

Superconductivity and Magnetism

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Received 2 July 2020

Abstract: The field of superconductivity which has more than one hundred years of history poses many challenges to the condensed matter physicists with the discovery of new materials with exotic properties defying older and accepted theory due to Bardeen, Cooper and Schriffer (BCS). Super-currents in superconductors are due to pairing of two electrons each carrying a charge $2e$ unlike individual electrons with charge e in ordinary current. In the superconducting state, electrical resistance completely vanishes. This super-current was believed to be due to paired two electrons arising from phonons which couple them. However, a large number of experiments clearly indicate that phonon mediated mechanism fails in the new superconductors. Already marching towards room temperature, superconductors show a promising trend as we are only 50 K away from room temperature. The million dollar question now is what binds the two electrons other than phonons? This seemingly simple question is not so simple. Superconductivity does not simply mean zero electrical resistance of the material. There are drastic changes in magnetic, optical and thermal properties and this obviously makes the problem complex. There is a huge collection of materials and some exhibiting exotic behaviour under pressure, applied magnetic field and alloying which leads to a number of unanswered questions. It is the field which has fetched maximum number of Nobel prizes in physics. Many more will get these awards in the years to come.

At present, it has pervaded all fields such as transportation engineering (Magnetically levitated trains), Medical resonance imaging, nuclear magnetic resonance, biological sensors (SQUID), nuclear reactors, particle accelerators, quantum computing and faster data transfer *etc.* The world's costliest experiment done on earth till date - a joint effort by about 100 countries, the superconducting super collider experiment to detect Higgs Boson made use of superconducting magnets. This has remained almost for 70 years, mostly

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as a low temperature phenomenon; the effects of which can be realised only at liquid helium temperatures. But, of late many materials have emerged which enables the above phenomenon to work at fairly higher temperatures making things more economical which gave impetus to search for materials with higher superconducting transition temperatures (T_c) until we reach room temperature which should be realised soon as we have reached already above 260 K.

Introduction

This article consists of a series of papers and the first paper deals with the fundamental phenomenon discovered by Holst and Onnes [1] in 1911 in mercury and their associated drastic property changes. Apart from Hg a large number of elements, compounds and alloys exhibited this phenomenon. Those superconductors that were found prior to 1979, whose properties were understood using Bardeen, Cooper and Schriffer (BCS) theory (1957) [2] based up on what are called Cooper pairs, where each pair consists of two electrons and the binding comes via phonons as mentioned earlier are called “conventional superconductors”. BCS theory will be discussed at greater length later. The validity of the theory became questionable from the discovery of new superconductors called as heavy fermion superconductors in 1979 and again, the cuprates in 1986, a path breaking discovery which raised the T_c values which went much beyond BCS or McMillan limit [3]. Moreover the new superconductors were found to carry magnetic moments which are in stark contrast with our age old understanding that magnetism and superconductivity are antagonistic to each other and hence the newer ones are called as “Unconventional Superconductors”. They cannot be explained employing phononic mechanism.

However, one should not jump to the wrong conclusion that the BCS mechanism cannot explain high T_c systems. It is Ashcroft who has been advocating that metallic hydrogen will be a room temperature superconductor and according to him it will be BCS superconductor, because of the lighter mass of the hydrogen atom [4]. Recent experiments show hydrogen containing compounds such as H_3S as well as the compound LaH_{10} , both under high pressures show T_c values of 203 K [5] and above 260 K respectively [6, 7]. Hence, any general statement made that BCS theory cannot be applied for high T_c superconductors is misleading. The time line of the discovery of superconductors is shown in Fig (1).

This paper will deal with the discovery of superconductivity in elements and compounds and the experimental aspects of these solids. The method of calculating T_c values employing McMillans formula [8] which is an outcome of the BCS formula, but in a easily calculable numerical form will be discussed. This serves as a verification of BCS formalism and the inputs required in the McMillans formula or the parameters associated with electrons and phonons of the system which are

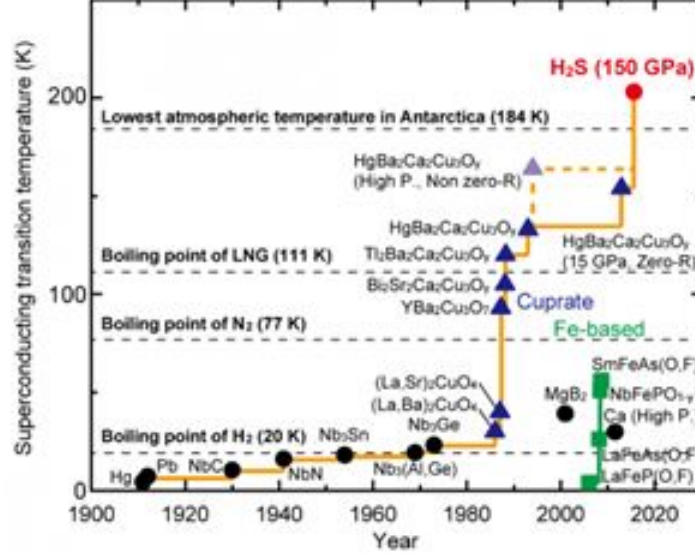


Fig 1. Timeline of superconductivity

the pre-requisites. The solid state problem requires a complete understanding of the atomic structures which were developed over the years. The determination of atomic potential and its evolution to calculate the solid state potential and finally obtaining the band structure will be discussed in the following sections which include density functional theory (DFT). The Band structure outputs will be required to calculate T_c of any solid. Prior to this, the origin and the basic properties related to the phenomenon of superconductivity will be discussed along with the simple minded free electron theory.

The origin of electrical resistivity and its temperature dependence are well known. Resistivity arises because of the scattering of the electrons by the ions which are constantly vibrating in the solid and as the temperature increases the amplitude of the ionic vibrations increase and hence, the scattering probability also increases leading to increased resistivity as shown by the basic relation.

$$R(T) = R_0(1 + \alpha T) \quad (1)$$

However, at low temperatures the linear relation does not hold good and is replaced by Bloch-Grüniesen relation [9]

$$\frac{\rho_{el-ph}(T)}{\rho_{\theta_D}} = \alpha_R \left(\frac{T}{\theta_D} \right)^5 \int_0^{\theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx, \quad (2)$$

which is valid for temperatures $T < \theta_D/10$, where θ_D is the Debye temperature. The power of T which one finds in the above relation actually varies from 4 to 7.

Mention should also be made of the empirical Matthiessens rule and its deviation in Cu based alloys and has been discussed [10], according to which,

$$\rho = \rho_{\text{res}} + \rho(T) \quad (3)$$

From the above relation, one understands the residual resistivity at $T = 0^\circ$ K is a measure of the degree of impurity contained in the material. On the other hand, a material free from impurity should have zero resistance at 0° K as shown in Fig (2).

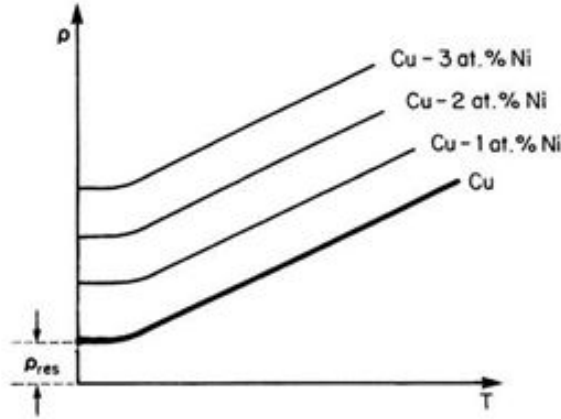


Fig 2. Variation of electrical resistivity with temperature for Cu and its alloy

The surprising observation made in the case of Hg where the electrical resistance fell abruptly to zero value at 4.17 K and this temperature T_c is called as critical temperature. This phenomenon was given the name superconductivity by Onnes and then renamed as superconductivity [11].

Not only does the electrical resistance become zero at the superconducting transition temperature, almost all the physical properties undergo changes which show very different trends when compared to those of the conventional metals as could be seen from the standard text books [12, 13, 14, 15]. In order to calculate T_c , one needs to know about the behaviour of electrons and such quantities as the Fermi energy (E_F), the density of states (DOS) at the Fermi energy ($D(E_F)$) and the scattering phase shifts which could be determined from the electronic band structure calculations which enable one to determine the energies of the electrons in solids as well as their eigen functions. This particular aspect will be dealt with in greater detail and this will be the main theme of this article. The success of the BCS theory will be shown by calculating T_c value of a HCP metal like technetium in this article. Other compounds and alloys will be discussed in the next article. Apart from this, it was found that pressure acts like one of the important parameters which drive some of the solids to acquire superconducting behaviour. As we

go further, we will understand the significance of the two factors: viz; Fermi surface and the parameter pressure playing important roles with respect to new materials. The predicting power of electronic band structure calculations has been found to be extraordinary which made Harrison [16] to lay the claim that given the atomic number(s) of the solid, it is possible to successfully determine ground state crystal structures, lattice constants, heat of formation, electronic specific heat coefficient, bulk modulus, magnetic structures, magnetic moments and structural and magnetic phase transitions, optical properties, positron life time calculations as well as superconducting transition temperature under pressure. Some of the typical examples will be discussed in depth and the density functional theory (DFT) based approach [17] seems to work very well. It was in 1937, the two Dutch scientists de Boer and Verwey [18] brought to light the inadequacy of the band structure approach as it miserably failed in dealing with NiO. This is the famous NiO problem where the experiment shows that NiO to be an antiferromagnetic insulator quite contrary to that of the band theory which shows it to be a metal. The failure of the band theory shows that the currently used exchange - correlations are inadequate. The term correlation is important and its meaning should be understood as NiO is a strongly correlated solid. All the newly found superconductors, heavy fermion superconductors, high T_c cuprates, iron based systems are either magnetic insulators or metals. The earlier understanding was that magnetism and superconductivity are antagonistic to each other and mutually exclusive. Hence, the discovery of new superconductors baffled the physicists as the conventional band structure will not work. Further the transition temperatures cross the McMillan or BCS limit and the need for new theoretical understanding became an urgent necessity, which eludes till date. Thus, this field has emerged as an outstanding area of research, offering several challenges for the condensed matter theorists. These newly found systems and their important properties will be outlined in the next paper. These solids come under the category of strongly correlated systems or Mott insulators [19].

The succeeding parts consist of pressure induced superconductors, listing and classifying of considerably a large number of new superconductors and a detailed description on the experimental aspects associated with them. The phase diagram, crystal structure, change in the magnetic behaviour up on doping or under the application of pressure or the magnetic field, leading to ultimately superconducting state which at many a times are surprisingly found to coexist with magnetism will be discussed. A detailed discussion on the failure of currently used band structure methods, in other words the high degree of the inability of the current exchange - correlation schemes will be discussed in the next section. It is remedied using the dynamical mean field theory (DMFT) and this being applied to Mott insulators in the place of the conventional band theory will be discussed. It includes the older BCS theory and will describe the two competing interactions with regard to the new materials viz; RKKY interaction which tries to develop a long range magnetic order-

ing as against Kondo interaction which tries to destroy magnetic ordering and the Doniach diagram and bring out the importance of Quantum Critical Point (QCP). Invariably, antiferromagnetic ordering present in the superconductors decreases up on application of external agency such as doping, pressure or magnetic field which leads a change in the exchange interaction. Detailed study of Heavy fermions, cuprates, iron arsenides and other systems will be discussed.

So far, several theories including spin fluctuations, valence fluctuations, etc. are in vogue and yet, there is no acceptable theory and hence no mathematical expression for T_c exists for these systems.

This article is meant to help beginners in understanding the phenomenon of superconductivity and introduce them to general underlying principles along with the classification of the newly found superconductors.

The first paper is divided into eight sections and the first section gives an introduction to the discovery of superconductivity and associated experimental observations. Section 2 deals with the early theoretical attempts made to understand the phenomenon. Outline of the procedure adopted to calculate T_c is described in section 3. Important aspects to understand exchange and correlation employing H atom, H_2 molecule and many electron systems are dealt with in detail in section 4, while a brief description of free electron theory is given together with the method of Linear Combination of Atomic Orbital in section 5, while the density functional theory is discussed in section 6. Section 7 is devoted to a description on the evolution of band structure methods. Section 8 describes the bands obtained for two HCP solids as well as the calculation of T_c of the metal technetium.

Section 1: Discovery of superconductivity and associated properties

Fig (3) shows the first observation made by Holst and Kammerlingh Onnes with regards to the variation of resistivity with temperature. It is again Onnes himself showed by his ingenuous experiment that the induced current in a current carrying coil lasted for ever and hence is called persistent current. Current induced in a coil having Ohmic resistance should decay exponentially following the relation

$$I(t) = I(0)e^{-Rt/L} \quad (4)$$

It is natural to ask as to whether this phenomenon is shown by all solids. Hence in the search of superconductors, 33 elemental solids were shown to exhibit this phenomenon and another 23 elemental solids in the periodic table showed superconductivity when subjected to high pressure as shown in Table 1. Among the elemental solids, Nb shows the highest superconducting transition temperature (T_c) of 9.3 K and under the application of pressure T_c of Li goes to 20 K [20].

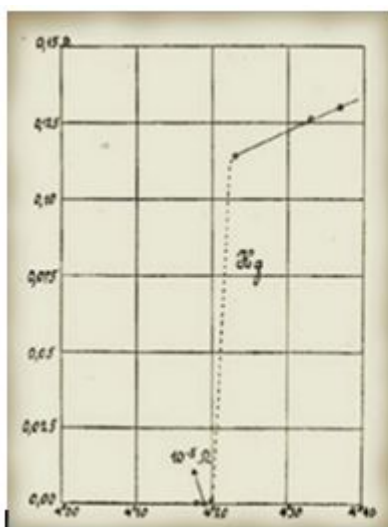


Fig 3. Variation of electrical resistance as a function of temperature for Hg.
 Source: Original picture taken from the notebook of Onnes.

Table 1: Known Superconductive Elements

KNOWN SUPERCONDUCTIVE ELEMENTS																																							
■ BLUE = AT AMBIENT PRESSURE ■ GREEN = ONLY UNDER HIGH PRESSURE																																							
1	IA	1	H	IA													2	He																					
2		3	Li	4	Be							5	B	6	C	7	N	8	O	9	F	10	Ne																
3		11	Na	12	Mg	IIIB	IYB	YB	YIB	YIIB	—	YII	—	IB	IIB	13	Al	14	Si	15	P	16	S	17	Cl	18	Ar												
4		19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr		
5		37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe		
6		55	Cs	56	Ba	57	*La	58	Hf	59	Ta	60	W	61	Re	62	Os	63	Ir	64	Pt	65	Au	66	Hg	67	Tl	68	Pb	69	Bi	70	Po	71	At	72	Rn		
7		87	Fr	88	Ra	89	+Ac	90	Rf	91	Ha	92	106	107	108	109	110	111	112																				

SUPERCONDUCTORS.ORG

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

Apart from elemental solids, as many as 5000 alloys and compounds show this phenomenon and some of them are given in Table 2 along with their T_c values. It could be seen that Nb_3Ge has the highest T_c of 23.2 K. Matthias [21] spent larger part of his lifetime to raise the value of T_c which drove him to the extent of writing “Stay away from theoreticians” as theories were unable to explain all aspects of the phenomenon.

Table 2: T_c of some Superconducting Elements and Inter-metallic compounds

Element	T_c (K)	Intermetallic compound	T_c (K)
Hg	4.17	Nb ₃ Ge	23.2
Nb	9.10	V ₃ Si	17.10
Pb	7.19	Nb ₃ Sn	18.05
Tc	11.20	ZrV ₂	11.0
Pb	7.0	YNi ₂ B ₂ C	15.5
Al	1.18	YBa ₂ Cu ₃ O ₇	90

Magnetic, thermal and optical properties and other associated phenomena such as isotopic effect etc. exhibited by these superconductors are neatly described in other sources discussed. However for the sake of completion and other compelling reasons which will enable one to distinguish the properties of these superconductors from the Unconventional superconductors, it is necessary to describe some of them in detail. Further, it should be stated that only the experiments give the clues in the formulations of theories.

Apart from T_c , the other two important characteristic parameters associated with superconductors are the Critical density J_c and critical magnetic fields H_c . It is noteworthy to remember that all the three parameters T_c , J_c and H_c are found to be higher in the newly found superconductors.

1) Silsbee rule: In 1916, Silsbee effect as described by Zwartz [22] in which it is found that there is a maximum current J_c , which can be passed through a superconducting wire, above which superconductivity is destroyed. The expression for J_c goes as

$$J_c = \frac{2H_c}{r}, \quad (5)$$

where r is the radius of the wire and H_c is called the critical magnetic field.

2) Meissner Effect: In 1933, Meissner and Oschenfeld [23] independently discovered that an applied magnetic field can destroy superconductivity. The field lines are completely expelled and hence it becomes a perfect diamagnet making the susceptibility to assume a value of $-\frac{1}{4\pi}$. There are two types of superconductors as shown in Fig (4).

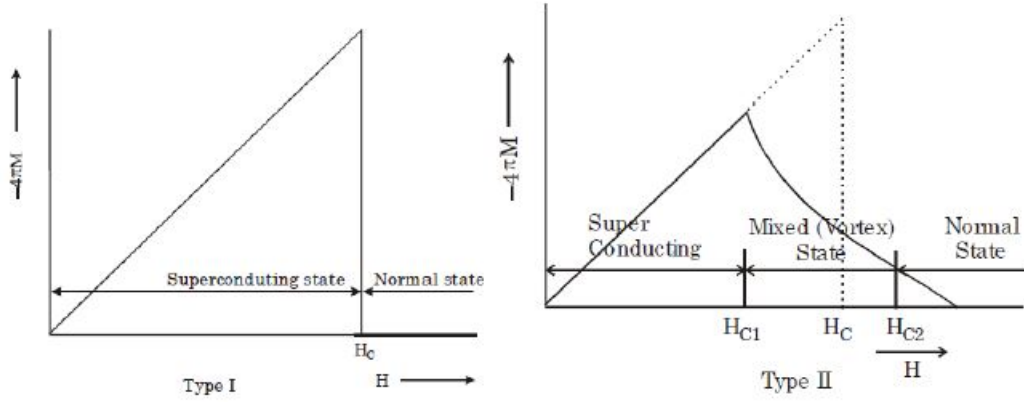


Fig. 4: Magnetisation versus applied magnetic field

3) **Specific Heat:** The specific heat of any solid can be written as:

$$C_v = C_e + C_l = \gamma T + \beta T^3. \tag{6}$$

C_e and C_l are respectively electronic and lattice specific heats. At low temperature, only electronic specific heat remains. It shows a discontinuous jump at T_c as shown in the Fig (5).

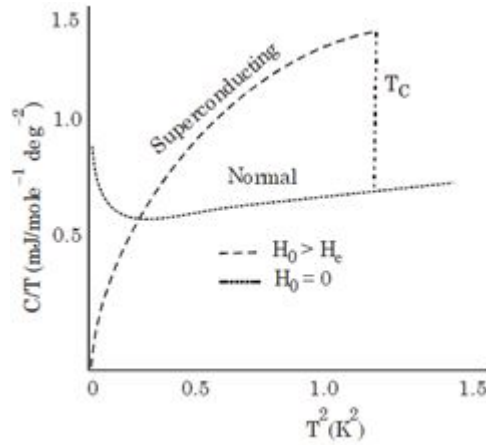


Fig. 5: Variation of specific heat with temperature

Thereafter it falls off exponentially, which follows

$$C_e(T) = A e^{-\Delta/(kT)} \tag{7}$$

The electronic specific co-efficient, is given by the expression which depends on the density of states at the Fermi energy (E_F).

This jump is too large for some of the superconductors, making the value of electronic specific heat coefficient quite large, which is of the order of Joules/ mole-K², instead of mJ/mole-K² as is found in the conventional superconductors. A typical example is $CeCu_2Si_2$ wherein Ce carries a magnetic moment - a magnetic material exhibiting superconductivity, which is inconsistent with what is known so far or unexplainable by the BCS theory. Hence, they form a new class of superconductors called “Heavy Fermion Superconductors”. The T_c values of this class are very low.

4) Energy Gap: The external influences by which superconductivity can be destroyed and making the material to revert back to the normal state should yield the energy required to break up the paired electrons each carrying a charge $2e$, which is responsible for superconductivity. This energy which takes the electron from the Fermi level to the next excited state is called the energy gap.

Several thermodynamical properties indicate exponential behaviour similar to that of the semiconductors, which made people to believe in the energy gaps to be possessed by superconductors too.

The optical absorption in the infrared region of the electromagnetic spectrum by these materials provide the direct proof and the measurement of these gaps [24, 25]. Fig (6) shows the optical absorption in elemental superconductors In and Nb .

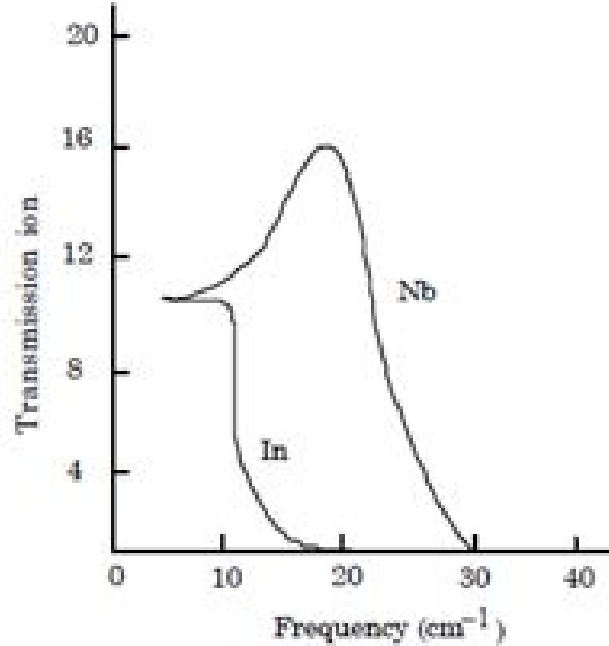


Fig. 6: Optical absorption by superconductors

Further, the application of the magnetic field can be used to destroy superconductivity, the experiments related to this can be applied to deduce the energy gap [26].

5) Characteristic Length Scales: London penetration depth and coherence length
 In 1950, Ginzburg -Landau [27] advanced a phenomenological theory and also from experimental investigations, it is found that superconducting materials have two characteristic length scales, the London penetration depth and the coherence length. The London penetration length (λ) refers to the exponential decay of the externally applied magnetic field inside a superconductor. It is given as,

$$\lambda = \sqrt{\frac{m}{\mu_0 n_s e^2}} \quad (8)$$

Where n_s is the density of superconducting electrons.

It is the distance where the flux density gets reduced to e^{-1} of the externally applied field at the surface. It is of the order of a few tens of nanometers.

Coherence length: In 1950, Ginzburg and Landau introduced the so called superconducting order parameter $\psi(r)$ to describe the non-locality of the superconducting property $|\psi(r)|^2 = n_s(r)$ (local density of superconducting electrons). The coherence length is defined as

$$\epsilon = \sqrt{\frac{\hbar^2}{2m\alpha(r)}}. \quad (9)$$

In the weak coupling BCS theory of s wave superconductor, it is related to Cooper pair size.

$$\epsilon_{BCS} = \frac{\hbar v_F}{\pi \Delta}. \quad (10)$$

v_F is the Fermi velocity and 2Δ is called the energy gap.

Type 1 and type -II Superconductors:

The criterion for type-I and type -II superconductors, lie in the values of the two length scales. If $\lambda/\xi < 0.71$, it is type I. On the other hand when $\lambda/\xi > 0.71$, it is type -II.

6) Isotope effect: It was noticed by Maxwell [28] and Reynold et al [29] that the superconducting transition temperature of Hg varied with its isotopic masses. The effect and the relation goes as

$$T_c M^\alpha = \text{constant}, \quad (11)$$

where M is the mass of the isotope.

As in any solid, atoms or ions are constantly vibrating and Frohlich [30] made an intelligent interpretation of the isotope effect viz, in explaining superconductivity.

Apart from electrons, the quanta of lattice vibrations, the phonons, should be taken into consideration. This obviously led to the foundation to the Bardeen-Cooper-Schriber (BCS) theory [31]. The value of α is 0.5 for monoatomic system. However, the value of the isotopic coefficient is zero for *Zr, Ru etc* and 0.07 for the first high temperature superconductor found. One even finds inverse isotope effect as PdH has a value of -0.2 and α for U is -2 [32].

Section 2: Early theories and calculation of superconductivity

In 1935, F and H. London [33] proposed a two fluid model, one consisting of normal fluid of concentration and the other that of superconducting fluid of concentration n_s .

$$n_n + n_s = n \quad (12)$$

But there was no understanding on how fermionic electrons could form a superfluid. Londons theory leads to

$$B(x) = B(0)e^{-x/\lambda}, \quad (13)$$

showing the exponential decrement of the field leading to a zero value inside the specimen. Londons theory together with Onsagers [34] suggestion led to the idea of flux quantisation

$$\phi_0 = \frac{hc}{2e}, \quad (14)$$

as found from the experiments.

Pippards Theory:

Experiments often show a magnetic penetration depth which is significantly larger than Londons prediction. Pippard [35] explained this on the basis of nonlocal electromagnetic response of the superconductor. According to him, the electrons forming the superfluid cannot be arbitrarily localised. Only, electrons with energies within kT of the Fermi energy can contribute appreciably.

This corresponds to a momentum range p determined by

$$\frac{kT_c}{\Delta p} = \frac{\partial \epsilon}{\partial p} \Big|_{\epsilon=E_F} = \frac{p}{m} \Big|_{\epsilon=E_F} = v_F, \quad (15)$$

leading to

$$\Delta p = \frac{kT_c}{v_F}. \quad (16)$$

Using Heisenbergs principle, we understand that the electrons cannot be localised on a scale smaller than

$$\Delta x = \frac{h}{\Delta p} = \frac{h v_F}{k T_c}. \quad (17)$$

Hence, Pippard introduced coherence length

$$\epsilon_0 = \frac{\alpha h v_F}{k T_c}. \quad (18)$$

ϵ_0 is the maximum extent of the electronic wave packet (or the size of Cooper Pair).

Ginzburg-Landau Theory:

Within London and Pippard theory, the superfluid density of electrons n is treated as a constant in space and time and it also does not include its dependence of temperature, magnetic field.

These deficiencies were done away with in the Ginzburg-London (G-L) theory which was developed as a generalised London theory in 1950.

Landau expressed the free energy of the system in terms of an order parameter to explain phase transitions. In this problem, the order parameter chosen was one particle wave function of superconducting electrons n_s . However, the spatial variation of n_s was neglected.

Ginzburg-Landau theory takes into account of magnetic field dependence, penetration depth and coherence length as discussed by Davide Zuliani [36]. It makes use of a complex order parameter ψ , where ψ is a function of temperature, magnetic field and spatial coordinates.

They obtained an expression for the difference in free energies in the superconducting and normal states near T_c in terms of the wave function. The expression for Londons penetration depth, now becomes

$$\lambda(T) = \frac{m^* c^2 b(T)}{4\pi g^2 n(T)} \quad (19)$$

BCS theory is able to successfully explain Meissner effect, discontinuous jump in the specific heat at T_c as well as the energy gap. It was McMillan who talked about maximum T_c ($T_{c,max}$) and he predicted highest T_c to be 40 K for the material V_3Si as shown in the table VIII of his paper [37] and also points out the importance of the phonon frequency. One of the greatest successes of the BCS theory, which will be discussed in the last part of this work, is that it enabled to successfully explain the experimentally observed superconducting transition temperatures of both elemental solids and alloys. From the BCS equation [38], McMillan gave a numerical expression which is easy to handle and it consists of the Fermi energy, density of states at

the Fermi energy (DOS), the scattering phase shifts and the square of the average phonon frequency which are used to calculate electron-phonon coupling strength. One of the major failures of the BCS Theory is that it did not have the predicting capability to find new superconductors.

Calculation of Superconducting transition temperature:

As mentioned earlier, McMillans expression which is used to calculate T_c is given by:

$$T_c = \frac{\theta_D}{1.45} \exp \left\{ \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right\}, \quad (20)$$

where θ_D is the Debye temperature, λ is the electron-phonon coupling constant and μ^* is the Coulomb pseudo potential which depends on DOS at E_F .

$$\lambda = \frac{N(0)\langle I^2 \rangle}{M\langle W^2 \rangle}, \quad (21)$$

where the numerator involves the Fermi energy, density of states at the Fermi energy and the scattering phase shifts suffered by the electron because of the Coulombic potential of the ion and the details of which can be seen elsewhere [39].

The numerator and denominator require the electronic and phononic band structure calculations.

By electronic band structure calculations, what we mean is the determination of the energy eigen values and eigen states of the freely moving electrons in the solid. It was mentioned in the isotopic effect ions in the lattice are vibrating and the vibrational frequencies are to be known.

Section 3: Description of H atom and H₂ molecule

All solids are made up of atoms and each atom has got what are known as Core electrons and valence electrons. Consider the case of Na atom whose atomic number is 11 and its electronic structure is $1s^2 2s^2 2p^6 3s^1$. All the electrons other than $3s^1$ are called Core electrons as they are tightly bound to the atom, while the $3s^1$ electron is the valence electron as it is loosely bound to the atom. The concept of valency is important and all the atomic properties are decided by the valence electrons. That is the reason as why we call first, second, etc., groups which have the same number of electrons. There is a one to one correspondence between atoms and solids. It is only the valence electrons or the outer most electrons in atoms that decide the properties and in the same way top most energy levels in solids are important, which as we will see later. It is important to note that the valence electrons of atoms become the conduction electrons in solids when a solid is formed, the loosely bound electrons of atoms become free and are able to wander throughout the solid, behaving like a gas

and hence was called as a free electron gas.

In order to understand solid state properties, one has to first understand atomic properties as solids are made up of atoms and the simplest atom is the hydrogen atom.

Hydrogen atom:

Our aim to see how an electron behaves when it is nearer to the nucleus and also in between two nuclei as our final aim is to describe the electron which is freely moving throughout the solid.

As H atom is a two body problem, the potential energy of the electron is exact and it is:

$$V(r) = -\frac{e^2}{r}, \quad (22)$$

where r is the distance between the electron and the proton. The Schrodinger equation to be solved is

$$\{-\nabla^2 + V(\mathbf{r})\}\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r}), \quad (23)$$

which in terms of spherical polar coordinates assumes the form:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi). \quad (24)$$

As r, θ and ϕ are independent, the above can be split up into three independent equations. In all the quantum mechanical problems, the quantisation comes out automatically through the application of the appropriate boundary condition. The energy eigen values and eigen functions are respectively,

$$E_n = -\frac{2\pi^2 m_e e^4}{n^2 h^2} \quad (25)$$

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi). \quad (26)$$

It is important to note that $R_{nl}(r)$ has $(n - l - 1)$ nodes or zero crossings as shown in the Fig.7.

This comes out of the property of the Laguerre polynomial found in the radial part of the Schrodinger equation which has $(n - l - 1)$ nodes. These nodal oscillations are a characteristic property of atomic functions. This is due to the large kinetic energy of the electron when it is closer to the nucleus to balance the high potential energy.

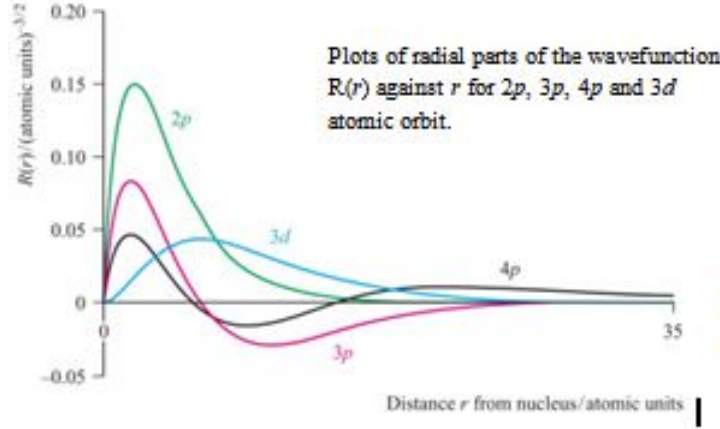


Fig. 7; Radial solution as a function of r

On the other hand, when the electron is in between two nuclei, the potential energy will be smooth as shown in the Fig (8). The potential energy can be averaged out and can be assumed to be a constant or can be made as zero for mathematical convenience. In the constant potential region, the Schrodinger equation now takes the form:

$$\nabla^2\psi + \left(\frac{2m}{\hbar^2}\right)(E - V_0)\psi = 0 \quad \text{or} \quad \nabla^2\psi + k^2\psi = 0. \quad (27)$$

The solution for the above is

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \quad (28)$$

The above is a plane wave as shown in Fig (8).

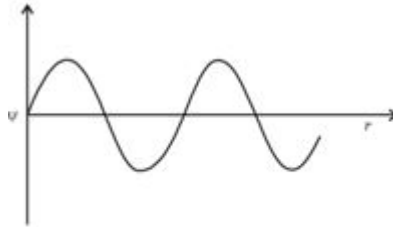


Fig 8. Plane wave solution

In reality, the true electron wave function will be as shown below (Fig 9). It is a combination of both the above two characteristics and that is how one describes the solid state wave function of an electron, as we shall see in the forthcoming description of electronic or band structure methods.

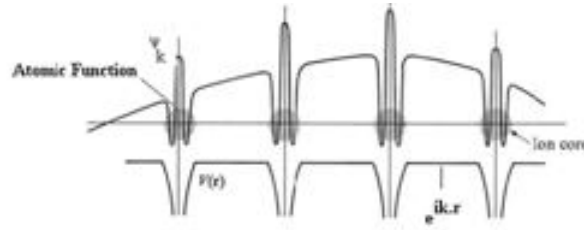


Fig 9. Schematic representation of the wave function of the electron in a solid

H₂ Molecule: Two electron system

Hartree method does not take into account the spin of the electron. A many electron system should take into account of the Pauli principle.

The Pauli Principle: Pauli principle states that the electron wave function should be anti-symmetric in character with respect to the exchange of space and spin coordinates when any two electrons are interchanged.

According to this, when the exchange operator P_{12} operates up on the two electron wave function, it should result in the wave function with a negative sign as shown below:

$$P_{12}\psi(1, 2) = \psi(2, 1) = -\psi(1, 2) \tag{29}$$

Pauli principle can be stated in a determinantal form as shown below.

$$\psi(1, 2) = \begin{vmatrix} \psi_A(r_1) & \psi_A(r_2) \\ \psi_B(r_1) & \psi_B(r_2) \end{vmatrix} \tag{30}$$

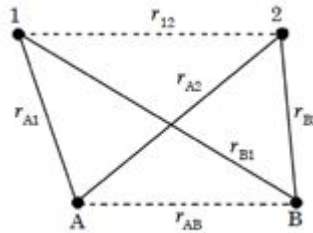


Fig.10: Hydrogen molecule

A and B refer to the two protons and 1 and 2 respectively refer to the two electrons. $\psi_A(r_1)$ refers to probability amplitude of electron 1 to be associated with the proton A (Fig 10). Electron 1 can also be associated with proton B as electrons are no longer particles because of the de Broglie matter wave concept. It is important to note that r_1 refers to the space coordinates $(x_1, y_1, z_1$ and the spin state) and the same holds good for the other electron.

The beauty of the determinantal wave function introduced by Slater [40] lies in the fact that each vertical column refers to a quantum state and if one puts 1=2, the determinant vanishes, showing the impossibility of forcing two electrons to occupy the same quantum state as required by the Pauli principle. Also, the anti-symmetric character of the wave function comes out automatically when the vertical columns (eigen states) are interchanged as the sign of the determinant gets changed.

Now we can write the wave functions for H_2 molecule as:

$$\psi(1, 2) = \psi_A(r_1)\psi_B(r_2) \quad (31)$$

or

$$\psi(1, 2) = \psi_A(r_2)\psi_B(r_1) \quad (32)$$

One can have linear combinations of the above.

$$\psi_+ = \frac{1}{\sqrt{2}} [\psi_A(r_1)\psi_B(r_2) + \psi_A(r_2)\psi_B(r_1)]; \quad (33)$$

$$\psi_- = \frac{1}{\sqrt{2}} [\psi_A(r_1)\psi_B(r_2) - \psi_A(r_2)\psi_B(r_1)]; \quad (34)$$

where $1/\sqrt{2}$ is the normalisation factor. The Potential Energy for the system is:

$$V = -e^2 \left[\frac{1}{r_{A1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B1}} + \frac{1}{r_{B2}} \right] + \frac{e^2}{r_{12}} \quad (35)$$

and the Hamiltonian is

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 + V(r) = \frac{e^2}{r} \quad (36)$$

The energies corresponding to different cases are

$$E = \frac{\int \psi_{\pm}^* H \psi_{\pm} d\tau}{\int \psi_{\pm}^* \psi_{\pm} d\tau} \quad (37)$$

The graph connecting E and the inter-proton distance is shown in the Fig (11).

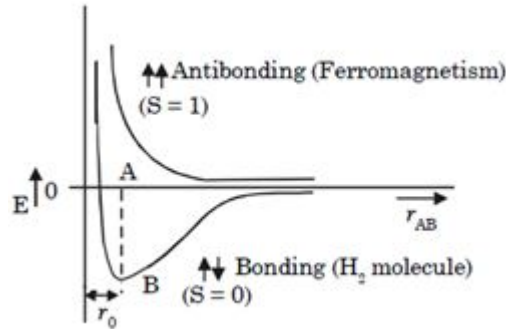


Fig.11: Bonding and antibonding between two H atoms

Also, the electronic charge density in the case of H_2 molecule can be calculated. The same can be obtained for solids also as shown for the Ge solid (Fig 12).

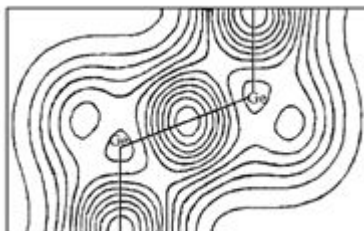


Fig.12: Electron density contour in Ge crystal

The bottom line of our discussions so far we had, can be extended to solids also. The points to be remembered are:

1. The wave function describing an electronic system should be anti-symmetric in nature with respect to interchange or exchange of two electrons with their space and spin coordinates.
2. The Hamiltonian for a solid will be written as done above and this will be used to evaluate the total energy of the system.
3. The graph connecting the total energy and inter atomic distance holds good in the solid also. The equilibrium interatomic separation can be obtained and compared with that obtained from X-ray diffraction experiments.
4. Also, the electronic charge density in the solid can be calculated and compared with the experimental values. We discussed here the H_2 molecule which is done for the two purposes: 1) the wave function being written as a second order determinant, which will be extended into a n th order determinant in the Hartee-Fock method and 2) the molecular wave function, being written in terms of atomic orbitals, leading to Linear Combination of Atomic Orbital (LCAO) method which in turn has leads to Linear Combination of Augmented Plane Waves (LAPW) or Linear Combination of Muffin Tin Orbitals (LMTO), etc. methods for the case of solids as will be seen later.

Section 4: Many electron systems Exchange and Correlation

The potential energy term used in the case just now dealt with is exact as it is a two body problem. Schrodinger obtained his celebrated equation in 1926. Immediately in 1927, Hartree [41] proposed a method to calculate the energy levels in electrons in atoms. When we deal with atoms having many electrons, then we come across the many electron wave function. They suggested a model in which every electron

moves independently in a potential arising from the rest of the electrons. The many electron wave function is written in terms one electron wave functions, as shown below:

$$\begin{aligned} P_{rs}\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_r, \mathbf{r}_s, \dots, \mathbf{r}_n) &= \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_s, \mathbf{r}_r, \dots, \mathbf{r}_n) \\ &= -\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_r, \mathbf{r}_s, \dots, \mathbf{r}_n) \end{aligned} \quad (38)$$

where $\mathbf{r}_1, \mathbf{r}_2, \dots$ refer to the space coordinates x_1, y_1, z_1 , and x_2, y_2, z_2, \dots . The total probability is written in terms of individual probabilities. They suggested a variational calculation by which E is minimised.

Electrons are charged particles which should repel each other. But, the above description does not lay any restriction on the motion of electrons, leading to the possibility of any number of electrons coming close to each other, which will raise the coulombic repulsion to a high value that will be unphysical.

Further, Paulis exclusion principle excludes the possibility of two electrons occupying the same quantum state.

Hartree-Fock equation: The Exchange

For the N electron system in an atom or a solid, following the H_2 molecular problem, the wavefunction is written in the form of the Slater determinant.

$$\psi(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \dots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \dots & \psi_2(\mathbf{r}_N) \\ \dots & \dots & \dots & \dots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \dots & \psi_N(\mathbf{r}_N) \end{vmatrix} \quad (39)$$

There should be clarity of understanding of the above determinant. The vertical columns with the parenthesis $(\mathbf{r}_1), (\mathbf{r}_2), \dots, (\mathbf{r}_N)$ refer to N quantum states. The first element in the determinant gives the probability amplitude of the electron 1 to be found in the first quantum state denoted by \mathbf{r}_1 and its square, obviously gives the probability of the electron 1 being found in the first quantum state. Electron 1 can also be associated with other quantum states $\psi_2 \dots \psi_N$, similar to what we saw in the case of H_2 molecule. It should be clear by now that the determinant indicates partial occupation of N electrons by the N quantum states. Hartree-Fock equation assumes the following form:

$$\begin{aligned} &\left\{ -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{r_1} + e^2 \sum_{j \neq 1}^N \frac{|\psi_j(r_j)|^2}{r_{ij}} dr_{ij} \right\} \psi_i \\ &- e^2 \sum_J^N \left[\frac{\psi_i^*(r_j) \psi_j(r_j)}{r_{ij}} dr_j \right] \psi_i(r_i) = \epsilon_i \psi_i(r_i). \end{aligned} \quad (40)$$

The term inside the curly brackets is just the Hartree operator. The extra term which appears in the equation (40) is called the exchange term which occurs as a consequence of the Pauli principle. The corresponding contribution to the total energy is called the exchange energy and is given by:

$$-e^2 \sum_J^N \left[\frac{\psi_i^*(r_j)\psi_j(r_j)}{r_{ij}} dr_j \right] \psi_i(r_i).$$

Hartree-Fock equation takes into account the Pauli principle and hence is able to keep electrons of the same spin away, leading to Fermi hole. Parallel spin correlations are taken care off. Hence,

$$\text{Exchange Energy} = E_{HF} - E_H. \quad (41)$$

Any beginner is strongly recommended to read excellent coverage of the above from [42, 43,44,45].

One can see the numerical values of the eigen values and eigen functions neatly tabulated for all the atoms in the periodic table by Herman and Skillman [46]. The difference in the total energy values in Cu ion under the Hartree and Hartree-Fock schemes are tabulated and can observe that the H-F eigen value is lower than the Hartree energy (Fig 13). This source book from IBM has been of immense value to obtain the energy bands of solids for a few decades. This essentially consists of finding the solution of the Schrodinger equation for atoms, it will be an integral part of the modern codes used today in all band structure methods.

Correlation:

Hartree-Fock thus takes care of parallel spin correlations via the Pauli principle. It is incapable of avoiding electrons with antiparallel spins coming closer to each other. As electrons are charged particles, any theoretical model built should take care of electrons in not coming close to each other, irrespective of the nature of spin. The term correlation means that one develops a scheme in which electrons with antiparallel spins too do not come closer to any electron. Hence, about every electron, there should a region or “exchange-correlation hole” into which no other electron of either spin can enter into. If one achieves this, then the energy of the electron will go down still further and this describes an ideal system as electrons are moving in a well correlated manner avoiding each other, with regard to the motion of the electrons in atoms, molecules or solids. The one electron energy now should be equivalent to experimental or exact eigen value. Following Pines, [47] the correlation energy is defined as

$$E_{\text{correlation}} = E_{\text{exact/experimental}} - E_{H-F} \quad (42)$$

and this is figuratively shown in Fig (13).

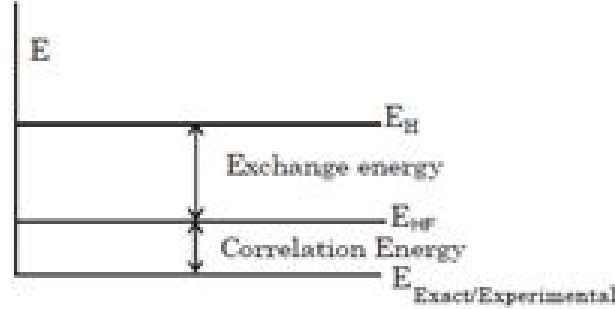


Fig 13. Exchange and Correlation energies

Exchange-Correlation Schemes:

A brief review of the exchange -correlation schemes will be made here and it has been a fertile area for several decades. It is impossible to have an accurate or exact exchange-correlation (XC) scheme to be found for a many body problem. Even though, Thomas, Fermi and others introduced electron density instead of dealing with many electron wavefunctions or determinantal wavefunctions, Slater [48] should be credited for having made great simplification to the Hartree-Fock model to obtain exchange potential taking into account what he called a fictitious exchange charge density, in analogy to the classical electrostatics which relates charge density and potential.

The exchange potential due to Slater becomes,

$$V_S = \left(-\frac{3}{\pi} \right) [3\pi^2 \rho(r)]^{1/3} \quad (43)$$

Sham, on the other hand used the variational principle and obtained the expression for the exchange term which is 2/3 of the above.

Thus, the Kohn-Sham-Gaspar [49, 50] exchange is

$$V_{\text{KSG}} = \left(-\frac{2}{\pi} \right) [3\pi^2 \rho(r)]^{1/3} \quad (44)$$

Slater in his series on this subject his last volume on "quantum theory of molecules and solids" which he wrote in 1974 [51] concludes that the more accurate XC potential will neither be full Slater exchange nor KSG XC. But it will be 5/6th of Slater exchange and until now, several minds have worked on this and it is true that all XC schemes are very close to what slater wrote. However, for several decades, large number of band structure calculations employed Slater exchange. More on this will be discussed in the next part.

Section 5: Free Electron Theory and LCAO Method

It was Sommerfield who proposed the free electron theory of metals. As stated earlier, the valence electrons of atoms become the free electrons or conduction electrons in metals which cause electrical and thermal conductivities. The energy of the electrons can be determined using the Schrodinger equation:

In the one dimensional model, for the simplifying the problem, it was assumed that the electron is moving in a constant potential and it was set equal to zero.

Under this condition, the Schrodinger equation reduces to:

$$\frac{\partial^2 \psi}{\partial x^2} + \left(\frac{2m}{\hbar^2} \right) E \psi = 0. \quad (45)$$

The above gives the eigen values

$$E = \frac{\hbar^2 k^2}{2m} \quad (46)$$

The eigen functions are given by

$$\psi(x) = e^{ikx}, \quad (47)$$

which are simply plane waves. It should be noted that the energy of the electron can be given only in terms of k for a free electron moving in a metallic solid, whereas we wrote the energy of the electron in the hydrogen atom in terms of the quantum number n .

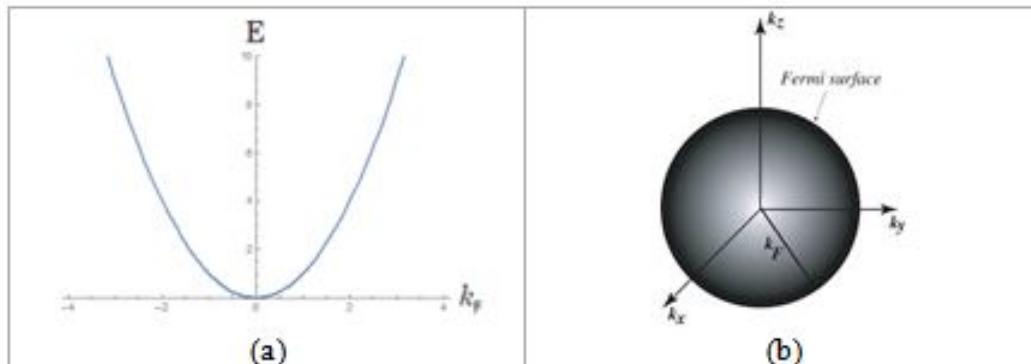


Fig 14. a) Free electron band structure b) Free electron Fermi surface

" n " is no longer a good quantum number to describe freely moving electrons and it is replaced by k , the wave vector and $\hbar k$ is the momentum. Now, the graph drawn between E and k is a parabola and it is called Sommerfields free electron parabola. It is the band structure of the free electron metal (Fig 14a). In the above expression,

$k = \frac{2\pi}{\lambda}$ and λ is found in the denominator which demands inverse or reciprocal or Fourier space. The unit cell in the momentum space is the Brillouin zone. The Brillouin zone for HCP solids is shown below (Fig 15). We will be concentrating on HCP B.Z as we will be discussing the band structures of the HCP solids Mg and Tc .

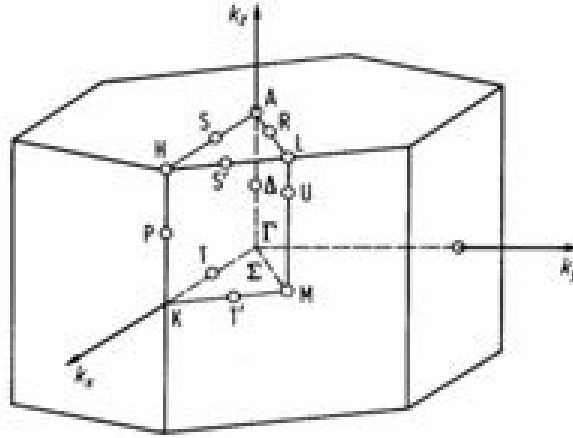


Fig 15. Brillouin zone of HCP lattice.

As there are 14 lattices for solids, their Brillouin zone and other related aspects can be seen in the books of Jones [52] and Benjamin Lax [53]. Band structure is nothing but energy-momentum relation. If the electron has a definite momentum, the corresponding energy value is known from the band structure. Following, the Pauli principle, we have to fill up the electrons in the band and the top most energy level is the Fermi level and the corresponding momentum is the Fermi momentum (Fig 14b).

The rigorous definition of a metal is that: A metal is one which has a Fermi surface [54] as semiconductors and insulators have their Fermi levels in the forbidden energy gap and cannot have Fermi surfaces. A sphere drawn with the Fermi momentum as the radius gives the Fermi surface. For real solids, the Fermi surface is not spherical and it will be complicated which can be obtained from band structure calculations and there are several experimental techniques to determine them [55, 56]. The density of states for electrons can be obtained by considering electrons to be in a potential energy well. The expression for the same can be obtained by phase space consideration as has been shown [57]. It assumes the form:

$$D(E) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}. \quad (48)$$

The DOS histogram, obtained from free electron theory is shown Fig (16).

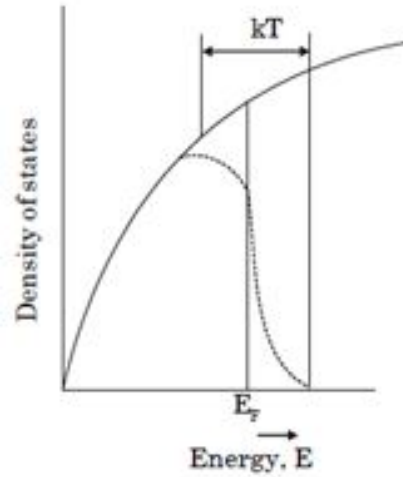


Fig 16. Density of states histogram.

Simple solids such as Al, Na, etc. will mimic this, while for most of the solids and especially transition metals, the surface will be complicated and these features can be seen in the book compiled by Papaconstantopoulous [58] where the band structure, DOS and Fermi level quantities of many solids in the periodic solids are given.

Molecular wave function: Linear Combination of Atomic Orbitals - (LCAO) Method

The molecular wave function was written as a linear combination of atomic orbitals. The atomic orbitals are the basis functions. Hence, the molecular orbital is

$$\psi = \sum_i c_i \psi_i, \quad (49)$$

where c_i are the mixing coefficients which are obtained by minimizing the energy of the system as given below:

$$E = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad (50)$$

If one applies to H₂O molecule, the basis set consists of two 1s states coming from two hydrogen atoms and 2s, 2p_x, 2p_y and 2p_z orbitals and in all, there will be six basis functions. Using the variational principle to solve the sixth order determinant, the six roots obtained are the energies for the six molecular orbitals produced. By plotting the energies for the different molecular orbitals by bending the molecule or by changing the bond angle the lowest energy is obtained and thus the eigenvalues and eigenfunctions are obtained. Free electron approximation and LCAO or tight binding approximation are the two extremes; while the former holds good for metals, the latter for molecules and insulators where the electrons are bound to the systems.

Section 6: Density Functional Theory

Hartree method makes use an N electron wave function or describing the N electrons in an atom as was seen earlier:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2) \cdots \psi(\mathbf{r}_N), \quad (51)$$

which has 3N variables. *viz*; $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_N, y_N, z_N)$.

Instead of employing Schrodinger equation containing wave functions, Thomas and Fermi proposed an atomic model containing electron density $\rho(r)$ which only three variables, thereby the problem is simplified. As this model did not yield the expected experimental values, Dirac included the exchange term as well. Also, Hartree-Fock method makes use of density of electrons. Hence density being used instead of wave functions is not new and the above mentioned methods form the forerunners to the Density Functional Formalism (DFT), which has become so much popular for describing the atoms, molecules and solids. DFT stands on two theorems proposed by Hohenberg and Kohn [59].

Theorem 1: The external potential V_{ext} , and hence the total energy is a unique functional of the electron density $n(r)$.

Theorem 2: The ground state energy can be obtained variationally: the density that minimises the total energy is the ground state density.

The reader can find the details from the original papers or several review papers available on this method [60]

Hohenberg-Kohn(H-K) theorems shows that the ground state energy can be obtained by minimising the energy functional:

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}} \right) \phi_i = \epsilon \phi_i \quad (52)$$

where $\rho(r)$ is the electronic density, $V(r)$ the external potential experienced by the nuclei due to any applied external electric field and the last term is the H-K functional. But, still one does not know as to how to calculate the charge density $\rho(r)$. Kohn and Sham [61] introduced a fictitious non interacting potential for an interacting electron system which lead to Schrodinger like single particle equations for each electron which are to be solved self consistently.

$$V_{\text{eff}} = V(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}). \quad (53)$$

The exchange-correlation part of the potential V_{xc} is given by

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}(\rho)}{\delta \rho(\mathbf{r})}. \quad (54)$$

The total energy of the system can be written as

$$E = \sum_i^N \varepsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}(\rho) - \int V_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}. \quad (55)$$

Finally, E_{xc} , non-coulombic part is unknown and there are more than one hundred exchange-correlation functionals. In this article, we discuss the potential constructed using Slater exchange whose form has been already given and this has been widely used. A few important and currently used exchange-correlation schemes will be presented in the next article.

Expressions for correlation parts alone were derived by Wigner for low electron densities and Gellmann and Bruckner at nuclear for high densities. Interested readers on Density functional theory should see the original papers.

Section 7: Evolution of Band Structure Calculations:

Electronic structure calculation rests on the two following approximations:

Born - Oppenheimer approximation:

Solids are made up of ions which are constantly in vibration leading to phonons as well as electrons. It will be too difficult to handle ions and electrons simultaneously and hence Born and Oppenheimer [62] decoupled the two as follows:

$$\psi_{\text{total}} = \psi_{\text{ions}} \cdot \psi_{\text{electrons}} \quad (56)$$

Since ionic masses are high, their motions can be neglected when compared to the motion of electrons. Hence, one concentrates on electrons ignoring the ionic part.

One electron approximation:

A solid may have N number of electrons and the dynamical motion of all the electrons cannot be dealt with at the same time as it will require N number of equations. Hence one resorts to one electron approximation, in which the motion of one electron in a spherically symmetrical potential which is obtained by superimposing the atomic potentials coming from the neighbouring atoms named as Muffin - Tin (MT) potential is constructed.

Wigner and Seitz cellular method:

Wigner and Seitz were the first to propose the methodology adopted to calculate the eigen values of electrons in solids as early as in 1934. They considered a spherically symmetric potential inside the Wigner-Seitz cell or the polyhedron, which is the unit cell or Wigner-Seitz cell of the solid. They wrote the wave function in terms of atomic orbitals and the wavefunction along with its derivative were matched at the boundary of the cell (Fig 17a). This, of course should be repeated in all directions which is a cumbersome process. Hence, they replaced the cell into a sphere of equal

volume (Fig 17b), an elegant way whereby the directional dependence of matching the wave function and its derivative are completely removed.

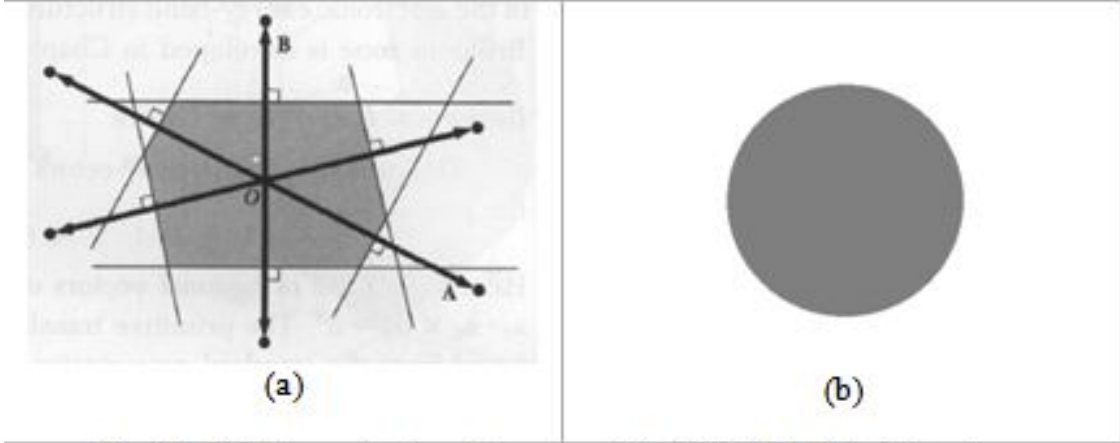


Fig 17. (a) Wigner-Seitz cell

Fig 17 (b) Muffin Tin sphere

Augmented Plane wave method:

This method was proposed by Slater in 1937 [63] and it is simple and a physically transparent method. The unit cell is divided into muffin tin spheres and the interstitial region. M.T spheres owe their name as the potential looks like the kitchen made muffins prepared at homes. This scheme is called augmented plane wave method as plane wave like nature describing the electronic behaviour in the interstitial region as discussed in the free electron theory earlier is added to atomic orbitals to describe the basis function. The solid state potential was obtained by superposing atomic potentials, which were determined by solving Hartree-Fock-Slater equations which are tabulated for all atoms from Helium to Lawrencium by Herman and Skillman as mentioned in the previous section 4. Also the atomic charge densities are known as they are to be used to find the exchange-correlation potential. Muffin tin potential is calculated taking into account the electrostatic potential arising out of the neighbouring atoms as expressed below:

$$V(r) = V_0(r) + \sum_i^{\text{neighbours}} V_0(a_i|r). \quad (57)$$

Fig (18) shows the unit cell which is divided into muffin spheres (M.T) where the potential will be spherically symmetric and the interstitial region where the potential is assumed to be constant. As one could see the Fig (9) shown earlier depicting the atomic wavefunction near the nuclei to demonstrate oscillatory nature or wiggles and plane waves when the electron is in the interstitial region.

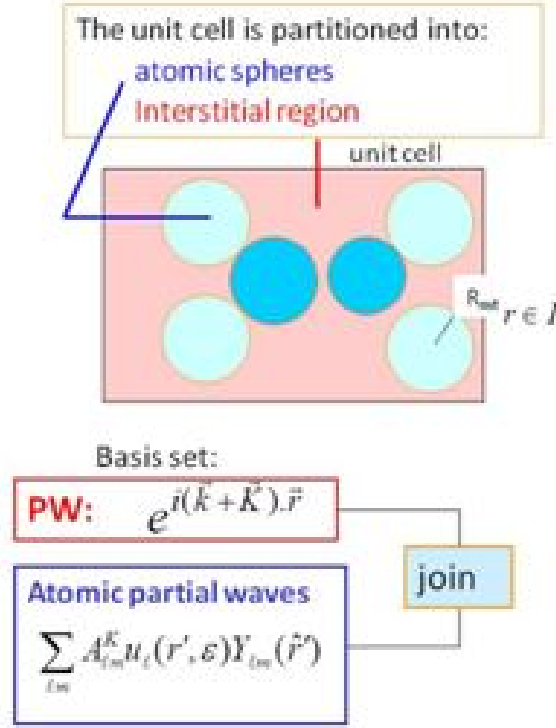


Fig 18. Atomic spheres, constant potential and basis functions

The features and the basis functions corresponding to different regions and the way they are combined are shown below:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_l \sum_m A_{lm} R_l(E, r) Y_{lm}(\theta, \phi) \quad \text{for } r < r_{MT} \quad (58)$$

$$= e^{i\mathbf{k} \cdot \mathbf{r}} \quad \text{for } r > r_{MT} \quad (59)$$

The wavefunction inside the M.T sphere and the outer region are matched at the sphere boundary. The APW wavefunctions assume the following form:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} 4\pi e^{i\mathbf{k} \cdot \mathbf{r}_v} \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{i^l j_l(k s_v) Y_{lm}^*(\hat{k}) Y_{lm}(\hat{\rho}) R_l(\rho)}{R_l(S_v)} & \text{for } r < r_{MT} \\ e^{i\mathbf{k} \cdot \mathbf{r}} & \text{for } r > r_{MT} \end{cases} \quad (60)$$

R_{nl} s are the radial solutions of the Schrodingers equation and J_l are the spherical Bessel functions. The position vectors \mathbf{r} and \mathbf{r}_v and the radius of the M.T sphere are shown in the diagram (Fig 19). J_l are the spherical Bessel functions.

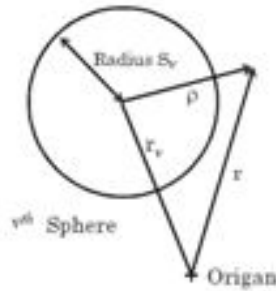


Fig 19. M.T sphere and the related coordinates

The wavefunction of the electron in the solid is:

$$\psi(k, r) = \sum_G C_{k+G} \phi_{k+G}(r) \quad (61)$$

where G s are reciprocal lattice vectors, which is continuous as well as its derivative at the sphere boundary. The higher angular momentum possessed by the electron near the nucleus requires large number of Reciprocal Lattice Vectors (RLVs) or higher G s are to be taken into effect. The order of the secular determinant depends up on the number of RLVS added. The APW secular determinant is of the form and unfortunately, the off diagonal terms contain the eigen values which can be determined only by finding the zeros of the determinant that occur for certain E values for a given k value and this is shown in the Fig (20a).

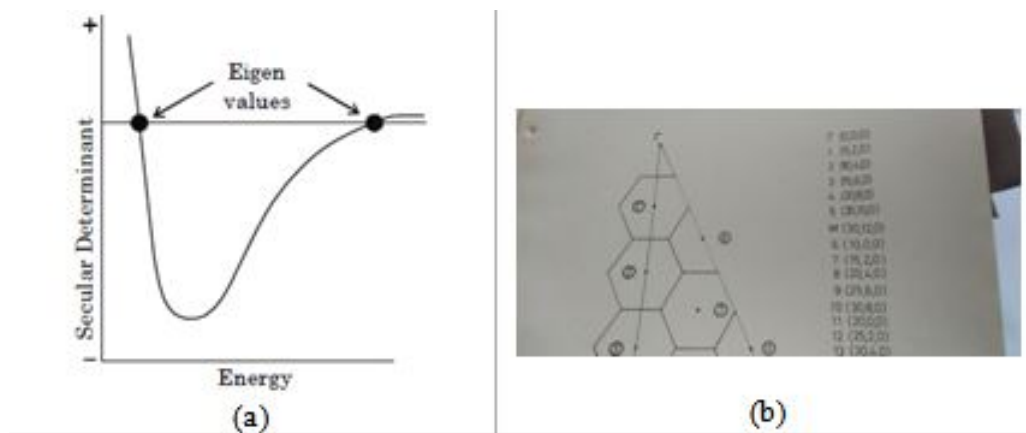


Fig 20.(a) Eigen value search

Fig 20 (b) A portion of 1/24th of Brillouin zone for HCP lattice

These E values are the energy eigen values sought. Any band structure calculation should lead to a relation connecting the energy eigen value E and the k vector

in the Brillouin zone. The details of this method can be seen in the book of Loucks [64], meant only for the APW method. It also has number of very relevant papers added to it at the end. In addition, it should be learnt as its linear version LAPW is the most widely method. Both LMTO and LAPW methods will be discussed in the next article.

As band structure calculations are very relevant for many applications, it is strongly recommended that for anyone who wants to master it, the following books and articles cited here are to be read and understood [65]. It will be worthy of having a glimpse on the calculated band structures compiled by Moruzzi et al [66]. Finally, every calculation is done for a particular purpose the validity of band structures should be verified from the experimental results and some of them are done with regard to the case studies which are discussed below. Mostly, of late many computer codes which are available in the market are purchased and used which finally leads to wrong interpretations of some of the results. The eigen values obtained for each k point and the connectivities of the bands are performed by taking into consideration the symmetry of the wave function or in other words employing the compatibility relations which are dictated by group theoretical considerations, which in turn are based on the symmetry of the crystal being considered. Tables showing compatibility relations are presented by Slater [67] as well as Joshi [68].

In this final part of the article, two case studies will be discussed, the first one on band structure of Mg and the second is on the calculation of the superconducting transition temperature using the results obtained by performing there band structures. The band structures were performed employing Kohn-Korringa-Rostkoer or Greens function method. [69].

Section 8: Electronic Band Structures

1. Band Structure of Mg:

We present below 1/24th part of the Brillouin zone for the HCP solid as well as the resulting band structures. The k points in the partitioned B.Z viz; Γ , K, M etc are the group theoretical notations assigned by BSW (Bouckert, Smoluchoswiski, Wigner) and the star or weightage of the wave vector decides the numerical values of the density of states and finally the Fermi energy as well as the Fermi surface. Subtleties associated with this can be appreciated by the reader if one goes through the paper of Burdick as mentioned earlier and most of the books and review articles reproduce the band structure, DOS and the Fermi surface of Cu from the work of Burdick. Band structure of Mg is reported here determined using one of the three different exchange schemes. (Fig 21). Now, the Fermi surface cross sections for Mg are shown in Fig (22) to make the reader to be aware of its the complex nature of it by comparing with the free electron spherical Fermi surface reported earlier. Fermi surface dimensions are compared with the experimentally obtained values and the

interested readers can refer to the original paper [70].

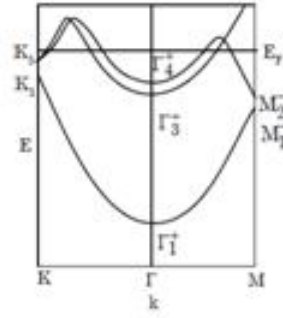


Fig 21. Band Structure of Mg

Table 3. Fermi Surface Dimensions

	Present calculations			Chatterjee and Sinha (1975)	Experimental
	V_c	V_H	V_{cc}		
2nd zone monster					
Γ-M inside	0.3603	0.3603	0.3738	0.349	0.370
Γ-M outside	0.4254	0.4282	0.4254	0.459	0.476
Γ-K inside	0.3455	0.3592	0.3730	0.342	0.370
Γ-K outside	0.6353	0.6078	0.6147	0.625	0.622
3rd zone cigar					
K-Γ	0.0449	0.0574	0.0552	0.050	0.067
K-M	0.0345	0.0460	0.0460	0.041	0.033
3rd zone lens					
Γ-A	0.0837	0.0797	0.0797	0.058	0.080
Γ-K	0.3592	0.3315	0.3247	0.251	0.312
Γ-M	0.3303	0.3140	0.3235	0.234	0.312
3rd and 4th zone pockets and butterflies					
L-H	0.1328	0.2292	0.1774	0.096	0.184
L-M	0.0864	0.0929	0.0664	0.023	0.043
A-L	0.0435	0.0367	0.0340	0.029	—
L-M	0.0864	0.0665	0.0532	0.044	—

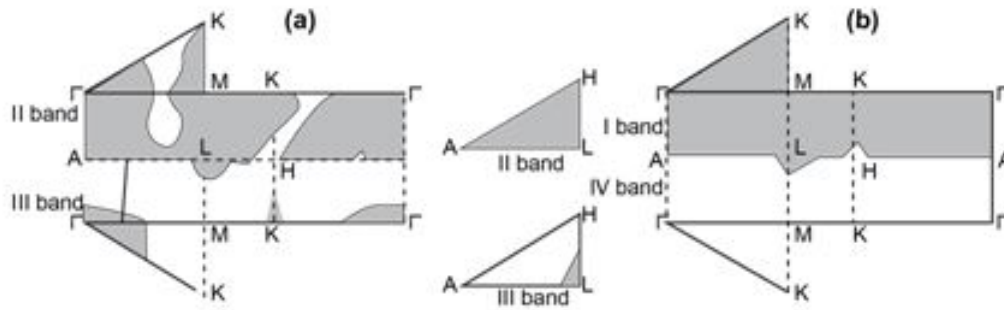


Fig 22. The Fermi cross-section in: (a), II and III and (b), bands I and IV, for the potential V_s regions of electrons are shaded

Some of the results obtained in the case of a HCP solid Mg and especially the values obtained for the electronic specific heat coefficient are given in the Table (3) and its importance will be seen in the future articles on the unconventional Non BCS superconductors whose specific heat coefficient values show a thousand fold increase.

Details regarding the KKR band structure method adopted here will be discussed in the next article.

2. Band Structure of Tc:

Superconductivity and Fermi surface are more relevant at present, especially after the discovery of high temperature superconductors. It was claimed by many eminent theoreticians that these high Tc systems will not have Fermi surfaces. It took almost a decade to disprove it and it is positron annihilation experiments which were the first to show the existence of the Fermi surface of high temperature superconductors which had tremendous impact on the theoreticians. Now all High Tc systems have Fermi surfaces and their significance has been realised. Moreover, this paper reported the first band structure calculation on the metal technetium [71]. The band structures were carried out with different XC schemes. The resulting band structures were used to evaluate the Fermi level quantities such as Fermi Energy, E_F , DOS at E_F and the scattering phase shifts which were fed into Gaspari-Gyorffy relation to evaluate the electron-phonon Coupling constant and hence Tc employing the McMillans formula and the calculated values are given in the Table (5).

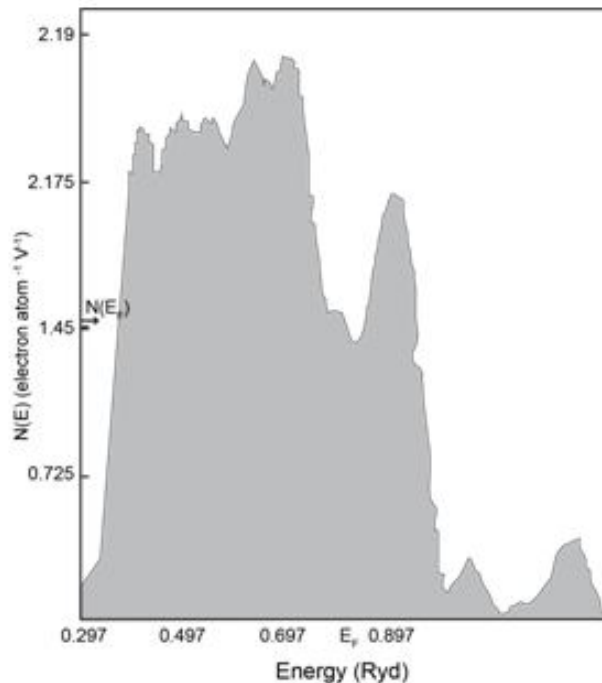


Fig 23. DOS of T_c for potential V_S

Table 4. Calculated Electronic Specific Heat coefficients for Tc with the electron-phonon interaction

Potential	γ_0 (mJ mol ⁻¹ deg ⁻²)	λ	$\gamma (= \gamma_0(1 + \lambda))$ (mJ mol ⁻¹ deg ⁻²)	$\gamma(\text{exp})$ (mJ mol ⁻¹ deg ⁻²)
V_S	3.277	0.305	4.27	4.84
V_H	2.640	0.828	4.82	4.84
V_{VS}	2.991	0.641	4.91	4.84

Table 5. Comparison of theoretical values of Tc with the experimental value

Potential	μ^*	λ (empirical)	λ (theory)	T_c (empirical) (K)	T_c (theory) (K)	T_c (exp) (K)
V_S	0.1512	0.476	0.305	1.004	0.005	7.73
V_H	0.1373	0.833	0.828	11.419	11.272	7.73
V_{VS}	0.1436	0.618	0.641	4.367	5.005	7.73

In view of the fact that T_c depends on a relation which contains exponential term, it is to be considered that the agreement between theory and experiment to be satisfactory. BCS theory was highly successful in many respects and especially in explaining pressure induced superconductivity which will be dealt with in the next article along with some of the high Tc systems.

Conclusion:

This introductory article should have given an overall understanding on band theory and how it can be applied to calculate superconducting transition temperature. Even though, BCS theory was built on phonon mechanism which was exhibited by many solids, it is missing in a few like Ru, Os etc and even the isotopic co-efficient assumes a negative value for uranium, which raises question on phonon mechanism, about which will see in the forthcoming article. It is worth revisiting this fundamental issue. Also, the applicability of BCS mechanism for super-hydrides at high pressure exhibiting high Tc values is a fascinating story to be probed.

The objective of this article is to remind the physicists of the two problems before us:

1) Deficiency in the Density Functional Method, which was successfully applied on hundreds of molecules and solids till the problems of NiO and high Tc parent compound La_2CuO_4 (Mott insulators) were brought into attention as the Conventional band structures show them to be metals instead of their insulating characteristics.

In this article, we have used conventional band structures which have been used in this article too and our calculations do not face any problem as they are non-magnetic, unlike the so called strongly correlated systems mentioned above.

2) Failure of BCS theory in explaining high temperature superconductors.

Real fall of BCS theory came to light with the discovery of the Heavy Fermion Superconductor, $CeCu_2Si_2$ exhibiting a thousand fold increase in the electronic specific heat coefficient compared to the phonon mediated BCS superconductors which were shown in table above. All BCS systems do show only milli joules regard to electronic specific heat coefficient. The discovery of high T_c superconductors, Copper oxides showing T_c values of 165 K and Iron arsenides with T_c of 65K clearly indicate the failure of BCS theory which gives an upper limit of 40 K.

The above two listed Nobel prize winning and most celebrated works: DFT due to W.Kohn and the other one, the BCS theory are in wanting, especially when we deal with magnetic materials.

Dynamical mean field theory (DMFT) to a certain extent solves the first problem. But, the second one has made physicists sleepless for the past forty years. Since the discovery of $CeCu_2Si_2$ in 1979 and the first high T_c parent superconductor La_2CuO_4 . Thousands of minds from all fields who jumped into this field, several thousand papers, more than one hundred theories to be proposed to be disposed is the present scenario of Condensed matter physics.

The key question is: Which "on" is responsible for the formation of cooper pair, other than phonon. several "On"s were proposed, but only to be discarded later. Or else should we break the electron and to build theories based on the quasi particles inside the electron: Holon and Spinon.

Acknowledgements:

One of the authors (R.A) gratefully acknowledges Prof.V.Devanathan, for having agreed to take me as his Ph.D student and also for giving me high degree of freedom, which enabled me to work in the areas of band structure, high pressure, and superconductivity during my Ph D years. One should gratefully appreciate his intellectual integrity by removing his name from my first paper on superconductivity, a part of my Ph.D work after expressing his view that he has not been following my work. The excellent freedom which I enjoyed gave me enough confidence to move on to other fields and make my students to work on both Theoretical and experimental superconductivity, aerospace materials and biomaterials along with my main area of Band structure. Prof V.D picked me along with a few others to go to IMSc during the visit of Abdus Salam, (N.L) who was the founder of ICTP, Trieste, Italy which became a great boon to many from third world countries to visit the center. He is highly thankful to ICTP to be a guest scientist many times which was a rich experience as it enabled him to meet several eminent scientists

and to interact with Profs.N.W.Ashcroft, G.Grimvall, B.L Gyorffy, W. Kohn (N.L), J.S.Schilling, and of course, my group head Prof.N.H March who were from several countries around the globe and whose papers and books are referred to in this article.

(R.A) wishes to thank Prof.Geetha Manivasagam, Director Center of theranostics, VIT, Vellore in identifying one of her old students from VIT with mechanical engineering background who is deeply interested in pursuing his Ph.D in quantum mechanics, theory of gravitation and related areas is my co-author and without whose hard work and perseverance, the paper could not have been completed. (R.A) would like to thank Prof K.Iyakutti and Dr R.S.Rao of BARC for the continuous support.

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