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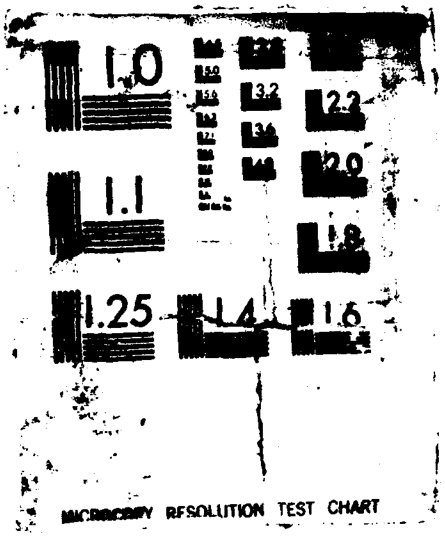
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Superconductivity as a Synchronous Spatial Alternation of Valence Bonds

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SUPERCONDUCTIVITY AS A SYNCHRONOUS SPATIAL ALTERNATION OF VALENCE BONDS

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A new theoretical model for superconductivity is proposed which depends on a pairing in real space (valence bonds). Pair-pair correlations establish an ordered array of such pairs and a synchronous alternation among equivalent coherent spatial arrays of valence bonds is considered as the origin of superconductivity. Simple metals with two valence electrons (e.g., Be, Zn, etc.) are used to illustrate the ideas. The new high T_c materials (based on substitutions in La_2CuO_4) will be considered elsewhere.

It has been traditional to view the electronic properties of metals by starting from the free electron gas model and adding various interactions necessary to explain the behavior of real metals. Another point of view (and the one adopted here) suggests starting at the opposite extreme - namely, the highly correlated Wigner lattice limit, in which the electrons have condensed onto localized sites of a lattice. Again, one would have to add the appropriate interactions necessary to describe the behavior of real metals. At first sight there appears little to be gained from the latter point of view, when so much of present solid state theory is based on the free electron gas model which has been so highly successful in advancing our understanding of metals. However, there are a number of problems in which a local real-space approach might offer complementary information and some additional novel insights. One such problem is the phenomenon of superconductivity.

A consistent theory of metals using the Wigner lattice (or highly correlated ground state) picture must also provide the basis for describing normal metal behavior. Thus, normal conductivity and other properties have to be described in terms of excitations within kT of the ground state which allow electron hopping in the lattice. The fact that metals are electron deficient materials, means there are many spatial configurations of the electrons (many spatial "boxes" into which electrons can be distributed) with very nearly the same energy. This leads to the high density of N-particle states within kT of the ground state. The philosophy in the present contribution is to start with a well defined model of the ground state (which also should be the basis of a description of superconductivity for those metals which exhibit the phenomenon) and leave to later work a discussion of normal metals as excitations from the ground state. This is in contrast to the usual approach which starts with a description of the normal metal and constructs the "special" superconducting ground state.

In order to motivate the discussion below it is necessary to consider some recent developments in our understanding of the chemical bond. It has been shown on the basis of wave functions which explicitly include electron correlation effects that the carbon atom exhibits essentially sp^3-like hybrid orbitals in its bonding in single,[1] double,[2,3] triple,[4] *conjugated bonds,*[5] *and other environments* such as $C\text{-}Li_n$ bonds.[6] This is in contrast to the conclusions of mean-field theory (e.g., molecular orbital theory) which find a variety of hybridizations (sp, sp^2, sp^3) depending upon the environment. These simple conclusions regarding carbon can be extended to sp-bonding in general.[7] Hence, it has been demonstrated that the geometrical structure of electron deficient 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 tetrahedrally distributed (minimization of Pauli repulsions). This is illustrated in Figure 1. In panel (a), two schematic representations of a C-H bond are shown. At the top, the schematic diagram represents the correlated nature of the two electron bond; a shorthand notation is shown at the bottom. In Fig. 1b, using the shorthand notation, the many-electron wave function of CH_4 is depicted; note the tetrahedral distribution of electron pairs. In Fig. 1c, the bonding in C_2H_4 is illustrated. Fig. 1d and Fig. 1e show the bonding for B_2H_6 and B_4H_{10} ; again in these cases note the tetrahedral distribution of electron pairs. Thus two simple principles provide a description of the bonding in molecules containing Li, Be, B and C ; a detailed discussion of bonding and structure in boron hydrides and carboranes will be given elsewhere.[8]

If this approach is applied to Be metal, a structure which has each Be atom tetrahedrally surrounded by four electron pairs would be anticipated. Starting with BeO, which has the wurtzite structure (two interpenetrating HCP lattices), replace each O atom with a pair of electrons localized in this vicinity. This achieves an HCP Be lattice with electron pairs in tetrahedral interstices of the lattice such that each Be atom has four electron pairs at tetrahedral positions. Such an array of electron pairs can be thought of as a Wigner-like lattice which might be a useful starting point for considering the ground state of the metal. There are some other aspects which must be considered before discussing the ground state however. One of them is the obvious question of just how reasonable the above description of Be might be. Is it at least consistent with known facts - for example, the charge distribution in Be metal? Is there any explicit theoretical evidence for such localization in metals at normal densities? It is necessary to digress briefly to address these important issues.

A very important contribution to the understanding of bonding in metals was made recently by McAdon and Goddard[9] who studied the electronic structure of many Li clusters using explicitly correlated many-electron wave functions. Their results demonstrate for many finite Li clusters that electrons occupy localized orbitals in *interstitial* regions between atoms. In particular, for three dimensional clusters, the orbitals localize in tetrahedral interstices of the cluster. This is analogous to the situation proposed above for Be. In fact, the positions of the interstitial electrons in Li clusters found from their quantitative calculations can be understood and predicted in terms of the two simple principles discussed above. Hence, there is sound theoretical evidence that the ground state of a metal (at least for finite systems) can be described in terms of localized orbitals. The next step is to test whether localized orbitals and interstitial electrons are consistent with the recent accurate determination of the charge density of Be metal.[10]

In order to study this aspect it is of interest to consider some recent results of cluster calculations of Be which were used to generate a charge density for the bulk metal.[11] In particular the HCP structure can be thought of as constructed from face-sharing tetrahedra of Be atoms separated by octahedral voids as shown in Fig. 2a. The Wigner lattice of electron pairs is the situation where all the upper tetrahedra (or lower tetrahedra) contain a pair of electrons. To construct a proper wave function a coherent superposition of these two alternative structures must be made (as in the representation of benzene by the two Kekule´ structures).[5] A cluster calculation was set up with the appropriate boundary conditions on the basis functions (appropriate to the solid) to allow a variational calculation of the form of wave function with the pair of electrons in a tetrahedral interstice. The charge density resulting from the superposition of component wave functions with such a pair of electrons in the upper tetrahedron and a pair in the lower tetrahedron was obtained (shown in Fig. 2b) and finally a periodic array of these charge densities superposed to obtain an approximate charge density in good agreement with experiment[10] and bulk band structure calculations.[12,13] Thus, the concept of a Wigner-like lattice of electron pairs largely localized to tetrahedral interstitial sites is consistent with the known charge density of Be. It is now possible, after this digression, to give a simple qualitative discussion of superconductivity in Be.

For the ground state of Be, a wave function now can be constructed which is a coherent superposition of two components. Each component describes the highly correlated Wigner-like lattice array of electron pairs all of which are in either the upper or lower tetrahedra. A schematic representation of these two components is shown in Fig. 3. The coherence of the pairs is manifest in this representation. At finite temperatures there will be situations where some pairs of electrons will be in "up"- tetrahedra while the majority are in "down"- tetrahedra (or *vice-versa*), as well as situations where pairs will be broken - resulting in one electron in some tetrahedra, three in others and/or single electrons in octahedra. Such finite temperature effects break the pairing and the coherence of the wave function responsible for superconductivity. In order to appreciate the coherence in an intuitive manner, it is useful to consider the benzene molecule.

In benzene it has been found[5] that an accurate description of the correlated many-electron ground state wave function is given in terms of a superposition of the two

Kekule´ structures shown in Fig. 4a. The correlated orbitals making up one of the Kekule´ structures are shown schematically in Fig. 4b. Considering a benzene molecule in the xy-plane, the ground state can be thought of as a superposition of the coherent motion of electron pairs about the z-axis in the clockwise and counter-clockwise directions. In the absence of a magnetic field there is no net current; however, in the presence of a magnetic field an overall phase is acquired because the two components no longer combine with opposite phases. This overall phase is characteristic of the coherent motion of the electron pairs of the benzene ring and is responsible for the well-known large diamagnetism of benzene. Thus, a synchronous spatial alternation of valence bonds in the presence of a magnetic field can produce a current. This same effect in Be is proposed as the origin of superconductivity in the metal. It is further proposed that this same mechanism is operative in the new oxide high T_c materials.

Mathematically, an approximate wave function which describes such a ground state can be constructed in the following manner. Define a local bond pair creation operator

$$b^+_L = 1/\sqrt{2} \sum_{\{k,l\}_L} c_{kl}\, a_l^+ a_k^+ \qquad (1)$$

which involves the set of orbitals $\{k,l\}_L$ available at site L, then define a general pair operator

$$b^+ = \sum_L d_L\, b^+_L \qquad (2)$$

which corresponds to the pair being moved to all appropriate sites in the solid. For the case of the Be example, this would be all the tetrahedral interstitial sites of the lattice. A Schafroth condensed pair wave function[14] then can be obtained by applying the pair creation operator b^+ to the vacuum state N/2 times, that is

$$\Psi_N = C_N (b^+)^{N/2} | 0 > \qquad (3)$$

where Ψ_N is the N-particle wave function for N/2 pairs with C_N a normalization constant. By a well-known procedure[15] it can be shown that for special choices of the c_{kl} and d_L in Eqs. (1) and (2)

$$\Psi_N = P_{N/2}\, \Psi_{BCS} \qquad (4)$$

i.e., the Schrafroth condensed pair wave function is identically equal to the BCS wave function projected onto the N-particle space (N/2 pairs).

However, to insure that the wave function conforms to the simple physical picture described above it is desirable to consider the general case and to project Ψ_N onto the "Wigner pair lattice" (WPL) subspace (*e.g.*, see Fig. 3), *i.e.*, define the wave function

$$\Psi_{SAB} = P_{WPL}\,\Psi_N \qquad (5)$$

which is the ground state in terms of a Synchronous spatial Alternation of valence Bonds (SAB). Of course, it is necessary to compare this wave function to $P_{WPL}P_{N/2}\Psi_{BCS}$ and to demonstrate that this projection does not destroy the crucial properties of $P_{N/2}\,\Psi_{BCS}$ responsible for the superconducting properties in simple metals. This concern is also applicable to a recently proposed model for the high T_c oxide superconductors.[16] Arguments can be made which make quite plausible the contention that Eq. (5) is a good representation of the ground state.[19] A discussion of excitations and finite temperature effects are much more easily carried out in a k-space representation such as employed in the BCS wave function.[20] A discussion of the ground state is much more visualizable however with the valence bond wave function. This situation regarding the ground state and excited state descriptions is characteristic of valence bond wave functions. Excitations from a valence bond ground state can be described but the algebra is rather more complicated.

An important point to emphasize about the wave function of Eq. (5) is the *synchronous* nature of the spatial alternation of valence bonds. In the benzene example of the two Kekule´ structures the concepts of synchronous and asynchronous do not arise (by construction it is synchronous) and thus the term "resonating valence bonds" is commonly used. In the case of metals, such as the Be example above, both synchronous and asynchronous behavior is possible. Pauling[21] proposed that normal metals are described by both synchronous and asynchronous alternation of valence bonds between atom-centered orbitals. However, for the phenomenon of superconductivity, the dominance of synchronous behavior and the suppression of asynchronous behavior is absolutely crucial as it is responsible for the coherence of the superconducting wave function.

It should be noted that the choice of Be (or other two valence electron metals) as a vehicle for discussion here was not entirely arbitrary. The more free electron like metals containing a single valence electron such as the alkalis and the noble metals (Cu, Ag, Au) are not superconductors (except for Cs at high pressure). Consider the noble metals and ignore the d-electrons as the valence electrons responsible for conduction are sp-like. The localized representation of the ground state (Wigner lattice) for the noble metals can be thought of as two interpenetrating FCC lattices with the ion cores on one lattice and the electrons on the other. There is one electron at each site on the "electron lattice." Thus there is little overlap of the interstitial electron orbitals (the pairing is weak), the electrons are also rather effectively screened from one another by the intervening ion cores. Such a situation for one-dimension is well described by a Heisenberg Hamiltonian approach.[9] This is likely to be the case in three-dimensions as well. As pair breaking excitations (magnons) can be formed at essentially no energy cost (remember the form of the magnon dispersion curve of 1-D Heisenberg model), superconductivity cannot be achieved. In principle, these metals can be made superconductors only by substantially increasing the overlap of the interstitial orbitals.

There are a number of novel aspects about this description of superconductivity. First, the coherence of the ground state wave function can be disturbed by either pair-breaking or asynchronous alternation of valence bonds. Second, the stabilization energy due to *synchronous* alternation of bonds (*e.g.*, "resonance energy" of Kekule´-Pauling description of benzene), E_{SAB}, is responsible for the gap. Third, E_{SAB} and the pair-breaking energy, E_{PB}, will be different in general. Fourth, the electron-phonon interaction is not responsible for the pairing. Fifth, E_{SAB} stabilizes a symmetric structure against alternative symmetry lowering distortions (recall the benzene molecule again) and thus the electron-phonon interaction is a critical component of superconductivity. Most of these novel aspects are unlikely to be of great consequence for ordinary metals and alloys, where the BCS theory and its generalizations provide a rather comprehensive explanation of the known experimental facts. The oxide materials however have a number of unique features for which the present model of superconductivity promises to provide insight.

A more complete description of the synchronous bond alternation model of superconductivity will be given elsewhere. Applications to the new high T_c oxide materials, as well as the treatment of normal metals from the Wigner lattice ground state description will be developed in future publications.

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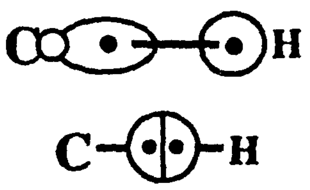
Figure Captions

Figure 1. Schematic representation of electronic structure and bonding in some molecules: (a) electron correlation in a C-H bond; (b) distribution of correlated electron pairs (CEPs) in CH_4; (c) CEPs in ethylene; (d) CEPs in diborane; (e) CEPs not involved in B-H bonds are shown by shaded circles, illustrating the correct topology of the molecule.

Figure 2. Beryllium metal structure: (a) the HCP lattice made up of face-sharing pairs of interstitial tetrahedra separated by octahedra; (b) charge density of wave function obtained by superposition of the amplitude of an electron pair in tetrahedron 1234 with the amplitude of a pair in the tetrahedron 1235, plotted in the plane of atoms 123 and atoms 145.

Figure 3. Schematic representation of alternative coherent distributions of electron pairs: Wigner-like lattices of electron pairs.

Figure 4. The benzene molecule as a coherent superposition of alternative bonding structures: (a) the Kekulé structures; (b) a schematic representation of the bonding in structure A around the ring from atom 1 to atom 6 in the plane perpendicular to the ring, showing the bent bonds.



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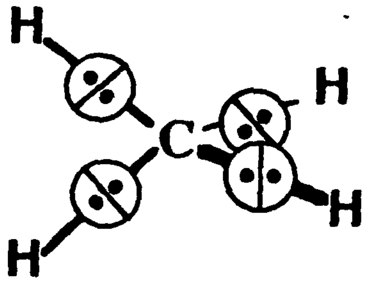

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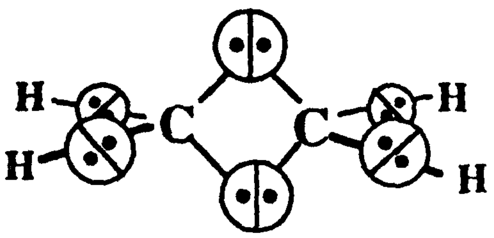

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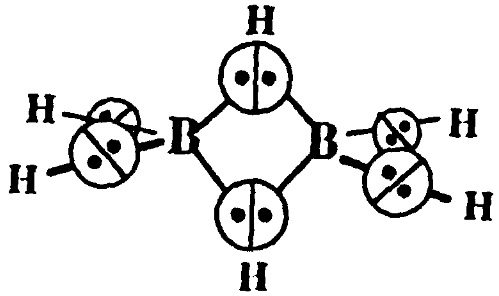

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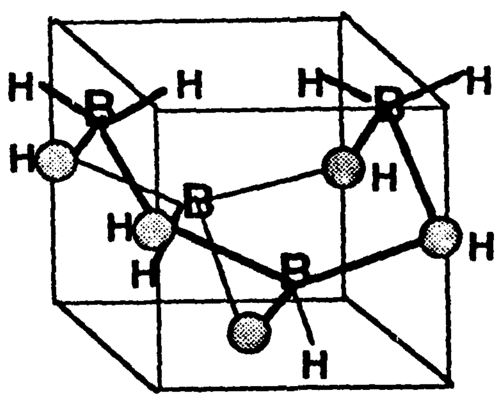

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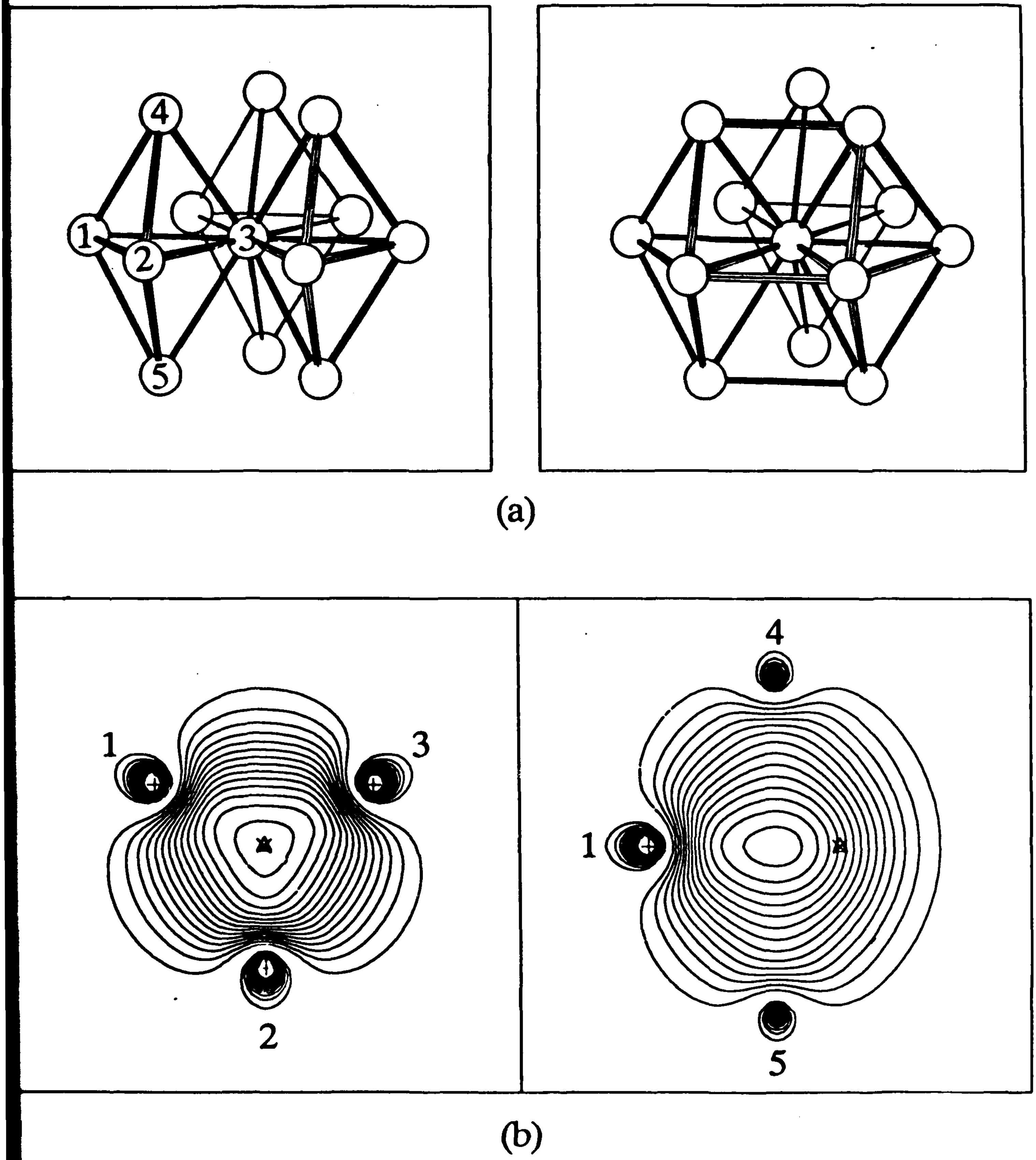
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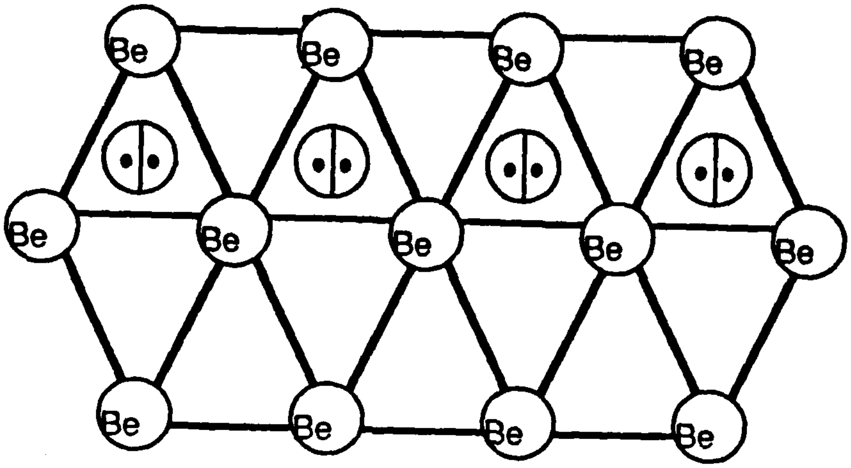
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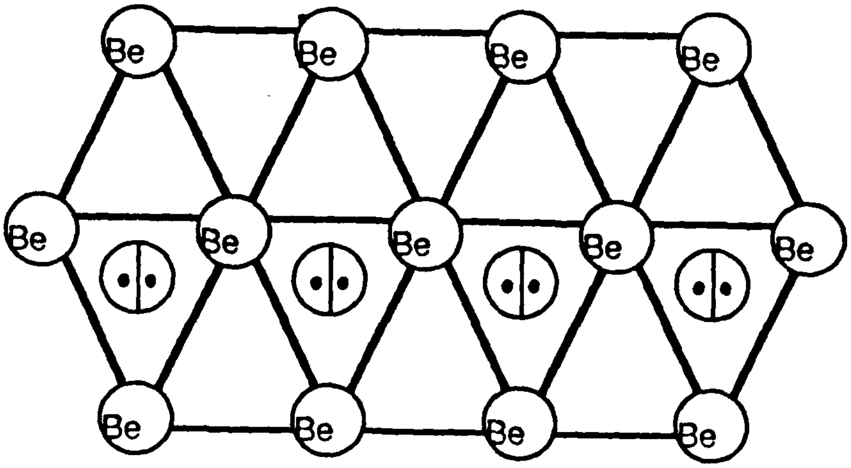
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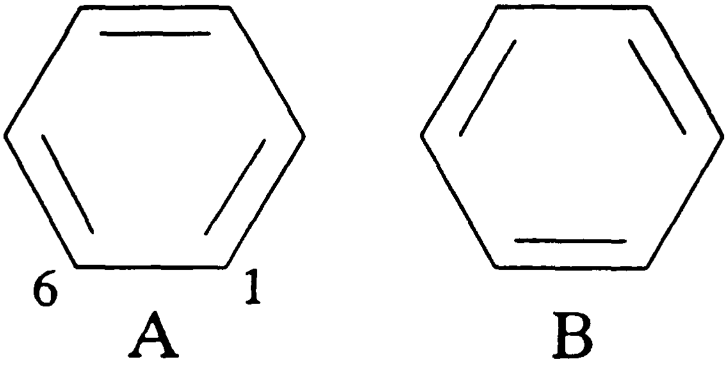

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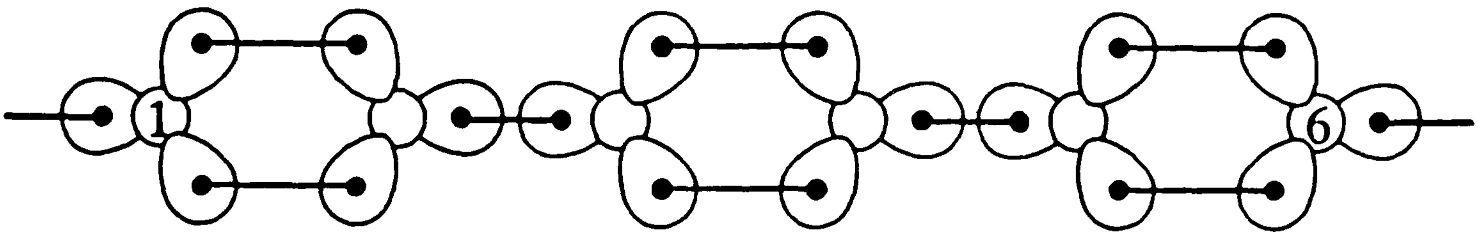

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