U_{\mu v} \cong -V$, the energy is:

$$W = E_0 - V \sum_{\mu v} a_\mu^* a_v, \tag{5}$$

and the lowest energy is obtained when all the a_v are the same. If there are m terms contributing in the expansion of the wave function, the result is: $W = E_0 - mV$. An energy gap parameter can be defined as:

$$\Delta = (E_0 - W) = V \sum_{\mu v} a_\mu^* a_v = mV. \tag{6}$$

Hence to produce a gap, one has to devise a physically meaningful wave function that has phase coherence and equal amplitudes for the Φ_v' and a potential U which is attractive (*i.e.*, leads to matrix elements $U_{\mu v} \cong -V$).

BCS chose to consider Eq. (3) in the form of Eq. (1), using Bloch functions as a basis set and working in reciprocal space. In this case E_0 becomes the Fermi energy E_F. They found a gap was achieved if: (1) the wave function was made up of pairs of electrons having opposite spins and opposite crystal momenta (**k**, -**k**) and (2) the potential U was an electron-electron attraction mediated by phonons, which has non-zero matrix elements, $U_{\mathbf{kk}'}$, for **k** values within a characteristic phonon energy $\hbar\omega_c$ above and below the Fermi surface.

An alternative procedure would be to employ Eq.(2), use a localized valence bond basis set, and work in real space. Such an approach has recently been suggested by the author.[6] In this model, the gap is produced by forming a ground state which is a superposition of a special class of terms, entering with equal amplitudes and phases and corresponding to a *spatial alternation of valence bonds*.[7,8] It turns out that this approach is mathematically very similar to the description of "resonance stabilization" in benzenoid molecules. In order to appreciate fully the concepts used in this approach as applied to solids, it is necessary to review some recent developments in understanding the chemical bond in molecules.

In the succeeding sections, an attempt is made to provide the following connections. First, the problem of electron correlation and the chemical bond for finite systems is considered. This leads to some generalizations which can be applied to solids. These, in turn, suggest that metals may be described by the highly correlated Wigner lattice limit as a starting point rather than the more traditional electron gas starting point. Next, this allows one to think of electron pairing in real space and make a connection to superconductivity. Finally, the connections among superconductivity, the spatial alternation of valence bonds (a particular form of "resonance") and the oxide materials will be discussed.

1.1 Digression: Comment on Band Theory and Oxides

It is worthwhile to recall some of the theoretical issues which have arisen in the past in describing simple transition metal oxides, as they are likely to have relevance in the high T_c oxide context. *Foremost among the issues is the adequacy of band theory to describe the* properties of these materials. Band theoretical calculations by Mattheiss[9] for CaO, TiO, VO, MnO, FeO, CoO and NiO found CaO to be an insulator and the other oxides to be metals. In fact, while experiment does find CaO to be an insulator and TiO and VO to be metals, the remaining oxides (MnO - NiO) are found to be antiferromagnetic insulators. Spin-polarized energy band calculations[10] found MnO and NiO to be semiconductors, but Mattheiss argued that similar calculations for FeO and CoO would yield metallic results. Thus it was concluded[9] that even spin-polarized band calculations are inadequate for the oxides MnO, FeO, CoO and NiO and that they should be considered as Mott insulators. This is in agreement with other approaches which stressed the importance of electronic correlation effects.[11]

Recent band structure results for the high T_c oxides by several groups[12-14] identify Cu 3d- O 2p interactions as the key to understanding the metallic and superconducting properties of these materials. However, the various issues associated with describing important correlation effects must be kept in mind.

2. NEW CONCEPTS OF CHEMICAL BONDING

The most common computational approach for molecules and clusters of atoms is the *molecular orbital* method, which describes the wave function as an antisymmetrized product of delocalized one-electron spin-orbitals in the Hartree-Fock approach or as a Hartree product of delocalized spin-orbitals in the local density functional approach. This is, of course, the finite analog of the band theoretic approach to solids where one uses Bloch functions instead of molecular orbitals. In each case the basis functions transform as irreducible representations of the appropriate symmetry group (point group for molecules or space group for solids) of the Hamiltonian. Using the Hartree-Fock wave function as a starting point there is a systematic procedure to carry out *ab initio* calculations which introduce various electron correlation effects. However, for the density functional approach, no well-defined method exists for adding electron correlation beyond the mean-field *local density* approximation. Hence, to study the systematics of electron correlation effects computationally (without using model Hamiltonians), one is forced to use *ab initio* methods on finite systems.

In the development to follow, the emphasis will be on the expansion of the wave function according to Eq. (2). Unlike the expansion in Eq. (1), in which the one electron basis functions (ϕ_j), the N-electron determinants (Φ_v) and the N-electron wave function all transform according to irreducible representations of the symmetry group, neither the basis functions (φ_j) nor the N-electron terms ($\Phi_v^{\ddagger}$) in Eq. (2) are symmetry functions. Only the full many-electron wave function has the symmetry of the Hamiltonian.

2.1 Molecules

The paradigm for *ab initio* correlated calculations on molecules has become the Hartree-Fock plus Configuration Interaction (HF + CI) approach. In this case the wave function is written as a linear combination of Slater determinants made up of orthogonal spatial orbitals (see Eq. 1). That is, for N electrons in a singlet state:

$$\Phi_\nu = \det \left[\left(\prod_{j(\nu)} \phi_j \right) \Theta_\nu \right], \tag{7}$$

with $<\Phi_\nu \mid \Phi_\mu> = \delta_{\nu\mu}$ and $<\phi_k \mid \phi_l> = \delta_{kl}$. However, another approach to the problem of correlation effects would be to consider the expansion given in Eq. 2, where the $\Phi_\nu^\ddagger$ are non-orthogonal and are made up of non-orthogonal spatial orbitals:

$$\Phi_\nu^\ddagger = \det \left[\left(\prod_{j(\nu)} \varphi_j \right) \Theta_\nu \right], \tag{8}$$

with $< \Phi_\nu^\ddagger \mid \Phi_\mu^\ddagger > \neq \delta_{\nu\mu}$ and $< \varphi_k \mid \varphi_l > \neq \delta_{kl}$. In each case Θ_ν is an N-electron spin function. Specifically,

$$\Theta_\nu = \sum_i c_i^\nu \theta_i, \tag{9}$$

where the θ_i are a set of linearly independent spin couplings spanning the N-electron spin space. The latter approach is vastly more complex mathematically. However, if the latter series is more rapidly convergent and the individual terms are more easily motivated physically than in the case of Eq. (1), the additional complexity may be worth the effort. This in fact is the case as illustrated below, hence this approach is adopted in the following discussion.

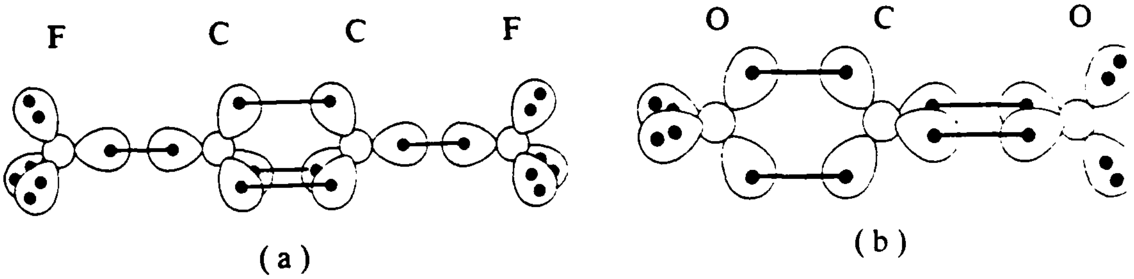
In some molecules, one term in Eq. (2) and one spin coupling in Θ_ν suffices to give a reasonable description of the electronic structure of interest. Then each of the spatial orbitals, one for each electron, can be determined self-consistently from a variational calculation.[15] The form of the wave function is:

$$\Phi^\ddagger = \det \left[\prod_j \varphi_j \, \theta \right], \tag{10}$$

where the spin function consists of singlet coupled pairs:

$$\theta = \prod_i^{(odd)} [\alpha(i)\,\beta(i+1) - \beta(i)\,\alpha(i+1)] \;/\sqrt{2}. \tag{11}$$

For the case of C_2F_2, the orbitals of $\Phi^\ddagger$ (*i.e.*, the φ_j of Eq. 8) are shown schematically in Fig. 1a. Note that all the orbitals are highly localized and are approximately tetrahedral hybrids. The dots denote that the orbitals are occupied by electrons; the lines denote which orbitals are coupled to form chemical bonds. For the "lone pairs" of electrons on the F atoms, the orbitals are shown as containing a pair of electrons. In fact, there are two orbitals for each pair - one for each electron, but the angular dependence of the two orbitals in a pair are practically identical, so the simplified representation of Fig. 1 is used. In order to obtain the identical description from Eq. (1), it would require an expansion of 2^{11} orthogonal determinants! It is interesting to observe that the usual description obtained by molecular orbital theory (one term in Eq. 1), consists of orbitals of σ and π symmetries. The results presented here[16] with electron correlation taken into account do not support such a description. Three equivalent bonds are energetically preferred for the carbon-carbon triple bond, not a σ and two π-bonds.



(a)

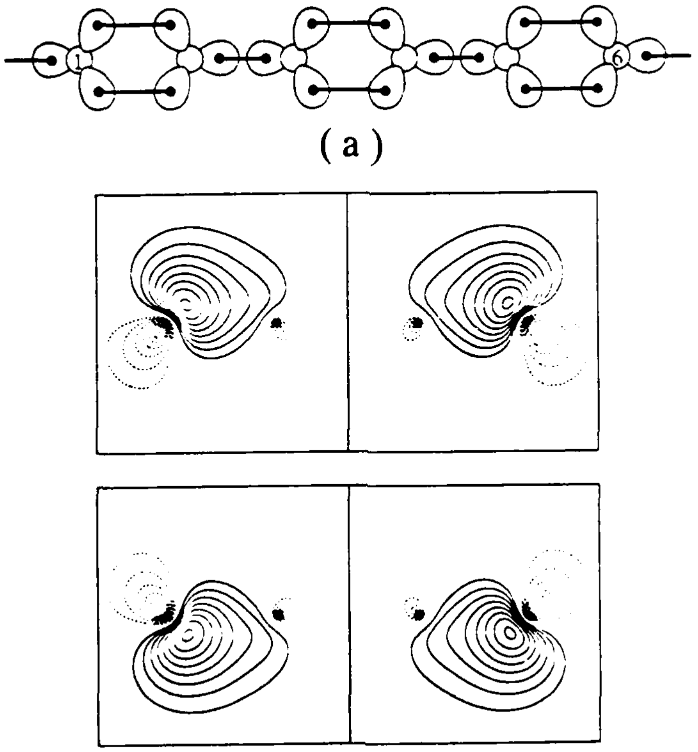
(b)

Figure 1. Schematic representation of multiple bonds: (a) the C-C triple bond in the C_2F_2 molecule; (b) the C-O double bonds in CO_2. Note the approximate tetrahedral hybrid nature of all the orbitals. The calculations on which this figure is based are described in the text (refs. 16 and 17).

Another example[17] is the case of CO_2 which has double bonds between the carbon atom and each of the oxygen atoms. In this molecule, two terms in Eq. (2), each with one spin coupling, are required to give a first order approximation. In Fig. 1b, a schematic representation of the orbitals of the first component are shown. Again, the atoms C and O exhibit localized orbitals which are essentially tetrahedral in nature. The second component of the wave function can be obtained from the first (see Fig. 1b) by a rotation of 90° about the internuclear axis, and the wave function is a coherent superposition of these two alternative structures. Thus in the case of double bonds there is also support for equivalent bent-bonds (Ω - bonds) as opposed to the molecular orbital concepts of σ and π–bonds.

A third example[18] to consider is benzene which has been the prototypic molecule for π-bonding. In Fig. 2a, a schematic representation of the carbon-carbon bonding in the ring is shown as obtained from the calculations. The wave function, Eq. (2), contains two terms (the two Kekule' structures of benzene) and in each there is an alternation of double and single bonds. However, the variational principle is found to favor approximately tetrahedral hybrids leading to equivalent bent bonds rather than sp^2 hybrids leading to π-bonds. In Fig. 2b, the orbitals forming a double bond in one of the Kekule' structures are shown.

In any of these cases, forcing the orbitals to become σ– and π-like (by imposing variational constraints) increases the calculated energy of the ground state, demonstrating that it is a worse solution. From these and other calculations, the conclusion is that the carbon atom and other atoms in this row of the periodic table (which have only s and p orbitals available) form essentially sp^3 hybrids regardless of their bonding environments. Furthermore, one may use this insight to formulate a simple method for predicting the molecular structure of sp-bonded molecules.[19] Namely, to first order, the structure of sp-bonded molecules arises as a consequence of two simple principles: (1) each atom shares electron pairs so as to achieve a closed shell configuration (the Lewis-Langmuir octet rule), and (2) the atoms arrange themselves so that the electron pairs about each atom are approximately tetrahedrally distributed (minimization of pair-pair repulsions). These principles are illustrated in Figs. 3 and 4. In Fig. 3a, two schematic representations of a C-H bond are shown. In the upper diagram, the correlated nature of the two electron bond is represented; a shorthand notation is given in the lower diagram. In Fig. 3b, using

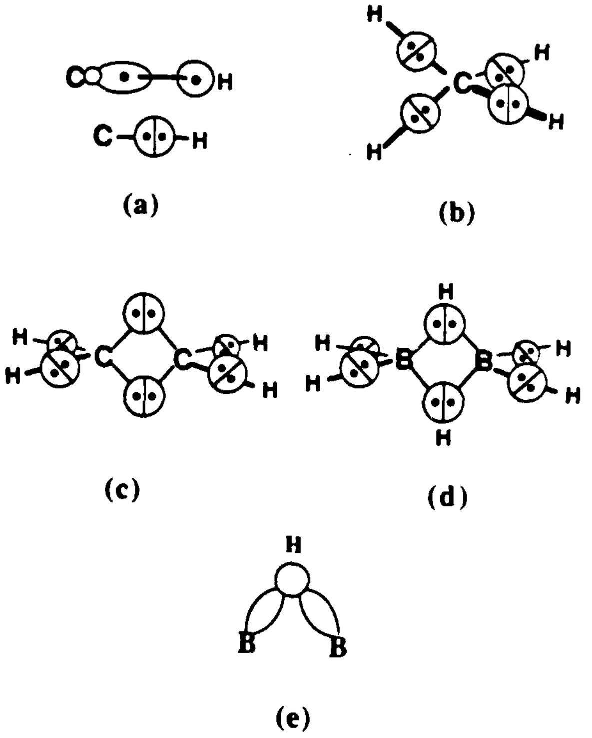


(a)

(b)

Figure 2. Bonding in the benzene molecule: (a) schematic representation of the orbitals forming the double and single bonds in one of the Kekule' structures; (b) calculated orbitals of one of the double bonds, with the upper orbitals forming one bond and the lower orbitals forming the other.

the shorthand notation, the many-electron wave function of CH_4 is depicted; note the tetrahedral distribution of electron pairs. In Fig. 3c, the bonding in C_2H_4 is illustrated;[20] observe that two electron pairs are shared by the carbon atoms. Fig. 3d shows the bonding for B_2H_6. The similarity to C_2H_4 is very clear in this representation. The molecule can be considered as arising from the removal of a proton from each carbon nucleus of C_2H_4 with the protons attaching themselves to the electron pairs shared by the resulting boron atoms in order to preserve charge neutrality. It must be kept in mind what the shorthand notation actually stands for. For example, the electron pair at a bridging H in Fig. 3d is shorthand for a situation which is more accurately represented in Fig. 3e. There are three orbitals, one from each atom, which have two electrons distributed among them. The two electrons are singlet coupled and the actual wave function will be a superposition of these various alternatives.



(a) (b)

(c) (d)

(e)

Figure 3. Schematic representations of bonding determined from the orbitals of correlated many-electron wave function: (a) the orbitals of a C-H bond showing "left-right" correlation of the bonding electron pair, together with a shorthand notation employed in the other diagrams; (b) diagram of the bonding in CH_4; (c) bonding in the C_2H_4 molecule, showing how electron pairs are shared between the two C atoms; (d) bonding in B_2H_6 showing the close correspondence to the C_2H_4 molecule; (e) the three orbitals among which two electrons are alternatively placed in a three-center two-electron bond (as in B_2H_6).

The electron distribution and bonding in B_4H_{10} is shown schematically in Fig. 4. Here a further simplification in notation is employed from that used in Fig. 3. The B-H two-center two-electron bonds (involving the four terminal hydrogen atoms) are now represented as dark connecting lines between the atoms. The electron pairs involved in three center bonds with hydrogen (bridging hydrogens) are not explicitly shown as the hydrogen atom marks the approximate position of the charge distribution center. The hybrids from the B atoms which share electron pairs are shown as light connecting lines. There is one pair of electrons which is not shared by a proton; it is shown as a shaded sphere.

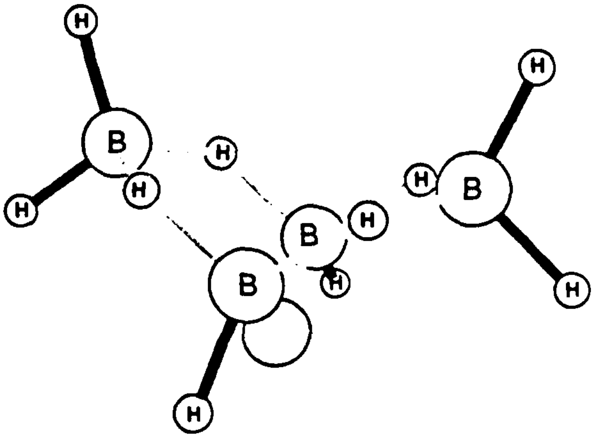


Figure 4. Schematic representation of B_4H_{10} wave function. The lighter connecting lines represent tetrahedral hybrid orbitals originating from the boron atoms. Two hybrids overlap to share an electron pair (denoted by shaded sphere); four such electron pairs are also shared with protons (bridging hydrogens) to create "three-center two-electron bonds." See text.

The concept of approximate tetrahedral hybrids for describing the bonding of C and B compounds is thus seen to be very useful and general. The fact that boron hydrides are electron-deficient molecules raises the possibility that the concept may be applicable to other electron deficient materials, for example, metal clusters and bulk metals. This is investigated next.

2.2 Metal Clusters

Recently, a very important contribution to the understanding of electronic structure in metals has been made by McAdon and Goddard[21]. They studied the electronic structure of many Li clusters using explicitly correlated many-electron wave functions and demonstrated that electrons in such clusters occupy localized orbitals in *interstitial* regions between the atoms. A schematic representation of some of their results is shown in Figs. 5 and 6. For one-dimensional chains of atoms (Fig. 5a) they found that one orbital localizes between each pair of atoms and is occupied by one electron. The orbitals in adjacent interstitial sites couple to form singlet pairs, *but* the dominant bonding is *via* the *one-electron bonds* formed by the interstitial electrons. In fact, all the electrons can be high spin coupled and the chain is still stable with respect to dissociation into Li atoms! This is quite different than the situation for normal covalent two-electron bonds. The origin of this behavior is the small overlap between the interstitial orbitals of the metal cluster, which then allows the calculated spin excitation spectrum to be accurately fit by a Heisenberg Hamiltonian model.

For the one-dimensional chain there are no low lying excitations (within kT) which could lead to electrical conductivity. However, for two-dimensional sheets there are a variety of low lying excited states. This is shown schematically in Fig. 5b. For these planar arrays of atoms, the orbitals localize into triangular interstices among three atoms with one electron in each orbital. Orbitals in adjoining interstices are singlet coupled in the ground state. In three-dimensional clusters, it was found that the orbitals localize into tetrahedral interstices with either one or two electrons in the tetrahedra, depending upon the cluster geometry. Fig. 6a shows a schematic representation of the results for the Li_{13}^+ fcc geometry. The cluster has eight tetrahedra about the central atom (labelled 1); four are occupied by correlated electron pairs. These pairs are shown in the figure as shaded spheres. One of these four tetrahedra is made up from the atoms labelled 1 to 4. The faces of the remaining four tetrahedra each contain one electron (shown as darker shaded spheres). These electrons are singlet coupled into pairs.

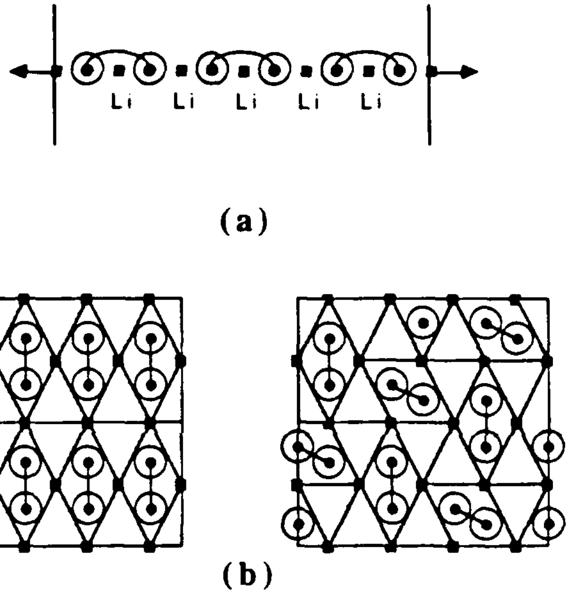


Figure 5. Schematic representations of one- and two-dimensional Li clusters: (a) linear chain of Li atoms, showing the interstitial orbitals localized between neighboring atoms with the orbitals occupied by a single electron and singlet coupling between adjacent orbitals; (b) two distributions of interstitial orbitals for planar arrays of Li atoms. See ref. 21.

For the three-dimensional clusters, some interesting questions to ask are: can we *predict* where the interstitial electrons should be without detailed calculations? Can the concept of interstitial electrons be used to think about bulk metals? If so, is it possible to predict where the interstitial electrons should be in the metal? What will be the consequences? For the moment, only the first question is considered. McAdon and Goddard[21] have presented some rules which are derived from their calculational results, but they are strictly empirical and lack a more fundamental basis. However, it has been found from our studies[22] that: (1) the tetrahedral hybrids offer a natural way to understand the electron distribution and predict the results of their cluster calculations; (2) tetrahedral hybrids provide insight about bulk metal alloys. Only one example is given here, namely, the Li_{13}^+ fcc cluster. In Fig. 6b, it is shown how each of the tetrahedral hybrid orbitals on the central atom overlap with hybrids from three other atoms so as to share an electron pair. This is the origin of the calculated results (see Fig. 6a) which show that four of the eight tetrahedra about the central atom contain electron pairs which are tetrahedrally oriented. The other interstitial electrons are each shared by three atoms with each atom contributing one tetrahedral hybrid orbital.

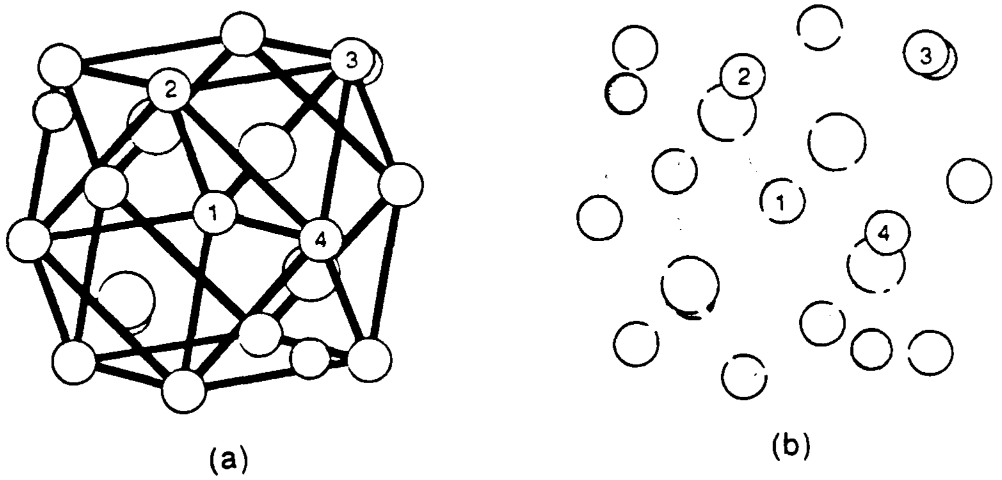


Figure 6. Li_{13}^+ fcc cluster: (a) schematic representation of results of ref. 21, showing electron pairs as lightly shaded spheres and single electrons as darker shaded spheres. The pairs are localized in tetrahedra such as formed by Li atoms 1,2,3 and 4; (b) the tetrahedral hybrids (shown as light lines) of the atoms overlap so as to optimally share electrons, which determines the positions of the interstitial electrons for the fcc cluster geometry.

Returning to the linear chain and two-dimensional clusters, one might ask how tetrahedral hybrids can explain the structures. Recall that the tetrahedral hybridization is a consequence of two effects: (1) the stability inherent in forming a closed shell of electrons about each atom (the octet rule) and (2) the minimization of pair-pair repulsions. If one chooses to arrange atoms in a way that tetrahedral hybrids cannot be effectively used (as in linear chains or two-dimensional structures), a rehybridization will be required in order to optimize the energy of the structure chosen. It should be clear, however, that the energy of the optimal 1-D and 2-D structures will be higher than for the optimal 3-D structures. This is in fact found by the calculations of McAdon and Goddard.[21] For the 1-D case, it is easily seen that the best overlap of orbitals is achieved for sp-hybridization, which leaves two orbitals unoccupied on each atom. For the 2-D case, it is the sp^2-hybridization which is most favorable, leaving one orbital/atom unoccupied.

The relative energy of the 1-D cluster is less favorable than for the 2-D cluster. In general, for atoms with s and p orbitals, the use of approximate hybridizations other than tetrahedral will raise the energy of the molecule or cluster.

Thus the concept of tetrahedral hybrids, together with the simple principles stated above (the octet rule and the minimization of pair-pair repulsions), provides a powerful way to understand the structure of molecules and clusters. This is a very different picture than provided by a non-correlated approach: molecular orbital theory .

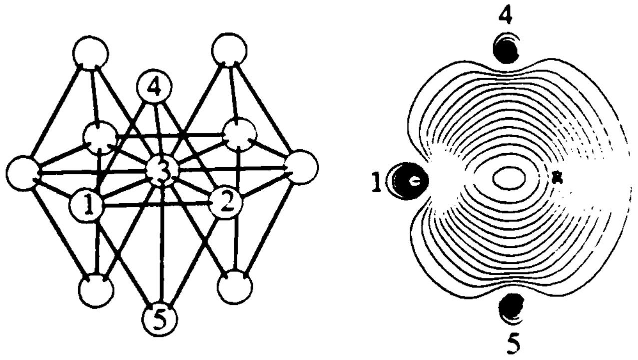
2.3 Solids

One of the potential advantages of using a framework based on localized orbitals is that these orbitals can have *transferability* from one system to another, *i.e.*, from molecule to molecule and molecule to solid. Thus the tetrahedral nature of the bonding in diamond, cubic-BN and BeO is not surprising. In fact, there are a large number of III-V and II-VI semiconductors involving only s and p orbitals in their bonding which have either zincblende or wurzite structures. Discussion of these semiconducting solids in terms of sp^3-hybrids is quite common.[23] However, from the above results on metal clusters, it might be anticipated that tetrahedral hybrids would be a useful concept with which to study bonding in simple metals. In fact the concepts of localized orbitals, tetrahedral hybrids and interstitial electrons obtained from studies of molecules and metal clusters suggest a rather different viewpoint for metallic solids than traditionally accepted.

If these concepts are applied to metallic Be or Zn, for example, a structure which has each metal atom tetrahedrally surrounded by four electron pairs would be anticipated. Starting with ZnO (or BeO), which has the wurzite structure (two interpenetrating hcp lattices), replace each O atom with a pair of electrons localized in this vicinity. This achieves an hcp metal lattice with electron pairs in tetrahedral interstices of the lattice such that each metal atom has four electron pairs distributed tetrahedrally about it. Such an array of electron pairs can be thought of as a useful starting point for considering the ground state properties of the metal.[6] There are, of course, two tetrahedra per electron pair into which electrons can be placed. The two ordered arrays of pairs are only a shorthand way of describing a large number of valence bond structures. Before proceeding down this path, however, it is reasonable to ask if this description is consistent with known facts - for example, the charge distribution of the metal. Fortunately, recent experimental work has produced a high quality charge density for the case of Be metal.[24]

In order to compare the results of localized electrons with this experimental data, it is necessary to describe some recent cluster calculations for Be which were used to generate a charge density for the bulk metal.[25] The hcp structure can be thought of as constructed from face-sharing tetrahedra of Be atoms separated by face-sharing octahedral voids as shown in

Fig. 7a. Considering just the atoms labelled 1 to 5, a cluster calculation was set up with boundary conditions appropriate to the solid.



(a) (b)

Figure 7. Atomic arrangement in hcp Be: (a) the lattice as network of face-sharing tetrahedra; (b) the calculated charge density in the plane of atoms 1,4,5 for the pair of tetrahedra labelled 1,2,3,4,5 .

The form of wave function with the pair of electrons in one of the tetrahedral interstices, *e.g.*, that defined by atoms 1,2,3 and 4, was determined by a variational calculation. The calculation was repeated for the pair in the tetrahedron defined by atoms 1,2,3 and 5. To construct a proper wave function for the pair of electrons, a coherent superposition of these two alternative structures must be made (as in the representation of benzene by the two Kekule' structures[18]). The charge density resulting from the superposition of these components (one with the pair in the upper tetrahedron and the other with the pair in the lower tetrahedron) was obtained and is shown in Fig. 7b. Finally a periodic array of these charge densities was superposed to obtain an approximate charge density in good agreement with experiment[25] and bulk band structure calculations.[26] Thus, the concept of electron pairs largely localized to tetrahedral interstitial sites is consistent with the known charge density of Be, even though it is not the commonly held view.

The traditional view has been to consider the electronic properties of metals by starting from the free electron gas model and constructing theories which incorporate various approximations to the electron-electron interactions in order to discuss the behavior of real metals. Another point of view, and the one adopted here, is suggested by the results discussed above - choose as the starting point the opposite extreme of highly correlated electrons localized at interstitial lattice sites. This viewpoint is not so radical as it may first sound; it is very similar to the electron lattice proposed by Wigner[27] fifty years ago to describe the electron gas at low density. Real metallic densities are roughly in the range of $2.5 < r_s < 5.5$, and it generally has been assumed (based on various theoretical estimates) that the Wigner lattice limit would correspond to much lower densities ($r_s > 10$-20). Thus, the emphasis has been on the development of theoretical techniques for the high density limit ($r_s < 1$) with the expectation that it offered a better chance of approaching densities of physical interest in metals. After many years of effort, however, a satisfactory theory for normal metallic densities is still elusive. The results for metal clusters using correlated wave functions suggest that the Wigner lattice idea may be more appropriate. The introduction of discrete atomic nuclei (rather than the uniform positive background of Wigner) is probably the crucial factor in stabilizing the electron lattice at normal metallic densities.

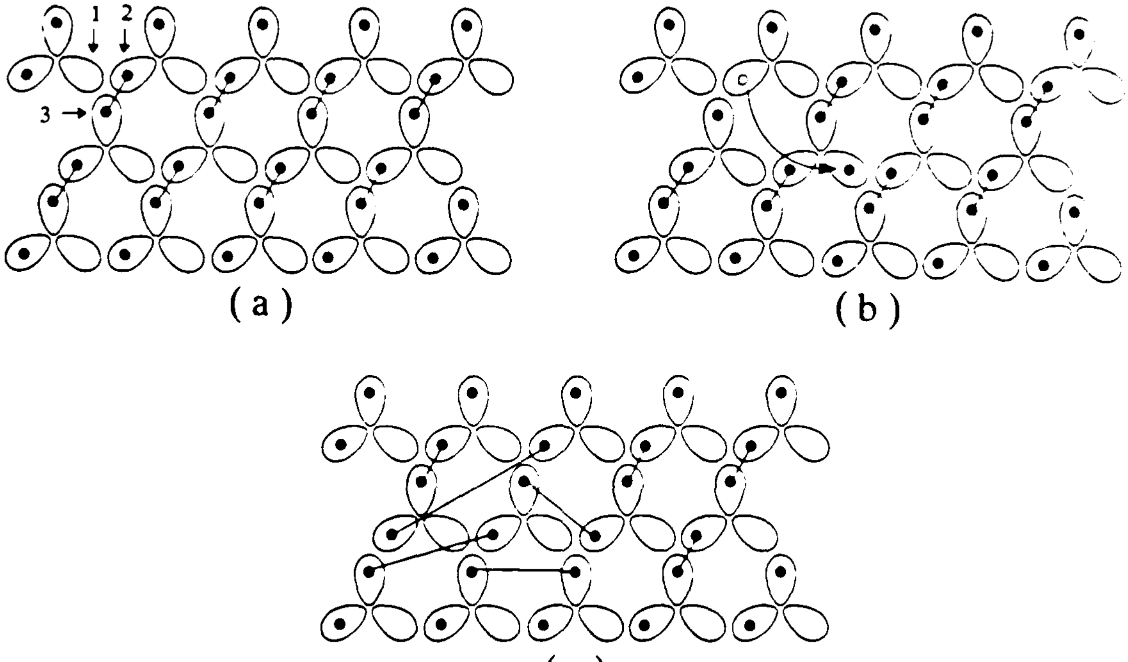
3. SUPERCONDUCTIVITY

Recently, the author proposed a connection between chemical bonding and superconductivity and argued for a formulation in real space.[6] It was proposed in this new model that the superconducting ground state is a coherent superposition of bonding structures which exhibit spatial alternation of valence bonds. With the background provided above, it should not seem unreasonable to formulate a description of metals, and certainly the ground state of metals, from a valence bond Ansatz. This approach is pursued here, and recent work by Robert Murphy and the author is reported upon.[7,8]

3.1 The Wigner Lattice and Normal Metals

In the Bloch theory of metals the one-electron basis set used is labelled according to the eigenfunctions of the kinetic energy operator (*i.e.*, by **k**). There is an intrinsic importance associated with the kinetic energy, while the potential energy (nuclear attraction and electron-electron repulsion) is treated in a secondary manner. In the valence bond theory of metals discussed here, just the opposite strategy is used. The potential energy (and local kinetic energy) is treated first with the (longer range) kinetic energy taken into account afterward.

To clarify the concepts involved, consider a simple two-dimensional case with trigonal hybrids and two electrons per atom. Figure 8 shows several valence bond structures for a small region of the 2-D lattice. In Fig. 8a, a representation of a Wigner-type lattice of pairs of electrons in trigonal interstices is given. As depicted, this clearly looks like an insulating state of valence bonds. There are two electrons in each interstitial region with bonds between orbitals of types 2 and 3. Other bonding arrangements would include bonds between types 1 and 2 and between 1 and 3. In order to describe normal metals, other energetically low-lying configurations have to be considered, such as the one in Fig. 8b, where three of the hybrids are occupied in one interstice and only one in another. The emphasis on the potential energy aspects of the problem are clearly illustrated in these diagrams where the electrons are localized in interstices and the distribution of pairs is such as to minimize pair-pair repulsions. However, there is no reason why the three electrons should be localized to a *particular* trigonal interstice as shown in Fig. 8b. There are other alternative positions which must be considered. In addition, such a localization would significantly raise the kinetic energy. The systematic treatment of configurations such as shown in Fig. 8b is necessary to describe normal metals starting from the valence bond or Wigner-lattice limit. Besides the types of configurations discussed so far there will be a large number based on alternative spin-couplings for a particular occupancy of orbitals. For example, an alternative spin coupling for the orbital configuration shown in Fig. 8a, is that given in Fig. 8c. For such "long bond" configurations, the singlet coupling and triplet coupling will be nearly identical in energy and spin fluctuations will be important. The theory of metals from this perspective is virtually unexplored.



(a) (b) (c)

Figure 8. Some representative valence bond structures in a small region of a two-dimensional lattice: (a) Wigner-like lattice of electron pairs; (b) example of a single particle excitation; (c) example of alternative spin couplings.

3.2 Kinetic Energy and Resonance

The simplest example is considered here in order to gain some insight,[28,29] namely the one electron case of H_2^+. Assume that the solution to this problem can be written in terms of a proton interacting with a hydrogen atom, *i.e.*, the wave function describes a proton on the right and a H atom on the left: (H, H^+). The full Hamiltonian is used, but this "localized" description of the wave function is used. The energy for this description, E_A, is repulsive for all values of the internuclear separation. Hence there is no bond! The problem, of course, is that the above description is not a proper wave function. A proper wave function for the system must be a linear combination of the two alternative structures : $(H, H^+) + (H^+, H)$, where there is an equal probability amplitude for the electron to be on the right or left proton. Now the energy is found to be: $E = E_A + T_X + V_X$, where T_X and V_X are the exchange kinetic energy and the exchange potential energy, respectively. The latter two terms arise from the "exchange" of the electron between the two protons. The exchange potential energy does not provide an attractive interaction over the whole range of internuclear distances. The only term which is attractive is T_X. Thus, the exchange kinetic energy is responsible for bonding! This also turns out to be the case for the prototype of the two-electron bond, H_2, which has been analyzed in detail.[28,29]

Thus, the superposition of alternative electron arrangements (exchanging electron positions among available orbitals) leads to the only attractive term, the exchange kinetic energy, present in the combined H + H^+ system. This kinetic energy stabilization also can be achieved in the one-electron case by allowing the electron to "delocalize" by forming a linear combination of atomic orbitals. These two descriptions are, of course, equivalent in the one electron case. In generalizing to N-electrons and the solid state however, the two approaches are no longer equivalent. Allowing each electron to delocalize (setting up Bloch states) and applying the canonical many-body theory to account for electron correlation effects is the usual procedure. Solving a set of local N-electron problems with correlation effects included and then taking a superposition of the local solutions is the valence bond approach. This superposition of terms (structures such as in Fig. 8c) will lower the kinetic energy and allow a **k** vector to be assigned to the N-electron state. Such a representation allows a description of the normal metal within a valence bond framework.

The coherent superposition of terms in Eq. (2) is frequently referred to as "resonance." However, this designation has come to mean so many things that it is necessary to specify what one is talking about. Consider a term in Eq. (2):

$$\Phi_v = \det[\,(\prod_{j(v)} \varphi_j)\,\Theta_v], \qquad \text{where} \quad \Theta_v = \sum_i c_i{}^{v}\,\theta_i. \qquad (12)$$

For any product of any set (v) of spatial orbitals φ_j in Φ_v, there will be $(2n!) / [n!\,(n+1)!] = \eta$ linearly independent singlet spin couplings θ_j which will contribute to the total singlet spin state Θ_v, where n is the number of electron pairs. If all $d_v = 0$ in Eq. (2), except for one, then the spatial orbitals are fixed; however there are still η terms from the spin-couplings. Such a wave function has been proposed by Anderson[30] to describe the superconductivity in Ba - and Sr - doped La_2CuO_4 and referred to by him as a "resonating valence bond" state or as a "quantum spin liquid."

Another use of the word "resonance" or "resonance structures" comes about if the orbitals in the $\Phi_v{}^{\ddagger}$ are not determined self-consistently, *i.e.*, they are atomic orbitals. Then, in order to obtain appropriate charge transfer from the atomic situation, ionic terms have to be introduced. In the qualitative valence bond scheme of Pauling many such terms were required in order to account for molecular charge distributions.

In the present context, neither of these meanings of the word "resonance" is appropriate. What is required to describe the physical situation envisioned here is a wave function in which there are different spatial terms (*i.e.*, there is a sum over ν), but the sum over the spin-couplings (Eq. 8) is restricted (usually to a single term). As described later this is referred to as a *spatial alternation of valence bonds*, or perhaps more succinctly, as "spatial resonance" in order to differentiate the physical situation from other uses of the word resonance.

3.3 Valence Bond Model of Superconductivity

If the superconducting ground state wave function is viewed as a superposition of structures, Eq. (2), such as schematically depicted in Fig. 8, why should a gap form? Here again, a comparison to a molecular situation is instructive. This time benzene and related molecules (benzenoid molecules) are relevant. These molecules have an anomolous stability and in a magnetic field exhibit large "diamagnetic ring currents"; two features in common with superconductors. However, the analogy goes even farther.

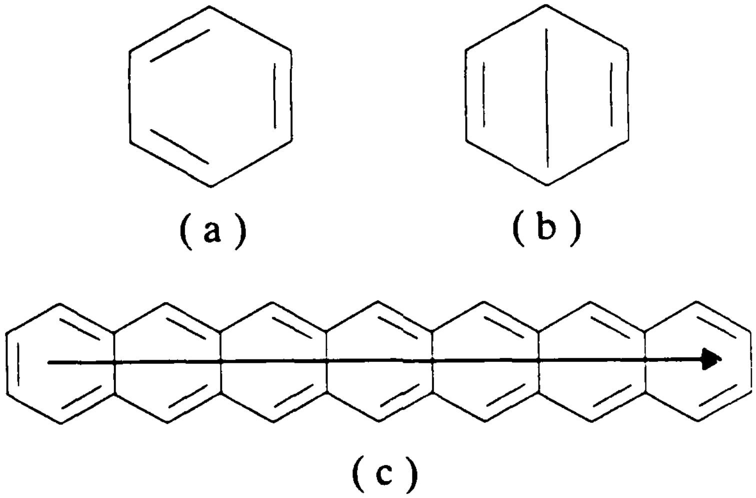


Figure 9.Valence bond structures: (a) one the Kekule' structures of benzene; (b) one of the Dewar structures of benzene; (c) one of several Kekule' structures in a polyacene in which the "benzene ring" can move down the chain.

For benzene, it has recently been demonstrated from quantitative calculations that only two structures, the Kekule' structures (see Fig. 9a) are needed to describe the ground state. Other structures (Fig. 9b) which involve long bonds contribute energetically very little to the ground state wave function. This result had been deduced from semiempirical theories many years ago, and has been the basis of the valence bond approach to benzenoid molecules.[31-33] The Kekule' structures, for example, describe the "delocalization" of the benzene ring in polyacenes (see Fig. 9c). In all these molecules the ground state wave function is made up of a superposition of Kekule'-like structures (no structures with long bonds, only those with nearest neighbor bonds). The coefficients in Eq. (2) for all Kekule' structures are taken to be identical; for large benzenoid systems these represent only a small fraction of the total number of valence bond structures. Furthermore, the matrix elements which convert one structure into another (off-diagonal matrix elements of the Hamiltonian) are set equal to a common value, determined empirically. Thus, the energy lowering associated with "resonance" in benzenoid molecules has a mathematical structure which parallels that of producing a gap in a superconductor as described in the Introduction. However, there is one very important difference.

In the benzenoid molecules the number of electrons and the number of available orbitals are equal, whereas in a metal there are more orbitals than electrons. The latter circumstance is necessary for transporting currents and super-currents. In the case of the oxide materials there are also more orbitals than electrons available, although it may be more convenient to think of the latter situation in terms of holes in occupied orbitals.

Thus it is proposed that the superconducting ground state wave function is composed of a superposition of Kekule'-like terms which enter with identical phases and essentially identical amplitudes. Such a combination produces the lowest kinetic energy. The energy of each of these terms will be nearly the same - all involve different ways of forming nearest neighbor bonds. Just as in the case of the benzenoid molecules there will be large numbers of off-diagonal matrix elements which are the same. This leads to an energy gap of

$$\Delta = \sum_{\mu \neq \nu}^{KS} U_{\mu\nu} \, a_\mu^* \, a_\nu \qquad (13)$$

if the lowest single-particle-like excitation has an energy approximately that of one of the Kekule' structures. The continuum of single-particle-like excitations is made up of the non-Kekule' valence bond structures (long bond structures) and higher kinetic energy sums of the Kekule' structures, in much the same fashion as excitations have been described previously in terms of many-electron basis states.[34] In Eq. (13) the sum is over Kekule' structures (KS), and as mentioned above the a_μ are nearly identical and large numbers of the matrix elements will be the same. At present, nothing more quantitative about the gap can be said. The discussion of several interesting aspects of the model must await the completion of work in progress.[8]

In this valence bond model of superconductivity, raising the temperature will eventually destroy the stability gained from the *spatial resonance* because the entropic term in the free energy will increase rapidly when the electron pairs take on the many other possible configurations that are available. There are clearly two factors which influence the gap size: the number of contributing Kekule'-like structures and the size of the off-diagonal matrix elements. The size of the matrix elements are strongly influenced by the degree of localization of the orbitals involved in the bonds within the given structures. The orbitals of oxygen involved in the high T_c oxides are much more compact than the orbitals of metal atoms in the usual superconducting metals. This is one of several factors contributing to the large gap in the oxide materials.

3.4 Oxides, Spatial Resonance, and High T_c

In order to discuss the new superconductors using the valence bond theory proposed, it must be shown that such a coherent spatial resonance can occur in these materials as a consequence of their local bonding. As an example of the concepts involved, recent work on the electronic structure of the SF_6 molecule is considered.[7] The S atom is in an octahedral environment not unlike that of the metal atoms in some of the oxides of interest. 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. The use of d-orbitals in the bonding, from a d^2sp^3 configuration for S, has been proposed frequently; however, many theoretical calculations show that there is rather little d involvement in the bonding. Understanding the bonding in this molecule continues to offer challenges.[35]

A novel interpretation of the electronic structure of SF_6 is obtained by considering the wave function as a coherent superposition of low symmetry generalized valence bond structures involving covalent bonding, ionic bonding and little sulfur d-orbital contribution. This superposition includes both intra-pair and inter-pair correlation effects while retaining a local picture of the bonding. Fig. 10a shows the geometry of the SF_6 molecule. The calculated results suggest that one may think of SF_6 as 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 on sulfur. The remaining four sulfur electrons left in a tetrahedral orientation on sulfur then form bonds to the equatorial fluorines. The inter-pair correlation introduced tetrahedral sp^3 orbitals bonding to the equatorial fluorines can be seen in Fig. 10b, wh schematic representation of the bonding results is shown. In particular, note that two pai electrons (denoted by shaded spheres) are pulled above the equatorial plane and two below, thus reducing the pair-pair repulsions. The choice of the axial direction for the ionic components is not unique. In order to obtain the wave function, a coherent superposition of six symmetrically equivalent, yet distinct structures is necessary:

$$\Psi = C \sum_{i=1}^{6} \Phi_i \ . \tag{14}$$

Such a coherent superposition of degenerate states leads to the well-known "resonance stabilization" and offers an explanation for the exceptional stability of this molecule.

In the oxide materials, much remains to be done in order to understand the electronic structure. However, the concepts of ionic and covalent bonds together with spatial resonance (as in the SF_6 molecule) are likely to play a significant role. The familiar chemical approach of treating the oxides as ionic solids is too simplistic to deal with many of the properties. On the other hand the band theoretic approaches of the physicist are also too simple; localization and correlation effects cannot be easily dismissed. High temperature superconductivity in ceramic oxides raises many unsettling questions about the present state of understanding in electronic structure theory.

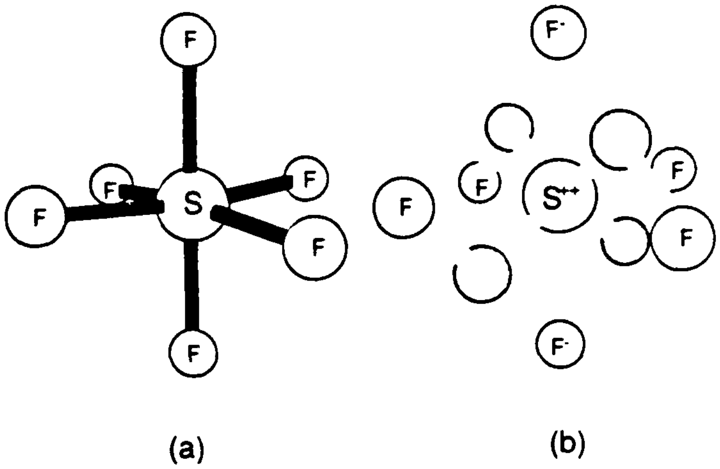


Figure 10. The SF_6 molecule: (a) showing the octahedral symmetry of the molecule; (b) schematic of the bonding in one of the valence bond structures, in which the shaded spheres represent electron pairs and the connecting "bars" represent tetrahedral hybrids.

4. SUMMARY

The thesis presented in this paper is that a common basis for understanding chemical bonding and superconductivity is provided in the framework of the valence bond theory of electronic structure. The valence bond approach considers local bonding and correlation effects in individual alternative valence bond *structures*, then takes care of kinetic energy effects by building a wave function which is a coherent superposition of these structures (*i.e.*, *spatial resonance*). The usual approach to solids is based on the Bloch method, where the kinetic energy for each electron is minimized first, with the correlation effects included afterward.

The BCS theory has taught us the essential requirements of a theory of superconductivity: there must be (1) a gap between the ground state and the spectrum of single-particle excitations, (2) a spatially long range phase-coherence of the electrons, (3) an effective attractive interaction between electrons and (4) a large number of essentially identical off-diagonal matrix elements. BCS, starting from a Bloch representation, met these requirements by using an electron-phonon interaction which produces an effective attractive electron-electron interaction between pairs of electrons with opposite spins and momenta (**k**, -**k**) and by constructing a ground state wave function from these electron pairs.

The valence bond theory described here starts with a large density of nearly degenerate valence bond structures. An in-phase coherent superposition of the Kekule'-type structures results in a ground state which is separated by an energy gap from the single-particle excitations *if* the off-diagonal matrix elements between Kekule' structures have approximately the same values. In benzenoid molecules the latter condition holds, and by analogy is expected to be valid in the more general context. However, a formal proof of this conjecture about the off-diagonal matrix elements for a realistic wave function of the solid is still lacking. If the conjecture is true for the solid, then all the necessary ingredients are in place to have a valence bond theory of superconductivity.

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