THE EFFECTIVE ELECTRON INTERACTION
IN THE THEORY OF SUPERCONDUCTIVITY

by

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ABSTRACT

The main contribution of this thesis is the
presentation of the theory of electrons in metals leading
to the theory of superconductivity in a lucid form. The
general form of the Hamiltonian of a metal is derived in
the second quantized formalism. The Frohlich transformation
which describes electron-electron interactions via the
lattice is discussed in detail and account is taken of
electron screening by introduction of plasma modes. The
BCS criterion for the occurence of superconductivity is
discussed and the BCS reduced Hamiltonian is obtained.
Finally, a critical summary of the various approximations
made in the theory is given.

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CHAPTER I

INTRODUCTION

The aim of this thesis is mainly pedagogical. The theory of electrons in metals leading up to the modern theory of superconductivity, as it is presented in the current literature, presents a formidable barrier to a graduate student beginning work in this field. Unfamiliar concepts, obscure approximations and lack of detail in calculations present difficulties which require a considerable amount of effort to overcome. It is hoped that this thesis will provide easier entry to the subject than has heretofore been possible. The second purpose of this work is to provide a critical summary of the numerous approximations which have been made throughout the theory.

It at first appears that superconductivity is a purely electronic phenomenon and is independent of the lattice. There is no appreciable change in the structure or other properties of the lattice in the transition to the superconducting state. In addition to the disappearance of all d.c. resistance below a critical temperature T_c, certain thermodynamic quantities behave discontinuously at the transition temperature. These indicate that a phase transition involving the conduction electrons occurs between the normal and superconducting states. F. and H. London[1] in 1935 developed a

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(1) H.London and F.London, Proc. Roy. Soc.(London) A149, 71(1935); Physica 2, 341 (1935).

satisfactory macroscopic theory of superconductivity which adequately described the electrodynamical properties of superconductors.

Early attempts to construct a microscopic theory based on the electrons in a metal met with little success. It was felt that due to the large mass of the ions in the metal relative to the mass of the electrons, the mobility of the ions would be too small to contribute at all to superconductivity. It was generally felt, that some purely electronic effect had hitherto been neglected in the theory of metals, and that consideration of this effect would satisfactorily explain superconductivity. However, in 1950, Frohlich[1] proposed a theory based on the interaction of electrons with lattice vibrations. He predicted an "isotope effect", in which the critical temperature T_c was dependent on the mass of the ions composing the metal. In the same year, Maxwell[2] and Reynolds[3] et. al. independently discovered this isotope effect experimentally, thus confirming Frohlich's hypothesis that superconductivity is related to the interaction of electrons with the lattice. Frohlich's 1950 theory of superconductivity was based on the electronic self energy, arising from the electron-phonon interaction, using perturbation

(1) H. Frohlich, Phys. Rev., 79, 845, (1950).

(2) E. Maxwell, Phys. Rev., 78, 477 (1950).

(3) Reynolds, Serin, Wright, and Nesbitt, Phys. Rev., 78, 487, (1950).

theory and failed to account for superconductivity. In the same year, Bardeen[1] independently performed a similar calculation using a variational method.

In 1952, Frohlich[2] described a canonical transformation of the Hamiltonian of a metal, neglecting the electronic coulomb interaction, in which the electron-phonon interaction led to an effective interaction between electrons. He showed that an attractive interaction was possible between electrons due to interactions via the vibrating lattice. This method was later extended by Nakajima[3] to take account of the coulomb interaction. In 1952, Bohm and Pines[4] using classical methods had shown that a dense gas of electrons contained collective (plasma) modes which tended to screen the field of individual electrons and that for long wavelengths, this collective motion was predominant, while for short wavelengths the individual particle aspects were important. These authors developed a quantum mechanical description of this phenomenon in 1953,[5] which was extended by Bardeen and Pines[6] in 1955 to take account of the coupled system of moving electrons and ions. They found that the long range coulomb interaction no longer appeared in the Hamiltonian but was

(1) Bardeen J., Phys.Rev., 79,167,(1950); Phys.Rev.,80,567,(1950)

(2) H. Frohlich, Proc. Roy. Soc.(London) A 215, 291,(1952)

(3) Nakajima S. Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, September 1953.

(4) D. Bohm and D. Pines, Phys. Rev., 85, 338, (1952)

(5) D. Bohm and D. Pines, Phys. Rev., 92, 609, (1953)

(6) J. Bardeen and D. Pines, Phys. Rev., 99, 1140, (1955).

described by high frequency plasma oscillations. Only a short range coulomb term remained.

In 1957, Bardeen, Cooper and Schrieffer[1] (hereafter referred to as BCS) presented a theory of superconductivity based on the off-diagonal parts of the electron Hamiltonian derived by Bardeen and Pines. This theory assumes correlations between pairs of electrons of opposite momentum and spin. Cooper[2] had earlier shown that two electrons interacting above a filled Fermi sphere by means of negative matrix elements could form a bound state. The BCS theory was found to explain nearly all the phenomena exhibited by superconductors. The theory has been criticized because of the sweeping simplifications used in the calculation, and the difficulty of giving more than vague justification for these simplifications. A more serious weakness is that the effective electron Hamiltonian is not gauge invariant and hence cannot adequately describe the electromagnetic proper-ties displayed by superconductors. Later work, notably by Anderson[3] and Rickayzen[4] has partially answered the question of lack of gauge invariance.

Chapter II of this thesis begins with a discussion of the adiabatic approximation and its range of validity. The adiabatic approximation assumes that the electrons follow the

(1) J. Bardeen, L.N. Cooper and J.R. Schrieffer, Phys. Rev., 108, 1175, (1957).

(2) L.N. Cooper, Phys. Rev. 104, 1189, (1956).

(3) Anderson P.W., Phys. Rev., 110, 827, (1958); Phys. Rev., 110, 985, (1958).

(4) Rickayzen, G., Phys. Rev., 111, 817, (1958).

motion of the ions at all frequencies and hence any interaction between them is velocity independent. The general form of the Hamiltonian of a metal is derived making use of this approximation and based on a model in which we consider ions oscillating about equilibrium positions and conduction electrons free to move throughout the solid without being concentrated at ion sites, but nevertheless subject to a periodic potential with the periodicity of the lattice. Use is made of the second quantized formalism in dealing with both electrons and phonons. Chapter III deals with the renormalization of the metal Hamiltonian. We require a model in which we can consider electrons largely moving independently of the lattice. This is obtained by means of the Frohlich transformation which in effect reorganizes the terms of the Hamiltonian by describing those electrons which contribute to the phonon part of the Hamiltonian in terms of lattice variables and those phonons which contribute to the electronic part of the Hamiltonian in terms of electron variables. We introduce plasma variables into the Hamiltonian to take proper account of the long range electronic Coulomb interaction. Chapter IV deals with the BCS theory of superconductivity. Here we have only attempted to show the physical reasoning for considering pair correlations and we discuss the BCS criterion for the occurrence of superconductivity. Chapter V is a summary of the approximations which are made in deriving the BCS reduced Hamiltonian.

The bulk of the material of this thesis is embodied in Chapters II and III, which is the quantum theory of

electron _interaction_ in metals in a fairly general form. The purpose of the thesis has not been to give a review of the theory of superconductivity since there has been a tremendous amount of work done on the theory since the original idea of BCS. Rather, the purpose of this thesis has been to review the theory of electrons in metals and indicate how the results are used in a theory of superconductivity.

CHAPTER II

QUANTUM THEORY OF ELECTRONS IN METALS

2.1 Basic Model of a Metal

It was first suggested by Drude that the electrical and thermal properties of metals might be correlated by assuming that metals contain free electrons in thermal equilibrium with the atoms of the solid. This hypothesis has led, after passing through several stages of development, to the present picture of a metal. The picture is as follows: the free neutral atoms out of which we construct a metal consist of nuclei surrounded by closed shells of electrons, which together constitute the ion cores, with additional valence electrons outside the closed shells. When the atoms are brought together to form a crystalline lattice, the ion cores occupy the regular array of sites which we associate with the crystal structure of a particular solid. The ion cores will oscillate about their equilibrium positions and will interact with the valence electrons which are no longer bound to individual ion cores but are free to move throughout the solid. These free electrons, with their wave functions extending throughout the lattice instead of being concentrated at individual lattice sites, form a background gas inside which the ion cores move. This gas is a plasma, capable of collective motion which tends to cancel the variations in electrostatic potential caused by the ionic motion. The individual electrons can also be scattered by the motion of the ion cores. One expects also that the free electrons will tend to screen their coulomb inter- actions with the vibrating ions. We shall now investigate the

criterion for considering the valence electrons and the ion cores as essentially decoupled from one another.

2.2 The Adiabatic Approximation [1]

From energy considerations, it appears plausible that the valence electrons tend to follow the motion of the ion cores so as to keep the system locally electrically neutral. If the electrons can effectively follow the motion of the ions at all frequencies, the motion of the electrons will be essentially adiabatic. In other words, we can assume that the electronic states depend only on the lattice configuration at a given instant and not on lattice dynamics. The criterion for the validity of this point of view can be determined by assuming that only small perturbative corrections arise from solutions based on the adiabatic approximation.

The exact Hamiltonian for a metal may be written

$$H = H_{el} + H_{ion} \qquad (2.1)$$

where H_{el} includes the kinetic energy of the electrons and the interaction of the electrons with the ions. If we consider the ions to be instantaneously in fixed positions, we have

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(1) The argument presented here is from a review article by G.V. Chester (1961): Advances in Physics, 10, 357 and is repeated for the sake of completeness.

for the Schrodinger equation satisfied by the electrons

$$H_{el}(\underline{R})\psi_n(\underline{r}/\underline{R}) = E_m\psi_n(\underline{r}/\underline{R}) \qquad (2.2)$$

where $\underline{r}$ represents the set of electron coordinates and $\underline{R}$ refers to the instantaneous positions of the ions. The wave function $\psi_n(\underline{r}/\underline{R})$ indicates that the electronic state is dependent on the instantaneous positions of the ions. The exact Schrodinger equation for the complete system can be written

$$H\Phi_m = \mathcal{E}_m\Phi_m \qquad (2.3)$$

where Φ_m is expanded in terms of the complete set of functions ψ_n as follows:

$$\Phi_m = \sum_n \chi_{mn}(\underline{R})\,\psi_n(\underline{r}/\underline{R}) \qquad (2.4)$$

If we substitute this expression into (2.3) and make use of (2.1) we obtain

$$(H_{el} + H_{ion})\sum_n \chi_{mn}(\underline{R})\psi_n(\underline{r}/\underline{R}) = \mathcal{E}_m\sum_n \chi_{mn}(\underline{R})\psi_n(\underline{r}/\underline{R}) \qquad (2.5)$$

We now allow for motion of the ions. We have $H_{ion} = T_{ion} + V_{ion}$ where T_{ion}, the kinetic energy operator for the ions is given as

$$T_{ion} = -\frac{\hbar^2}{2M}\sum_j \nabla_{R_j}^2 \qquad (2.6)$$

We have assumed a monatomic crystal so that all the ions have the same mass. We multiply (2.5) on the left by $\psi_n^*(\underline{r}/\underline{R})$ and integrate over the electronic coordinates to obtain

$$(V_{ion} + E_n)\chi_{mn} - \frac{\hbar^2}{2M}\sum_j\int \psi_n{}^*\nabla_{R_j}^2\sum_{n'}\chi_{mn'}\psi_{n'}d\underline{r} = \mathcal{E}_m\chi_{mn} \quad (2.7)$$

In obtaining this result we have made use of (2.6). If we
now let

$$A_{nn'} = -\frac{\hbar^2}{M}\sum_j\int\psi_n{}^*\nabla_{R_j}\psi_{n'}d\underline{r}\cdot\nabla_{R_j}$$

and   (2.8)

$$B_{nn'} = -\frac{\hbar^2}{2M}\sum_j\int\psi_n{}^*\nabla_{R_j}^2\psi_{n'}d\underline{r}$$

we have

$$(T_{ion} + V_{ion} + E_n + B_{nn})\chi_{mn} + \sum_{n\neq n'}C_{nn'}\chi_{mn'} = \mathcal{E}_m\chi_{mn} \quad (2.9)$$

where we have let $C_{nn'} = A_{nn'} + B_{nn'}$.

Equation (2.9) is a matrix operator equation of the
form $\mathcal{H}\hat{\chi}_m = \mathcal{E}_m\hat{\chi}_m$ where $\hat{\chi}_m$ stands for the column vector
$[\chi_{m1}, \chi_{m2}, \cdots \chi_{mn}, \cdots]$ and $\mathcal{H}$ has matrix elements
$\mathcal{H}_{nn'} = (T_{ion} + V_{ion} + E_n + B_{nn})\delta_{nn'} + C_{nn'}$. If we set
$C_{nn'} = 0$ our matrix operator is diagonal. Each $\hat{\chi}_m$ which is a
solution has therefore just one non-zero component. The
expanded wave function (2.4) has therefore just one component
for each value of m, $\Phi_m = \chi_{mn}\psi_n$. From the discussion
preceeding (2.2) it can be seen that for this case the elect-
ronic motion is completely adiabatic, since the wave function
for the electronic system is the same electronic wave function
which we wrote when we considered the ions instantaneously at
rest. The $C_{nn'}$ are the terms which lead to non-adiabatic

motion. We shall now obtain an estimate of the importance
of the non-adiabatic terms by employing perturbation techniques.

If we treat the $C_{nn'}$ as small, then to first order
of perturbation theory

$$\delta \chi_{mn} = \sum_{n'} \frac{C_{nn'} \chi_{mn'}^{(0)}}{E_n - E_{n'}} \qquad (2.10)$$

where $\delta \chi_{mn}$ is the non-adiabatic distortion of the wave
function $\chi_{mn}^{(0)}$ and $\chi_{mn'}^{(0)}$ is a solution of (2.9) with $C_{nn'} \chi_{mn'}^{(0)}$
set equal to zero. If $\delta \chi_{mn}$ is small compared to χ_{mn}, the
adiabatic approximation is valid. $\delta \chi_{mn}$ will be small if
$C_{nn'} \chi_{mn'}^{(0)}$ is small compared to a typical energy denominator.

We shall now estimate the order of magnitude of
$C_{nn'} \chi_{mn'}^{(0)}$. We consider $A_{nn'} \chi_{mn'}^{(0)}$ which equals

$-\frac{\hbar^2}{M} \sum_j \int \psi_n^* \nabla_{R_j} \psi_{n'} \, d\underline{r} \cdot \nabla_{R_j} \chi_{mn'}^{(0)}$. We can replace $-\frac{i\hbar}{M} \nabla_{R_j}$

by the velocity operator $\underline{v}_j$ of the jth ion. In order to
obtain a reasonable estimate we shall replace $\underline{v}_j \chi_{mn'}^{(0)}$ by $\bar{v}$,
the mean value of the velocity of the ions in the lattice.
We therefore have

$$|A_{nn'}| \leq \hbar \bar{v} \left| \sum_j \int \psi_n^* \nabla_{R_j} \psi_{n'} d\underline{r} \right| \qquad (2.11)$$

We consider now the Schrodinger equation

$$H_{el} \psi_{n'} = E_{n'} \psi_{n'}$$

which on writing H_{el} explicitly becomes

$$\left\{-\frac{\hbar^2}{2m}\nabla_{\underline{r}}^2 + V_{int}(\underline{r}/\underline{R})\right\}\psi_{n'}(\underline{r}/\underline{R}) = E_{n'}\psi_{n'}(\underline{r}/\underline{R}) \tag{2.12}$$

V_{int} is the electron-ion interaction and enters this expression since H_{el} contains this interaction as well as the electronic kinetic energy. If we operate on this equation with $\sum_j \nabla_{\underline{R}_j}$ and then multiply on the left with ψ_n^* and integrate over the electron coordinates we obtain

$$\sum_j \int \psi_n^* \nabla_{\underline{R}_j}\psi_{n'}\,d\underline{r} = \sum_j \frac{(\nabla_{\underline{R}_j}V_{int})_{nn'}}{E_{n'}-E_n} \tag{2.13}$$

As the ions in the lattice move about, the potential energy of the lattice is changed by a small amount. This extra potential will introduce a distortion of the electronic wave functions. We can expand the electron ion interaction term as

$$\sum_j V_{int}(\underline{r}/\underline{R}_j) = \sum_j V_{int}(\underline{r}/\underline{R}_j^o) + \sum_j(\underline{R}_j - \underline{R}_j^o)\cdot\nabla_{\underline{R}_j}V_{int}(\underline{r}/\underline{R}_j^o) + \cdots$$

where $\underline{R}_j^o$ are the ion equilibrium positions. We assume we need only consider the first order terms as contributing to the extra potential. For a reasonable estimate of the effect of this term, we replace $(\underline{R}_j - \underline{R}_j^o)$ by ℓ, the average displacement of the ions from equilibrium. Using this value, the distortion of the electronic function ψ_n becomes

$$\delta\psi_n = \ell\sum_{n'}\frac{(\sum_j\nabla_{\underline{R}_j}V_{int})_{nn'}}{E_{n'}-E_n}\psi_{n'} \tag{2.14}$$

from standard first order perturbation theory.

For an appreciable distortion of the electronic wave function we require that

$$\ell \, \frac{(\sum_{j} \nabla_{R_j} \cdot V_{int})_{mn'}}{E_{n'} - E_{n}} \sim 1 \qquad (2.15)$$

If we combine this with (2.13) we find

$$\left| \sum_{j} \int \psi_{n}^{*} \nabla_{R_j} \psi_{n'} \, d\underline{r} \right| \sim \frac{1}{\ell} \qquad (2.16)$$

where ℓ is the average distance the ions have to move to produce an appreciable distortion in ψ_{n}. If we were to follow a similar procedure we would find that $B_{mn'}$ is small in magnitude compared to $A_{mn'}$. We have therefore that $C_{mn'} \chi_{mn'}^{(0)}$

$$\sim \frac{\hbar \bar{v}}{\ell} \chi_{mn'}^{(0)}.$$

We now consider the energy denominators of (2.10). The matrix elements $C_{mn'}$ connect states that differ by single electron excitations. The Pauli Exclusion Principle forbids all transitions except those from an occupied to an unoccupied state. The majority of such states have an energy separation of the order of η, the Fermi energy. For most transitions, $E_{n'} - E_{n}$ will therfore be of the order of η. This is not true of transitions from just below to just above the Fermi surface, but the number of occupied states just below the Fermi surface is small. For the case where the denominators are of the order of the Fermi energy we have

$$\frac{C_{mn'}}{E_{n'} - E_{n}} \sim \frac{\hbar \bar{v}}{\ell \eta}$$

We know that $\bar{v} \sim 10^{5}$ cm/sec, $\eta \sim 5$ ev. and ℓ cannot be much less than 10^{-8} cm. Using these values, we find that

$$\frac{C_{mm'}}{E_{m'} - E_{m}} \sim 2 \times 10^{-3} .$$

If this estimate is correct, then the non-adiabatic correction to the wave function is very small and the adiabatic approximation is valid.

We now wish to estimate where the adiabatic approximation breaks down. Non-adiabatic terms have to be considered if the distortion $\delta \chi_{mm}$ is of the same order of magnitude as $\chi_{mm}^{(o)}$; if $\frac{C_{mm'}}{E_{m'} - E_{m}} \sim 1$. Using the above values for $\bar{v}$ and ℓ we find that this occurs when

$$|E_{m'} - E_{m}| \leq 10^{-14} \text{ ergs} \sim \hbar \omega_{max}$$

where ω_{max} is the maximum lattice frequency. We therefore define a "danger zone" of electrons that lie within $\hbar \omega_{max}$ of the Fermi surface. Since the adiabatic approximation loses validity in this "danger zone", any property of the solid which depends on these electrons must be calculated by taking into consideration the non-adiabatic terms in the equations of motion.

2.3 Derivation of the Hamiltonian

(a) Preliminary Discussion

If we assume that spin-orbit and spin-spin interactions of the electrons can be neglected, we can write for the Hamiltonian describing a metal

$$H = \sum_{i} \frac{p_i^2}{2m} + \sum_{i,j} v(\underline{r}_i - \underline{R}_j) + H_{ion\text{-}ion} + H_{coul} \qquad (3.a.1)$$

The subscript i labels the valence electrons and j refers to the ions. In this model, we are assuming that the valence electrons are completely separated from the closed shells of bound electrons which make up the ion cores so that there is no exchange between these two groups of electrons. If we consider N ions in our metal, for electric neutrality we require zN valence electrons where z is the valence of the atoms forming the metal. The first term of (3.a.1) is the kinetic energy of the valence electrons and the second term represents the interaction between these electrons and the ion cores. We are assuming that this interaction energy is independent of ion velocities by considering an interaction which depends only on the instantaneous positions of the ions. We are thus in effect using the adiabatic approximation which was discussed in the preceeding section. $H_{ion\text{-}ion}$ includes the kinetic energy as well as the coulomb and exchange repulsion of the ion cores. H_{coul} represents the coulomb interaction of the valence electrons.

In order to eliminate infinities in the separate terms of eq. (3.a.1), since we shall be considering an infinite crystal, we suppose that there is subtracted from the electron-ion interaction the interaction of a uniform negative charge with a uniform positive charge, from the electron-electron

interaction the self energy of a uniform negative charge, and from the ion-ion interaction the self energy of a uniform positive charge. The positive charge density can be written as

$$\rho_{ion}(\underline{r}) = \rho_{ion}^{\circ} + \widetilde{\rho}_{ion}(\underline{r})$$

where ρ_{ion}° is constant and represents a uniform positive charge density. Also we can write for the negative charge density

$$\rho_{el}(\underline{r}) = \rho_{el}^{\circ} + \widehat{\rho}_{el}(\underline{r})$$

Since the system is electrically neutral, $\rho_{el}^{\circ} = -\rho_{ion}^{\circ}$. The total energy which we are subtracting is given by

$$\frac{1}{2}\int d\tau\, d\tau' \frac{(\rho_{ion}^{\circ})^2}{|\underline{r} - \underline{r}'|} + \frac{1}{2}\int d\tau\, d\tau'' \frac{(\rho_{el}^{\circ})^2}{|\underline{r} - \underline{r}'|} + \int d\tau\, \frac{d\tau'(\rho_{el}^{\circ}\,\rho_{ion}^{\circ})}{|\underline{r} - \underline{r}'|}$$

It can be seen that the total energy subtracted from the separate terms of (3.a.1) exactly equals zero. In the Hamiltonian (3.a.1) therefore, H_{coul} is actually the coulomb energy of the valence electrons measured relative to the self energy of a uniform distribution of negative charge and $H_{ion-ion}$ contains the coulomb energy of the ions measured relative to the self energy of a uniform distribution of positive charge.

(b) <u>Lattice Vibrations</u>

We consider a set of identical, charged, small ionic cores interacting through repulsive forces, largely Coulomb. We shall assume that we have an infinite lattice made up of these cores so that surface effects may be

neglected, and we shall impose periodic boundary conditions
on our system. We shall assume further that the minimum of
potential energy of a lattice of ion cores devoid of valence
and conduction electrons corresponds to a lattice configuration
identical to that of the real crystal. If this is not true,
then small oscillations of the "empty" lattice about the
real crystal equilibrium sites cannot be defined. Since we
wish to describe these oscillations in terms of normal modes
we must assume the existence of this minimum of potential
energy. In deriving the Hamiltonian which describes the
lattice vibrations, or the phonon Hamiltonian, we shall employ
a method similar to that of Peierls.[2]

We let $\underline{u}_j$ be the displacement of an atom from
its equilibrium position $\underline{R}_j^o$. $\underline{R}_j^o$ is the equilibrium
position of the j'th ion relative to the origin. Then

$$\underline{u}_j = \delta \underline{R}_j = \underline{R}_j - \underline{R}_j^o \qquad (3.b.1)$$

If we let U_o be the potential energy of our system at
equilibrium including the self energy of a uniform positive
charge, we may expand the potential energy U in a Taylor
series:

$$U - U_o = \sum_{j,j'} \tfrac{1}{2} A_{jj'} \underline{u}_j \, \underline{u}_{j'} + \sum_{j,j',j''} \tfrac{1}{6} B_{jj'j''} \underline{u}_j \, \underline{u}_{j'} \, \underline{u}_{j''} + \cdots \qquad (3.b.2)$$

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(2)   Peierls R.E., (1955):   Quantum Theory of Solids.
(Oxford: University Press).

where $\underset{\approx}{A}$ and $\underset{\approx}{B}$ are tensors of second and third rank respectively connecting the components of the vectors which follow. The subscripts in this equation refer to the positions of the ions and not to the coordinate axes. The ratio of A to B has dimensions of length. For reasonable forces we assume that this ratio is of the order of the ionic spacing. If the ionic displacements are small compared to this distance, we need only consider quadratic terms in the expansion for the potential energy. There are no linear terms in the expansion since the first derivative must vanish at equilibrium. Since the tensor $\underset{\approx}{A}_{jj'}$ is related to the force constant between the ions at positions j and j', if we assume that the forces between the ions depend only on the relative distances between the ions and not on directions of displacement, the tensors $\underset{\approx}{A}$ are symmetric in their indices. Considering only quadratic terms in the above expansion we have

$$U - U_o = \sum_{j,j'} \tfrac{1}{2} \underline{u}_j \cdot \underset{\approx}{A}_{jj'} \cdot \underline{u}_{j'} \tag{3.b.3}$$

from which, employing Hamilton's classical equations of motion, we obtain the equations of motion for our system

$$M \, \underset{\ \ }{\overset{\bullet\bullet}{\underline{u}}}_j = - \sum_{j'} \underset{\approx}{A}_{jj'} \cdot \underline{u}_{j'} \tag{3.b.4}$$

where M is the mass of each of the identical ions.

We now wish to determine the normal modes of our system, that is vibrations in which all ions oscillate with the same angular frequency, Ω radians/second. These normal

frequencies, which are determined solely from ion-ion interactions, will not be those of the real crystal which contains many conduction electrons. The presence of the electrons in the real crystal alters the ion-ion interaction and leads to a renormalization of the normal frequencies. This point will be discussed in greater detail at a later stage. We verify that the ions all have the same amplitude of oscillation but differ in phase. We therefore write

$$\underline{u}_j = e^{-i\Omega t + i\underline{k}\cdot\underline{R}_j^o}\ u_o\ \underline{\varepsilon}_o \qquad\qquad (3.b.5)$$

where $\underline{k}$ is some vector to be determined from periodic boundary conditions, $\underline{R}_j^o$ is again a vector from the origin to the ion at the lattice site specified by j, $\underline{\varepsilon}_o$ is a unit polarization vector and u_o is the amplitude of the displacement of the ion occupying the site $j = 0$ at $t = 0$. On substituting this expression for $\underline{u}_j$ into (3.b.4) we obtain the equation

$$M\Omega^2\ \underline{\varepsilon}_o = \sum_{j'} \underline{\underline{A}}_{jj'}\cdot\underline{\varepsilon}_o\ e^{i\underline{k}\cdot(\underline{R}_{j'}^o - \underline{R}_j^o)} \qquad\qquad (3.b.6)$$

In order to obtain the correct values for $\underline{k}$, we apply our periodic boundary conditions. If we consider a cube of volume V and length L, the components of $\underline{k}$ must satisfy the relations $e^{ik_1 L} = e^{ik_2 L} = e^{ik_3 L} = 1$. The components of $\underline{k}$ are therefore real and are given by $\dfrac{2\pi n_1}{L}$, $\dfrac{2\pi n_2}{L}$, and $\dfrac{2\pi n_3}{L}$ where n_1 , n_2, and n_3 are integers. It can be seen that the

vectors $\underline{k}$ and $\underline{k}'$ refer to the same normal mode of vibration if $(\underline{k} - \underline{k}') \cdot \underline{R}_j^o$ is a multiple of 2π for any j. If we introduce reciprocal lattice vectors $\underline{q}$ such that $e^{i\underline{q}\cdot\underline{R}_j^o} = 1$ for any j, any two vectors $\underline{k}$ and $\underline{k}'$ are equivalent in defining normal modes if they differ by a lattice vector of the reciprocal lattice.

Since there are N independent values of $\underline{k}$ in the first Brillouin zone we have 3N independent modes of vibration. There are three different modes of vibration for each value of $\underline{k}$ which are solutions of (3.b.6), since this is a vector equation and the $\underline{\underline{A}}$ are tensors of second rank. In general, these solutions have different frequencies Ω. We label these solutions $\underline{\xi}_o(\underline{k}, \sigma)$ and $\Omega(\underline{k}, \sigma)$ where σ takes on values 1, 2 or 3. We can express the most general displacement as a linear superposition of particular solutions with arbitrary coefficients.

$$\underline{u}_j = \sum_{\underline{k},\sigma} C_{\underline{k},\sigma} \, e^{-i\Omega(\underline{k},\sigma)t + i\underline{k}\cdot\underline{R}_j^o} \, u_o(\underline{k},\sigma) \, \underline{\xi}_o(\underline{k},\sigma)$$

For the sake of convenience we write this as

$$\underline{u}_j = (NM)^{-\frac{1}{2}} \sum_{\underline{k},\sigma} q_{\underline{k},\sigma}(t) \, e^{i\underline{k}\cdot\underline{R}_j^o} \, \underline{\xi}_o(\underline{k},\sigma) \qquad (3.b.7)$$

where $q_{\underline{k},\sigma}(t) = q_{\underline{k},\sigma}(0) \, e^{-i\Omega(\underline{k},\sigma)t}$. On substituting (3.b.7) into (3.b.4) and making use of (3.b.6) we find that $q_{\underline{k},\sigma}(t)$ satisfies the equation

$$\ddot{q}_{\underline{k},\sigma} + \left\{\Omega(\underline{k},\sigma)\right\}^2 q_{\underline{k},\sigma} = 0 \qquad (3.b.8)$$

which agrees with the time dependence above. If we assume

that $\Omega(-\underline{k}) = \Omega(\underline{k})$, we find that $\underline{\mathcal{E}}_o^*(\underline{k},\sigma) = \underline{\mathcal{E}}_o(-\underline{k},\sigma)$ by taking the complex conjugate of (3.b.6) since $A_{jj'}$ is necessarily a real quantity. Also, since the ionic displacements are real, from (3.b.7) we have

$$q_{-\underline{k},\sigma} = q^*_{\underline{k},\sigma} \qquad (3.b.9)$$

We now wish to show that

$$\sum_{j} M\left\{\underline{\mathcal{E}}_o(\underline{k},\sigma)\, e^{i\underline{k}\cdot\underline{R}_j^o}\right\}^* \cdot \left\{\underline{\mathcal{E}}_o(\underline{k}',\sigma')\, e^{i\underline{k}'\cdot\underline{R}_j^o}\right\} = 0 \qquad (3.b.10)$$

unless $\underline{k} = \underline{k}'$ and $\sigma = \sigma'$. We consider first the sum $S = \sum_{j} e^{i(\underline{k}' - \underline{k})\cdot\underline{R}_j^o}$. Suppose each lattice point of the crystal to be displaced by a particular lattice vector $\underline{R}^o$. This changes every lattice point into another lattice point, since we are considering an infinite crystal, and hence merely relabels the terms of the sum while the value of the sum doesn't change. However, each term of the sum is multiplied by the factor $e^{i(\underline{k}' - \underline{k})\cdot\underline{R}^o}$ and hence the entire sum is multiplied by this amount. We have that $S = S\, e^{i(\underline{k}' - \underline{k})\cdot\underline{R}^o}$. Either $S = 0$ or $\underline{k}' - \underline{k}$ is a vector of the reciprocal lattice. For the sum not to vanish, $\underline{k}$ and $\underline{k}'$ must be equivalent. Therefore $S = \sum_{j} e^{i(\underline{k}' - \underline{k})\cdot\underline{R}_j^o} = N\,\delta_{\underline{k},\underline{k}'}$ for a lattice composed of N ions. We now consider $M\underline{\mathcal{E}}_o^*(\underline{k},\sigma)\cdot \underline{\mathcal{E}}_o(\underline{k},\sigma')$. We multiply (3.b.6) on the left by $\underline{\mathcal{E}}_o^*(\underline{k},\sigma)$ to obtain

$$M\Omega^2(\underline{k},\sigma')\,\underline{\mathcal{E}}_o^*(\underline{k},\sigma)\cdot\underline{\mathcal{E}}_o(\underline{k},\sigma') = \sum_{j}\underline{\mathcal{E}}_o^*(\underline{k},\sigma)\cdot A_{jj'}\cdot\underline{\mathcal{E}}_o(\underline{k},\sigma')e^{i\underline{k}\cdot(\underline{R}_{j'}^o - \underline{R}_j^o)}$$

Taking the complex conjugate of this expression and interchanging σ and σ' we have

$$M\Omega^2(\underline{k},\sigma)\,\underline{\mathcal{E}}_o^*(\underline{k},\sigma)\cdot\underline{\mathcal{E}}_o(\underline{k},\sigma') = \sum_{j'}\underline{\mathcal{E}}_o(\underline{k},\sigma')\cdot A_{jj'}\cdot\underline{\mathcal{E}}_o^*(\underline{k},\sigma)e^{-i\underline{k}\cdot(\underline{R}_{j'}^o - \underline{R}_j^o)}$$

Since $\underset{=}{A}_{j,j'}$ Depends only on the relative positions of the ions we have that $\underset{=}{A}_{j,j'} = \underset{=}{A}_{j',j}$. Also since $\underset{=}{A}_{j,j'}$ is symmetric in its unwritten spatial indices we have that

$$\underset{\sim}{\mathcal{E}}_0{}^*(\underline{k}, \sigma) \cdot \underset{=}{A}_{j,j'} \cdot \underset{\sim}{\mathcal{E}}_0(\underline{k}, \sigma') = \underset{\sim}{\mathcal{E}}_0(\underline{k}, \sigma') \cdot \underset{=}{A}_{j,j'} \cdot \underset{\sim}{\mathcal{E}}_0{}^*(\underline{k}, \sigma)$$

Since we are considering an infinite crystal, we can consider the ions as symmetric about any ion j. Therefore on subtraction of the above two expressions we have

$$M \left[\Omega^2(\underline{k}, \sigma') - \Omega^2(\underline{k}, \sigma) \right] \underset{\sim}{\mathcal{E}}_0{}^*(\underline{k}, \sigma) \cdot \underset{\sim}{\mathcal{E}}_0(\underline{k}, \sigma') = 0$$

We see that (3.b.10) is true provided $\Omega^2(\underline{k}, \sigma) \neq \Omega^2(\underline{k}, \sigma')$. If more than one normal vibration for a given $\underline{k}$ have the same frequency, the $\underset{\sim}{\mathcal{E}}_0(\underline{k}, \sigma)$ are not uniquely determined since the set of linear homogeneous equations (3.b.6) has more than one independent solution. In this case, we choose our basic set of solutions such that (3.b.10) is true if $\underline{k} \neq \underline{k}'$ and $\sigma \neq \sigma'$. We have therefore the result

$$\sum_{j} M \left\{ \underset{\sim}{\mathcal{E}}_0(\underline{k}, \sigma) e^{i\underline{k} \cdot \underline{R}_j^o} \right\}^* \cdot \left\{ \underset{\sim}{\mathcal{E}}_0(\underline{k}', \sigma') e^{i\underline{k}' \cdot \underline{R}_j^o} \right\} = NM \delta_{\underline{k}, \underline{k}'} \delta_{\sigma, \sigma'} \quad (3.b.11)$$

We wish now to relabel our equations by letting ν stand for j and the three space directions and φ stand for $\underline{k}$ and σ. $\mathcal{E}_\nu(\varphi)$ is then one of the components of $\underset{\sim}{\mathcal{E}}_0(\underline{k}, \sigma) e^{i\underline{k} \cdot \underline{R}_j^o}$. Instead of (3.b.11) we write for the orthogonality relation

$$\sum_{\nu} M \, \mathcal{E}_\nu{}^*(\varphi) \, \mathcal{E}_\nu(\varphi') = NM \delta_{\varphi, \varphi'} \quad (3.b.12)$$

and the most general form for a component of displacement for a given ion may be written in analogy with (3.b.7) as

$$u_\nu = (NM)^{-\frac{1}{2}} \sum_{\varphi} q(\varphi)\, \mathcal{E}_\nu(\varphi) \qquad\qquad (3.b.13)$$

If we multiply this expression by $M\, \mathcal{E}_\nu(\varphi)$ and sum over ν we obtain

$$\sum_\nu M\, \mathcal{E}_\nu^*(\varphi) u_\nu = \sum_\nu \frac{M}{(MN)^{\frac{1}{2}}} \mathcal{E}_\nu^*(\varphi) \sum_{\varphi'} q(\varphi')\, \mathcal{E}_\nu(\varphi')$$

which with the aid of (3.b.12) gives

$$\sum_\nu M\, \mathcal{E}_\nu^*(\varphi)\, u_\nu = q(\varphi)(MN)^{\frac{1}{2}} \qquad\qquad (3.b.14)$$

or

$$q(\varphi) = \frac{M}{(MN)^{\frac{1}{2}}} \sum_\nu \mathcal{E}_\nu^*(\varphi)\, u_\nu \qquad\qquad (3.b.15)$$

Substituting this into (3.b.13) and simplifying we obtain

$$u_\nu = \frac{1}{N} \sum_\varphi \mathcal{E}_\nu(\varphi) \sum_{\nu'} \mathcal{E}_{\nu'}^*(\varphi)\, u_{\nu'}$$

and since this must be true for arbitrary displacements we have the completeness relation

$$\sum_\varphi \mathcal{E}_\nu(\varphi)\, \mathcal{E}_{\nu'}^*(\varphi) = N\, \delta_{\nu,\nu'} \qquad\qquad (3.b.16)$$

We now wish to investigate the energy of the system of ions. From classical mechanics we can write for the kinetic energy of the ions

$$T = \tfrac{1}{2} \sum_\nu M\, \dot{u}_\nu^2 = \frac{1}{2N} \sum_{\nu,\varphi,\varphi'} \mathcal{E}_\nu(\varphi)\, \dot{q}(\varphi)\, \mathcal{E}_\nu(\varphi')\, \dot{q}(\varphi')$$

Since $\mathcal{E}_\nu(-\varphi) = \mathcal{E}_\nu^*(\varphi)$ and $q(-\varphi) = q^*(\varphi)$ we have with the aid of (3.b.12) that

$$T = \tfrac{1}{2} \sum_{\varphi} \dot{q}*(\varphi)\, \dot{q}(\varphi) \tag{3.b.17}$$

If we revert to our former explicit notation we have

$$T = \tfrac{1}{2} \sum_{\underline{k},\sigma} |\dot{q}_{\underline{k},\sigma}|^2 \tag{3.b.18}$$

If we substitute for $\underline{u}_j$ from (3.b.7) into (3.b.3) and make use of (3.b.4) we obtain

$$U - U_0 = \tfrac{1}{2} \sum_{\underline{k},\sigma} \left\{ \Omega(\underline{k},\sigma) \right\}^2 |q_{\underline{k},\sigma}|^2 \tag{3.b.19}$$

The total energy of our system is therefore

$$E = \tfrac{1}{2} \sum_{\underline{k},\sigma} \left\{ |\dot{q}_{\underline{k},\sigma}|^2 + \left\{ \Omega(\underline{k},\sigma) \right\}^2 |q_{\underline{k},\sigma}|^2 \right\} \tag{3.b.20}$$

This expression for the energy resembles the energy of a set of decoupled harmonic oscillators. We shall make use of this resemblance to quantize the system. For quantization of a harmonic oscillator we require the conditions

$$\left[\dot{u}_{\nu}(\varphi),\ u_{\nu'}(\varphi') \right] = -\frac{i\hbar}{M}\, \delta_{\nu,\nu'}\, \delta_{\varphi,\varphi'} \tag{3.b.21}$$

$$\left[\dot{u}_{\nu}(\varphi),\ \dot{u}_{\nu'}(\varphi') \right] = \left[u_{\nu}(\varphi),\ u_{\nu'}(\varphi') \right] = 0$$

If we make use of (3.b.15) we obtain

$$\left[\dot{q}*(\varphi),\, q(\varphi') \right] = \frac{M}{N} \sum_{\nu,\nu'} \mathcal{E}_{\nu}*(\varphi')\, \mathcal{E}_{\nu'}(\varphi) \left[\dot{u}_{\nu},\, u_{\nu'} \right]$$

which with (3.b.21) and (3.b.12) becomes

$$\left[\dot{q}*(\varphi),\, q(\varphi') \right] = -i\hbar\, \delta_{\varphi,\varphi'} \tag{3.b.22}$$

We therefore see that $q(\varphi)$ and $\dot{q}*(\varphi)$ are canonically

conjugate variables. We label $\dot{q}*(\varphi) = p(\varphi)$ and $\dot{q}(\varphi) = p*(\varphi)$.[1] If we revert again to our former explicit notation we have

$$\left[p_{k,\sigma}, q_{k',\sigma'} \right] = - i\hbar \, \delta_{k,k'} \, \delta_{\sigma,\sigma'} \qquad (3.b.23)$$

Equation (3.b.18) becomes

$$T = \frac{1}{2} \sum_{k,\sigma} p*_{k,\sigma} \, p_{k,\sigma} \qquad (3.b.24)$$

and (3.b.19) is now

$$U - U_0 = \frac{1}{2} \sum_{k,\sigma} \left\{ \Omega(\underline{k},\sigma) \right\}^2 q*_{k,\sigma} \, q_{k,\sigma} \qquad (3.b.25)$$

The total Hamiltonian for the system of ions or the phonon Hamiltonian, is therefore

$$H_{ph} = \frac{1}{2} \sum_{k,\sigma} \left[p*_{k,\sigma} \, p_{k,\sigma} + \left\{ \Omega(\underline{k},\sigma) \right\}^2 q*_{k,\sigma} q_{k,\sigma} \right] \qquad (3.b.26)$$

We have shown that for each value of $\underline{k}$ which describes normal modes, the three different modes of oscillation are orthogonal. We assume that two of these components are transverse and that one is longitudinal. If we examine only the longitudinal component, the phonon Hamiltonian becomes

$$H_{ph} = \frac{1}{2} \sum_{k} (p*_{k} \, p_{k} + \Omega_{k}^2 q*_{k} \, q_{k}) \qquad (3.b.27)$$

Since we have shown that two different $\underline{k}'$ are equivalent in defining normal modes of vibration if they differ by a vector of the reciprocal lattice, in the expression above whenever $\underline{k}$ runs out of the first Brillouin zone the q_{k} refers to the

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(1) We introduce these variables in order to establish a connection with the phonon Hamiltonian of Bardeen J. and Pines D., Phys. Rev. 99, 1140 (1955).

corresponding $\underline{k}$ in the first zone. In subsequent work we shall assume that electrons interact only with the longitudinal component of the lattice waves. The two transverse frequencies are in this approximation determined entirely from ion-ion interactions. Calculation of the longitudinal frequencies of the real crystal, however, requires consideration of the electron lattice interaction.

We now wish to introduce creation and annihilation operators for the lattice waves. These are required for facilitating later calculations. If we substitute $-\underline{k}$ for $\underline{k}$ in (3.b.27), since the summation over $\underline{k}$ is symmetric and since $q_{\underline{k}}^* = q_{-\underline{k}}$ and $p_{\underline{k}}^* = p_{-\underline{k}}$,

$$H_{ph} = \tfrac{1}{2} \sum_{\underline{k}} (p_{\underline{k}}^* \, p_{\underline{k}} + \Omega_{-\underline{k}}^2 \, q_{\underline{k}}^* \, q_{\underline{k}}) \tag{3.b.28}$$

Since H_{ph} is real

$$H_{ph} = \tfrac{1}{2} \sum_{\underline{k}} (p_{\underline{k}}^* \, p_{\underline{k}} + (\Omega_{\underline{k}}^*)^2 q_{\underline{k}}^* \, q_{\underline{k}}) \tag{3.b.29}$$

We have therefore that $\Omega_{\underline{k}}^2 = \Omega_{-\underline{k}}^2 = (\Omega_{\underline{k}}^*)^2$. The frequencies will be real so we take $\Omega_{\underline{k}} = \Omega_{-\underline{k}} = \Omega_{\underline{k}}^*$. We define an operator $b_{\underline{k}}$ and its hermitian conjugate $b_{\underline{k}}^*$ as

$$b_{\underline{k}} = \frac{1}{\sqrt{2\hbar\Omega_{\underline{k}}}} (p_{\underline{k}}^* - i \, \Omega_{\underline{k}} q_{\underline{k}})$$

$$b_{\underline{k}}^* = \frac{1}{\sqrt{2\hbar\Omega_{\underline{k}}}} (p_{\underline{k}} + i \, \Omega_{\underline{k}} q_{\underline{k}}^*) \tag{3.b.30}$$

Solving for $p_{\underline{k}}$, $p_{\underline{k}}^*$, $q_{\underline{k}}$ and $q_{\underline{k}}^*$ we obtain the results

$$p_{\underline{k}} = \sqrt{\frac{\hbar\Omega_{\underline{k}}}{2}} \, (b_{\underline{k}}^* + b_{-\underline{k}})$$

$$p_{\underline{k}}^* = \sqrt{\frac{\hbar\Omega_{\underline{k}}}{2}} \, (b_{-\underline{k}}^* + b_{\underline{k}}) \tag{3.b.31}$$

$$q_{\underline{k}} = i \sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}} (b_{\underline{k}} - b_{-\underline{k}}^{*})$$

$$q_{\underline{k}}^{*} = i \sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}} (b_{-\underline{k}} - b_{\underline{k}}^{*})$$

Making use of the commutation relations for the $q_{\underline{k}}$ and $p_{\underline{k}}$ we obtain

$$\left[b_{\underline{k}}, b_{\underline{k}'}^{*} \right] = \delta_{\underline{k},\underline{k}'}$$

and   (3.b.32)

$$\left[b_{\underline{k}}, b_{\underline{k}'} \right] = \left[b_{\underline{k}}^{*}, b_{\underline{k}'}^{*} \right] = 0$$

If we substitute (3.b.31) into (3.b.27) and note that the summation over $\underline{k}$ in this Hamiltonian is symmetric we have

$$H_{ph} = \sum_{\underline{k}} \frac{\hbar\Omega_{\underline{k}}}{2} (b_{\underline{k}} b_{\underline{k}}^{*} + b_{\underline{k}}^{*} b_{\underline{k}}) \qquad (3.b.33)$$

Making use of (3.b.32) this becomes

$$H_{ph} = \sum_{\underline{k}} \hbar \Omega_{\underline{k}} (b_{\underline{k}}^{*} b_{\underline{k}} + \tfrac{1}{2}) \qquad (3.b.34)$$

We recognize the commutation relations (3.b.22) as those used to describe Bose-Einstein type particles. The quanta of energy of the system described by (3.b.34) are called phonons. $b_{\underline{k}}^{*}$ and $b_{\underline{k}}$ are respectively creation and annihilation operators for phonons of wave number $\underline{k}$ and $b_{\underline{k}}^{*} b_{\underline{k}}$ is the occupation number of the phonon state.

(c) Electron - Lattice Interaction

If we consider the electron-ion interaction term $\sum_{i,j} v(\underline{r}_i - \underline{R}_j)$, which we wrote in (3.a.1), we may following

the example of Bardeen and Pines[1] expand this term in powers of $(\underline{R}_j - \underline{R}_j^o)$ about the ion equilibrium sites and obtain to first order

$$\sum_{i,j} v(\underline{r}_i - \underline{R}_j) = \sum_{i,j} v(\underline{r}_i - \underline{R}_j^o) - \sum_{i,j}(\underline{R}_j - \underline{R}_j^o)\cdot \nabla_{\underline{R}_j} v(\underline{r}_i - \underline{R}_j^o) \qquad (3.c.1)$$

From (3.b.1) we see that $\underline{R}_j - \underline{R}_j^o = \underline{u}_j$. If we substitute from (3.b.7) into (3.c.1) we have

$$\sum_{i,j} v(\underline{r}_i - \underline{R}_j) = \sum_{i,j} v(\underline{r}_i - \underline{R}_j^o) - (NM)^{-\frac{1}{2}} \sum_{i,j,k} \underline{\mathcal{E}}_k \cdot \nabla_{\underline{R}_j} v(\underline{r}_i - \underline{R}_j^o) q_k e^{i\underline{k}\cdot\underline{R}_j^o} \qquad (3.c.2)$$

In obtaining this expression we have assumed that the electrons interact only with the longitudinal component of the lattice waves. This assumption neglects anisotropic effects and is not really valid particularly for short wave-lengths. The resulting equations, however, are less complex. We shall call the second term of (3.c.2) the electron-phonon interaction Hamiltonian and write

$$H_{int} = -(NM)^{-\frac{1}{2}} \sum_{i,j,k} \underline{\mathcal{E}}_k \cdot \nabla_{\underline{R}_j} v(\underline{r}_i - \underline{R}_j^o) \, q_k \, e^{i\underline{k}\cdot\underline{R}_j^o} \qquad (3.c.3)$$

The valence electrons see a potential $V(\underline{r})$ due to the ions where

$$V(\underline{r}) = \sum_j v(\underline{r} - \underline{R}_j^o) \qquad {}^{(2)} \qquad (3.c.4)$$

(1) Bardeen J. and Pines D., (1955) Phys. Rev., 99, 1140.

(2) This potential is different from that written by Bardeen and Pines. They consider in addition the subtraction of the potential due to a uniform positive charge.

We shall combine $V(\underline{r})$ with the kinetic energy of the valence electrons and write for the electronic part of the Hamiltonian neglecting the electronic coulomb interaction

$$H_{el} = \sum_i \left[\frac{p_i^2}{2m} + V(\underline{r}_i) \right] \qquad (3.c.5)$$

In configuration space, the coulomb interaction between electrons is given as

$$\mathcal{V}(\underline{r}_i - \underline{r}_j) = \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{|\underline{r}_i - \underline{r}_j|} \qquad (3.c.6)$$

We shall require $\mathcal{V}(\underline{r})$ expressed in terms of wave vectors $\underline{k}$. We therefore expand $\mathcal{V}(\underline{r})$ in a Fourier series

$$\mathcal{V}(\underline{r}) = \frac{e^2}{r} = \sum_{\underline{k}'} V_{\underline{k}'} e^{i\underline{k}' \cdot \underline{r}} \qquad (3.c.7)$$

where we have normalized in a box of unit volume. If we multiply this expression through on the left by $\int e^{-i\underline{k} \cdot \underline{r}} \, dr$ we obtain

$$\int \frac{e^2}{r} e^{-i\underline{k} \cdot \underline{r}} \, dr = \sum_{\underline{k}'} V_{\underline{k}'} \int e^{i(\underline{k}' - \underline{k}) \cdot \underline{r}} \, dr$$

$$= \sum_{\underline{k}'} V_{\underline{k}'} \, \delta_{\underline{k}, \underline{k}'}$$

or $\qquad V_{\underline{k}} = \int \frac{e^2}{r} e^{-i\underline{k} \cdot \underline{r}} \, dr \qquad (3.c.8)$

This integral does not converge. In order to evaluate the integral we introduce a convergence factor $e^{-\lambda r}$ into the integral where λ is a positive real constant. This convergence factor effectively screens the coulomb field of each electron so that the range of the field is no longer infinite. We have therefore

$$V_{\underline{k}} = \lim_{\lambda \to 0} e^2 \int_0^{2\pi} \int_{-1}^{1} \int_0^{\infty} d\phi \, d\omega \, r^2 dr \, \frac{e^{-irk\omega - \lambda r}}{r}$$

$$= \lim_{\lambda \to 0} \frac{4\pi e^2}{(-ik)} \left[\frac{ik}{(ik)^2 - \lambda^2} \right] \tag{3.c.9}$$

If we now let λ go to zero we have

$$V_{\underline{k}} = \frac{4\pi e^2}{k^2} \tag{3.c.10}$$

Substituting this into (3.c.7) we have

$$\mathcal{V}(\underline{r}) = \sum_{\underline{k}} \frac{4\pi e}{k^2} \, e^{i\underline{k} \cdot \underline{r}} \tag{3.c.11}$$

If we collect terms from (3.c.5), (3.c.3) and (3.c.11) making use of (3.c.6) we have for the total electronic part of the Hamiltonian

$$H = \sum_{i} \left[\frac{p_i^2}{2m} + V(\underline{r}_i) \right] - (NM)^{-\frac{1}{2}} \sum_{i,j,\underline{k}} \underline{\mathcal{E}}_{\underline{k}} \cdot \nabla_{R_j} v(\underline{r}_i - \underline{R}_j^o) \, q_{\underline{k}} \, e^{i\underline{k} \cdot \underline{R}_j^o}$$

$$+ \frac{1}{2} \sum_{i \neq j, \underline{k}} \frac{4\pi e^2}{k^2} \, e^{i\underline{k} \cdot (\underline{r}_i - \underline{r}_j)} \tag{3.c.12}$$

We wish now to introduce the second quantized formalism in which the electrons are described by occupation numbers.[1] We first introduce field operators $\varphi(\underline{r})$ and $\varphi^*(\underline{r})$ which obey the commutation rules for fermions

$$\left[\varphi^*(\underline{r}), \, \varphi(\underline{r}') \right]_+ = \delta(\underline{r} - \underline{r}')$$

and

$$\left[\varphi(\underline{r}), \, \varphi(\underline{r}') \right]_+ = \left[\varphi^*(\underline{r}), \, \varphi^*(\underline{r}') \right]_+ = 0 \tag{3.c.13}$$

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(1) Fukuda N., (1960): Brandeis University 1960 Institute in Theoretical Physics. (Brandeis, 1960)

The anticommutation relation is based on the fact that fermions require antisymmetric wave vectors for their description. In the second quantized formalism, the Hamiltonian (3.c.12) is written

$$H = \int \varphi^*(\underline{r})\left[\frac{p^2}{2m} + V(\underline{r})\right]\varphi(\underline{r})dr$$

$$-(NM)^{-\frac{1}{2}}\int \varphi^*(\underline{r})\sum_{j,\underline{k}}\mathcal{E}_{\underline{k}}\cdot\nabla_{\underline{R}_j}v(\underline{r} - \underline{R}_j^{\circ})q_{\underline{k}}\,e^{i\underline{k}\cdot\underline{R}_j^{\circ}}\varphi(\underline{r})dr \qquad (3.c.14)$$

$$+\int dr\,dr'\,\varphi^*(\underline{r})\varphi^*(\underline{r}')\sum_{\underline{k}}\frac{2\pi e^2}{k^2}e^{i\underline{k}\cdot(\underline{r} - \underline{r}')}\varphi(\underline{r}')\varphi(\underline{r})$$

$$-\int dr\,\varphi^*(\underline{r})\sum_{\underline{k}}\frac{2\pi e}{k^2}\varphi(\underline{r})$$

We label the terms in the first, second, and third and fourth lines of this expression as H_{el}, H_{int}, and H_{coul} respectively. Since H_{coul} can be written in configuration space as

$$H_{coul} = \frac{1}{2}\sum_{i,j,\underline{k}}\frac{4\pi e^2}{k^2}e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} - \frac{1}{2}\sum_{i,\underline{k}}\frac{4\pi e}{k^2}$$

the second quantized formalism leads to the third and fourth lines of (3.c.14).

We shall choose as a basis for the field operators the complete orthonormal set of Bloch states related to the Hamiltonian (3.c.12). The Bloch functions are a set of one particle functions $\psi_{\underline{k}}(\underline{r})$ for the electrons which apply to a crystal with the ions fixed in equilibrium positions. The Bloch equation for the one particle functions is given as

$$\left[\frac{p^2}{2m} + V(\underline{r})\right] \psi_{\underline{k}}(\underline{r}) = E_{\underline{k}} \psi_{\underline{k}}(\underline{r}) \qquad (3.c.15)$$

where $V(\underline{r})$ is defined in (3.c.4) and $V(\underline{r} + \underline{l}) = V(\underline{r})$ where $\underline{l}$ is any lattice vector. The Bloch theorem states that

$$\psi_{\underline{k}}(\underline{r} + \underline{l}) = e^{i\underline{k}\cdot\underline{l}} \psi_{\underline{k}}(\underline{r}) \qquad (3.c.16)$$

The electrons are described in an extended zone scheme so that the wave vector $\underline{k}$ is not necessarily in the first Brillouin zone. For free electrons the Bloch functions are normalized plane waves. However, for electrons in a periodic lattice

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}} u_{\underline{k}}(\underline{r}) \qquad (3.c.17)$$

where $u_{\underline{k}}(\underline{r})$ is a function having the periodicity of the lattice such that $u_{\underline{k}}(\underline{r} + \underline{l}) = u_{\underline{k}}(\underline{r})$. The functions $\psi_{\underline{k}}(\underline{r})$ are orthogonal in the sense that

$$\int \psi_{\underline{k}}^*(\underline{r}) \psi_{\underline{k}'}(\underline{r}) dr = \delta_{\underline{k},\underline{k}'} \qquad (3.c.18)$$

In these expressions we have assumed the Bloch functions to be normalized in a box of unit volume.

We now expand the field operators $\varphi(\underline{r})$ and $\varphi^*(\underline{r})$ in terms of the complete set of single particle Bloch functions

$$\varphi(\underline{r}) = \sum_{\underline{k}} c_{\underline{k}} \psi_{\underline{k}}(\underline{r})$$

$$\qquad (3.c.19)$$

$$\varphi^*(\underline{r}) = \sum_{\underline{k}} c_{\underline{k}}^* \psi_{\underline{k}}^*(\underline{r})$$

Making use of (3.c.13) and (3.c.18) we find

$$\left[c^*_{\underline{k}}, \ c_{\underline{k}'}\right]_+ = \delta_{\underline{k},\underline{k}'}$$

and

$$(3.c.20)$$

$$\left[c_{\underline{k}}, \ c_{\underline{k}'}\right]_+ = \left[c^*_{\underline{k}}, \ c^*_{\underline{k}'}\right]_+ = 0$$

$c_{\underline{k}}$ and $c^*_{\underline{k}}$ are respectively annihilation and creation operators for electrons in the state $\underline{k}$. The product $c^*_{\underline{k}} c_{\underline{k}}$ is the occupation number of the electronic state $\underline{k}$.

If we make use of (3.c.14) and (3.c.19) we find that

$$H_{el} = \int \sum_{\underline{k},\underline{k}'} c^*_{\underline{k}} \ c_{\underline{k}'} \ \psi_{\underline{k}}^*(\underline{r}) \left[\frac{p^2}{2m} + V(\underline{r})\right] \psi_{\underline{k}'}(\underline{r}) \ dr$$

which with the aid of (3.c.15) and (3.c.18) becomes

$$H_{el} = \sum_{\underline{k}} E_{\underline{k}} \ c^*_{\underline{k}} \ c_{\underline{k}} \qquad (3.c.21)$$

We also have

$$H_{int} = -(NM)^{-\frac{1}{2}} \int \sum_{\underline{k},\underline{k}'} c^*_{\underline{k}'} \ c_{\underline{k}} \ \psi_{\underline{k}}^* \left[\sum_{j,\underline{k}} \mathcal{E}_{\underline{k}} \cdot \nabla_{\underline{R}_j} v(\underline{r} - \underline{R}_j^o) q_{\underline{k}} e^{i\underline{k}\cdot\underline{R}_j^o}\right] \psi_{\underline{k}} \ dr \quad (3.c.22)$$

If we change the origin of the j'th term to $\underline{R}_j^o$ we have, making use of the Bloch theorem (3.c.14), that

$$H_{int} = -(NM)^{-\frac{1}{2}} \int \sum_{\underline{k},\underline{k}'} c^*_{\underline{k}'} \ c_{\underline{k}} \ \psi_{\underline{k}}^* \left[\sum_{\underline{k}} \mathcal{E}_{\underline{k}} \cdot \nabla_{\underline{R}} v(\underline{r}) q_{\underline{k}}\right] \psi_{\underline{k}} \sum_j e^{i(\underline{k} + \underline{k} - \underline{k}')\cdot\underline{R}_j^o} \ dr$$

$$(3.c.23)$$

This last sum vanishes unless

$$\underline{k} + \underline{k} - \underline{k}' = \underline{g} \qquad (3.c.24)$$

where $\underline{g}$ is a vector of the reciprocal lattice including zero. Since we are considering our Bloch functions in the extended zone scheme, $\underline{k}$ assumes all values. We therefore have that

$$H_{int} = \sum_{K,k} c_{K+k}^* \, c_K \, q_k \, v_{k,K}^i$$

where $v_{K,k}^i$ is defined as

$$v_{K,k}^i = -(NM)^{-\frac{1}{2}} \int \psi_{K+k}^* \left\{ \sum_{j,k} \mathcal{E}_k \cdot \nabla_{R_j} v(\underline{r} - \underline{R}_j^o) \, e^{-i\underline{k}\cdot\underline{R}_j^o} \right\} \psi_K \, dr$$

Bardeen and Pines assume this coefficient to be independent of $\underline{k}$. In other words, the electron-phonon interaction is independent of the electronic state. They write therefore

$$H_{int} = \sum_{K,k} c_{K+k}^* \, c_K \, q_k \, v_k^i \tag{3.c.25}$$

where

$$v_k^i = -(NM)^{-\frac{1}{2}} \int \psi_{K+k}^* \left\{ \sum_{j,k} \mathcal{E}_k \cdot \nabla_{R_j} v(\underline{r} - \underline{R}_j^o) \, e^{-i\underline{k}\cdot\underline{R}_j^o} \right\} \psi_K \, dr \tag{3.c.26}$$

With the aid of (3.c.14) and (3.c.19) we obtain the coulomb term

$$H_{coul} = \frac{1}{2} \sum_k \frac{4\pi e^2}{k^2} \int dr\,dr' \sum_{K_1,K_2,K_3,K_4} c_{K_1}^* c_{K_2}^* c_{K_3} c_{K_4} \left\{ \psi_{K_1}^*(\underline{r}) \, e^{i\underline{k}\cdot\underline{r}} \, \psi_{K_4}(\underline{r}) \right.$$
$$\left. \times \, \psi_{K_2}^*(\underline{r}') \, e^{-i\underline{k}\cdot\underline{r}'} \, \psi_{K_3}(\underline{r}') \right\} - \frac{1}{2} \sum_{K,k} \frac{4\pi e^2}{k^2} c_K^* c_K \tag{3.c.27}$$

If we shift the origin of each of these integrals by a lattice vector and again make use of the Bloch theorem as above we obtain

$$H_{coul} = \frac{1}{2} \sum_k \frac{4\pi e^2}{k^2} \int dr\,dr' \sum_{K_1,K_2} c_{K_1}^* c_{K_2}^* c_{K_2+k} c_{K_1-k} \left\{ \psi_{K_1}^*(\underline{r}) e^{i\underline{k}\cdot\underline{r}} \psi_{K_1-k}(\underline{r}) \right.$$
$$\left. \times \, \psi_{K_2}^*(\underline{r}') e^{-i\underline{k}\cdot\underline{r}'} \psi_{K_2+k}(\underline{r}') \right\} - \frac{1}{2} \sum_{K,k} \frac{4\pi e^2}{k^2} C_K^* C_K$$

$$= \frac{1}{2} \sum_{k,K_1,K_2} M_k^2 \, c_{K_1}^* c_{K_2}^* c_{K_2+k} c_{K_1-k} - \frac{1}{2} \sum_{k,K} M_k^2 \, c_K^* c_K \tag{3.c.28}$$

For free electrons $M_{\underline{k}}^{\lambda}$ is equal to $\dfrac{4\pi e^2}{k^2}$ and is the Fourier coefficient for the expansion of the coulomb energy. If we make use of the commutation relation (3.c.20) we have

$$H_{coul} = \tfrac{1}{2} \sum_{\underline{k},\underline{k_1},\underline{k_2}} M_{\underline{k}}^{\lambda}\, c_{\underline{k_2}}^{*}\, c_{\underline{k_2}+\underline{k}}\, c_{\underline{k_1}}^{*}\, c_{\underline{k_1}-\underline{k}} - \sum_{\underline{k},\underline{k}} M_{\underline{k}}^{\lambda}\, c_{\underline{k}}^{*}\, c_{\underline{k}} \qquad (3.c.29)$$

The second term on the right hand side of this expression can be combined with (3.c.21) to give a constant, additive (infinite) term to the Bloch energies $E_{\underline{k}}$.

In configuration space the density of particles is given by $\rho(\underline{r}) = \sum_{i=1}^{N} \delta(\underline{r} - \underline{r}_i)$, where N is the number of particles per unit volume. In the second quantized formalism it can be shown that the density operator is equivalent to $\rho(\underline{r}) = \psi^{*}(\underline{r})\,\psi(\underline{r})$. We define the density fluctuation operator as the Fourier transform of $\rho(\underline{r})$

$$\rho_{\underline{k}} = \int \rho(\underline{r})\, e^{-i\underline{k}\cdot\underline{r}}\, dr \qquad (3.c.30)$$

In the second quantized formalism, making use of (3.c.19) this becomes

$$\rho_{\underline{k}} = \int \sum_{\underline{k},\underline{k}'} c_{\underline{k}'}^{*}\, c_{\underline{k}}\, \psi_{\underline{k}'}^{*}(\underline{r})\, e^{-i\underline{k}\cdot\underline{r}}\, \psi_{\underline{k}}(\underline{r})\, dr \qquad (3.c.31)$$

Employing the same argument used to obtain (3.c.28) we obtain

$$\rho_{\underline{k}} = \sum_{\underline{k}} c_{\underline{k}-\underline{k}}^{*}\, c_{\underline{k}} \int \psi_{\underline{k}-\underline{k}}^{*}(\underline{r})\, e^{-i\underline{k}\cdot\underline{r}}\, \psi_{\underline{k}}(\underline{r})\, dr$$

which for the free electron case becomes

$$\rho_{\underline{k}} = \sum_{\underline{k}} c_{\underline{k}-\underline{k}}^{*}\, c_{\underline{k}} \qquad (3.c.32)$$

The term in $\underline{k} = 0$ corresponds to a uniform background of particles since $\langle \rho_o \rangle = N$, the average particle density for a box of unit volume. We note that $\rho_{-\underline{k}} = \rho_{\underline{k}}^* = \sum_{\underline{k}} c_{\underline{k}}^* c_{\underline{k} - \underline{k}}$. For electrons in a periodic potential, (3.c.32) does not represent the density fluctuation operator. However, we shall employ this notation keeping in mind that $\rho_{\underline{k}}$ is not an actual density fluctuation operator unless we are considering free electrons. Making use of (3.c.32) in (3.c.25) and (3.c.29) we get

$$H_{int} = \sum_{\underline{k}} q_{\underline{k}} v_{\underline{k}}^i \rho_{-\underline{k}} \tag{3.c.33}$$

and

$$H_{coul} = \tfrac{1}{2} \sum_{\underline{k}} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}} \tag{3.c.34}$$

Making use of the expression for $q_{\underline{k}}$ in (3.b.31) we have

$$H_{int} = \sum_{\underline{k}} i \sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}} (b_{\underline{k}} - b_{-\underline{k}}^*) v_{\underline{k}}^i \rho_{-\underline{k}}$$

$$= i \sum_{\underline{k}} \sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}} (v_{\underline{k}}^i b_{\underline{k}} \rho_{\underline{k}}^* - v_{-\underline{k}}^i b_{\underline{k}}^* \rho_{\underline{k}})$$

Since $v_{-\underline{k}}^i = (v_{\underline{k}}^i)^*$ we have

$$H_{int} = i \sum_{\underline{k}} (D_{\underline{k}}^i b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^{i*} b_{\underline{k}}^* \rho_{\underline{k}}) \tag{3.c.35}$$

where the elements $D_{\underline{k}}^i$ are given as

$$D_{\underline{k}}^i = \sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}} v_{\underline{k}}^i \tag{3.c.36}$$

(d) Summary

The final Hamiltonian of the system can be written

as in Bardeen and Pines

$$H = H_1 + H_{tr} + H_{ion\text{-}ion} \tag{3.d.1}$$

where from equations (3.b.27), (3.c.21), (3.c.33) and (3.c.34)

$$H_1 = \tfrac{1}{2}\sum_{k}(p_k^* \, p_k + \Omega_k^2 q_k^* \, q_k) + \sum_{k}E_k c_k^* \, c_k \tag{3.d.2}$$

$$+ \sum_{k} q_k v_k^i \, \rho_{-k} + \tfrac{1}{2}\sum_{k} M_k^2 \, \rho_{-k}\,\rho_k$$

The first term on the right hand side of this expression, or the longitudinal phonon Hamiltonian, was derived by considering only ion-ion interactions. This expression will be renormalized when we deal further with the electrons in interaction with the lattice vibrations. H_{tr} in (3.d.1) represents the transverse lattice vibrations and is uniquely determined from ion-ion interactions since we have assumed that electrons interact only with the longitudinal component. $H_{ion\text{-}ion}$ represents the interaction energy of the ions at their equilibrium sites. In subsequent work we shall be only concerned with H_1. If we write H_1 in terms of phonon creation and annihilation operators we have that

$$H_1 = \sum_{k}E_k c_k^* \, c_k + \sum_{k} h\,\Omega_k (b_k^* \, b_k + \tfrac{1}{2})$$

$$\tag{3.d.3}$$

$$+ i \sum_{k}(D_k^i \, b_k \, \rho_k^* - D_k^* \, b_k^* \, \rho_k) + \tfrac{1}{2}\sum_{k} M_k^2 \, \rho_{-k}\,\rho_k$$

CHAPTER III

RENORMALIZATION OF THE ELECTRON-LATTICE INTERACTION

3.1 Motivation for Renormalization

In Chapter II we derived the phonon Hamiltonian
by considering only ion-ion interactions. We mentioned,
however, that the presence of the valence electrons in the
lattice will affect the ion-ion forces and lead to different
phonon frequencies. The vibrating lattice affects the
electronic states as well, so that the valence electrons
cannot be treated simply as a free electron gas. We now wish
to reorganize our Hamiltonian in such a way that part of the
phonons contribute to the electronic part of the Hamiltonian
and part of the electrons contribute to the phonon Hamiltonian.
Mathematically this can be done by means of a unitary trans-
formation which effectively introduces new lattice variables
in terms of original lattice and electron variables and new
electron variables in terms of original lattice and electron
variables. In this way we can obtain a description of the
system in which the electrons and the ions are to some extent
decoupled from one another and the electron lattice interaction
is as small as possible. If we consider a new phonon variable
b'_k where

$$b'_k = U b_k U^{-1}$$

where U depends on original lattice and electron variables
then b'_k contains contributions from the original electron

variables as well as the original lattice variables.
Similarly, the new electron variables include contributions
from the phonons. If we express the transformed Hamiltonian
in terms of original variables, the requirement that the
electrons and phonons be decoupled will lead to renormalized
phonon frequencies and the electron-phonon interaction will
contribute to an effective electron-electron interaction.
Frohlich[1] first performed a unitary transformation of this
form in which, however, he did not take account of the electron
coulomb interaction. Nakajima[2] introduced a method by means
of which the coulomb interaction could be accounted for as
well. In section 3.2 we shall perform a transformation using
the methods of Frohlich and of Nakajima.

3.2 Frohlich's Canonical Transformation

The starting point of this section is the Hamil-
tonian which was derived in Chapter II, equation (3.d.3)

$$H' = \sum_{k} E_{k} c_{k}^{*} c_{k} + \sum_{k} h \, \Omega_{k} (b_{k}^{*} b_{k} + \tfrac{1}{2})$$

$$\tag{2.1}$$

$$+ i \sum_{k} (D_{k}^{i} b_{k} \rho_{k}^{*} - D_{k}^{i*} b_{k}^{*} \rho_{k}) + \tfrac{1}{2} \sum_{k} M_{k}^{2} \rho_{-k} \rho_{k}$$

We wish to transform this Hamiltonian so that our system will

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(1) Frohlich H. (1952), Proc. Roy. Soc., A, 215, 291.

(2) Nakajima S. Proceedings of the International Conference on
Theoretical Physics, Kyoto and Tokyo, September 1953.

be described by electrons and phonons which are essentially decoupled from one another. If S is an operator satisfying $S* = -S$ then e^S is a unitary operator and we can perform a unitary transformation of the form

$$H = e^{S*} H' e^S = e^{-S} H' e^S \qquad (2.2)$$

H is the transformed Hamiltonian and describes the same system as H'. If we expand the exponentials in power series we have

$$H = (1 - S + \frac{S^2}{2} \ldots)H'(1 + S + \frac{S^2}{2} + \ldots)$$

which on gathering terms becomes

$$H = H' - [S, H'] + \frac{1}{2}[S, [S, H']] + \cdots \qquad (2.3)$$

where the brackets represent the usual commutators.

Frohlich considers a form for S which is relatively simple and well suited for the calculation (2.3) using the form for H' given in (2.1). He considers

$$S = \sum_{\underline{k}} S_{\underline{k}} \text{ where } S_{\underline{k}} = -\gamma_{\underline{k}} b_{\underline{k}} + \gamma_{\underline{k}}* b_{\underline{k}}* = -S_{\underline{k}}* \qquad (2.4)$$

and
$$\gamma_{\underline{k}} = \sum_{\underline{K}} \phi(\underline{K}, \underline{k}) \, c_{\underline{K}}* \, c_{\underline{K}-\underline{k}}$$

$$\gamma_{\underline{k}}* = \sum_{\underline{K}} \phi*(\underline{K}, \underline{k}) \, c_{\underline{K}-\underline{k}}* \, c_{\underline{K}} \qquad (2.5)$$

$\phi(\underline{K}, \underline{k})$ is a c number which is assumed small, of the same order of magnitude as the $D_{\underline{k}}^i$ making S small also, and will be determined in such a way as to approximate the model which was discussed in section 3.1 as closely as possible.

If our transformed Hamiltonian is to give a physically reasonable picture of the metal, the terms in $b_{\underline{k}}^{*} b_{\underline{k}}$ in the phonon variables will describe normal modes. We thus assume that any reasonable transformed wave function which describes the system will give negligible expectation values for other quadratic terms such as $b_{\underline{k}}^{2}$, $b_{\underline{k}} b_{\underline{k'}}$, $b_{\underline{k}}^{*} b_{\underline{k'}}$, etc. where $\underline{k} \neq \underline{k'}$. If we follow this hypothesis then we can neglect terms with $S_{\underline{k}} S_{\underline{k'}}$ if $\underline{k} \neq \underline{k'}$. From (2.3) and (2.4) we have therefore

$$H = H' + \sum_{\underline{k}} \left\{ -\left[S_{\underline{k}}, H' \right] + \tfrac{1}{2} \left[S_{\underline{k}}, \left[S_{\underline{k}}, H' \right] \right] \right\} + \cdot \cdot \cdot \quad (2.6)$$

This calculation can be performed using the Hamiltonian H' as it is written in (2.1). The calculation is more amenable to direct physical interpretation, however, if we modify H' as was done by both Frohlich and Nakajima by introducing renormalized phonon frequencies and new interaction parameters. We write

$$H' = H_{o} + H_{1} + H_{2} \quad (2.7)$$

where H_{o}, H_{1} and H_{2} are respectively zeroth, first and second order quantities. Writing these out explicitly we have

$$H_{o} = \sum_{\underline{k}} E_{\underline{k}} c_{\underline{k}}^{*} c_{\underline{k}} + \sum_{\underline{k}} \hbar \omega_{\underline{k}} b_{\underline{k}}^{*} b_{\underline{k}} + \tfrac{1}{2} \sum_{\underline{k}} \hbar \Omega_{\underline{k}} \quad (2.8)$$

$$H_{1} = \sum_{\underline{k}} H_{1\underline{k}} = i \sum_{\underline{k}} (D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^{*} - D_{\underline{k}}^{*} b_{\underline{k}}^{*} \rho_{\underline{k}})$$

$$+ \tfrac{1}{2} \sum_{\underline{k}} M_{\underline{k}}^{2} \rho_{-\underline{k}} \rho_{\underline{k}} \quad (2.9)$$

$$H_2 = \sum_{k} H_{2k} = i \sum_{k} \left[(D_{k}^{i} - D_{k}) b_{k} \rho_{k}^{*} - (D_{k}^{i*} - D_{k}^{*}) b_{k}^{*} \rho_{k} \right]$$

$$+ \sum_{k} \hbar (\Omega_{k} - \omega_{k}) b_{k}^{*} b_{k} \qquad (2.10)$$

where ω_{k} is the renormalized lattice frequency and D_{k} are new electron-phonon interaction matrix elements. We have assumed here that the renormalization of the phonon energies leads to a second order small quantity. Since D_{k} and D_{k}^{i} are first order small quantities, their difference will be of at least second order.

We shall evaluate (2.6) by collecting terms in order of magnitude and shall neglect terms of order greater than the second. We therefore rewrite (2.6) making use of (2.7)

$$H = H_o + H_1 - \sum_{k} \left[S_{k}, H_o \right]$$

$$+ H_2 - \sum_{k} \left[S_{k}, H_{1k} \right] + \frac{1}{2} \sum_{k} \left[S_{k}, \left[S_{k}, H_o \right] \right] \qquad (2.11)$$

The calculation of the required commutation relations is carried out explicitly in Appendix I. The results are merely stated here. From equation (6) of this appendix we have

$$\left[S_{k}, \sum_{k'} E_{k'} c_{k'}^{*} c_{k'} \right] = \sum_{K} (E_{k} - E_{k-k}) \left\{ b_{k} \phi(\underline{K}, \underline{k}) c_{k}^{*} c_{k-k} + h.c. \right\}$$

where h.c. stands for hermitian conjugate and from equation (8)

$$\left[S_{k}, \sum_{k'} \hbar \omega_{k} b_{k}^{*} b_{k'} \right] = - \sum_{K} \hbar \omega_{k} \left\{ \phi(\underline{K}, \underline{k}) b_{k} c_{k}^{*} c_{k-k} + h.c. \right\}$$

Combining these two expressions we have

$$-\sum_{k}\left[S_{k},H_{o}\right] = \sum_{K,k}(E_{K-k} - E_{K} + \hbar\omega_{k})\left\{\phi(\underline{K},\underline{k})b_{k}c_{K}^{*}c_{K-k} + h.c.\right\} \quad (2.12)$$

From equation (15) of this appendix we obtain

$$\sum_{k}\tfrac{1}{2}\left[S_{k},\left[S_{k},H_{o}\right]\right] = -\sum_{K,k}(E_{K-k} - E_{K} + \hbar\omega_{k})b_{k}^{*}b_{k}\left|\phi(\underline{K},\underline{k})\right|^{2}(n_{K-k} - n_{K})$$

$$+ \tfrac{1}{2}\sum_{K,k}(E_{K-k} - E_{K} + h\omega_{k})\left\{\phi(\underline{K},\underline{k})\rho_{k}^{*}\gamma_{k}^{*} + h.c.\right\} \quad (2.13)$$

where we have written n_{K} for $c_{K}^{*}c_{K}$. From equation (23)

$$-\sum_{k}\left[S_{k},H_{1k}\right] = -\sum_{K,k}(n_{K-k} - n_{K})\left[iD_{k}\phi^{*}(\underline{K},\underline{k}) + h.c.\right]b_{k}^{*}b_{k}$$

$$+ i\sum_{k}\left\{D_{k}\rho_{k}^{*}\gamma_{k}^{*} - D_{k}^{*}\gamma_{k}\rho_{k}\right\}$$

$$- \tfrac{1}{2}\sum_{K,k}M_{k}^{2}(n_{K-k} - n_{K})(b_{k}\phi(\underline{K},\underline{k})\rho_{k}^{*} + h.c.) \quad (2.14)$$

In obtaining this last expression, non-diagonal terms in $\left[S_{k},\rho_{k}\right]$ and $\left[S_{k},\rho_{k}^{*}\right]$ have been neglected. This neglect is equivalent to the random phase approximation which is discussed in more detail in section 3.3. We are in effect neglecting terms in $\sum_{K,K'}c_{K}^{*}c_{K'}$ relative to $\sum_{K}c_{K}^{*}c_{K}$ where $\underline{K}' \neq \underline{K}$. Since $\sum_{K}c_{K}^{*}c_{K}$ is equivalent to ρ_{o}, the average particle density, we are considering only average values in the summation. If we substitute (2.12), (2.13) and (2.14) into (2.11) we can write

$$H = H^{(0)} + H^{(1)} + H^{(2)} \quad (2.15)$$

where $H^{(j)}$ is of order j in small quantities :

$$H^{(0)} = H_{o} \quad (2.16)$$

$$H^{(1)} = H_1 - \sum_{\underline{k}} \left[S_{\underline{k}}, H_0 \right]$$

$$= \sum_{\underline{K},\underline{k}} \left\{ \left[(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi(\underline{K},\underline{k}) + iD_{\underline{k}} \right] b_{\underline{k}} C_{\underline{K}}^* C_{\underline{K}-\underline{k}} + h.c. \right\}$$

$$+ \tfrac{1}{2} \sum_{\underline{k}} M_{\underline{k}}^2 \, \rho_{-\underline{k}} \, \rho_{\underline{k}} \tag{2.17}$$

and

$$H^{(2)} = H_2 - \sum_{\underline{k}} \left[S_{\underline{k}}, H_{1\underline{k}} \right] + \tfrac{1}{2} \sum_{\underline{k}} \left[S_{\underline{k}}, \left[S_{\underline{k}}, H_0 \right] \right]$$

$$= i \sum_{\underline{k}} \left\{ D_{\underline{k}} \rho_{\underline{k}}^* \gamma_{\underline{k}}^* - D_{\underline{k}}^* \gamma_{\underline{k}} \rho_{\underline{k}} \right\}$$

$$+ \tfrac{1}{2} \sum_{\underline{K},\underline{k}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \left\{ \phi(\underline{K},\underline{k}) \rho_{\underline{k}}^* \gamma_{\underline{k}}^* + h.c. \right\}$$

$$+ \sum_{\underline{k}} \left\{ \left[i(D_{\underline{k}}^i - D_{\underline{k}}) - \tfrac{1}{2} M_{\underline{k}}^2 \sum_{\underline{K}} \phi(\underline{K},\underline{k})(n_{\underline{K}-\underline{k}} - n_{\underline{K}}) \right] b_{\underline{k}} \rho_{\underline{k}}^* + h.c. \right\}$$

$$+ \sum_{\underline{k}} b_{\underline{k}}^* b_{\underline{k}} \left\{ \hbar(\Omega_{\underline{k}} - \omega_{\underline{k}}) - \sum_{\underline{K}} \left[(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) |\phi(\underline{K},\underline{k})|^2 \right. \right.$$

$$\left. \left. + i(D_{\underline{k}} \phi^*(\underline{K},\underline{k}) - D_{\underline{k}}^* \phi(\underline{K},\underline{k})) \right] (n_{\underline{K}-\underline{k}} - n_{\underline{K}}) \right\} \tag{2.18}$$

We can obtain a value for $\phi(\underline{K},\underline{k})$ by eliminating terms linear in $b_{\underline{k}}$ in $H^{(1)}$. This eliminates the electron-phonon interaction as completely as possible. We must take into account the possibility of vanishing denominators which would give a divergent series. Therefore following Frohlich (1952) op.cit. we write

$$\phi(\underline{K},\underline{k}) = -\frac{iD_{\underline{k}}(1 - \Delta(\underline{K},\underline{k}))}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}} \tag{2.19}$$

where $\Delta(\underline{K},\underline{k}) \equiv \Delta^2(\underline{K},\underline{k}) = \begin{matrix} 1 \\ 0 \end{matrix}$ if $(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}})^2 \begin{matrix} < \Gamma_{\underline{k}}^2 \\ > \Gamma_{\underline{k}}^2 \end{matrix}$

The function Δ is introduced here to prevent $\phi(\underline{K},\underline{k})$ from becoming infinite. The energy Γ_k is chosen large enough to make the series in $\phi(\underline{K},\underline{k})$ converge. We notice that we are consistent with our former assumption that $\phi(\underline{K},\underline{k})$ be of the same order of magnitude as D_k. We can solve for D_k by eliminating the terms linear in b_k in $H^{(2)}$. We therefore set

$$D_k^i - D_k = -\tfrac{1}{2}M_k^2 \sum_K \phi(\underline{K},\underline{k})(\overline{n}_{K-k} - \overline{n}_K)$$

where we have replaced the operators n_{K-k} and n_K by their expectation values $\overline{n}_{K-k}$ and $\overline{n}_K$. Hence the electron-lattice interaction depends on the electronic state of the system.[1]
With the aid of (2.19) we have

$$D_k^i - D_k = -\tfrac{1}{2}M_k^2 \sum_K \frac{(\overline{n}_{K-k} - \overline{n}_K)D_k(1 - \Delta(\underline{K},\underline{k}))}{E_{K-k} - E_K + \hbar\omega_k}$$

or

$$D_k = \frac{D_k^i}{1 - \frac{2\pi e^2}{k^2}\sum_K \frac{(\overline{n}_{K-k} - \overline{n}_K)(1 - \Delta(\underline{K},\underline{k}))}{E_{K-k} - E_K + \hbar\omega_k}} \tag{2.20}$$

We can solve for ω_k by eliminating terms quadratic in b_k in $H^{(2)}$. We set

$$\hbar(\Omega_k - \omega_k) = \sum_K \left\{(E_{K-k} - E_K + \hbar\omega_k)|\phi(\underline{K},\underline{k})|^2\right.$$

$$\left. + i(D_k\phi^*(\underline{K},\underline{k}) - D_k^*\phi(\underline{K},\underline{k})\right\}(\overline{n}_{K-k} - \overline{n}_K) \tag{2.21}$$

where we have again replaced the quantum mechanical operators

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(1) In Chapter II we had assumed that this matrix element is independent of $\underline{K}$. This assumption is probably still valid if we restrict our calculations to a narrow band of electrons.

$n_{\underline{K}-\underline{k}}$ and $n_{\underline{k}}$ by their expectation values. Making use of (2.19) we have

$$\hbar(\Omega_{\underline{k}} - \omega_{\underline{k}}) = \sum_{\underline{k}} \frac{|D_{\underline{k}}|^2 (1 - \Delta(\underline{K}, \underline{k}))}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}}} (\bar{n}_{\underline{k}} - \bar{n}_{\underline{k}-\underline{k}}) \qquad (2.22)$$

We see that the phonon frequencies will depend on the electronic state of the system since the values $\bar{n}_{\underline{k}}$ and $\bar{n}_{\underline{K}-\underline{k}}$ depend on the state.

If we consider (2.19) we are left with

$$H^{(1)} = i \sum_{\underline{k}} (D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^* b_{\underline{k}}^* \rho_{\underline{k}}) \Delta(\underline{K}, \underline{k})$$
$$+ \tfrac{1}{2} \sum_{\underline{k}} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}} \qquad (2.23)$$

Making use of (2.20) and (2.21) we have

$$H^{(2)} = \sum_{\underline{k},\underline{k}} \left\{ \left[\tfrac{1}{2}(E_{\underline{K}-\underline{k}} = E_{\underline{K}} + \hbar\omega_{\underline{k}}) \phi(\underline{K},\underline{k}) + iD_{\underline{k}} \right] \rho_{\underline{k}}^* \gamma_{\underline{k}}^* + h.c. \right\}$$

which with the aid of (2.19) and (2.5) becomes

$$H^{(2)} = -\tfrac{1}{2} \sum_{\underline{K},\underline{K}',\underline{k}} \frac{|D_{\underline{k}}|^2 (1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} (c_{\underline{K}}^* c_{\underline{K}-\underline{k}} c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} + h.c.) \qquad (2.24)$$

If we substitute (2.24), (2.23) and (2.8) into (2.15) we have for our transformed Hamiltonian to second order

$$H = \sum_{\underline{K}} E_{\underline{K}} c_{\underline{K}}^* c_{\underline{K}} + \sum_{\underline{k}} \hbar\omega_{\underline{k}} b_{\underline{k}}^* b_{\underline{k}} + \sum_{\underline{k}} \tfrac{1}{2}\hbar\Omega_{\underline{k}}$$

$$+ i \sum_{\underline{k}} (D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^* b_{\underline{k}}^* \rho_{\underline{k}}) \Delta(\underline{K},\underline{k}) + \tfrac{1}{2} \sum_{\underline{k}} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}}$$

$$- \tfrac{1}{2} \sum_{\underline{K},\underline{K}',\underline{k}} \frac{|D_{\underline{k}}|^2 (1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} (c_{\underline{K}}^* c_{\underline{K}-\underline{k}} c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} + h.c.) \qquad (2.25)$$

We wish to express H completely in terms of $\omega_{\underline{k}}$ and in this way eliminate the term in $\Omega_{\underline{k}}$, the unrenormalized phonon frequency. If we consider (2.22), this can be rewritten following the example of Frohlich, op. cit. as

$$\hbar(\Omega_{\underline{k}} - \omega_{\underline{k}}) = \sum_{\underline{K},\underline{K}'} \frac{|D_{\underline{k}}|^2 (1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} \left[c_{\underline{K}}^* c_{\underline{K}-\underline{k}}, c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} \right]$$

Since $\Delta^2 = \Delta$ and $\left[c_{\underline{K}}^* c_{\underline{K}-\underline{k}}, c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} \right] = \delta_{\underline{K},\underline{K}'}(n_{\underline{K}} - n_{\underline{K}-\underline{k}})$. We rewrite this in the form

$$-\tfrac{1}{2} \sum_{\underline{k}} \left\{ |D_{\underline{k}}|^2 \sum_{\underline{K},\underline{K}'} \frac{(1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} c_{\underline{K}}^* c_{\underline{K}-\underline{k}} c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} - \hbar(\Omega_{\underline{k}} - \omega_{\underline{k}}) \right\}$$

$$= -\tfrac{1}{2} \sum_{\underline{k}} \left\{ |D_{\underline{k}}|^2 \sum_{\underline{K},\underline{K}'} \frac{(1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} c_{\underline{K}}^* c_{\underline{K}-\underline{k}} \right\}$$

$$= -\tfrac{1}{2} \sum_{\underline{k}} \left\{ |D_{\underline{k}}|^2 \sum_{\underline{K},\underline{K}'} \frac{(1 + \Delta(\underline{K}-\underline{k},-\underline{k}))(1 - \Delta(\underline{K}'-\underline{k},-\underline{k}))}{E_{\underline{K}'} - E_{\underline{K}'-\underline{k}} + \hbar\omega_{\underline{k}}} c_{\underline{K}}^* c_{\underline{K}'-\underline{k}} c_{\underline{K}'-\underline{k}}^* c_{\underline{K}} \right\}$$

$$(2.26)$$

Making use of this relation we can write

$$-\tfrac{1}{2} \sum_{\underline{K},\underline{K}',\underline{k}} \frac{|D_{\underline{k}}|^2 (1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} (c_{\underline{K}}^* c_{\underline{K}-\underline{k}} c_{\underline{K}'-\underline{k}}^* c_{\underline{K}'} + h.c.)$$

$$= -\tfrac{1}{2} \sum_{\underline{k}} \left\{ \hbar(\Omega_{\underline{k}} - \omega_{\underline{k}}) + \sum_{\underline{K},\underline{K}'} \left[\frac{|D_{\underline{k}}|^2 (1 + \Delta(\underline{K},\underline{k}))(1 - \Delta(\underline{K}',\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} \right. \right.$$

$$\left. \left. - |D_{\underline{k}}|^2 \frac{(1 + \Delta(\underline{K}-\underline{k},-\underline{k}))(1 - \Delta(\underline{K}'-\underline{k},-\underline{k}))}{E_{\underline{K}'-\underline{k}} - E_{\underline{K}'} + \hbar\omega_{\underline{k}}} \right] c_{\underline{K}'}^* c_{\underline{K}'-\underline{k}} c_{\underline{K}-\underline{k}}^* c_{\underline{K}} \right\}$$

$$= -\tfrac{1}{2} \sum_{\underline{k}} \left\{ \hbar(\Omega_{\underline{k}} - \omega_{\underline{k}}) - \sum_{\underline{K},\underline{K}'} \frac{2\hbar\omega_{\underline{k}}|D_{\underline{k}}|^2 c_{\underline{K}'}^* c_{\underline{K}'-\underline{k}} c_{\underline{K}-\underline{k}}^* c_{\underline{K}}}{(E_{\underline{K}'-\underline{k}} - E_{\underline{K}'})^2 - (\hbar\omega_{\underline{k}})^2} \right\} \qquad (2.27)$$

If we substitute this expression into (2.25), the transformed Hamiltonian becomes

$$H = \sum_{\underline{k}} E_{\underline{k}} c_{\underline{k}}^* c_{\underline{k}} + \sum_{\underline{k}} \hbar \omega_{\underline{k}} (b_{\underline{k}}^* b_{\underline{k}} + \tfrac{1}{2})$$

$$+ i\sum_{\underline{k}} (D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^* b_{\underline{k}}^* \rho_{\underline{k}}) \Delta(K,\underline{k}) + \tfrac{1}{2} \sum_{\underline{k}} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}}$$

$$+ \sum_{\underline{k},\underline{k}',\underline{k}} \frac{\hbar \omega_{\underline{k}} |D_{\underline{k}}|^2}{(E_{\underline{k}'} - E_{\underline{k}'+\underline{k}})^2 - (\hbar \omega_{\underline{k}})^2} c_{\underline{k}'+\underline{k}}^* c_{\underline{k}'} c_{\underline{k}-\underline{k}}^* c_{\underline{k}} \quad (2.28)$$

The first term in this Hamiltonian refers to the energy of free Bloch particles whose states are described by occupation numbers $c_{\underline{k}}^* c_{\underline{k}}$. The second term describes the phonon energy. The frequency $\omega_{\underline{k}}$ however depends on the electronic state $\underline{K}$ as was shown earlier (equation (2.22)). The third term of (2.28) refers to absorption or emission of vibrational quanta by the electrons and vanishes unless energy is conserved within a range $\Gamma_{\underline{k}}$. The fourth term is the coulomb interaction energy of the electrons and the last term is an effective interaction between electrons due to the lattice vibrations, or phonons. This Hamiltonian has the same form as that derived by Frohlich apart from the electronic coulomb energy term. However, his expressions for $\Omega_{\underline{k}}$ and $D_{\underline{k}}^i$ were supposed to include the effect of screening by the electrons, so that $(\omega_{\underline{k}} - \Omega_{\underline{k}})$ could reasonably be considered second order. Our expressions for unrenormalized phonon frequencies $\Omega_{\underline{k}}$ and interaction parameters $D_{\underline{k}}^i$ do not include electron screening, and the coulomb term in (2.28) does not adequately describe the electrostatic interaction in a many-electron system. This point is discussed in detail in the next section, in which the phonon renormalization is further elucidated. We have treated the electrons as exhibiting only individual particle motion, whereas in fact the electrons in a metal are capable of collective motion as well. This collective motion tends

to screen the coulomb interactions between electrons. This
point is discussed in detail in the next section.

3.3 Plasma Variables for the Electrons

(a) Theoretical Background

It was shown by Bohm and Pines (1952),[1] that a
dense gas of electrons, interacting via coulomb forces,
displays aspects of both collective and individual particle
motion. The analysis was performed classically by
considering the equations of motion of the Fourier
coefficients of the density fluctuation operator. The
collective behaviour is describable in terms of generalized
coordinates which involve all of the electron coordinates.
These coordinates refer to a normal mode of oscillation,
called the "plasma" oscillation. The electron density is
found to oscillate with a frequency

$$\omega_p = \left(\frac{4\pi n e^2}{m} \right)^{\frac{1}{2}} \tag{3.a.1}$$

called the plasma frequency, where n is the total number
of electrons. In their equation of motion, Bohm and
Pines also have a term which is present even in the absence
of interactions and is due to the random thermal motion of
the individual particles. These authors found that the
organized collective behaviour is predominant in phenomena

(1) Bohm D. and Pines D., (1952), Phys. Rev., 85, 338.

connected with distances greater than λ_D where λ_D is the classical Debye length, while for distances less than this length, the individual particle aspects are the most important. Therefore, there is a maximum wave vector $\underline{k}$ above which organized behaviour is not possible and where the individual particle aspect need only be considered.

In a subsequent paper, Bohm and Pines (1953)[1] have given a quantum mechanical description of the behaviour of a dense electron gas based on the long range coulomb interactions of the electrons. They consider the electron Hamiltonian in the form:

$$H' = \sum_i \frac{p_i^2}{2m} + 2\pi e^2 \sum_{\underline{k}, i, j} \frac{e^{i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)}}{k^2} - 2\pi n e^2 \sum_{\underline{k}} \frac{1}{k^2} \quad (3.a.2)$$

where the last term refers to the self-energy of the n electron system. An equivalent Hamiltonian is introduced in terms of the longitudinal vector potential of the electromagnetic field $\underline{A}(\underline{x})$ where $\underline{A}(\underline{x})$ is Fourier analyzed in the form

$$\underline{A}(\underline{x}, t) = (4\pi c^2)^{\frac{1}{2}} \sum_{\underline{k}} Q_{\underline{k}} \, \underline{\mathcal{E}}_{\underline{k}} \, e^{i\underline{k}\cdot\underline{x}} \quad (3.a.3)$$

The electric field intensity is therefore

$$\underline{E}(\underline{x}, t) = - (4\pi)^{\frac{1}{2}} \sum_{\underline{k}} \dot{Q}_{\underline{k}} \, \underline{\mathcal{E}}_{\underline{k}} \, e^{i\underline{k}\cdot\underline{x}}$$

$$= (4\pi)^{\frac{1}{2}} \sum_{\underline{k}} P_{\underline{k}} \, \underline{\mathcal{E}}_{\underline{k}} \, e^{i\underline{k}\cdot\underline{x}} \quad (3.a.4)$$

---

(1) Bohm D. and Pines D., (1953), Phys. Rev., 92, 609.
The argument is repeated here for the sake of completeness.

In terms of these variables, the equivalent Hamiltonian becomes

$$H = \sum_i \frac{p_i^2}{2m} + \frac{e}{m}(4\pi)^{\frac{1}{2}} \sum_{i,k} \underline{\mathcal{E}}_k \cdot (\underline{p}_i - \frac{\hbar k}{2}) Q_k e^{i\underline{k}\cdot\underline{x}_i}$$

$$+ \frac{2\pi e^2}{m} \sum_{i,k,l} \underline{\mathcal{E}}_k \cdot \underline{\mathcal{E}}_l \, Q_k Q_l e^{i(\underline{k} + \underline{l})\cdot\underline{x}_i} - \sum_k \frac{1}{2} P_k P_{-k}$$

$$- 2\pi n e^2 \sum_k \frac{1}{k^2} \tag{3.a.5}$$

This Hamiltonian expresses the correct equation of motion when used in conjunction with a set of subsidiary conditions acting on the wave function of the system

$$\xi_k \psi = 0 \tag{3.a.6}$$

where $$\xi_k = P_{-k} - i(\frac{4\pi e^2}{k^2})^{\frac{1}{2}} \sum_i e^{-i\underline{k}\cdot\underline{x}_i} \tag{3.a.7}$$

ξ_k is proportional to the k'th Fourier component of $\nabla \cdot \underline{E}(\underline{x}) - 4\pi \rho(\underline{x})$ and hence the subsidiary condition insures that Maxwell's equations will be satisfied. Equation (3.a.7) serves to provide a relationship between the Fourier components of the electronic density $\rho_k = \sum_i e^{-i\underline{k}\cdot\underline{x}_i}$ and a set of field variables P_k. In order to decouple the electron variables from the new field quantities, Bohm and Pines relate the field variables to the plasma modes by performing a canonical transformation which relates the P_k to the ρ_k, since for long wavelengths, the density fluctuations are almost entirely collective motion. As a generator for the transformation, the authors use

$$S = -i \sum_{|\underline{k}|<|\underline{k}_c|,\, i} \left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}} Q_{\underline{k}}\, e^{i\underline{k}\cdot\underline{x}_i}$$

$$= -i \sum_{|\underline{k}|<|\underline{k}_c|} \left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}} Q_{\underline{k}}\, \rho_{\underline{k}}^{*} \qquad\qquad (3.a.8)$$

The summation is limited to terms in $|\underline{k}|<|\underline{k}_c|$ since from classical theory these are the only values of $\underline{k}$ for which collective behaviour can occur. Using this generator of a unitary transformation, the transformed Hamiltonian is found to consist of the kinetic energy of the electrons, a simple interaction between the electrons and the collective field, a Hamiltonian appropriate to a set of decoupled harmonic oscillators representing a collective field

$$H_{osc} = -\frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} \left(P_{\underline{k}} P_{-\underline{k}} + \omega_p^2 Q_{\underline{k}} Q_{-\underline{k}}\right) \qquad\qquad (3.a.9)$$

with a frequency ω_p which is just the plasma frequency (3.a.1), and the short range part of the electron coulomb interaction. This method has been extended by Bardeen and Pines[1] to treat the coupled system of moving electrons and ions. The method of Bardeen and Pines is discussed in (b).

(b) The Method of Bardeen and Pines

In their quantum mechanical treatment of the dense electron gas, Bohm and Pines effectively added new degrees of freedom to their original Hamiltonian by introducing a set of new field variables. In order to insure that the energy of

(1) Bardeen J. and Pines D., (1955), Phys. Rev., 99, 1140.

the system was unchanged and that the number of degrees of freedom was kept constant, a set of subsidiary conditions were required to operate on the wave function of the system. The new field variables were related to the collective oscillations of the electron gas by means of a unitary transformation. Following the example of Bardeen and Pines we shall employ this sort of procedure to treat the collective description of coupled electron-ion motion. We hope in this way to obtain the effective coulomb interaction between electrons and account for the effect of electron screening on the electron-phonon interaction and on the phonon frequencies.

We begin with the total Hamiltonian for the metal which we derived in Chapter II, (3.d.2)

$$H_1 = \sum_k E_k c_k^* c_k + \tfrac{1}{2} \sum_k (p_k^* p_k + \Omega_k^2 q_k^* q_k)$$

$$+ \sum_k q_k v_k^i \rho_{-k} + \tfrac{1}{2} \sum_k M_k^2 \rho_{-k} \rho_k \qquad (3.b.1)$$

Following Bohm and Pines, a field energy term is added to this initial Hamiltonian. The new field variables will be related to the normal modes of collective motion of the electrons by means of a canonical transformation. We assume that in the presence of ionic motion there still exists a maximum wave vector $\underline{k}_c$ above which collective motion cannot occur. We have therefore for our new Hamiltonian

$$H = H_1 + \sum_{|\underline{k}| < |\underline{k}_c|} P_k^* P_k \qquad (3.b.2)$$

$P_{\underline{k}}$ are variables as yet undefined which commute with all variables in H_1. We impose a set of subsidiary conditions on the combined system wave function

$$P_{\underline{k}} \Psi \;=\; 0 \quad \text{for} \quad (|\underline{k}| < |\underline{k}_c|) \tag{3.b.3}$$

We now seek a canonical transformation which will transform H to include a set of independent plasma modes. In the case of the free electron gas, the transformation related the field variables to the electron density fluctuations $\rho_{\underline{k}}$. Since we are now considering electrons in interaction with phonons, we are led to believe that a plasma mode will contain both electronic density fluctuations and phonon coordinates. We therefore require a transformation which relates the $P_{\underline{k}}$ to both $\rho_{\underline{k}}$ and the phonon coordinate $q_{\underline{k}}$.

In analogy with the electron gas problem, Bardeen and Pines consider a transformation generated by

$$S \;=\; \sum_{|\underline{k}| < |\underline{k}_c|} (iM_{\underline{k}} \, \rho_{-\underline{k}} + u_{\underline{k}} q_{-\underline{k}}) \, Q_{\underline{k}} \tag{3.b.4}$$

where $Q_{\underline{k}}$ is taken to be a coordinate conjugate to the field momentum $P_{\underline{k}}$ such that

$$\left[P_{\underline{k}} , Q_{\underline{k}'} \right] \;=\; - \, i\hbar \delta_{\underline{k}, \underline{k}'} \tag{3.b.5}$$

$M_{\underline{k}}^2$ occurring in (3.b.1) is just equal to $\dfrac{4\pi e^2}{k^2}$ and $u_{\underline{k}}$ is a real constant which will be determined later in a self consistent manner. If we use the above generator for our transformation, the subsidiary condition (3.b.3) becomes

$$e^{-iS/\hbar} \, P_{\underline{k}} \, e^{iS/\hbar} \, \Psi' = 0 \qquad\qquad |\underline{k}| < |\underline{k}_c| \qquad (3.b.6)$$

where Ψ' is the transformed wave function. On expanding
this in a power series and collecting terms we have

$$\left\{ P_{\underline{k}} + \frac{i}{\hbar}\left[P_{\underline{k}}, S\right] - \frac{1}{2\hbar^2}\left[\left[P_{\underline{k}}, S\right], S\right] + \cdot \cdot \cdot \right\}\Psi' = 0 \qquad |\underline{k}| < |\underline{k}_c|$$

$$(3.b.7)$$

Since $P_{\underline{k}}$ commutes with all variables in H_1, we have

$$\left[P_{\underline{k}}, S\right] = \sum_{|\underline{k}|<|\underline{k}_c|} (iM_{\underline{k}'}\, \rho_{-\underline{k}'} + u_{\underline{k}'} q_{-\underline{k}'})\left[P_{\underline{k}}, Q_{\underline{k}'}\right] \qquad (3.b.8)$$

which with the aid of (3.b.5) becomes

$$\left[P_{\underline{k}}, S\right] = -\, i\hbar(iM_{\underline{k}}\rho_{-\underline{k}} + u_{\underline{k}} q_{\underline{k}}) \qquad (3.b.9)$$

Since $\left[\rho_{-\underline{k}}, S\right] = 0$ and $\left[q_{\underline{k}}, S\right] = 0$, the subsidiary condition
becomes

$$\left[P_{\underline{k}} + iM_{\underline{k}}\rho_{-\underline{k}} + u_{\underline{k}} q_{-\underline{k}}\right]\Psi' = 0 \qquad |\underline{k}| < |\underline{k}_c| \qquad (3.b.10)$$

In analogy with (3.b.7), the transformed Hamiltonian takes
the form

$$H^T = H + \frac{i}{\hbar}\left[H, S\right] - \frac{1}{2\hbar^2}\left[\left[H, S\right], S\right] + \cdots \qquad (3.b.11)$$

The explicit calculations required in (3.b.11) are done in
Appendix II. We merely state the results of these calculations
here. We have for the transformed Hamiltonian, neglecting
higher order terms, as in the Fröhlich transformation using
(3.b.1) and (3.b.2)

$$H^T = \sum_{k} E_k c_k^* c_k + \frac{1}{2} \sum_{|k|<|k_c|} \left[p_k^* p_k + (\Omega_k^2 - u_k^2) q_k^* q_k \right]$$

$$+ \frac{1}{2} \sum_{|k|<|k_c|} \left[P_k^* P_k + u_k^2 Q_k^* Q_k \right]$$

$$+ \frac{1}{2\hbar^2} \sum_{|k,k'|<|k_c|, \, k} M_k M_{k'} Q_k Q_{k'} (E_k - 2E_{k-k} + E_{k-k-k}) \, \rho_{k+k'}^*$$

$$+ \sum_{|k|<|k_c|} (v_k^i - iM_k u_k) q_k \rho_{-k} + \sum_{|k|<|k_c|} u_k p_k Q_k$$

$$- \frac{1}{\hbar} \sum_{|k|<|k_c|, \, k} (E_k - E_{k-k}) M_k Q_k c_k^* c_{k-k}$$

$$+ \frac{1}{2} \sum_{|k|>|k_c|} (p_k^* p_k + \Omega_k^2 q_k^* q_k) + \sum_{|k|>|k_c|} v_k^i q_k \rho_{-k}$$

$$+ \frac{1}{2} \sum_{|k|>|k_c|} M_k^2 \rho_{-k} \rho_k \qquad\qquad (3.b.12)$$

To simplify this expression we wish to make use of the random
phase approximation in the third line of this expression.
We have from Chapter II that $\rho_{k+k'} = \sum_i e^{i(\underline{k} + \underline{k}') \cdot \underline{r}_i}$ The
mean value of this expression is zero except for the case
where $\underline{k} + \underline{k}' = 0$. In this case the value is independent of
$\underline{r}_i$, the particle coordinates and is given by n if we consider
n electrons per unit volume. The mean deviation in this case
is just $\sqrt{n}$ [1] or $\frac{1}{\sqrt{n}}$ times smaller than the mean value itself.
The i in our summation corresponds to Tomanaga's n and our
$\rho_{k+k'}$ to his F. In a metal there are about 10^{12} electrons/cm^3
and hence the mean deviation is negligible relative to the

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(1) A proof of this is given by
    Tomonaga S., (1955), Prog. of Th. Phys., 13, No. 5.

mean value. We are therefore safe in assuming that $\rho_{k+k'} = 0$ unless $\underline{k} = -\underline{k}'$. This is called the random phase approximation. It is based on the fact that for a system of n particles distributed randomly in a unit volume, the random phases $i\underline{\lambda}\cdot\underline{r}_j$ produce a mean value n for ρ_λ. In expressions like (3.b.12) containing other variables $Q_k Q_k$, it is convenient to approximate $\rho^*_{k+k'}$ by its mean value. Making use of this approximation, the term in the third line becomes

$$\frac{n}{\hbar^2} \sum_{|k|<|k_c|} M_k M_k Q_{-k} Q_k (E_k - E_{k-k})$$

(3.b.13)

since we have n electrons per unit volume. If we introduce the effective mass approximation

$$E_k = \frac{\hbar^2 K^2}{2m}$$

(3.b.14)

this reduces to

$$\frac{2\pi e^2 n}{m} \sum_{|k|<|k_c|} Q^*_k Q_k$$

(3.b.15)

which with the aid of (3.a.1) becomes

$$\sum_{|k|<|k_c|} \frac{\omega_p^2}{2} Q^*_k Q_k$$

(3.b.16)

where ω_p is the plasma frequency. We see that the field energy term introduced in (3.b.2) and the introduction of generalized coordinates in (3.b.4) leads to oscillator like terms in collective variables. This formalism is a convenient form for expressing the collective motion. Making use of the effective mass approximation in the fifth line of

(3.b.12), we find that this expression reduces to

$$- \sum_{\substack{|k|<|k_c| \\ K}} M_{\underline{k}} \frac{\hbar}{m} \underline{k} \cdot (\underline{K} - \tfrac{1}{2}\underline{k}) \, c_{\underline{K}}^{*} \, c_{\underline{K}-\underline{k}} \, Q_{\underline{k}} \tag{3.b.17}$$

If we rewrite (3.b.12) making use of (3.b.16) and (3.b.17), the collective Hamiltonian becomes

$$H = \sum_{\underline{K}} E_{\underline{K}} c_{\underline{K}}^{*} c_{\underline{K}} + \tfrac{1}{2} \sum_{|k|<|k_c|} \left[p_{\underline{k}}^{*} p_{\underline{k}} + (\Omega_{\underline{k}}^{2} - u_{\underline{k}}^{2}) q_{\underline{k}}^{*} q_{\underline{k}} \right]$$

$$+ \tfrac{1}{2} \sum_{|k|<|k_c|} \left[P_{\underline{k}}^{*} P_{\underline{k}} + (\omega_p^{2} + u_{\underline{k}}^{2}) Q_{\underline{k}}^{*} Q_{\underline{k}} \right]$$

$$+ \sum_{|k|<|k_c|} (v_{\underline{k}}^{i} - iM_{\underline{k}} u_{\underline{k}}) q_{\underline{k}} P_{-\underline{k}} + \sum_{|k|<|k_c|} u_{\underline{k}} P_{\underline{k}} Q_{\underline{k}}$$

$$- \sum_{\substack{|k|<|k_c| \\ K}} M_{\underline{k}} \frac{\hbar}{m} \underline{k} \cdot (\underline{K} - \tfrac{1}{2}\underline{k}) \, c_{\underline{K}}^{*} \, c_{\underline{K}-\underline{k}} \, Q_{\underline{k}}$$

$$+ \tfrac{1}{2} \sum_{|k|>|k_c|} (p_{\underline{k}}^{*} p_{\underline{k}} + \Omega_{\underline{k}}^{2} q_{\underline{k}}^{*} q_{\underline{k}}) + \sum_{|k|>|k_c|} v_{\underline{k}}^{i} q_{\underline{k}} P_{-\underline{k}}$$

$$+ \tfrac{1}{2} \sum_{|k|>|k_c|} M_{\underline{k}}^{2} P_{-\underline{k}} P_{\underline{k}} \tag{3.b.18}$$

The term in the second line of this expression is a Hamiltonian appropriate to a set of decoupled harmonic oscillators, oscillating with a frequency $\sqrt{\omega_p^{2} + u_{\underline{k}}^{2}}$. This term describes the plasma field in terms of normal modes which is what we desired. The first two terms in the above Hamiltonian contain the one electron Bloch energies and the phonon energy respectively. We note that the phonon frequencies have been renormalized by the introduction of collective electron coordinates. The first term in the third line describes the electron-phonon interaction which likewise

has been modified for long wavelengths by the consideration
of the collective motion of the electrons. The next term is
a weak phonon-plasma interaction which is customarily
neglected. The term in the fourth line is an interaction
between the individual electrons and the plasma. Since there
is a great disparity between the frequencies of the individual
electrons and the frequency of oscillation of the plasma,
this interaction will be small. The remaining terms in the
Hamiltonian describe the short wave phonon field, the short
range electron-phonon interaction, and the short range
coulomb interaction of the electrons. None of these terms
are modified by the consideration of plasma variables. We
note that we no longer have a long range coulomb interaction
between electrons. This is because the collective motion of
the electrons screens out the field of any given electron
within a range given by $\underline{k}_c$. We now wish to transform this
Hamiltonian in order to eliminate the electron-phonon
interaction as completely as possible as was done in 3.2.
We shall also determine $u_{\underline{k}}$ in a self-consistent way. We
shall do this by means of the Frohlich transformation
introduced in section 3(a).

(c) Frohlich's Transformation Reconsidered

In order to treat the electrons and phonons as decoupled from one another as was done in 3.2, we shall perform the Frohlich transformation on our collective Hamiltonian (3.b.18). This will be done by considering separately the long range and short range parts of the Hamiltonian. Since the short range terms are unaffected by the introduction of plasma variables, this part of the Hamiltonian is transformed exactly the same way as in 3.2, except as a generator of the transformation we take $S = \sum_{|k|>|k_c|} S$ instead of (2.4). We need therefore consider only the long range part of the collective Hamiltonian.

From (3.b.18), we write for the long range part of the Hamiltonian

$$
H_{\ell.r.} = \sum_{k} E_{k} c^{*}_{k} c_{k} + \tfrac{1}{2} \sum_{|k|<|k_c|} \left[p^{*}_{k} p_{k} + (\Omega^{2}_{k} - u^{2}_{k}) q^{*}_{k} q_{k} \right]
$$

$$
+ \tfrac{1}{2} \sum_{|k|<|k_c|} \left[P^{*}_{k} P_{k} + (\omega^{2}_{p} + u^{2}_{k}) Q^{*}_{k} Q_{k} \right]
$$

$$
+ \sum_{|k|<|k_c|} (v^{i}_{k} - i M_{k} u_{k}) q_{k} P_{-k} + \sum_{|k|<|k_c|} u_{k} p_{k} Q_{k}
$$

$$
- \sum_{|k|<|k_c|, K} M_{k} \frac{\hbar}{m} k \cdot (K - \tfrac{1}{2}k) c^{*}_{k} c_{k-k} Q_{k} \qquad (3.c.1)
$$

The subsidiary condition acting on the wave function of the system is from (3.b.10)

$$
\left[P_{k} + i M_{k} \rho_{-k} + u_{k} q_{-k} \right] \Psi' = 0 \qquad |k| < |k_c| \qquad (3.c.2)
$$

We now introduce phonon creation and annihilation operators as in Chapter II. From (3.b.31) of that chapter we have

$$q_{\underline{k}} = i\sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}}(b_{\underline{k}} - b^*_{-\underline{k}})$$

and

$$p_{\underline{k}} = \sqrt{\frac{\hbar\Omega_{\underline{k}}}{2}}(b^*_{\underline{k}} + b_{-\underline{k}}) \tag{3.c.3}$$

Making use of this expression we have

$$\frac{1}{2}\sum_{|\underline{k}|<|\underline{k}_c|}\left[p^*_{\underline{k}}\,p_{\underline{k}} + \Omega^2_{\underline{k}}q^*_{\underline{k}}\,q_{\underline{k}}\right] = \sum_{|\underline{k}|<|\underline{k}_c|}\hbar\Omega_{\underline{k}}(b^*_{\underline{k}}\,b_{\underline{k}} + \tfrac{1}{2}) \tag{3.c.4}$$

and

$$-\frac{1}{2}\sum_{|\underline{k}|<|\underline{k}_c|}u^2_{\underline{k}}\,q^*_{\underline{k}}\,q_{\underline{k}} \simeq -\sum_{|\underline{k}|<|\underline{k}_c|}\frac{\hbar}{2\Omega_{\underline{k}}}u^2_{\underline{k}}\,(b^*_{\underline{k}}\,b_{\underline{k}} + \tfrac{1}{2}) \tag{3.c.5}$$

where in the latter expression we have neglected terms in $b_{\underline{k}}b_{-\underline{k}}$ and their hermitian conjugate since we expect that the screening effect will not couple phonon modes and for the actual ground state wave function the expectation value of quantities like these will vanish. We also have

$$\sum_{|\underline{k}|<|\underline{k}_c|}(v^i_{\underline{k}} - iM_{\underline{k}}u_{\underline{k}})q_{\underline{k}}\,\rho_{-\underline{k}} = i\sum_{|\underline{k}|<|\underline{k}_c|}(\eta^i_{\underline{k}}b_{\underline{k}}\,\rho^*_{\underline{k}} - \eta^{i*}_{\underline{k}}b^*_{\underline{k}}\,\rho_{\underline{k}})$$
$$\tag{3.c.6}$$

where we have defined $\eta^i_{\underline{k}}$ to be

$$\eta^i_{\underline{k}} = \sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}}(v^i_{\underline{k}} - iM_{\underline{k}}u_{\underline{k}}) \tag{3.c.7}$$

If we substitute (3.c.4), (3.c.5) and (3.c.6) into (3.c.1), and make use of (3.c.3) we have for the long range Hamiltonian

$$H_{l.h.} = \sum_{\underline{k}} E_{\underline{k}} c_{\underline{k}}^* c_{\underline{k}} + \sum_{|\underline{k}|<|\underline{k}_c|} \hbar \Omega_{\underline{k}} (b_{\underline{k}}^* b_{\underline{k}} + \tfrac{1}{2})$$

$$- \sum_{|\underline{k}|<|\underline{k}_c|} \frac{\hbar}{2\Omega_{\underline{k}}} u_{\underline{k}}^2 (b_{\underline{k}}^* b_{\underline{k}} + \tfrac{1}{2})$$

$$+ i \sum_{|\underline{k}|<|\underline{k}_c|} (\eta_{\underline{k}}^i b_{\underline{k}} \rho_{\underline{k}}^* - \eta_{\underline{k}}^{i*} b_{\underline{k}}^* \rho_{\underline{k}}) + \sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}} \sqrt{\frac{\hbar \Omega_{\underline{k}}}{2}} (b_{\underline{k}}^* + b_{-\underline{k}}) Q_{\underline{k}}$$

$$- \sum_{|\underline{k}|<|\underline{k}_c|, \underline{K}} M_{\underline{k}} \frac{\hbar}{m} \underline{k} \cdot (\underline{K} - \tfrac{1}{2}\underline{k}) \, c_{\underline{k}}^* c_{\underline{K}-\underline{k}} Q_{\underline{k}} \qquad (3.c.8)$$

We now transform this part of the Hamiltonian in the same way we transformed the Hamiltonian in 3.2. However, since there is no coulomb term in (3.c.8), there is no need to introduce new electron-phonon interaction matrix elements into the Hamiltonian. We employ as a generator for the transformation[1]

$$S = \sum_{|\underline{k}|<|\underline{k}_c|} S_{\underline{k}} \qquad \text{where } S_{\underline{k}} = -\gamma_{\underline{k}} b_{\underline{k}} + \gamma_{\underline{k}}^* b_{\underline{k}}^* \qquad (3.c.9)$$

and
$$\gamma_{\underline{k}} = \sum_{\underline{K}} \phi(\underline{K}, \underline{k}) \, c_{\underline{K}}^* c_{\underline{K}-\underline{k}}$$

$$\qquad\qquad\qquad (3.c.10)$$

$$\gamma_{\underline{k}}^* = \sum_{\underline{K}} \phi^*(\underline{K}, \underline{k}) \, c_{\underline{K}-\underline{k}}^* c_{\underline{K}}$$

The transformation of the plasma-phonon interaction term gives

$$\sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}} \sqrt{\frac{\hbar \Omega_{\underline{k}}}{2}} \sum_{\underline{K}} (\phi(\underline{K}, \underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}} + h.c.) Q_{\underline{k}}$$

This term is much smaller than the electron-plasma interaction term since here the coefficient is of at least second order where $u_{\underline{k}}$ is assumed first order small. in small quantities, We therefore neglect this relative to the electron-plasma interaction. We also neglect the

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(1) Again $\phi(\underline{K}, \underline{k})$ is assumed to be a first order small quantity.

transformation of the electron-plasma interaction since this will lead to second order small quantities linear in $b_{\underline{k}}$ which is small relative to the electron-phonon interaction term. As in 3.2 we obtain therefore

$$\phi(\underline{K},\underline{k}) = -\frac{i\eta_{\underline{k}}^i(1 - \Delta(K,k))}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}}} \qquad |\underline{k}| < |\underline{k}_c| \qquad (3.c.11)$$

accurate to first order, and

$$\hbar(\Omega_{\underline{k}} - \frac{u_{\underline{k}}^2}{2\Omega_{\underline{k}}} - \omega_{\underline{k}}) = \sum_{\underline{K}} \frac{|\eta_{\underline{k}}^i|^2(1 - \Delta(K,k))}{E_{\underline{k}-\underline{k}} - E_{\underline{k}} + \hbar\omega_{\underline{k}}}(\bar{n}_{\underline{k}} - \bar{n}_{\underline{k}-\underline{k}})$$
$$(3.c.12)$$

where $\omega_{\underline{k}}$ is the renormalized phonon frequency. Comparing (3.c.12) with (2.22), neglecting $\hbar\omega_{\underline{k}}$ in the denominator on the right hand side in each case, we can see the effect of screening embodied in $u_{\underline{k}}$ in (3.c.12) on the long range phonon frequencies. We again note that the long range phonon frequencies depend also on the electronic state of the system. The transformed long range Hamiltonian (3.c.8) becomes

$$H_{\ell.n.}^T = \sum_{\underline{k}} E_{\underline{k}} c_{\underline{k}}^* c_{\underline{k}} + \sum_{|\underline{k}|<|\underline{k}_c|} \hbar\omega_{\underline{k}} b_{\underline{k}}^* b_{\underline{k}} + \frac{1}{2}\sum_{|\underline{k}|<|\underline{k}_c|} \hbar\omega_{\underline{k}}$$
$$+ i\sum_{|\underline{k}|<|\underline{k}_c|}(\eta_{\underline{k}}^i b_{\underline{k}} \rho_{\underline{k}}^* - \eta_{\underline{k}}^{i*} b_{\underline{k}}^* \rho_{\underline{k}})\Delta(K,\underline{k})$$
$$+ \frac{1}{2}\sum_{|\underline{k}|<|\underline{k}_c|}\left[P_{\underline{k}}^* P_{\underline{k}} + (u_{\underline{k}}^2 + \omega_p^2)Q_{\underline{k}}^* Q_{\underline{k}}\right]$$
$$+ \sum_{\substack{|\underline{k}|<|\underline{k}_c| \\ \underline{K},\underline{K}'}} \frac{\hbar\omega_{\underline{k}}|\eta_{\underline{k}}^i|^2}{(E_{\underline{K}'} - E_{\underline{K}'+\underline{k}})^2 - (\hbar\omega_{\underline{k}})^2} c_{\underline{K}'+\underline{k}}^* c_{\underline{K}'} c_{\underline{K}-\underline{k}}^* c_{\underline{K}}$$
$$+ \sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}}\sqrt{\frac{\hbar\Omega_{\underline{k}}}{2}}(b_{\underline{k}}^* + b_{-\underline{k}})Q_{\underline{k}}$$
$$- \sum_{|\underline{k}|<|\underline{k}_c|,\underline{K}} M_{\underline{k}}\frac{\hbar}{m}\underline{k}\cdot(\underline{K} - \frac{1}{2}\underline{k})c_{\underline{K}}^* c_{\underline{K}-\underline{k}} Q_{\underline{k}} \qquad (3.c.13)$$

We now wish to determine the value of the constant $u_{\underline{k}}$. This is done in a self consistent way by eliminating terms

to the same order of accuracy in the subsidiary condition as in the Hamiltonian. On substituting from (3.c.3) into [1] (3.c.2), the subsidiary condition becomes

$$\left[P_{\underline{k}} + iM_{\underline{k}} \rho_{-\underline{k}} + i\sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}} u_{\underline{k}} (b_{-\underline{k}} - b_{\underline{k}}^{*}) \right] \Psi' = 0 \qquad (3.c.14)$$

for $|\underline{k}| < |\underline{k}_c|$. We now transform the subsidiary condition with the aid of (3.c.9). Considering only diagonal terms in the commutator $\left[S_{\underline{k}}, \rho_{-\underline{k}} \right]$, we have

$$\left[S_{\underline{k}}, \rho_{-\underline{k}} \right] = \sum_{\underline{K}} \phi^{*}(\underline{K}, \underline{k}) b_{\underline{k}}^{*} (n_{\underline{K}-\underline{k}} - n_{\underline{K}}) \qquad (3.c.15)$$

Eliminating terms linear in $b_{\underline{k}}^{*}$ in the transformed subsidiary condition, we have therefore

$$u_{\underline{k}} = - M_{\underline{k}} \sum_{\underline{K}} \frac{\phi^{*}(\underline{K}, \underline{k})(n_{\underline{K}-\underline{k}} - n_{\underline{K}})}{\sqrt{\frac{\hbar}{2\Omega_{\underline{k}}}}}$$

which on making use of (3.c.11) becomes

$$u_{\underline{k}} = -iM_{\underline{k}} \sum_{\underline{K}} \frac{(v_{\underline{k}}^{i} - iM_{\underline{k}} u_{\underline{k}})(1 - \Delta(\underline{K}, \underline{k}))(n_{\underline{K}-\underline{k}} - n_{\underline{K}})}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}}} \qquad (3.c.16)$$

If we neglect all higher order terms in S then from (3.c.16) [1] the subsidiary condition becomes

$$\left[P_{\underline{k}} + iM_{\underline{k}} \rho_{-\underline{k}} \right] \Psi'' = 0 \qquad |\underline{k}| < |\underline{k}_c| \qquad (3.c.17)$$

Finally, we note that the transformed short range Hamiltonian is from (2.27)

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[1] $\Psi'' = e^{S_2}\Psi' = e^{S_2}e^{S_1}\Psi$, where Ψ, Ψ', and Ψ'' occur in (3.b.3), (3.c.14), and (3.c.17), and where S_1, the generator of the Bohm-Pines transformation is given in (3.b.4) and S_2, the generator of the Frohlich transformation is given in (3.c.9).

$$H_{e,h}^T = \sum_{\underline{K}} E_{\underline{K}} c_{\underline{K}}^* c_{\underline{K}} + \sum_{|\underline{k}|>|k_c|} \hbar\omega_{\underline{k}}(b_{\underline{k}}^* b_{\underline{k}} + \tfrac{1}{2})$$

$$+ i \sum_{|\underline{k}|>|k_c|,\underline{K}} (D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^* b_{\underline{k}}^* \rho_{\underline{k}}) \Delta(\underline{K},\underline{k})$$

$$+ \sum_{|\underline{k}|>|k_c|,\underline{K},\underline{K}'} \frac{\hbar\omega_{\underline{k}} |D_{\underline{k}}|^2 c_{\underline{K}'+\underline{k}}^* c_{\underline{K}'} c_{\underline{K}-\underline{k}}^* c_{\underline{K}}}{(E_{\underline{K}'} - E_{\underline{K}'+\underline{k}})^2 - (\hbar\omega_{\underline{k}})^2}$$

$$+ \tfrac{1}{2} \sum_{|\underline{k}|>|k_c|} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}} \qquad\qquad (3.c.18)$$

3.4 The Effective Electron Hamiltonian

Making use of (3.c.13) and (3.c.18), the complete transformed Hamiltonian in terms of plasma variables is

$$H = \sum_{\underline{K}} E_{\underline{K}} c_{\underline{K}}^* c_{\underline{K}} + \sum_{\underline{k}} \hbar\omega_{\underline{k}}(b_{\underline{k}}^* b_{\underline{k}} + \tfrac{1}{2})$$

$$+ i \sum_{|\underline{k}|<|k_c|,\underline{K}} (\eta_{\underline{k}}^i b_{\underline{k}} \rho_{\underline{k}}^* - \eta_{\underline{k}}^{i*} b_{\underline{k}}^* \rho_{\underline{k}}) \Delta(\underline{K},\underline{k})$$

$$+ i \sum_{|\underline{k}|>|k_c|,\underline{K}} (D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^* b_{\underline{k}}^* \rho_{\underline{k}}) \Delta(\underline{K},\underline{k})$$

$$+ \tfrac{1}{2} \sum_{|\underline{k}|<|k_c|} \left[P_{\underline{k}}^* P_{\underline{k}} + (u_{\underline{k}}^2 + \omega_p^2) Q_{\underline{k}}^* Q_{\underline{k}} \right] + \sum_{|\underline{k}|<|k_c|} u_{\underline{k}} \sqrt{\frac{\hbar\Omega_{\underline{k}}}{2}} (b_{\underline{k}}^* + b_{-\underline{k}}) Q_{\underline{k}}$$

$$- \sum_{|\underline{k}|<|k_c|,\underline{K}} M_{\underline{k}} \frac{\hbar}{m} \underline{k}\cdot(\underline{K} - \tfrac{1}{2}\underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}} Q_{\underline{k}}$$

$$+ \sum_{|\underline{k}|<|k_c|,\underline{K},\underline{K}'} \frac{\hbar\omega_{\underline{k}} |\eta_{\underline{k}}^i|^2}{(E_{\underline{K}'} - E_{\underline{K}'+\underline{k}})^2 - (\hbar\omega_{\underline{k}})^2} c_{\underline{K}'+\underline{k}}^* c_{\underline{K}'} c_{\underline{K}-\underline{k}}^* c_{\underline{K}}$$

$$+ \sum_{|\underline{k}|>|k_c|,\underline{K},\underline{K}'} \frac{\hbar\omega_{\underline{k}} |D_{\underline{k}}|^2}{(E_{\underline{K}'} - E_{\underline{K}'+\underline{k}})^2 - (\hbar\omega_{\underline{k}})^2} c_{\underline{K}'+\underline{k}}^* c_{\underline{K}'} c_{\underline{K}-\underline{k}}^* c_{\underline{K}}$$

$$+ \tfrac{1}{2} \sum_{|\underline{k}|>|k_c|} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}} \qquad\qquad (4.1)$$

where we omit the second order electron-plasma term which arises from transformation with S, of the plasma-phonon term in (3.c.8). If we write the purely electronic part of this Hamiltonian, we have

$$H_{el} = \sum_{k} E_{k} c_{k}^{*} c_{k} + \sum_{|k|<|k_c|,k,k'} \frac{\hbar \omega_{k} |\eta_{k}^{i}|^{2}}{(E_{k'} - E_{k'+k})^{2} - (\hbar \omega_{k})^{2}} c_{k'+k}^{*} c_{k'} c_{k-k}^{*} c_{k}$$

$$+ \sum_{|k|>|k_c|,k,k'} \frac{\hbar \omega_{k} |D_{k}|^{2}}{(E_{k'} - E_{k'+k})^{2} - (\hbar \omega_{k})^{2}} c_{k'+k}^{*} c_{k'} c_{k-k}^{*} c_{k} + \frac{1}{2} \sum_{|k|>|k_c|} M_{k}^{2} \rho_{-k} \rho_{k} \qquad (4.2)$$

The second and third terms of this expression represent an effective electron-electron interaction produced by the exchange of virtual phonons. This is the part of the total Hamiltonian for a metal which Bardeen, Cooper and Schrieffer use as a starting point in their theory of superconductivity.[1] In spite of the fact that the phonon frequencies were shown to be dependent on the electronic state of the system, the authors neglect the phonon Hamiltonian in their theory. The assumption here is that the phonon frequencies are not altered appreciably by the transition to the superconducting state so that the frequency change can be accounted for by means of perturbation theory once the electronic wave function for the superconducting state has been obtained. BCS neglect also the plasma part of the Hamiltonian since the plasma energies are very high and will not be significantly excited at low temperatures and hence will play no direct role in superconductivity. The electron-plasma interaction is also

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(1) Bardeen J., Cooper L.N., and Schrieffer J.R., Phys. Rev., (1957), <u>108</u>, 1175.

neglected since this interaction is very weak. The ratio of ion to electron plasma frequencies is of the order $\sqrt{\frac{m}{M}}$ where m is the electron mass and M the ionic mass. We therefore expect these waves of different frequencies to interact weakly and we hence neglect the phonon-plasma term also.[1]

From (3.c.7) we have

$$\left|\eta_{\underline{k}}^{i}\right|^{2} = \frac{\hbar}{2\Omega_{\underline{k}}}\left(\left|v_{\underline{k}}^{i}\right|^{2} + M_{\underline{k}}^{2}\, u_{\underline{k}}^{2}\right) \tag{4.3}$$

Making use of (3.c.16) this becomes

$$\left|\eta_{\underline{k}}^{i}\right|^{2} = \frac{\hbar}{2\Omega_{\underline{k}}}\left(\left|v_{\underline{k}}^{i}\right|^{2} + \frac{M_{\underline{k}}^{4}}{\hbar}\frac{1}{2\Omega_{\underline{k}}}\left|\eta_{\underline{k}}^{i}\right|^{2}\left[\sum_{\underline{K}}\frac{(1 - \Delta(\underline{K},\underline{k}))(n_{\underline{K}-\underline{k}} - n_{\underline{K}})}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}}}\right]^{2}\right)$$

or

$$\left|\eta_{\underline{k}}^{i}\right|^{2} = \frac{\frac{\hbar}{2\Omega_{\underline{k}}}\left|v_{\underline{k}}^{i}\right|^{2}}{1 - M_{\underline{k}}^{4}\left[\sum_{\underline{K}}\frac{(1 - \Delta(\underline{K},\underline{k}))(n_{\underline{K}-\underline{k}} - n_{\underline{K}})}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}}}\right]^{2}} \tag{4.4}$$

From (2.20) with the aid of (3.c.36) from Chapter II we have

$$\left|D_{\underline{k}}\right|^{2} = \frac{\frac{\hbar}{2\Omega_{\underline{k}}}\left|v_{\underline{k}}^{i}\right|^{2}}{1 - M_{\underline{k}}^{2}\left[\sum_{\underline{K}}\frac{(n_{\underline{K}-\underline{k}} - n_{\underline{K}})(1 - \Delta(\underline{K},\underline{k}))}{E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}}}\right]} \tag{4.5}$$

BCS replace $\left|\eta_{\underline{k}}^{i}\right|^{2}$ in (4.2) by $\left|D_{\underline{k}}\right|^{2}$, assuming that for small values of $\underline{k}$, the difference is not too great. Making use of this approximation, they write for the effective electron Hamiltonian of the system

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(1) See Note at end of Chapter.

$$H_{\mathscr{el.}} = \sum_{\underline{k}} E_{\underline{k}} \ c_{\underline{k}}^{*} \ c_{\underline{k}}$$

$$+ \sum_{\underline{k},\underline{k}',\underline{k}'} \frac{\hbar \omega_{\underline{k}} \ |D_{\underline{k}}|^2}{(E_{\underline{k}'} - E_{\underline{k}'+\underline{k}})^2 - (\hbar \omega_{\underline{k}})^2} \ c_{\underline{k}'+\underline{k}}^{*} \ c_{\underline{k}'} c_{\underline{k}-\underline{k}}^{*} \ c_{\underline{k}}$$

$$+ \tfrac{1}{2} \sum_{|\underline{k}|>|\underline{k}_c|} M_{\underline{k}}^2 \ \rho_{-\underline{k}} \ \rho_{\underline{k}} \qquad\qquad (4.6)$$

This Hamiltonian can be shown to commute with the total

number operator $N = \sum_{\underline{k}} c_{\underline{k}}^{*} \ c_{\underline{k}}$ and hence the total number of

particles is conserved. The total number of electrons in the

system and the energy will thus be simultaneous eigenvalues

of the wave function describing this system. However, $H_{\mathscr{el}}$
in (4.6) is not gauge invariant, and thus cannot be easily
used to describe electromagnetic properties.

Note:

We wish to make an estimate of the coupling between

the electrons and the plasma. From (4.1) the interaction

coefficient is given by

$$M_{\underline{k}} \ \frac{\hbar}{m} \ \underline{k} \cdot (\underline{K} - \tfrac{1}{2}\underline{k})$$

We replace the vectors by their absolute values and since

$M_{\underline{k}}^{\mathscr{a}} = \frac{4\pi e^2}{k^2}$ obtain

$$(4\pi e^2)^{\tfrac{1}{2}} \ \frac{\hbar}{m} \ (K - \tfrac{1}{2}k)$$

In order to obtain a most liberal estimate of this coupling,

we let $k = 0$ and replace K by K_F where K_F is the value of K

at the Fermi surface. We have that $K_F = (3\pi^2 n)^{1/3}$ where n is

the electron density. The coupling constant is therefore

given by

$$\frac{eh}{\pi^{1/2}m} (3n)^{1/3} \pi^{-2/3}$$

which approximately equals 4×10^{-5}. We see therefore that the interaction is very weak.

If we consider the bare phonon frequency, since the b's refer to unrenormalized phonons, we treat the ions as a plasma and obtain

$$\Omega_{\underline{k}}^2 = \frac{4 \pi N z^2 e^2}{M}$$

where N is the number of ions per unit volume and z is the valence. From (3.a.1)

$$\omega_p^2 = \frac{4 \pi n e^2}{m}$$

where $n = zN$. The ratio $\frac{\omega_p^2}{\Omega_{\underline{k}}^2}$ is therefore given by $\frac{M}{zm}$.
Therefore the ratio of ionic to plasma frequencies is of the order of $\sqrt{\frac{m}{M}}$ as was stated above.

CHAPTER IV

THE BCS THEORY OF SUPERCONDUCTIVITY

4.1 Introduction

In 1957, Bardeen, Cooper and Schrieffer[1] pre-
sented a theory of superconductivity based on electronic
pair correlations which was able to account for nearly all
of the experimental phenomena which a superconductor exhibits.
The theory is based on the effective interaction between
electrons due to the exchange of virtual phonons which we
derived in Chapter III. As was mentioned in the last chapter,
these authors do not take account of the phonon part of the
total Hamiltonian of the metal in the formulation of their
theory. Since the phonons are assumed to be effectively
decoupled from the electrons as a result of the Frohlich
transformation, they should not affect a theory based on the
electrons. However, we did show that the phonon frequencies
are dependent on the electronic state and hence the phonon
frequencies will be changed upon the transition of the metal
to the superconducting state. BCS assume that this change
can be accounted for by means of perturbation theory once the
electronic state function has been obtained. The plasma part
of the total Hamiltonian is also neglected since, as we have
shown, the plasma frequencies are too high to be easily
excitable and hence the plasma modes will not be expected to

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(1) J. Bardeen, L.N. Cooper and J.R. Schrieffer, Phys. Rev.,
108, 1175, (1957).

have much effect on the transition to the superconducting state.

In this chapter we are going to illustrate how the BCS reduced Hamiltonian is obtained from the effective electron Hamiltonian which was derived in Chapter III. BCS choose a simple trial wave function to describe the superconducting state in terms of their reduced Hamiltonian. We shall merely indicate the form of the wave function chosen but we shall not perform any explicit calculations.

4.2 The Reduced BCS Hamiltonian

From Chapter III, equation (4.6) we have the simplified effective electron Hamiltonian for a metal

$$H = \sum_{\underline{k}} E_{\underline{k}} n_{\underline{k}} + H_{coul} + \sum_{\underline{k},\underline{k}',\underline{k}} \frac{\hbar \omega_{\underline{k}} |D_{\underline{k}}|^2}{(E_{\underline{k}'} - E_{\underline{k}'+\underline{k}})^2 - (\hbar \omega_{\underline{k}})^2} c^*_{\underline{k}'+\underline{k}} c_{\underline{k}'} c^*_{\underline{k}'-\underline{k}} c_{\underline{k}} \tag{2.1}$$

BCS have neglected the effect of the screening by the plasma oscillations on the "phonon" interaction. We call the last term of (2.1) the phonon interaction since it arises due to exchange of virtual phonons between electrons. As we saw in Chapter III, BCS replace $\left|\eta^i_{\underline{k}}\right|^2$ (equation (4.4)) by $\left|D_{\underline{k}}\right|^2$ (equation (4.5)) in the effective electron Hamiltonian for long wavelengths. The Hamiltonian (2.1) can be written

$$H = H_o + H_I \tag{2.2}$$

where H_I is the sum of the last two terms of (2.1) and can be written as

$$H_1 = -\sum_{\underline{k},\underline{k}',\underline{k}} V_{\underline{k}',\underline{k}} \; c^*_{\underline{k}'+\underline{k}} \; c_{\underline{k}'} \; c^*_{\underline{k}-\underline{k}} \; c_{\underline{k}} \tag{2.3}$$

since $H_{coul} = \frac{1}{2} \sum_{|\underline{k}|>|k_d|} M^2_{\underline{k}} \; \rho_{-\underline{k}} \; \rho_{\underline{k}}$ and $\rho_{-\underline{k}} \; \rho_{\underline{k}} = \sum_{\underline{k}',\underline{k}} c^*_{\underline{k}'+\underline{k}} \; c_{\underline{k}'} \; c^*_{\underline{k}-\underline{k}} \; c_{\underline{k}}.$

where $V_{\underline{k}',\underline{k}} = -\left[\dfrac{\hbar\omega_{\underline{k}} \; |D_{\underline{k}}|^2}{(E_{\underline{k}'} - E_{\underline{k}'+\underline{k}})^2 - (\hbar\omega_{\underline{k}})^2} + \frac{1}{2} M^2_{\underline{k}} \right] \Theta(k-k_c)$

where $k = |\underline{k}|$, and $\Theta(x) = \begin{matrix} 0 \text{ for } & x<0 \\ 1 & x>0 \end{matrix}$

If we consider the self energy terms of H_1, these are

$$\sum_{\underline{k},\underline{k}'} V_{\underline{k}',0} \; c^*_{\underline{k}'} \; c_{\underline{k}'} \; c^*_{\underline{k}} \; c_{\underline{k}} = \sum_{\underline{k},\underline{k}'} V_{\underline{k}',0} \; n_{\underline{k}'} \; n_{\underline{k}} = \sum_{\underline{k}'} V_{\underline{k}',0} \; n_{\underline{k}'} \; N_{op} \tag{2.5}$$

These terms can be absorbed into the Bloch energies and lead to a renormalization of the Bloch energies of the electrons. Since from (2.4) $V_{\underline{k}',0}$ is a constant we can write

$$H = \sum_{\underline{k}} E'_{\underline{k}} \; n_{\underline{k}} + H_{coul} + \sum_{\substack{\underline{k},\underline{k}' \\ \underline{k}\neq 0}} \frac{\hbar\omega_{\underline{k}} \; |D_{\underline{k}}|^2}{(E_{\underline{k}'} - E_{\underline{k}'+\underline{k}}) - (\hbar\omega_{\underline{k}})^2} \; c^*_{\underline{k}'+\underline{k}} \; c_{\underline{k}'} \; c^*_{\underline{k}-\underline{k}} \; c_{\underline{k}} \tag{2.6}$$

where

$$E'_{\underline{k}} = E_{\underline{k}} - N \; V_{\underline{k}',0} \tag{2.7}$$

since $\sum_{\underline{k}'} n_{\underline{k}'} = N$, the total number of particles. The theory of Bardeen, Cooper and Schrieffer is based only on the off diagonal terms of the above interaction; the terms in the ''phonon'' interaction for which $\underline{k} \neq 0$. This is because the self energy terms lead to too large a difference between the normal and superconducting state energies. They assume that the self energy is essentially the same in the two states. We not let $\mathcal{E}_{\underline{k}} = E'_{\underline{k}} - \zeta$ where ζ is the Fermi energy $\zeta = \frac{\hbar^2 K_F^2}{2m}$. We also introduce spin indices into the Hamiltonian (2.6) since

these are necessary for further development. Spin indices could have been carried through all the previous development but would have made no difference to the present result. We write therefore for the Hamiltonian apart from a constant energy term with σ denoting spin

$$H = \sum_{|\underline{k}| > K_F} \mathcal{E}_{\underline{k}} \, n_{\underline{k},\sigma} + \sum_{|\underline{k}| < K_F} |\mathcal{E}_{\underline{k}}| \, (1 - n_{\underline{k},\sigma}) + H_{coul}$$

$$+ \sum_{\substack{\underline{k},\underline{k}',\underline{k} \\ \sigma,\sigma'}} \frac{\hbar \omega_{\underline{k}} |D_{\underline{k}}|^2}{(\mathcal{E}_{\underline{k}'} - \mathcal{E}_{\underline{k}'+\underline{k}})^2 - (\hbar \omega_{\underline{k}})^2} \, c^*_{\underline{k}'+\underline{k},\sigma} c_{\underline{k}',\sigma} \, c^*_{\underline{k}-\underline{k},\sigma'} c_{\underline{k},\sigma'} \quad (2.8)$$

Since $NV_{\underline{k}',0}$ is a constant we have that $E_{\underline{k}'} - E_{\underline{k}'+\underline{k}}$ is equal to $E_{\underline{k}'} - E_{\underline{k}'+\underline{k}}$ and hence we can replace $E_{\underline{k}'} - E_{\underline{k}'+\underline{k}}$ by $\mathcal{E}_{\underline{k}'} - \mathcal{E}_{\underline{k}'+\underline{k}}$ in the denominator of the last term. In the second term of (2.8) we have $\sum_{|\underline{k}| < K_F} |\mathcal{E}_{\underline{k}}| (1 - n_{\underline{k},\sigma})$ since $c_{\underline{k},\sigma} \, c^*_{\underline{k},\sigma}$ is the occupation number of a hole below the Fermi surface with momentum $-\underline{K}$. [1]

The last term in the Hamiltonian (2.8) is called the "phonon" interaction as mentioned previously since it arises from virtual exchange of phonons between electrons. This "phonon" interaction will be attractive when the energy difference $\Delta \mathcal{E}$ between the electronic states involved is less than the phonon energy $\hbar \omega$; when $|\mathcal{E}_{\underline{k}} - \mathcal{E}_{\underline{k}+\underline{k}}| < \hbar \omega_{\underline{k}}$. BCS take as their criterion for the occurence of supercon- ductivity the condition that this attractive "phonon" inter- action dominate the repulsive coulomb interaction for those

(1) Fukuda N., (1960): Brandeis University 1960 Institute in Theoretical Physics. (Brandeis, 1960)

matrix elements which are of importance in the superconducting wave function. This criterion can therefore be expressed as

$$-V \equiv \left\langle \frac{-2|D_k|^2}{\hbar \omega_k} + \frac{4\pi e^2}{k^2} \right\rangle_{AV} < 0 \qquad (2.9)$$

In order to describe the ground state of a superconductor, we require a low energy state. Cooper[1] considered the problem of a pair of electrons interacting above a quiescent Fermi sphere through negative matrix elements. He found that the pair of electrons was able to form a quasi-bound state; the lowest energy eigenvalue of the system was separated from the continuum by a volume (i.e. number) independent binding energy. If the matrix elements of our interaction were negative in sign, we could therefore form a low energy state by forming a linear combination of basis functions with expansion coefficients of the same sign. The interaction energy would then be given by the number of configurations connected to some given configuration times an average matrix element.

However, for a general configuration of Fermi-Dirac particles, the sign of the matrix elements depends on the occupation of the states which are unaffected by the interaction.[2] In the interaction, we are considering a pair of

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(1) L.N. Cooper, Phys. Rev., 104, 1189, (1956).

(2) This argument is implied by BCS in their paper but not actually presented.

particles taken from the state $(\underline{K}_1, \underline{K}_2)$ to the state $(\underline{K}_1', \underline{K}_2')$ by means of the operator

$$c*(\underline{K}_2') \ c(\underline{K}_2) \ c*(\underline{K}_1') \ c(\underline{K}_1) \tag{2.10}$$

We require that a system of Fermi-Dirac particles be described by an antisymmetric wave function. This means that the sign of the state function changes for each interchange of particle coordinates or momenta. Therefore the sign of a relative matrix element connecting two states by means of (2.10) apart from the coefficient is given by $(-1)^{N+N'}$ where N and N' are the total number of occupied states between $\underline{K}_1$ and $\underline{K}_2$ in the initial state and $\underline{K}_1'$ and $\underline{K}_2'$ in the final state respectively. In general, N+N' is equally likely to be even or odd, so that matrix elements will alternate in sign and we cannot therefore obtain a coherent low energy state. In order to form such a low energy state, we require a subset of configurations between which matrix elements are predominantly negative. This can be done by associating the electrons in pairs, such that if any member of a pair is occupied, the other is also. N and N' will therefore always be even as will N+N' and hence the matrix element is always negative since from (2.9) we are considering a negative coefficient. Since the interaction conserves momentum

$$\underline{K}_1 + \underline{K}_2 = \underline{K}_1' + \underline{K}_2' \tag{2.11}$$

there will be a maximum number of pair-wise interactions

and therefore the largest interaction energy if the total momentum of all the pairs is the same. In considering the interaction of Fermi-Dirac particles, there is a further interaction, which occurs only between particles of parallel spin, called the exchange energy, which tends to weaken the total energy of interaction. Since we desire as large an interaction as possible, we consider pairs in which the electrons have opposite spin. For describing the ground state, we consider pairs whose total momentum is zero,

$$\underline{K}_1 + \underline{K}_2 = \underline{K} = 0 \tag{2.12}$$

We shall now consider the reduced problem in which we think about configurations in which the electron states are occupied in pairs such that if $\underline{k}, \sigma$ is occupied, $-\underline{k}, -\sigma$ is occupied. We define, therefore, annihilation and creation operators for pairs as follows:

$$d_{\underline{k}} = c_{-\underline{k}\downarrow} c_{\underline{k}\uparrow}$$

$$d_{\underline{k}}^* = c_{\underline{k}\uparrow}^* c_{-\underline{k}\downarrow}^* \tag{2.13}$$

If we make use of the commutation rules for the c's from Chapter II, equation (3.c.20)

$$\left[c_{\underline{k},\sigma} , c_{\underline{k}',\sigma'}^* \right]_+ = \delta_{\underline{k},\underline{k}'} \delta_{\sigma,\sigma'}$$

$$\left[c_{\underline{k},\sigma} , c_{\underline{k}',\sigma'} \right]_+ = \left[c_{\underline{k},\sigma}^* , c_{\underline{k}',\sigma'}^* \right]_+ = 0 \tag{2.14}$$

we can show the following relations for the $d_{\underline{k}}$:

$$\left[d_{\underline{k}}, d_{\underline{k}'}^{*} \right]_{-} = (1 - n_{\underline{k}\uparrow} - n_{-\underline{k}\downarrow}) \delta_{\underline{k},\underline{k}'}$$

$$\left[d_{\underline{k}}, d_{\underline{k}'} \right]_{-} = 0$$

$$\left[d_{\underline{k}}, d_{\underline{k}'} \right]_{+} = 2 d_{\underline{k}} d_{\underline{k}'} (1 - \delta_{\underline{k},\underline{k}'}) \qquad (2.15)$$

From the second of these relations and from algebraic consid-
erations it would appear that the third relation should be
$\left[d_{\underline{k}}, d_{\underline{k}'} \right]_{+} = 2 d_{\underline{k}} d_{\underline{k}'}$. However, consideration of the commutation
relations for the c's shows that the above is the correct
expression. The second of these relations is a relation
satisfied by bosons. The other two relations are not, however.
Therefore, the superconducting transition is not a Bose-
Einstein condensation, with the ground state containing $\frac{N}{2}$
Bose-like electron pairs (each with spin zero) all in the same
zero-momentum state as had been conjectured by Schafroth.[1]
Schafroth's contribution of focussing attention on the pair
correlations, as the basic mechanism in superconductivity was
one of the major steps toward the present theory although it
is rarely acknowledged.

We can write our electron Hamiltonian (2.8) as

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(1) Schafroth, M.R., Phys. Rev., 96, 1442, (1954).

$$H = \sum_{|\underline{k}|>K_F} \mathcal{E}_{\underline{k}} \, n_{\underline{k},\sigma} + \sum_{|\underline{k}|<K_F} |\mathcal{E}_{\underline{k}}| \; (1 - n_{\underline{k},\sigma})$$

$$- \sum_{\underline{k},\underline{k}',\underline{k},\sigma,\sigma'} V_{\underline{k},\underline{k}'} \, c^{*}_{\underline{k}'+\underline{k},\sigma} c_{\underline{k}',\sigma} c^{*}_{\underline{k}-\underline{k},\sigma'} c_{\underline{k},\sigma'} \tag{2.16}$$

where $V_{\underline{k},\underline{k}'}$ is defined in equation (2.4). Since we wish to
consider only pair configurations in which the members of the
pair have opposite spin and momentum, the operators $n_{\underline{k},\sigma}$ and
$d^{*}_{\underline{k}} d_{\underline{k}}$ will have the same expectation value, for any wave
function which adequately describes the system. We can there-
fore rewrite the first two terms of (2.16) in terms of pair
operators as

$$2 \sum_{|\underline{k}|>K_F} \mathcal{E}_{\underline{k}} d^{*}_{\underline{k}} d_{\underline{k}} + 2 \sum_{|\underline{k}|<K_F} |\mathcal{E}_{\underline{k}}| \, d_{\underline{k}} d^{*}_{\underline{k}} \tag{2.17}$$

The factor of 2 enters since for each value of $\underline{K}$ there are
two electrons, each of energy $\mathcal{E}_{\underline{k}}$, forming the pair. The
interaction term can be written

$$V_{\underline{k},\underline{k}'} c^{*}_{\underline{k}'+\underline{k},\sigma} \left(\delta_{\underline{k}',\underline{k}-\underline{k},\sigma'} - c^{*}_{\underline{k}-\underline{k},\sigma'} c_{\underline{k}',\sigma} \right) c_{\underline{k},\sigma'}$$

$$= V_{\underline{k},\underline{k}'} c^{*}_{\underline{k}'+\underline{k},\sigma} c_{\underline{k}'+\underline{k},\sigma}$$

$$+ V_{\underline{k},\underline{k}'} c^{*}_{\underline{k}'+\underline{k},\sigma} c^{*}_{\underline{k}-\underline{k},\sigma'} c_{\underline{k},\sigma'} c_{\underline{k}',\sigma} \tag{2.18}$$

The first term on the right hand side cannot be expressed in
terms of pairs and so we neglect it in our reduced Hamiltonian.
If we consider only pairs whose total momentum is zero, we
can write for the last term

$$V_{\underline{k}'',\underline{k}'} \, d^{*}_{\underline{k}''} d_{\underline{k}'} \tag{2.19}$$

where we have substituted $\underline{K}''$ for $\underline{K}' + \underline{k}$. BCS assume that the terms containing pairs whose total momentum is not zero and which are neglected in reduced Hamiltonian will not contribute to the ground state appreciably and can be treated by perturbation theory. Making use of (2.17) and (2.19) we write for the reduced Hamiltonian

$$H_{red} = 2 \sum_{|\underline{k}| > K_F} \mathcal{E}_{\underline{k}} \, d^{*}_{\underline{k}} \, d_{\underline{k}} + 2 \sum_{|\underline{k}| < K_F} |\mathcal{E}_{\underline{k}}| \, d_{\underline{k}} d^{*}_{\underline{k}}$$

$$- \sum_{\underline{k},\underline{k}'} V_{\underline{k},\underline{k}'} \, d^{*}_{\underline{k}} \, d_{\underline{k}'} \qquad\qquad (2.20)$$

It is this part of the total interaction that BCS consider to be the most important in describing the properties of superconductors. The reduced Hamiltonian (2.20) is found to commute with the total number operator $N = \sum_{\underline{k},\sigma} c^{*}_{\underline{k},\sigma} c_{\underline{k},\sigma}$, and hence a wave function can be found to describe the system such that the energy and the total number of particles are simultaneous eigenvalues of the wave function.

The most general wave function of the system which we are considering is

$$\Psi = \sum_{\underline{k}_1, \cdots \underline{k}_N} A(\underline{K}_1, \underline{K}_2, \cdots \underline{K}_{\frac{N}{2}}) \, d^{*}_{\underline{k}_1} \, d^{*}_{\underline{k}_2} \cdots d^{*}_{\underline{k}_{\frac{N}{2}}} \, |0\rangle$$

$$\qquad\qquad (2.21)$$

where the summation extends over all distinct pair configurations. BCS relax the requirement that the total number of electrons be an eigenvalue of the wave function and construct a wave function by making a Hartree-like approximation.

This means that the probability of finding two pair states occupied in the ground state of the many electron system is equal to the product of the probabilities of finding each pair state occupied. The wave function having this property which BCS write is

$$\Psi_0 = \prod_{\underline{k}} (\alpha_{\underline{k}} + \beta_{\underline{k}} d_{\underline{k}}^* \mid 0 \rangle \qquad (2.22)$$

with $\alpha_{\underline{k}}$ and $\beta_{\underline{k}}$ real and $\alpha_{\underline{k}}^2 + \beta_{\underline{k}}^2 = 1$ for all $\underline{K}$. $\beta_{\underline{k}}^2$ is the probability that the pair state is occupied and $\alpha_{\underline{k}}^2$ is the probability that it is not occupied. BCS calculate the ground state energy variationally using this wave function and the reduced Hamiltonian (2.20) subject to the constraint that the total number of particles be conserved

$$\left\langle \Psi_0 \middle| \sum_{\underline{k},\sigma} c_{\underline{k},\sigma}^* c_{\underline{k},\sigma} \middle| \Psi_0 \right\rangle = N \qquad (2.23)$$

In order to treat excited states, BCS decompose the total state into states in which they consider single particle excitations and states in which they consider excited pairs. They write a wave function in the form

$$\Psi_{exc} = \prod_{\underline{k}(G)} (\alpha_{\underline{k}} + \beta_{\underline{k}} d_{\underline{k}}^*) \prod_{\underline{k}'(P)} (\alpha_{\underline{k}'} d_{\underline{k}'}^* - \beta_{\underline{k}'}) \prod_{\underline{k}''(S)} c_{\underline{k}''}^* \mid 0 \rangle \qquad (2.24)$$

where G, P and S specify the states occupied by ground pairs, excited pairs and single particles respectively. The energy of the excited states is evaluated by using the reduced Hamiltonian as well as the Bloch energies for single particles.

Valatin[1] and Bogolubov[2] independently found that the ground state vector of BCS is related to new collective fermion variables, in terms of which one obtains a simple classification of the excited states and which greatly simplify the calculation. The new variables are given as

$$\xi^{*}_{k,\sigma} = \alpha_k\, c^{*}_{k,\sigma} - \varepsilon(\sigma)\, \beta_k\, c_{-k,-\sigma}$$

and

$$\xi_{k,\sigma} = \alpha_k\, c_{k,\sigma} - \varepsilon(\sigma)\, \beta_k\, c^{*}_{-k,-\sigma} \qquad (2.25)$$

where the α_k and β_k are the same as used above and

$$\varepsilon(\sigma) = \begin{array}{l} 1 \\ -1 \end{array} \quad \text{for} \quad \begin{array}{l} \sigma = \uparrow \\ \sigma = \downarrow \end{array}$$

The operators ξ^{*} and ξ are Fermion operators and satisfy the commutation relations for such operators. These operators lead to a "quasi particle" concept since $\xi^{*}_{k,\sigma}$ may be thought of as creating a quasi-particle satisfying Fermi statistics. Valatin showed that the products

$$\left| \Psi_{k_1,\sigma_1;\, k_2,\sigma_2;\, \cdots\, k_m,\sigma_m} \right\rangle = \xi^{*}_{k_1,\sigma_1}\, \xi^{*}_{k_2,\sigma_2}\, \cdots\, \xi^{*}_{k_m,\sigma_m} \left| \Psi_0 \right\rangle \qquad (2.26)$$

form a complete orthonormal set of state vectors and are just the BCS excited states. In particular, the states $\xi^{*}_{k,\sigma} \left| \Psi_0 \right\rangle$ and $\xi^{*}_{k,\sigma}\, \xi^{*}_{-k,-\sigma} \left| \Psi_0 \right\rangle$ represent a "single particle" and a "real

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(1) Valatin, J.G., Nuovo Cimento, 7, 843, (1958).

(2) Bogolubov, N.N., Nuovo Cimento 7, 794, (1958).

pair" excited state respectively.

4.3 Criticism of the Theory

The main criticism originally put forth against the BCS theory was the lack of detailed justification of approximations made in the derivation. Since the original publication of this theory, independent work by Bogolubov[1] et. al. who solved the electron-phonon interaction problem differently agrees with the final BCS formulae for the ground state and one fermion excited states to first order approximation.

The most serious objection to the BCS theory is the lack of gauge invariance in the effective electron Hamiltonian. BCS chose a special gauge for the vector potential and derived a Meissner effect from this. Schafroth[2] has argued that this choice of a gauge is an independent assumption of the theory and is equivalent to assuming a Meissner effect itself. Anderson[3] has attempted to justify the BCS approach by showing that the reduced Hamiltonian is approximately gauge invariant and that consideration of the plasma oscillations should favour the choice of gauge.

(1) Bogolubov, N.N., Zubarev, D.N., and Tserkovnikov, Yu.A., Doklady Akad. Nauk. S.S.S.R. 117, 788, (1957).

(2) Schafroth, M.R., Solid State Physics, (1960), volume 10, pp. 471. ed: Seitz and Turnbull.

(3) Anderson, P.W., Phys. Rev., 110, 827, (1958).

Schafroth does not consider this argument to be valid since the relation of the BCS reduced Hamiltonian to the rigorous many electron Hamiltonian is not well defined. The method of Anderson has been extended by Rickayzen[1] to give a gauge invariant calculation of the Meissner effect by stressing the collective aspects of the theory of Bardeen, Cooper and Schrieffer.

Since the BCS theory has had such widespread success in describing the experimental situation, one must conclude that the type of pair correlations which their trial wave function singles out from the effective electron interaction is the basic mechanism of superconductivity. The major difficulty remaining is to adequately derive a many electron Hamiltonian (if this is possible) for various superconducting systems which will not lose gauge invariance in the approximating processes. Once gauge invariance has been lost, predictions concerning electromagnetic phenomena are impossible or at best uncertain.

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(1) Rickayzen, G., Phys. Rev., 111, 817, (1958).

CHAPTER V

SUMMARY

In this chapter we shall attempt to summarize the physical assumptions corresponding to the approximation made in the foregoing theory, apart from the more straightforward approximations such as neglect of second order small quantities in series expansions. We shall discuss the approximations made in obtaining the general Hamiltonian for a metal, in renormalizing the Hamiltonian and in obtaining the reduced BCS Hamiltonian.

The first approximation which we made was in assuming that the valence electrons in a metal are completely separated from the closed shells of bound electrons and that the adiabatic approximation could be used to write down the Hamiltonian for a metal. We showed in Chapter II that the adiabatic approximation was valid except for the electrons which lie within a distance $\hbar\,\omega_{max}$ of the Fermi surface where ω_{max} is the maximum lattice frequency. For electrons lying within this zone, non-adiabatic terms must be taken into account in the equation of motion. According to the BCS theory it is the electrons within this zone which are responsible for superconductivity. Chester[1] argues that in order to give a mathematically consistent description

(1) Chester, G.V., Advances in Physics, 10, 357, (1961), page 363.

of electrons for the purpose of a theory of superconductivity, non-adiabatic terms should be accounted for. We assumed in obtaining the phonon Hamiltonian that anharmonic terms in the lattice potential energy could be neglected. There was no justification for this assumption, but rather the theory was constructed to be consistent with it since no new anharmonic terms were introduced by the Frohlich transformation. In obtaining a general form for the Hamiltonian of a metal we also assumed that the valence electrons interact only with the longitudinal lattice vibrations. This assumption neglects anisotropic effects and is not rigorous particularly for short wavelengths. This approximation is not really necessary for developing the theory but it does help to reduce the complexity of the resulting equations.

In performing the Frohlich transformation in Chapter III, we assumed the quadratic terms in $b_k b_{k'}$, $b_k^* b_{k'}$, b_k^2 etc. could be neglected for $\underline{k} \neq \underline{k}'$. We argued that if the transformation and the model is adequate, the wave function describing the system would give zero expectation value for these quantities. In renormalizing the metal Hamiltonian use has been made of the random phase approximation. This procedure has been widely used, but proof of its validity usually depends on the specific system under consideration and is not straightforward. We have also made use of the effective mass approximation assuming the effective mass to

be constant whereas, in fact, it depends on the wave number. This approximation, however, does not affect the BCS theory since explicit use is not made of the term in which this approximation arises. In obtaining the transformed Hamiltonian we have not been consistent in considering terms to second order since we neglected the second order contributions from electron-plasma and phonon-plasma interactions, but we attempted to justify the neglect by energy considerations.

BCS have neglected a considerable portion of the metal Hamiltonian in obtaining their effective electron Hamiltonian. As was mentioned in Chapter III, they neglect the phonon energies, the plasma energies, the electron-plasma interaction, the phonon-plasma interaction and the residual electron-phonon interaction. The model which they consider enables them to neglect the phonon and electron-phonon energies, while energy considerations allow them to neglect the remaining terms. The most serious effect of neglecting these terms is the resulting lack of gauge invariance in the remaining Hamiltonian. BCS also neglect the effect of plasma screening on the effective electron interaction via the lattice. They assume a coefficient of the same form for both long wavelengths and short wavelengths whereas, in fact, we showed that the coefficients were different. These authors claim that the difference is small at long wavelengths and that the approximation is justified. BCS also neglect a

number of terms in obtaining their reduced Hamiltonian from the effective electron Hamiltonian. In particular, they neglect the terms which do not lead to pairwise interactions between electrons. This procedure is best characterized as a choice of simple trial wave function rather than as a physical approximation in the Hamiltonian. This simplicity may in some cases be expressed in terms of physical approximations. BCS also neglect pairs of electrons for which the total momentum is not equal to zero in obtaining the reduced Hamiltonian. They assume that terms of this sort have little effect on the ground state and can be treated as a perturbation.

The approximations made in the theory lead to a model of a metal in which the electrons and lattice are considered to be distinctly separated. Since there are a number of superconductors which do not satisfy the rigid restrictions which have been imposed in obtaining the theory, but still satisfy the predictions which the theory makes, we anticipate that the electron-lattice interaction problem might be treated in a different way which, however, would lead to essentially the same results. The main theoretical points which led to the development of the theory of superconductivity and which have been discussed here are the Frohlich transformation which indicated how to accurately describe the interaction between electrons due to the lattice and the BCS idea that superconductivity was due to Cooper pair correlations between the interacting electrons.

APPENDIX I

COMMUTATION RELATIONS REQUIRED FOR FROHLICH TRANSFORMATION

From Chapter III, equation (2.11) we have

$$H = H_0 + H_1 - \sum_{\underline{k}} \left[S_{\underline{k}}, H_0 \right]$$

$$+ H_2 - \sum_{\underline{k}} \left[S_{\underline{k}}, H_{1\underline{k}} \right] + \tfrac{1}{2} \sum_{\underline{k}} \left[S_{\underline{k}}, \left[S_{\underline{k}}, H_0 \right] \right] \tag{1}$$

where from (2.8)

$$H_0 = \sum_{\underline{K}} E_{\underline{K}} c_{\underline{K}}^* c_{\underline{K}} + \sum_{\underline{k}} \hbar \omega_{\underline{k}} b_{\underline{k}}^* b_{\underline{k}} + \tfrac{1}{2} \sum_{\underline{k}} \hbar \Omega_{\underline{k}} \tag{2}$$

and from (2.9)

$$H_{1\underline{k}} = i(D_{\underline{k}} b_{\underline{k}} \rho_{\underline{k}}^* - D_{\underline{k}}^* b_{\underline{k}}^* \rho_{\underline{k}}) + \tfrac{1}{2} M_{\underline{k}}^2 \rho_{-\underline{k}} \rho_{\underline{k}} \tag{3}$$

From (2.4) we have

$$S_{\underline{k}} = - \gamma_{\underline{k}} b_{\underline{k}} + \gamma_{\underline{k}}^* b_{\underline{k}}$$

with

$$\gamma_{\underline{k}} = \sum_{\underline{K}} \phi(\underline{K}, \underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}}$$

$$\gamma_{\underline{k}}^* = \sum_{\underline{K}} \phi^*(\underline{K}, \underline{k}) c_{\underline{K}-\underline{k}}^* c_{\underline{K}} \tag{4}$$

We wish now to derive the relations required in (1). From Chapter II, equations (3.c.20) we obtain the relation

$$c_{\underline{K}}^* c_{\underline{\ell}} c_{\underline{q}}^* c_{\underline{h}} - c_{\underline{q}}^* c_{\underline{h}} c_{\underline{K}}^* c_{\underline{\ell}} = \delta_{\underline{\ell},\underline{q}} c_{\underline{K}}^* c_{\underline{h}} - \delta_{\underline{K},\underline{h}} c_{\underline{q}}^* c_{\underline{\ell}} \tag{5}$$

We consider first

$$\left[S_{\underline{k}}, \sum_{\underline{K}'} E_{\underline{K}'} c_{\underline{K}'}^* c_{\underline{K}'}\right] = \sum_{\underline{K}'} \left\{ (-\gamma_{\underline{k}} b_{\underline{k}} + \gamma_{\underline{k}}^* b_{\underline{k}}^*) E_{\underline{K}'} c_{\underline{K}'}^* c_{\underline{K}'} \right.$$

$$\left. - E_{\underline{K}'} c_{\underline{K}'}^* c_{\underline{K}'} (-\gamma_{\underline{k}} b_{\underline{k}} + \gamma_{\underline{k}}^* b_{\underline{k}}^*) \right\}$$

which with the aid of (4) can be written

$$\sum_{\underline{K},\underline{K}'} E_{\underline{K}'} b_{\underline{k}} \phi(\underline{K},\underline{k}) \left\{ -c_{\underline{K}}^* c_{\underline{K}-\underline{k}} c_{\underline{K}'}^* c_{\underline{K}'} + c_{\underline{K}'}^* c_{\underline{K}'} c_{\underline{K}}^* c_{\underline{K}-\underline{k}} \right\}$$

$$+ \sum_{\underline{K},\underline{K}'} E_{\underline{K}'} b_{\underline{k}}^* \phi^*(\underline{K},\underline{k}) \left\{ c_{\underline{K}-\underline{k}}^* c_{\underline{K}} c_{\underline{K}'}^* c_{\underline{K}'} - c_{\underline{K}'}^* c_{\underline{K}'} c_{\underline{K}-\underline{k}}^* c_{\underline{K}} \right\}$$

Using equation (5) this reduces to

$$\left[S_{\underline{k}}, \sum_{\underline{K}'} E_{\underline{K}'} c_{\underline{K}'}^* c_{\underline{K}'}\right] = \sum_{\underline{K}} (E_{\underline{K}} - E_{\underline{K}-\underline{k}}) b_{\underline{k}} \phi(\underline{K},\underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}}$$

$$+ \sum_{\underline{K}} (E_{\underline{K}} - E_{\underline{K}-\underline{k}}) b_{\underline{k}}^* \phi^*(\underline{K},\underline{k}) c_{\underline{K}-\underline{k}}^* c_{\underline{K}}$$

$$= \sum_{\underline{K}} (E_{\underline{K}} - E_{\underline{K}-\underline{k}}) \left\{ b_{\underline{k}} \phi(\underline{K},\underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}} + h.c. \right\} \quad (6)$$

We consider now

$$\left[S_{\underline{k}}, \sum_{\underline{k}'} \hbar \omega_{\underline{k}'} b_{\underline{k}'}^* b_{\underline{k}'}\right]$$

$$= \sum_{\underline{k}',\underline{K}} \left\{ \hbar \omega_{\underline{k}'} \phi(\underline{K},\underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}} (-b_{\underline{k}} b_{\underline{k}'}^* b_{\underline{k}'} + b_{\underline{k}'}^* b_{\underline{k}'} b_{\underline{k}}) \right.$$

$$\left. + \hbar \omega_{\underline{k}'} \phi^*(\underline{K},\underline{k}) c_{\underline{K}-\underline{k}}^* c_{\underline{K}} (b_{\underline{k}}^* b_{\underline{k}'}^* b_{\underline{k}'} - b_{\underline{k}'}^* b_{\underline{k}'} b_{\underline{k}}^*) \right\}$$

Making use of the commutation relations (3.b.32) from Chapter II, this becomes

$$-\sum_{\underline{K}} \hbar \omega_{\underline{k}} \left\{ \phi(\underline{K},\underline{k}) c_{\underline{K}}^* c_{\underline{K}-\underline{k}} b_{\underline{k}} + \phi^*(\underline{K},\underline{k}) c_{\underline{K}-\underline{k}}^* c_{\underline{K}} b_{\underline{k}}^* \right\} \quad (7)$$

Therefore we have

$$\left[S_{\underline{k}}, \sum_{\underline{k}} \hbar \omega_{\underline{k}'} b^{*}_{\underline{k}} b_{\underline{k}} \right] = - \sum_{\underline{k}} \hbar \omega_{\underline{k}} \left\{ \phi(\underline{K}, \underline{k}) b_{\underline{k}} c^{*}_{\underline{K}} c_{\underline{K}-\underline{k}} + h.c. \right\} \tag{8}$$

Combining (6) and (8) we have therefore

$$-\sum_{\underline{k}} \left[S_{\underline{k}}, H_0 \right] = \sum_{\underline{K}, \underline{k}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \left\{ \phi(\underline{K}, \underline{k}) b_{\underline{k}} c^{*}_{\underline{K}} c_{\underline{K}-\underline{k}} + h.c. \right\} \tag{9}$$

Making use of (9) and (4) we have

$$S_{\underline{k}} \left[S_{\underline{k}}, H_0 \right] = (\gamma_{\underline{k}} b_{\underline{k}} - \gamma^{*}_{\underline{k}} b^{*}_{\underline{k}}) \left\{ b_{\underline{k}} \sum_{\underline{K}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi(\underline{K}, \underline{k}) c^{*}_{\underline{K}} c_{\underline{K}-\underline{k}} \right.$$

$$\left. + b^{*}_{\underline{k}} \sum_{\underline{K}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi^{*}(\underline{K}, \underline{k}) c^{*}_{\underline{K}-\underline{k}} c_{\underline{K}} \right\}$$

If we neglect terms in $b^2_{\underline{k}}$, etc. this can be written

$$-\sum_{\underline{K}, \underline{K}'} \left\{ b^{*}_{\underline{k}} b_{\underline{k}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi^{*}(\underline{K}', \underline{k}) \phi(\underline{K}, \underline{k}) c^{*}_{\underline{K}'-\underline{k}} c_{\underline{K}'} c^{*}_{\underline{K}} c_{\underline{K}-\underline{k}} \right.$$

$$\left. + b_{\underline{k}} b^{*}_{\underline{k}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi(\underline{K}', \underline{k}) \phi^{*}(\underline{K}, \underline{k}) c^{*}_{\underline{K}'} c_{\underline{K}'-\underline{k}} c^{*}_{\underline{K}-\underline{k}} c_{\underline{K}} \right\} \tag{10}$$

In the same way we can show that

$$\left[S_{\underline{k}}, H_0 \right] S_{\underline{k}} =$$

$$-\sum_{\underline{K}, \underline{K}'} \left\{ b_{\underline{k}} b^{*}_{\underline{k}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi(\underline{K}, \underline{k}) \phi^{*}(\underline{K}', \underline{k}) c^{*}_{\underline{K}} c_{\underline{K}-\underline{k}} c^{*}_{\underline{K}'-\underline{k}} c_{\underline{K}'} \right.$$

$$\left. + b^{*}_{\underline{k}} b_{\underline{k}} (E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar \omega_{\underline{k}}) \phi^{*}(\underline{K}, \underline{k}) \phi(\underline{K}', \underline{k}) c^{*}_{\underline{K}-\underline{k}} c_{\underline{K}} c^{*}_{\underline{K}'} c_{\underline{K}'-\underline{k}} \right\} \tag{11}$$

If we make use of the fact that

$$\left[b_{\underline{k}}, b^{*}_{\underline{k}} \right] = 1 \tag{12}$$

we have on subtracting the first lines of (10) and (11)

$$\sum_{\underline{K},\underline{K}'}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\phi(\underline{K},\underline{k})\phi^*(\underline{K}',\underline{k})\left\{(c^*_{\underline{K}} c_{\underline{K}-\underline{k}} c^*_{\underline{K}'-\underline{k}} c_{\underline{K}'} -\right.$$

$$\left. c^*_{\underline{K}'-\underline{k}} c_{\underline{K}'} c^*_{\underline{K}} c_{\underline{K}-\underline{k}})b^*_{\underline{k}} b_{\underline{k}} + c^*_{\underline{K}} c_{\underline{K}-\underline{k}} c^*_{\underline{K}'-\underline{k}} c_{\underline{K}'}\right\}$$

which with the aid of (5) becomes

$$\sum_{\underline{K},\underline{K}'}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\phi(\underline{K},\underline{k})\phi^*(\underline{K}',\underline{k})\left\{(c^*_{\underline{K}} c_{\underline{K}'}\delta_{\underline{K},\underline{K}'}\right.$$

$$\left. - c^*_{\underline{K}'-\underline{k}} c_{\underline{K}-\underline{k}}\delta_{\underline{K},\underline{K}'})b^*_{\underline{k}} b_{\underline{k}} + c^*_{\underline{K}} c_{\underline{K}-\underline{k}} c^*_{\underline{K}'-\underline{k}} c_{\underline{K}'}\right\}$$

$$= - \sum_{\underline{K}}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\left|\phi(\underline{K},\underline{k})\right|^2(n_{\underline{K}-\underline{k}} - n_{\underline{K}})\, b^*_{\underline{k}} b_{\underline{k}}$$

$$+ \sum_{\underline{K}}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\phi(\underline{K},\underline{k})c^*_{\underline{K}} c_{\underline{K}-\underline{k}}\,\gamma_{\underline{k}}^* \qquad (13)$$

Taking the difference of the second lines of (10) and (11) we obtain

$$- \sum_{\underline{K}}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\left|\phi(\underline{K},\underline{k})\right|^2(n_{\underline{K}-\underline{k}} - n_{\underline{K}})b^*_{\underline{k}} b_{\underline{k}}$$

$$+ \sum_{\underline{K}}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\phi^*(\underline{K},\underline{k})\gamma_{\underline{k}} c^*_{\underline{K}-\underline{k}} c_{\underline{K}} \qquad (14)$$

In these last two expressions we have written $n_{\underline{K}'}$ for $\sum_{\underline{K}'} c^*_{\underline{K}'} c_{\underline{K}'}$. If we combine (13) and (14) we have that

$$\tfrac{1}{2}\sum_{\underline{k}}\left[S_{\underline{k}},\left[S_{\underline{k}},H_o\right]\right] = - \sum_{\underline{K},\underline{k}}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})b^*_{\underline{k}} b_{\underline{k}}\left|\phi(\underline{K},\underline{k})\right|^2(n_{\underline{K}-\underline{k}} - n_{\underline{K}})$$

$$+ \tfrac{1}{2}\sum_{\underline{K},\underline{k}}(E_{\underline{K}-\underline{k}} - E_{\underline{K}} + \hbar\omega_{\underline{k}})\left\{\phi(\underline{K},\underline{k})\rho_{\underline{k}}^* \gamma_{\underline{k}}^* + h.c.\right\} \qquad (15)$$

We now wish to evaluate the remaining commutator required in (1). We consider first

$$\left[S_{\underline{k}}, \rho_{\underline{k}}\right] = \sum_{\underline{k}'}\left\{\left(-\gamma_{\underline{k}}b_{\underline{k}} + \gamma_{\underline{k}}^{*}b_{\underline{k}}^{*}\right)c_{\underline{k}'-\underline{k}}^{*}c_{\underline{k}'}\right.$$

$$\left. - c_{\underline{k}'-\underline{k}}^{*}c_{\underline{k}'}\left(-\gamma_{\underline{k}}b_{\underline{k}} + \gamma_{\underline{k}}^{*}b_{\underline{k}}^{*}\right)\right\}$$

$$= \sum_{\underline{K},\underline{k}'}\left[-\phi(\underline{K},\underline{k})b_{\underline{k}}\left\{c_{\underline{K}}^{*}c_{\underline{K}-\underline{k}}c_{\underline{k}'-\underline{k}}^{*}c_{\underline{k}'} - c_{\underline{k}'-\underline{k}}^{*}c_{\underline{k}'}c_{\underline{K}}^{*}c_{\underline{K}-\underline{k}}\right\}\right.$$

$$\left. + \phi^{*}(\underline{K},\underline{k})b_{\underline{k}}^{*}\left\{c_{\underline{K}-\underline{k}}^{*}c_{\underline{K}}c_{\underline{k}'-\underline{k}}^{*}c_{\underline{k}'} - c_{\underline{k}'-\underline{k}}^{*}c_{\underline{k}'}c_{\underline{K}-\underline{k}}^{*}c_{\underline{K}}\right\}\right]$$

which with the aid of (5) becomes

$$\sum_{\underline{K},\underline{k}'}\left[-\phi(K,k)b_{\underline{k}}\left(c_{\underline{K}}^{*}c_{\underline{k}'}\delta_{\underline{K},\underline{k}'} - c_{\underline{k}'-\underline{k}}^{*}c_{\underline{K}-\underline{k}}\delta_{\underline{K},\underline{k}'}\right)\right.$$

$$\left. + \phi^{*}(\underline{K},\underline{k})b_{\underline{k}}^{*}\left(c_{\underline{K}-\underline{k}}^{*}c_{\underline{k}'}\delta_{\underline{K},\underline{k}'-\underline{k}} - c_{\underline{k}'-\underline{k}}^{*}c_{\underline{K}}\delta_{\underline{k}',\underline{K}-\underline{k}}\right)\right] \qquad (16)$$

If we consider only diagonal terms in this expansion we have

$$\left[S_{\underline{k}}, \rho_{\underline{k}}\right] = \sum_{\underline{K}}\phi(\underline{K},\underline{k})b_{\underline{k}}(n_{\underline{K}-\underline{k}} - n_{\underline{K}}) \qquad (17)$$

In the same way we find that

$$\left[S_{\underline{k}}, \rho_{-\underline{k}}\right] = \sum_{\underline{K}}\phi^{*}(\underline{K},\underline{k})b_{\underline{k}}^{*}(n_{\underline{K}-\underline{k}} - n_{\underline{K}}) \qquad (18)$$

We consider also

$$\left[S_{\underline{k}}, b_{\underline{k}}\right] = \gamma_{\underline{k}}^{*}b_{\underline{k}}^{*}b_{\underline{k}} - b_{\underline{k}}\gamma_{\underline{k}}^{*}b_{\underline{k}}^{*}$$

which becomes on making use of (12)

$$\left[S_{\underline{k}}, b_{\underline{k}}\right] = -\gamma_{\underline{k}}^{*} \qquad (19)$$

In the same way we show that

$$\left[S_{\underline{k}}, b_{\underline{k}}^{*} \right] = - \gamma_{\underline{k}} \tag{20}$$

We consider now

$$\left[S_{\underline{k}}, i(D_{\underline{k}} \rho_{\underline{k}}^{*} b_{\underline{k}} - D_{\underline{k}}^{*} b_{\underline{k}}^{*} \rho_{\underline{k}}) \right.$$

$$= i D_{\underline{k}} \left\{ \left[S_{\underline{k}}, \rho_{\underline{k}}^{*} \right] b_{\underline{k}} + \rho_{\underline{k}}^{*} \left[S_{\underline{k}}, b_{\underline{k}} \right] \right\}$$

$$- i D_{\underline{k}}^{*} \left\{ b_{\underline{k}}^{*} \left[S_{\underline{k}}, \rho_{\underline{k}} \right] + \left[S_{\underline{k}}, b_{\underline{k}}^{*} \right] \rho_{\underline{k}} \right\}$$

Making use of (17), (18), (19) and (20) this becomes

$$\left[S_{\underline{k}}, i(D_{\underline{k}} \rho_{\underline{k}}^{*} b_{\underline{k}} - D_{\underline{k}}^{*} b_{\underline{k}}^{*} \rho_{\underline{k}}) \right]$$

$$= b_{\underline{k}}^{*} b_{\underline{k}} \sum_{\underline{k}} (n_{\underline{K}-\underline{k}} - n_{\underline{k}}) \left[i D_{\underline{k}} \phi^{*}(\underline{K},\underline{k}) + h.c. \right]$$

$$- i D_{\underline{k}} \rho_{\underline{k}}^{*} \gamma_{\underline{k}}^{*} + i D_{\underline{k}}^{*} \gamma_{\underline{k}} \rho_{\underline{k}} \tag{21}$$

If we consider

$$\left[S_{\underline{k}}, \tfrac{1}{2} M_{k}^{2} \rho_{-k} \rho_{\underline{k}} \right] = \tfrac{1}{2} M_{k}^{2} \left\{ \left[S_{\underline{k}}, \rho_{-k} \right] \rho_{\underline{k}} + \rho_{-k} \left[S_{\underline{k}}, \rho_{\underline{k}} \right] \right\}$$

this becomes with the aid of (17) and (18)

$$\tfrac{1}{2} M_{k}^{2} \sum_{\underline{k}} (n_{\underline{K}-\underline{k}} - n_{\underline{k}})(b_{\underline{k}} \phi(\underline{K},\underline{k}) \rho_{\underline{k}}^{*} + h.c.) \tag{22}$$

Combining (21) and (22) we have

$$- \sum_{\underline{k}} \left[S_{\underline{k}}, H_{1\underline{k}} \right] = - \sum_{\underline{k},\underline{k}} (n_{\underline{K}-\underline{k}} - n_{\underline{k}}) \left[i D_{\underline{k}} \phi^{*}(\underline{K},\underline{k}) + h.c. \right] b_{\underline{k}}^{*} b_{\underline{k}}$$

$$\tag{23}$$

$$+ i \sum_{\underline{k}} \left\{ D_{\underline{k}} \rho_{\underline{k}}^{*} \gamma_{\underline{k}}^{*} - D_{\underline{k}}^{*} \gamma_{\underline{k}} \rho_{\underline{k}} \right\} - \tfrac{1}{2} \sum_{\underline{k},\underline{k}} M_{k}^{2} (n_{\underline{K}-\underline{k}} - n_{\underline{k}})(b_{\underline{k}} \phi(\underline{K},\underline{k}) \rho_{\underline{k}}^{*} + h.c.)$$

APPENDIX II

CALCULATION OF THE COLLECTIVE HAMILTONIAN

From Chapter III, equation (3.b.11), we have that the collective Hamiltonian can be written

$$H^T = H + \frac{i}{\hbar}\left[H,S\right] - \frac{1}{2\hbar^2}\left[\left[H,S\right],S\right] + \cdots \cdots \qquad (1)$$

where from (3.b.1) and (3.b.2)

$$H = \sum_{\underline{k}} E_{\underline{k}}\, c^{*}_{\underline{k}}\, c_{\underline{k}} + \frac{1}{2}\sum_{\underline{k}}(p^{*}_{\underline{k}}\, p_{\underline{k}} + \Omega^2_{\underline{k}} q^{*}_{\underline{k}}\, q_{\underline{k}}) + \sum_{|\underline{k}|<|\underline{k}_c|} P^{*}_{\underline{k}}\, P_{\underline{k}}$$

$$+ \sum_{\underline{k}} q_{\underline{k}} v^{i}_{\underline{k}}\, \rho_{-\underline{k}} + \frac{1}{2}\sum_{\underline{k}} M^2_{\underline{k}}\, \rho_{-\underline{k}}\, \rho_{\underline{k}} \qquad (2)$$

and from (3.b.4)

$$S = \sum_{|\underline{k}|<|\underline{k}_c|}(iM_{\underline{k}}\, \rho_{-\underline{k}} + u_{\underline{k}} q_{-\underline{k}})\, Q_{\underline{k}} \qquad (3)$$

The first line of (2) contains zeroth order terms and the second line contains first order terms. We assume that S is a first order small quantity. We consider first

$$\left[\rho_{-\underline{k}},S\right] = \sum_{|\underline{k}'|<|\underline{k}_c|} iM_{\underline{k}'} Q_{\underline{k}'}\left[\rho_{-\underline{k}},\rho_{-\underline{k}'}\right]$$

since $\rho_{-\underline{k}}$ commutes with $q_{-\underline{k}}$. This equals

$$\sum_{|\underline{k}|<|\underline{k}_c|} iM_{\underline{k}'} Q_{\underline{k}'} \sum_{\underline{k},\underline{k}'}(c^{*}_{\underline{k}}\, c_{\underline{k}-\underline{k}}\, c^{*}_{\underline{k}'}\, c_{\underline{k}'-\underline{k}'} - c^{*}_{\underline{k}'}\, c_{\underline{k}'-\underline{k}'}\, c^{*}_{\underline{k}}\, c_{\underline{k}-\underline{k}})$$

$$= \sum_{\underline{k},\underline{k}',|\underline{k}'|<|\underline{k}_c|} iM_{\underline{k}'} Q_{\underline{k}'}(c^{*}_{\underline{k}}\, c_{\underline{k}'-\underline{k}}\, \delta_{\underline{k}',\underline{k}-\underline{k}} - c^{*}_{\underline{k}'}\, c_{\underline{k}-\underline{k}}\, \delta_{\underline{k},\underline{k}'-\underline{k}'})$$

$$= \sum_{|\underline{k}'|<|\underline{k}_c|,\underline{k}} iM_{\underline{k}'} Q_{\underline{k}'}(c^{*}_{\underline{k}}\, c_{\underline{k}-\underline{k}-\underline{k}'} - c^{*}_{\underline{k}}\, c_{\underline{k}-\underline{k}-\underline{k}'}) = 0 \qquad (4)$$

In the same way we show that $\left[\rho_k, S\right] = 0$. Therefore we have

$$\left[\tfrac{1}{2}\sum_k M_k^2 \rho_{-k}\, \rho_k \,, S\right] = 0 \tag{5}$$

and

$$\left[\sum_k v_k^i\, q_k\, \rho_{-k}\,,\, S\right] = 0 \tag{6}$$

since $\left[q_k, q_{-k}\right] = 0.$

We consider now

$$\tfrac{i}{\hbar}\left[\sum_{k'} E_{k'} c_{k'}^* \, c_{k'}\,, S\right] = \tfrac{i}{\hbar}\sum_{\substack{|k|<|k_c| \\ k, k'}} E_{k'}(i M_k Q_k)(c_{k'}^* \, c_{k'}\, c_k^* \, c_{k-k} - c_k^* \, c_{k-k}\, c_{k'}^* \, c_{k'})$$

since $\rho_{-k} = \sum_k c_k^* \, c_{k-k}$ and the c's commute with q_k. Making use of (4) of Appendix I, this becomes

$$\tfrac{i}{\hbar}\left[\sum_{k'} E_{k'} c_{k'}^* \, c_{k'}\,, S\right] = -\tfrac{1}{\hbar}\sum_{\substack{|k|<|k_c| \\ k}} (E_k - E_{k-k}) M_k Q_k c_k^* \, c_{k-k} \tag{7}$$

We consider now

$$-\tfrac{1}{2\hbar^2}\left[\left[\sum_{k'} E_{k'} c_{k'}^* \, c_{k'}\,, S\right], S\right]$$

$$= \tfrac{-1}{2\hbar^2}\sum_{\substack{|k|<|k_c| \\ k, k, k'}} M_k (E_k - E_{k-k})(i M_{k'}) Q_k Q_{k'}(c_k^* \, c_{k-k}\, c_{k'}^* \, c_{k'-k'} - c_k^* \, c_{k'-k'} c_{k'}^* \, c_{k-k})$$

$$= \tfrac{1}{2\hbar^2}\sum_{\substack{k, k'|<|k_c| \\ k}} M_{k'} M_k Q_{k'} Q_k (E_k - 2E_{k-k} + E_{k-k-k'})\, \rho_{k+k'}^* \tag{8}$$

We now look at the relation

$$\tfrac{i}{\hbar}\left[\tfrac{1}{2}\sum_{k'}(p_{k'}^* \, p_{k'} + \Omega_{k'}^2 q_{k'}^* \, q_{k'})\,, S\right]$$

$$= \tfrac{i}{2\hbar}\sum_{k',|k|<|k_c|} u_k Q_k (p_{k'}^* \, p_{k'} q_k^* - q_k^* \, p_{k'}^* \, p_{k'})$$

since $q_{-k} = q_k^*$ and $\left[q_k, q_{k'}\right] = 0$. This becomes

$$\frac{1}{2\hbar} \sum_{k',|k|<|k_c|} u_k Q_k (p_{k'}^* \, p_{k'} \, q_k^* \; - \; (p_{k'}^* \, q_k^* \; + \; i\hbar\delta_{k',k}) \, p_{k'})$$

$$= \frac{1}{2\hbar} \sum_{k',|k|<|k_c|} u_k Q_k (- \, i\hbar p_{k'} \delta_{k,k'} \; + \; p_{k'}^* \, p_{k'} \, q_k^* \; - \; p_{k'}^* \, (p_{k'} q_k^* \; + \; i\hbar\delta_{k,-k'}))$$

We therefore have

$$\frac{1}{\hbar}\left[\frac{1}{2} \sum_{k'} (p_{k'}^* \, p_{k'} \; + \Omega_k^2 \, q_{k'}^* \, q_{k'}), S \right] \; = \; \sum_{|k|<|k_c|} u_k p_k Q_k \tag{9}$$

We have from (9) that

$$- \frac{1}{2\hbar^2} \left[\left[\frac{1}{2} \sum_{k'} (p_{k'}^* \, p_{k'} \; + \Omega_k^2 \, q_{k'}^* \, q_{k'}), S \right], S \right] = \frac{1}{2\hbar} \left[\sum_{|k|<|k_c|} u_k Q_k p_k, S \right]$$

$$= \frac{1}{2\hbar} \sum_{|k,k'|<|k_c|} u_k Q_k u_{k'} Q_{k'} (-i\hbar) \delta_{k,-k'}$$

$$= \frac{1}{2} \sum_{|k|<|k_c|} u_k u_{-k} Q_k Q_{-k}$$

$$= \frac{1}{2} \sum_{|k|<|k_c|} u_k^2 \, Q_k Q_{-k}^* \tag{10}$$

since $Q_k^* = Q_k$ and $u_{-k} = - \, u_k$.

We now have

$$\frac{1}{\hbar}\left[\frac{1}{2} \sum_{|k|<|k_c|} P_k^* \, P_k, S \right]$$

$$= \frac{1}{2\hbar} \sum_{|k,k'|<|k_c|} (iM_{k'} \, p_{-k'} + u_{k'} q_{-k'}) \left\{ P_k^* \left[P_k, Q_{k'} \right] \; + \; \left[P_k^*, Q_{k'} \right] P_k \right\}$$

From Chapter III, (3.b.5) we have

$$\left[P_k, Q_{k'} \right] = -i\hbar \, \delta_{k,k'} \tag{11}$$

Hence

$$\frac{1}{\hbar}\left[\frac{1}{2} \sum_{|k|<|k_c|} P_k^* \, P_k, S \right] = \sum_{|k|<|k_c|} (iM_k \, p_{-k} + u_k q_{-k}) P_k^* \tag{12}$$

We also have with the aid of (12),

$$- \frac{1}{2\hbar^2} \left[\left[\frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} P_{\underline{k}}^* \ P_{\underline{k}} \ , S \right], S \right]$$

$$= \frac{1}{2\hbar} \sum_{|\underline{k},\underline{k}'|<|\underline{k}_c|} (iM_{\underline{k}} \, \rho_{-\underline{k}} + u_{\underline{k}} q_{\underline{k}}) (iM_{\underline{k}'} \, \rho_{-\underline{k}'} + u_{\underline{k}'} q_{\underline{k}'}) \left[P_{\underline{k}}^* \ , Q_{\underline{k}'} \right]$$

which becomes

$$- \frac{1}{2\hbar^2} \left[\left[\frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} P_{\underline{k}}^* \ P_{\underline{k}} \ , S \right], S \right] = \frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} M_{\underline{k}}^2 \, \rho_{-\underline{k}} \rho_{\underline{k}}$$

$$+ i \sum_{|\underline{k}|<|\underline{k}_c|} M_{\underline{k}} u_{\underline{k}} q_{\underline{k}} \rho_{-\underline{k}} + \frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}}^2 \, q_{\underline{k}}^* \ q_{\underline{k}} \qquad (13)$$

From Chapter III, (3.b.10) we have for the subsidiary condition

$$P_{\underline{k}}^* \Psi' = (iM_{\underline{k}} \, \rho_{-\underline{k}} - u_{\underline{k}} q_{\underline{k}}) \Psi' \qquad (14)$$

If we substitute the right hand side of this expression for $P_{\underline{k}}^*$ into (12) we have

$$\frac{i}{\hbar} \left[\frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} P_{\underline{k}}^* \ P_{\underline{k}} \ , S \right] = - \sum_{|\underline{k}|<|\underline{k}_c|} M_{\underline{k}}^2 \, \rho_{-\underline{k}} \rho_{\underline{k}} - 2i \sum_{|\underline{k}|<|\underline{k}_c|} M_{\underline{k}} u_{\underline{k}} q_{\underline{k}} \rho_{-\underline{k}}$$

$$- \sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}}^2 \, q_{\underline{k}}^* \ q_{\underline{k}} \qquad (15)$$

If we add (14) and (15) we have

$$\frac{i}{\hbar} \left[\frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} P_{\underline{k}}^* \ P_{\underline{k}} \ , S \right] - \frac{1}{2\hbar^2} \left[\left[\frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} P_{\underline{k}}^* \ P_{\underline{k}} \ , S \right], S \right]$$

$$\qquad (16)$$

$$= - \frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} M_{\underline{k}}^2 \, \rho_{-\underline{k}} \rho_{\underline{k}} - i \sum_{|\underline{k}|<|\underline{k}_c|} M_{\underline{k}} u_{\underline{k}} q_{\underline{k}} \rho_{-\underline{k}} - \frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}}^2 \, q_{\underline{k}}^* \ q_{\underline{k}}$$

If we neglect all terms of order higher than second, we obtain for our collective Hamiltonian making use of equations (5), (6), (7), (8), (9), (10), (16) and (2)

$$H^T = \sum_{\underline{k}} E_{\underline{k}} c^*_{\underline{k}} c_{\underline{k}} + \frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} \left[p^*_{\underline{k}} p_{\underline{k}} + (\Omega^2_{\underline{k}} - u^2_{\underline{k}}) q^*_{\underline{k}} q_{\underline{k}} \right]$$

$$+ \frac{1}{2} \sum_{|\underline{k}|<|\underline{k}_c|} \left[P^*_{\underline{k}} P_{\underline{k}} + u^2_{\underline{k}} Q^*_{\underline{k}} Q_{\underline{k}} \right]$$

$$+ \frac{1}{2\hbar^2} \sum_{\substack{|\underline{k},\underline{k}'|<|\underline{k}_c| \\ \underline{k}}} M_{\underline{k}'} M_{\underline{k}} Q_{\underline{k}'} Q_{\underline{k}} (E_{\underline{k}} - 2E_{\underline{k}-\underline{k}} + E_{\underline{k}-\underline{k}-\underline{k}'}) \rho^*_{\underline{k}+\underline{k}'}$$

$$+ \sum_{|\underline{k}|<|\underline{k}_c|} (v^i_{\underline{k}} - iM_{\underline{k}} u_{\underline{k}}) q_{\underline{k}} \rho_{-\underline{k}} + \sum_{|\underline{k}|<|\underline{k}_c|} u_{\underline{k}} P_{\underline{k}} Q_{\underline{k}}$$

$$- \frac{1}{\hbar} \sum_{|\underline{k}|<|\underline{k}_c|, \underline{k}} (E_{\underline{k}} - E_{\underline{k}-\underline{k}}) M_{\underline{k}} Q_{\underline{k}} c^*_{\underline{k}} c_{\underline{k}-\underline{k}}$$

$$+ \frac{1}{2} \sum_{|\underline{k}|>|\underline{k}_c|} (p^*_{\underline{k}} p_{\underline{k}} + \Omega^2_{\underline{k}} q^*_{\underline{k}} q_{\underline{k}}) + \sum_{|\underline{k}|>|\underline{k}_c|} v^i_{\underline{k}} q_{\underline{k}} \rho_{-\underline{k}}$$

$$+ \frac{1}{2} \sum_{|\underline{k}|>|\underline{k}_c|} M^2_{\underline{k}} \rho_{-\underline{k}} \rho_{\underline{k}} \qquad\qquad (17)$$