Superconductivity, a Physical Chemical Perspective

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Superconductivity arises when solids have conducting bands (singly occupied wave functions) that do not have intrinsic electron-nuclear scattering (Fermi contact) and the temperature is low enough to eliminate partial wave scattering of electrons. This means that the conducting bands do not include ***s*** basis functions (atomic quantum numbers l ,m = 0), and the temperature is low enough so that electron scattering in conduction bands with $l > 0$ is negligible. In most cases, the transition to superconductivity involves a breakdown in the Born-Oppenheimer approximation that separates degenerate electronic states as distinct electron-phonon states. In the case of molecular wires, and related materials, based on $\boldsymbol{\pi}$-electron conjugation the transition to superconductivity may not be a first order phase transition but rather a continuous phase transition. The theory presented here is not in conflict with the standard model for superconductivity, BCS theory. Azimuthal quantum numbers (l) do not appear in BCS theory. The formulations of the two theories are distinct. Experimental data shows two blocks of superconducting elements at one bar appear near the center of the periodic table of the elements. The location of these blocks appears to depend on the lowest energy states of the metallic conductors. The details show the direct involvement of electron orbital angular momentum in the appearance of superconductivity. Conduction band electron orbital angular momentum in the elements is used to account for the central pattern of one bar superconductivity in the periodic table. The lack of superconductivity in Ni, Pd, Pt, Cu, Ag, and Au, all of which are excellent conductors, is due to their lowest energy conduction band being a ***s*** basis-set band, which will always have Fermi contact electron scattering resistivity. The confirmation of this band for copper can be seen in the zero slope of resistivity *v.* temperature at the lowest temperatures for the purest samples of this metal. ***s*** basis set conduction bands cannot be superconducting at any temperature because of Fermi contact induced resistivity. Beryllium's superconductivity is the result of the very low temperature (0.026 K) degeneracy between 2***s*** and 2***p*** conduction bands. In the orbital angular momentum model of superconductivity the energy gap that is known to appear in superconducting states is caused by spin-orbit coupling. The magnetic field associated with carrier motion in the superconducting state couples with the spin angular momentum of the electrons and creates a low energy state. Bosonic conductors, such as ring currents in closed shell aromatic hydrocarbons, are not capable to directly becoming superconductors. This is because in the absence of a magnetic field, the ground state of a conductor is no conduction, as David Bohm proved in 1949. In the presence of a magnetic field for Bosonic systems, there is no spin-orbit coupling to generate an energy gap to stabilize the superconducting state.

I. INTRODUCTION

The recent demonstration of fermionic superconductivity[1] calls for a review of our understanding of the subject. The experiments by Kenzelmann, *et al.*[1], presented strong evidence for femionic superconductivity with normal Meissner Ochsenfeld behavior. This means that the view of the London brothers[2,3] that the Meissner Ochsenfeld effect[4] indicates a bosonic state for superconductivity is not necessarily correct. The Meissner Ochsenfeld effect demonstrated that a superconductor will expel an external magnetic field,[4] and it will prevent the intrusion of a magnetic field with field strength below H_c, the critical field strength, with the exception of a molecularly thin layer (less than a bond length) on the superconductor's surface.[5]

There are a number of other superconducting systems that are intrinsically fermionic. Examples include the organic radical cation superconductors,[6] which have received extensive study. In order for the conducting bands in these systems to become bosonic, it would be necessary to form the dication of the conducting organic ligand. This process is energetically out of the range of possibility. Furthermore, experimental ^{77}Se Knight shifts have demonstrated the existence of triplet states in this class of superconductors.[7] These experiments were conducted with bis-tetramethyl-tetraselenafulvalene hexafluorophosphate.

Organic radical ion systems in which the conduction band is anionic are also well known.[8] Cs_3C_{60} has a critical temperature, T_c, 10 K higher[9] than its Rb counterpart.[8] The critical temperature for superconductivity is also strongly pressure dependent.[9] Charge on the C_{60} ion is assumed to be 3-, which is appropriate for the empirical formula of the A_3C_{60} species. Carbon ions with three negative charges are previously unknown, and seem unlikely on electron repulsion grounds, particularly for a system of 2***p*** basis functions. It would be possible to determine the charge on the C_{60} and the associated metal by integrated x-ray diffraction. High quality crystals are required for these experiments.

Formation of doubly ionized, bosonic states in these systems is even less likely than in the case of radical cations. If the starting conductor is the C_{60}^{3-}, it would be necessary to form C_{60}^{4-} and C_{60}^{2-} to obtain a bosonic state. The dianion state for the parent C_{60} appears to be metastable in the gas phase.[10] The gas-phase lifetime for C_{60}^{2-} as prepared by lazer desorption from solid C_{60} was estimated as ~ms.[10] The electron affinity of C_{60} is quoted as 2.65 eV,[11] and the electron affinity for the C_{60} monoanion is estimated as being of the order of 0.1 to 0.4 eV,[10] insufficient energy to ionize atomic Cs. Formation of C_{60}^{4-} would be very strongly endothermic. Solid state formation of a bosonic pair in an anionic C_{60} conduction band would require a significant increase in the potential of the system, as it would be necessary to transfer an electron from the stabilized monoanion wavefunction to an intrinsically less binding dianion wavefunction in the most favorable case. There is no evidence that supports the availability of the energy necessary for this electron transfer.

An antiferromagnetic phase has been reported for body center cubic crystals of Cs_3C_{60},[11] along with a purely electronic phase transition to superconductivity. Quoting from the abstract for ref. 11 concerning the phase transition, “with a dependence of the transition temperature on pressure-induced changes of anion packing density that is not explicable by Bardeen-Cooper-Schrieffer (BCS) theory.” Isotope effects on the transition temperature and other parameters for K_3C_{60}, were also unexplained by BCS theory.[12]

Electron capture by the C_{84} fullerene was reported to give the dianion, C_{84}^{2-}.[13,14] This same dianion is known in the solid state as an insulator, K_3C_{84}.[15] The failure of the bosonic dianion, C_{84}^{-2}, as a conductor is expected (see below.) The conductivity of K_3C_{60} is consistent with the C_{60} being present in the material as the radical anion.

Paramagnetic chemical shifts in nmr experiments are known as Knight shifts. These temperature dependent shifts are due to the presence of unpaired electrons in the system. Literature on the Knight shift in superconductors is long in duration,[16] and substantial in scope. SciFinder Scholar found more than 650 references under the concept, 'Knight shift superconductivity,' in 2009. All of the major classes of superconductors have shown a Knight shift, see, e.g., the study by Fisk, *et al,* on the Knight shift in a high temperature superconductor.[17] In that study, the axial part of the Knight shift showed linear behavior with T at copper sites in the high T_c superconductor, $YBa_2Cu_3O_7$ powder.[17]

The Knight shift was considered an unresolved problem in the original paper by Bardeen, Cooper, and Schrieffer on superconductivity.[18] Knight shifts in Type I superconductors like mercury[16] show that the magnetic susceptibility within those superconductors is not purely bosonic, magnetic susceptibility, -4π.[4] This observation leads to the conclusion that the information available from magnetic susceptibility measurements on a superconductor is limited to the fact that the external magnetic field does not penetrate the bulk of the superconductor. The recent literature shows that the question of the Knight shift in superconductors does not yet have a consensus solution[19].

The ^{13}C Knight shift for Rb_3C_{60} has been examined in some detail including 85% ^{13}C substitution.[12] The experiments were interpreted in terms of the C_{60}^{3-} ion.

In the systems that show Knight shifts the highest energy electrons in the system must be the unpaired electrons. This can be confirmed at the highest levels of *ab initio* molecular orbital theory.[20] As a consequence unpaired electrons will necessarily be in the conduction bands for any material that shows a Knight shift.

Superconductivity in $CeCoIn_5$[1] is the clearest case of a fermionic superconductor. The examples of organic radical ion superconductors[6-9] are certainly consistent with their being fermionic superconductors. Observation of Knight shifts in both anionic[12] and cationic[7] organic superconductors provides direct evidence of the fermionic character of the superconducting state. With these observations, and the previously mentioned failures of BCS theory to account for the results of recent experiments, it seems appropriate to re-examine the foundations of the general subject of superconductivity.

This paper deals with the fundamental aspects of superconductivity from a chemical perspective. The chemical structural aspects of magnetoresistance and resistivity in metals are respectively the subjects of the following manuscripts.[21,22] All three of these subjects are indexed under solid state physics; however, there are significant chemical insights that shed light on these topics as shown here. The stimulus for presenting this work at this time comes from the experimental observations by Kenzelmann, *et al.*[1] that superconducting states of matter can be host to electron spin angular momentum that couples directly with ordinary ferromagnetism, and the experimental results with A_3C_{60} samples (A symbolizes an alkali metal atom) that cannot fit in the BCS framework.[11,12] A beginning on the large project of rethinking the theory of superconductivity is presented here.

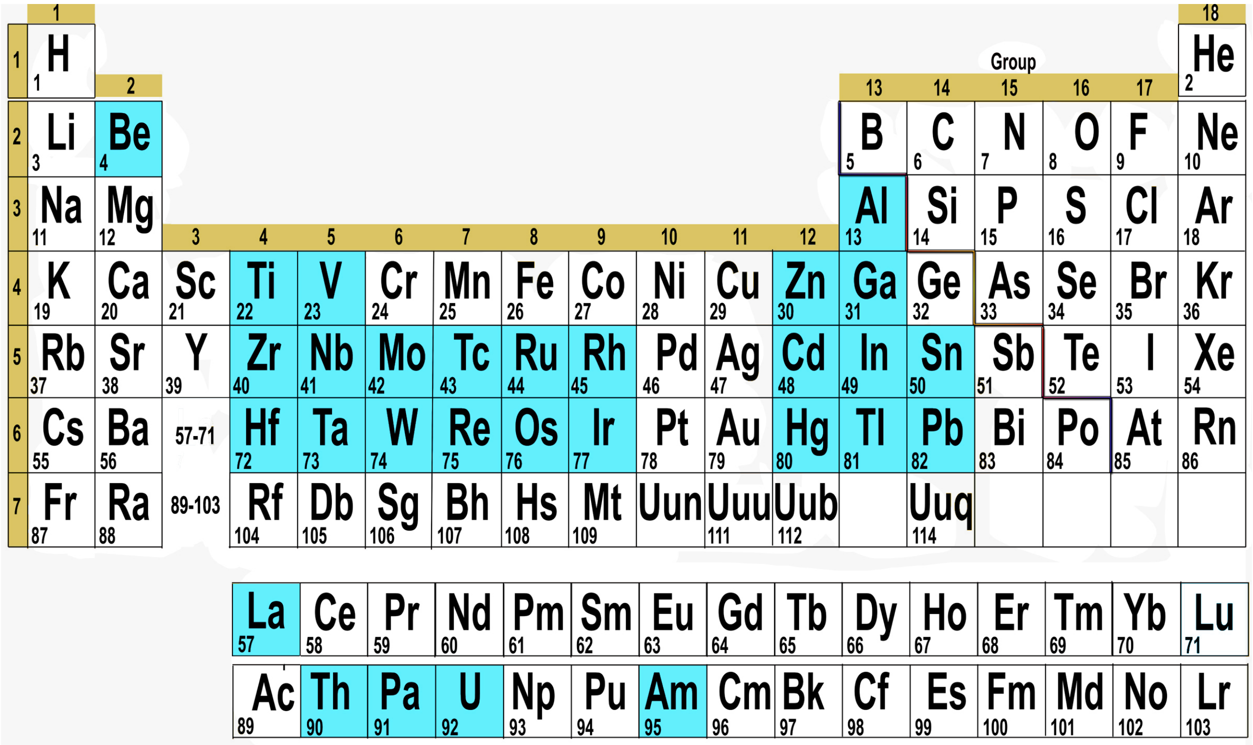
Chemistry can be described as a study in electron orbital angular momentum. Total orbital angular momentum is a very important periodic property of atoms. This quantum characteristic of mater plays a central role in electron transport in metals and other materials. Nonetheless electron orbital angular momentum has received relatively little attention in the discussion of electronic theory of materials. One reason for this is the fact that the energetic effects of orbital angular momentum are extremely small. The accuracy of high level quantum mechanical calculations of molecular or metallic properties of materials have had error bars of the same magnitude as the energy gap due to spin-orbit coupling,[20] ~*k*T at 300 K.

Wave functions for metals extend over the entire lattice and give rise to specific metallic properties.[23,24] Metallic color, luster, and photo ionization threshold are three of many examples of wave mechanically controlled properties of metals. To deepen our understanding of the phenomenological basis for superconductivity in metals we will examine the quantum mechanics of metals as metals without making electron plasma-like approximations. We will not need to solve, or even set up, complete wave functions for metals to develop an understanding of how they work, and how their eigenvalues will scale. That we cannot exactly solve the wave equations for metals does not mean that solutions do not exist, nor does it mean that metals are somehow exempt from the basic rules of quantum mechanics for molecules.

The models for magnetoresistance,[21] and resistivity[22] in the following papers.are quantum mechanical models based on the understanding of electron orbital angular momentum and its role in partial wave electron scattering. It is remarkable that a fully quantum mechanical model for resistivity that explicitly allows for superconductivity already exists in the literature in the form of partial wave electron nuclear scattering.[22] Resistivity and superconductivity are both quintessentially quantum mechanical phenomenon. Resistivity in metals has two major components (1) promotion energy required to form conduction bands and (2) electron nuclear scattering in the lattice.[22] In conductors in which all of the orbitals contributing to the conducting band have orbital angular momentum greater than zero, the material is a superconductor, if the temperature is low enough so that partial wave electron-nuclear scattering in the conduction band is negligible.[22] Superconductivity involves a state that has no resistivity,[18] no electron scattering from Fermi contact or partial wave scattering with nuclei. States of this kind are possible if their conducting bands contain only basis functions that have $l > 0$, and if the temperature is low enough so that partial wave electron scattering can be neglected. This theory is simple and it provides a tool for looking for new superconductors.

Table 1 is the periodic table to the elements,[25] in which the elements that are superconductors at one bar are indicated by blue shading.[26] If we focus our attention on the two blocks of superconductors located near the center of the table, the first thing that we notice is the fact that the two blue blocks are separated by the columns for the nickel and copper families of transition elements. Both of these families are excellent normal conductors of electricity, yet none of the the elements are superconductors in their normal structures at ambient pressures. The reason for this stems from the fact that all six of these elements have ground state ***s*** basis

Table 1: Periodic Table of the elements,[25] showing the superconductors at one bar.[26]



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	57-71	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	89-103	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Uun	Uuu 111	Uub 112		Uuq 114				

La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

conducting bands. Carriers in these bands produce resistance through the mechanism of Fermi contact at the lowest temperatures attainable.[22]

Table 1 shows that there are 29 elements that are superconductors at one bar. All of them are metals. The parameter that generates the pattern seen in Table 1 is the electron orbital angular momentum of the lowest energy conduction bands in metals at one bar.

The existence of isolated conducting, presumably ***p*** band, states in the lanthanides and actinides is expected. The superconductivity of beryllium, Be, is not expected, and must be explained if electron orbital angular momentum is indeed involved in superconductivity. Beryllium has two charge carriers, and the largest known elemental perpendicular Hall coefficient, $+14.8*10^{-10}$ m^3/C.[27]

The only superconductors in Table 1 that are vertically associated with other superconductors are in the two blocks of superconductors at the center of the table. There are no alkali metal or alkaline earth superconductors at one bar. The copper and nickel families of transition metals have no superconducting members.

Approximately one third of the metals in the periodic table are superconductors at one bar (29 of 87 metallic elements.) The recently named metallic elements in row 7 (atomic numbers 104-109) have not to our knowledge been examined for superconductivity. They are likely to be superconductors if sufficient quantities and nuclear stability are available for the experiments. If all of the new metals are superconductors the fraction of superconducting metals at one bar will still be below 1/3.

The pattern displayed in Table 1 cannot be an accident. The source of the pattern is not yet rigorously clear.

Differential compressibility of wavefunctions with the same principal quantum number and different azimuthal quantum numbers is the reason for the large pressure effects on superconductivity that have been observed for many elements.[28] Changes in pressure can cause changes in lowest energy conduction bands for metals.[28] Changes in pressure can induce Mott transitions.[29-31] It is no surprise that adding pressure or thin film as variables makes the pattern of superconductors in the periodic table difficult to understand.[26] The basis for the effects of pressure on conductivity are: 1) differential energy effects of compression of wavefunctions with the same principal quantum number and different azimuthal quantum numbers; and 2) pressure effects on structural arrangement of atoms in the material. For modest pressures the relative orbital energy effects are the most important. In thin films the density of states is much lower than it is in three dimensional metals. This means that thin films will have more isolated conduction bands than are available in the normal metals.

Hirsch presented a careful and extensive statistical study of the correlations between thirteen normal state properties of the elements and critical temperatures at one bar.[32] None of the correlations were strong (maximum $r^2 \sim 0.12$). He found the largest correlations for heat capacity, magnetic susceptibility, and atomic volume. He found the greatest predictive power for superconductivity of the element in its bulk modulus, work function, and Hall coefficient,[32] though this power was small. With the exception of atomic number, Hirsch did not consider quantum mechanical properties of the elements, nor did he look at other parameters directly linked to an element's position in the periodic table.

Our statistical interest is in the pattern shown in Table 1.[33] Unfortunately data is generally not available on the orbital structure of the conduction bands for elements at the superconducting critical temperature, or the lowest temperatures examined. It is possible to construct probable models for the many cases where there is no data; however, elimination of the bias that is introduced by having a specific model in mind is a major difficulty.

II. CLASSES OF ELECTRON CONDUCTORS

There are distinct well known classes of electron conductors. The classes are (1) fermionic: these are standard electron conductors in electronic circuits; and (2) bosonic: these are even electron, spin paired, molecular conducting systems, such as the π-electron system in benzene, the archetypical aromatic hydrocarbon, or coronene, $C_{24}H_{12}$, a polynuclear aromatic hydrocarbon that has often been used as a model for graphene. There are a small group of odd-electron molecules that have an odd number of π-electrons.[34] These molecules could be a distinct subsystem; however, in principle it is possible to incorporate these molecules into fermionic conductors.

Figure 1 presents a scheme for Fermionic electrical conduction. Fermionic conductors employ electrons or holes as charge carriers. In either case the charge carrier wavefunction is a single electron wavefunction. The conductor can, as a consequence, be part of an electronic circuit. Fermionic conductors repeatedly carry a charge from A to B as part of a circuit. Bosonic electron conductors are also well known. They are conductors of pairs of electrons, each pair is a boson, see Figs 2 and 3. The ring current in benzene, C_6H_6, when this molecule is placed in a magnetic

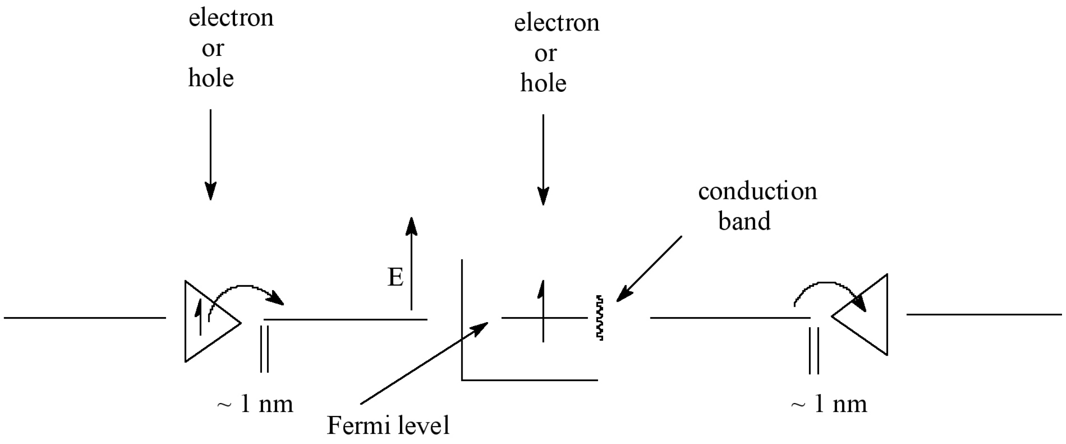


Figure 1: Fermionic electrical conductor. The two edges of the drawing are meant to represent the source/sink for the conduction of either electrons or holes.

field, is an example of bosonic conduction, that has received substantial experimental and theoretical attention. Bosonic circuits will not, on their own, become superconducting at low temperatures. This is because the ground state of a conductor in the absence of a magnetic field is no conduction.[35] In a bosonic conductor there is no spin-orbit coupling to stabilize the superconducting state. Without this small stabilization energy any superconducting state will return to normal conduction through dissipative stochastic processes. There is no Knight shift in a bosonic conductor, because all of the electron spins in the system are paired.

Figure 2: A doubly occupied topologically circular wavefunction for the highest occupied orbital of a bosonic conductor.

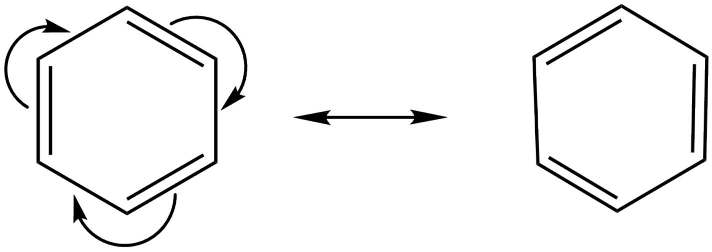


Figure 3: Two lowest energy resonance forms for benzene, an example of bosonic conduction.

The presence of a Knight shift in a molecular system is an indication that the system cannot be bosonic. The wavefunctions harboring the unpaired spins that are responsible for the Knight shift are intrinsically higher in energy than the doubly occupied wavefunctions for the system. These wavefunctions must be either the conduction bands or just below the conduction bands in energy, and the system is described as fermionic.

Bosonic conduction happens in molecules with mobile π-electron systems. Benzene is the primary archetype of these systems. One of the best experimental proofs that this kind of conduction occurs is the nmr chemical shifts of nuclei attached inside and outside the macrocyclic ring of molecules like porphine. The chemical shift difference between those two sets of nuclei can be larger than 10 ppm in selected cases. The chemical shift is caused by an induced ring current that opposes the applied nmr primary field on the periphery of the macrocyclic ring in molecules like benzene (Fig. 3).[36]

Bosonic conduction systems are closed systems, or open systems with equipotential input and output. When current is carried by the highest occupied wavefunction and the lowest vacant wave function in the same spin paired molecule, bond formation occurs if charge is actually transferred. These systems are Mott insulators. They are only conductors because of delocalization of bonding electron pairs. The insulating properties of K_3C_{84} (see above) are an example of a molecular ionic bosonic conductor.[15]

III. ELECTRON-PHONON COUPLING AND BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION IN TYPE I SUPERCONDUCTIVITY.

Type I superconductors were discovered by H. Kamerlingh Onnes in 1911,[37] through low temperature studies of resistivity in mercury. In superconductors, there is a phase transition with a discontinuity in the heat capacity at a critical temperature, T_c.[38,39] Aa the temperature decreases below T_c, the number of states that can accept conducting electrons usually undergoes a substantial increase.

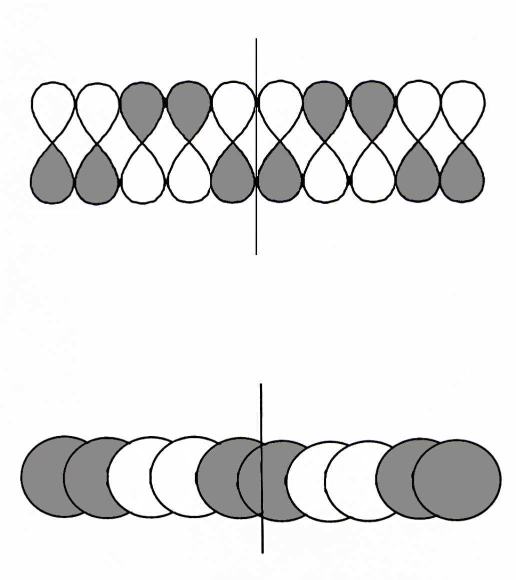
A perturbation molecular orbital[49] model of a metal can be a manageable substitute for a full molecular orbital treatment in this analysis of superconductivity. This model will allow us to examine some qualitative properties of the wave functions in the conduction bands of both metals and nonmetals. The individual bands can be built in pieces starting in the same manner as the first row diatomics.[40] This approach retains the fundamental quantum mechanical features that we need in the wave functions. In this model the orbitals are still molecular orbitals with associated principal, azimuthal, and magnetic quantum numbers. The Pauli exclusion principle operates, and the individual orbitals are normalized and orthogonal. These quantum mechanical features are essential to understanding the details of superconductivity. In the way of contrast, in a liquid of fermions, every electron is in an independent wave function, and the wave functions are not associated with orbital angular momentum quantum numbers.

The highest energy-conducting band of ordinary metallic conductors at low temperatures, can contain a mixture of ***s***, ***p***, and potentially higher orbital angular momentum atomic basis functions. To keep the system as simple, and as close to reality, as possible we use only one value of electron orbital angular momentum per conduction band. In any case degenerate bands with distinct electron orbital angular momenta will not mix as long as electron orbital angular momentum is explicitly considered. For our purposes, the symmetry properties of the ***d***, and ***f*** basis functions are the same as those of the ***p*** basis functions, so we will only discuss the latter. The electron scattering amplitudes[22] of ***d,*** and ***f*** basis functions are superior to those of ***p*** basis functions from the point of view of superconductivity; however, our interest at this point is symmetry. The derivatives of the electron radial distribution for ***p, d,*** and ***f*** orbitals at the origin for each atom are zero. None of these orbitals are involved in Fermi contact. With reference to a symmetry plane, all three sets of orbitals have similar properties. They are anti-symmetric for reflection in a plane that contains one of their nodal axes.

The Feynman band theory of solids[24] treats the molecular orbital relationships in metallic conductors. Here we discuss bonding in metals using perturbation molecular orbital theory[40] within the context of band theory. We need to keep track of the basis sets for the various bands, so we will need to stay in a normal coordinate system and give up the advantages of working in reciprocal space (*k* space).

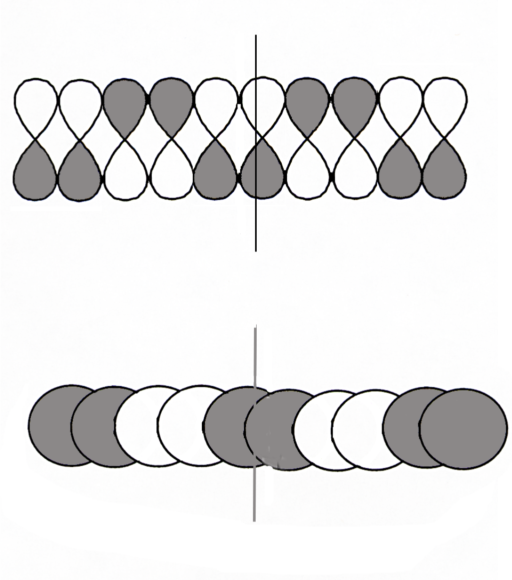
The valence band of the metal contains the core electrons and the metal bonding electrons. Moving up the energy scale for wave functions the next set of orbitals are either vacant or partially filled bonding valence level orbitals, such as in the alkali metals, group 1A, and the group 1B metals, Cu, Ag, Au, or non-bonding molecular orbitals of any metallic element. Nonbonding orbitals form for every atomic orbital type used to build odd fragment molecular orbitals for a metal. Anti-bonding molecular orbitals are generally at the top of the band structure for each specific band. Anti-bonding orbitals for the core electrons can have energies in the range of the valence bands.

The fact that wave functions in a metal lattice are more complex than we suggest because of overlaps in three dimensions between ranks of metal cores makes no difference to the one dimensional arguments used here. The three-dimensional orbitals, regardless of their complexity, must conform to the one-dimensional symmetry properties of the collection of atoms. The simple argument will work as well as a much more complex three-dimensional one. We use grey scale to indicate phase, ○ indicates positive phase and ● indicates a negative phase, or the reverse. Orbital drawing (1) shows two sets of a string of ten atoms with symmetric bonding wavefunctions of ***s*** and $\boldsymbol{p_y}$ type (orbital coefficients all set to ± 1 for the purposes of illustrating symmetry.) These two symmetric orbitals would not be distinguishable if they were at the same energy. Since the density of orbitals in the conduction band is high it is likely that the ***s*** and ***p*** wavefunctions in (1) will be only the order of a vibrational quantum different in energy at some temperature not far from 0 K.



(1)

Orbital phase diagram (2) illustrates a possible arrangement for the same orbitals, this time with the symmetry removed by an appropriate vibrational motion. If the assumptions of the Born-Oppenheimer approximation[41,42] breakdown under these conditions the two sets of wavefunctions can be distinguished. If one band has become superconducting, the system will drop into that state.



(2)

Phonons are the eigen values of nuclear wavefunctions. When the electronic and nuclear coordinates are separated in the Born-Oppenheimer approximation each group of particles has its own wave functions and eigen states.[43-45]

Phonons are electromagnetic quanta generated by the motion of nuclei in a crystal lattice following Maxwell's equations. When the Born-Oppenheimer approximation holds in molecular systems the nuclei behave like classical particles so classical equations, like those of Maxwell are appropriate. The frequencies associated with these states are of the order of terahertz, 10^{12} Hz. The electromagnetic energy associated with such a state is roughly 10^{-3} times the energy of the Fermi level in a metal. These orders or magnitude are in the correct ranges for breakdown[41-45] of the Born-Oppenheimer approximation due to electronic-nuclear coupling in symmetric (or antisymmetric) electronic states.

The features that are necessary for Type I superconductivity are two degenerate or near degenerate conduction band wavefunctions of the same symmetry and different orbital angular momentum (basis set). The ***s*** basis set orbital is a conduction-orbital and is half occupied. The ***p*** basis set orbital of the same symmetry is either a conduction-orbital or a vacant-orbital and just above the ***s*** orbital in energy. As the temperature decreases the ***p*** basis orbital will decrease in energy faster than the ***s*** basis orbital, as the ***p*** basis orbital approaches a state of zero electron scattering faster than its counterpart. Once the condition of zero electron scattering is achieved in the ***p*** basis orbital, both states will become electron-nuclear states with distinct symmetries and the phase transition will occur.

This argument may be somewhat clearer when cast in terms of the ***s*** and ***p*** basis wavefunctions discussed above using Kamerlingh Onnes' example of Hg. Mercury has a ground state electronic structure of $\ldots 6\boldsymbol{s}^{2}5\boldsymbol{d}^{10}$. Hall probe measurements show there are two electron charge carriers per atom in mercury.[46] This indicates that the lowest energy conduction bands for Hg will have 6***s*** and 6***p*** basis sets. These two basis sets are well separated in energy at 300 K.

Temperature dependence of resistivity, electron scattering[22] in 6***s*** orbitals is zero. Temperature dependence of resistivity in 6***p*** orbitals follows T^2.[22] This means that as the temperature decreases the energies of the 6***p*** conduction band orbitals will decrease with reference to those of the 6***s*** conduction band. In cases where there is orbital degeneracy between the two bands, this will have no effect until a vacant 6***p*** wavefunction attains the state of zero electron scattering. That temperature corresponds to T_c. At that temperature the combination of a phonon state with the ***s*** and ***p*** basis states will create new nuclear-electronic states that are distinguishable from one another, so the superconducting state will take all of the current and the phase transition will occur. A superconducting potential drop is generated by spin-orbit coupling with the superconducting magnetic field. In the case of lead, the electron-phonon interaction in the energy gap, has received detailed experimental examination.[47]

The nuclear-electronic transition that is responsible for initiating superconductivity is directly analogous to the corresponding coupling that destroys the symmetry of orbitally degenerate systems in the Jahn-Teller Theorem.[48] When the Born-Oppenheimer approximation breaks down, the coordinates of the electrons can no longer be treated independently from the nuclear coordinates. Here the nuclear and electronic wave functions couple in such a way that the ***p*** (l = 1) basis orbitals become available to accept supercurrent electrons in an electron-nuclear symmetry state that is unique compared to other available ***s*** basis conducting bands. The electronic potential associated with the ***p*** (l = 1) basis orbitals is intrinsically lower than that of corresponding ***s*** basis orbitals at T_c because of the lack of electron nuclear scattering in the ***p*** (l = 1) basis orbitals. The energy gap in superconductivity is generated through spin-orbit coupling due to the presence of the magnetic field generated by a supercurrent. It appears from this analysis that superconductivity is a bootstrap operation. The development of the energy gap that is essential for a sustained supercurrent requires the development of a magnetic field, which is dependent on spin-orbit coupling in the superconducting state. It is physically reasonable that this system will work, but it will be delicate at the onset of superconductivity. Without the presence of charge carriers, the phase transition can occur but there will be no energy gap with which to create a persistent superconducting magnetic field. In the Kamerlingh Onnes experiment,[37] the resistance of the mercury was measured with a bridge under conditions of no current.

Isotope effects on T_c,[49,50] and superconducting transitions, are often directly analogous to those found in the Jahn-Teller effect.[48] They are the direct consequence of breakdown of the Born-Oppenheimer approximation for the electronic-vibronic system.

Isotope effects on T_c in organic ***p*** basis superconductors are another matter. The phase transition in the organic superconductors is a temperature dependent phase transition in a single basis set conductor. The isotope effect reflects the vibrational coupling to the temperature dependence of the ***p*** basis electron nuclear scattering. The phase transition is a continuous phase transition.[51] Both the unusual isotope effects,[12] and the pure electronic phase transition,[11] can be understood within the context of this model.

Type II superconductors differ from Type I superconductors in some important details. Type II superconductors contain vortex domains and electron spin magnetism, that is not present in Type I superconductors.[5]

High temperature superconductors are a distinct class of materials.[52] At the critical temperature, a breakdown in the Born-Oppenheimer approximation[41,42] of a similar type to that described above opens access to a ***d*** basis conducting band and superconductivity follows. Electron scattering at a given temperature is much smaller (roughly three orders of magnitude) in ***d*** basis function orbitals than it is in ***p*** basis function orbitals.[22] The relatively high T_c for these superconductors is directly linked to the ***d*** basis functions for the conduction band. These observations point to the fact that the conduction band in these materials does not involve the oxygen atoms, or any other second or third row main group atom. The well known ***d*** wave character of these materials is a direct consequence of the ***d*** basis conduction band. Higher temperature superconductors may be attainable if systems can be found that utilize exclusively ***f*** basis functions for the conduction band. These systems are likely to be doped actinide oxides, nitrides or sulfides. The probability for success of this venture seems guarded because ***f*** basis functions are doubly inner shell and ***f - f*** bonds are not known to be strong. Higher temperature superconductors might also be available for other ***d*** basis function conductors that have stronger bonds between individual cores than those found in the cuprates.

Table 2 shows a first order analysis (taken from Ref. 22) of the ratio of electron scattering amplitude for $l > 0$ to ***s*** basis function conduction bands. Table 2 assumes that all of the bond strengths in the compared systems are identical. This assumption is surely not true. Nonetheless the table can provide a rough guide to the probability of superconductivity being associated with a given conduction band.

Molecular wires that have well defined **π** conjugation using *p* basis functions have an intrinsic superconducting architecture. The question of superconductivity in these materials revolves around the magnitude of the electron scattering in the *p*

Table 2: Approximate electron-nuclear scattering amplitude ratios as a function of temperature and azimuthal quantum number.

Temperature	300 K	200 K	100 K	10 K	1 K
p/*s*	$7*10^{-5}$	$5*10^{-5}$	$2*10^{-5}$	$2*10^{-6}$	$2*10^{-7}$
d/*s*	$5*10^{-9}$	$2*10^{-9}$	$6*10^{-10}$	$6*10^{-12}$	$6*10^{-14}$
f/*s*	$4*10^{-13}$	$1*10^{-13}$	$1*10^{-14}$	$1*10^{-17}$	$1*10^{-20}$

conducting orbitals. The ratio of the scattering cross sections for *p* to *s* electrons at 300 K[22] is roughly 10^{-4}. This 10,000 fold, or so, decrease in resistivity will not be sufficient to sustain superconductivity. At 1 K the same ratio in Table 2[22] is about 10^{-7}. This decrease in resistivity may sustain superconductivity. A decrease in the magnitude of r_o, the scattering range, one order of magnitude would decrease the ratio by two orders of magnitude. For the purposes of our approximate calculations we chose the scattering range as the negative of the Bohr radius.[22] The scattering range is the analog of the phase shift in x-ray scattering.[22]

Single-walled carbon nanotubes in zeolite have been observed to be superconducting at 15 K.[53] Graphitic multilayer materials have recently appeared in the literature.[54] Graphene samples have exceptionally low resistivities at ambient temperature. Undoped graphene bilayers did not demonstrate superconductivity,[55] and gave a temperature dependence of resistivity consistent with a *s* basis set conduction band[22,55] for the neutral bilayer (see Fig. 3d of ref. 55 reproduced as Fig. 3 of ref. 22). In the Geim group experiment,[55] undoped graphene is bosonic and a Mott insulator, for specific resistance below ~7 kΩ. Doped graphene demonstrated a supercurrent as part of a Josephson junction at 30 mK.[54] In hole doped graphene, the transition from the normal to superconducting state should not be a first order phase transition. There should be no change in the density of states at the transition. Resistivity in the ***p*** basis π-conduction band will be temperature dependent. The phase transition in 3D systems will be continuous.[51] Graphene is only two dimensional so a phase transition is not possible. The transition temperature may be dependent upon the size of the sample. Dependence of transition temperature on sample thickness is known for lead.[56]

IV. SUPERCONDUCTING ENERGY GAP

David Bohm was the first to point out the fact that spin-orbit coupling will generate an energy-gap that will make sustained superconductivity possible (see p. 504 top of column 2, ref. 35). It is worth noting that Bohm's extension of the Bloch Theorem indicates that a sustained supercurrent would not be stable in a bosonic system in the absence of an external magnetic field. Our unpublished experiments with the ring current in coronene were in complete agreement with Bohm's theoretical prediction.[57] The energy-gap generated by spin-orbit coupling of electron angular momenta is very small. The measured energy gap for superconductivity is known to be of this order of magnitude.[58,59]

V. DISCUSSION

THE PATTERN OF SUPERCONDUCTORS AT ONE BAR

The feature that determines the pattern of the superconductors in Table 1 is the nature of the basis functions for the ground state conduction band of the elements. If the ground state conduction band has ***s*** basis orbitals the element will not be superconducting because its conduction will have Fermi contact electron scattering at the lowest possible temperatures. The ground state conduction band for the alkali metals, Li-Fr, is *ns*. None of these elements are superconducting at one bar. Li and Cs are column 1 metals that are superconductors at high pressures.[26] Elevated pressure, changes the relative energies of conduction bands because of differential compressibility as a function of *l* .[28]

Both theory[22] and experiment indicate that ultra pure copper metal has zero slope for partial wave electron scattering (resistivity) *v*. T in the temperature range below 10 K.[60,61] This is a clear indication that systems with ***s*** basis conduction bands cannot participate in superconductivity, because Fermi contact electron scattering will produce resistivity even at the lowest temperatures.

The alkaline earth metals, Be-Ra, have a closed ns^2 subshell that is not conducting. The ground state conducting band is ns^1, which should not be superconducting. Be is both a bulk and film superconductor.[26] Band structure and the Fermi surface for Be have been carefully examined. Auger spectra[62] and molecular orbital calculations[63] have shown that the ***s*** and ***p*** bands for Be are strongly overlapped. Because of the relatively high specific resistivity of Be very high current densities are not realistic for this material. As long as the current is low enough so that the lowest energy conduction band only samples the highest conducting orbitals, 2***p***, Be will be superconducting at sufficiently low temperatures. More recently *ab initio* theoretical studies,[64] and inelastic x-ray scattering studies[65] have amplified these results.

Of the superconducting elements rhodium has the lowest critical temperature, 325 μK.[66] Tungsten is next, critical temperature, 0.015 K.[67] Its critical magnetic field estimated at 0 K is 1.15 G.[67] Be is next in critical temperature at 0.026 K,[68] and its estimated critical field is 1.08 G. The amount of data here is insufficient to draw any clear conclusions. From the data it appears that superconductivity for beryllium is marginal, and that it depends upon sampling only the highest energy portions of the ground state conduction bands for the element. These are the 2***p*** basis bands. The high pressure superconductivity of Ca, Sr, and Ba have been discussed in terms of ***s*** – ***d*** electron transitions under pressure.[28,67]

The ***ns*** *-**np*** energy gap increases as you proceed to the right and down the periodic table. Classically this relative shift in orbital energies is known as the "inert pair" effect. In elements like Pb. for example, the outer ***s*** electrons tend to be inert, and the usual valence often contracts by two. The relative orbital energy gap is also responsible for the fact that the 3***d*** transition metals Cr-Co are not in the group of superconducting elements at one bar.

Cu, Ag, and Au all have ***s*** basis wave functions that are bonding, vacant, and lower in energy than any bands made up from basis sets with $l > 0$. The same is true the nickel family (column 10, Table 1). None of these columns in the periodic table are expected to show superconductivity at one bar.

Alloys of copper family elements, Cu, Ag, Au, with elements in the boron family, column 13 of Table 1, Ga, In, Tl, could show superconductivity, and should have interesting properties. Some of these possibilities have received attention.[69] The literature on superconducting compounds and solutions of non-superconducting elements is both long standing and extensive.[70]

Carbon, tin, and lead are the only members of the carbon family that demonstrate supercurrents at one bar. Carbon does so only for structural reasons involving the formation of delocalized π-electron systems that structurally avoid involvement with carbon's 2***s*** electrons. It seems highly probable that tin and lead are superconductors as two electron conductors utilizing ground state ***np*** conduction bands.

Antimony and bismuth are the only metallic members of Group V (column 15 in Table 1). The atomic ground state for these semimetals is closed sub-shell, as a result their specific resistance is relatively high. The text book number of carriers for Sb and Bi from Hall effect experiments is 5.[71] If this relatively large number of carriers is maintained at low temperatures, the ground state conduction bands will involve both ***ns*** and (*n*+1)***s*** bands. The lowest energy conducting bands in the system will be *ns.* Neither of these elements is expected to be a superconductor at one bar. Bismuth as a conductor has been of recent interest because like graphene its conducting electrons behave as Dirac fermions.[72]

The conducting states that lead to superconductivity in the lanthanides and actinides are not immediately clear. The La atomic ground state is [Xe]$6s^2 5\boldsymbol{d}^1$. A simple analysis suggests that La should be one electron/hole conductor. Electron promotion to wavefunctions that would provide delocalized bonds in the lanthanides and actinides would seem to be required. Atomic resistivity for La, ~1,800 Ω-atom is exceeded only by Sc, Mn, Hg, and 12 other lanthanides.[22]

The number of reports of one bar superconductivity for Lu is very limited.[73] We removed Lu from the group of superconducting elements at one bar[26] because none of the subsequent investigators of Lu's superconductivity confirmed it was a superconductor at one bar. Lutetium's atomic resistivity is an order of magnitude lower than that of lanthanum at ~180 Ω-atom.[22] This makes it even more unlikely that lutetium is in fact a superconductor at one bar pressure (because the band gap for conductivity is quite small, suggesting involvement of 6***s*** electrons in the ground state conduction band) and further justifies our removing it from the list of one bar superconducting elements.[26]

The pattern of superconductivity in the actinides is different from the lanthanides. This is due to the small differences in the relative gaps between the outer ***s***, ***p***, and ***d*** conduction bands for these two groups of elements. As one might expect the radioactivity of the actinides appears to have limited the number of reports of superconductivity in these elements.[74]

Perturbation theory predicts that metallic states of H_2 or Xe at low temperatures and high pressures will not show superconductivity. Going up in energy from the valence band in the high pressure metallic state for either element, one would encounter a set of vacant bonding ***s*** based wave functions. These wave functions will be lower in energy than the corresponding bonding ***p*** based functions. In this case there will be no way to evade the presence of the ***s*** basis in the lowest energy conduction band. These materials will not be superconductors. Experiments on this subject for Xe in 2000[31] demonstrated a semi-conductor to metal transition in Xe in the pressure range of 121 to 138 GPa. The material showed no sign of superconductivity down to a temperature of 27 mK.[31]

BOSONIC SUPERCURRENTS

Electron orbital angular momentum has considerable influence on electron lattice scattering and provides a predictive model for superconductivity in materials. In light of this model, the aromatic ring current observed in nuclear magnetic resonance[36] when observed at sufficiently low temperatures is a supercurrent. This supercurrent will not, however, be self sustaining since there is no energy gap in bosonic systems. The much smaller ring currents seen in σ bonded rings would not be a supercurrent because bonding in these systems involves ***s*** basis functions.

The supercurrent in aromatic rings would show zero carriers in a Hall probe experiment, because the system is closed shell and has no half filled orbitals. The reason for no response in a Hall probe experiment is that the bosonic current is not responsive to an electric field in first order. This means that without the introduction of spins these systems could not be a useful part of any circuit. It also means that this system has no mechanism for generating an energy gap. We have made a serious attempt to observe a supercurrent in coronene, $C_{12}H_{10}$. None was observed.[57]

One of the major strengths of this approach to superconductivity arrises in the treatment of superconductor communication with non-superconducting power supplies and related circuitry. In this treatment the wavefunctions for superconductors are the same wavefunctions involved in non-superconducting current flow. No spin inversions are required. The open shell/closed shell nature of the system is not changed by the phase transition to superconductivity. In this model it is easy to understand how ordinary power supplies can be used to increase the magnetic field in a superconductor that has just been initialized at T_c, and has a thermally generated minimal magnetic field. Ease of understanding follows from the fact that both the power supply and the superconductor are fermionic systems. In the BCS model the power supply is fermionic and the superconductor is bosonic. Electronic communication between these two states is formally statistically forbidden.

SUMMARY

Superconductivity occurs when conducting electrons move in states that have no contributions from zero orbital angular momentum atomic wave functions and no partial wave scattering of conducting electrons. For Type I superconductors, these states arise at low temperatures by electron-phonon interactions, directly analogous to the Jahn-Teller Effect.

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