THE ELECTRONIC ENERGIES AND WAVEFUNCTIONS OF METALS

BY

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ABSTRACT

The plasma oscillation theory of Bohm and Pines represents a big advance in the theory of electron gases. Its main application has been to obtain an understanding of correlation phenomena in the conduction bands of metals. Bohm and Pines in their original work dealt only with the special case of the free electron gas. The work described in this thesis is mainly concerned with investigating the way in which their results are modified when one is dealing with the conduction electrons of metals.

Two distinct methods of attacking this problem are described in the main body of the thesis. One of these uses Bohm and Pines' formalism together with the effective mass theory developed by various authors. It is shown that provided certain effects can be neglected this approach yields a theory of conduction electrons similar to Bohm and Pines free electron gas theory. Unfortunately some of the effects neglected have turned out to be important.

The other method depends upon developing the plasma oscillation theory in rather a different manner from that used by Bohm and Pines. This approach recognises the close connection between the plasma oscillations and the dielectric properties of electron gases. It avoids some of the awkward features of Bohm and Pines' formalism but has the disadvantage as originally developed of being a semi-classical theory rather than a proper quantum mechanical treatment.

In a series of three papers submitted as subsidiary matter it has been shown how, starting from first principles, it is possible to construct a theory of plasma oscillations which is of the same character as the dielectric theory. This in itself is a complete theory of plasma oscillations applicable to the conduction electrons of metals and free from the difficulties of Bohm and Pines' formalism.

PREFACE

The work described in this thesis, apart from where acknowledgement has been given and the introductory matter of chapters one and two, is all original although some of the results were obtained independently and at about the same time by workers elsewhere. None of it has been submitted for a degree in any other University.

The work described in chapter three has been published in the Proceedings of the Physical Society (1954), and that described in chapter four has been published as a research note and a paper in the Proceedings of the Physical Society (1955). The three papers submitted as subsidiary matter have all been accepted for publication in the Proceedings of the Royal Society (1957).

It is a pleasure to acknowledge the benefit of the valuable advice and encouragement I have received from by supervisor, Professor H. Jones, during the course of this work. I should also like to thank Dr. S. Raimes for much valuable advice and encouragement during my period at Imperial College and Dr. B. H. Flowers and Dr. W. M. Lomer for their continued help and encouragement during my stay at A.E.R.E. Finally, I should like to thank Dr. J. S. Bell and Mr. R. S. Leigh for much stimulating discussion during the later stages of this work.

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LIST OF SYMBOLS

This list contains only symbols used widely throughout the main body of the thesis. The definitions of other symbols will be found at the places at which they are introduced.

The convention that underlining indicates the vector character of a symbol has been used universally; second rank tensor quantities have been indicated by a double underlining.

$\underline{\underline{\alpha}}_{\omega\underline{k}}$		Fourier component of the polarizability tensor
$\alpha_{\omega\underline{k}}$	$=$	$\hat{\underline{k}} \cdot \underline{\underline{\alpha}}_{\omega\underline{k}} \cdot \hat{\underline{k}}$
$\underline{D}_{\omega\underline{k}}$		Fourier component of the electric displacement
$D_{\omega\underline{k}}$	$=$	$\hat{\underline{k}} \cdot \underline{D}_{\omega\underline{k}}$
e		electronic charge
e		base of Naperian logarithms
E		total energy of system
$E_{\underline{k}}$		energy of Bloch wave function with wave vector $\underline{k}$
$E_{\underline{k}n}$		as E but for wave function belonging to n^{th} zone
$\underline{E}_{\omega\underline{k}}$		Fourier component of the electric field
$E_{\omega\underline{k}}$	$=$	$\hat{\underline{k}} \cdot \underline{E}_{\omega\underline{k}}$
$\underline{\underline{\epsilon}}_{\omega\underline{k}}$		Fourier component of complex dielectric tensor
$\epsilon_{\omega\underline{k}}$	$=$	$\hat{\underline{k}} \cdot \underline{\underline{\epsilon}}_{\omega\underline{k}} \cdot \hat{\underline{k}}$
$\hbar$		Plank's constant/2π
H		Hamiltonian
$H_{s.r.}$		Short-range part of the Coulomb interaction Hamiltonian
$\underline{k}$		wave vector
k	$=$	$\lvert \underline{k} \rvert$
$\hat{\underline{k}}$	$=$	$\underline{k}/k$

k_c	cut-off wave vector
$\underline{k}_i$	wave vector of the i^{th} electron
χ	Boltzmann's constant (except on page 101 where it is extinction coefficient)
m	mass of an electron
$\underline{\underline{m}}^*$	effective mass tensor
n	density of electrons (except on page 101 where it is the refractive index)
$N_{\underline{k}n}$	the occupation number of the state ($\underline{k}$, n)
$\underline{p}_i$	momentum of the i^{th} electron
$p_{\underline{k}}$	momentum of the plasma oscillator with wave vector $\underline{k}$
$q_{\underline{k}}$	co-ordinate of the plasma oscillator with wave vector $\underline{k}$
r_s	radius of sphere whose volume is equal to the volume per electron
$\underline{r}_i$	position vector of i^{th} electron
$\underline{\underline{\sigma}}_{\omega\underline{k}}$	Fourier component of conductivity tensor
$\sigma_{\omega\underline{k}}$ =	$\hat{\underline{k}} \cdot \underline{\underline{\sigma}}_{\omega\underline{k}} \cdot \hat{\underline{k}}$
T	absolute tempserature
$U(\underline{r})$	periodic potential in crystal
$u_{\underline{k}}(\underline{r})$	periodic part of the Bloch wave function
$\varphi(\underline{r})$	Wannier function (chapter three)
$\varphi(\underline{r},t)$	electric potential (chapter four)
$\psi_{\underline{k}}$	Bloch wave function with wave vector $\underline{k}$
$\psi_{\underline{k}n}$	Bloch wave function with wave vector $\underline{k}$ belonging to n^{th} zone

ω	frequency
ω_p	plasma frequency
$\omega_{\underline{k}}$	frequency of plasma oscillator with wave vector $\underline{k}$

INTRODUCTION

Within recent years much progress has been made in the understanding of the quantum mechanics of systems consisting of large numbers of interacting particles. One of the most interesting features of the behaviour of such systems is the existence of the so-called collective modes of behaviour. These are special modes of motion which depend upon co-operative effects involving large numbers of particles and are controlled by the interactions between the particles. A typical example is a sound wave in a gas.

One of the earliest examples of a treatment of a quantum mechanical system in which the role played by the collective motions was recognised is Bohm and Pines' theory of the degenerate free electron gas (Bohm and Pines 1953, Pines 1953). Their treatment is based upon a study of the plasma oscillations which can occur in this system; it enabled them to calculate various properties of the system such as the energy of the ground state.

This work of Bohm and Pines is of considerable importance in the theoretical study of the solid state. In conventional band theory the correlation effects due to the interactions of the electrons are neglected and each conduction electron is regarded as moving in the field of the ion cores and in some sort of average field due to the rest of the electrons. For many years considerable uncertainty had existed as to the importance of the correlation effects and the manner in which they were to be treated. However, the degenerate electron gas can be

regarded as a very crude model of the conduction band of a metal, so that Bohm and Pines' theory sheds considerable light on this problem. It is then natural to ask in what way Bohm and Pines' results are modified when the theory is applied to the conduction electrons of a metal i.e. to electrons moving in the periodic field of the ion cores. The work described in this thesis originated in an investigation of this problem.

The earliest attempt to determine the effect upon the plasma oscillations of a periodic background potential was made by Wolff (1953) who used a time-dependent self-consistent field method. His main result was that in the expression for the plasma frequency one should replace the ordinary electronic mass by an average of the effective masses over the occupied electronic states. Wolff's treatment was not a complete theory starting from first principles as Bohm and Pines' is. Part of the work described in this thesis (chapter three) is an attempt to obtain Wolff's result from first principles by generalising Bohm and Pines' theory so as to apply to electrons moving in a periodic potential. It was found possible to do this making use of the effective mass theory developed by Slater (1949) and Adams (1952). It was shown that Wolff's result obtained provided the effects of virtual inter-zone transitions could be neglected, and this work has since been published (Hubbard 1954). It was thought, however, that the neglect of the inter-zone transitions might be a source of serious error and an attempt (not described in this thesis) was made to generalise the theory to include these effects. However, there were

difficulties connected with the convergence of a perturbation series which arises and this work was abandoned in favour of a different method described below. Nevertheless, other authors (Adams 1955, Kanazawa 1955, Pines and Nozieres 1957) have continued to investigate the effect of these inter-zone transitions using Bohm and Pines formalism with some success.

An entirely different line of attack upon the problem is represented by the 'dielectric' approach to the plasma oscillation theory. This theory was developed by the author (Hubbard 1955A) and simultaneously and independently by several others (Mott 1954, Frohlich and Pelzer 1955), and has been described in chapter four of this thesis. This method depends upon a recognition of the close connection between the theory of plasma oscillations and the dielectric properties of an electron gas. It has several advantages over Bohm and Pines' treatment. One of these is that it is as easily applicable to a metal as to a free electron gas, the only difference being in their dielectric properties. It has the further advantage of allowing one easily to handle the damping of the plasma oscillations, a problem which cannot be very adequately treated using Bohm and Pines' formalism and represents the chief drawback of their method. Associated with this damping problem in Bohm and Pines' theory is the necessity to introduce an ill-defined cut-off length which is automatically avoided in the dielectric treatment.

Although the dielectric theory has these advantages over Bohm and Pines', it suffers from a serious disadvantage. Whereas Bohm and Pines' is a complete theory starting from first principles, the dielectric

method has the character of a phenomenological theory. It is therefore highly desirable to investigate whether it is possible to develop the dielectric theory from first principles. Such an investigation is a natural continuation of the work described in chapter Four. It has, in fact, been found possible to do this using a perturbation theory method and the techniques of field theory. This work has been written up as a series of three papers (all of which have been accepted for publication in the Proceedings of the Royal Society) which are submitted as subsidiary matter in this thesis.

These three papers in themselves represent a self-contained theory. It is shown in them how, starting from the formally exact solution to the many-body problem represented by an infinite perturbation series, one can, by carrying out suitable partial summations in the perturbation series, obtain a theory which yields all the major results of Bohm and Pines and yet avoids the difficulties of the damping, the cut-off and the subsidiary conditions. The physical interpretation of the various manipulations which are carried out is found to correspond to the ideas behind the dielectric theory. In the third paper it is shown how the theory can be formally extended to apply to the case of electrons moving in a periodic potential. In a sense this work supercedes the work described in the main body of the thesis.

CHAPTER ONE.

CORRELATION EFFECTS IN METALS.

§1 The Independent Particle Model.

If one makes certain plausible simplifying assumptions (see, for example, Seitz, 1940, Chapter VI), one can regard the conduction band of a metal as a system whose Hamiltonian is

$$H = \sum_i \left[\frac{1}{2m} \underline{p}_i^2 + U(\underline{r}_i) \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\underline{r}_i - \underline{r}_j|} \qquad (1.1)$$

where $\underline{r}_i$ and $\underline{p}_i$ are the position and momentum vectors of the i th electron of the band; the first term of (1.1) represents the kinetic energy of the electrons, the second their potential energy in the field $U(\underline{r})$ of the ion cores, and the last term represents the mutual Coulomb interaction energy of the electrons.

In most applications of the theory one is concerned with the ground state of this system and those states close to the ground state in energy. An important problem in the theory of metals is therefore the determination of the energies and wave functions of the low energy stationary states of the Hamiltonian (1.1).

If it were not for the presence of the last term in (1.1), this would be a relatively straightforward problem. However, the presence of this term makes the problem a many-body problem, and it is from this many-body nature of the problem that its main difficulties derive. In

other branches of quantum mechanics in which the many-body problem is met with the general approach to its solution has been through the independent particle model. This model is equivalent physically to the assumption that the electrons can be regarded, at least approximately, as moving independently of each other in a potential field which represents a sort 'smoothed out' interaction with the remaining electrons of the system. Formally it is represented by the assumption that the wave functions Ψ of the stationary states of (1.1) can be approximately represented as a products of 'independent electron' wave functions, each of which depends only upon the co-ordinates of one of the electrons.

$$\Psi(\underline{r}_1, \underline{r}_2, \ldots \underline{r}_n) = \psi_1(\underline{r}_1)\psi_2(\underline{r}_2)\ldots\psi_n(\underline{r}_n) \qquad (1.2)$$

It is easily seen that the wave function (1.2) represents electrons moving independently of each other, for the probability that the i th electron is at $\underline{r}$ is just given by

$$\frac{|\Psi(\underline{r}_1, \ldots \underline{r}_{i-1}, \underline{r}, \underline{r}_{i+1}, \ldots \underline{r}_n)|^2}{\int |\Psi|^2 d\underline{r}_i} = \frac{|\psi_i(\underline{r})|^2}{\int |\psi_i(\underline{r})|^2 d\underline{r}} \qquad (1.3)$$

which is independent of the $\underline{r}$ s of the other electrons.

Actually, even in the approximation represented by the independent particle model, (1.2) it not a satisfactory wave function, for electrons are known to obey Fermi-Dirac statistics, and this requires that the wave function of a stationary state of the Hamiltonian (1.1) be anti-symmetric in the co-ordinates of the different electrons, whereas (1.2) is symmetric. To remedy this defect the approximate wave function (1.2) can be replaced

by the determinant

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(\underline{r}_1) & \psi_2(\underline{r}_1) & \dots & \psi_n(\underline{r}_1) \\ \psi_1(\underline{r}_2) & \psi_2(\underline{r}_2) & \dots & \psi_n(\underline{r}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\underline{r}_n) & \psi_2(\underline{r}_n) & \dots & \psi_n(\underline{r}_n) \end{vmatrix} \qquad (1.4)$$

In the case of this wave function it is no longer true that the probability of finding the i th electron at $\underline{r}$ is independent of the coordinates of the other electrons. In fact, (1.4) contains certain correlations between the motions of the different electrons; these correlations represent the tendency of electrons with the same spin to keep away from one another as a result of the action of the exclusion principle, giving rise to the so-called 'Fermi hole'. These correlations should, however, be carefully distinguished from those other correlations brought about by the mutual repulsion of the electrons, which are not included in the wave function (1.4), and whose treatment is the main concern of the work of this thesis. In future the term correlation will be understood to mean these latter correlations rather than those arising from the exclusion principle.

If one makes the assumption that the wave functions of the stationary states of (1.1) can be represented in the forms (1.2) or (1.3), then the problem of determining these stationary states is reduced to that of determining the independent particle wave functions ψ_i in such a way as to make (1.2) or (1.4) as good an approximation

to the true wave function of the stationary state as possible. This is a fairly straightforward problem; the wave functions (1.2) or (1.4) can be regarded as trial functions subject to variation by variation of the ψ_i s, and the best ψ_i s can then be determined by application of the variation principle (see, for example, Schiff, 1949, p. 169)

$$0 = \delta \int \Psi^* H \Psi \, d\underline{r}_1 d\underline{r}_2 \ldots d\underline{r}_n \tag{1.5}$$

In the case of the wave function (1.2) it is found that this will be the best approximation to the true wave function if the ψ_i s satisfy the Hartree equations (Hartree, 1928)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U + e^2 \sum_{j \neq i}' \int \frac{|\psi_j(\underline{r}')|^2}{|\underline{r} - \underline{r}'|} d\underline{r}' \right] \psi_i(\underline{r}) = E_i \psi_i \tag{1.6}$$

and it is found that, in the cases of principal interest (those in which the stationary state has the multiplicity one), the wave function (1.4) will be the best approximation to the true wave function when the ψ_i s satisfy the Hartree-Fock equations (Fock, 1930)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U + e^2 \sum_j \int \frac{|\psi_j(\underline{r}')|^2}{|\underline{r} - \underline{r}'|} d\underline{r}' \right] \psi_i$$

$$- e^2 \sum_j \sum_{\underline{\sigma}'} \int \frac{\psi_j^*(\underline{r}', \underline{\sigma}') \psi_i(\underline{r}', \underline{\sigma}')}{|\underline{r} - \underline{r}'|} d\underline{r}' \, \psi_j(\underline{r}) = E_i \psi_i \tag{1.7}$$

It will be seen that (1.6) has the same form as the ordinary Schrödinger equation for a single electron moving in a certain (self-consistent) field, whilst (1.7) has the same form except for the

presence of a more general 'exchange potential'. Thus in the independent particle model not only do the electrons move independently of one another, but they also move according to the ordinary Schrödinger equation, adding greatly to the ease with which the various phenomena can be visualised from the point of view of this model.

To summarise, making the assumptions involved in the independent particle model, the problem of determining the stationary states of (1.1) is reduced to that of solving the Schrödinger type equations (1.6) or (1.7) self-consistently; the actual wave functions could then be determined in this approximation by substitution of the solutions of (1.6) or (1.7) into (1.2) or (1.4); the corresponding energies of these wave functions can then be obtained from

$$E = \int \underline{\Psi}^* H \underline{\Psi} \, d\underline{\tau}_1 \, d\underline{\tau}_2 \ldots d\underline{\tau}_n \qquad (1.8)$$

It should be noted that, although both the Hartree and the Hartree-Fock schemes have been dealt with here, the Hartree-Fock is the more correct theoretically, since it takes into account those correlations in the electronic motion brought about by the exclusion principle.

§2 Correlation Phenomena.

In the previous section the independent particle model has been briefly described. In this section the extent to which it is successful in explaining the properties of solids will be discussed.

At first sight it might seem that, because strong correlations in the motions of the electrons must evidently be brought about by the

Coulomb repulsion, this model would be rather unsuccessful. This expectation is, however, by no means borne out by experiment. In fact, as will be illustrated below, the situation seems to be that the independent particle model gives a good qualitative account of the properties of solids, and it is only when the theory is applied quantitatively that its short-comings are noticeable.

One of the most important deductions which can be made from the independent particle model is the Brillouin zone structure of solids. In (1.1) the potential U is a periodic function of position because of the regular arrangement of the ion cores in the crystalline lattice. It is true in most cases that, because of the periodicity of U, the self-consistent potentials appearing in the Hartree and Hartree-Fock equations (1.6) and (1.7) are also periodic with the same period (the only exceptions to this rule seem to be antiferromagnetic substances in which the period of the self-consistent field may be a multiple of the period of U). Then equation (1.7) becomes the Schrödinger equation of a particle moving in a periodic field. The application of group theoretic methods now leads to the deduction of the familiar Bloch form

$$\psi_{\underline{k}} = e^{i\underline{k}\cdot\underline{r}}\, u(\underline{r}), \quad u \text{ periodic}, \tag{2.1}$$

for the solutions of (1.7), and to the whole Brillouin zone scheme.

This deduction of the zone scheme from the independent particle

model is by far the greatest success of this model, for this scheme explains, at least qualitatively, a very wide range of the observed properties of solids, and its general correctness can be regarded as well established.

The independent particle model has not only been successful in predicting the Brillouin zone structure of solids; the treatment of the electrons as though they move independently of each other has also lead to qualitatively correct deductions concerning a wide range of metallic phenomena. For example, in conductivity theory the electrons are usually treated upon this basis, and the deductions concerning conduction phenomena in solids made from this theory are in very fair agreement with experiment in a large number of cases. Thus it would seem that the independent particle model gives at least a qualitatively correct picture of the behaviour of the electrons in a solid.

It is now natural to ask to what extent the model also gives a quantitatively correct account of the properties of solids. This question is much more difficult to answer. The chief cause of this uncertainty is the lack of accurate band structure calculations based upon the Hartree-Fock equations (1.7); in fact, no complete self-consistent field calculation has ever been carried out for a solid. Consequently it is very difficult to make anything other than very rough quantitative deductions from the theory, and an accurate comparison of the predictions of the model with experiment is not in

general possible. For these reasons, to answer this question one has to rely upon rather indirect evidence from the atomic case, and upon the results obtained in the rather special case of the alkali metals, whose band structures are fairly well known.

In the atomic case one is rather better placed to judge the accuracy of the Hartree-Fock scheme, for accurate solutions of the Hartree-Fock equations are available for a large number of different atoms. Using these solutions it is possible to calculate in the approximation represented by the independent particle model the cohesive energy of the atom, and compare this directly with the experimentally measured cohesive energy, thus obtaining a direct test of the accuracy of the independent particle in predicting the ground state energy of the system. The results of this comparison in the cases of the atoms of Be and C have been discussed by Seitz (1940); the general conclusion is that the independent particle model's predictions of the cohesive energies of these atoms are wrong by about 0.5 eV. per electron of the atom.

The alkali metals, and in particular sodium, present a particularly favourable case for testing the accuracy of the independent particle model and assessing the importance of correlation effects. The reason for this is that the band structures of these metals can be said to be fairly well known. In fact, there are very good reasons for supposing that these band structures are fairly accurately given by formulae of the type

$$E_{\underline{k}} = E_0 + \frac{\hbar^2 k^2}{2m^*} \qquad (2.2)$$

where E_o is the energy of the state $\underline{k} = 0$, and m^* is an 'effective mass'; detailed calculations in the cases of Na (Howarth and Jones, 1952) and Li (Kohn and Rostocker, 1954) confirm this type of band structure. Further, the energy E_o can be calculated very accurately by the Wigner and Seitz cellular method, and m^* can be estimated by Bardeen's method (Bardeen, 1938).

The band structure represented by (2.2) is a free electron-like band structure, that is, its $\underline{k}$-dependence is of the same type as that of a free electron gas. It might therefore be expected that the correlation phenomena occurring in a metal with the band structure (2.2) would be rather similar to those occurring in a free electron gas. It is therefore of interest to consider the predictions of the Hartree-Fock scheme concerning the properties of a free electron gas, and to compare these predictions with the experimentally determined properties of the alkali metals. This is the subject of the next section.

§3 Correlation Phenomena in a Free Electron Gas.

In this context a 'free electron gas' will be taken to mean a system of electrons moving in a background of positive charge of just such a density as to render the system as a whole electrically neutral. This background will have no effect on the details of the motion of the electrons, but will serve to prevent the system from flying apart under the mutual repulsions of the electrons; it will also give a contribution

$e\phi$ (3.1)

to the potential energy of each electron, where ϕ is the (constant) potential due to the background of positive charge.

With the definition of a free electron gas just given, the Hamiltonian of the system will be just (1.1) with $U(\underline{r}) = e\phi$ = constant. In this case the Hartree-Fock equations (1.7) reduce to

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + e\phi + e^2\sum_j \int \frac{|\psi_j(\underline{r}')|^2}{|\underline{r}-\underline{r}'|}\,d\underline{r}'\right]\psi_i - e^2\sum_j \sum_{\underline{\sigma}'} \int \frac{\psi_j^*(\underline{r}',\underline{\sigma}')\,\psi_i(\underline{r}',\underline{\sigma}')}{|\underline{r}-\underline{r}'|}\,d\underline{r}'\,\psi_j = E_i\,\psi_i \tag{3.2}$$

It is not difficult to verify that the solutions of the equations (3.2) are just any set of free electron wave functions

$$\psi_i = e^{i\underline{k}_i\cdot\underline{r}}\,u_{s_i}(\underline{\sigma}_i) \tag{3.3}$$

multiplied by arbitary spin functions; here $\underline{\sigma}_i$ is the spin vector of the i th electron and $u_{s_i}(\underline{\sigma}_i)$ the spin function; s_i takes the values ± 1 corresponding to the two possible spin directions. In fact, if one substitutes (3.3) into (3.2), then one obtains

$$\left[\frac{\hbar^2 k_i^2}{2m} + e\phi + \sum_j \int \frac{e^2\,d\underline{r}'}{|\underline{r}-\underline{r}'|}\right]e^{i\underline{k}_i\cdot\underline{r}} - \sum_j \delta_{s_i s_j}\int \frac{e^{i(\underline{k}_i-\underline{k}_j)\cdot\underline{r}'}}{|\underline{r}-\underline{r}'|}\,d\underline{r}'\,e^{i\underline{k}_j\cdot\underline{r}} = E_i\,e^{i\underline{k}_i\cdot\underline{r}} \tag{3.4}$$

The second and third terms cancel as a consequence of the assumption that the background of positive charge is of such a density as to render the system electrically neutral. To evaluate the fourth term on the left one uses the well known Fourier expansion of $1/|\underline{r}-\underline{r}'|$:

$$\frac{1}{|\underline{r}-\underline{r}'|} = \sum_{\underline{k}} \frac{4\pi}{k^2} e^{i\underline{k}\cdot(\underline{r}-\underline{r}')} \tag{3.5}$$

This leads to the result

$$e^2 \int \frac{e^{i(\underline{k}_i-\underline{k}_j)\cdot\underline{r}'}}{|\underline{r}-\underline{r}'|} d\underline{r}' = \frac{4\pi e^2}{|\underline{k}_i-\underline{k}_j|^2} e^{i(\underline{k}_i-\underline{k}_j)\cdot\underline{r}} \tag{3.6}$$

for this term, and it is seen that (3.2) is satisfied provided

$$E_i = \frac{\hbar^2 k_i^2}{2m} - \sum_j \frac{4\pi e^2 \delta_{s_i s_j}}{|\underline{k}_i-\underline{k}_j|^2} \tag{3.7}$$

Thus it is possible to obtain an exact solution of the Hartree-Fock equations in the case of a free electron gas and these solutions are given by (3.3) and (3.7).

Having obtained these solutions, it is now possible to determine the properties of a free electron gas as predicted by the Hartree-Fock scheme and to compare these predictions with the observed properties of the alkali metals.

The first and most important of these properties is the cohesive energy of the system. As mentioned above, any set of free electron wave functions (3.3) will give a solution of (3.2); the case of principal interest is, however, the case in which these wave functions are chosen so that the system has the lowest possible energy, and this choice corresponds to a Fermi distribution in which all the states with k s less than a certain k_0 are occupied and all the other states are unoccupied; it will in future be assumed that this is the case being

dealt with unless otherwise indicated.

The cohesive energy of the system can be calculated by substituting the solutions (3.3) into (1.4), and (1.4) into (1.8). The result is

$$E = \sum_{\underline{k}} \frac{\hbar^2 k^2}{2m} - \sum_{\underline{k},\underline{k}'} \frac{2\pi e^2}{|\underline{k}-\underline{k}'|^2} \tag{3.8}$$

where the sums over $\underline{k}$ and $\underline{k}'$ range over the Fermi distribution. The first term represents the kinetic energy of the electrons and the second the 'exchange' energy. The sums over $\underline{k}$ and $\underline{k}'$ can be evaluated and give

$$-\frac{0.916}{r_s} \text{ Rhyd. per electron if } r_s \text{ is expressed in B.U.,} \tag{3.9}$$

where r_s is the mean inter-electronic distance defined by

$$\frac{4\pi}{3} r_s^3 = \frac{1}{n} \tag{3.10}$$

where n is the electronic density; r_s is related to the k_o of the Fermi by

$$k_o = \left(\frac{9\pi}{4}\right)\frac{1}{r_s} \tag{3.11}$$

To compare the cohesive energy calculated above with the experimentally determined cohesive energy of Na it is necessary to take into account the E_o in (2.2) and the fact that in Na the potential U is not actually uniform; the first factor gives an additional term nE_o in the cohesive energy, and the second factor gives rise to a 'Coulomb' term in the cohesive energy. When these corrections have been taken into account it is found that the calculated cohesive energy of Na actually

differs from the experimentally determined cohesive energy by a 'correlation' energy of about .064 Rhyd. per electron. This is a measure of the inaccuracy in the calculation of the cohesive energy on the basis of the independent particle model due to the neglect of correlation effects. It is seen that this correlation energy is about 1 eV. per electron, which is of about the same order as the corresponding effect in the atomic case.

The other properties of a free electron gas which will be investigated here are mainly concerned with the actual variation of $E_{\underline{k}}$ with $\underline{k}$ as given by (3.7). In the case when the electrons occupy a Fermi distribution the sum in (3.7) can be evaluated and gives

$$E_{\underline{k}} = \frac{\hbar^2 k^2}{2m} - \frac{e^2 k_0}{\pi}\left[2 + \frac{k_0^2 - k^2}{k_0 k} \log\left|\frac{k_0 + k}{k_0 - k}\right| \right] \qquad (3.12)$$

Several deductions can be made from this result. The most important of these is that the Hartree-Fock scheme predicts that, in a free electron gas, the density of states vanishes at the Fermi surface. In fact, a plot of the density of states curve for $r_s = 3.96$ B.U. (appropriate to Na) will be of the form shown in Fig.1.

The vanishing of the density of states at the Fermi surface in the Hartree-Fock scheme has a very profound effect upon the predictions of the theory concerning a number of important properties which depend critically upon this quantity. Amongst the more important of these quantities are the electronic specific heat, the spin paramagnetism and the conductivity. In fact, it has been shown by Wohlfarth (1950)

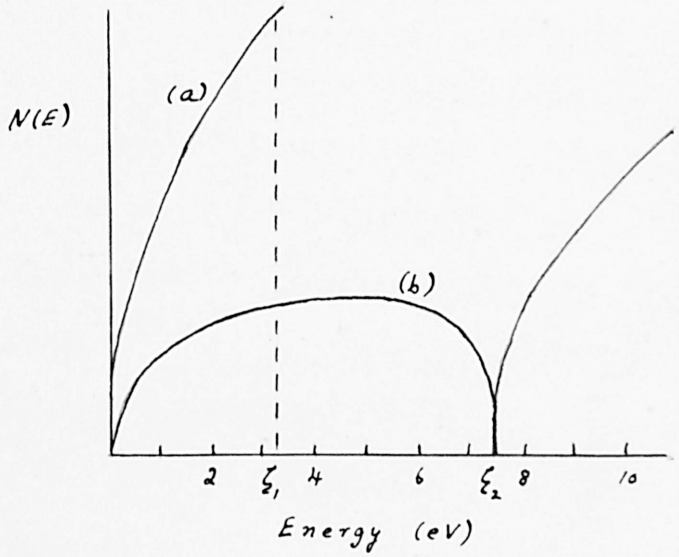


Fig. 1. Density of states curve for Na as predicted by the Hartree-Fock scheme (curve (b)). The curve (a) is the corresponding free electron curve without taking the exchange energy into account. The Fermi surfaces are at ζ_1 and ζ_2 respectively.

implied by (3.12) leads to a low temperature variation of the electronic specific heat according to a T/logT law (T is the absolute temperature); the experimentally determined low temperature specific heat actually varies linearly with T. In the same way the predictions of the Hartree-Fock scheme concerning the paramagnetism and conductivity are not borne out by experiment; it must therefore be conclude that the prediction of this scheme concerning the density of states at the Fermi surface is in poor agreement with experiment.

Two further predictions of the Hartree-Fock scheme concerning the soft X-ray emission spectrum of Na will finally be mentioned. It should first be noticed from Fig. 1 that the bandwidth of the conduction of Na predicted by the Hartree-Fock scheme is c. 7.5 eV.; this is actually about three times as large as the bandwidth of the conduction band of Na as determined from the X-ray emission spectrum. Finally, Landsberge (1949) found that the use of the Hartree-Fock scheme gave wrong predictions concerning the shape of the 'tail' of the X-ray emission spectrum of Na. He further suggested that this discrepancy would be removed if one arbitarily replaced the ordinary Coulomb interaction ($1/r$) between the electrons by a short range screened interaction of the form

$$\frac{e^{-\kappa r}}{r} \qquad (3.13)$$

The arbitary assumption of this interaction instead of the usual Coulomb interaction would also remove the difficulties concerning the density of states at the Fermi surface; it would not, however, lead to a correct value for the cohesive energy of metallic Na.

It can be concluded from the above discussion that, although the independent particle model usually leads to correct qualitative deductions concerning the properties of solids, when it is applied quantitatively it is unsatisfactory, at least in the case of the alkali metals, the only case in which a satisfactory quantitative test of the theory can be made.

§4 Previous Calculations of the Correlation Energy.

In the preceeding section it has been seen that the predictions of the independent particle model are often quantitatively incorrect as a result of the neglect of the correlations in the electronic motions brought about by the Coulomb interaction of the electrons. One of the properties of a metal which is incorrectly predicted by the Hartree-Fock scheme is the cohesive energy, and the difference between the actual cohesive energy and the cohesive energy predicted from the Hartree-Fock scheme has come to be called the correlation energy. There have been a number of attempts to calculate this energy previous to the plasma oscillation theory of Bohm and Pines with which the work of this thesis is mainly concerned, and two of them, the correlation energy calculation of Wigner (1934, 1938) and that of Macke (1950), will be briefly described in this section.

There is one case in which the correlation energy can be quite easily calculated. This is the case in which the electronic density and the kinetic energy of the electrons are low (if the electrons occupy a Fermi distribution a low density implies a low kinetic energy). In this case the most stable arrangement of the electrons is, according to Madelung type calculations (Madelung, 1909, 1910), a body-centred cubic lattice, and the corresponding energy of the system is (relative to a uniform distribution of negative charge of the same density)

$$-\frac{1.492}{r_s} \text{ Rhyd.} \qquad (4.1)$$

per electron. Of this energy, $0.916/r_s$ per electron is exchange energy according to (3.9), so that the correlation energy in this case must be just

$$-\frac{0.576}{r_s} \quad \text{Rhyd.} \tag{4.2}$$

per electron.

In Wigner's calculation this result is combined with a calculation (to be outlined shortly) of the correlation energy of a high density system of electrons to give an approximate interpolation formula

$$-\frac{0.576}{r_s+5.1} \quad \text{Rhyd.} \tag{4.3}$$

for the correlation energy per electron.

In Wigner's calculation of the correlation energy of a high density electron gas he only considered the correlations between the motions of the electrons with opposite spins. This is reasonable because the correlations in the motions of the electrons brought about by the exclusion principle (the Fermi hole) tend, in any case, to keep electrons with the same spin apart, so that the effect of the Coulomb repulsion in keeping them apart is much reduced, and the greater part of the correlation energy arises from the correlations in the motions of electrons with opposite spins.

If all the electronic states are doubly occupied (that is both the corresponding spin states are occupied), then in the Hartree-Fock

scheme, in calculating the energy of the system, the wave function (1.4) can be replaced by

$$\begin{vmatrix} \psi_1(\underline{r}_1) & \psi_2(\underline{r}_1) & \dots & \psi_{N/2}(\underline{r}_1) \\ \psi_1(\underline{r}_2) & \psi_2(\underline{r}_2) & \dots & \psi_{N/2}(\underline{r}_2) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \psi_1(\underline{r}_{\frac{N}{2}}) & \psi_2(\underline{r}_{\frac{N}{2}}) & \dots & \psi_{N/2}(\underline{r}_{\frac{N}{2}}) \end{vmatrix} \begin{vmatrix} \psi_1(\underline{s}_1) & \psi_2(\underline{s}_1) & \dots & \psi_{N/2}(\underline{s}_1) \\ \psi_1(\underline{s}_2) & \psi_2(\underline{s}_2) & \dots & \psi_{N/2}(\underline{s}_2) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \psi_1(\underline{s}_{\frac{N}{2}}) & \psi_2(\underline{s}_{\frac{N}{2}}) & \dots & \psi_{N/2}(\underline{s}_{\frac{N}{2}}) \end{vmatrix}$$

(4.4)

where the $\underline{r}_i$ s are the co-ordinates of the electrons with one spin and the $\underline{s}_i$ s are the co-ordinates of the electrons with the opposite spin direction. This wave function already includes (as (1.4) does) the correlations between the motions of the electrons brought about by the exclusion principle, but does not contain the correlations between the motions of electrons with opposite spins brought about by the Coulomb interaction. To include these latter correlations, Wigner generalised the wave function (4.4) to one of the form

$$\begin{vmatrix} \psi_1'(\underline{r}_1;\underline{s}_1,\underline{s}_2,\dots\underline{s}_{\frac{N}{2}}) & \dots & \psi_{N/2}(\underline{r}_1;\underline{s}_1,\dots\underline{s}_{\frac{N}{2}}) \\ \psi_1'(\underline{r}_2;\underline{s}_1,\underline{s}_2,\dots\underline{s}_{\frac{N}{2}}) & \dots & \psi_{N/2}(\underline{r}_2;\underline{s}_1,\dots\underline{s}_{\frac{N}{2}}) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \psi_1'(\underline{r}_{\frac{N}{2}};\underline{s}_1,\underline{s}_2,\dots\underline{s}_{\frac{N}{2}}) & \dots & \psi_{N/2}'(\underline{r}_{\frac{N}{2}};\underline{s}_1,\dots\underline{s}_{\frac{N}{2}}) \end{vmatrix} \begin{vmatrix} \psi_1(\underline{s}_1) & \dots & \psi_{N/2}(\underline{s}_1) \\ \psi_1(\underline{s}_2) & \dots & \psi_{N/2}(\underline{s}_2) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \psi_1(\underline{s}_{\frac{N}{2}}) & \dots & \psi_{N/2}(\underline{s}_{\frac{N}{2}}) \end{vmatrix}$$

(4.5)

in which the wave functions of the electrons with one spin depend parametrically upon the co-ordinates of the electrons of opposite spin. The independent electron wave functions ψ' and ψ could now be determined by the application of the variation principle (1.5). The wave functions thus obtained could then be substituted into (4.5) and the total energy calculated. Because of analytic difficulties in carrying through this calculation, Wigner restricted himself to the case of high electronic densities. He then constructed the formula (4.3) so that the correlation energy given by it joins smoothly to this result for high densities and to (4.2) for low densities.

Macke (1950) calculated the correlation energy of a free electron gas directly by treating the Coulomb interaction between the electrons as a perturbation and summing part of the perturbation series. The perturbation series for the energy of the ground state is just

$$E = E_0 + V_{00} + \sum_n{}' \frac{V_{0n} V_{n0}}{E_0 - E_n} + \sum_{n,n'}{}' \frac{V_{0n} V_{nn'} V_{n'0}}{(E_0 - E_n)(E_0 - E_{n'})} + \ldots \qquad (4.6)$$

where 0 is the ground state (the determinant of free electron wave functions corresponding to a Fermi distribution), n, n',... are excited states, and $V_{nn'}$ is the matrix element of the Coulomb interaction between the states n and n'.

The first term of (4.6) is just the kinetic energy of the electrons of the Fermi distribution in the absence of the interaction. Direct calculation of V_{00} shows that this term just coincides with the exchange energy of the electrons as calculated in §3. The remaining terms in the

series must, therefore, represent the correlation energy, and the leading term of this is the second order perturbation term. Unfortunately, however, it is found that when this second order term is calculated it diverges logarithmically. An important point which emerges from this calculation is that this divergence is actually due to the possibility of the system making virtual transitions from the ground state to excited states in which one electron is excited to a state just above the Fermi surface, and that the importance of such transitions arises from the long-range nature of the Coulomb interaction.

Since a finite result must evidently be obtained if the perturbation calculation is carried to an infinite order, Macke concluded that there must be terms amongst the higher order terms of the perturbation series which corrected the divergence of the second order term. He then went on to pick out these terms and to combine them with the second order term to obtain a finite result for the correlation energy which is in good agreement with Wigner's formula (4.3). He further showed that the same result could be obtained by assuming that the Coulomb interaction is replaced by an interaction of the form

$$\frac{e^{-\kappa r}}{r} \tag{4.7}$$

calculating the energy so far as the second order perturbation term, and then using the variational principle to find the best value for κ. He actually finds that this best value of κ is given by

$$\kappa = \frac{1}{r_s}\sqrt{\frac{e^2}{r_s}\Big/\frac{\hbar^2 k_0^2}{2m}} \tag{4.8}$$

The two most important correlation calculations previous to the theory of BP have been described above. Whilst there does not seem much doubt that the results which were obtained are substantially correct, these calculations do not fulfill all the requirements of useable theory of correlation phenomena. For, as has been pointed out in §2, whilst the independent particle model leads to quantitatively incorrect results, the general picture of the electronic motion which it presents is found to be in good agreement with the observed properties of solids. A complete theory of correlation effects should therefore show why this is so, and should in fact retain those features of the independent particle model (such as the zone scheme) which have been found to be in good agreement with experiment. However, the two calculations which have been described above are purely formal calculations of a particular quantity rather than theories giving a complete account of the correlation phenomena and showing how the independent particle aspects of the motion arise. The qualitative success of the independent particle model leads one to suspect that a theory of the required nature exists; such a theory has,

in fact, been developed recently, namely the plasma oscillation theory of Bohm and Pines, and this theory is the subject of the remainder of the present thesis.

CHAPTER TWO.

THE FREE ELECTRON GAS THEORY.

In this chapter, as a preliminary to the description of the work with which this thesis is mainly concerned, a description of the BP plasma oscillation theory of the free electron gas will be given. The description which will be given here is mainly concerned with the quantum mechanical version of the theory, as presented in BP 1953 and by Pines (1953), since space does not permit a description of the interesting classical versions of the theory.

§5 Introduction to the Plasma Oscillation Theory.

By a plasma is meant here a system which, whilst electrically neutral as a whole, is made up of positively and negatively charged particles. For example, a system consisting of electrons and positive ions, such as a metal, is a plasma; it is for this reason that the study of plasmas is of interest in the theory of solids.

Because it is made up of charged particles which are free to react to any electric field acting on them, a plasma exhibits certain characteristic electrical properties. Two of these are of particular interest. The first of these is the tendency of a plasma to remain field-free. This tendency arises from the fact that if some disturbance should generate an internal field in the plasma, then the charged particles will tend to move as a result of the action of the field on them in such a way as to screen

out this field (the field polarises the plasma). Because of the inertia of the particles this screening is not, however, instantaneous. Suppose some disturbance in the plasma creates an excess of positive charge in some region of the plasma; then this charge will attract the negatively charged particles and repel the positively charged particles; if the mean free path of the negative particles in the plasma is sufficiently long, then these particles will accelerate towards the disturbance and will then overshoot and move away from the disturbance again, recreating the original excess of positive charge, to which they will now again be attracted. In this way the initial disturbance will set up a sort of oscillation, the negative particles oscillating about the centre of the disturbance; exactly similar considerations hold for the positively charged particles. Thus it is possible to set up in a plasma certain types of oscillation, the so-called plasma oscillations. The possibility of sustaining such oscillations is the second of the characteristic properties of a plasma referred to above.

These plasma oscillations were first investigated (classically) by Tonks and Langmuir (1929), who found that, in a plasma made up of particles with mass m and charge e, in which the particle density is n, the long wave length oscillations had the frequency $(4\pi ne^2/m)^{1/2}$. Further investigations of the classical case by Bohm and Gross (1949) showed that if these oscillations were resolved into travelling waves with wave vectors $\underline{k}$, then the frequency of each wave was related to its wave vector by the dispersion relation

$$\omega_k^2 = \omega_p^2 + \overline{V^2} k^2 \qquad (5.1)$$

where $\overline{V^2}$ is the mean V^2 of the particles of the plasma. These authors also discussed the generation and damping of the plasma oscillations.

The more recent investigations of these oscillations have been carried out by Bohm and Pines (BP 1951, 1952, 1953; Pines, 1953). These investigations have shown that a fairly complete account of the phenomena brought about in a plasma by the long-range part of the Coulomb interaction can be given in terms of these oscillations. It is from this possibility that the importance of the theory of these oscillations in relation to correlation phenomena in electron gases arises.

These authors have also given a quantum mechanical version of the theory, and have used this theory to obtain a value for the correlation energy of a free electron gas and to investigate other correlation phenomena. It is this theory which forms the starting point for the work of this thesis, and which will be described in the remaining sections of this chapter.

Before going on to describe this theory in detail, a general picture of the behaviour of a plasma in terms of this theory will be given. According to the theory a plasma exhibits two types of behaviour simultaneously, on the one hand a medium-like behaviour as exemplified by the plasma oscillations, and on the other hand a particle-like behaviour similar to that of the particles of an ordinary gas. The

motion of each particle can, in fact, be regarded as made up of two components. One of these components of its motion is exactly similar to that of a particle in a gas of similar particles, all of which interact through a weak, screened interaction (the short-range part of the Coulomb interaction). Superposed on this component of the motion is the other, collective component, which consists of small oscillations at the plasma frequency. The oscillatory motions of all the electrons in any region are all in phase with one another and tend to maintain and reinforce each other through the long-range part of the Coulomb interaction. Thus it is to be expected that the plasma can be represented, at least approximately, by a system of particles interacting via a screened interaction together with a set of oscillators representing the plasma oscillations; this is, in fact, the description which was developed by BP, and the details of which are given in the remaining sections of this chapter.

§6 The Transition to the Collective Description of a Free Electron Gas.

In this and the following sections the free electron gas theory as developed by Bohm and Pines (Bohm and Pines, 1953; Pines, 1953) will be described. BP have called the description of a plasma in terms of its plasma oscillations the collective description of the system, since these oscillations are a result of the collective behaviour of the electrons. In this section the way in which the transition from the

ordinary description in terms of a set of particles interacting with one another via their Coulomb interactions to the collective description can be made in the quantum mechanical case will be described.

The system which will be dealt with here is a system consisting of N electrons moving in a background of positive charge of just such a density as to render the system as a whole electrically neutral, and interacting with one another via their Coulomb interactions. The Hamiltonian of such a system is (see (1.1))

$$H = \sum_i \frac{1}{2m} p_i^2 + \sum_{i \neq j} \sum_k \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{6.1}$$

Here the Coulomb interaction has been expanded in terms of its Fourier components according to (3.5). The Fourier component with $\underline{k} = 0$ just cancels the energy of the electrons due to their interaction with the positive background charge, and has therefore been omitted from the sum.

To separate the long- and short-range parts of the interaction, the Fourier series in (6.1) is now split into two parts, one part containing all the terms with $\underline{k}$ s such that $k < k_c$, where k_c is some suitable constant, and the other part containing all the remaining terms. The first part represents the long-range part of the interaction and the latter part the short-range part. In making the transition to the collective description it is only the first part which is transformed. It is convenient to include in the term representing the long-range part of the interaction also a term representing the long-range part of the Coulomb self-energies of the electrons and to subtract this

part out in an extra term. When all these changes have been carried through the Hamiltonian becomes

$$H = \sum_i \frac{1}{2m} p_i^2 + \sum_{i,j}{}' \sum_{k<k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + H_{s.r.} \tag{6.2}$$

where

$$H_{s.r.} = \sum_{i \neq j} \sum_{k>k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{6.3}$$

represents the short-range interaction.

In order to represent the plasma oscillations in terms of oscillators it is necessary to introduce suitable oscillator co-ordinates. In doing so no new degrees of freedom will be introduced, since at the same time a set of subsidiary conditions, equal in number to the number of oscillator co-ordinates introduced, will also be introduced. It is convenient to introduce these oscillator co-ordinates q_k and their conjugate momenta p_k formally by adding to the Hamiltonian (6.2) the terms

$$-\frac{1}{2} \sum_{k<k_c} p_k p_{-k} \tag{6.4}$$

and imposing the subsidiary conditions

$$p_k \Psi = 0 \quad , \quad k<k_c \tag{6.5}$$

on the wave functions.

The new Hamiltonian is

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i,j} \sum_{k<k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} - \sum_{k<k_c} \left(\frac{2\pi n e^2}{k^2} + p_k p_{-k} \right) + H_{s.r.} \,. \tag{6.6}$$

It follows at once from (6.5) that if Ψ is any eigenfunction of (6.6) satisfying (6.5), then Ψ is also an eigenfunction of (6.3) belonging to the same eigenvalue. Thus it is sufficient, in order to determine the eigenvalues and eigenfunctions of (6.3), to determine those of (6.6) which satisfy the condition (6.5).

The next step in the transition to the collective description is made by means of a unitary transformation,

$$O \rightarrow e^{-\frac{i}{\hbar}S} O e^{\frac{i}{\hbar}S} \tag{6.7}$$

where O is any operator and S is the function generating the transformation. In the present case the function S is chosen to be

$$S = -i \sum_i \sum_{k<k_c} \left(\frac{4\pi e^2}{k^2} \right)^{\frac{1}{2}} q_k e^{i\underline{k}\cdot\underline{r}_i} \tag{6.8}$$

The transformed operators may be conveniently evaluated by means of the expansion

$$e^{-\frac{i}{\hbar}S} O e^{\frac{i}{\hbar}S} = O + \frac{i}{\hbar}[O,S] + \frac{1}{2}\left(\frac{i}{\hbar}\right)^2 [[O,S],S] + \ldots \tag{6.9}$$

One finds, in fact, that the transformed operators are given by

$$\underline{r}_i \rightarrow \underline{r}_i \,, \qquad q_k \rightarrow q_k \tag{6.10a}$$

$$p_i \rightarrow p_i + \sqrt{4\pi e^2} \sum_{k<k_c} q_k \hat{\underline{k}} e^{i\underline{k}\cdot\underline{r}_i} \tag{6.10b}$$

$$p_k \rightarrow p_k - i\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}} \sum_i e^{i\underline{k}\cdot\underline{r}_i} \tag{6.10c}$$

Substituting these results into (6.6) and (6.5), the new Hamiltonian and subsidiary conditions become

$$H = \sum_i \frac{1}{2m}\left[p_i + \sqrt{4\pi e^2} \sum_{k<k_c} q_k \hat{\underline{k}} e^{i\underline{k}\cdot\underline{r}_i} \right]^2$$

$$- \tfrac{1}{2} \sum_{k<k_c} p_k p_{-k} - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + H_{s.r.} \tag{6.11}$$

and

$$\left[p_k - i\left(\frac{4\pi e^2}{k^2}\right)^{\frac{1}{2}} \sum_i e^{i\underline{k}\cdot\underline{r}_i} \right] \Psi = 0 \quad , \quad k < k_c \, . \tag{6.12}$$

The next, and final, step in the transition is the application of the so-called 'random phase approximation' (RPA for short). To do this it is first necessary to expand the brackets in the first term of (6.11). When this is done one obtains

$$H = \sum_i \frac{p_i^2}{2m} + \frac{\sqrt{4\pi e^2}}{m} \sum_i \sum_{k<k_c} \hat{k} \cdot (p_i - \tfrac{1}{2}\hbar k) q_k e^{ik \cdot r_i}$$

$$+ \frac{2\pi e^2}{m} \sum_i \sum_{k,k'<k_c} (\hat{k} \cdot \hat{k}') q_k q_{k'} e^{i(k+k') \cdot r_i}$$

$$- \frac{1}{2} \sum_{k<k_c} p_k p_{-k} - \sum_{k<k_c}' \frac{2\pi ne^2}{k^2} + H_{s.r.} \quad . \tag{6.13}$$

The RPA can now be applied to the third term of (6.13). In this term the sum over i reduces to a sum of the form

$$\sum_i e^{i(k+k') \cdot r_i} \tag{6.14}$$

If instead of a sum an integral were present here, the integral would reduce to 0 unless $k + k' = 0$. But, if k is short, corresponding to a wave length considerably greater than the inter-particle spacing (r_s), then this sum can to a good approximation be replaced by this integral. It has therefore to be concluded that, unless $k + k' = 0$, the sum (6.14) is small compared to the corresponding sum when $k + k' = 0$. The RPA consists of neglecting in the third term of (6.13) those terms in which $k + k' \neq 0$. This is obviously equivalent to the transition from a particle-like to a medium-like description, and is the real crux of the theory. That it is in the present case a valid approximation can be verified by using perturbation theory to calculate the contribution of the neglected terms to the energy; it is found that their contribution is indeed negligible.

When this approximation has been made the Hamiltonian (6.13) reduces to

$$H = \sum_i \frac{p_i^2}{2m} + \frac{\sqrt{4\pi e^2}}{m} \sum_i \sum_{k<k_c} \hat{k} \cdot (p_i - \tfrac{1}{2}\hbar k) q_k e^{ik \cdot r_i}$$

$$- \frac{1}{2} \sum_{k<k_c} \left(p_k p_{-k} + \frac{4\pi n e^2}{m} q_k q_{-k} \right) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + H_{s.r.} .$$

(6.15)

The various terms of this Hamiltonian have simple interpretations. The first term represents the kinetic energy of the electrons, the third is the Hamiltonian of a set of oscillators with frequency ω_p , the plasma oscillators, the second term represents an interaction between the particles and the oscillators, whose effects are to be studied shortly, and finally, the last term represents a screened interaction between the particles.

Suppose that for the moment the particle-oscillator interaction term and $H_{s.r.}$ are neglected. Then the Hamiltonian is separable, and the wave function of a stationary state of the system will be the product of an oscillator wave function and a particle wave function. Thus, in this approximation, the two types of behaviour, the collective behaviour represented by the oscillators, and the particle-like behaviour represented by the particles interacting via the screened interaction, have already been separated. In fact, the eigenfunction of (6.14) representing the oscillators in the ground state (this will be their usual state, since the quantum $\hbar\omega_p$ is of the order of several electron volts, much greater

than either $\varkappa T$ or the kinetic energy of an electron at the top of the Fermi distribution) and the particles in momentum states $\underline{k}_1, \underline{k}_2, \ldots$ will be, neglecting the short-range interaction and the particle-oscillator interaction

$$\Psi = \prod_{k<k_c} \exp\left\{-\frac{|p_k|^2}{2\hbar\omega_p}\right\} \cdot \begin{vmatrix} e^{i\underline{k}_1\cdot\underline{r}_1} & \cdots & e^{i\underline{k}_N\cdot\underline{r}_1} \\ \vdots & & \vdots \\ e^{i\underline{k}_1\cdot\underline{r}_N} & \cdots & e^{i\underline{k}_N\cdot\underline{r}_N} \end{vmatrix} \qquad (6.16)$$

This result is only obtained by making a number of approximations. The effect of $H_{s.r.}$ will be to modify the particle wave function; from Macke's calculations and those given later in the present chapter it seems that this effect can be adequately treated by means of perturbation theory. A further approximation is the neglect of the subsidiary conditions; it has, however, been shown by BP (1953) that if the wave function (6.15) is non-degenerate then it will automatically satisfy these conditions. This result applies particularly to the important case of the ground state wave function which is non-degenerate. The effects of the RPA are found by perturbation theory to be negligible. The last approximation was the neglect of the particle-oscillator interaction; the effects brought about by the inclusion of this interaction will next be investigated.

BP studied the effects brought about by the particle-oscillator interaction by making a further unitary transformation which eliminates the explicit

interaction and replaces it by terms which can easily be interpreted. The details of this calculation will not be given here since they are exactly similar to (and are, in fact, a special case of) a calculation performed in the next chapter. It is sufficient to say that a function S can be found having the property

$$\frac{i}{\hbar}[H_0, S] = -H_I \tag{6.17}$$

where

$$H_0 = \sum_i \frac{p_i^2}{2m} - \frac{1}{2}\sum_{k<k_c}\left(p_k p_{-k} + \omega_p^2 q_k q_{-k}\right) - \sum_{k<k_c}\frac{2\pi e^2}{k^2} \tag{6.18}$$

and

$$H_I = \frac{\sqrt{4\pi e^2}}{m}\sum_i\sum_{k<k_c}\hat{k}\cdot\left(p_i - \tfrac{1}{2}\hbar k\right) q_k\, e^{i\underline{k}\cdot\underline{r}_i} \tag{6.19}$$

and that this function generates the unitary transformation which is used.

If now the transformed Hamiltonian is calculated by means of the expansion (6.9), it is found, using (6.16), that it is given by

$$H \to H_0 - \frac{i}{2\hbar^2}[H_I, S] + \ldots \tag{6.20}$$

Thus the interaction H_I no longer appears in the Hamiltonian, but is replaced by other terms, the leading one being

$$-\frac{i}{2\hbar^2}[H_I, S] \tag{6.21}$$

This term clearly represents the effects of the interaction H_I ; fortunately its various terms, which can be calculated directly from H_I and S, are susceptible to simple interpretations once the RPA has been used. It is in fact, found that this term represents three effects:

(i) a change in the oscillator frequency; the new frequency of an oscillator with co-ordinate q_k is given by

$$1 = \frac{4\pi e^2}{m} \sum_i \frac{1}{\left(\omega - \frac{\hbar}{m} \underline{k} \cdot \underline{p}_i\right)^2 - \frac{\hbar^2 k^4}{4m^2}} \qquad (6.22)$$

where ω is the new frequency;

(ii) a change in the particle energy; an additional term

$$- \frac{n'}{3n} \sum_i \frac{p_i^2}{2m} \qquad (6.23)$$

appears in the Hamiltonian, where n' is the number of oscillators per unit volume ($= k_c^3/6\pi^2$); this term is clearly equivalent to a change in effective mass from m to

$$m^* = m\left(1 - \frac{n'}{3n}\right)^{-1} \qquad (6.24)$$

(iii) a long-range, but screened, velocity-dependent interaction between the particles of the form

$$- \frac{2\pi e^2}{m} \sum_{i \neq j} \sum_{k<k_c} \frac{(\hat{\underline{k}} \cdot \underline{p}_i)(\hat{\underline{k}} \cdot \underline{p}_j)}{\omega_p^2 + k^4 v^2} e^{i\underline{k} \cdot (\underline{r}_i - \underline{r}_j)} \qquad (6.25)$$

this interaction is very weak and can often be neglected.

The effects described above will be fairly small provided the parameter

$$\alpha = \left\langle \left(\frac{\underline{k} \cdot \underline{p}_i}{m\omega} \right)^2 \right\rangle_{AV.} \qquad (6.26)$$

is small; the smallness of this parameter is also the condition for the unitary transformation method of eliminating H_I used here to be successful. It is found in practice that for the cases of principal interest that α is between 1/16 and 1/20, and this is sufficiently small. In this case the effects arising from the higher order terms in the expansion (6.18) are negligible.

Thus after the elimination of H_I the Hamiltonian becomes

$$H = \sum_i \frac{p_i^2}{2m^*} - \frac{1}{2}\sum_{k<k_c} \left(p_k p_{-k} + \omega_k^2 q_k q_{-k} \right) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + H_{s.r.} + H_{r.p.} \qquad (6.27)$$

which is separable. Further, the transformation of the subsidiary conditions yields for the transformed subsidiary conditions

$$\sum_i \frac{1}{\omega_k^2 - \left[\frac{\hbar}{m} \underline{k} \cdot \underline{p}_i - \frac{\hbar k^2}{2m} \right]^2} e^{i\underline{k}\cdot\underline{r}_i} \Psi = 0 \quad , \quad k<k_c \qquad (6.28)$$

which affects only upon the particle co-ordinates. Thus a complete separation of the particle and collective aspects of the system has been achieved (as far as terms of the order α^2).

§7 The Collective Description.

As a result of a series of unitary transformations and a number of valid approximations, the problem of determining the eigenvalues of (6.1) has been reduced to that of determining the eigenvalues of (6.27) subject to the subsidiary conditions (6.28). The Hamiltonian (6.27) now provides

the collective description of the system; in this section the nature of this description will be discussed.

The essential feature of the Hamiltonian (6.27) is that it is separable into two parts, one part,

$$H_{osc.} = -\frac{1}{2}\sum_{k<k_c}\left(p_k p_{-k} + \omega_k^2 q_k q_{-k}\right) - \sum_{k<k_c}\frac{2\pi n e^2}{k^2} \tag{7.1}$$

being the Hamiltonian of the plasma oscillators, and the other part being the Hamiltonian

$$H_{part.} = \sum_i \frac{p_i^2}{2m^*} + H_{s.r.} + H_{r.p.} \tag{7.2}$$

of a system of particles interacting with one another via the interactions $H_{s.r.}$ (6.3) and $H_{r.p.}$ (6.25).

As a result of this separation it is permissible to treat the system as though it consisted of two systems, one consisting of the oscillators and the other of the particles. Because the quantum of energy $\hbar\omega$ of the oscillators is very large ($\sim$10 eV.), the system will tend to behave so far as a wide range of effects are concerned as though it consisted of just the particle part. For example, if any term is added into (6.1) representing some perturbation due to an external electric or magnetic field, then when the various unitary transformations have been performed, and the RPA applied, there will result additional terms in (6.27), one representing the interaction of the external field with the oscillators, and one representing its interaction with the particles. In general the

term representing the interaction with the oscillators will have little effect, since the energies of the lowest excited states of the oscillator system are so much above the energy of the ground state. Thus the system will tend to behave as though it consisted of just the particle part. There are, however, some phenomena in which the interaction with the oscillators is important, and these phenomena, to be discussed in §8, are of particular interest from the point of view of the present theory as confirming the general correctness of the theory and providing direct information concerning the actual plasma frequencies.

Since the oscillator system is easily understood, and in most applications it is the particle system which is important, the rest of this section will be devoted to the discussion of this system. The Hamiltonian (7.2) represents a system of particles of mass m^* interacting with one another through the interaction $H_{r.p.}$, which is very weak and will be neglected, and via the weak, screened interaction $H_{s.r.}$. But this system is just the same as that represented by (6.1) except that the Coulomb interaction has been replaced by a screened interaction, and the mass has been changed. Since the interaction is now weak and short-range, it is to be expected that the independent particle model discussed in the preceeding chapter may now be applied successfully to treat this system, since it was seen in §3 that most of the difficulties of this model when applied to metals arose from the long-range part of the interaction. Thus it is possible to show from the present theory that the independent particle model should give a good description of the behaviour of the

system provided that in this model the ordinary Coulomb interaction between the particles is replaced by a screened interaction. But this latter modification is just what was required in order to correct the wrong results obtained in the ordinary theory as a result of the use of the Hartree-Fock scheme. Thus the present theory gives a good account of the reasons for the success of the independent particle model, and shows how it should be corrected where it is wrong.

Apart from the phenomena to be discussed in § 8, there is one particular case in which the oscillator system cannot be ignored. This is in the calculation of the correlation energy. It was pointed out in § 3 that one of the difficulties in arbitarily postulating that the electrons interacted through a screened interaction was that this led to a wrong value for the cohesive energy. This difficulty is avoided in the present theory by taking into account the contribution to the ground state energy made by the zero-point energy of the plasma oscillators.

In calculating the ground state energy of the system it is permissible to neglect the subsidiary conditions and also to treat $H_{s.r.}$ as a perturbation. Because of the short-range nature of $H_{s.r.}$ this perturbation calculation will not meet with the difficulties encountered by Macke (see § 3) in treating the Coulomb interaction as a perturbation.

If the oscillator and particle systems are in their ground states, the ground state eigenfunction of (6.27) will be, neglecting $H_{s.r.}$,

$$\Psi = \prod_{k<k_c} \exp\left\{-\frac{|p_k|^2}{2\hbar\omega_k}\right\} \begin{vmatrix} e^{i\underline{k}_1\cdot\underline{r}_1} & \cdots & e^{i\underline{k}_1\cdot\underline{r}_N} \\ \vdots & & \vdots \\ e^{i\underline{k}_N\cdot\underline{r}_1} & \cdots & e^{i\underline{k}_N\cdot\underline{r}_N} \end{vmatrix} \tag{7.3}$$

where the $\underline{k}_i$ make up a Fermi distribution. The corresponding energy will be

$$E = \sum_i \frac{\hbar^2 k_i^2}{2m^*} - \sum_{k<k_c} \left\{\frac{\hbar\omega_k}{2} - \frac{2\pi ne^2}{k^2}\right\} \tag{7.4}$$

If now $H_{S.R.}$ is introduced as a perturbation, the first order perturbation term is found to be

$$-\sum_{\substack{i\neq j \\ |\underline{k}_i-\underline{k}_j|>k_c}}' \frac{2\pi e^2}{|\underline{k}_i-\underline{k}_j|^2} \tag{7.5}$$

This is just that part of the exchange energy (3.7) due to the short-range part of the Coulomb interaction.

The second order perturbation term will be the leading term of the correlation energy due to the short-range interaction. Its calculation involves only a slight modification of Macke's calculation (1950) and had been performed by Pines (1954). The result is finite, the divergence which appeared in Macke's calculation being due to the long-range part of the Coulomb interaction which is no longer present.

Thus the total energy of the system is given by

$$E = \sum_i \frac{\hbar^2 k_i^2}{2m^*} + \sum_{k<k_c} \left(\frac{\hbar\omega_k}{2} - \frac{2\pi n e^2}{k^2} \right) - \sum_{\substack{i,j \\ |\underline{k}_i - \underline{k}_j| > k_c}} \frac{2\pi e^2}{|\underline{k}_i - \underline{k}_j|^2} + \mathcal{E}_{corr.}^{(s.r.)} \qquad (7.6)$$

where $\mathcal{E}_{corr.}^{(s.r.)}$ is the short-range correlation energy.

Before direct calculations of the energy of the system can be made from this result it is first necessary to choose a value for k_c. k_c was a parameter introduced to separate the long- and short-range parts of the interaction, and its choice will effect the extent to which $H_{s.r.}$ is screened. An optimum choice of k_c can easily be determined using the variational principle (1.5); k_c can be regarded as a variational parameter in the expression (7.6) for the total energy of the system and can be determined by the requirement that it make the total energy a minimum.

Pines (1953) has made detailed numerical calculations of k_c and the energy given by (7.6) for electronic densities corresponding to those occurring in metals, and has obtained good agreement with Wigner's formula (4.3) for the correlation energy and with the experimentally determined cohesive energies of the alkali metals.

§8 The Small Angle Scattering of Fast Electrons.

It was mentioned in the preceeding section that there are certain phenomena in which the effects due to the oscillator part of the system are observable. The most important of these, apart from the calculation of the correlation energy, is the small angle, inelastic scattering of fast electrons in transversing a solid.

It was first observed by Ruthemann (1948) and Lang (1948) that if, when a beam of fast electrons is passed through a metal foil, those electrons which have undergone very small angle inelastic scattering are collected, then the resulting energy loss spectrum shows definite, very sharp peaks. The origin of these sharp peaks was difficult to understand because the only obvious scattering processes would be expected to give rather broad peaks if anything at all.

However, it will now be shown that the theory developed in this chapter gives a reasonable account of these peaks. They appear in the present theory as a result of the energy loss of an electron due to its interaction with the plasma oscillators. As these oscillators nearly all have the same frequency ω, they all give rise to energy losses in quanta of $\hbar\omega$, thus giving rise to a sharp peak in the energy loss spectrum.

A fast electron passing through the electron gas can be represented by the addition to (6.1) of terms of the form

$$\frac{1}{2m}\underline{P}^2 + \sum_i \frac{e^2}{|\underline{r}_i - \underline{R}|} = \frac{1}{2m}\underline{P}^2 + \sum_i \sum_k \frac{4\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{R})} \qquad (8.1)$$

where $\underline{P}$ is the momentum and $\underline{R}$ the position of the fast electron. When the first unitary transformation (6.7) is performed these terms will be unaffected; after the transformation it is possible to use the subsidiary conditions (6.12) to transform those terms with $k < k_c$ in (8.1). When this is done one obtains in (6.27) the additional terms (neglecting

the second unitary transformation which only gives rise to small effects)

$$\frac{1}{2m}\underline{P}^2 + \sum_{k<k_c}\left(\frac{4\pi e^2}{k^2}\right)^{1/2} \rho_k e^{-i\underline{k}\cdot\underline{R}} + \sum_i \sum_{k>k_c} \frac{4\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{R})} \tag{8.2}$$

The last term of (8.2) represents a short-range interaction between the fast electron and the electrons of the gas, and will give rise to mainly large angle scattering of the fast electron. The second term represents an interaction between the fast electron and the plasma oscillators, and it is this term which gives rise to the small angle inelastic scattering of the electrons. It will be seen that this term, regarded as a perturbation, gives rise to transitions of the system in which an oscillator is excited from the ground state to its first excited state, taking up energy $\hbar\omega$ from the fast electron, and in which the electron is scattered from the state with momentum $\underline{P}$ to a state with momentum $\underline{P} - \hbar\underline{k}$. Since $k < k_c$, $\hbar\underline{k}$ will be small compared to $\underline{P}$ and the electron will only be scattered through a small angle as stated. Since the energy of the electron is absorbed in quanta of $\hbar\omega$ in such processes, there will be a sharp peak in the energy loss spectrum at this energy, and at multiples of this energy.

The mean free path for energy loss by this process can be calculated directly from (8.2) using the usual perturbation theoretic methods. The result is that the rate of energy loss per unit path length of a fast electron with velocity v is

$$\frac{2\pi ne^4}{mv^2} \log \frac{k_c^2 m^2 v^2}{\omega^2}$$

(8.3)

It has been verified experimentally in a number of cases (in particular Be and Al) that the observed peaks in the energy loss spectra are at about the energy $\hbar\omega$ as predicted above, and the correctness of the result (8.3) for the mean free path for energy loss by this mechanism has also been verified in these cases. In other cases, however, much more complicated energy loss spectra than those predicted by the above theory have been obtained experimentally. The interpretation of these more complex spectra will be returned to in Chapter Four.

CHAPTER THREE.

THE EFFECTIVE MASS TREATMENT.

It has been seen in the preceeding chapter that Bohm and Pines' plasma oscillation treatment gives a good account of correlation phenomena in a free electron gas. The principal interest in this treatment from the point of view of the theory of solids lies in its application to correlation phenomena in the conduction bands of metals. However, a free electron gas is only a very idealised model of a conduction band. Nevertheless, it seems evident that some treatment closely analagous to the free electron gas treatment can be given for the electrons of a conduction band; the construction of such a treatment has been the main aim of the work to be described in this thesis.

In a metal there are two main additional effects which are not represented in the free electron gas model. The first of these is the presence of the periodic potential field. This field has a profound effect upon the electronic motion in a metal, and can be expected to modify such phenomena as the plasma oscillations very considerably in many cases. The second additional effect is the presence of the ion cores. It might be expected that these ion cores will be polarised by the electric fields associated with the plasma oscillations and will thereby exert an influence on them.

The attempts to generalise BP's free electron gas treatment to the

case of the electrons in a metal have followed two main lines. The first and earlier of these lines, which has been developed by the present author (Hubbard, 1954) and others (Adams, 1955; Kanazawa, 1955) makes use of the so-called 'effective mass equation'. Essentially what is done is to transform the Hamiltonian (1.1) into the corresponding Hamiltonian in Adams' crystal momentum representation (Adams 1952, 1953). In this representation the Hamiltonian assumes a form very similar to the Hamiltonian (6.1) of a free electron gas, and it is possible to proceed to the collective description along lines very similar to those of § 6. In this chapter a description of the simple version of this theory developed by the present author will be given.

The second approach to the generalisation of BP's theory has been through the 'dielectric' treatments. These treatments arise from the recognition that BP's free electron gas treatment is really equivalent in essentials to treating the long-range part of the electron-electron interaction as though the gas were a homogeneous dielectric medium possessing the dielectric properties appropriate to a free electron gas. When this is recognised it is at once evident that the theory can be generalised so as to apply to a solid by merely treating the long-range interaction in the solid as though the solid were a dielectric medium with the appropriate dielectric properties. This approach enables one to give a much more general and complete treatment than is possible through the effective mass treatments, and will be developed in chapters four.

§9 The Transformation to the Crystal Momentum Representation.

In the remainder of this chapter a simple version of the effective mass treatment will be described. This treatment will only apply to the case in which only one of the Brillouin zones is occupied, and even then will neglect the sometimes important inter-zone transitions (see §14). Nevertheless, the treatment developed here illustrates the main features of the effective mass treatments, and the extension of the theory developed here to cover more general cases is very straightforward, if somewhat cumbersome.

The general problem is that of determining the eigenvalues and eigenfunctions of the Hamiltonian (1.1). It will be assumed for the purpose of the present treatment that the solutions of the corresponding independent particle problem, namely the solutions of the Hartree-Fock equations (1.7), are already known.

The first step in the treatment is to transform the Hamiltonian (1.1) to the corresponding Hamiltonian in the crystal momentum representation. In making this transformation it is not very convenient to transform the short-range part of the interaction. It is therefore necessary to separate the long- and short-range parts of the interaction before making the transformation. This is done in the same way as in the free electron gas case by expanding the interaction term of (1.1) in Fourier series according to (3.5). It is now found that the term with $\underline{k}=0$ in this expansion just cancels with $n\overline{U}$, where $\overline{U}$ is the mean strength of the potential field $U(\underline{r})$ (the term with $\underline{k}=0$ in the

Fourier expansion of $U(\underline{r})$) and n is the electronic density, as a consequence of the electrical neutrality of the system as a whole; carrying out this cancellation and writing $U'(\underline{r}) = U(\underline{r}) - \overline{U}$, the Hamiltonian (1.1) now becomes

$$H = \sum_i \left[\frac{p_i^2}{2m} + U'(\underline{r}_i) \right] + \sum_{i \neq j} \sum_{k}{}' \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{9.1}$$

where the prime on $\sum_k{}'$ means omit the term with $\underline{k} = 0$ in the summation.

To separate the long- and the short-range parts of the interaction, the interaction term is split into two parts in exactly the same way as in the free electron case (see 6); this gives

$$H = \sum_i \left[\frac{p_i^2}{2m} + U'(\underline{r}_i) \right] + \sum_{i \neq j} \sum_{k<k_c}{}' \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} + H_{s.r.} \tag{9.2}$$

where

$$H_{s.r.} = \sum_{i \neq j} \sum_{k>k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{9.3}$$

is the short-range part of the interaction. It is hoped that it will be possible as in the free electron case to choose k_c in such a way that $H_{s.r.}$ represents a weak, short-range interaction which can be treated as a perturbation. If this is so, this term may be dropped from the Hamiltonian, the effects brought about by it being afterwards investigated by means of perturbation theory. The Hamiltonian then becomes

$$H = \sum_i \left[\frac{p_i^2}{2m} + U'(\underline{r}_i) \right] + \sum_{i \neq j} \sum_{k<k_c}{}' \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{9.4}$$

and this is the Hamiltonian which will be transformed.

The present treatment is restricted to the case in which the conduction electrons occupy only one Brillouin zone (in the reduced zone scheme) and does not contemplate the possibility of inter-zone transitions to other zones. With these restrictions it is only necessary in the present treatment to consider the Bloch wave functions $\psi_{\underline{k}}$ belonging to one zone; these wave functions will have the form

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u_{\underline{k}}(\underline{r}) \tag{9.5}$$

and will satisfy the Schrödinger equation

$$H_0(\underline{p},\underline{r})\,\psi_{\underline{k}} \equiv \left[\frac{p^2}{2m} + U'(\underline{r})\right]\psi_{\underline{k}} = E(\pm\underline{k})\,\psi_{\underline{k}} \tag{9.6}$$

where $E(\pm\underline{k})$ is the corresponding energy.

If the interaction between the electrons were neglected, then an eigenfunction of (9.4) would have the form (neglecting also the exclusion principle)

$$\Phi_0 = \psi_{\underline{k}_1}(\underline{r}_1)\, u_{s_1}(\underline{\sigma}_1)\, \psi_{\underline{k}_2}(\underline{r}_2)\, u_{s_2}(\underline{\sigma}_2) \cdots \psi_{\underline{k}_n}(\underline{r}_n)\, u_{s_n}(\underline{\sigma}_n) \tag{9.7}$$

where $\underline{\sigma}_i$ is the spin vector of the i th electron, $(\underline{k}_1, s_1)$, $(\underline{k}_2, s_2)$, ... $(\underline{k}_n, s_n)$ are the wave vectors and spin numbers ($s_i = \pm 1$) of the occupied states, and the $u_{s_i}(\underline{\sigma}_i)$ s are the spin functions.

(9.7) can be written in another way which is instructive for the present purpose. To do this it is necessary to introduce the Wannier

functions (Wannier, 1937)

$$\varphi(\underline{r}) = N^{-\frac{1}{2}} \sum_{\underline{k}}' \psi_{\underline{k}}(\underline{r}) \tag{9.8}$$

where the sum runs over the whole Brillouin zone. These functions have two important properties; the first is that any Bloch wave function can be expanded in terms of the $\varphi(\underline{r} - \underline{R})$ s, where $\underline{R}$ is a lattice vector, according to

$$\psi_{\underline{k}}(\underline{r}) = N^{-\frac{1}{2}} \sum_{\underline{R}}' e^{i\underline{k}\underline{R}} \varphi(\underline{r}-\underline{R}) \tag{9.9}$$

the second property is that they have the orthonormality property

$$\int \varphi^*(\underline{r}-\underline{R}) \varphi(\underline{r}-\underline{R}') \, d\underline{r} = \delta(\underline{R}-\underline{R}') \tag{9.10}$$

Using (9.9), the wave function (9.7) can be written in the form

$$\Phi = \sum_{\underline{R}_1, \underline{R}_2, \ldots \underline{R}_n} \sum_{\alpha_1, \alpha_2, \ldots \alpha_n} \left\{ e^{i(\underline{k}_1 \cdot \underline{R}_1 + \underline{k}_2 \cdot \underline{R}_2 + \ldots + \underline{k}_n \cdot \underline{R}_n)} \delta_{\alpha_1 s_1} \delta_{\alpha_2 s_2} \ldots \delta_{\alpha_n s_n} \right\}$$

$$\times \varphi(\underline{r}_1 - \underline{R}_1) \varphi(\underline{r}_2 - \underline{R}_2) \ldots \varphi(\underline{r}_n - \underline{R}_n)$$

$$\times u_{\alpha_1}(\underline{\sigma}_1) u_{\alpha_2}(\underline{\sigma}_2) \ldots u_{\alpha_n}(\underline{\sigma}_n) \tag{9.11}$$

This expression for the wave function Φ_0 is of interest because it is of the form

$$\Phi_0 = \sum_{\underline{R}_1, \ldots \underline{R}_n} \sum_{\alpha_1, \ldots \alpha_n} \mathcal{F}(\underline{R}_1, \ldots \underline{R}_n; \alpha_1, \ldots \alpha_n) \varphi(\underline{r}_1 - \underline{R}_1) \ldots \varphi(\underline{r}_n - \underline{R}_n) u_{\alpha_1}(\underline{\sigma}_1) \ldots u_{\alpha_n}(\underline{\sigma}_n) \tag{9.12}$$

with

$$\Psi = e^{i(\underline{k}_1\cdot\underline{R}_1 + \cdots + \underline{k}_n\cdot\underline{R}_n)}\,\delta_{\alpha_1 s_1}\,\delta_{\alpha_2 s_2}\cdots\delta_{\alpha_n s_n} \qquad (9.13)$$

which is just the wave function of a free electron gas when the interactions between the electrons are neglected. This suggests that if now Φ is an eigenfunction of (9.4) when the interaction between the electrons is taken into account, then when it is expanded according to (9.12), the function Ψ obtained may resemble the BP wave function for a free electron gas; this is, in fact, found to be so.

Let Φ be any eigenfunction of (9.4) belonging to the energy E, and suppose that it can be expanded in the form

$$\Phi = \sum_{\underline{R}_1,\ldots\underline{R}_n}\ \sum_{\alpha_1,\ldots\alpha_n} \Psi(\underline{R}_1,\ldots\underline{R}_n;\alpha_1,\ldots\alpha_n)\,\varphi(\underline{r}_1-\underline{R}_1)\cdots\varphi(\underline{r}_n-\underline{R}_n)\,u_{\alpha_1}(\underline{\sigma}_1)\cdots u_{\alpha_n}(\underline{\sigma}_n) \qquad (9.14)$$

where Ψ is some as yet unknown function. The assumption that it can be expanded in this way is the main restriction of the present theory, since it implies that all the electrons belong to the Brillouin zone corresponding to the Wannier function $\varphi(\underline{r})$, and does not allow the possibility of inter-zone transitions to be taken into account.

Since Φ satisfies the equation $H\Phi = E\Phi$, will satisfy some corresponding equation. This equation is quite easily derived using the method given in the Appendix to Slater's paper (1949); it is only necessary to multiply $(H - E)\Phi = 0$ by

$$\varphi^*(\underline{r}_1-\underline{R}_1')\cdots\varphi^*(\underline{r}_n-\underline{R}_n')\,u^*_{\alpha_1'}(\underline{\sigma}_1)\cdots u^*_{\alpha_n'}(\underline{\sigma}_n)$$

and integrate over the co-ordinates $\underline{r}_i$ and sum over the spin co-ordinates $\underline{\sigma}_i$. One thus obtains on carrying out the spin summation

$$\sum_{\underline{R}_1,\underline{R}_2,\ldots\underline{R}_n} \Psi(\underline{R}_1,\ldots\underline{R}_n;\alpha_1',\ldots\alpha_n') \int \varphi^*(\underline{r}_1-\underline{R}_1')\ldots\varphi^*(\underline{r}_n-\underline{R}_n')$$

$$\times\left[-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_{i\neq j}\sum_{k<k_c}\frac{2\pi e^2}{k^2}e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)} - E\right]\varphi(\underline{r}_1-\underline{R}_1)\ldots\varphi(\underline{r}_n-\underline{R}_n)$$

$$\times\ d\underline{r}_1 d\underline{r}_2\ldots d\underline{r}_n$$

$$= 0$$

(9.15)

Using the orthonormality properties (9.10), the last term in square brackets gives a contribution $E\,\Psi(\underline{R}_1',\underline{R}_2',\ldots\underline{R}_n';\alpha_1',\alpha_2',\ldots\alpha_n')$. The contribution from the second term in square brackets is also easily calculated. Because this term represents the long-range part of the interaction it is a 'slowly varying' function in the sense of Slater's paper; because it is slowly varying this term hardly affects the orthogonality of the Wannier functions in the integration and one has

$$\int\varphi^*(\underline{r}_i-\underline{R}_i')\varphi^*(\underline{r}_j-\underline{R}_j')e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\varphi(\underline{r}_i-\underline{R}_i)\varphi(\underline{r}_j-\underline{R}_j)\,d\underline{r}_i d\underline{r}_j \approx e^{i\underline{k}\cdot(\underline{R}_i-\underline{R}_j)}\delta(\underline{R}_i-\underline{R}_i')\delta(\underline{R}_j-\underline{R}_j') \tag{9.16}$$

Using this and the orthogonality properties (9.10), the second term in square brackets of (9.15) gives

$$\sum_{i\neq j}\sum_{k<k_c}\frac{2\pi e^2}{k^2}e^{i\underline{k}\cdot(\underline{R}_i'-\underline{R}_j')}\Psi(\underline{R}_1',\ldots\underline{R}_n';\alpha_1',\ldots\alpha_n') \tag{9.17}$$

The contribution from the first term in the square brackets of (9.15) can be calculated by the method used in the Appendix to Slater's paper (1949); the result is

$$\sum_i E\left(\frac{\hbar}{i}\frac{\partial}{\partial\underline{R}_i'}\right)\Psi(\underline{R}_1',\ldots\underline{R}_n';\alpha_1',\ldots\alpha_n') \tag{9.18}$$

where $E(\hbar \underline{k})$ is given by (9.6).

Combining all these results, it is seen that Ψ satisfies the 'effective mass' equation

$$\left[\sum_i E(\underline{p}_i) + \sum_{i \neq j} \sum_{k<k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \right] \Psi = E \Psi \tag{9.19}$$

where small $\underline{r}_i$ s have been written in place of the $\underline{R}_i$ s, and $\underline{p}_i$ has been written in place of $(\hbar/i)(d/d\underline{r}_i)$; $\underline{p}_i$ and $\underline{r}_j$ satisfy the usual commutation relations

$$[\underline{p}_i, \underline{r}_j] = \frac{\hbar}{i} \delta_{ij} \underline{I} \tag{9.20}$$

between canonically conjugate variables.

It should be noticed that $\Psi(\underline{r}_i)$ is only defined when $\underline{r}_i$ = lattice vector; in this connection the following remarks concerning the interpretation of the operator $\underline{p}_i$ should be noted. It is not at once obvious what is meant by the application of the differential operator $E(\underline{p})$ to a function which is defined only for discrete values of the argument $\underline{r}$ ($\underline{r}$ = lattice vector). The essential point is, however, that $E(\hbar\underline{k})$ is regarded as a periodic operator in $\underline{k}$-space having the periodicity of the reciprocal lattice; this is not in contradiction to the definition of $E(\hbar\underline{k})$ by (9.6) since this only defines E within the first Brillouin zone; this definition has, in fact, been continued throughout the whole of $\underline{k}$-space by the periodicity requirement. If now $E(\underline{p})$ is expanded in Fourier series, since it is periodic, the expansion will have the form

$$E(\underline{p}) = \sum_{\underline{R}}' E_{\underline{R}} \exp\left\{ \frac{i}{\hbar} \underline{R} \cdot \underline{p} \right\} \tag{9.21}$$

where the $\underline{R}$ s are lattice vectors. If $E(\underline{p})$ is now applied to a function $F(\underline{r})$ of $\underline{r}$, then one has from (9.21)

$$E(\underline{p})\,F(\underline{r}) = \sum_{\underline{R}} E_{\underline{R}}\, \exp\left\{\underline{R}\cdot\frac{d}{d\underline{r}}\right\} F(\underline{r})$$

$$= \sum_{\underline{R}} E_{\underline{R}}\, F(\underline{r}+\underline{R}) \qquad (9.22)$$

where use has been made of the result, derived from the Taylor's theorem expansion of $F(\underline{r}+\underline{R})$,

$$\exp\left\{\underline{x}\cdot\frac{d}{d\underline{r}}\right\} F(\underline{r}) = F(\underline{r}+\underline{x}) \qquad (9.23)$$

(this result was used to derive (9.18)).

If $\underline{r}$ = lattice vector, then the right hand side of (9.22) only involves the values of $F(\underline{r})$ at the points $\underline{r}$ = lattice vector, and is meaningful although $F(\underline{r})$ is only defined at such points; thus a definite meaning is given to $E(\underline{p})F(\underline{r})$ when $\underline{r}$ = lattice vector, the only case of interest. All the operators involving $\underline{p}$ which are used in the following sections are derived from $E(\underline{p})$ and are also periodic, and their application to $\mathcal{Y}$ is therefore meaningful. One could, in fact, have written all the work of this and the following sections in terms of expansions of the same type as that appearing on the right hand side of (9.22) and dispense with the operator $\underline{p}$ altogether; one would then obtain exactly the same results, but written in a more cumbersome notation. Thus it may be concluded that although $\mathcal{Y}$ is defined only for discrete values of its arguments, one may work quite safely with

the operators $\underline{p}$ provided that it is always borne in mind in interpreting any result that it has the meaning given by an equation of the type (9.22).

Thus it is seen that if Φ is an eigenfunction of the H of (9.4) belonging to the eigenvalue E, then the corresponding Ψ of (9.14) satisfies the eigenvalue equation (9.19), the eigenvalue again being E. Thus the operator

$$H = \sum_i' E(p_i) + \sum_{i \neq j}' \sum_{k<k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{9.24}$$

can be regarded as the Hamiltonian in the new representation.

The Hamiltonian (9.24) bears a close resemblance to the free electron gas Hamiltonian (6.1), and one can now proceed to the collective description along the lines of § 6; it is for this reason that the transformation to the crystal momentum representation is useful.

There is one further point which has to be considered. Electrons satisfy the exclusion principle and it is therefore required that be antisymmetric against the interchange of any pair of electronic ordinates $(\underline{r}_i, \sigma_i)$, $(\underline{r}_j, \sigma_j)$; this imposes on Ψ the condition that it also be antisymmetric against any similar interchange of co-ordinates as is easily seen from (9.14).

To summarise, within the restricted form of the theory developed here, it is sufficient, in order to determine the eigenvalues of and eigenfunctions of (1.1) satisfying the exclusion principle, to determine the eigenvalues and eigenfunctions of (9.24) satisfying the exclusion principle, when the eigenvalue of (1.1) will be that of

(9.24) and the eigenfunction of (1.1) will be given in terms of that of (9.24) by (9.14).

§10 The Transition to the Collective Description.

Having now obtained the Hamiltonian (9.24) in a form analagous to (6.1), one can proceed to the collective description along the lines of §6, generalising the theory of §6 everywhere to cover the present case.

If one adds the terms (6.4) to the Hamiltonian (9.24), imposes on $\mathcal{Y}$ the subsidiary conditions (6.5), and makes the unitary transformation generated by (6.8), then, using (6.10), one obtains the transformed Hamiltonian

$$H = \sum_i T_i + \sum_{k<k_c} \tfrac{1}{2} v_k (\rho_k \rho_{-k} - N) + \sum_{i<j} \sum_{k<k_c} v_k \left(e^{i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)} - 1 \right) \tag{10.1}$$

analagous to (6.11), and the same transformed subsidiary conditions (6.12) as in the free electron case.

The next step is to apply the RPA. In order to do this it is necessary to expand the first term of (10.1) in powers of q_k. This is not straightforward on account of the lack of commutativity of the terms in curly brackets. However, the effect of the unitary transformation on $E(\underline{p})$ can be alternatively evaluated using the expansion (6.9); when this is done the transformed $E(\underline{p})$ is obtained in the form of an expansion in powers of the q_ks since S is linear in the q_k. The expansion obtained is

$$E\left\{ p_i + \sqrt{4\pi e^2} \sum_{k<k_c} \hat{k}\, q_k e^{i\underline{k}\cdot\underline{r}_i} \right\} = E(p_i)$$

$$+ \sqrt{4\pi e^2} \sum_{k<k_c} M_1(p_i;\underline{k})\, q_k\, e^{i\underline{k}\cdot\underline{r}_i}$$

$$+ \frac{4\pi e^2}{2!} \sum_{k,k'<k_c} M_2(p_i;\underline{k},\underline{k}')\, q_k q_{k'}\, e^{i(\underline{k}+\underline{k}')\cdot\underline{r}_i}$$

$$+ \frac{(4\pi e^2)^{3/2}}{3!} \sum_{k,k',k''<k_c} M_3(p_i;\underline{k},\underline{k}',\underline{k}'')\, q_k q_{k'} q_{k''}\, e^{i(\underline{k}+\underline{k}'+\underline{k}'')\cdot\underline{r}_i}$$

$$+ \quad \ldots \qquad (10.2)$$

where evaluation of the commutators shows that

$$M_1(p;\underline{k}) = \frac{1}{\hbar k}\left\{ E(p) - E(p-\hbar\underline{k}) \right\} = \hat{k}\cdot\left\{ \nabla E(p) - \tfrac{\hbar}{2}\underline{k}\cdot\nabla\nabla E(p) + \ldots \right\} \qquad (10.3a)$$

$$M_2(p;\underline{k},\underline{k}') = \frac{1}{\hbar^2 k k'}\left\{ E(p) - E(p-\hbar\underline{k}) - E(p-\hbar\underline{k}') + E(p-\hbar\underline{k}-\hbar\underline{k}') \right\}$$

$$= (\hat{k}\cdot\nabla)(\hat{k}'\cdot\nabla) E(p) + \ldots$$

$$M_3(p;\underline{k},\underline{k}',\underline{k}'') = \frac{1}{\hbar^3 k k' k''}\left\{ E(p) - E(p-\hbar\underline{k}) - E(p-\hbar\underline{k}') - E(p-\hbar\underline{k}'') \right. \qquad (10.3b)$$

$$\left. + E(p-\hbar\underline{k}-\hbar\underline{k}') + E(p-\hbar\underline{k}-\hbar\underline{k}'') + E(p-\hbar\underline{k}'-\hbar\underline{k}'') - E(p-\hbar\underline{k}-\hbar\underline{k}'-\hbar\underline{k}'') \right\}$$

$$= (\hat{k}\cdot\nabla)(\hat{k}'\cdot\nabla)(\hat{k}''\cdot\nabla) E(p) + \ldots$$

(10.3c)

and the general law of formation of the $M_n(\underline{p}, \underline{k}, \underline{k}', \ldots)$ can be inferred.

Using (10.2) the transformed Hamiltonian can now be written

$$H = \sum_i E(\underline{p}_i) + \sqrt{4\pi e^2} \sum_{i,k<k_c} M_1(\underline{p}_i;\underline{k}) q_k e^{i\underline{k}\cdot\underline{r}_i}$$

$$+ \frac{4\pi e^2}{2!} \sum_{i,k,k'<k_c} M_2(\underline{p}_i;\underline{k},\underline{k}') q_k q_{k'} e^{i(\underline{k}+\underline{k}')\cdot\underline{r}_i}$$

$$+ \frac{(4\pi e^2)^{3/2}}{3!} \sum_{i,k,k',k''<k_c} M_3(\underline{p}_i;\underline{k},\underline{k}',\underline{k}'') q_k q_{k'} q_{k''} e^{i(\underline{k}+\underline{k}'+\underline{k}'')\cdot\underline{r}_i} + \ldots$$

$$- \frac{1}{2} \sum_{k<k_c} \rho_k \rho_{-k} - \sum_{k<k_c} \frac{2\pi n e^2}{k^2}$$

(10.4)

The RPA can now be applied to the terms of (10.4) involving $M_2, M_3, \ldots$ Each of these terms involves a sum over the i s of the type

$$\sum_i e^{i(\underline{k}+\underline{k}'+\ldots)\cdot\underline{r}_i}$$

(10.5)

which is of the same form as (6.14). In the case of (6.14) it was deduced that the sums of this form with $\underline{k} + \underline{k}' + \ldots \neq 0$ were negligible compared to those for which $\underline{k} + \underline{k}' + \ldots = 0$. In the present case one has to be a little more careful since the $\underline{r}_i$ s no longer range over all space but can only take the values $\underline{r}_i$ = lattice vector. In the case of (6.14) the RPA was deduced by noticing that the sum (6.14) was to a good approximation equal to the integral

$$n \int e^{i(\underline{k}+\underline{k}'+\ldots)\cdot\underline{r}} d\underline{r}$$

if $\underline{k}$ was small. In the present case the corresponding argument is that

the sum (10.5) is to a good approximation equal to the sum

$$\sum_{\underline{R}}' e^{i(\underline{k}+\underline{k}'+\ldots)\cdot\underline{R}}$$

if $\underline{k}$ is small. But this sum vanishes unless $\underline{k} + \underline{k}' + \ldots = \underline{K}$, where $\underline{K}$ is a reciprocal lattice vector. Thus it can be concluded in the present case that the sums of the form (10.5) for which $\underline{k} + \underline{k}' + \ldots \neq \underline{K}$ are negligible compared to those for which the equality holds.

In the present treatment since only the electrons occupying one zone are being dealt with it is almost certain that $k_c < \frac{1}{2} K_{min}$, where K_{min} is the shortest of the reciprocal lattice vectors apart from $\underline{K} = 0$. If this is so, then in the case of the term of (10.4) involving M_2, $\underline{k} + \underline{k}' = \underline{K}$ is only possible when $\underline{K} = 0$. Consequently in the present treatment one can again apply the RPA to this term in the same way as in the free electron case, concluding that in the sum over $\underline{k}$ and $\underline{k}'$ in the term involving M_2 the terms for which $\underline{k} + \underline{k}' \neq 0$ are negligible compared to those for which the equality holds.

When the RPA has been applied the Hamiltonian (10.4) becomes

$$H = \sum_i E(p_i) + \sqrt{4\pi e^2} \sum_{i,k<k_c} M_1(p_i;\underline{k}) q_k e^{i\underline{k}\cdot\underline{r}_i}$$

$$- \frac{1}{2}\sum_{k<k_c}{}' p_k p_{-k} + 2\pi e^2 \sum_{i,k<k_c} M_2(p_i;\underline{k},-\underline{k}) q_k q_{-k}$$

$$+ \frac{(4\pi e^2)^{3/2}}{3!} \sum_{i,k,k'<k_c} \sum_{K} M_3(p_i;\underline{k},\underline{k}',\underline{K}-\underline{k}-\underline{k}') q_k q_{k'} q_{K-k-k'} + \ldots$$

(10.6)

This is the Hamiltonian in the present case analagous to (6.15) in the free electron case. Its various terms have interpretations similar to those of (6.15): the first term represents the energy of the particles including their potential energy in the periodic field; the third term is the Hamiltonian of a set of oscillators; the second term represents an interaction between the oscillators and the particles; finally, the remaining terms (apart from the self-energy term), which have no analogue in (6.15), represent a weak interaction between the oscillators.

If all but the first, third and last terms of (10.6) are neglected (all the other terms are expected to be comparatively small), the Hamiltonian becomes

$$H = \sum_i E(p_i) - \frac{1}{2}\sum_{k<k_c}\left\{p_k p_{-k} + 4\pi e^2 \sum_i M_2(p_i;\underline{k},-\underline{k})\right\} - \sum_{k<k_c}\frac{2\pi n e^2}{k^2} \tag{10.7}$$

This Hamiltonian is separable into a set of independent particle Hamiltonians and a set of oscillator Hamiltonians. This separability is not affected by the appearance in the oscillator Hamiltonians of the particle variables $\underline{p}_i$ since, as H does not involve the $\underline{r}_i$ s, H and $\underline{p}_i$ and hence H and $M_2(\underline{p}_i;\underline{k},-\underline{k})$ are simultaneously diagonal.

The general form of an (antisymmetric) eigenfunction of (10.7) is

$$\Psi = \prod_{k<k_c} h_{n_k}(p_k)\, e^{-\frac{|p_k|^2}{2\pi\omega_k}} \begin{vmatrix} e^{i\underline{k}_1\cdot\underline{r}_1}u_{s_1}(\sigma_1) & \cdots & e^{i\underline{k}_N\cdot\underline{r}_1}u_{s_N}(\sigma_1) \\ \vdots & & \vdots \\ e^{i\underline{k}_1\cdot\underline{r}_N}u_{s_1}(\sigma_N) & \cdots & e^{i\underline{k}_N\cdot\underline{r}_N}u_{s_N}(\sigma_N) \end{vmatrix} \tag{10.8}$$

where the $\underline{k}_i$ s are N wave vectors, the u_{s_i} s are N spin functions, h_n is the Hermite polynomial of order n, n_k takes the values 0,1,2,...corresponding to the states of the oscillator with co-ordinate q_k, and where ω_k is given by the dispersion relation

$$\omega_k^2 = 4\pi e^2 \sum_i' M_1(\hbar\underline{k}_i;\underline{k},-\underline{k}) \tag{10.9}$$

That the wave function (10.8) subject to (10.9) is an eigenfunction of (10.7) corresponding to the energy

$$E = \sum_i' E(\hbar\underline{k}_i) + \sum_{k<k_c} \left\{ \hbar\omega_k\left(n_k+\tfrac{1}{2}\right) - \frac{2\pi ne^2}{k^2} \right\} \tag{10.10}$$

can easily be verified directly; that the set of wave functions (10.8) exhausts all possible antisymmetric eigenfunctions of (10.7) can be seen by noticing that the set (10.8) is a complete set with respect to antisymmetric functions of $\underline{r}_i$ and p_k.

Using (10.3a) the dispersion relation (10.9) can be written

$$\begin{aligned}\omega_k^2 &= \frac{4\pi e^2}{\hbar^2 k^2} \sum_i' \left\{ E(\hbar\underline{k}_i+\hbar\underline{k}) + E(\hbar\underline{k}_i-\hbar\underline{k}) - 2E(\hbar\underline{k}_i) \right\} \\ &= 4\pi e^2\, \hat{\underline{k}} \cdot \left\{ \sum_i' \nabla\nabla E(\hbar\underline{k}_i) \right\} \cdot \hat{\underline{k}} + \ldots \\ &= 4\pi ne^2\, \hat{\underline{k}} \cdot \langle (\underline{m}^*)^{-1} \rangle_{AV} \cdot \hat{\underline{k}} + \ldots\end{aligned} \tag{10.11}$$

where the average is over the occupied levels.

It is seen that in the present case, in contrast to the free electron

case, the oscillator frequency ω_k may depend upon the direction of the wave vector $\underline{k}$; the frequencies are, in fact, determined by the average over the occupied levels of $(\underline{m}^*)^{-1}$, where $\underline{m}^*$ is the effective mass tensor. If this average over $(\underline{m}^*)^{-1}$ is a multiple of the unit tensor, as it will be in all crystals with cubic type structures since the multiples of the unit tensor are the only tensors with cubic symmetry, then all the oscillator frequencies given by (10.11) will be the same and will be given by

$$\omega_k^2 = 4\pi n e^2 \left\langle \left(\frac{1}{m^*}\right) \right\rangle \qquad (10.12)$$

where $\langle (1/m^*) \rangle$ is the average of $1/m^*$ over the occupied states. In the case of other crystal structures such as the hexagonal structures $\underline{m}$ will often be anisotropic and the oscillators with wave vectors in different directions will have different frequencies.

The above results have been obtained by neglecting the oscillator-particle and oscillator-oscillator interaction. Whilst it is expected that the oscillator-oscillator interaction will be small enough to be treated by perturbation theory, this is not so for the oscillator-particle interaction, and in the next section this latter interaction will be treated by a further unitary transformation along the lines of the free electron case.

§11 The Treatment of the Particle-Oscillator Interaction.

In this section the effects of the particle-oscillator interaction term of (10.6) will be investigated by means of a further unitary

transformation. For the moment the small terms representing the oscillator-oscillator interaction will be dropped from the Hamiltonian since these terms can in any case be treated at the present stage by perturbation theory. Then the Hamiltonian H of (10.6) becomes

$$H = H_0 + H_I \tag{11.1}$$

where H_0 is the Hamiltonian (10.7) and

$$H_I = \sqrt{4\pi e^2} \sum_{i,k<k_c}' M_1(p_i;\underline{k}) q_k e^{i\underline{k}\cdot\underline{r}_i} \tag{11.2}$$

The aim will be, as in the free electron case, to determine a generator S of a unitary transformation such that

$$\frac{i}{\hbar}[H_0, S] = -H_I \tag{11.3}$$

The transformed Hamiltonian will then be given, using the expansion (6.9), by

$$H \to H_0 + \sum_{n=1}^{\infty} \left(\frac{i}{\hbar}\right)^n [H_I, S]_n \left\{\frac{1}{n!} - \frac{1}{(n+1)!}\right\} \tag{11.4}$$

and the main effects of H_I will be represented by the term $\frac{i}{2\hbar}[H_I, S]$; it will be found that the various contributions to this term will have simple interpretations.

The success of this method depends upon the rapidity of the convergence of the series in (11.4). The rate of convergence of this series is measured by the smallness of the parameter

$$\alpha = \left\langle \left[\frac{\underline{k} \cdot \nabla E(\underline{k})}{\omega} \right]^2 \right\rangle_{Av}$$

relative to 1. This parameter is exactly analagous to the parameter α (6.26) in the free electron gas case, and, in fact, a rough estimate shows that provided $m^* > 1$ the α in the present case will be of the same order as in the free electron gas (if anything, somewhat smaller). Consequently it can be concluded that in the present case $\alpha \sim 1/20$, and the series in (11.4) will be quite rapidly convergent.

In order to construct the required S it is convenient to introduce instead of the oscillator variables q_k and p_k the creation and destruction operators a_k^*, a_k defined by

$$q_k = \left(\frac{\hbar}{2\omega_k'}\right)^{\frac{1}{2}} (a_k - a_{-k}^*) \quad , \quad p_k = i\left(\frac{\hbar\omega_k'}{2}\right)^{\frac{1}{2}} (a_k^* + a_{-k}^*) \tag{11.5}$$

where ω_k' is an as yet undetermined frequency. It is easily found from the commutation relations for q_k and p_k that the a_k s and a_k^* s satisfy the commutation relations

$$[a_k, a_{k'}] = [a_k^*, a_{k'}^*] = 0 \qquad [a_k, a_{k'}^*] = \delta_{kk'} \tag{11.6}$$

The parts of the Hamiltonian H_0 and H_I can now be written in terms of the creation and destruction operators:

$$H_0 = \sum_i E(\underline{k}_i) + \sum_{k<k_c} \frac{\hbar\omega_k'}{2} (a_k a_k^* + a_k^* a_k) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2}$$

$$+ \sum_{k<k_c} \left(\frac{\hbar}{4\omega_k'}\right) (\omega_k^2 - \omega_k'^2)(a_k a_k^* + a_k^* a_k - a_k a_{-k} - a_k^* a_{-k}^*) \tag{11.7}$$

$$H_I = \sqrt{4\pi e^2} \sum_{i,k<k_c}' \left(\frac{\hbar}{2\omega_k'}\right)^{1/2} \left\{ M_1(p_i;\underline{k}) a_k e^{i\underline{k}\cdot\underline{r}_i} - e^{-i\underline{k}\cdot\underline{r}_i} a_k^* M_1(p_i;\underline{k}) \right\} \tag{11.8}$$

The required S is now given by

$$S = -i\hbar \sum_{i,k<k_c}' \left(\frac{\hbar}{2\omega_k'}\right)^{\frac{1}{2}} \left\{ F(p_i;\underline{k}) a_k e^{i\underline{k}\cdot\underline{r}_i} + e^{-i\underline{k}\cdot\underline{r}_i} a_k^* F(p_i;\underline{k}) \right\} \tag{11.9}$$

where

$$F(p,\underline{k}) = \sqrt{4\pi e^2} \; \frac{M_1(p,\underline{k})}{\hbar\omega_k' + E(p-\hbar\underline{k}) - E(p)} \tag{11.10}$$

That the S given by (11.9) does actually satisfy (11.3) can easily be verified using the commutation relations (11.6). It remains now to evaluate the terms in the series in (11.4) to determine the effects of H_I. The leading term of this series is $(i/2\hbar)[H_I,S]$. This term can be evaluated directly from the expressions (11.8) and (11.9) for H_I and S using the commutation relations (11.6). If the random phase approximation is used in the result thus obtained, one obtains

$$\begin{aligned}
\frac{i}{2\hbar}[H_I,S] = {} & \sqrt{4\pi e^2} \sum_{i,k<k_c}' \left(\frac{\hbar}{4\omega_k'}\right) \left\{ M_1(p_i+\hbar\underline{k},\underline{k}) F(p_i+\hbar\underline{k},\underline{k}) - M_1(p_i,\underline{k}) F(p_i,\underline{k}) \right\} \\
& \times \left(a_k a_k^* + a_k^* a_k - a_k a_{-k} - a_k^* a_{-k}^* \right) \\
& - \sqrt{4\pi e^2} \sum_{i\neq j}' \sum_{k<k_c}' \left(\frac{\hbar}{4\omega_k'}\right) \left\{ M_1(p_i,\underline{k}) F(p_j+\hbar\underline{k},\underline{k}) e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)} \right. \\
& \left. - e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)} M_1(p_i,\underline{k}) F(p_j+\hbar\underline{k}) \right\} \\
& - \sqrt{4\pi e^2} \sum_{i,k<k_c}' \left(\frac{\hbar}{4\omega_k'}\right) \left\{ M_1(p_i,\underline{k}) F(p_i,\underline{k}) + M_1(p_i+\hbar\underline{k},\underline{k}) F(p_i+\hbar\underline{k},\underline{k}) \right\}
\end{aligned} \tag{11.11}$$

(11.11) gives the leading term of the series in (11.4) Since all the other terms of the series are of the order α smaller than this term and $\alpha \sim 1/20$, these other terms can to a good approximation be neglected. The transformed Hamiltonian then becomes $H_0 + (i/2\hbar)[H_I, S]$, which can be written using (11.11)

$$H = H_{parc.} + H_{osc.} + H_{r.p.} \tag{11.12}$$

where

$$H_{parc.} = \sum_i E(p_i) - \sqrt{4\pi e^2} \sum_{ik<k_c} \left(\frac{\hbar}{4\omega_k'}\right) \left[M_1(p_i+\hbar k, k) F(p_i+\hbar k, k) + M_1(p_i, k) F(p_i, k) \right] \tag{11.13}$$

and

$$H_{osc.} = \sum_{k<k_c} \frac{\hbar\omega_k'}{2} (a_k a_k^* + a_k^* a_k) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + \sum_{k<k_c} \left(\frac{\hbar}{4\omega_k'}\right) \left[\omega_k^{*2} - \omega_k'^2 + \sqrt{4\pi e^2} \sum_i \left\{ M_1(p_i+\hbar k, k) F(p_i+\hbar k, k) - M_1(p_i, k) F(p_i, k) \right\} \right] \times (a_k a_k^* + a_k^* a_k - a_k a_{-k} - a_k^* a_{-k}^*) \tag{11.14}$$

and

$$H_{r.p.} = -\sqrt{4\pi e^2} \sum_{i \neq j} \sum_{k<k_c} \left(\frac{\hbar}{4\omega_k'}\right) \left[M_1(p_i, k) F(p_j+\hbar k, k)\, e^{ik\cdot(r_i - r_j)} - e^{-ik\cdot(r_i - r_j)} M_1(p_i, k) F(p_j+\hbar k, k) \right] \tag{11.15}$$

If now ω_k' is chosen to satisfy

$$\omega_k'^2 = \omega_k^{*2} + \sqrt{4\pi e^2} \sum_i \{ M_1(p_i + \hbar k, k) F(p_i + \hbar k, k) - M_1(p_i, k) F(p_i, k) \} \tag{11.16}$$

then $H_{osc.}$ reduces to

$$H_{osc.} = \sum_{k<k_c} \frac{\hbar\omega_k'}{2} (a_k a_k^* + a_k^* a_k) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} \tag{11.17}$$

which is just the sum of a set of oscillator Hamiltonians. If further $E'(\underline{p})$ is defined by

$$E'(p_i) = E(p_i) - \sqrt{4\pi e^2} \sum_{k<k_c} \left(\frac{\hbar}{m\omega_k'} \right) [M_1(p_i + \hbar k, k) F(p_i + \hbar k, k) - M_1(p_i, k) F(p_i, k)] \tag{11.18}$$

then the Hamiltonian (11.12) can be written

$$H = \sum_i E'(p_i) + \sum_{k<k_c} \frac{\hbar\omega_k'}{2} (a_k a_k^* + a_k^* a_k) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + H_{r.p.} \tag{11.19}$$

This Hamiltonian is apart from the term $H_{r.p.}$ of the same form as (10.7) except that the oscillator Hamiltonians are now written in terms of the creation and destruction operators. The effects of taking the particle-oscillator interaction H_I into account can now be seen by comparing (11.19) with (10.7). Three effects are observed:

(i) $E(\underline{p})$ has been replaced by $E'(\underline{p})$ given by (11.18); since $E(\hbar\underline{k})$ was defined in terms of the energy surfaces (9.6), this change is equivalent to a modification of the energy surfaces;

(ii) ω_k^* has been replaced by the ω_k' given by the dispersion relation (11.16); thus the frequencies of the plasma oscillators are

modified by the particle-oscillator interaction;

(iii) an additional term $H_{r.p.}$ has appeared in the Hamiltonian; inspection of this term shows that it represents a weak, screened, long-range, velocity-dependent interaction between the particles. In the case of a free electron gas BP found that H was very weak, and this is almost certainly the case here; consequently $H_{r.p.}$ can be quite reasonably treated by perturbation theory. If now the oscillator-oscillator interaction terms of (10.6) are again included in the Hamiltonian (actually these terms should first be transformed by the unitary transformation which has just been made, but since these terms are already small, and the effects of the transformation would be α times smaller, these latter effects may be neglected), the Hamiltonian becomes

$$H = \sum_i E'(p_i) + \sum_{k<k_c} \frac{\hbar\omega_k'}{2}(a_k a_k^* + a_k^* a_k) - \sum_{k<k_c} \frac{2\pi n e^2}{k^2} + H_p \tag{11.20}$$

where

$$H_p = H_{r.p.} + \frac{(4\pi e^2)^{3/2}}{3!} \sum_i \sum_{k,k'<k_c} \sum_{\substack{K \\ |\underline{k}+\underline{k}'-\underline{K}|<k_c}} M_3(p_i; \underline{k}, \underline{k}', \underline{K}-\underline{k}-\underline{k}') q_k q_{k'} q_{K-k-k'} + \cdots \tag{11.21}$$

includes all the small terms which can be treated as perturbations (the terms neglected in the random phase approximation could also be included here for the sake of completeness).

To complete the transformation it remains only to determine the form of the transformed subsidiary conditions. Direct calculation

with the help of the dispersion relation (11.16) shows that the transformed subsidiary conditions are

$$\sum_i \frac{1}{\hbar^2\omega_k'^2 - [E(p_i) - E(p_i - \hbar k)]^2} e^{i\underline{k}\cdot\underline{r}_i} \Psi = 0 , \quad k<k_c . \tag{11.22}$$

It is seen that, as in the free electron case, after transforming away the particle-oscillator interaction the subsidiary conditions only affect the particle variables.

The transformation to the collective description has now been completed, the system being represented by the Hamiltonian (11.20) together with the subsidiary conditions (11.22). Before going on to discuss the collective description in this case it is convenient to simplify the expressions (11.16), (11.19) and (11.15). This may be done by substituting in these expressions for F from (11.10), for M_1 from (10.3a), and expanding in powers of α ; the results are

$$\omega_k'^2 = \omega_k''^2 - \frac{8\pi e^2}{\hbar^4 k^2 \omega_k'} \sum_i' [E(p_i + \hbar k) - E(p_i)]^3 + \ldots \tag{11.23}$$

$$E'(p) = E(p) - 2\pi e^2 \sum_{k<k_c}' \frac{[E(p+\hbar k) - E(p)]^2}{\hbar^2 k^2 \omega_k'^2} + \ldots \tag{11.24}$$

and

$$H_{r.p.} = \sum_{i\neq j}' \sum_{k<k_c}' \frac{8\pi e^2}{\hbar\omega_k'} [\hat{k}\cdot\nabla E(p_i)][\hat{k}\cdot\nabla E(p_j)] e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} + \ldots \tag{11.25}$$

§12 The Collective Description.

The collective description of the system is now given by the Hamiltonian (11.20). This Hamiltonian has a very close formal resemblance to the Hamiltonian (6.27) of the free electron case (except for the different treatment of $H_{s.r.}$ in the present case), and most of the remarks which were made in § 7 concerning the collective description of a free electron gas are applicable here. It has again been shown that the system behaves as though it consisted of two distinct systems, a particle system and an oscillator system. Again in the majority of phenomena only the particle part of the system will be concerned, and this part will behave very much as though the independent particle model were accurate owing to the removal of the long-range part of the Coulomb interaction. The small angle, inelastic scattering of fast electrons could again be treated along the lines of § 8, and it would now be found that the electrons lost their energy in quanta of $\hbar\omega_k$ where ω_k is given by the dispersion relation (11.23) or approximately by (10.11). Thus it is seen that the effect of the periodic field upon the collective behaviour of the system is to modify the details of the free electron results rather than to introduce any important new effects.

Of particular interest is the determination of the energy levels of the system. In calculating these it is necessary to take into consideration the short-range interaction $H_{s.r.}$. The general form of an

eigenfunction of the Hamiltonian (11.20) will be, neglecting the small term H_p,

$$\Psi = \prod_{k<k_c} h_{n_k}(p_k)\, e^{-\frac{|p_k|^2}{2\hbar\omega_k'}} \begin{vmatrix} e^{i\underline{k}_1\cdot\underline{r}_1} u_{s_1}(\underline{\sigma}_1) & \cdots & e^{i\underline{k}_N\cdot\underline{r}_1} u_{s_N}(\underline{\sigma}_1) \\ \vdots & & \vdots \\ e^{i\underline{k}_1\cdot\underline{r}_N} u_{s_1}(\underline{\sigma}_N) & \cdots & e^{i\underline{k}_N\cdot\underline{r}_N} u_{s_N}(\underline{\sigma}_N) \end{vmatrix} \tag{12.1}$$

where $\underline{k}_i$ etc. have the same meaning as in (10.8), and the corresponding energy, neglecting H_p and $H_{s.r.}$, is

$$E = \sum_i E'(\hbar\underline{k}_i) + \sum_{k<k_c} \left\{ \hbar\omega_k'\left(n_k + \tfrac{1}{2}\right) - \frac{2\pi n e^2}{k^2} \right\} \tag{12.2}$$

Whilst the contribution to the energy of H_p is probably small enough to be neglected quite safely (as is shown by calculating it perturbation theoretically and considering plausible band structures $E(\underline{p})$), the contribution of $H_{s.r.}$ can certainly not be neglected. As was pointed out at the beginning it is generally possible to treat $H_{s.r.}$ as a perturbation (or by the Hartree-Fock scheme if necessary, see below). Since $H_{s.r.}$ was not transformed, to calculate its contribution to the energy by perturbation theory it is necessary to use the untransformed wave function Φ of (9.14) rather than the Ψ of (12.1). It should be noticed that the Ψ in (9.4) is not actually the Ψ of (12.1), but is this latter wave function transformed by the unitary transformation generated by S (11.9), i.e. is $\exp\{-(i/\hbar)S\}\,\Psi$. Thus Φ is

given in terms of Ψ by

$$\Phi = \sum_{\underline{R}_1,\ldots\underline{R}_N} \sum_{\alpha_1,\ldots\alpha_N} U \Psi(\underline{R}_1,\ldots\underline{R}_N;\alpha_1,\ldots\alpha_N)\, \varphi(\underline{r}_1-\underline{R}_1)\ldots\varphi(\underline{r}_N-\underline{R}_N)\, u_{\alpha_1}(\underline{\sigma}_1)\ldots u_{\alpha_N}(\underline{\sigma}_N) \tag{12.3}$$

where

$$U = \exp\left\{-\frac{i}{\hbar} S\right\} \tag{12.4}$$

It has already been seen that the effects introduced by S are of the order $\alpha \sim 1/20$; therefore not too great an error is introduced into Φ by neglecting S and putting $U = 1$. Using (12.1) and (9.8), Φ can then be written

$$\Phi = \prod_{k<k_c} h_{n_k}(p_k)\, e^{-\frac{|p_k|^2}{2\hbar\omega_k}} \begin{vmatrix} \psi_{\underline{k}_1}(\underline{r}_1)\, u_{s_1}(\underline{\sigma}_1) & \cdots & \psi_{\underline{k}_N}(\underline{r}_1)\, u_{s_N}(\underline{\sigma}_1) \\ \vdots & & \vdots \\ \psi_{\underline{k}_1}(\underline{r}_N)\, u_{s_1}(\underline{\sigma}_N) & \cdots & \psi_{\underline{k}_N}(\underline{r}_N)\, u_{s_N}(\underline{\sigma}_N) \end{vmatrix} \tag{12.5}$$

where Φ is now regarded as a function of the q_k s as well as the $\underline{r}_i$ s; the subsidiary conditions (11.22) will then imply a similar set of conditions on Φ thus restoring the correct number of degrees of freedom.

The contribution of $H_{s.r.}$ to the energy can now be calculated perturbation theoretically. $H_{s.r.}$ acts only upon the particle variables; the first term of the perturbation series representing its contribution to the energy is

$$\frac{1}{2} \sum_{i\neq j} \left\{ (ij|H_{s.r.}|ij) - (ij|H_{s.r.}|ji) \right\} \tag{12.6}$$

where the sum over i and j runs over the occupied levels and

$$(ij|H_{s.r.}|k\ell) = \delta_{s_i s_k}\delta_{s_j s_\ell}\int \psi_i^*(\underline{r})\psi_j^*(\underline{r}')H_{s.r.}(\underline{r}-\underline{r}')\psi_k(\underline{r})\psi_\ell(\underline{r}')\,d\underline{r}\,d\underline{r}' \tag{12.7}$$

This is just the ordinary expression according to the independent particle model for the contribution to the energy of the Coulomb interaction except that this interaction is now replaced by $H_{s.r.}$; the first term represents the classical 'Coulomb' energy and the second the quantum mechanical exchange energy.

The second term in the perturbation series is

$$\sum_{i,i'}\frac{|H_{ii'}|^2}{E_i - E_{i'}} + \sum_{ij,i'j'}\frac{|H_{ij,i'j'}|^2}{E_i + E_j - E_{i'} - E_{j'}} \tag{12.8}$$

where

$$H_{ii'} = \sum_{k\neq i}\left\{(ik|H_{s.r.}|i'k) - (ik|H_{s.r.}|ki')\right\} \tag{12.9}$$

and

$$H_{ij,i'j'} = (ij|H_{s.r.}|i'j') - (ij|H_{s.r.}|j'i') \tag{12.10}$$

where the sums over i and j run over the occupied levels and the sums over i' and j' run over the unoccupied levels; E_i, E_j etc. are the energies of the levels i, j and are given by $E'(\underline{p}_i)$, $E'(\underline{p}_j)$,... This term represents the leading term of the short-range correlation energy.

It should now be noticed that although in the free electron case $H_{s.r.}$ can usually be quite safely treated as a perturbation except in the case of very low electronic densities, in the case of a metal this simple

treatment will often break down. The reason for this is that, whereas in the free electron case the electrons are fairly randomly distributed, in the case of a metal, because of the action of the periodic potential field, the electrons will tend to pile up in the neighbourhoods of the atomic nuclei, producing a periodic variation in the electronic density which in turn gives rise to a comparatively strong periodic field; this field just represents the screening of the nuclei by the piling up of electrons near them. Since this field is periodic, if it were expanded in Fourier series, only those components for which $\underline{k}$ = reciprocal lattice vector would appear; but, since $k_c < K_{min}$, all these components are contained in $H_{s.r.}$, and all the effects of the screening will be contained in $H_{s.r.}$. Because these effects are comparatively large the perturbation-theoretic treatment of $H_{s.r.}$ may very well break down; in the case of the leading term (12.8) of the short-range correlation energy these effects are represented by the large first term of (12.8).

There is, however, a remedy for this difficulty, and this will be the subject of the next section.

§13 The Hartree-Fock Treatment of the Short-Range Interaction.

The original aim was to determine the eigenvalues and eigenfunctions of the Hamiltonian (1.1), and the work of the preceeding sections has shown that, apart from the difficulty with $H_{s.r.}$, the wave function (12.5)

for any given choice of the $\underline{k}_i$ and s_i s represents a good approximation to an eigenfunction of (1.1). In this section it will be shown how it is possible for any given choice of the $\underline{k}_i$s and s_is to construct a wave function similar in form to (12.5) but which avoids the difficulty with $H_{s.r.}$.

Suppose that the $\psi'_{\underline{k}_i}$ s are the solutions of the self-consistent equations

$$\left[\frac{p^2}{2m} + U'(\underline{r}) + \sum_j' \int H_{s.r.}(\underline{r}-\underline{r}')\,|\psi'_{\underline{k}_j}(\underline{r}')|^2 d\underline{r}'\right]\psi'_{\underline{k}_i}(\underline{r})$$

$$- \sum_j' \int \psi'^{*}_{\underline{k}_j}(\underline{r}')\, H_{s.r.}(\underline{r}-\underline{r}')\,\psi'_{\underline{k}_i}(\underline{r}')\,d\underline{r}'\,.\,\psi'_{\underline{k}_i}(\underline{r}) = E^{HF}(\hbar\underline{k}_i)\,\psi'_{\underline{k}_i}(\underline{r})$$

(13.1)

for a given choice of the $\underline{k}_i$ s and s_i s, where

$$\psi'_{\underline{k}_i}(\underline{r}) = e^{i\underline{k}_i\cdot\underline{r}}\,u_{\underline{k}_i}(\underline{r}) \quad , \quad u_{\underline{k}_i} \text{ periodic}.$$

(13.2)

The Hamiltonian (1.1) can now be rewritten

$$H = \sum_i H_i + \sum_{i\neq j}\sum_{k<k_c} \frac{2\pi e^2}{k^2}\, e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)} + H'_{s.r.}$$

(13.3)

where

$$H_i = \frac{p_i^2}{2m} + \sum_j' \int H_{s.r.}(\underline{r}_i-\underline{r})\,|\psi'_{\underline{k}_j}(\underline{r})|^2 d\underline{r} + A(\underline{r}_i) + U'(\underline{r}_i)$$

(13.4)

and

$$H'_{s.r.} = H_{s.r.} - \sum_{i,j}' \int H_{s.r.}(\underline{r}_i-\underline{r})\,|\psi'_{\underline{k}_j}(\underline{r})|^2 d\underline{r} - \sum_i' A(\underline{r}_i)$$

(13.5)

in which A is the operator defined by

$$A\,\psi(\underline{r})\,u_s(\sigma) = \sum_i \delta_{ss_i}\,\psi'_{\underline{k}_i}(\underline{r})\,u_{s_i}(\sigma)\int \psi'^{*}_{\underline{k}_i}(\underline{r}')\,H_{s.r.}(\underline{r}-\underline{r}')\,\psi(\underline{r}')\,d\underline{r}' \tag{13.6}$$

and is the short-range analogue of the Dirac exchange operator (Dirac, 1930).

Let it now be supposed that $H'_{s.r.}$ is small and can be treated as a perturbation; this will actually be found to be so; it is, in fact, $H'_{s.r.}$ which is small rather than $H_{s.r.}$. Then $H'_{s.r.}$ can be dropped from the Hamiltonian and its effects investigated afterwards by perturbation theory. The resulting Hamiltonian can then be transformed to the crystal momentum representation by expanding Φ according to (9.14), except that now instead of expanding it in terms of the $\phi(\underline{r}-\underline{R})$ s defined by (9.8) it must be expanded in terms of the $\phi'(\underline{r}-\underline{R})$ s, where

$$\varphi'(\underline{r}) = \sum_{\underline{k}} \varphi_{\underline{k}}'(\underline{r}) \tag{13.7}$$

in which the $\varphi_{\underline{k}}'$ s are the solutions of the equations

$$\left[\frac{p^2}{2m} + U'(\underline{r}) + \sum_i \int H_{s.r.}(\underline{r}-\underline{r}')\,|\psi'_{\underline{k}_i}(\underline{r}')|^2\,d\underline{r}' + A(\underline{r})\right]\psi_{\underline{k}}' = E^{HF}(\underline{k})\,\psi_{\underline{k}}' \tag{13.8}$$

in the case $\underline{k} = \underline{k}_i$, where $\underline{k}_i$ is the wave vector of one of the occupied levels $\psi_{\underline{k}}'$ will coincide with the solution $\psi'_{\underline{k}_i}$ of (13.3); for other $\underline{k}$ s the $\psi_{\underline{k}}'$ will be 'virtual orbitals'.

When the transformation to the crystal momentum representation is made in the manner indicated, it is found that the transformed Hamiltonian becomes instead of (9.24)

$$H = \sum_i E^{HF}(p_i) + \sum_{i,j} \sum_{k<k_c} \frac{2\pi e^2}{k^2} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \tag{13.9}$$

This has exactly the same form as (9.24) except that $E(\underline{p})$ has been replaced by $E^{HF}(\underline{p})$. The work of sections §10 and §11 can then proceed exactly as before except for the replacement of E by E^{HF} everywhere. Thus the Hamiltonian will be reduced in the collective description to

$$H = \sum_i E'^{HF}(p_i) + \sum_{k<k_c} \left\{ \frac{\hbar\omega_k}{2}(a_k a_k^* + a_k^* a_k) - \frac{2\pi e^2}{k^2} \right\} + H_p' \tag{13.10}$$

where E'^{HF}, ω_k and H'_p are given by the relations (11.24), (11.23) and (11.25) with E replaced by E^{HF}. Further, the wave function Φ of (12.5) will now be replaced by

$$\Phi = \prod_{k<k_c} h_{n_k}(p_k)\, e^{-\frac{|p_k|^2}{2\hbar\omega_k}} \begin{vmatrix} \psi'_{\underline{k}_1}(\underline{r}_1)u_{s_1}(\underline{\sigma}_1) & \cdots & \psi'_{\underline{k}_N}(\underline{r}_1)u_{s_N}(\underline{\sigma}_1) \\ \vdots & & \vdots \\ \psi'_{\underline{k}_1}(\underline{r}_N)u_{s_1}(\underline{\sigma}_N) & \cdots & \psi'_{\underline{k}_N}(\underline{r}_N)u_{s_N}(\underline{\sigma}_N) \end{vmatrix} \tag{13.11}$$

It now only remains to calculate the contribution to the energy of $H'_{s.r.}$. This will be given by formulae (12.6), (12.8) with $H_{s.r.}$ replaced by $H'_{s.r.}$. Direct calculation now shows that the first term of the perturbation series becomes

$$-\frac{1}{2} \sum_{i,j} \left\{ (ij|H_{s.r.}|ij) - (ij|H_{s.r.}|ji) \right\} \tag{13.12}$$

which is just the negative of (12.6). In the expression (12.8), the first (and large) term is the contribution to the short-range correlation

energy of virtual transitions from the initial state to states in which one electron is excited, whilst the second term arises from virtual transitions to states in which two electrons are excited. The important point about the replacement of $H_{s.r.}$ by $H'_{s.r.}$ is that the matrix elements of $H'_{s.r.}$ from the initial state to excited states in which only one electron is excited now vanish identically, as can easily be verified by direct computation. Consequently when the leading term of the short-range correlation energy due to $H'_{s.r.}$ is calculated no term analagous to the first term of (12.8) appears; thus the large term in (12.8) is eliminated, and the correlation energy becomes of the same order as in the free electron case and can be safely treated by perturbation theory (since evidently the higher order perturbation terms are reduced in just the same way as the second is). The leading term of the short-range correlation energy now becomes

$$\sum_{i,j,i',j'} \frac{|H_{ij,i'j'}|^2}{E_i+E_j-E_{i'}-E_{j'}} \qquad (13.13)$$

where $H_{ij,i'j'}$ is again given by (12.10). What has actually been done above is that the screening of the nucleus by the electrons has been represented by the Hartree-Fock field, thus removing it from $H_{s.r.}$ and replacing the latter by $H'_{s.r.}$ which gives rise to just the same sort of correlation effects as in a free electron gas.

To summarise, what has been shown in this section is as follows. For any given choice of the $\underline{k}_i$s and s_is, the wave function (13.11) will

be, apart from the small perturbation by $H'_{s.r.}$ and H_{sx}, an eigenfunction of the H of (1.1) provided the ψ'_{k_i} s are the solutions of the Hartree-Fock equations (13.1) with a screened interaction, and that the E^{HF} s given by the solutions of the equations (13.8) are used in calculating ω_k and E'^{HF}. The corresponding energy will be to a good approximation

$$E = \sum_i{}' E'^{HF}(\hbar k_i) + \sum_{k<k_c} \left\{ \hbar\omega_k (n_k + \tfrac{1}{2}) - \frac{2\pi e^2}{k^2} \right\} + \langle H'_p \rangle$$

$$- \tfrac{1}{2} \sum_{ij}{}' \left\{ (ij|H_{s.r.}|ij) - (ij|H_{s.r.}|ji) \right\} + \sum_{i,j,i',j'} \frac{|H_{ij,i'j'}|^2}{E_i + E_j - E_{i'} - E_{j'}} \qquad (13.14)$$

One last point should be mentioned. This concerns the choice of k_c. Throughout all the above work k has been a parameter, and it appears implicitly in the expressions (13.14) for the energy. This parameter can now be regarded as a variational parameter, and its best value will be the value which minimises the total energy (13.14). The determination of such a k_c theoretically would be very complex, since k_c enters in a complex way through its affect upon the solution of the equations (13.1) and (13.8) ($H_{s.r.}$ depends upon k_c).

§ 14 Criticisms of the Effective Mass Treatment.

In this section the scope of the treatment given in the previous sections will be discussed together with certain criticisms of it which exist.

(i) The neglect of the inter-zone transitions. In the treatment given above only the electrons belonging to a single zone have been

treated, and only the possibility of virtual intra-zone transitions have been considered, since the total wave function Φ of the system was expanded in terms of a single Wannier function ϕ or ϕ', which from (9.8) or (13.7) is equivalent to expanding Φ in terms of the wave functions ψ_k of one zone. However, it is possible for the electric field associated with the plasma oscillations to cause both real and virtual inter-zone transitions of the electrons analagous to the intra-zone transitions brought about in the above theory by the particle-oscillator interaction. If the virtual inter-zone transitions were taken into account then the details of the effects (discussed in § 11) brought about by the particle-oscillator interaction would be modified, although the nature of the effects would not be altered. Treatments along the lines of the treatment presented in this chapter but including the inter-zone transitions have been given by Adams (1955) and Kanazawa (1955) using either the more refined effective mass theory developed by Adams (1952, 1953) or the second quantisation method. Both these authors concluded that these effects might be quite important, although it is difficult to estimate their magnitude without a definite knowledge of the band structures and certain matrix elements.

(ii) The neglect of the core electron polarisation. An additional but similar effect to the last one is the neglect of the core electron polarisation. It may be expected that the electric field associated with the plasma oscillations will not only give rise to transitions of the conduction electrons but also to transitions of the core electrons

above the Fermi surface; these transitions are again of two kinds, real and virtual; the real transitions will be discussed in (iii). The virtual transitions are equivalent to the polarisation of the ion cores by the plasma field. This polarisation may be expected to react upon the plasma oscillations and effect the details of the whole collective description, without changing the general picture. Another similar effect is the polarisation of the lattice by the plasma oscillations due to the small accelerations of the ion cores produced by the plasma field; this effect will be very small.

(iii) The neglect of damping of the oscillations. In (i) and (ii) above the possibility of electrons making real transitions from the conduction band or the ion core levels to states above the Fermi surface has been mentioned. In such real transitions energy must be conserved, so that it is only possible for an electron to be elevated to a higher energy level as a result of the particle-oscillator interaction if at the same time one of the plasma oscillators passes into a state of lower energy. Thus this possibility only affects oscillators in excited states, and will then give rise to a damping of the oscillator down to the ground state. Under normal conditions there are only a very small number of oscillators in excited states in a metal since $\hbar\omega_p >> \kappa T$, and this effect will be quite unimportant. In Ruthemann and Lang type experiments, however, oscillators will be excited by the passage of the fast electron and this damping will give rise to a certain half-life for an oscillator in the excited state which will in turn give rise to a certain broadening of the

plasma absorbtion peak. This damping has been discussed from the point of view of the effective mass treatment by Kanazawa (1955).

(iv) Difficulties with the subsidiary conditions. In the above treatment the subsidiary conditions have been practically ignored as they were in BP's original free electron treatment. One could again show that in the case of a non-degenerate state the subsidiary conditions are automatically satisfied and rely upon this to demonstrate that the calculation of the ground state energy is correct. On the other hand, so far as a general treatment is concerned, there is no satisfactory treatment, as far as the author is aware, of solving eigenvalue problems subject to this sort of subsidiary condition. The subsidiary conditions remain one of the awkward features of BP's formalism.

CHAPTER FOUR.

THE DIELECTRIC APPROACH.

In the preceeding chapter the method of generalising the BP free electron gas theory by making use of the crystal momentum representation has been described. In this chapter an alternative method of generalisation will be described.

It has been seen in the previous chapters that the main difficulty in the treatment of the electronic interactions arises from the long-range nature of the Coulomb interaction. When the Coulomb interaction has been replaced by a screened interaction the Hartree-Fock scheme becomes adequate. Thus, in order to obtain a satisfactory treatment of the electronic interactions, it is necessary to obtain some proper treatment of the long-range part of the interaction, after which the short-range part can be treated perturbation-theoretically or by means of the Hartree-Fock scheme. This treatment of the long-range interaction is just what BP's theory and the effective mass generalisation of it provide. In this chapter, however, a more direct approach to the problem of treating the long-range interaction will be made.

In treating the long-range interaction there is fortunately an important simplification which can be made and upon which the successful treatment of the long-range interaction by the plasma theory rests. This simplification arises from the fact that, provided the electronic density is sufficiently high, so far as the long-range interaction is

concerned the metal or free electron gas can be regarded as a medium. For if the distance over which the long-range interaction acts is rather greater than the inter-electronic spacing, the positions of the actual individual electrons have little effect upon the long-range field, only the average positions of many electrons being important.

Since so far as the long-range interaction is concerned the electrons constitute to a good approximation a medium, it is reasonable to treat this interaction according to the ordinary theory of the electromagnetic field in dielectric media, the appropriate dielectric properties being ascribed to the medium. This is what will be called the dielectric approach and it is this approach which will be devloped in the present chapter. It will be found that when this approach is applied to a free electron gas it leads to essentially the same results as BP's theory, and consequently can be regarded as a generalisation of this theory. That it is, in fact, a very wide generalisation of this theory can be seen at once; for example, effects such as the ion core polarisation can be taken into account at once by merely taking into account their influence upon the dielectric properties of the medium whilst such phenomena as the damping can be interpreted in terms of the complex part (the conductivity) of the dielectric constant.

This type of treatment of the long-range part of the Coulomb interaction is not new but was first developed by Fermi (1940) in connection with that part of the stopping power of materials for fast changed particles due to 'long-range' collisions; its connection with the plasma

theory of BP and the correlation problem seems only to have been realised recently, (Fröhlich and Pelzer, 1955, Hubbard, 1955) however. Refinements of Fermi's theory have been made by various authors (Halpern and Hall, 1948, Kramers, 1947, A.Bohr, 1948), and the treatment of the small angle, inelastic scattering of fast electrons given in § 17 is, in fact, only a refinement of these theories.

There is one important difficulty in the developement of this theory. This is that, although the classical version of the theory can be developed very straightforwardly, the resulting theory is rather difficult to quantise. Only in the very special case of a free electron gas is the quantisation easy and in this case the ordinary BP theory is reproduced. For this reason in the present chapter only a semi-classical version of the theory will be developed. This version of the theory is sufficient to indicate the main results but a true quantum mechanical theory would, of course, be desirable.

§ 15 The Semi-Classical Version of the Dielectric Theory.

In this section the semi-classical version of the theory will be developed in detail. In the remaining sections of this chapter the theory developed here will be applied to obtain certain results.

Since the dielectric theory is only applicable to the long-range part of the Coulomb interaction, it is necessary as a first step to separate the long- and short- range parts of the electric field. This can be done by the usual device of expanding the electric field in Fourier series and separating this series into two parts. The electric field $\underline{E}(\underline{r},t)$ is expanded thus:

$$\underline{E}(\underline{r},t) = \sum_{k} \underline{E}_{k}(t)\, e^{i\underline{k}\cdot\underline{r}} \tag{15.1}$$

and the long-range part of it, $\underline{E}_{l.r.}$ is taken to be

$$\underline{E}_{l.r.} = \sum_{k<k_c} \underline{E}_{k}(t)\, e^{i\underline{k}\cdot\underline{r}} \tag{15.2}$$

where k_c is some suitably chosen parameter, whilst the remainder

$$\underline{E}_{s.r.} = \underline{E} - \underline{E}_{l.r.} \tag{15.3}$$

is the short-range part of the field. In the remainder of this chapter only the long-range part $\underline{E}_{l.r.}$ of $\underline{E}$ will be considered, and the subscript l.r. will be dropped, it being understood that only the long-range part is being dealt with.

The long-range field will now be treated in accordance with the dielectric approach as though the solid were a continuous dielectric medium (instead of a collection of point electrons). The dielectric properties of such a medium can be described by a (complex) frequency-dependent, $\underline{k}$-dependent (see Appendix A) dielectric tensor $\underline{\underline{\epsilon}}_{k\omega}$. This tensor relates the Fourier components $\underline{E}_{k\omega}$ of the electric field, given by

$$\underline{E}(\underline{r},t) = \sum_{k\omega} \underline{E}_{k\omega}\, e^{i\underline{k}\cdot\underline{r} + i\omega t} \tag{15.4}$$

to the corresponding Fourier components $\underline{D}_{k\omega}$ of the displacement $\underline{D}(\underline{r},t)$ through the equation

$$\underline{\underline{\epsilon}}_{k\omega} \cdot \underline{E}_{k\omega} = \underline{D}_{k\omega} \tag{15.5}$$

In the present case it is only the longitudinal part of the electric field which is of interest since this represents the Coulomb interactions between the electrons whilst the transverse part only represents the weak magnetic interactions which will be neglected. If the transverse part of the field is neglected then $\underline{E}_{\omega k}$ can be written $\hat{\underline{k}}\, E_{\omega k}$ and $\underline{D}_{\omega k}$ can be similarly written $\hat{\underline{k}}\, D_{\omega k}$; (15.5) then becomes

$$\epsilon_{\omega k} E_{\omega k} = D_{\omega k} \tag{15.6}$$

where

$$\epsilon_{\omega k} = \hat{\underline{k}} \cdot \underline{\underline{\epsilon}}_{\omega k} \cdot \hat{\underline{k}} \tag{15.7}$$

The theory is now very straightforward. The equation (15.6) can be used to obtain a simple relationship between the electric field in the metal and the charge distribution generating it, taking into account the fact that the electric field polarises the metal. This latter polarisation is just equivalent to the ordinary correlations in the electronic motion, for it represents the movements of the electrons to screen out the field acting on them, and it is just these movements which are called the electronic correlations.

In addition to (15.6) it is necessary to use the equation

$$\mathrm{div}\, \underline{D} = 4\pi\rho \tag{15.8}$$

relating the displacement to the charge density $\rho(\underline{r},t)$ generating the field; it is also convenient to introduce the scalar potential $\phi(\underline{r},t)$:

$$-\nabla\phi = \underline{E} \tag{15.9}$$

Combining the Fourier transforms of the equations (15.8), (15.9) with (15.5), one can easily obtain the relation

$$\epsilon_{\omega k}\,\phi_{\omega k} = \frac{4\pi}{k^2}\,\rho_{\omega k} \tag{15.10}$$

relating the scalar potential ϕ to the charge density ρ generating the field.

One point should particularly be noticed here. This is that the charge density ρ in (15.10) will not be the charge density corresponding to the actual distribution of the electrons; it is what the charge density would be if there were no correlations i.e. if the medium were not polarised. The charge density of the actual distribution of the electrons is the charge density in (15.10) together with the charge distribution corresponding to the polarisation. From this point of view the electronic motion has been broken up into two parts. One part represents what the motion of the electrons would be in the absence of the long-range interaction, whilst the other part represents the reaction of the electrons to the long-range field; the charge distribution corresponding to the first part of the motion is the ρ in (15.10) whilst the charge distribution corresponding to the second part of the motion is the charge distribution

corresponding to the polarisation. The important point about (15.10) is that it involves only the charge distribution corresponding to the uncorrelated motion (which is so much easier to deal with), the correlation effects having been taken into account by the use of the dielectric constant.

(15.10) summarises the dielectric theory; all the results of the semi-classical theory can be obtained from it. One consequence of the equation (15.10) is of particular importance. Suppose for some ω ($= \omega_k$) $\epsilon_{\omega k}$ vanishes. Then according to (15.10), the corresponding $\phi_{\omega k}$ is indeterminate. Thus the equation (15.10) does not determine ϕ uniquely, but all the $\phi_{\omega k}$ s such that the corresponding $\epsilon_{\omega k}$ vanishes are indeterminate. Thus the general solution of (15.10) is of the form

$$\rho_{\omega k} = \frac{4\pi}{k^2 \epsilon_{\omega k}} \rho_{\omega k} + A_k^{(1)} \delta(\omega - \omega_k^{(1)}) + A_k^{(2)} \delta(\omega - \omega_k^{(2)}) + \cdots \qquad (15.11)$$

where the $A_k^{(1)}$, $A_k^{(2)}$,... are arbitary constants, and $\omega_k^{(1)}$, $\omega_k^{(2)}$,... are the frequencies at which $\epsilon_{\omega k}$ vanishes. Thus it is seen that the electric field consists of two parts, one corresponding to the particular solution of (15.10) and the other to the complementary function. This exactly parallels the case of the radiation field in vacua; there is in that case a particular integral representing the ~~magnetic~~ interactions of the particles and a complementary function representing the photons which are present. In the present case the particular integral represents the residual interactions between the particles (corresponding to the

H of BP), whilst the complementary function represents longitudinal oscillations of the electric field. When this oscillating field is resolved into travelling waves, the part with wave vector $\underline{k}$ resolves into parts which oscillate with the frequencies $\omega_k^{(1)}$, $\omega_k^{(2)}$, ... Thus it is seen that the dielectric theory leads quite naturally to the concept of longitudinal oscillations in an electron gas and shows that the frequencies of these oscillations are the frequencies at which $\epsilon_{\omega k} = 0$. It is natural to identify these oscillations in the case of a free electron gas with BP's plasma oscillations, and this identification will be confirmed in the next section by showing that their frequencies agree.

The possibility of longitudinal oscillations which has just been discussed depends upon the vanishing of $\epsilon_{\omega k}$ at some frequency- or frequencies. In general the real part of $\epsilon_{\omega k}$ will vanish at some frequencies, but the actual complex $\epsilon_{\omega k}$ will not unless the imaginary part vanishes at the same frequencies. This is just what is to be expected in the classical case for the imaginary part of $\epsilon_{\omega k}$ represents the conductivity which will have a damping effect upon the oscillations. Thus according to a classical treatment there will be no sustained oscillations. However, the situation is rather different in the quantum mechanical case provided the damping is not too strong. In the quantum mechanical case the situation will be that whilst the damping is able to damp an oscillator in an excited state down to the ground state, the damping cannot destroy the zero-point oscillations.

Thus in the quantum mechanical case it is expected that zero-point oscillations will exist at the frequencies at which the real part of $\epsilon_{\omega k}$ vanishes, and that if in any way the oscillators become excited, then they will be damped down to the ground state at a rate which is proportional to the imaginary part of $\epsilon_{\omega k}$ at the oscillator frequency. This result gives a simple rule for calculating the oscillation frequencies in solids; it is only necessary to calculate $\epsilon_{\omega k}$ and determine the frequency at which the real part vanishes. A discussion of these frequencies upon this basis will be given in the next section.

§16 The Oscillation Frequencies of Solids.

To be able to discuss the plasma frequencies in solids it is necessary to have a general expression for the dielectric constant . Unfortunately, a careful calculation of $\epsilon_{\omega k}$ leads to an expression to which it is difficult to give a simple physical interpretation. In this section, therefore, in order to render the results more surveyable, an approximate expression for $\epsilon_{\omega k}$ will be used.

The approximate expression for $\epsilon_{\omega k}$ which will be used has been briefly derived in Appendix A; the modifications to it which arise in a more careful treatment have also been indicated there. $\underline{\underline{\epsilon}}_{\omega k}$ can be expressed in the form

$$\underline{\underline{\epsilon}}_{\omega k} = 1 + 4\pi \underline{\underline{\alpha}}_{\omega k} + \frac{4\pi}{i\omega} \underline{\underline{\sigma}}_{\omega k} \tag{16.1}$$

where $\underline{\underline{\alpha}}_{\omega k}$ and $\underline{\underline{\sigma}}_{\omega k}$ are the (real) polarisability and conductivity tensors.

$\epsilon_{\omega k}$ can correspondingly be written

$$\epsilon_{\omega k} = 1 + 4\pi\alpha_{\omega k} + \frac{4\pi}{i\omega}\sigma_{k\omega} \tag{16.2}$$

where $\alpha_{\omega k} = \hat{k}\cdot\underline{\underline{\alpha}}_{\omega k}\cdot\hat{k}$ and $\sigma_{k\omega} = \hat{k}\cdot\underline{\underline{\sigma}}_{\omega k}\cdot\hat{k}$. The calculation of Appendix A gives the expressions

$$\alpha_{\omega k} = -\frac{Ne^2}{m} + \frac{2e^2}{m^2\hbar\omega}\sum_{\underline{k}',n,n}' \frac{N_{\underline{k}'n}\,|M_{\underline{k}'+\underline{k},n';\underline{k}'n}|^2\,\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}}{\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2} \tag{16.3}$$

and

$$\sigma_{\omega k} = \frac{\pi e^2}{m^2\hbar\omega}\sum_{\underline{k}',n,n}' N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'})\,|M_{\underline{k}'+\underline{k},n';\underline{k}'n}|^2 \times\left[\delta(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}-\omega) - \delta(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}+\omega)\right] \tag{16.4}$$

for $\alpha_{\omega k}$ and $\sigma_{\omega k}$, where

$$\hbar\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} = E_{\underline{k}'+\underline{k},n'} - E_{\underline{k}'n} \tag{16.5}$$

$$M_{\underline{k}'+\underline{k},n';\underline{k}'n} = \int \psi^*_{\underline{k}'+\underline{k},n'}\, e^{i\underline{k}\cdot\underline{x}}\,\hat{k}\cdot\left(\underline{p}+\tfrac{1}{2}\hbar\underline{k}\right)\psi_{\underline{k}'n}\,d\underline{x} \tag{16.6}$$

and where N is the total electronic density (core and conduction electrons), $\psi_{\underline{k}n}$ is the Bloch wave function belonging to the n th zone and to reduced wave vector $\underline{k}$, $E_{\underline{k}n}$ is the corresponding energy and $N_{\underline{k}n}$ the corresponding occupation number (= 0, 1, 2). The sums over $\underline{k}'$ run over the first Brillouin zone and the sums over n and n' run over all the Brillouin zones including the core electron levels.

These results will first be used to discuss the free electron gas case. A free electron gas can be regarded as a metal with a single Brillouin zone which extends throughout the whole of $\underline{k}$-space.

Substituting the free electron wave functions into (16.3) gives

$$\alpha_{\omega k} = -\frac{Ne^2}{m\omega^2} + \frac{2e^2}{m^2\hbar\omega}\sum_{\underline{k}'}\frac{N_{\underline{k}'}\left[\hbar\underline{k}\cdot(\underline{k}'+\tfrac{1}{2}\underline{k})\right]^3 k}{\left[\frac{\hbar}{m}\underline{k}\cdot(\underline{k}'+\tfrac{1}{2}\underline{k})\right]^2-\omega^2} \qquad (16.7)$$

where the subscripts n and n' have been dropped. ~~This expression is actually exact in the special case of free electrons.~~ The condition for the plasma frequency ω_k is $\alpha_{\omega k} = -\frac{1}{4\pi}$; using the expression (16.7) for $\alpha_{\omega k}$ in this, one obtains after some re-arrangement the equation

$$1 = \frac{4\pi e^2}{m}\sum_{\underline{k}'}\frac{N_{\underline{k}'}}{\left(\omega-\frac{\hbar}{m}\underline{k}\cdot\underline{k}'\right)^2-\frac{\hbar^2k^4}{4m^2}} \qquad (16.8)$$

for the oscillation frequency ω_k (there is only one ω_k for each $\underline{k}$ in this case). This expression agrees exactly with BP's dispersion relation (6.22), thus confirming the identification of these oscillations with BP's plasma oscillations. Investigation of the expression (16.4) for the conductivity shows that this will actually vanish at the plasma frequency provided $\hbar\omega_k$ is greater than the Fermi energy. This exact vanishing of $\sigma_{\omega k}$ is only the result of using the approximate expression (16.4) for $\sigma_{\omega k}$, but the actual damping will, in fact, be quite small.

The application of the formula $\alpha_{\omega k} = -\frac{1}{4\pi}$ to calculate the oscillation frequencies of actual solids will now be considered. It is first convenient to transform the expression (16.3) using a generalisation of the ordinary f-sum rule; the result is

$$1 + 4\pi\alpha_{\omega_{\underline{k}}} = 1 - \frac{4\pi e^2}{\hbar^2\omega^2}\sum_{\underline{k}'n} N_{\underline{k}'n}(\hat{\underline{k}}\cdot\nabla)(\hat{\underline{k}}\cdot\nabla)E_{\underline{k}'n} + \ldots.$$

$$+ \frac{8\pi e^2}{\hbar m^2}\sum_{\underline{k}'n}\frac{N_{\underline{k}'n}\,|M_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2\,\omega_{\underline{k}'+\underline{k},n;\underline{k}'n}}{\omega^2(\omega^2_{\underline{k}'+\underline{k},n;\underline{k}'n} - \omega^2)}$$

$$+ \frac{8\pi e^2}{\hbar m^2}\sum_{\underline{k}'n}\sum_{n'\neq n}\frac{N_{\underline{k}'n}\,|M_{\underline{k}'+\underline{k},n';\underline{k}'n}|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}(\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2)} \qquad (16.9)$$

The sum in the first term is just $\mathcal{N}$ times the average of $\hat{\underline{k}}\cdot(1/\underline{\underline{m}}^*)\cdot\hat{\underline{k}}$ over the occupied levels. In the case of nearly free electron-like metals it is expected that the second and third terms of (16.9) will be small compared to the first. If this term is neglected, then one obtains the expression

$$\omega^2_{\underline{k}} = \omega^2_{\underline{k}o} \equiv \frac{4\pi e^2}{\hbar^2}\sum_{\underline{k}'n} N_{\underline{k}'n}(\hat{\underline{k}}\cdot\nabla)(\hat{\underline{k}}\cdot\nabla)E_{\underline{k}'n} \qquad (16.10)$$

which agrees with the effective mass treatment in the first approximation (10.11). If now the ω_k given by (16.10) is substituted for ω_k in the second and third terms of (16.9), one obtains the next approximation

$$\omega^2_{\underline{k}} = \omega^2_{\underline{k}o} + \frac{8\pi e^2}{\hbar m^2}\sum_{\underline{k}'n}\frac{N_{\underline{k}'n}\,|M_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2\,\omega_{\underline{k}'+\underline{k},n;\underline{k}'n}}{\omega^2_{\underline{k}o}(\omega^2_{\underline{k}'+\underline{k},n;\underline{k}'n} - \omega^2_{\underline{k}o})}$$

$$+ \frac{8\pi e^2}{\hbar m^2}\sum_{\underline{k}'n}\sum_{n'\neq n}\frac{N_{\underline{k}'n}\,|M_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}(\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2_{\underline{k}o})} \qquad (16.11)$$

for ω_k.

The second and third terms of (16.11) can now be split up (artificially it is true) into several parts which have simple interpretations. These parts are as follows:

(i) those terms in which n = n' correspond to a conduction band zone; these terms are of exactly the same kind as those arising from the particle-oscillator interaction in the expressions (6.22) and (11.16) in the free electron case and the effective mass treatment; they represent the effect upon the oscillation frequency of the intra-zone transitions induced by the plasma field;

(ii) those terms in which n corresponds to a conduction band zone and the n' to one of the higher zones; these terms represent the effect upon the plasma frequency of the inter-zone transitions discussed in (i) of § 14;

(iii) those terms in which n corresponds to a core level and n' corresponds to one of the higher zones; these terms represent the effect upon the oscillation frequency of the core polarisation which can be interpreted in terms of virtual transitions of the core electrons (see (ii) of § 14).

Thus it is seen that the expression (16.11) contains all the main factors affecting the oscillation frequency which were neglected in the effective mass treatment. It will not always be possible to use the approximation procedure (16.10), (16.11) to solve the equation

$$0 = 1 - \frac{4\pi e^2}{k^2\omega^2} \sum_{\underline{k}'n} N_{\underline{k}'n} (\hat{\underline{k}}\cdot\nabla)(\hat{\underline{k}}\cdot\nabla) E_{\underline{k}'n} + \ldots$$

$$+ \frac{8\pi e^2}{\hbar^2 m} \sum_{\underline{k}'n} \frac{N_{\underline{k}'n} \, |M_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2 \omega_{\underline{k}'+\underline{k},n;\underline{k}'n}}{\omega^2(\omega^2_{\underline{k}'+\underline{k},n;\underline{k}'n} - \omega^2)}$$

$$+ \frac{8\pi e^2}{\hbar^2 m} \sum_{\underline{k}'n} \sum_{n'\neq n} \frac{N_{\underline{k}'n} \, |M_{\underline{k}'+\underline{k},n';\underline{k}'n}|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}(\omega^2_{\underline{k}'+\underline{k},n;\underline{k}'n} - \omega^2)} \qquad (16.12)$$

(from (16.9)) for the plasma frequency; nevertheless, it is evident that the same interpretations can be given to the various terms of (16.12) as were given to the terms of (16.11).

Without discussing specific band structures little more can be said concerning the factors affecting the oscillation frequencies apart from discussing the effects of replacing the approximate expression (16.3) by a more accurate expression; such a discussion is rather difficult, but an indication of the effects has been given in Appendix B.

There are, however, two alternative methods of obtaining information concerning the oscillation frequencies, both experimental. These methods will be the subject of the next section.

§17. Experimental Methods of Investigating the Dielectric Behaviour

Apart from the theoretical calculations of the preceding section there are at present at least two experimental methods of obtaining direct information concerning the dielectric behaviour of a metal. The first of these methods is by investigation of the optical properties of the metal and the second is the investigation of the small angle, inelastic scattering of fast electrons in transversing the metal (see § 8).

Since the theory of the optical spectra of solids is very well-known, very little will be said concerning it here. It is sufficient to remark that in many crystal structures (including all crystals with cubic type symmetries) the dielectric tensor $\underline{\underline{\epsilon}}_{k\omega}$ of (15.5) is a multiple of the unit tensor and is, in fact $\underline{\underline{\epsilon}}_{k\omega} \equiv \underline{\underline{1}}$. In this case the solid will exhibit the same dielectric behaviour with respect to both the transverse and

longitudinal electromagnetic fields. But the dielectric behaviour with respect to transverse fields governs the optical properties of the solid; in fact, the polarisability and conductivity ~~are~~ at the frequency are related to the refractive index n and the extinction coefficient κ at the same frequency by

$$n^2 - \kappa^2 = 1 + 4\pi\alpha_{\omega\underline{k}}$$
$$n\kappa\omega = 2\pi\sigma_{\omega\underline{k}} \qquad (17.1)$$

where $\underline{k}$ is the wave vector of the optical radiation. Thus direct measurement of n and κ over a range of ω will give direct information concerning ~~and~~ $\epsilon_{k\omega}$ for certain values of $\underline{k}$; it is not expected that either the polarisability or the conductivity will vary very greatly with $\underline{k}$, so that the measurement of the optical properties will give a good indication of the general behaviour of these quantities with . Unfortunately the region of ω of principal interest in connection with the dielectric theory ($\hbar\omega \sim$ 5-20 eV) corresponds to the far ultra-violet region of the spectrum and practically no measurements of the optical properties of solids in this region have as yet been made. Thus it is only possible in one ortwo cases to use this method at present. Amongst these cases is the important case of the alkali metals for which the results of Ives and Briggs (1936, 1937) are available; in these cases it is observed that the metals become very nearly transparent at what corresponds to the free-electron plasma frequency (the optical theory predicts that this will occur at the frequency at which the real part of the dielectric constant vanishes i.e. at the plasma frequency, provided the damping is

not too strong); thus it is confirmed that the plasma frequencies of these metals are at practically the free electron gas frequencies and that the damping of the oscillations is quite small.

The theory of the small angle, inelastic scattering of electrons and its connection with the dielectric properties of solids seems to be less well known and will be developed here in a little more detail.

The problem is to determine the energy loss spectrum and angular distribution of those electrons which have undergone inelastic scattering through small angles within a solid. The treatment which will be given is very similar to the Weizacker-Williams method of treating scattering problems (Weizacker, 1934, Williams, 1935; see also Heitler 1954, App. 6) and can be regarded as a refinement of the stopping power treatments of the authors cited in the introduction to this chapter.

The scattering arises from the interaction of the fast electron with the electrons of the metal, and since the angle of scattering is small, the momentum exchange $\hbar\underline{k}$ in the scattering process must also be small, and therefore $\underline{k}$ must be small; thus it is the long-range part of the Coulomb interaction which is responsible for the small angle scattering, and consequently this scattering can be quite reasonably treated on the basis of the dielectric approach developed in §15.

The presence of the fast electron in the metal will give rise to an electric field which, when the polarisation of the metal by the field has been taken into account, will be given in terms of the charge distribution representing the fast electron by (15.10). This field may now be regarded

as a perturbation acting on the electrons of the metal; as such it will cause the electrons to make real transitions to excited states above the Fermi surface, and each electron which makes such a transition will absorb a certain energy and momentum from the fast electron thus giving rise to the inelastic scattering. This picture is not contrary to the picture developed in §8 of the absorbtion of energy from the fast electron as being due to the excitation of plasma oscillations for it could be interpreted in the following way: the fast electron excites a plasma oscillation, but after a certain time (governed by its half-life due to damping processes) this oscillation will be damped down to the ground state by an electron absorbing its energy and making a transition to a state above the Fermi surface; it is the rate of these latter transitions which will be calculated by means of the dielectric theory.

The charge distribution due to a fast electron with velocity $\underline{v}$ passing through a solid will be

$$\rho(\underline{r},t) = e\,\delta(\underline{r}-\underline{v}t) \tag{17.2}$$

and the corresponding Fourier transform of ρ will be

$$\rho_{\omega\underline{k}} = e\,\delta(\omega + k_{\parallel} v) \tag{17.3}$$

where $v = |\underline{v}|$ and $k_{\parallel}$ is the component of $\underline{k}$ parallel to $\underline{V}$. According to (15.10) the corresponding field in the solid will have a scalar potential whose Fourier components are given by

$$\varphi_{\omega\underline{k}} = \frac{4\pi e}{k^2 \epsilon_{\omega\underline{k}}} \delta(\omega + v k_n) \tag{17.4}$$

If the corresponding field

$$\varphi(\underline{r},t) = \sum_{\underline{k}\,\omega} \varphi_{\omega\underline{k}} \, e^{i\underline{k}.\underline{r} + i\omega t} \tag{17.5}$$

is regarded as a perturbation acting on the metal electrons and the ordinary time-dependent perturbation theory is applied, it is found that the component of (17.5) involving $\phi_{\omega\underline{k}}$ will only give rise to transitions in which the electron making the transition acquires momentum $\hbar\underline{k}$ and energy $\hbar\omega$, and that the rate of such transitions is proportional to $|\phi_{\omega\underline{k}}|^2$. Each time an electron makes such a transition the fast electron suffers a corresponding loss of energy and momentum; thus it has to be concluded that the rate at which the fast electron makes transitions in which it loses momentum $\hbar\underline{k}$ and energy $\hbar\omega$ is proportional to $|\varphi_{\omega\underline{k}}|^2$. The constant of proportionality is most conveniently calculated by calculating the total rate of energy loss of the field associated with the $\phi_{\omega\underline{k}}$ component. The total rate of energy loss of the field is

$$R = \int \overline{\underline{J}(\underline{r},t) \cdot \underline{E}(\underline{r},t)} \, d\underline{r}$$

$$= \sum_{\underline{k}} \sum_{\omega=-\infty}^{\infty} \underline{J}_{\omega\underline{k}} \cdot \underline{E}_{-\omega,-\underline{k}} \tag{17.6}$$

where the bar indicates the time average, $\underline{J}(\underline{r},t)$ is the current vector and $\underline{J}_{\omega\underline{k}}$ is its Fourier transform. It can easily be shown from the

ordinary theory of dielectrics that

$$\underline{J}_{\omega\underline{k}} = (i\omega \underline{\underline{\alpha}}_{\omega\underline{k}} + \underline{\underline{\sigma}}_{\omega\underline{k}}) \cdot \underline{E}_{\omega\underline{k}} \tag{17.7}$$

so that R can be written

$$R = \sum_{\underline{k}} \sum_{\omega=-\infty}^{\infty} \underline{E}_{-\omega,-\underline{k}} \cdot (i\omega \underline{\underline{\alpha}}_{\omega\underline{k}} + \underline{\underline{\sigma}}_{\omega\underline{k}}) \cdot \underline{E}_{\omega\underline{k}} \tag{17.8}$$

Putting $\underline{E}_{\omega\underline{k}} = \hat{\underline{k}} E_{\omega\underline{k}}$, using $E_{-\omega,-\underline{k}} = -E^{*}_{\omega\underline{k}}$ which follows from the reality of $\underline{E}$, and using the Fourier transform of (15.9), (17.8) becomes

$$R = \sum_{\underline{k}} \sum_{\omega=-\infty}^{\infty} k^2 (i\omega \alpha_{\omega\underline{k}} + \sigma_{\omega\underline{k}}) |\varphi_{\omega\underline{k}}|^2$$

$$= 2 \sum_{\underline{k}} \sum_{\omega=0}^{\infty} k^2 \sigma_{\omega\underline{k}} |\varphi_{\omega\underline{k}}|^2 \tag{17.9}$$

where the sum over ω of the term involving $\alpha_{\omega\underline{k}}$ just cancels. Inspection of (17.9) shows that the rate of energy loss of the field associated with the component $\phi_{\omega\underline{k}}$ is

$$2k^2 \sigma_{\omega\underline{k}} |\varphi_{\omega\underline{k}}|^2 \tag{17.10}$$

Thus the rate $P(\underline{k}, \omega)$ of transitions in which the fast electron loses momentum $\hbar\underline{k}$ and energy $\hbar\omega$ is given by

$$P(\underline{k},\omega) = \frac{2k^2 \sigma_{\omega\underline{k}}}{\hbar\omega} |\varphi_{\omega\underline{k}}|^2 \tag{17.11}$$

Substituting for $\phi_{\omega\underline{k}}$ from (17.4) one obtains the formula

$$P(\underline{k},\omega) = \frac{32\pi e^2}{\hbar\omega k^2} \frac{\sigma_{\omega\underline{k}}}{|\epsilon_{\omega\underline{k}}|^2} \delta(\omega + vk_{\parallel}) \tag{17.12}$$

This result gives a complete account of the energy loss spectrum and the angular distribution of scattered electrons due to 'long-range' collisions. The angle of scattering is related to $\underline{k}$ by

$$\theta = \hbar k_\perp / mv \tag{17.13}$$

where $k_\perp$ is the component of $\underline{k}$ perpendicular to $\underline{v}$.

Various results can be obtained from (17.12) by integrating over the variables involved. The probability per unit path length of an electron being scattered through an angle between θ and $\theta+d\theta$ and losing energy $\hbar\omega$ is given by

$$\frac{2\pi k_\perp dk_\perp}{v(2\pi)^3}\int_{-\infty}^{\infty} P(\underline{k},\omega)\,dk_\parallel = \frac{8e^2}{\hbar\omega v^2}\,\frac{\sigma_{\omega\underline{k}}}{|\epsilon_{\omega\underline{k}}|^2}\,\frac{\theta\,d\theta}{\theta^2+\left(\frac{\hbar\omega}{mv^2}\right)^2} \tag{17.14}$$

since $mv^2 \gg \hbar\omega$, the scattering is seen to have a very strong maximum near to $\theta = 0$. The probability of an electron being scattered through an angle less than θ and losing energy $\hbar\omega$ is (neglecting the small $\underline{k}$-dependence of $\epsilon_{\omega\underline{k}}$ and $\sigma_{\omega\underline{k}}$ since most of the contribution to the integral comes from one region of $\underline{k}$)

$$\frac{8e^2}{\hbar\omega v^2}\frac{\sigma_\omega}{|\epsilon_\omega|^2}\int_0^\theta \frac{\theta\,d\theta}{\theta^2+\left(\frac{\hbar\omega}{mv^2}\right)^2} = \frac{4e^2}{\hbar\omega v^2}\,\frac{\sigma_\omega}{|\epsilon_\omega|^2}\,\log\left\{1+\theta^2\left(\frac{mv^2}{\hbar\omega}\right)^2\right\} \tag{17.15}$$

whilst, putting $\theta = \hbar k_c/mv$, the total rate of energy loss due to 'long-range' collisions is

$$\frac{4e^2}{\hbar v^2}\int_0^\infty \frac{\sigma_\omega}{|\epsilon_\omega|^2}\,\log\frac{k_c^2+(\omega/v)^2}{(\omega/v)^2}\,d\omega \tag{17.16}$$

per unit path length.

If these results are now applied to a free electron gas, the difficulty is met with that both $\sigma_{\omega\underline{k}}$ and $\epsilon_{\omega\underline{k}}$ vanish at $\omega = \omega_{\underline{k}}$ ~~over a large range of~~ and P according to (17.12) becomes indeterminate. This difficulty can be avoided by formally introducing a very small damping proportional to γ (there will always be some sources of small damping); then one finds

$$\left.\begin{aligned} \sigma_{\omega\underline{k}} &= \frac{\omega_{\underline{k}}^2}{4\pi}\,\frac{\gamma}{\omega^2+\gamma^2} \\ |\epsilon_{\omega\underline{k}}|^2 &= 1 - \frac{\omega_{\underline{k}}^2}{\omega^2+\gamma^2} + \frac{\gamma^2}{\omega^2} \end{aligned}\right\} \quad \omega \text{ near } \omega_{\underline{k}}\,, \tag{17.17}$$

where $\omega_{\underline{k}}$ is the oscillation frequency given by (6.22). Calculating the ratio $\sigma_{\omega\underline{k}}/|\epsilon_{\omega\underline{k}}|^2$ from (17.17) and letting $\gamma \to +0$, one obtains

$$\lim_{\gamma\to+0} \frac{\sigma_{\omega\underline{k}}}{|\epsilon_{\omega\underline{k}}|^2} = \frac{\omega_{\underline{k}}^2}{8}\,\delta(\omega-\omega_{\underline{k}}) \quad , \ \omega \text{ near } \omega_{\underline{k}}, \tag{17.18}$$

Putting this result into (17.12) it is seen that a free electron gas will absorb energy in quanta of $\hbar\omega_{\underline{k}}$ from a fast electron in agreement with the results obtained in § 8. There is an additional small source of energy loss. For a free electron gas, from (16.14),

$$\sigma_{\omega\underline{k}} = \frac{\pi e^2\omega}{\hbar k^2} \sum_{\underline{k}'}{}' N_{\underline{k}'}(1-N_{\underline{k}'+\underline{k}})\,\delta\left\{\frac{\hbar}{m}\,\underline{k}\cdot(\underline{k}'+\tfrac{1}{2}\underline{k})-\omega\right\} \tag{17.19}$$

when this together with the appropriate $\epsilon_{\omega\underline{k}}$ is put into (17.12) a small absorbation of energy from the fast electron at frequencies other than the plasma frequency is found to occur; this just corresponds to the absorbation represented by the second term of Eqn. 48 of Pines (1953).

Neglecting this term, the total rate of energy loss of the per unit path of a fast electron in a free electron gas is found to be

$$\frac{2\pi n e^4}{mv^2} \log \frac{k_c^2 m^2 v^2}{\omega_p^2} \qquad (17.20)$$

per unit path length, in agreement with the result of Pines (1953) quoted in § 8, and with the earlier calculation (along similar lines to the present) of Kramers (1947).

Thus it is seen that in the case of a free electron gas the formula (17.12) leads to the same results as the earlier treatments. Consider now its application to a real solid. From the formulae (16.3), (16.4), it is seen that in a real solid it is quite possible for $\sigma_{\omega\underline{k}}$ and $\epsilon_{\omega\underline{k}}$ to vary in a quite complicated way with ω ; consequently, it is quite possible for the P given by (17.12) to also vary in a complex way, thus giving rise to a complicated energy loss spectrum. Unfortunately, in the absence of accurate band structure calculations it is not possible to deduce the actual energy loss spectra theoretically from (17.12) in order to make a comparison with the experimental results; it does seem from a preliminary investigation of the results obtained by Jull (1955), however, that so far as the non-transition metals of the lower part of the periodic table are concerned, an almost free electron calculation of $\sigma_{\omega\underline{k}}$ and $\epsilon_{\omega\underline{k}}$ will when used in (17.12) lead to good agreement with the experimental results.

An alternative approach (Frolich and Pelzer, 1955) is to compare the energy loss spectra with the optical spectra, eliminating $\sigma_{\omega\underline{k}}$ and $\epsilon_{\omega\underline{k}}$ between (17.12) and (17.1); here again the lack of the required optical

measurements does not allow this method to be used in many cases at present.

APPENDIX A

In this appendix we describe the calculation of the dielectric properties of a metal neglecting the Coulomb interaction between the electrons.

Let $\psi_{\underline{k}n}$ be the Bloch wave function in the reduced zone scheme with wave vector $\underline{k}$ belonging to the n^{th} band and let $E_{\underline{k}n}$ be its energy. Further let $N_{\underline{k}n}$ be the occupation number ($= 0,1$) of the state $\psi_{\underline{k}n}$ in the ground state of the metal. Suppose now that an electric field $\underline{E}(\underline{x},t) = -\nabla\varphi$ is applied to the metal where

$$\varphi(\underline{x},t) = \varphi_{\omega\underline{k}}\, e^{i\underline{k}\cdot\underline{x} + i\omega t} + \varphi^{*}_{\omega\underline{k}}\, e^{-i\underline{k}\cdot\underline{x} - i\omega t} \tag{A1}$$

This field will act on the wave functions $\psi_{\underline{k}'n}(\underline{x},t)$ and perturb them into some other wave functions $\psi'_{\underline{k}'n}(\underline{x},t)$. Using time dependent perturbation theory it can easily be shown that $\psi'_{\underline{k}'n}$ is given by

$$\begin{aligned}\psi'_{\underline{k}'n}(\underline{x},t) = {} & \psi_{\underline{k}'n}\, e^{-\frac{i}{\hbar}E_{\underline{k}'n}t} \\ & + \frac{2\pi e}{i\hbar}\varphi_{\omega\underline{k}}\, e^{i\omega t - \frac{i}{\hbar}E_{\underline{k}'n}t} \sum_{n'} (1 - N_{\underline{k}'+\underline{k},n'})\, \psi_{\underline{k}'+\underline{k},n'}\, M'_{\underline{k}'+\underline{k},n';\underline{k}'n} \\ & \qquad \times \delta_{-}\left\{ \frac{E_{\underline{k}'+\underline{k},n'} - E_{\underline{k}'n}}{\hbar} + \omega \right\} \\ & + \frac{2\pi e}{i\hbar}\varphi^{*}_{\omega\underline{k}}\, e^{-i\omega t - \frac{i}{\hbar}E_{\underline{k}'n}t} \sum_{n'} (1 - N_{\underline{k}'-\underline{k},n'})\, \psi_{\underline{k}'-\underline{k},n'}\, M'_{\underline{k}'-\underline{k},n';\underline{k}'n} \\ & \qquad \times \delta_{-}\left\{ \frac{E_{\underline{k}'-\underline{k},n'} - E_{\underline{k}'n}}{\hbar} - \omega \right\}\end{aligned} \tag{A2}$$

where

$$M'_{\underline{k}'n';\underline{k}n} = \int \psi^*_{\underline{k}'n'} e^{i(\underline{k}'-\underline{k})\cdot\underline{x}} \psi_{\underline{k}n}\, d\underline{x} \qquad (A3)$$

and

$$\delta_-(u) = \frac{1}{2\pi}\int_{-\infty}^{0} e^{iut}\, dt = \frac{1}{2\pi i}\frac{P}{u} + \frac{1}{2}\delta(u) \qquad (A4)$$

In obtaining (A2) we have made use of the selection rule that

$$\int \psi^*_{\underline{k}''n'} e^{i\underline{k}\cdot\underline{x}} \psi_{\underline{k}'n}\, d\underline{x}$$

$\underline{k}'' = \underline{k}'+\underline{k}$

vanishes unless ~~$\underline{k}'' = \underline{k}'$~~ and have used (A4) to evaluate the time integrals.

The perturbation of the charge density, $\delta\rho(\underline{x},t)$, due to the application of the electric field is given by

$$\delta\rho(\underline{x},t) = e\sum_{\underline{k}'n} N_{\underline{k}'n}\left\{|\psi'_{\underline{k}'n}(\underline{x},t)|^2 - |\psi_{\underline{k}'n}(\underline{x},t)|^2\right\} \qquad (A5)$$

If we now insert the $\psi'_{\underline{k}'n}$ given by (A2) into (A5) we obtain

$$\begin{aligned}
\delta\rho(\underline{x},t) &= \frac{2\pi e^2}{i\hbar}\varphi_{\omega\underline{k}}\, e^{i\omega t}\sum'_{\underline{k}',n,n'} N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'})\,\psi^*_{\underline{k}'n}\,\psi_{\underline{k}'+\underline{k},n'}\,M'_{\underline{k}'+\underline{k},n';\underline{k}'n}\,\delta_-\left\{\frac{E_{\underline{k}'+\underline{k},n'}-E_{\underline{k}'n}}{\hbar}+\omega\right\} \\
&+ \frac{2\pi e^2}{i\hbar}\varphi^*_{\omega\underline{k}}\, e^{-i\omega t}\sum'_{\underline{k}',n,n'} N_{\underline{k}'n}(1-N_{\underline{k}'-\underline{k},n'})\,\psi^*_{\underline{k}'n}\,\psi_{\underline{k}'-\underline{k},n'}\,M'_{\underline{k}'-\underline{k},n';\underline{k}'n}\,\delta_-\left\{\frac{E_{\underline{k}'-\underline{k},n'}-E_{\underline{k}'n}}{\hbar}-\omega\right\} \\
&+ \text{complex conjugate} \\
&= \frac{2\pi e^2}{i\hbar}\varphi_{\omega\underline{k}}\, e^{i\underline{k}\cdot\underline{x}+i\omega t} \\
&\times\Bigg[\sum'_{\underline{k}',n,n'} N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'})\,u^*_{\underline{k}'n}\,u_{\underline{k}'+\underline{k},n'}\,M'_{\underline{k}'+\underline{k},n';\underline{k}'n}\,\delta_-\left\{\frac{E_{\underline{k}'+\underline{k},n'}-E_{\underline{k}'n}}{\hbar}+\omega\right\} \\
&- \sum'_{\underline{k}',n,n'} N_{\underline{k}'n}(1-N_{\underline{k}'-\underline{k},n'})\,u_{\underline{k}'n}\,u^*_{\underline{k}'-\underline{k},n'}\,M'^*_{\underline{k}'-\underline{k},n';\underline{k}'n}\,\delta_+\left\{\frac{E_{\underline{k}'-\underline{k},n'}-E_{\underline{k}'n}}{\hbar}-\omega\right\}\Bigg] \\
&+ \text{complex conjugate}
\end{aligned} \qquad (A6)$$

where we have written

$$\psi_{\underline{k}'n} = e^{i\underline{k}'\cdot\underline{x}}\, u_{\underline{k}'n} \quad , \quad u_{\underline{k}'n} \text{ periodic}, \tag{A7}$$

and

$$\delta_+(u) = \delta_-^*(u) = \frac{1}{2\pi}\int_0^\infty e^{iut}\,dt = -\frac{1}{2\pi i}\cdot\frac{P}{u} + \frac{1}{2}\,\delta(u) \tag{A8}$$

It will be seen from (A6) that $\delta\rho$ is of the form

$$\delta\rho = \left[\varphi_{\omega\underline{k}}\, e^{i\underline{k}\cdot\underline{x}+i\omega t} + \varphi^*_{\omega\underline{k}}\, e^{-i\underline{k}\cdot\underline{x}-i\omega t}\right] K_{\omega\underline{k}}(\underline{x}) \quad , \quad K_{\omega\underline{k}} \text{ periodic}, \tag{A9}$$

Thus the application of the field (A1) gives rise to a charge disturbance which has the same form as φ apart from a periodic modulation. It is this modulation which gives rise to a part of the local field correction (see Appendix B). Here we neglect this correction and form from $\delta\rho$ its Fourier component $\delta\rho_{\omega\underline{k}}$. From (A6) this is given by

$$\delta\rho_{\omega\underline{k}} = \frac{2\pi e^2}{i\hbar}\varphi_{\omega\underline{k}}\left[\sum_{\underline{k}'nn'} N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'})\left|M'_{\underline{k}'+\underline{k},n';\underline{k}'n}\right|^2\delta_-\left\{\frac{E_{\underline{k}'+\underline{k},n'}-E_{\underline{k}'n}}{\hbar}+\omega\right\}\right.$$

$$\left. -\sum_{\underline{k}'nn'} N_{\underline{k}'n}(1-N_{\underline{k}'-\underline{k},n'})\left|M'_{\underline{k}'-\underline{k},n';\underline{k}'n}\right|^2\delta_+\left\{\frac{E_{\underline{k}'-\underline{k},n'}-E_{\underline{k}'n}}{\hbar}-\omega\right\}\right] \tag{A10}$$

where we have used

$$M'_{\underline{k}'n';\underline{k}n} = \int u^*_{\underline{k}'n'}\, u_{\underline{k}n}\, d\underline{x} \tag{A11}$$

and

$$M'^*_{\underline{k}'n';\underline{k}n} = M'_{\underline{k}n;\underline{k}'n'} \tag{A12}$$

If we substitute for the δ_- and δ_+ functions from (A4) and (A8) and re-arrange we obtain

$$\delta\rho_{\omega\underline{k}} / \varphi_{\omega\underline{k}} = \frac{e^2}{\hbar} \sum_{\underline{k}'nn'}' N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'}) \left| M'_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2 \times \left[-\frac{2\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}}{\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2} + i\pi\delta(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega) - i\pi\delta(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} + \omega) \right] \tag{A13}$$

where we have introduced the abbreviation

$$\omega_{\underline{k}'n';\underline{k}n} = \frac{E_{\underline{k}'n'} - E_{\underline{k}n}}{\hbar} \tag{A14}$$

From the ordinary theory of dielectrics it can be shown that

$$4\pi\alpha_{\omega\underline{k}} = -\frac{4\pi}{k^2} Re \frac{\delta\rho_{\omega\underline{k}}}{\varphi_{\omega\underline{k}}}$$

$$\frac{4\pi}{\omega}\sigma_{\omega\underline{k}} = \frac{4\pi}{k^2} Im \frac{\delta\rho_{\omega\underline{k}}}{\varphi_{\omega\underline{k}}} \tag{A15}$$

where Re and Im mean the real and imaginary parts. Comparing with (A13) we have

$$1 + 4\pi\alpha_{\omega\underline{k}} = 1 + \frac{8\pi e^2}{\hbar k^2} \sum_{\underline{k}'nn'}' \frac{N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'}) \left| M'_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2 \omega_{\underline{k}'+\underline{k},n';\underline{k}'n}}{\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2} \tag{A16}$$

$$\frac{4\pi}{\omega}\sigma_{\omega\underline{k}} = \frac{4\pi e^2}{\hbar k^2} \sum_{\underline{k}'nn'}' N_{\underline{k}'n}(1-N_{\underline{k}'+\underline{k},n'}) \left| M'_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2 \times \left[\delta(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega) - \delta(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} + \omega) \right] \tag{A17}$$

We can transform these results with the help of certain identities.

The wave function $\psi_{\underline{k}n}$ will satisfy a Schrodinger equation of the form

$$H\psi_{\underline{k}n} \equiv \left[\frac{1}{2m}\underline{p}^2 + U(\underline{x})\right]\psi_{\underline{k}n} = E_{\underline{k}n}\psi_{\underline{k}n} \tag{A18}$$

From the ordinary commutation relations we have

$$\left[H, e^{i\underline{k}\cdot\underline{x}}\right] = \frac{\hbar}{m} e^{i\underline{k}\cdot\underline{x}}\,\underline{k}\cdot\left(\underline{p} + \tfrac{1}{2}\hbar\underline{k}\right) \tag{A19}$$

$$\left[\left[H, e^{i\underline{k}\cdot\underline{x}}\right], e^{-i\underline{k}\cdot\underline{x}}\right] = -\frac{\hbar^2 k^2}{m} \tag{A20}$$

Taking the matrix element of (A19) between the states $\psi_{\underline{k}'n}$ and $\psi_{\underline{k}'+\underline{k},n'}$ and using (A18) we have

$$\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}\, M'_{\underline{k}'+\underline{k},n';\underline{k}'n} = \frac{k}{m}\int \psi^*_{\underline{k}'+\underline{k},n'} e^{i\underline{k}\cdot\underline{x}}\,\hat{\underline{k}}\cdot\left(\underline{p} + \tfrac{1}{2}\hbar\underline{k}\right)\psi_{\underline{k}'n}\, d\underline{x} \equiv \frac{k}{m} M_{\underline{k}'+\underline{k},n';\underline{k}'n} \tag{A21}$$

We can use this result to rewrite (A16) and (A17)

$$1 + 4\pi\alpha_{\omega\underline{k}} = 1 + \frac{8\pi e^2}{\hbar m^2}\sum'_{\underline{k}'nn'} \frac{N_{\underline{k}'n}\left(1 - N_{\underline{k}'+\underline{k},n'}\right)\left|M_{\underline{k}'+\underline{k},n';\underline{k}'n}\right|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}\left(\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2\right)} \tag{A22}$$

$$\frac{4\pi}{\omega}\sigma_{\omega\underline{k}} = \frac{4\pi^2 e^2}{\hbar m^2\omega^2}\sum'_{\underline{k}'nn'} N_{\underline{k}'n}\left(1 - N_{\underline{k}'+\underline{k},n'}\right)\left|M_{\underline{k}'+\underline{k},n';\underline{k}'n}\right|^2 \times\left[\delta\left(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega\right) - \delta\left(\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} + \omega\right)\right] \tag{A23}$$

We can further notice that the term in (A22) involving $N_{\underline{k}'+\underline{k},n'}\, N_{\underline{k}'n}$

cancels identically when the summation is performed so that we can rewrite (A22) as

$$1 + 4\pi\alpha_{\omega\underline{k}} = 1 + \frac{8\pi e^2}{\hbar m^2} \sum_{\underline{k}'n n'}' \frac{N_{\underline{k}'n} \left| M_{\underline{k}+\underline{k},n';\underline{k}'n} \right|^2}{\omega_{\underline{k}+\underline{k},n';\underline{k}'n} \left(\omega^2_{\underline{k}+\underline{k},n';\underline{k}'n} - \omega^2\right)} \tag{A24}$$

We can use the result (A20) to carry out a further transformation of (A24). If we take the matrix element of (A20) between the wave function $\psi_{\underline{k}'n}$ and itself we obtain on simplifying and using (A18)

$$1 = \frac{1}{m\hbar} \sum_{n'}' \left\{ \frac{\left| M_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}} + \frac{\left| M_{\underline{k}'-\underline{k},n';\underline{k}'n} \right|^2}{\omega_{\underline{k}'-\underline{k},n';\underline{k}'n}} \right\} \tag{A25}$$

from which

$$N = \sum_{\underline{k}'n}' N_{\underline{k}'n} = \frac{2}{\hbar m} \sum_{\underline{k}'n n'}' \frac{N_{\underline{k}'n} \left| M_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}} \tag{A26}$$

where N is the number of electrons. Combining (A24) and (A26) we have

$$1 + 4\pi\alpha_{\omega\underline{k}} = 1 - \frac{8\pi e^2}{\hbar m^2} \frac{\hbar m N}{2\omega^2} + \frac{8\pi e^2}{\hbar m^2} \sum_{\underline{k}'n n'}' \frac{N_{\underline{k}'n} \left| M_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n}} \left\{ \frac{1}{\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2} + \frac{1}{\omega^2} \right\}$$

$$= 1 - \frac{4\pi N e^2}{m\omega^2} + \frac{8\pi e^2}{\hbar m^2} \sum_{\underline{k}'n n'}' \frac{N_{\underline{k}'n} \left| M_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2 \omega_{\underline{k}'+\underline{k},n';\underline{k}'n}}{\omega^2 \left(\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2\right)} \tag{A27}$$

which is equation (16.3) of the text.

For small $\underline{k}$ one can made a yet another transformation of (A24). From (A21) one has for small $\underline{k}$

$$|M_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2 \omega^{-1}_{\underline{k}'+\underline{k},n;\underline{k}'n} + |M_{\underline{k}'-\underline{k},n;\underline{k}'n}|^2 \omega^{-1}_{\underline{k}'-\underline{k},n;\underline{k}'n}$$

$$= \frac{m^2}{k^2}\left[|M'_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2 \omega_{\underline{k}'+\underline{k},n;\underline{k}'n} + |M_{\underline{k}'-\underline{k},n;\underline{k}'n}|^2 \omega_{\underline{k}'-\underline{k},n;\underline{k}'n}\right]$$

$$\approx \frac{m^2}{\hbar k^2}\left[E_{\underline{k}'+\underline{k},n} + E_{\underline{k}'-\underline{k},n} - 2E_{\underline{k}'n}\right]$$

$$= \frac{m^2}{\hbar}(\hat{\underline{k}}\cdot\nabla)(\hat{\underline{k}}\cdot\nabla) E_{\underline{k}'n} + \ldots$$

(A28)

since for small $\underline{k}$

$$M'_{\underline{k}'+\underline{k},n;\underline{k}'n} = \int u^*_{\underline{k}'+\underline{k},n} u_{\underline{k}'n}\, d\underline{x} \approx 1$$

(A29)

From (A28) one has the result

$$2\sum_{\underline{k}'n} N_{\underline{k}'n}\left[\frac{|M_{\underline{k}'+\underline{k},n;\underline{k}'n}|^2}{\omega_{\underline{k}'+\underline{k},n;\underline{k}'n}} + \frac{|M_{\underline{k}'-\underline{k},n;\underline{k}'n}|^2}{\omega_{\underline{k}'-\underline{k},n;\underline{k}'n}}\right] = \frac{m^2}{\hbar}\sum_{\underline{k}'n} N_{\underline{k}'n}(\hat{\underline{k}}\cdot\nabla)(\hat{\underline{k}}\cdot\nabla)E_{\underline{k}'n} + \ldots$$

(A30)

which when combined with (A24) gives

$$1 + 4\pi\alpha_{\omega\underline{k}} = 1 - \frac{4\pi e^2}{\hbar^2\omega^2} \sum_{\underline{k}'n} N_{\underline{k}'n} (\hat{\underline{k}}\cdot\nabla)(\hat{\underline{k}}\cdot\nabla) E_{\underline{k}'n} + \ldots$$

$$+ \frac{8\pi e^2}{\hbar m^2} \sum_{\underline{k}'n} \frac{N_{\underline{k}'n} \left| M_{\underline{k}'+\underline{k},n;\underline{k}'n} \right|^2 \omega_{\underline{k}'+\underline{k},n;\underline{k}'n}}{\omega^2 \left(\omega^2_{\underline{k}'+\underline{k},n;\underline{k}'n} - \omega^2 \right)}$$

$$+ \frac{8\pi e^2}{\hbar m^2} \sum_{\underline{k}'n}' \sum_{n'\neq n} \frac{N_{\underline{k}'n} \left| M_{\underline{k}'+\underline{k},n';\underline{k}'n} \right|^2}{\omega_{\underline{k}'+\underline{k},n';\underline{k}'n} \left(\omega^2_{\underline{k}'+\underline{k},n';\underline{k}'n} - \omega^2 \right)}$$

(A31)

reproducing equation (16.9) of the text.

APPENDIX B

In the preceding appendix an account was given of an approximate calculation of the dielectric properties of a metal. In this section we shall comment on the defects of that calculation. There are two of these. Firstly the electrons were treated as though they were independent, that is their Coulomb interactions were neglected; secondly, to obtain equation (A10) we neglected the periodic modulation of the electric field in the interior of the metal. Both these effects contribute to what is normally referred to as the local field correction.

Let us first discuss the manner in which the results of appendix A are modified when the Coulomb interactions of the electrons are taken into account. We shall work with the eigenfunctions of the total Hamiltonian of the system. These will satisfy an eigenvalue of the form

$$\left[\sum_i \frac{1}{2m} p_i^2 + \sum_i U(\underline{x}_i) + \sum_{i \neq j} \frac{e^2}{|\underline{x}_i - \underline{x}_j|} \right] \Psi(\underline{x}_1, \underline{x}_2, \ldots) = E \Psi \tag{B1}$$

where $U(\underline{x})$ is the periodic potential. The Hamiltonian in (B1) is invariant against the symmetry operation of adding a lattice vector $\underline{R}$ to all the $\underline{x}_i$. It follows at once that each of its eigenfunctions must be of the form

$$\Psi_{\underline{k}n}(\underline{x}_1, \underline{x}_2, \ldots) = e^{i\underline{k}\cdot\underline{X}} \Phi_{\underline{k}n}(\underline{x}_1, \underline{x}_2, \ldots) \tag{B2}$$

where

$$\underline{X} = \frac{1}{N} \sum_i \underline{x}_i \tag{B3}$$

and $\Phi_{\underline{k}n}$ is a function with the property

$$\Phi_{\underline{k}n}(\underline{x}_1+\underline{R}, \underline{x}_2+\underline{R}, \ldots, \underline{x}_N+\underline{R}) = \Phi_{\underline{k}n}(\underline{x}_1, \underline{x}_2, \ldots \underline{x}_N) \tag{B4}$$

where $\underline{R}$ is any lattice vector.

Suppose that the system is in the state represented by the wave function $\Psi_{\underline{k}'n}$ and is perturbed by an electric field derived from the potential function

$$\varphi(\underline{x},t) = \varphi_{\omega\underline{k}} e^{i\omega t + i\underline{k}\cdot\underline{x}} + \varphi^*_{\omega\underline{k}} e^{-i\omega t - i\underline{k}\cdot\underline{x}} \tag{B5}$$

The perturbing term in the Hamiltonian representing the electric field will be

$$H' = e\left\{ \varphi_{\omega\underline{k}} e^{i\omega t} \sum_i e^{i\underline{k}\cdot\underline{x}_i} + \varphi^*_{\omega\underline{k}} e^{-i\omega t} \sum_i e^{-i\underline{k}\cdot\underline{x}_i} \right\} \tag{B6}$$

If we represent the perturbed wave function by $\Psi'_{\underline{k}'n}(t)$, then it can be shown using time dependent perturbation theory that to the first order in

$$\begin{aligned}\Psi'_{\underline{k}'n}(t) = {} & \Psi_{\underline{k}'n} e^{-\frac{i}{\hbar}E_{\underline{k}'n}t} \\ & + \frac{2\pi e}{i\hbar}\varphi_{\omega\underline{k}} e^{i\omega t - \frac{i}{\hbar}E_{\underline{k}'n}t} \sum_{n'} \Psi_{\underline{k}'+\underline{k},n'}(\Psi_{\underline{k}'+\underline{k},n'}, \rho_{-k}\Psi_{\underline{k}'n})\,\delta_-\left\{\frac{E_{\underline{k}'+\underline{k},n'} - E_{\underline{k}'n}}{\hbar} - \omega\right\} \\ & + \frac{2\pi e}{i\hbar}\varphi^*_{\omega\underline{k}} e^{-i\omega t - \frac{i}{\hbar}E_{\underline{k}'n}t} \sum_{n'} \Psi_{\underline{k}'-\underline{k},n'}(\Psi_{\underline{k}'-\underline{k},n'}, \rho_k\Psi_{\underline{k}'n})\,\delta_-\left\{\frac{E_{\underline{k}'-\underline{k},n'} - E_{\underline{k}'n}}{\hbar} + \omega\right\}\end{aligned} \tag{B7}$$

where

$$\rho_k = \sum_i e^{-i\underline{k}\cdot\underline{x}_i} \tag{B8}$$

and use has been made of the selection rule

$$(\Psi_{\underline{k}''n'} \rho_{-k} \Psi_{\underline{k}'n}) = 0 \quad \text{unless} \quad \underline{k}'' = \underline{k} + \underline{k}' + \underline{K} \tag{B9}$$

where $\underline{K}$ is any reciprocal lattice vector. We have introduced the convention that $\Psi_{\underline{k}+\underline{K},n} = \Psi_{\underline{k}n}$ since the $\underline{k}$ in (B2) is determined only up to an arbitary reciprocal lattice vector by the translational properties of $\Psi_{\underline{k}n}$. The perturbation of the charge distribution by the electric field is given by

$$\delta\rho(\underline{x},t) = e\left\{(\Psi'_{\underline{k}'n}(t)\ \rho(\underline{x})\ \Psi'_{\underline{k}'n}(t)) - (\Psi_{\underline{k}'n}\ \rho(\underline{x})\ \Psi_{\underline{k}'n})\right\} \tag{B10}$$

Substituting from (B7) into (B10) we obtain after some re-arrangement

$$\begin{aligned}\delta\rho(\underline{x},t) = {} & \frac{2\pi e^2}{i\hbar}\varphi_{\omega\underline{k}}\, e^{i\omega t} \\ & \times\Big[\sum_{n'}(\Psi_{\underline{k}'n}\rho(\underline{x})\Psi_{\underline{k}'+\underline{k},n'})(\Psi_{\underline{k}'+\underline{k},n'}\rho_{-k}\Psi_{\underline{k}'n})\,\delta_-\left\{\frac{E_{\underline{k}'+\underline{k},n'}-E_{\underline{k}'n}}{\hbar}-\omega\right\} \\ & -\sum_{n'}(\Psi_{\underline{k}'n}\rho(\underline{x})\Psi_{\underline{k}'-\underline{k},n'})(\Psi_{\underline{k}'-\underline{k},n'}\rho_{k}\Psi_{\underline{k}'n})\,\delta_+\left\{\frac{E_{\underline{k}'-\underline{k},n'}-E_{\underline{k}'n}}{\hbar}+\omega\right\}\Big] \\ & + \text{complex conjugate}\end{aligned} \tag{B11}$$

an equation analagous to (A6). We now note using the selection rule (B9) that

$$\begin{aligned}(\Psi_{\underline{k}'n}\rho(\underline{x})\Psi_{\underline{k}'+\underline{k},n'}) &= \sum_{\underline{k}''} e^{i\underline{k}''\cdot\underline{x}}(\Psi_{\underline{k}'n}\rho_{\underline{k}''}\Psi_{\underline{k}'+\underline{k},n'}) \\ &= e^{i\underline{k}\cdot\underline{x}}\sum_{\underline{K}} e^{i\underline{K}\cdot\underline{x}}(\Psi_{\underline{k}'n}\rho_{\underline{k}+\underline{K}}\Psi_{\underline{k}'+\underline{k},n'})\end{aligned} \tag{B12}$$

enabling us to rewrite (B11)

$$\delta\rho(\underline{x},t) = \frac{2\pi e^2}{i\hbar}\varphi_{\omega\underline{k}}\, e^{i\underline{k}\cdot\underline{x}+i\omega t}$$

$$\times\Big[\sum_{n',\underline{K}} e^{i\underline{K}\cdot\underline{x}}\,(\Psi_{\underline{k}'n}\rho_{\underline{k}+\underline{K}}\Psi_{\underline{k}'+\underline{k},n'})(\Psi_{\underline{k}'+\underline{k},n'}\rho_{-\underline{k}}\Psi_{\underline{k}'n})\,\delta_-\Big\{\frac{E_{\underline{k}'-\underline{k},n'}-E_{\underline{k}'n}}{\hbar}-\omega\Big\}$$

$$-\sum_{n',\underline{K}} e^{i\underline{K}\cdot\underline{x}}\,(\Psi_{\underline{k}'n}\rho_{-\underline{k}+\underline{K}}\Psi_{\underline{k}'-\underline{k},n'})(\Psi_{\underline{k}'-\underline{k},n'}\rho_{\underline{k}}\Psi_{\underline{k}'n})\,\delta_+\Big\{\frac{E_{\underline{k}'+\underline{k},n'}-E_{\underline{k}'n}}{\hbar}+\omega\Big\}\Big]$$

$$+\ \text{complex conjugate} \qquad \text{(B13)}$$

Thus the expression we obtain for $\delta\rho$ is again of the form (A9). If we proceed as before and neglect the periodic modulation and only calculate the Fourier component $\delta\rho_{\omega\underline{k}}$, we find

$$\delta\rho_{\omega\underline{k}} = \frac{2\pi e^2}{i\hbar}\varphi_{\omega\underline{k}}\sum_{n'}\Big[\,|(\Psi_{\underline{k}'+\underline{k},n'}\rho_{-\underline{k}}\Psi_{\underline{k}'n})|^2\,\delta_-\Big\{\frac{E_{\underline{k}'+\underline{k},n'}-E_{\underline{k}'n}}{\hbar}-\omega\Big\}$$

$$-\,|(\Psi_{\underline{k}'-\underline{k},n'}\rho_{\underline{k}}\Psi_{\underline{k}'n})|^2\,\delta_+\Big\{\frac{E_{\underline{k}'-\underline{k},n'}-E_{\underline{k}'n}}{\hbar}+\omega\Big\}\Big] \qquad \text{(B14)}$$

This expression has the same form as (A10) and we can now go on to derive results similar to those obtained in appendix A. Thus the outcome is that even when the Coulomb interactions are taken into account the results have the same form as those derived in appendix A, the difference being in the type of matrix element and the energies which appear. Because of these differences we cannot give quite the same simple interpretations of the various terms arising in the dispersion relation for the plasma frequency which we did in §16 of the thesis. However, if we considered

how the eigenstates $\Psi_{\underline{k}'m}$ of (B1) arose from the eigenstates of the same Hamiltonian without the Coulomb interactions as the Coulomb interaction were adiabatically switched on we should find that we could give roughly the same interpretations. We make no further comment here, only noting that corrections of the type discussed here arise even in the case of a free electron gas.

We now go on to consider the second feature contributing to the local field correction, namely the periodic modulation of the electric field in the interior of the crystal.

Let us suppose that an external field $\varphi^{(e)}(\underline{x},t)$ of the form (B5) is applied to the crystal and that it induces in the interior of the crystal an electric field whose potential function is $\varphi(\underline{x},t)$ and a charge displacement given by $\delta\rho(\underline{x},t)$. Then we shall have

$$\varphi(\underline{x},t) = \varphi^{(e)}(\underline{x},t) + \int \frac{\delta\rho(\underline{x}',t)\,d\underline{x}'}{|\underline{x}-\underline{x}'|} \tag{B15}$$

Now each Fourier component $\varphi_{\omega\underline{k}}$ of φ induces a charge displacement given by (A9), so that

$$\begin{aligned}\delta\rho(\underline{x},t) &= \sum_{\omega\underline{k}} \varphi_{\omega\underline{k}}\, e^{i\omega t + i\underline{k}\cdot\underline{x}}\, K_{\omega\underline{k}}(\underline{x}) \\ &= \int G'(\underline{x},\underline{x}';t,t')\,\varphi(\underline{x}',t')\,d\underline{x}'dt'\end{aligned} \tag{B16}$$

where

$$G(\underline{x},\underline{x}';t,t') = \sum_{\omega\underline{k}} e^{i\omega(t-t')+i\underline{k}\cdot(\underline{x}-\underline{x}')}\, K_{\omega\underline{k}}(\underline{x}) \tag{B17}$$

Substituting this result back into (B15) we have the integral equation

$$\varphi(\underline{x},t) = \varphi^{(e)}(\underline{x},t) + \int G(\underline{x},\underline{x}';t,t')\,\varphi(\underline{x}';t')\,d\underline{x}'dt' \tag{B18}$$

for $\varphi(\underline{x},t)$, where

$$G(\underline{x},\underline{x}';t,t') = \int \frac{G'(\underline{x}'',\underline{x}';t,t')\,d\underline{x}''}{|\underline{x}-\underline{x}''|} \tag{B19}$$

Since G depends only on the difference of the time arguments we can obtain a partial solution of (B18) by taking the Fourier transforms of all quantities with respect to their time arguments. We then obtain from (B18)

$$\varphi_\omega(\underline{x}) = \varphi^{(e)}_\omega(\underline{x}) + \int G_\omega(\underline{x},\underline{x}')\,\varphi_\omega(\underline{x}')\,d\underline{x}' \tag{B20}$$

where

$$\varphi(x,t) = \int \varphi_\omega(\underline{x})\, e^{i\omega t}\, d\omega \tag{B21}$$

with a similar definition for $\varphi^{(e)}_\omega$ and

$$G_\omega(\underline{x},\underline{x}') = \sum_{\underline{k}} \int \frac{e^{i\underline{k}\cdot(\underline{x}''-\underline{x}')}\,K_{\omega\underline{k}}(\underline{x}'')\,d\underline{x}''}{|\underline{x}-\underline{x}''|} \tag{B22}$$

To solve the integral equation (B20) we introduce the eigenfunctions $\chi_{\omega i}(\underline{x})$ of the corresponding homogeneous integral equation; these functions satisfy the equation

$$\chi_{\omega i}(\underline{x}) = \lambda_{\omega i} \int G_\omega(\underline{x},\underline{x}')\,\chi_{\omega i}(\underline{x}')\,d\underline{x}' \tag{B23}$$

where $\lambda_{\omega i}$ is the eigenvalue corresponding to $\chi_{\omega i}$. It can be shown that corresponding to each eigenfunction $\chi_{\omega i}$ there is an eigenfunction $\tau_{\omega i}$ of the associated homogeneous integral equation belonging to the same eigenvalue $\lambda_{\omega i}$ i.e. satisfying

$$\tau_{\omega i}(\underline{x}) = \lambda_{\omega i} \int G_\omega(\underline{x}', \underline{x})\, \tau_{\omega i}(\underline{x}')\, d\underline{x}' \qquad \text{(B24)}$$

and that these functions after suitable normalisation and orthogonalisation of functions belonging to the same eigenvalue have the orthonormality property

$$\int \tau_{\omega i}(\underline{x})\, \chi_{\omega j}(\underline{x})\, d\underline{x} = \delta_{ij} \qquad \text{(B25)}$$

The kernel G_ω of the integral equation (B23) has the symmetry property

$$G_\omega(\underline{x}+\underline{R}, \underline{x}'+\underline{R}) = G_\omega(\underline{x}, \underline{x}') \qquad \text{(B26)}$$

where $\underline{R}$ is any lattice vector. It follows at once that its eigenvalues form a band structure and may be denoted by $\lambda_{\omega \underline{k} n}$ where $\underline{k}$ is a wave vector lying in the first Brillouin zone and n is an integral subscript which distinguishes the various bands. The corresponding eigenfunctions will have the Bloch form

$$\chi_{\omega \underline{k} n} = e^{i\underline{k}\cdot\underline{x}}\, X_{\omega \underline{k} n}(\underline{x}) \qquad \text{(B27)}$$

where $X_{\omega \underline{k} n}$ is a periodic function of $\underline{x}$. Similarly the corresponding eigenfunction $\tau_{\omega \underline{k} n}$ will have the form

$$\tau_{\omega \underline{k} n} = e^{-i\underline{k}\cdot\underline{x}} T_{\omega \underline{k} n} \tag{B28}$$

where $T_{\omega \underline{k} n}$ is periodic.

We may now solve (B20) by expanding φ_ω in terms of the $\chi_{\omega \underline{k} n}$:

$$\varphi_\omega(\underline{x}) = \sum_{\underline{k} n}' \varphi_{\omega \underline{k} n} \chi_{\omega \underline{k} n}(\underline{x}) \tag{B29}$$

Substituting this expansion into (B20) we can obtain using (B23) and (B25)

$$\varphi_{\omega \underline{k} n} = \varphi^{(e)}_{\omega \underline{k} n} + \lambda_{\omega \underline{k} n} \varphi_{\omega \underline{k} n} \tag{B30}$$

where

$$\varphi^{(e)}_{\omega \underline{k} n} = \int \varphi^{(e)}_\omega(\underline{x})\, \tau_{\omega \underline{k} n}(\underline{x})\, d\underline{x} \tag{B31}$$

Equation (B30) has the immediate solution

$$\varphi_{\omega \underline{k} n} = \frac{\varphi^{(e)}_{\omega \underline{k} n}}{1 - \lambda_{\omega \underline{k} n}} \tag{B32}$$

so that

$$\varphi_\omega(\underline{x}) = \sum_{\underline{k} n}' \frac{\varphi^{(e)}_{\omega \underline{k} n}}{1 - \lambda_{\omega \underline{k} n}} \chi_{\omega \underline{k} n}(\underline{x}) \tag{B33}$$

We now note that if $\varphi^{(e)}_\omega$ has the form $e^{i\underline{k}\cdot\underline{x}}$ then

$$\varphi^{(e)}_{\omega \underline{k}' n} = \int e^{i\underline{k}\cdot\underline{x} - i\underline{k}'\underline{x}} T_{\omega \underline{k}' n}(\underline{x})\, d\underline{x} = 0 \quad \text{unless} \quad \underline{k}' = \underline{k} \tag{B34}$$

Thus

$$\varphi_{\omega}(\underline{x}) = \rho^{(e)}_{\omega\underline{k}}\, e^{i\underline{k}\cdot\underline{x}} \sum_{n}{}' \frac{\mu_{\omega\underline{k}n}}{1-\lambda_{\omega\underline{k}n}} X_{\omega\underline{k}n}(\underline{x}) \tag{B35}$$

where

$$\mu_{\omega\underline{k}n} = \int T_{\omega\underline{k}n}(\underline{x})\, d\underline{x} \tag{B36}$$

and φ is of the form $e^{i\underline{k}\cdot\underline{x}+i\omega t}$ times a periodic function of $\underline{x}$. The Fourier component $\varphi_{\omega\underline{k}}$ of φ is given by

$$\varphi_{\omega\underline{k}} = \int \varphi_{\omega}(\underline{x})\, e^{-i\underline{k}\cdot\underline{x}}\, d\underline{x} = \rho^{(e)}_{\omega\underline{k}} \sum_{n}{}' \frac{\mu_{\omega\underline{k}n}\,\xi_{\omega\underline{k}n}}{1-\lambda_{\omega\underline{k}n}} \tag{B37}$$

where

$$\xi_{\omega\underline{k}n} = \int X_{\omega\underline{k}n}(\underline{x})\, d\underline{x} \tag{B38}$$

Since according to the ordinary theory of dielectrics $\varphi_{\omega\underline{k}} = \varphi^{(e)}_{\omega\underline{k}}/\epsilon_{\omega\underline{k}}$, we have

$$\frac{1}{\epsilon_{\omega\underline{k}}} = \sum_{n}{}' \frac{\mu_{\omega\underline{k}n}\,\xi_{\omega\underline{k}n}}{1-\lambda_{\omega\underline{k}n}} \tag{B39}$$

We see from this result that $\epsilon_{\omega\underline{k}}$ vanishes whenever the right hand side of (B39) becomes infinite i.e. whenever one of the $\lambda_{\omega\underline{k}n}$ satisfies $\lambda_{\omega\underline{k}n} = 1$. Thus the plasma resonances are at the frequencies at which there exist non-trivial $\chi(\underline{x})$ satisfying the equation

$$\chi(\underline{x}) = \int G_{\omega}(\underline{x},\underline{x}')\,\chi(\underline{x}')\, d\underline{x}' \tag{B40}$$

This is physically sensible because comparing with (B20) we see that this

is the condition that an internal field can exist in the crystal in the absence of an external perturbing field.

In general, of course, there will be no frequencies at which the equation $\lambda_{\omega \underline{k} n} = 1$ will be exactly satisfied. However, we may argue as in §15 that the plasma frequencies are those at which the real part of $\lambda_{\omega \underline{k} n}$ is equal to 1 and the imaginary part is small. Then at these frequencies it will be possible for weakly damped oscillations to exist in the crystal. Thus it is possible even when the periodic modulation of the field is taken into account to discuss the oscillation frequencies in terms of the dielectric theory.

It is easily seen that in the case of a free electron gas there is no correction of the type discussed above since there is no possibility of a periodic modulation of the field; this is an old result due to Darwin (1934, 1943). Thus in the case of a free electron gas and free electron like metals this type of local field correction will have no effect on the oscillation frequencies.

SUBSIDIARY MATTER

"The Description of Collective Motion in Terms of Many-Body Perturbation Theory".

"The Description of Collective Motion in Terms of Many-Body Perturbation Theory II".

"The Description of Collective Motion in Terms of Many-Body Perturbation Theory III".

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The description of collective motions in terms of many-body perturbation theory

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In this and a succeeding paper it is shown how a theory equivalent to the Bohm & Pines collective motion theory of the electron plasma can be derived directly from a perturbation series which gives in principle an exact solution of the many-body problem. This result is attained by making use of a diagrammatic method of analysis of the perturbation series. By a process analogous to the elimination of photon self-energy parts from the electrodynamic S matrix it is found possible to simplify the perturbation series, introducing a modified interaction between the particles. A useful integral equation for this modified interaction can be set up, and it is shown how the energy of the system can be expressed in terms of the modified interaction. The close connexion between this approach and the dielectric theory of plasma oscillations is indicated.

1. Introduction

Within recent years much attention has been given in the study of the quantum mechanical many-body problem to the collective modes of motion which may be present (Bohm & Pines 1953; Tomonaga 1955; Bohr & Mottelson 1953). Two main theories of collective motion have been developed, that of Tomonaga (1955), and the superfluous co-ordinate type of theory introduced by Bohm & Pines (1953). In the Tomonaga theory a transformation of variables is made in such a way that some of the new co-ordinates are directly related to the collective modes of motion, whilst the remaining new co-ordinates are associated with internal modes of motion. In the superfluous co-ordinate treatment certain auxiliary variables are introduced together with an equal number of subsidiary conditions to preserve the correct number of degrees of freedom, and a transformation is made in such a way that the new auxiliary variables are related to the collective motion, whilst the original co-ordinates when transformed are related to the internal motion. If the collective modes being studied have real physical significance, then it will be found in both these methods that the Hamiltonian is, to a good approximation, separable in the new co-ordinates, and a separation of the collective motion is thereby obtained.

Though these methods are quite successful, they have certain unsatisfactory features. In the Tomonaga method it is generally found that when the Hamiltonian has been separated the problem of finding the eigenvalues of the internal motion part is very difficult. In the superfluous co-ordinate treatment one does not meet with this difficulty but with an equivalent one; this is that it is difficult to find eigenfunctions satisfying the subsidiary conditions. In addition, both theories suffer from the difficulty of not being able to treat very easily the interaction between the collective and internal modes of motion, or the intimately related problem of the damping of the collective motion; where the damping is small this is not a very

serious problem, but in certain cases, e.g. the application of the Bohm & Pines theory to metals, it may be quite serious. We shall see later that this problem of treating the damping is also intimately connected with the problem of the cut-off in the Bohm & Pines theory of the electron plasma (1953).

In the case of the electron plasma an alternative type of theory of a different character from those described above has been developed. In this 'dielectric' theory (Mott 1954; Fröhlich & Pelzer 1955; Hubbard 1955*a*, *b*) one argues along semi-classical lines, regarding the electron gas as a dielectric medium. From this point of view one thinks of the electrons as interacting with one another like particles in the dielectric medium represented by the remaining electrons; their interaction is therefore modified and screened. The plasma oscillations are thought of as being the polarization waves in the dielectric medium. This approach has advantages over the other two approaches in that it can easily treat the damping problem, and does not attempt so complete a separation of the collective and internal modes of motion, the one going smoothly over into the other; it suffers from the disadvantages of being a phenomenological theory and difficult to quantize satisfactorily.

It is the purpose of this and a succeeding paper (Hubbard 1957) to develop yet another approach to the collective motion problem which is applicable to the electron plasma, and to similar systems, and which we hope combines the advantages of the treatments described above and yet is free of their disadvantages. This theory is based upon an (infinite) perturbation series which provides in principle an exact solution to the many-body problem and therefore contains all the physical effects including the collective motion. The various contributions to this perturbation series can be conveniently analyzed making use of diagrams similar to Feynman diagrams (Goldstone 1957). It is now argued that we may be able to simplify our perturbation series by a process exactly analogous to the elimination of photon self-energy parts in the analysis of the S-matrix in quantum electrodynamics (see, for example, Dyson 1949). This is in fact so, and the analysis shows that we need only retain in our perturbation series terms corresponding to diagrams free from these parts, provided everywhere in the perturbation series we replace the ordinary interaction between the particles by a modified interaction.

To establish the connexion between this apparently formal device for simplifying the perturbation series and the collective motion problem let us now consider the physical interpretation of what we shall do. Just as in the electrodynamic case, we can regard the diagrams used in the analysis of the perturbation series as representing the actual physical process which gives rise to the corresponding contribution to the perturbation series. Interpreting the parts of diagrams analogous to photon self-energy parts in this way, we can see that they correspond to the modification of the ordinary interaction between particles by the polarization of the medium represented by the remaining particles; we shall refer to these as polarization parts. Thus, the elimination of these parts and the replacement of the ordinary interaction by the modified interaction in the perturbation series is exactly equivalent to going over to the viewpoint of the dielectric theory described above, so that we may expect our theory to be equivalent to the other theories of collective motion. This expectation is in fact borne out by detailed calculation.

The present paper develops the theory in a general form, and the detailed treatment of the electron plasma is reserved for a succeeding paper. Since the diagrammatic analysis is used in a different (although equivalent) form to that given by Goldstone (1957), it is developed afresh in §§ 2 to 4. In § 5 are discussed certain simplifications which arise when one considers the case of a uniform gas; in the remainder of the paper it is assumed that we are dealing with this case.

Section 6 proceeds with the main programme; the polarization parts are eliminated and the modified interaction introduced. In § 7 an integral equation is derived for the modified interaction which very greatly simplifies its calculation. Finally, in § 8 it is shown how the energy of the system can be expressed exactly in terms of the modified interaction. This result will enable us to calculate correlation energies directly from the modified interaction which in turn can be calculated easily using the integral equation.

2. The diagrammatic analysis of the perturbation series

We shall consider the problem of determining the energy spectrum and wave functions of a gas of Fermi–Dirac particles interacting with one another through an instantaneous two-body potential and moving so slowly that relativistic effects can be neglected; we include also the case in which the particles move in an external potential field. The Hamilton for such a system is

$$H = H_0 + H', \tag{1}$$

where H_0 includes the kinetic energy of the particles and their potential energy in the external field, and H' is the interaction energy of the particles. H' will be treated as a perturbation.

One way in which we may develop the perturbation series for H' is by making use of the adiabatic approximation. We consider the interaction H' to be slowly switched on between $t = -\infty$ and $t = 0$, and to be slowly switched off between $t = 0$ and $t = +\infty$; then a system which at $t = -\infty$ is in an eigenstate Ψ_0 of H_0 will between $t = -\infty$ and $t = 0$ slowly change into an eigenstate of H. This result has been proved by Gell-Mann & Low (1951) in the following form: if Ψ_0 is an eigenstate of H_0 belonging to the energy E_0, then

$$\Psi = \lim_{\alpha \to +0} S_\alpha(0, -\infty)\,\Psi_0 / (\Psi_0 \,|\, S_\alpha(0, -\infty) \,|\, \Psi_0) \tag{2}$$

is an eigenstate of H belonging to the energy

$$E = E_0 + \Delta E = E_0 + \lim_{\alpha \to +0} (\Psi_0 \,|\, H' S_\alpha(0, -\infty) \,|\, \Psi_0) / (\Psi_0 \,|\, S_\alpha(0, -\infty) \,|\, \Psi_0), \tag{3}$$

where $S_\alpha(t, t')$ is the solution of the equation

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} S_\alpha(t, t') = H_\alpha(t)\, S_\alpha(t, t'), \tag{4}$$

satisfying the boundary condition $S_\alpha(t', t') = 1$, and

$$H_\alpha(t) = \mathrm{e}^{(\mathrm{i}/\hbar) H_0} H' \mathrm{e}^{-(\mathrm{i}/\hbar) H_0} \mathrm{e}^{-\alpha |t|}. \tag{5}$$

The parameter α is seen to govern the rate of switching on and off of the interaction; the limit $\alpha \to +0$ means that the potential is switched on infinitely slowly, the condition for the exactness of the adiabatic approximation.

We can now obtain a perturbation series for Ψ by solving (4) by iteration. To do this we replace (4) by the integral equation

$$S_\alpha(t) = 1 + \frac{1}{i\hbar}\int_{-\infty}^{t} H_\alpha(t')\, S_\alpha(t')\, dt', \tag{6}$$

incorporating the boundary condition at $t = -\infty$ (in future we shall for brevity write $S_\alpha(t, -\infty)$ as $S_\alpha(t)$). Iteration of (6) gives

$$\begin{aligned} S_\alpha(t) &= 1 + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{n-1}} dt_n\, H_\alpha(t_1)\, H_\alpha(t_2) \ldots H_\alpha(t_n) \\ &= 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{1}{i\hbar}\right)^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \ldots \int_{-\infty}^{t} dt_n\, P[H_\alpha(t_1)\, H_\alpha(t_2) \ldots H_\alpha(t_n)], \end{aligned} \tag{7}$$

where P is the chronological ordering operator; this is the perturbation series we shall use.

Our interaction Hamilton can be written in the notation of field theory

$$H' = \frac{1}{2}\int \overline{\psi}(\mathbf{x}')\, \psi(\mathbf{x}')\, v(\mathbf{x}-\mathbf{x}')\, \overline{\psi}(\mathbf{x})\, \psi(\mathbf{x})\, d\mathbf{x}\, d\mathbf{x}' - \tfrac{1}{2} N v(0), \tag{8}$$

where $v(\mathbf{x}-\mathbf{x}')$ is the mutual potential energy of two particles at $\mathbf{x}$ and $\mathbf{x}'$, N is the number of particles in the system, and $\overline{\psi}(\mathbf{x})$, $\psi(\mathbf{x})$ are the particle field operators. These can be written

$$\left.\begin{aligned} \psi(\mathbf{x}) &= \sum_i u_i(\mathbf{x})\, \eta_i, \\ \overline{\psi}(\mathbf{x}) &= \sum_i \overline{u}_i(\mathbf{x})\, \overline{\eta}_i, \end{aligned}\right\} \tag{9}$$

where the $u_i(\mathbf{x})$ are the eigenfunctions of the one-particle Hamiltonian,

$$\left[\frac{p^2}{2m} + U(\mathbf{x})\right] u_i(\mathbf{x}) = E_i\, u_i(\mathbf{x}), \tag{10}$$

in which $\mathbf{p}$ is the momentum and $U(\mathbf{x})$ the external potential. The operators $\overline{\eta}_i$ and η_i are creation and destruction operators for the particle in the state i; since our particles obey Fermi–Dirac statistics they satisfy the anticommutation relations

$$[\eta_i, \eta_j]_+ = [\overline{\eta}_i, \overline{\eta}_j]_+ = 0, \quad [\eta_i, \overline{\eta}_j]_+ = \delta_{ij}. \tag{11}$$

In (8) spinor indices are suppressed since their inclusion only requires a trivial generalization of the theory. The second term in (8) subtracts the self-energies of the particles due to the interaction v, since these are included together with the mutual interactions of the particles in the first term of (8). (If the potential is singular at the origin $v(0)$ is not defined. We can, however, easily introduce a suitable limiting procedure. If we Fourier transform v, $v(\mathbf{x}) = \int v(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{x}}\, d\mathbf{k}$, then we can work with $v_K(\mathbf{x}) = \int_{k<K} v(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{x}} d\mathbf{k}$, for which $v_K(0)$ is defined, and take the limit $K \to \infty$ at the end of the calculation.)

To obtain our perturbation series in a suitable form for computation we now have to substitute (8) into (5) and (5) into (7). Before doing this it is convenient to include the (constant) second term of (8) in H_0 and to symmetrize the first term; H' then becomes

$$H' = \frac{1}{4}\int v(\mathbf{x}-\mathbf{x}')\,[\overline{\psi}(\mathbf{x}')\,\psi(\mathbf{x}')\,\overline{\psi}(\mathbf{x})\,\psi(\mathbf{x}) + \overline{\psi}(\mathbf{x})\,\psi(\mathbf{x})\,\overline{\psi}(\mathbf{x}')\,\psi(\mathbf{x}')]\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'. \quad (12)$$

Putting (12) into (5) we can easily obtain

$$H_\alpha(t) = \frac{1}{4}\int \mathrm{d}x \int \mathrm{d}x'\, v_\alpha(x-x')\,[\overline{\psi}(x')\,\psi(x')\,\overline{\psi}(x)\,\psi(x) + \overline{\psi}(x)\,\psi(x)\,\overline{\psi}(x')\,\psi(x')], \quad (13)$$

where x stands for $(\mathbf{x}, t)$ and x' for $(\mathbf{x}', t')$,

$$v_\alpha(x-x') = v(\mathbf{x}-\mathbf{x}')\,\delta(t-t')\,\mathrm{e}^{-\alpha|t|}, \quad (14)$$

and

$$\psi(x) = \psi(\mathbf{x}, t) = \sum_i u_i(x)\,\eta_i = \sum_i u_i(\mathbf{x})\,\mathrm{e}^{-(\mathrm{i}t/\hbar)E_i}\,\eta_i,$$

$$\overline{\psi}(x) = \sum_i \overline{u}_i(x)\,\overline{\eta}_i. \quad (15)$$

Substituting (13) into (7) we obtain

$$\begin{aligned} S_\alpha(t) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!}\left(\frac{1}{4\mathrm{i}\hbar}\right)^n \int^t \mathrm{d}x_1 \int^t \mathrm{d}x_2 \ldots \int^t \mathrm{d}x_n \int^t \mathrm{d}x_1' \ldots \int^t \mathrm{d}x_n' \\ \times v_\alpha(x_1-x_1')\,v_\alpha(x_2-x_2')\ldots v_\alpha(x_n-x_n') \\ \times P[\overline{\psi}(x_1')\,\psi(x_1')\,\overline{\psi}(x_1)\,\psi(x_1) + \overline{\psi}(x_1)\,\psi(x_1)\,\overline{\psi}(x_1')\,\psi(x_1'), \ldots \\ \ldots, \overline{\psi}(x_n')\,\psi(x_n')\,\overline{\psi}(x_n)\,\psi(x_n) + \overline{\psi}(x_n)\,\psi(x_n)\,\overline{\psi}(x_n')\,\psi(x_n')], \end{aligned} \quad (16)$$

where $\int^t \mathrm{d}x$ means the integral over all that part of space-time behind the surface t.

We can conveniently analyze the P product in (16) by making use of Wick's theorem (Wick 1950). This analysis can be simplified if we notice that we are interested only in the operation of S_α on the particular eigenstate Ψ_0 of H_0. We shall, henceforth, assume that Ψ_0 is a non-degenerate eigenstate of H_0 in which certain definite states i are occupied. Then we can conveniently take the state Ψ_0 as a 'redefined vacuum state' (Salam 1953) and resolve $\overline{\psi}$ and ψ according to

$$\psi = \psi^+ + \psi^-, \quad \overline{\psi} = \overline{\psi}^+ + \overline{\psi}^-, \quad (17)$$

where

$$\psi^-(x) = \sum_i^{\text{unocc.}} u_i(x)\,\eta_i \quad \text{(destroys particles)},$$

$$\psi^+(x) = \sum_i^{\text{occ.}} u_i(x)\,\eta_i \quad \text{(creates holes)},$$

$$\overline{\psi}^-(x) = \sum_i^{\text{occ.}} \overline{u}_i(x)\,\overline{\eta}_i \quad \text{(destroys holes)},$$

$$\overline{\psi}^+(x) = \sum_i^{\text{unocc.}} \overline{u}_i(x)\,\overline{\eta}_i \quad \text{(creates particles)}. \quad (18)$$

Here the terms occupied and unoccupied refer to the state of occupation of the state i in Ψ_0. We then have the result

$$\psi^-(x)\,\Psi_0 = \overline{\psi}^-(x)\,\Psi_0 = 0. \tag{19}$$

To take advantage of the result (19) we resolve the P product in (16) in such a way as to move all the operators ψ^+, $\overline{\psi}^+$ to the left and all the operators ψ^-, $\overline{\psi}^-$ to the right. This analysis can be performed quite straightforwardly using Wick's theorem. When this analysis has been completed we can reject all terms involving ψ^- and $\overline{\psi}^-$ by virtue of (19). Only one special point arises in this analysis. This is that, whereas in the case dealt with by Wick all operators with the same time argument either commuted or were already arranged as an S product, this is not so in the present case and one has to allow for contractions between operators with the same time argument.

When the analysis has been completed, it is found that the various terms contributing to $S_\alpha(t)\,\psi_0$ (the terms not involving ψ^- or $\overline{\psi}^-$) can be conveniently classified in terms of certain diagrams similar to Feynmann diagrams, there being a contribution to $S_\alpha(t)\,\psi_0$ corresponding to each diagram. We proceed at once to the prescription for drawing these diagrams and for calculating the corresponding contribution to $S_\alpha(t)$.

The diagrams will be of orders 1, 2, ..., corresponding to the contributions arising from different order terms of (16). The prescription for drawing an nth order diagram is as follows:

(i) Mark n points on the diagram and label these $x_1, x_2, \ldots, x_n$; mark a further n points and label with $x_1', \ldots, x_n'$; join the pairs of points x_i, x_i' by 'interaction' lines (broken lines in the diagrams of this paper).

(ii) Draw directed 'particle' lines, one entering and one leaving each point; these lines may run between points or from a point to itself or from a point to the edge of the diagram or from the edge of the diagram to a point.

The different nth order diagrams are obtained by drawing in the particle lines in all possible ways. It will be noted that the particle lines form closed polygons and open polygonal arcs, so that to every particle line running inwards from the edge of the diagram there is one running out connected to it by a chain of particle lines.

The contributions to $S_\alpha(t)$ corresponding to a given diagram is a certain integral which can be written down from the following prescription:

(i) For every interaction line $x_i x_i'$ introduce a factor $v(x_i - x_i')$ into the integrand.

(ii) For every particle line running from a point y(= some x_i or x_i') to the edge of the diagram introduce a factor $\overline{\psi}^+(y)$ into the integrand, and for every particle line running from the edge of the diagram to a point y introduce a factor $\psi^+(y)$ into the integrand. The ψ^+ and $\overline{\psi}^+$ are to be arranged so that if $\psi^+(y)$ corresponds to the incoming line of one of the open polygonal arcs and $\overline{\psi}^+(z)$ to the corresponding outgoing line, then $\overline{\psi}^+(z)$ is adjacent to and on the left of $\psi^+(y)$.

(iii) For every particle line running from a point y to a point $z\,(\neq y)$ introduce a factor $S(z, y)$ into the integrand.

(iv) For every particle line running from a point y to itself introduce a factor $\rho(y)$ into the integrand.

(v) Integrate with respect to $\mathrm{d}x_1\mathrm{d}x_2\ldots\mathrm{d}x_n\mathrm{d}x'_1\ldots\mathrm{d}x'_n$ over the region of space-time behind the surface t.

(vi) Multiply the integral by $(2\mathrm{i}\hbar)^{-n}(n!)^{-1}(-1)^p$, where p is the number of closed particle loops in the diagram.

The quantity $\rho(x)$ is just the charge density corresponding to Ψ_0, namely

$$\rho(x) = \sum_{}^{\text{occ.}} \overline{u}_i(\mathbf{x})\, u_i(\mathbf{x}), \tag{20}$$

whilst the quantity $S(x', x)$ is a propagator given by

$$S(x', x) = \epsilon(t'-t) \sum_{i}^{\text{unocc.}} u_i(x')\,\overline{u}_i(x) - \epsilon(t-t') \sum_{i}^{\text{occ.}} u_i(x')\,\overline{u}_i(x), \tag{21}$$

where

$$\epsilon(t) = 1 \quad \text{if} \quad t > 0$$
$$= 0 \text{ otherwise.}$$

The function $S(x, x')$ is the solution of the equation

$$\left[\mathrm{i}\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 - U(\mathbf{x})\right] S(x, x') = \delta(\mathbf{x}-\mathbf{x}')\,\delta(t-t'), \tag{22}$$

which reduces to $\frac{1}{2} - \rho(\mathbf{x}, \mathbf{x}')$ when $t = t'$, where $\rho(\mathbf{x}, \mathbf{x}')$ is the ordinary density matrix corresponding to the state Ψ_0:

$$\rho(\mathbf{x}, \mathbf{x}') = \sum_{i}^{\text{occ.}} u_i(\mathbf{x})\,\overline{u}_i(\mathbf{x}'). \tag{23}$$

As an example of the above prescriptions we give the contribution to $S_\alpha(t)$ corresponding to the diagram shown in figure 1 (*a*); it is

$$-\frac{1}{4!}\left(\frac{1}{2\mathrm{i}\hbar}\right)^4 \int \mathrm{d}x_1\,\mathrm{d}x_2\,\mathrm{d}x_3\,\mathrm{d}x_4\,\mathrm{d}x'_1\,\mathrm{d}x'_2\,\mathrm{d}x'_3\,\mathrm{d}x'_4\; v_\alpha(x_1-x'_1)\, v_\alpha(x_2-x'_2)\, v_\alpha(x_3-x'_3)\, v_\alpha(x_4-x'_4)$$
$$\times\, \overline{\psi}^+(x_4)\,\psi^+(x_1)\,\overline{\psi}^+(x'_3)\,\psi^+(x'_1)\,S(x_4, x'_4)\,S(x'_4, x_3)\,S(x_3, x_1)\,S(x'_3, x_2)\,S(x_2, x'_1)\,\rho(x'_2). \tag{24}$$

3. The linked-cluster expansion

The linked-cluster expansion was first suggested by Brueckner (1955) and has been proved by Goldstone (1957) using the diagrammatic method of analysis of the perturbation series. The necessity for this result arises because the ordinary perturbation series for the energy, including that derived above, contain terms which diverge more strongly than N, the number of particles in the system, as $N \to \infty$. Such terms can have no physical significance and must cancel out against each other: we should, therefore, be able to eliminate them from the series, which is done in the linked-cluster expansion. This elimination will be carried out easily and naturally in this section using the diagrammatic analysis.

Before proceeding to develop the linked-cluster expansion it is first convenient to classify the diagrams in a certain way. We shall say that two diagrams belong to the same class if they have the same basic structure, i.e. if they have the same arrangement of vertices, interaction and particle lines and differ only in the labelling of their vertices; for example, the diagrams shown in figures 1 (*a*) and (*b*) belong to the same

class since they have the same basic structure shown in figure 1 (*c*). It is seen that each class is associated with a certain basic structure.

It can be seen from the prescription of § 2 that if two diagrams G, G' belong to the same class their contributions to $S_\alpha(t)$ are integrals which differ only by a permutation of the variables of integration, and are therefore equal. Thus all the diagrams of the same class give an equal contribution, and the contribution of the whole class is the contribution of a typical member multiplied by the number of diagrams in the class.

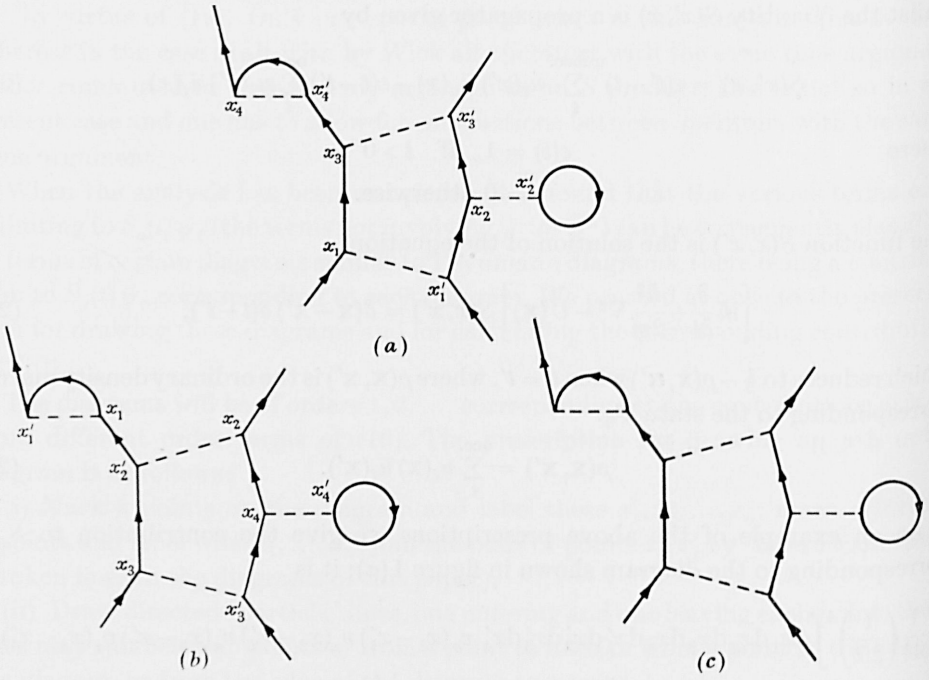


FIGURE 1

Let us consider how many diagrams there are in a given class. Let G be a typical member of a class Γ of order n, i.e. a class whose associated structure has n interaction lines. We can obtain all the other members of the class by performing certain permutations of the labels x_i, x'_i of the vertices of G. The permutations of the labels which lead to diagrams agreeing with the prescriptions of § 2 are those which leave the pairs x_i, x'_i connected by interaction lines in G still connected by interaction lines after the permutation. The only permutations which do this can be built up from the following types of permutation:

(i) simultaneous permutations of the x_i and x'_i in the same way;

(ii) the interchange of any pair x_i, x'_i.

The number of distinct permutations which can be built up from these is $2^n n!$. If the application of every one of these permutations to the labels of G led to a diagram distinct from G, then this would be the number of diagrams in the class. However, it may be that the application of some of these permutations to G leads to diagrams which are not topologically distinct from G; for example, the diagrams shown in

figures 2 (*a*) and (*b*) which are obtainable from one another by a permutation of labels are topologically equivalent and must not be counted separately. Suppose the number of permutations which take G into diagrams topologically equivalent to itself is $g(\Gamma)$ (this number is a function of the structure Γ rather than of the particular diagram); then we can easily show that the number of diagrams in the class is in fact $2^n n!/g(\Gamma)$.

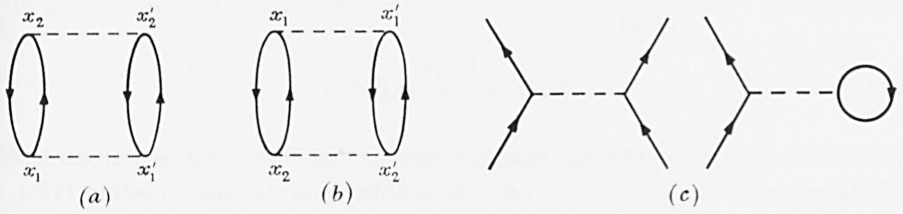


FIGURE 2

If we denote the contribution of a diagram G to $S_\alpha(t)$ by $S_\alpha(t, G)$ and the contribution of the class Γ to which G belongs by $S_\alpha(t, \Gamma)$, then we have

$$S_\alpha(t, \Gamma) = \frac{2^n n!}{g(\Gamma)} S_\alpha(t, G). \tag{25}$$

We can now develop the linked-cluster expansion. A structure Γ may or may not fall into two or more unconnected parts; in the former case we shall say that it is an unlinked, in the latter case linked. For example, the structure shown in figure 1 (*c*) is linked whilst that shown in figure 2 (*c*) is unlinked. It should be noticed that this definition of linked and unlinked diagrams is not quite the same as that used by Goldstone (1957).

An unlinked structure Γ can be resolved into a set of linked structures; if the unlinked structure Γ is made up of p_1 linked structures Γ_1, p_2 linked structures Γ_2 etc., we shall write

$$\Gamma = p_1 \Gamma_1 + p_2 \Gamma_2 + \ldots.$$

Let G be a typical diagram with the structure Γ. Using the prescription of § 2 we can easily prove that

$$S_\alpha(t, G) = \frac{1}{n!} [n_1! \, S_\alpha(t, G_1)]^{p_1} [n_2! \, S_\alpha(t, G_2)]^{p_2} \ldots,$$

where $G_1, G_2 \ldots$ are typical diagrams with the structures $\Gamma_1, \Gamma_2, \ldots$, n is the order of Γ, and $n_1, n_2 \ldots$ are the orders of Γ_1, Γ_2, etc. Using (25) we obtain

$$S_\alpha(t, \Gamma) = \frac{1}{g(\Gamma)} [g(\Gamma_1) \, S_\alpha(t, \Gamma_1)]^{p_1} [g(\Gamma_2) \, S_\alpha(t, \Gamma_2)]^{p_2} \ldots. \tag{26}$$

Finally it can be seen that

$$g(\Gamma) = p_1! p_2! \ldots [g(\Gamma_1)]^{p_1} [g(\Gamma_2)]^{p_2} \ldots, \tag{27}$$

so that

$$S_\alpha(t, \Gamma) = \frac{1}{p_1! p_2! \ldots} [S_\alpha(t, \Gamma_1)]^{p_1} [S_\alpha(t, \Gamma_2)]^{p_2} \ldots. \tag{28}$$

Let $\Gamma_1, \Gamma_2, \ldots$ be the set of all linked structures; if in (26) we allow $p_1, p_2, \ldots$ to run over all the values $0, 1, 2, \ldots$, then we obtain all possible structures. Since $S_\alpha(t)$ is the sum of the contributions from all possible structures we have

$$\begin{aligned} S_\alpha(t) &= \sum_{p_1=0}^{\infty} \sum_{p_2=0}^{\infty} \cdots \frac{1}{p_1! p_2! \ldots} [S_\alpha(t, \Gamma_1)]^{p_1} [S_\alpha(t, \Gamma_2)]^{p_2} \ldots \\ &= \exp\{S_\alpha(t, \Gamma_1)\} \exp\{S_\alpha(t, \Gamma_2)\} \ldots \\ &= \exp\{S_{L\alpha}(t)\}, \end{aligned} \tag{29}$$

where

$$S_{L\alpha}(t) = \sum_{\Gamma}^{\text{linked}} S_\alpha(t, \Gamma), \tag{30}$$

and we have made use of the fact that the various $S_\alpha(t, G)$ commute with each other; this is because all the ψ^+ and $\overline{\psi}^+$ operators anticommute (see equation (18)), and each $S_\alpha(t, G)$ contains an even number of these. Thus we see that $S_\alpha(t)$ can be expressed in terms of $S_{L\alpha}$, the sum of the contributions from linked diagrams.

Let us now resolve $S_{L\alpha}(t)$ into two parts

$$S_{L\alpha}(t) = S^{(0)}_{L\alpha}(t) + S'_{L\alpha}(t), \tag{31}$$

$S^{(0)}_{L\alpha}(t)$ containing the contributions from all linked 'vacuum' diagrams, that is, diagrams with no particle lines running to or from the edge of the diagram, and $S'_{L\alpha}(t)$ the contributions from all linked diagrams with external lines; $S^{(0)}_{L\alpha}(t)$ contains no operators and is a c number.

Substituting (31) into (29) and (29) into (2) and dividing out by the c number $\exp\{S^{(0)}_{L\alpha}(0)\}$, we obtain

$$\Psi = \lim_{\alpha \to +0} \exp\{S'_{L\alpha}(0)\} \Psi_0 / (\Psi_0 \mid \exp\{S'_{L\alpha}(0)\} \mid \Psi_0). \tag{32}$$

It will be shown in the next section that $S'_{L\alpha}(t)$ is continuous as $\alpha \to +0$ whilst $S^{(0)}_{\alpha L}(t)$ diverges like $1/\alpha$; thus, dropping a normalization factor,

$$\Psi = \exp\{S'_L(0)\} \Psi, \tag{33}$$

where

$$S'_L(0) = \lim_{\alpha \to +0} S'_{L\alpha}(0).$$

We shall see in the next section that the energy shift ΔE can be derived from $S^{(0)}_{L\alpha}(t)$, i.e. from a series involving only the linked terms; this series does not contain terms diverging more strongly than N and so is free from the difficulty mentioned at the beginning of this section.

4. The evaluation of integrals

In this section we perform as an illustration the evaluation of the integral representing the contribution of a simple diagram to $S_\alpha(0)$. The result obtained is typical of the general case, and we can deduce from it certain properties of the $S_\alpha(0, G)$; furthermore, these results afford a link between the present formalism and that of Goldstone.

The diagram whose evaluation we shall perform is that shown in figure 3 (*a*). The corresponding contribution to $S_\alpha(0)$ is according to the prescription of § 2

$$\frac{1}{2}\left(\frac{1}{2i\hbar}\right)^2\int_{-\infty}^{0}dt_1\int_{-\infty}^{0}dt_2\int d\mathbf{x}_1\,d\mathbf{x}_2\,d\mathbf{x}_1'\,d\mathbf{x}_2'\,v(\mathbf{x}_1-\mathbf{x}_1')\,v(\mathbf{x}_2-\mathbf{x}_2')\,e^{\alpha(t_1+t_2)}$$
$$\times S(\mathbf{x}_2,t_2;\mathbf{x}_1,t_1)\,S(\mathbf{x}_2',t_2;\mathbf{x}_1',t_1)\,\bar{\psi}^+(\mathbf{x}_2,t_2)\,\psi^+(\mathbf{x}_1,t_1)\,\bar{\psi}^+(\mathbf{x}_2',t_2)\,\psi^+(\mathbf{x}_1',t_1), \quad (34)$$

where we have already performed the integrations over t_1' and t_2'. Because of the nature of the function S (equation (21)), it is convenient to divide the integration

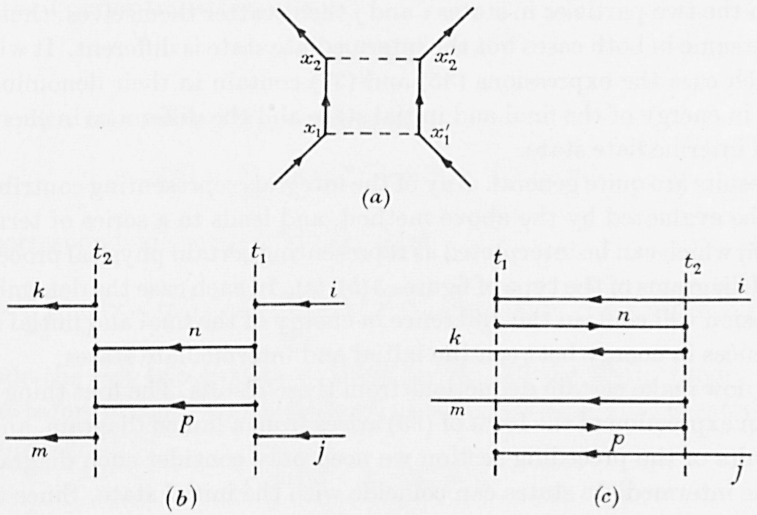


FIGURE 3

over t_1 and t_2 into two parts, one part arising from the region in which $t_2 > t_1$ and the other from the region in which $t_2 < t_1$. Substituting for S from (21) and for $\bar{\psi}^+$, ψ^+, from (18), we have for the first part of the integral

$$\frac{1}{2}\left(\frac{1}{2i\hbar}\right)^2\sum_{i,j}^{\text{occ.}}\sum_{kmnp}^{\text{unocc.}}\int\bar{u}_k(\mathbf{x}_2)\,\bar{u}_m(\mathbf{x}_2')\,v(\mathbf{x}_2-\mathbf{x}_2')\,u_n(\mathbf{x}_2)\,u_p(\mathbf{x}_2')\,d\mathbf{x}_2\,d\mathbf{x}_2'$$
$$\times\int\bar{u}_n(\mathbf{x}_1)\,\bar{u}_p(\mathbf{x}_1')\,v(\mathbf{x}_1-\mathbf{x}_1')\,u_i(\mathbf{x}_1)\,u_j(\mathbf{x}_1')\,d\mathbf{x}_1\,d\mathbf{x}_1'\int_{-\infty}^{0}dt_2\int_{-\infty}^{t_2}dt_1$$
$$\times\exp\left\{\alpha(t_1+t_2)+\frac{i}{\hbar}(E_k+E_m-E_n-E_p)t_2+\frac{i}{\hbar}(E_n+E_p-E_i-E_j)t_1\right\}\bar{\eta}_k\eta_i\bar{\eta}_m\eta_j$$
$$=\frac{1}{8}\sum_{ij}^{\text{occ.}}\sum_{kmnp}^{\text{unocc.}}\frac{(km\,|\,v\,|\,np)\,(np\,|\,v\,|\,ij)}{(E_k+E_m-E_i-E_j+2i\hbar\alpha)\,(E_n+E_p-E_i-E_j+i\hbar\alpha)}\bar{\eta}_k\eta_i\bar{\eta}_m\eta_j, \quad (35)$$

where
$$(km\,|\,v\,|\,np)=\int\bar{u}_k(\mathbf{x})\,\bar{u}_m(\mathbf{x}')\,v(\mathbf{x}-\mathbf{x}')\,u_n(\mathbf{x})\,u_p(\mathbf{x}')\,d\mathbf{x}\,d\mathbf{x}'. \quad (36)$$

A similar evaluation of the second part of the integral gives

$$\frac{1}{8}\sum_{ijnp}^{\text{occ.}}\sum_{km}^{\text{unocc.}}\frac{(km\,|\,v\,|\,np)\,(np\,|\,v\,|\,ij)}{(E_k+E_m-E_i-E_j+2i\hbar\alpha)\,(E_k+E_m-E_n-E_p+i\hbar\alpha)}\bar{\eta}_k\eta_i\bar{\eta}_m\eta_j. \quad (37)$$

The similarity of these results to the terms of the ordinary perturbation series is at once recognizable.

The two terms (35) and (37) may be represented diagrammatically as in figures 3(*b*), (*c*); these diagrams are obtained from (*a*) by arranging t_1 and t_2 in particular orders and labelling the lines rather than the vertices. Figure 3(*b*) represents a process in which two particles in states i and j interact and scatter into states n and p, and re-interact and scatter into states m and k; thus the whole process is a scattering of particles out of the states i and j into the states k and m via the intermediate state n, p. Similarly, figure 3(*c*) represents a process in which two particles scatter themselves into states k and m leaving holes in the states n and p into which the two particles in states i and j then scatter themselves; thus the final state is the same in both cases but the intermediate state is different. It will be seen that in each case the expressions (35) and (37) contain in their denominators the difference in energy of the final and initial state and the difference in energy of the initial and intermediate state.

These results are quite general. Any of the integrals representing contributions to $S_\alpha(0)$ can be evaluated by the above method, and leads to a series of terms of the form of (35) which can be interpreted as representing certain physical processes with the help of diagrams of the type of figures 3(*b*), (*c*). In each case the denominators of the expression will contain the difference in energy of the final and initial state and the differences in energy between the initial and intermediate states.

We can now make certain deductions from these results. The first thing to notice is that if an expression of the form of (35) arises from a linked diagram, and in view of the results of the preceding section we need only consider such diagrams, then none of the intermediate states can coincide with the initial state. Since the latter has been assumed to be non-degenerate, it follows that the energy of none of the intermediate states can coincide with that of the initial state. If, further, the final state is different from the initial state, as it is in all the terms contributing to $S'_{L\alpha}(0)$, then the energy of the final state will be different from that of the initial state. Thus, in the case of terms contributing to $S'_{L\alpha}(0)$, none of the energy differences in the denominators is zero; it follows at once (see (35)) that each of these terms is continuous as $\alpha \to +0$, and that $S'_{L\alpha}(0)$ is continuous $\alpha \to +0$. Thus $\lim S'_{L\alpha}(0)$ as $\alpha \to +0$ exists, and may be evaluated putting $\alpha = 0$ at the beginning of the calculation.

The situation with $S^{(0)}_{L\alpha}(0)$ is different, however. In the case of terms contributing to $S^{(0)}_{L\alpha}(0)$ the initial and final states coincide (although the intermediate states are different from the initial state), and the corresponding energy difference vanishes giving rise to a factor α in the denominator. Thus $S^{(0)}_{L\alpha}(0)$ diverges like $1/\alpha$ as $\alpha \to +0$.

We should now like to consider the calculation of the energy shift ΔE. This is given by (3). It may, however, be more conveniently calculated using a formula given by Gell-Mann & Low; it is shown in an appendix that it can be derived from $S^{(0)}_{L\alpha}(\infty)$, and is given by the following prescription: *write down the sum of all integrals contributing to* $S^{(0)}_{L\alpha}(\infty)$ *(one from each vacuum diagram); introduce into the integrand of each of these integrals a factor* $i\hbar\delta(t_1)$ *and put* $\alpha = 0$; *the resulting sum gives* ΔE.

In the remainder of this paper we shall devote our attention to the calculation of ΔE.

5. The uniform gas case

The theory of the preceding sections was general in the sense that H_0 was supposed to include not only the kinetic energy of the particles but also their potential energy in an external field. In the remaining sections of this paper we shall for simplicity restrict ourselves to the case in which the external field is constant and the particles form a uniform gas; it is hoped to deal with the general case later.

In the case of a uniform gas it is convenient to resolve the H' of (8) into two parts. Suppose the Fourier transform of v is

$$v(\mathbf{x}) = \sum_{\mathbf{k}} u(\mathbf{k})\, e^{i\mathbf{k}.\mathbf{x}}. \tag{38}$$

Then we split v into two parts according to

$$v(\mathbf{x}) = \sum_{k \neq 0} u(\mathbf{k})\, e^{i\mathbf{k}.\mathbf{x}} + u(0) = v'(\mathbf{x}) + u(0). \tag{39}$$

We can correspondingly write H' in the form

$$H' = \frac{1}{2}\int d\mathbf{x}\, d\mathbf{x}'\, \overline{\psi}(\mathbf{x}')\, \psi(\mathbf{x}')\, v'(\mathbf{x}-\mathbf{x}')\, \overline{\psi}(\mathbf{x})\, \psi(\mathbf{x})\, d\mathbf{x}\, d\mathbf{x}' + \tfrac{1}{2}N^2 u(0) - \tfrac{1}{2}N v(0) \tag{40}$$

and include the last two (constant) terms in H_0. All the above theory then goes through as before except that v is replaced by v' everywhere. The potential v' has the useful property

$$\int v'(\mathbf{x}-\mathbf{x}')\, d\mathbf{x}' = 0. \tag{41}$$

We can now make an important deduction concerning the perturbation series in the case of a uniform gas. This is that *in the case of a uniform gas those diagrams which contain a part which is attached to the rest of the diagram by only a single interaction line give no contribution $S_\alpha(t)$ or any derived quantities.* To prove this let us consider the contribution of a diagram of the type shown in figure 4 (*a*), where the two parts I'' and I''' are connected by only the single interaction line shown. If in the integral representing the contribution of this diagram we perform all the integrations except those over $\mathbf{x}$ and $\mathbf{x}'$, we must obtain an expression of the form

$$\int F(\mathbf{x})\, v'(\mathbf{x}-\mathbf{x}')\, G(\mathbf{x}')\, d\mathbf{x}\, d\mathbf{x}'. \tag{42}$$

However, since the gas is uniform and has no natural origin of co-ordinates, F and G must be independent of $\mathbf{x}$ and $\mathbf{x}'$, so that it reduces to an integral over $v'(\mathbf{x}-\mathbf{x}')$ which must vanish by virtue of (41). Thus we can omit all diagrams of this type.

In future we shall drop the prime on v', it being always understood that we are working with v'.

6. The elimination of polarization parts

As pointed out in the introduction, the main point of introducing the diagrammatic analysis in the present theory is that it enables us easily to recognize those parts of the perturbation series which represent polarization effects. We are now in a position to investigate this.

Let us consider the physical interpretation of the *subdiagram* shown in figure 4 (*b*). The net effect of this subdiagram is that the two incoming particles scatter off each other, not through the ordinary direct interaction but via a closed particle loop. More generally, the subdiagram shown in figure 4 (*c*), where the circle is meant to represent some set of closed particle loops and interaction lines connected to the rest of the diagram by only the two interaction lines shown, represents the scattering of two particles through some more complicated process which, however, returns all the particles involved to their original states. Our hypothesis, which will be borne out by further calculation, is that these subdiagrams represent the polarization effect referred to in the introduction, and that they can be eliminated from the perturbation series by replacing the ordinary interaction by a modified interaction.

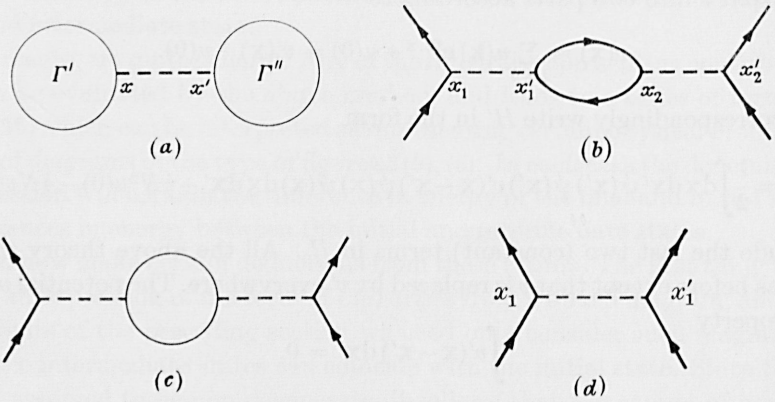


FIGURE 4

The way in which such subdiagrams can be eliminated from the perturbation series is already familiar in quantum electrodynamics, being exactly analogous to the elimination of photon self-energy parts (Dyson 1949). Let Γ be some structure. Then it may or may not be that Γ contains some polarization part, i.e. some connected part without external lines attached to the rest of the structure by only two interaction lines; in the former case we shall say that Γ is (polarization) reducible, in the latter case that Γ is irreducible. It is obvious that we can obtain all reducible structures by inserting polarization parts in place of interaction lines in irreducible structures.

Let us consider as an example the diagram shown in figure 4 (*b*), regarding this now as a complete diagram rather than as a subdiagram of some larger diagram. This is a reducible diagram contributing to $S'_L(t)$, obtainable from the irreducible diagram shown in figure 4 (*d*) by substituting the polarization part shown in figure 6 (*a*) for its interaction line. The contributions to $S'_L(t)$ of the diagrams of figures 4 (*b*), (*d*) are

$$\frac{1}{2!}\left(\frac{1}{2i\hbar}\right)^2\int^t dx_1\int^t dx'_1\int^t dx_2\int^t dx'_2\, v(x_1-x'_1)\, v(x_2-x'_2)$$
$$\times\, \overline{\psi}^+(x_1)\,\psi^+(x_1)\,\overline{\psi}^+(x'_2)\,\psi^+(x'_2)\,S(x'_1,x_2)\,S(x_2,x'_1) \qquad (43)$$

and

$$\frac{1}{1!}\left(\frac{1}{2i\hbar}\right)\int^t dx_1\int^t dx'_1\, v(x_1-x'_1)\,\overline{\psi}^+(x_1)\,\psi^+(x_1)\,\overline{\psi}^+(x'_1)\,\psi^+(x'_1). \qquad (44)$$

It will be seen that (43) is obtainable from (44) (apart from an unimportant change in the integration variable) by:

(i) multiplying by $1!/2!$, the ratio of the factorials of the orders of the diagrams;

(ii) by replacing $v(x-x')$ in (44) by the quantity

$$\frac{1}{2i\hbar}\int^t \mathrm{d}x \int^t \mathrm{d}x'\, v(x_1-x)\, v(x_1'-x')\, S(x,x')\, S(x',x) \tag{45}$$

which is just the contribution to (43) of the interaction and particle lines of the polarization part of figure 6 (a) with the integrations at the vertices performed. This result is typical; the contribution of a reducible diagram is the same as that of the corresponding irreducible diagram except that the v's are replaced by functions of the type (45) corresponding to the various polarization parts which have been inserted in place of interaction lines, and the whole integral has been multiplied by the ratio of the factorials of the orders.

We can enunciate this result more precisely as follows. If G is a reducible diagram obtained by substituting the polarization part Γ'_{s_1} for the interaction line x_1x_1', Γ'_{s_2} for x_2x_2', etc., of the irreducible diagram G' (introducing the convention that if the line x_ix_i' of G' is left unchanged we say it has been replaced by the polarization part Γ'_0), then

$$S(t,G) = \frac{n'!}{n!} S(t,G';\ W'_t(\Gamma'_{s_1}),\ W'_t(\Gamma'_{s_2}),\ldots), \tag{46}$$

where n and n' are the orders of G and G', $S(t,G';\ W'_t(\Gamma'_{s_1}),\ W'_t(\Gamma'_{s_2}),\ldots)$ means that integral for $S(t,G')$ with the $v(x_i-x_i')$ replaced by the functions $W'_t(x_i',x_i,\Gamma'_{s_i})$, and $W'_t(x',x,\Gamma'')$ is the expression which arises from the polarization part Γ'' in the same way that (45) arises from the polarization part of figure 6 (a), remembering that in the case of the special polarization part Γ_0 this is just $v(x-x')$.

Let Γ be a reducible structure contributing to $S'_L(t)$, i.e. with external lines. Then it can be seen that Γ arises from some unique irreducible structure Γ''. Consider the total contribution to $S'_L(t)$ of all the diagrams with structures which reduce to a given irreducible structure Γ''. A straightforward counting of diagrams shows now that this total contribution is given by the expression

$$\frac{n'!\,2^{n'}}{g(\Gamma'')} \sum_{\Gamma'_{s_1}} \sum_{\Gamma'_{s_2}} \ldots S(t,G';W_t(\Gamma'_{s_1}),W_t(\Gamma'_{s_2}),\ldots), \tag{47}$$

where the sums run over all polarization parts, and

$$W_t(x',x,\Gamma'') = \frac{2^m}{g(\Gamma'')}\, W'_t(x',x,\Gamma''), \tag{48}$$

where $g(\Gamma'')$ is the g factor of the polarization part Γ'', defined to be the number of permutations of the *internal* interaction lines of Γ'' which take it into itself (these g factors are exactly analogous to those of §3), and m is its order, defined to be the number of *internal* interaction lines of Γ'' plus one.

Since $S(t,G';\ W_t(\Gamma'_{s_1}),\ W_t(\Gamma'_{s_2}),\ldots)$ depends linearly upon the $W_t(\Gamma'_s)$ we can write (47) as

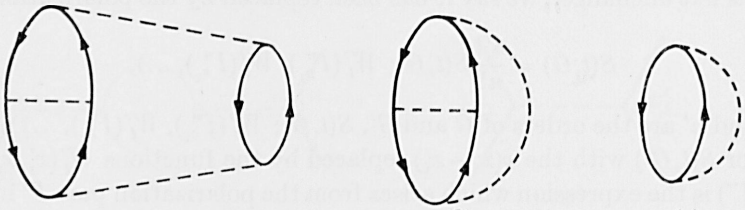
$$S(t,\Gamma';\mathscr{V}_t,\mathscr{V}_t,\ldots), \tag{49}$$

using (25), where

$$\mathscr{V}_t(x',x) = \sum_{\Gamma'} W_t(x',x,\Gamma'_s). \tag{50}$$

Thus, we see that the contribution to $S_L(t)$ of all diagrams reducing to the structure Γ' can be expressed in terms of the contribution of the class Γ' by replacing v everywhere by $\mathscr{V}_t$. Since every diagram contributing to $S_L(t)$ is uniquely reducible, we see that $S_L(t)$ can be expressed as a sum over contributions from irreducible diagrams by replacing v by $\mathscr{V}_t$ in all the integrals. Thus $\mathscr{V}_t$ plays the part of a modified interaction. In order to calculate the perturbed wave function we shall be interested in $\mathscr{V}_0$.

We have shown above how the perturbation series for the perturbed wave function can be contracted by introducing a modified interaction. Let us now consider the perturbation series for the energy shift ΔE. This has been expressed as a sum over vacuum diagrams in §4. We could proceed as above and reduce this to a sum over irreducible vacuum diagrams by replacing v everywhere by $\mathscr{V}_\infty$ (since the time integrations run up to $t = \infty$ in the case of ΔE) except for one feature. Whereas every diagram contributing to $S'_L(t)$ is uniquely reducible, this is not true for vacuum diagrams in general. For example, the diagram shown in figure 5 (*a*) could be reduced to either of the diagrams shown in figures 5 (*b*) or (*c*) by regarding either the right hand or the left hand part as the polarization part.



(*a*) (*b*) (*c*)

FIGURE 5

The fact that the reduction may not be unique can be overcome by demanding that every vacuum diagram be reduced in such a way that the point x_1 remain in the irreducible residue; any vacuum reducible diagram can always be reduced in this way provided that it contains no part which is connected to the rest of the diagram by only a single interaction line, and we have shown in the preceding section that such diagrams can be omitted. Furthermore, it is necessary to reduce the diagrams contributing to ΔE in this way, otherwise the factor $i\hbar\delta(t_1)$ would appear in some polarization part and spoil the theory.

Taking this point into account, we find by counting diagrams that the total contribution to ΔE of all diagrams which reduce to a given irreducible structure Γ' is

$$\frac{2^{n'}n'!}{g(\Gamma')}\sum_{\Gamma_{s_1}}\sum_{\Gamma_{s_2}}\cdots\frac{n'}{n'+n_{s_1}+n_{s_2}+\ldots}\Delta E(G';\, W_\infty(\Gamma'_{s_1}), W_\infty(\Gamma'_{s_2}), \ldots), \tag{51}$$

where G' is a typical diagram with the structure Γ' and n_s is the order of the polarization part Γ_s. Because of the factor $(n'+n_{s_1}+n_{s_2}+\ldots)^{-1}$, we cannot perform the sum in the simple way we did in (47). However, we notice that if we regard the interaction v as being linearly proportional to some coupling constant λ, then $\Delta E(G';\, W_\infty(\Gamma'_{s_1}), W_\infty(\Gamma'_{s_2}), \ldots)$ varies as $\lambda^{n'+n_{s_1}+n_{s_2}+\cdots}$. Thus we can write (51) as

$$\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\frac{2^{n'}n'!}{g(\Gamma')}\sum_{\Gamma'_{s_1}}\sum_{\Gamma_{s_2}}\ldots n'\,\Delta E\,(G';\, W_\infty(\Gamma'_{s_1}), W_\infty(\Gamma''_{s_2})\ldots). \tag{52}$$

We can now perform the sum as we did in (47) and obtain

$$\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} \frac{2^{n'} n'!}{g(\Gamma')} n' \Delta E(G'; \mathscr{V}_\infty, \mathscr{V}_\infty \ldots), \tag{53}$$

enabling us to express ΔE as a sum over irreducible diagrams. In this case we replace v by $\mathscr{V}_\infty$ (which will be written $\mathscr{V}$ for short in future); it is this quantity $\mathscr{V}_\infty$ that we regard as the real modified interaction rather than the more general $\mathscr{V}_t$, since in the calculation of all observable quantities, such as ΔE, $\mathscr{V}_\infty$ will turn up rather than $\mathscr{V}_t$.

7. An integral equation for $\mathscr{V}$

In the preceding section we have introduced the modified interaction and expressed it in terms of an infinite series. In this section we should like to consider some of its properties.

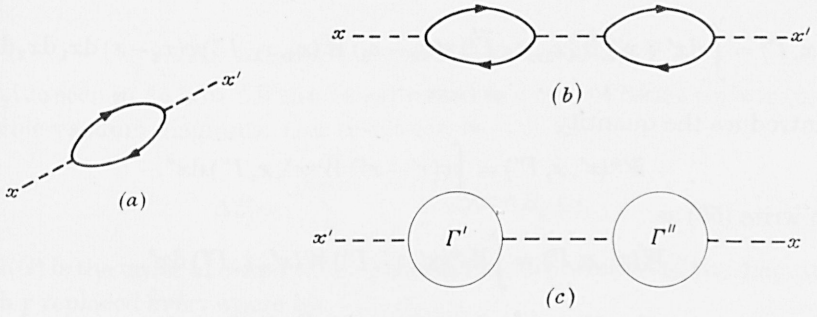


Figure 6

We first notice that in the case of a uniform gas $\mathscr{V}(x', x)$ is a function of $x - x'$ only. For so far as the space co-ordinates are concerned it can only be a function of $\mathbf{x} - \mathbf{x}'$ because of the spatial homogeneity of the system. Also each of the integrals in the series for $\mathscr{V}$ (equation (50) with $t = \infty$) is an integral whose time integrations run from $-\infty$ to $+\infty$ and whose integrands are products of factors each of which depends only upon time differences (see e.g. (45)); consequently $\mathscr{V}(x', \boldsymbol{x})$ can depend only upon $t' - t$, and is therefore a function of $x' - x$. It should further be noticed that there is no reason why $\mathscr{V}$ should vanish when $t \neq t'$, so that the modified interaction $\mathscr{V}$ will not in general be an instantaneous interaction like v but a sort of retarded interaction.

We shall now see how we can set up an integral equation for $\mathscr{V}$ which will enable us to express it in terms of a series more rapidly convergent than (50). Let Γ be any polarization structure. Then it may or may not be that Γ consists of two or more parts which are only connected by single interaction lines. In the first case we shall say that Γ is an improper polarization structure, in the latter case that it is a proper polarization structure. For example, the polarization structure shown in figure 6 (*a*) is a proper structure whilst that shown in figure 6 (*b*) is an improper one.

Let Γ be some improper polarization structure. Then Γ can be uniquely resolved as shown in figure 6 (*c*) into a proper structure Γ' and some other polarization structure Γ'', proper or improper. Let us introduce as follows the quantity $\overline{W}(x', x, \Gamma)$

related to $W_\infty(\Gamma)$ (to be written $W(\Gamma)$ for brevity in future). It will be seen from the prescription of the previous section for $W(\Gamma)$ that it can be written in the form

$$W(x', x, \Gamma) = \int v(x' - x'')\, \overline{W}(x'', x''', \Gamma)\, v(x''' - x)\, \mathrm{d}x''\, \mathrm{d}x''', \tag{54}$$

the two v's being those corresponding to the two outgoing lines of the polarization structure, and $\overline{W}$ containing the contribution from all the internal interaction and particle lines with the appropriate integrations performed. For example, in the case of the polarization part shown in figure 6 (a) (see (45)) $\overline{W}$ will be

$$\overline{W}(x', x) = \frac{1}{\mathrm{i}\hbar} S(x', x)\, S(x, x'). \tag{55}$$

We can now prove that the contribution of the polarization part resolved as in figure 6 (c) can be written

$$W(x', x, \Gamma) = \int v(x' - x_1)\, \overline{W}(x_1, x_2, \Gamma')\, v(x_2 - x_3)\, \overline{W}(x_3, x_4, \Gamma'')\, v(x_4 - x)\, \mathrm{d}x_1\, \mathrm{d}x_2\, \mathrm{d}x_3\, \mathrm{d}x_4. \tag{56}$$

If we introduce the quantity

$$W^*(x', x, \Gamma') = \int v(x' - x'')\, \overline{W}(x'', x, \Gamma')\, \mathrm{d}x'', \tag{57}$$

we can write (56) as

$$W(x', x, \Gamma) = \int W^*(\mathrm{x}', x'', \Gamma')\, W(x'', x, \Gamma'')\, \mathrm{d}x''. \tag{58}$$

Let us now consider the contribution to $\mathscr{V}$ of all those improper polarization structures which give rise to a given proper structure Γ' when resolved as in figure 6 (c). This is evidently obtained by summing over all structures Γ'' apart from Γ_0 on the right-hand side of (58), and is given by

$$\int W^*(x', x'', \Gamma') \sum_{\Gamma'' \neq \Gamma_0} W(x'', x, \Gamma'')\, \mathrm{d}x'' \tag{59}$$

If we add to this the contribution of Γ' itself to $\mathscr{V}$, which from (54) and (57) is given by

$$\int W^*(x', x'', \Gamma')\, v(x'' - x)\, \mathrm{d}x, \tag{60}$$

we obtain

$$\int W^*(x', x'', \Gamma') [v(x'' - x') + \sum_{\Gamma'' \neq \Gamma_0} W(x'', x, \Gamma'')]\, \mathrm{d}x'' = \int W^*(x', x'', \Gamma')\, \mathscr{V}(x'', x)\, \mathrm{d}x'' \tag{61}$$

for the total contribution to $\mathscr{V}$ of the proper diagram Γ' and all the improper ones which give Γ' on resolution. To obtain $\mathscr{V}$ we now have to sum this expression over all proper polarization parts Γ' and add the contribution of the polarization part Γ_0 which is just $v(x - x')$. Defining

$$\mathscr{V}^*(x', x) = \sum_{\Gamma' \neq \Gamma_0}^{\text{proper}} W(x', x, \Gamma'), \tag{62}$$

we have

$$\mathscr{V}(x', x) = v(x' - x) + \int \mathscr{V}^*(x', x'')\, \mathscr{V}(x'', x)\, \mathrm{d}x''. \tag{63}$$

Thus we have derived an integral equation which gives $\mathscr{V}$ in terms of $\mathscr{V}^*$. This is desirable because the series (62) is very much more rapidly convergent than (50). The solution of (63) presents no particular difficulty in the uniform gas because all the quantities involved depend upon the differences in their arguments and the equation may be solved by Fourier transformation.

We should like to complete this section with a comment on the physical interpretation of the result (62). The modified interaction between two particles can be regarded as a superposition of their direct interaction and the interaction of each with the polarization field of the other. These two interactions are represented by the first and second terms on the right-hand side of (62). The polarization produced at any point by one of the particles depends, however, not upon the direct field of the particle at that point, but upon the modified field; this is represented in (63) by the dependence of the second term upon $\mathscr{V}$, $\mathscr{V}^*(x', x'')$ representing the field at x' due to the polarization at the point x''.

8. An expression for ΔE in terms of V

We have seen in §6 how ΔE can be expressed as a sum of terms corresponding to irreducible vacuum diagrams. Our result can be written

$$\Delta E = \sum_{G}^{\text{irreducible vacuum}} \int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} n(G)\, \Delta E_v(G), \tag{64}$$

where $n(G)$ is the order of G and $\Delta E_v(G)$ means the contribution of the diagram G to ΔE with v replaced everywhere by $\mathscr{V}$.

Suppose now that G is some irreducible vacuum diagram. If we break the interaction line $x_1 x_1'$, the diagram may or may not fall into two separate parts. If it does, then it is of the form shown in Figure 4(*a*), and we have seen in §5 that such diagrams give no contribution. If it does not, then breaking this interaction line leads to some proper irreducible polarization part Γ (since G was assumed to be irreducible).

It can now be proved that if on breaking the line $x_1 x_1'$ in the diagram G we obtain the polarization part Γ, then

$$\Delta E_v(G) = \int \mathrm{d}x_1 \int \mathrm{d}x_1'\, \mathrm{i}\hbar\delta(t_1)\, \mathscr{V}(x_1 - x_1')\, \overline{W}_v(x_1, x_1', \Gamma)\, \frac{g(\Gamma)}{n(G)!\, 2^{n(G)}}, \tag{65}$$

where $\overline{W}_v(x', x, \Gamma)$ is the same as $\overline{W}(x', x, \Gamma)$ except that v has been replaced everywhere by $\mathscr{V}$.

If we substitute (65) into (64), our sum over diagrams reduces to a sum over irreducible polarization structures, each structure being counted a certain number of times. Counting of diagrams shows that this sum reduces to

$$\Delta E = \frac{1}{2} \int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} \int \mathrm{d}x_1 \int \mathrm{d}x_1'\, \mathrm{i}\hbar\delta(t_1)\, \mathscr{V}(x_1 - x_1') \sum_{\Gamma \neq \Gamma_0}^{\text{proper irreducible}} \overline{W}_v(x_1', x_1, \Gamma). \tag{66}$$

Defining the quantity

$$\overline{\mathscr{V}}(x', x) = \sum_{\Gamma \neq \Gamma_0}^{\text{proper irreducible}} \overline{W}_v(x', x, \Gamma) = \sum_{\Gamma \neq \Gamma_0}^{\text{proper}} \overline{W}(x', x\Gamma), \tag{67}$$

we see that (66) can be written

$$\Delta E = \frac{1}{2}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}x_1 \int \mathrm{d}x_1' \, \mathrm{i}\hbar\delta(t_1)\,\overline{\mathscr{V}}(x_1, x_1')\,\mathscr{V}(x_1', x_1). \tag{68}$$

The quantity $\overline{\mathscr{V}}$ is closely related to $\mathscr{V}$. We have in fact (57), (62) and (67)

$$\mathscr{V}^*(x', x_1) = \int \overline{\mathscr{V}}(x', x'')\, v(x''-x)\,\mathrm{d}x, \tag{69}$$

and $\mathscr{V}$ is related to $\mathscr{V}^*$ by (62); thus (68) is in effect an expression for ΔE in terms of $\mathscr{V}$. Using the result (68), we obtain the expression

$$E = \sum_i^{\text{occ.}} E_i - \tfrac{1}{2}Nv(0) + \tfrac{1}{2}N^2 u(0) + \frac{\mathrm{i}\hbar}{2}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}x_1 \int \mathrm{d}x_1' \, \delta(t_1)\,\mathscr{V}(x_1, x_1')\,\overline{\mathscr{V}}(x_1', x_1) \tag{70}$$

for the energy of a uniform interacting gas, where the E_i are those of equation (10). In the case of a uniform gas the first term of (70) is just the kinetic energy of the particles in the occupied states together with their potential energy in any constant background potential which is present.

9. Summary of results

In this paper the following results have been obtained.

(i) It has been shown how the perturbation series for the many-body problem may be expressed as a sum of terms each of which is associated with a certain diagram.

(ii) This has been reduced to a series of terms (linked-cluster expansion) corresponding to linked diagrams.

(iii) A series has been obtained for the energy shift ΔE due to the interaction, each term of which is associated with a certain 'vacuum' diagram.

(iv) In the case of a uniform gas it has been shown that some of the terms of this series give no contribution and may be omitted.

(v) This series has been reduced to one over irreducible vacuum diagrams, i.e. over diagrams containing no polarization parts, by introducing a modified interaction $\mathscr{V}$ in place of the ordinary interaction v. An infinite series has been given for $\mathscr{V}$.

(vi) An integral equation has been obtained for $\mathscr{V}$ in terms of a quantity $\mathscr{V}^*$ which is given by an infinite series much more rapidly convergent than that for $\mathscr{V}$.

(vii) Finally, the energy shift and the energy of the whole system have been expressed in terms of the modified interaction $\mathscr{V}$; the latter is calculated from the integral equation the rapidly convergent series for $\mathscr{V}^*$ replaces the original perturbation series.

In a later paper these results will be applied to calculate the correlation energy of a free-electron gas, and it will be shown that essentially the same results as those of Bohm & Pines (1953) can be obtained by taking only the first term of the series for $\mathscr{V}^*$ and making allowance for certain exchange terms.

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Appendix. The calculation of ΔE

To calculate ΔE we start from a formula given by Gell-Mann & Low (1951), namely

$$\Delta E = \lim_{\alpha \to +0} i\hbar\alpha\lambda \frac{\partial}{\partial \lambda} \ln (\Psi_0 \mid S_\alpha(0, -\infty) \mid \Psi_0), \tag{A 1}$$

where λ is the coupling constant of the interaction. Using the same method as Gell-Mann & Low we can also derive the formula

$$\Delta E = -\lim_{\alpha \to +0} i\hbar\alpha\lambda \frac{\partial}{\partial \lambda} \ln (\Psi_0 \mid S_\alpha^{-1}(\infty, 0) \mid \Psi_0). \tag{A 2}$$

Furthermore, we have

$$S_\alpha(\infty, -\infty) = S_\alpha(\infty, 0)\, S_\alpha(0, -\infty), \tag{A 3}$$

from which

$$S_\alpha^{-1}(\infty, 0) = S_\alpha(0, -\infty)\, S_\alpha^{-1}(\infty, -\infty) \tag{A 4}$$

It was shown in § 3 that

$$S_\alpha(\infty, -\infty)\, \Psi_0 = \exp \{S_{L\alpha}^{(0)}(\infty) + S'_{L\alpha}(\infty)\}\, \Psi_0. \tag{A 5}$$

Since Ψ_0 is non-degenerate and $S_\alpha(\infty, -\infty)$ connects only states with the same energy in the limit as $\alpha \to +0$, we see that $S'_{L\alpha}(\infty, -\infty) \to 0$ as $\alpha \to +0$. From (A 1), (A 2), (A 4) and (A 5) we have

$$\begin{aligned}
\Delta E &= \lim_{\alpha \to +0} -i\hbar\alpha\lambda \frac{\partial}{\partial \lambda} \ln (\Psi_0 \mid S_\alpha(0) [\exp \{S'_{L\alpha}(\infty)\}]^{-1} \exp \{-S_{L\alpha}^{(0)}(\infty)\} \mid \Psi_0) \\
&= \lim_{\alpha \to +0} -i\hbar\alpha\lambda \frac{\partial}{\partial \lambda} [\ln (\Psi_0 \mid S_\alpha(0) \mid \Psi_0) - S_{L\alpha}^{(0)}(\infty)] \\
&= -\Delta E + \lim_{\alpha \to +0} i\hbar\alpha\lambda \frac{\partial}{\partial \lambda} S_{L\alpha}^{(0)}(\infty).
\end{aligned} \tag{A 6}$$

Thus

$$\Delta E = \tfrac{1}{2} \lim_{\alpha \to +0} i\hbar\alpha\lambda \frac{\partial}{\partial \lambda} S_{L\alpha}^{(0)}(\infty). \tag{A 7}$$

Now $S^{(0)}_{L\alpha}(\infty)$ is a sum of terms corresponding to vacuum diagrams. When all the integrations in an nth order diagram except those over $t_1, t_2, \ldots, t_n$ have been performed, we shall have an expression of the form

$$\int \mathrm{d}t_1 \ldots \int \mathrm{d}t_n \, U_\alpha(t_1, t_2, \ldots, t_n). \tag{A 8}$$

We can split this up into $n!$ terms by making different time orderings. In each of these terms we can perform the time integrations in any particular order; let us agree to always perform the integration over t_1 last. When we have performed all the integrations apart from that over t_1 in any term we end up with an expression of the form

$$\int_{-\infty}^{\infty} \mathrm{d}t_1 \, \mathrm{e}^{-\alpha|t_1|+\mathrm{i}Et_1} \, M \, \mathrm{e}^{-(n-1)\alpha|t_1|-\mathrm{i}Et_1} + O(1), \tag{A 9}$$

where the factor $\exp\{-\alpha|t_1| + \mathrm{i}Et_1\}$ arises from the corresponding factor in U_α and the term $\exp\{-(n-1)\alpha|t_1| - \mathrm{i}Et_1\}$ arises from the performance of the remaining integrations. Performing the integration in (A 9) gives $2M/n\alpha + O(1)$. The operation $\lambda(\mathrm{d}/\mathrm{d}\lambda)$ on the contribution to $S^{(0)}_{L\alpha}(\infty)$ of an nth order term just multiplies it by n. Thus the contribution of the term (A 9) to ΔE is just

$$\lim_{\alpha \to +0} \tfrac{1}{2}\mathrm{i}\hbar\alpha n \left\{\frac{2M}{n\alpha} + O(1)\right\} = \mathrm{i}\hbar M. \tag{A 10}$$

Let us now compare this result with

$$\int_{-\infty}^{\infty} \mathrm{d}t_1 \ldots \int_{-\infty}^{\infty} \mathrm{d}t_n \mathrm{i}\hbar\delta(t_1) \, U_0(t_1, t_2, \ldots, t_n), \tag{A 11}$$

which arises from (A 8) by inserting a factor $\mathrm{i}\hbar\delta(t_1)$ into the integrand and putting $\alpha = 0$. If we evaluate this by splitting it into terms with different time orderings and perform the integration over t_1 last, we find that the term which corresponds to (A 9) is when all the integrations except that over t_1 have been performed

$$\int_{-\infty}^{\infty} \mathrm{d}t_1 \mathrm{i}\hbar\delta(t_1) \, M \, \mathrm{e}^{\mathrm{i}Et_1 - \mathrm{i}Et_1} = \mathrm{i}\hbar M, \tag{A 12}$$

which agrees with (A 11), the terms written $O(1)$ in (A 9) disappearing when $\alpha = 0$. Thus the insertion of a factor $\mathrm{i}\hbar\delta(t_1)$ into the integrand of (A 8) and putting $\alpha = 0$ has the same effect as operating with $\mathrm{i}\hbar\lambda(\mathrm{d}/\mathrm{d}\lambda)\alpha$ and taking the limit as $\alpha \to +0$. Thus we obtain the prescription of § 4.

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The description of collective motions in terms of many-body perturbation theory

II. The correlation energy of a free-electron gas

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The theory developed in a previous paper is applied to calculate the correlation energy of a free-electron gas. The theory involves no cut-off and gives a uniform description of collective motion effects in the long-range limit and of particle motion effects in the short-range limit. It is shown that in the lowest order the theory agrees with Bohm & Pines's plasma oscillation theory in the long-range limit, but is inadequate in the short-range limit. The theory is approximately evaluated to the next order, which is correct in the short-range limit, and is applied to calculate the correlation energy at several gas densities; the results are in good agreement with those of Bohm & Pines.

1. Introduction

In a previous paper (Hubbard 1957), which will be referred to as I, a method of analyzing the perturbation series for the many-body problem was described, which, it was stated, would lead to a theory equivalent to Bohm & Pines's (1953) plasma oscillation theory when applied to a free electron gas. In this paper the general theory of I is applied to a free-electron gas and this claim in part substantiated.

Bohm & Pines's theory has had three principal applications. These are

(i) to the calculation of the correlation energy of a free-electron gas;

(ii) to the interpretation of the energy loss spectra of fast electrons passing through thin metal films;

(iii) to give a theoretical basis to the 'independent particle' picture normally used in the discussion of metallic properties.

The present paper is concerned purely with the first application, i.e. the application of the theory developed in I to calculate the correlation energy of a free-electron gas. It is hoped in a later paper to deal with the items (ii) and (iii) above in terms of the theory developed in I.

In § 2 of this paper the expression given in I for the total energy of the system is transformed into a form more suitable for calculation and the integral equation giving $\mathscr{V}$ in terms of $\mathscr{V}^*$ is solved. In § 3 $\mathscr{V}^*$ is calculated in the lowest order for the ground state of an electron gas, and in § 4 the nature of the results obtained is investigated; it is found that the theory is adequate in the long-range limit but inadequate in the short-range limit. In § 5 it is shown that to make the theory correct in the short-range limit one has to carry the calculation of $\mathscr{V}^*$ to the next lowest order, and this calculation is performed approximately. Finally, in § 6 the results of numerical computations are quoted and compared with Bohm & Pines's theory.

2. The calculation of the correlation energy

The system considered is the same as that discussed by Bohm & Pines (1953), namely an infinite electron gas moving in a uniform background of positive charge of such a density as to make the system as a whole electrically neutral. The Hamiltonian of this system can be written

$$H = \sum_i \frac{1}{2m} p_i^2 + \sum_{i \neq j} \sum_{k \neq 0} \frac{2\pi e^2}{k^2} e^{i\mathbf{k}.(\mathbf{x}_i - \mathbf{x}_j)}, \tag{1}$$

in which the first term represents the kinetic energy of the electrons and the second term their mutual Coulomb interactions. The term with $\mathbf{k} = 0$ in the Fourier expansion of the Coulomb interaction has been removed because it is exactly cancelled out by the potential energy of the electrons in the background of positive charge.

In I it was shown that each eigenstate of the perturbed system (regarding the interaction between the electrons as the 'perturbation') could be associated with an eigenstate of the unperturbed system from which it evolves as the interaction is slowly switched on. The Hamiltonian of the unperturbed system consists of the first term of (1), the eigenfunctions of which are determinants of plane waves. Thus, each eigenstate of the unperturbed system is completely specified by saying which plane waves are present in the determinant, i.e. which plane-wave states are occupied. If the quantities $N_{\mathbf{k}}$ are defined by

$$\left.\begin{aligned} N_{\mathbf{k}} &= 1 \quad \text{if state } \mathbf{k} \text{ is occupied,} \\ N_{\mathbf{k}} &= 0 \quad \text{if state } \mathbf{k} \text{ is unoccupied,} \end{aligned}\right\} \tag{2}$$

then any eigenstate of the unperturbed system is specified by giving its occupation numbers $N_{\mathbf{k}}$. Further, each state of the perturbed system can be specified by giving the occupation numbers in the unperturbed state from which it arises when the interaction is slowly switched on.

In the present paper the correlation energy of that state of the perturbed system which arises from the ground state of the unperturbed system is calculated. The latter state is that in which all the plane-wave states below the Fermi surface are occupied and all those above are empty, i.e. the ordinary Fermi ground-state distribution. Whilst it is not quite obvious that the state which arises adiabatically from this one is the ground state of the perturbed system, this is taken to be so for the moment and we assume that we are calculating the correlation energy in the ground state of the perturbed system. Although it is our main purpose in this paper to calculate this ground-state correlation energy, much of the work of this section and the next section up to equation (24) is general and applicable to any distribution $N_{\mathbf{k}}$.

In I the expression (equation (70))

$$E = \sum_{\mathbf{k}} N_{\mathbf{k}} E_{\mathbf{k}} - \tfrac{1}{2} N v(0) + \tfrac{1}{2} N^2 u(0) + \frac{i\hbar}{2} \int_0^\lambda \frac{d\lambda}{\lambda} \int dx \int dx' \, \delta(t) \mathscr{V}(x', x) \, \overline{\mathscr{V}}(x, x') \tag{3}$$

for the energy of the state arising from a given unperturbed state was given. In this expression $N = \sum_{\mathbf{k}} N_{\mathbf{k}}$ is the total number of particles in the system (the system is now assumed to be enclosed in a very large box and surface effects are neglected), the

$E_{\mathbf{k}}$ are the energies of the individual particle states of the unperturbed system, $v(0)$ is the interaction energy at zero separation and $u(0)$ is the component with $\mathbf{k} = 0$ in the Fourier expansion of the interaction. The quantity λ is the interaction coupling constant, and $\curlyvee$ and $\overline{\curlyvee}$ are the modified interaction and a related quantity discussed extensively in I; these latter quantities depend implicitly on the occupation numbers $N_{\mathbf{k}}$ (see § 3).

In the present application the individual particle states are the plane waves $e^{i\mathbf{k}.\mathbf{x}}$, the corresponding energies being given by $E_{\mathbf{k}} = \hbar^2 k^2/2m$. Thus for a ground-state Fermi distribution the first term of (2) is $(3/5)NE_F$, where E_F is the Fermi energy. Further, in the present case $u(0) = 0$ since the Fourier component with $\mathbf{k} = 0$ in the interaction term of (1) has been removed, whilst

$$v(0) = \int \frac{2\pi e^2}{k^2} \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}.$$

This integral diverges, but the divergence is cancelled by a corresponding divergence in the last term of (3); as was pointed out in I these divergences lead to no difficulty since a suitable limiting procedure can easily be found. Combining these results one can write (3) as

$$E = \tfrac{3}{5}NE_F - \int \frac{2\pi Ne^2}{k^2} \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} + \frac{i\hbar}{2} \int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} \int \mathrm{d}x \int \mathrm{d}x' \delta(t)\, \curlyvee(x, x')\, \overline{\curlyvee}(x', x), \tag{4}$$

which can be rewritten

$$E = \tfrac{3}{5}NE_F + N\epsilon_{\mathbf{exch.}} + \left\{ \frac{i\hbar}{2} \int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} \int \mathrm{d}x \int \mathrm{d}x' \delta(t)\, \curlyvee(x, x')\, \overline{\curlyvee}(x', x) - \int \frac{2\pi Ne^2}{k^2} \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} - N\epsilon_{\mathbf{exch.}} \right\}, \tag{5}$$

where $\epsilon_{\mathbf{exch.}}$ is the ordinary exchange energy per particle given by

$$\epsilon_{\mathbf{exch.}} = -\frac{1}{N} \sum_{\mathbf{k}', \mathbf{k}''}^{\mathrm{occ.}} \frac{2\pi e^2}{|\mathbf{k}' - \mathbf{k}''|^2} = -\frac{0{\cdot}916}{r_s} \mathrm{Ry}$$

and r_s is the radius of a sphere whose volume equals the volume per electron. The terms in the bracket in (5) constitute what is normally defined to be the correlation energy; to calculate this quantity it is necessary to calculate $\curlyvee$ and $\overline{\curlyvee}$.

The quantities $\curlyvee$, $\curlyvee^*$ and $\overline{\curlyvee}$ are related (see I) by the equations

$$\curlyvee(x', x) = v(x' - x) + \int \curlyvee^*(x', x'')\, \curlyvee(x'', x)\, \mathrm{d}x'', \tag{6}$$

$$\curlyvee^*(x', x) = \int \overline{\curlyvee}(x', x'')\, v(x'' - x)\, \mathrm{d}x'', \tag{7}$$

where $v(x - x') = v(\mathbf{x} - \mathbf{x}')\, \delta(t - t')$ and $v(\mathbf{x} - \mathbf{x}')$ is the ordinary interaction, the Coulomb interaction in the case of an electron gas. The quantity $\curlyvee^*$ can be expressed as an infinite series of terms, each term being associated with a proper polarization part (see I); $\curlyvee$ can also be expressed as an infinite series of terms corresponding to polarization parts (proper and improper), but since this series is

much less rapidly convergent than that giving $\mathscr{V}^*$, $\mathscr{V}$ is most conveniently calculated from (6). Since in the case of a uniform gas the quantities $\mathscr{V}(x', x)$, $\mathscr{V}^*(x', x)$ and $\overline{\mathscr{V}}(x', x)$ are functions of the differences of their arguments only, one can solve (6) at once by introducing their Fourier transforms:

$$\mathscr{V}(x', x) = \frac{1}{2\pi}\int \mathrm{d}\mathbf{k} \int \mathrm{d}\omega\, \mathscr{V}(\mathbf{k}, \omega)\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot(\mathbf{x}'-\mathbf{x})+\mathrm{i}\omega(t'-t)} \tag{8}$$

with similar definitions for $\mathscr{V}^*(\mathbf{k}, \omega)$ and $\overline{\mathscr{V}}(\mathbf{k}, \omega)$. When these transforms are introduced into equations (6) and (7) one obtains

$$\mathscr{V}(\mathbf{k}, \omega) = v(\mathbf{k}) + \mathscr{V}^*(\mathbf{k}, \omega)\, \mathscr{V}(\mathbf{k}, \omega) \tag{9}$$

and

$$\mathscr{V}^*(\mathbf{k}, \omega) = v(\mathbf{k})\, \overline{\mathscr{V}}(\mathbf{k}, \omega), \tag{10}$$

where $v(\mathbf{k})$ is the Fourier component of the ordinary potential $v(\mathbf{x}-\mathbf{x}')$, given by $v(\mathbf{k}) = 4\pi e^2/k^2$ in the case of a Coulomb potential. Equation (9) can be solved immediately to give

$$\mathscr{V}(\mathbf{k}, \omega) = \frac{v(\mathbf{k})}{1 - \mathscr{V}^*(\mathbf{k}, \omega)}. \tag{11}$$

Introducing the Fourier transforms of $\mathscr{V}$ and $\overline{\mathscr{V}}$ into (5), carrying out the integrations and dividing by N, one obtains making use of (10) and (11) the expression

$$\epsilon_{\mathrm{corr.}} = \frac{\mathrm{i}\hbar}{4\pi n}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\int \mathrm{d}\omega\, \frac{\mathscr{V}^*(\mathbf{k}, \omega)}{1 - \mathscr{V}^*(\mathbf{k}, \omega)} - \int \frac{2\pi e^2}{k^2}\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} - \epsilon_{\mathrm{exch.}} \tag{12}$$

for the correlation energy per electron, where n is the number of electrons per unit volume.

If one now writes

$$\mathscr{V}^*(\mathbf{k}, \omega) = A(\mathbf{k}, \omega) + \mathrm{i}\Sigma(\mathbf{k}, \omega), \tag{13}$$

where $A(\mathbf{k}, \omega)$ and $\Sigma(\mathbf{k}, \omega)$ are the real and imaginary parts of $\mathscr{V}^*(\mathbf{k}, \omega)$, and notices that the expression (12) must be real, one obtains

$$\epsilon_{\mathrm{corr}} = \frac{\hbar}{4\pi n}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\int \mathrm{d}\omega\, \frac{-\Sigma(\mathbf{k}, \omega)}{[1 - A(\mathbf{k}, \omega)]^2 + \Sigma^2(\mathbf{k}, \omega)} - \int \frac{2\pi e^2}{k^2}\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} - \epsilon_{\mathrm{exch.}}. \tag{14}$$

This is a general expression for the correlation energy. It remains now only to calculate A and Σ; in the next section this calculation is performed approximately.

3. The modified interaction

In I the quantity $\overline{\mathscr{V}}$ was defined (equation (67)) to be the sum over all proper polarization diagrams apart from Γ_0 of certain quantities $\overline{W}$

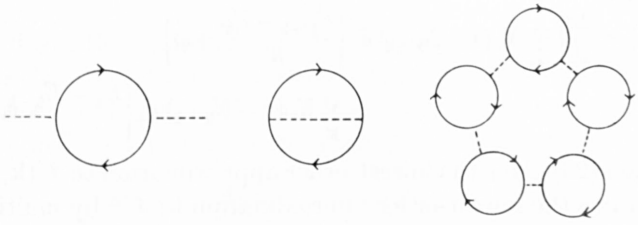
$$\overline{\mathscr{V}}(x', x) = \sum_{\Gamma+\Gamma_0}^{\text{proper}} \overline{W}_\Gamma(x', x).$$

Taking the Fourier transform of this relation, one has

$$\overline{\mathscr{V}}(\mathbf{k}, \omega) = \sum_{\Gamma+\Gamma_0}^{\text{proper}} \overline{W}_\Gamma(\mathbf{k}, \omega), \tag{15}$$

where $\overline{W}_\Gamma(\mathbf{k}, \omega)$ is the Fourier transform of $\overline{W}_\Gamma(x', x)$, the latter in a uniform gas being a function of the difference of its arguments only. It is hoped that this latter series is

rapidly convergent; it has therefore been approximated to by its leading term, that corresponding to the simplest of all polarization diagrams, shown in figure 1 (*a*). It is actually found that this approximation is sufficient to give the effects associated with the plasma oscillations to the same accuracy as Bohm & Pines calculated them, but that the retention of only this single term leads to significant inaccuracies in the calculation of the particle aspects due to the omission of certain exchange terms. This latter point and the way in which it can be approximately allowed for is dealt with in § 5 of this paper.



(*a*) (*b*) (*c*)

FIGURE 1

In I the expression (equation (55)) for the $\overline{W}$ corresponding to the polarization part shown in figure 1 (*a*) was given; it is

$$\overline{W}(x',x) = -\frac{1}{\mathrm{i}\hbar} S(x',x)\, S(x,x'), \tag{16}$$

where $S(x',x)$ is the particle propagator given in I, equation (21). In the case of a free electron gas this becomes

$$S(x',x) = \epsilon(t'-t) \sum_{\mathbf{k}}^{\text{unocc.}} \exp\left\{\mathrm{i}\mathbf{k}.(\mathbf{x}'-\mathbf{x}) - \frac{\mathrm{i}}{\hbar} E_{\mathbf{k}}(t'-t)\right\}$$
$$-\epsilon(t-t') \sum_{\mathbf{k}}^{\text{occ.}} \exp\left\{\mathrm{i}\mathbf{k}.(\mathbf{x}'-\mathbf{x}) - \frac{\mathrm{i}}{\hbar} E_{\mathbf{k}}(t'-t)\right\}, \tag{17}$$

where
$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}. \tag{18}$$

Putting (17) into (16), one obtains

$$\overline{W}(x'-x) = \frac{1}{\mathrm{i}\hbar}\left[\epsilon(t'-t) \sum_{\mathbf{k}'}^{\text{unocc.}} \sum_{\mathbf{k}''}^{\text{occ.}} \exp\left\{\mathrm{i}(\mathbf{k}'-\mathbf{k}'').(\mathbf{x}'-\mathbf{x}) - \frac{\mathrm{i}}{\hbar}(E_{\mathbf{k}'}-E_{\mathbf{k}''})(t'-t)\right\}\right.$$
$$\left.+\epsilon(t-t') \sum_{\mathbf{k}'}^{\text{occ.}} \sum_{\mathbf{k}''}^{\text{unocc.}} \exp\left\{\mathrm{i}(\mathbf{k}'-\mathbf{k}'').(\mathbf{x}'-\mathbf{x}) - \frac{\mathrm{i}}{\hbar}(E_{\mathbf{k}'}-E_{\mathbf{k}''})(t'-t)\right\}\right], \tag{19}$$

from which, on Fourier transformation, one has

$$\overline{W}(\mathbf{k},\omega) = \frac{2\pi}{\mathrm{i}\hbar}\left[\sum_{\mathbf{k}'}^{\text{unocc.}} \sum_{\mathbf{k}''}^{\text{occ.}} \delta(\mathbf{k}'-\mathbf{k}''-\mathbf{k})\, \delta_{-}\left\{\frac{E_{\mathbf{k}'}-E_{\mathbf{k}''}}{\hbar}+\omega\right\}\right.$$
$$\left.+\sum_{\mathbf{k}'}^{\text{occ.}} \sum_{\mathbf{k}''}^{\text{unocc.}} \delta(\mathbf{k}'-\mathbf{k}''-\mathbf{k})\, \delta_{+}\left\{\frac{E_{\mathbf{k}'}-E_{\mathbf{k}''}}{\hbar}+\omega\right\}\right], \tag{20}$$

where δ_+ and δ_- are the positive and negative frequency parts of the δ function given by

$$\delta_+(x) = -\frac{1}{2\pi i}\frac{P}{x} + \tfrac{1}{2}\delta(x), \tag{21}$$

$$\delta_-(x) = \frac{1}{2\pi i}\frac{P}{x} + \tfrac{1}{2}\delta(x), \tag{22}$$

and P means principal value.

It is convenient now to introduce the quantities $N_{\mathbf{k}}$ defined in (2) and re-arrange (20) into the form

$$\overline{W}(\mathbf{k},\omega) = \frac{2\pi}{i\hbar}\Big[\sum_{\mathbf{k}'} N_{\mathbf{k}'}(1-N_{\mathbf{k}'+\mathbf{k}})\,\delta_-\Big\{\frac{E_{\mathbf{k}'+\mathbf{k}}-E_{\mathbf{k}'}}{\hbar}+\omega\Big\} + \sum_{\mathbf{k}'} N_{\mathbf{k}'}(1-N_{\mathbf{k}'-\mathbf{k}})\,\delta_+\Big\{\frac{E_{\mathbf{k}'}-E_{\mathbf{k}'-\mathbf{k}}}{\hbar}+\omega\Big\}\Big]. \tag{23}$$

The expression (23) gives the lowest-order approximation to $\mathscr{V}(\mathbf{k},\omega)$. According to (10), one obtains the lowest-order approximation to $\mathscr{V}^*$ by multiplying this by $v(\mathbf{k}) = 4\pi e^2/k^2$; if one does this, substitutes for the δ functions in (23) from (21) and (22), and re-arranges, one obtains the expression

$$\mathscr{V}^*(\mathbf{k},\omega) = \frac{4\pi e^2}{m}\sum_{\mathbf{k}'} N_{\mathbf{k}'}\frac{P}{\Big(\omega-\frac{\hbar}{m}\mathbf{k}.\mathbf{k}'\Big)^2-\frac{\hbar^2k^4}{4m^2}} - i\frac{4\pi^2e^2}{\hbar k^2}\sum_{\mathbf{k}'} N_{\mathbf{k}'}(1-N_{\mathbf{k}'+\mathbf{k}})\Big[\delta\Big\{\frac{E_{\mathbf{k}'+\mathbf{k}}-E_{\mathbf{k}'}}{\hbar}-\omega\Big\}+\delta\Big\{\frac{E_{\mathbf{k}'+\mathbf{k}}-E_{\mathbf{k}'}}{\hbar}+\omega\Big\}\Big] \tag{24}$$

for $\mathscr{V}^*(\mathbf{k},\omega)$ in the lowest-order approximation. The real part of this expression gives A and the imaginary part Σ to the present degree of approximation. It will be noticed that the real part coincides with the polarizability of a free electron gas calculated in the lowest order (Hubbard 1955) and that Σ differs from the corresponding conductivity in that the sum rather than the difference of the two δ functions appears.

In the case when the electrons occupy a ground-state Fermi distribution the sums in (24) can be evaluated quite straightforwardly. The results can be conveniently expressed in terms of the reduced variables

$$\left.\begin{aligned} x &= k/k_F, \\ y &= \hbar\omega/E_F. \end{aligned}\right\} \tag{25}$$

It is found that $\Sigma(x,y)$ (Σ and A are functions of $k = |\mathbf{k}|$ only since the Fermi distribution is isotropic) is given for $y>0$ by

$$\begin{aligned} \Sigma(x,y) &= 0 \quad \text{when} \quad y > x(x+2), \\ &= 0 \quad \text{when} \quad x>2 \quad \text{and} \quad y<x(x-2), \\ &= -\frac{\pi}{2}\frac{\xi}{x^3}\Big[1-\frac{1}{4}\Big(\frac{y}{x}-x\Big)^2\Big] \\ &\qquad \text{when} \quad x>2 \quad \text{and} \quad x(x-2)<y<x(x+2), \\ &\qquad \text{or when} \quad x<2 \quad \text{and} \quad x(2-x)<y<x(x+2); \\ &= -\frac{\pi}{2}\frac{\xi y}{x^3} \quad \text{when} \quad x<2 \quad \text{and} \quad 0<y<x(2-x) \end{aligned} \tag{26}$$

whilst for $y<0$ Σ is given by $\Sigma(x,-y)=\Sigma(x,y)$. A is given for all x and y by

$$A(x,y) = -\frac{\xi}{x^3}\left[x+\frac{1}{2}\left\{1-\frac{1}{4}\left(\frac{y}{x}-x\right)^2\right\}\ln\left|\frac{y-x(x+2)}{y-x(x-2)}\right|\right.$$
$$\left.+\frac{1}{2}\left\{1-\frac{1}{4}\left(\frac{y}{x}+x\right)^2\right\}\ln\left|\frac{y+x(x+2)}{y+x(x-2)}\right|\right], \tag{27}$$

where ξ is the quantity $$\xi = \frac{e^2k_F}{\pi}\Big/E_F = 0{\cdot}33\,r_s \tag{28}$$

and r_s is the radius in Bohr units (B.U. $=\hbar^2/me^2$) of a sphere whose volume is equal to the volume per electron. It will be noticed that to the present degree of approximation the gas density only enters Σ and A as a multiplicative constant.

For small x and $y \gg x(x+2)$, the expression (27) reduces approximately to

$$A(x,y) = -y_P^2/y^2, \tag{29}$$

where y_P is the reduced plasma frequency given by

$$y_P = \frac{\hbar\omega_P}{E_F} = \frac{\hbar}{E_F}\left(\frac{4\pi ne^2}{m}\right)^{\frac{1}{2}}. \tag{30}$$

4. The general nature of the results

To evaluate the correlation energy to the present degree of approximation one must now substitute (26) and (27) into (14) and evaluate the integral. If the reduced variables x and y are introduced into (14) and the angular part of the $\mathbf{k}$ integration performed (Σ and A depend only upon the length of $\mathbf{k}$), then one obtains

$$\epsilon_{\text{corr.}} = \frac{3}{4\pi}E_F\int_0^\lambda\frac{\mathrm{d}\lambda}{\lambda}\int_0^\infty x^2\,\mathrm{d}x\int_0^\infty \mathrm{d}y\,\frac{-\Sigma(x,y)}{[1-A(x,y)]^2+\Sigma^2(x,y)} - \int\frac{2\pi e^2}{k^2}\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} - \epsilon_{\text{exch.}}. \tag{31}$$

It is useful to investigate the contributions to the integral in (31) arising from different parts of the xy plane; this can be conveniently done with the aid of the diagram of the plane given in figure 2. On this diagram the lines oc and bd whose equations are $y=x(x+2)$ and $y=x(x-2)$ have been drawn together with that part of the line $A(x,y)=1$ lying outside the region $cobd$ for a typical value of ξ, namely $\xi = 1{\cdot}33$ (ef). According to (26) Σ vanishes except in the region between the lines oc and obd. It might be thought therefore that it is only this region of the plane which gives any contribution to the integral in (31). However, one must be cautious because along the line $A(x,y)=1$ the integrand becomes indeterminate.

If the calculation had been carried to a higher degree of approximation, i.e. in the calculation of Σ one had included terms corresponding to more complicated polarization parts than that shown in figure 1 (a), then it would have been found that Σ was different from zero everywhere in the plane. Nevertheless, if it is supposed that the calculation retaining only the first term is a good approximation, then it follows that although Σ does not vanish outside of the region $cobd$, it is small

outside this region. One can then sensibly approximate by taking the limit of the integrand of (14) as $\Sigma \to 0$ in the region outside *cobd*. Taking this limit one obtains

$$\lim_{\Sigma \to -0} \frac{-\Sigma}{[1-A]^2+\Sigma^2} = \pi\delta[1-A]. \tag{32}$$

Thus the integrand has a δ function singularity along the part of the line $A(x, y) = 1$ lying in the region outside *cobd*.

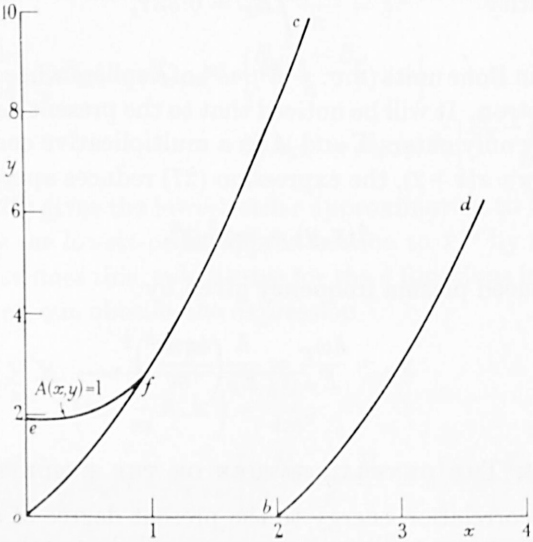


FIGURE 2. Diagram of the xy plane; the lines $y = x(x+2)$ and $y = x(x-2)$ (*oc* and *bd*) are shown, together with that part of the line $A(x, y) = 1$ lying outside *cobd* for $r_s = 4$ (*ef*).

For small x one can evaluate the contribution of this singularity to the integral by using the approximation (29) for A; one obtains

$$\begin{aligned}\frac{\hbar}{4\pi n}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\int_{-\infty}^{\infty} \frac{E_F}{\hbar}\,\mathrm{d}y\,\pi\delta\left\{1-\frac{y_P^2}{y^2}\right\} \\ = \frac{1}{4n}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\int_{-\infty}^{\infty} \mathrm{d}y\, E_F \frac{y_P}{2}[\delta(y-y_P)+\delta(y+y_P)] \\ = \frac{1}{4n}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\hbar\omega_P. \end{aligned} \tag{33}$$

Now $\omega_P \propto e \propto \lambda^{\frac{1}{2}}$ since $\lambda = e^2$ is the coupling constant, so that the performance of the λ integration yields a factor 2, giving

$$\frac{1}{n}\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\frac{\hbar\omega_P}{2}. \tag{34}$$

Thus, for small x the contribution of the singularity to the correlation energy is just what one would ordinarily call the zero-point energy of the plasma oscillations. Since $1-A$ is always the real part of the dielectric constant, whose vanishing gives the plasma frequency, one may interpret the total contribution of the singularity as representing the contribution to the energy of the collective oscillations of the gas.

Having pointed out the existence of a contribution to the integral from the region of the plane outside *obcd* and its connexion with the collective motion, we now consider a simpler method of evaluating the integral (31). According to the calculation of §3, Σ and A are linearly proportional to the coupling constant λ. Using this fact one can immediately perform the λ integration in (31) to obtain

$$\epsilon_{\text{corr.}} = \frac{3}{4\pi} E_F \int_0^\infty x^2 \, \mathrm{d}x \int_0^\infty \mathrm{d}y \tan^{-1} \frac{-\Sigma(x,y)}{1-A(x,y)} - \int \frac{2\pi e^2}{k^2} \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} - \epsilon_{\text{exch.}}, \tag{35}$$

where one must always take the branch lying between 0 and π of the many-valued inverse tangent. In those regions where $\Sigma = 0$ in the first approximation we take the limit as $\Sigma \to -0$ of the integrand; this limit will be 0 in the region in which $A < 1$ and will be π in the region in which $A > 1$. Thus, in figure 2 the integrand in (35) will be between 0 and π in the region *cobd* since Σ is non-zero in this region, will be π in the region *efo* since $\Sigma = 0$ and $A > 1$ in this region, and will be zero in all other parts of the plane. There are good reasons for thinking of the contribution from the region *efo* as being associated with the collective motion and of the contribution from the region *cobd* as being associated with the particle motion; it will be noticed that the contribution from the region *efo* for small x is again of the form (34), and that for small x this is almost the whole of the contribution.

From (24) one can obtain

$$\begin{aligned} -\frac{\hbar}{4\pi n} \int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \int \mathrm{d}\omega \, . \, \Sigma(\mathbf{k},\omega) &= \frac{1}{n} \int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \int \mathrm{d}\omega \, \frac{\pi e^2}{k^2} \\ &\times \sum_{\mathbf{k}'} N_{\mathbf{k}'}(1 - N_{\mathbf{k}'+\mathbf{k}}) \left[\delta\left(\frac{E_{\mathbf{k}'+\mathbf{k}} - E_{\mathbf{k}'}}{\hbar} - \omega \right) + \delta\left(\frac{E_{\mathbf{k}'+\mathbf{k}} - E_{\mathbf{k}'}}{\hbar} + \omega \right) \right] \\ &= \frac{1}{n} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \frac{2\pi e^2}{k^2} \sum_{\mathbf{k}'} N_{\mathbf{k}'}(1 - N_{\mathbf{k}'+\mathbf{k}}) \\ &= \int \frac{2\pi e^2}{k^2} \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} - \epsilon_{\text{exch.}}, \end{aligned} \tag{36}$$

since

$$\sum_{\mathbf{k}'} N_{\mathbf{k}'} = n$$

and

$$\frac{1}{n} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \frac{2\pi e^2}{k^2} \sum_{\mathbf{k}'} N_{\mathbf{k}'} N_{\mathbf{k}'+\mathbf{k}} \tag{37}$$

is the exchange energy per particle. Thus one can substitute the left-hand side of (36) for the last two terms of (35). If the left-hand side is written in terms of the reduced variables x and y one obtains

$$\epsilon_{\text{corr.}} = -\frac{3}{4\pi} E_F \int_0^\infty x^2 \, \mathrm{d}x \int_0^\infty \mathrm{d}y \left\{ \tan^{-1} \frac{\Sigma(x,y)}{1-A(x,y)} - \Sigma(x,y) \right\}. \tag{38}$$

As $x \to \infty$, Σ and $A \to 0$ like $1/x^3$, so that the integrand of (38) tends to 0 like $1/x^4$ and the integral is convergent for large x; thus the divergences in the first and second terms on the right-hand side of (31) cancel.

We should like to complete this section by commenting on how the theory behaves in the limits of small and large x. Going back to equation (35), it has already been

pointed out that the contribution of the first term is given for small x by equation (34) and represents the zero point of the plasma oscillations. The second term represents a subtraction of the self-energies of the electrons, whilst the third term cancels out the long-range part of the exchange energy. Thus, in the limit of small x, the results agree exactly with those Bohm & Pines obtain in the long-range limit (Pines 1953).

For large x, Σ and A become small and one can expand the denominator in the first term of the integrand of (38) in powers of Σ and A. If one carries out this expansion and performs the various integrations, one obtains an expansion for the correlation energy which consists of a subset of the terms of the original perturbation series, namely, all those terms which correspond to diagrams of the type shown in figure 1 (*c*), consisting of rings of the polarization parts shown in figure 1 (*a*). One has, of course, only obtained a subset of the terms of the original perturbation series because only the leading term corresponding to the polarization part of figure 1 (*a*) was retained in calculating $\mathscr{V}^*$.

If one performs the expansion of the first term of the integrand of (38) described in the preceding paragraph, then the two leading terms correspond to the diagrams of figures 1 (*b*) and 3 (*a*). The leading term, corresponding to figure 1(*b*), is

$$-\frac{3}{4\pi} E_F \int_0^\infty x^2 \, \mathrm{d}x \int_0^\infty \mathrm{d}y \, \Sigma(x, y), \tag{39}$$

which cancels out the second term in the integrand of (38). Thus, in the limit of large x the leading term in the correlation energy is that corresponding to the diagram of figure 3 (*a*). If one evaluates the contribution of this diagram to the correlation energy directly, one obtains the expression

$$64\pi^2 \sum_{\mathbf{k}} \frac{1}{k^4} \sum_{\substack{k_1 < k_F \\ |\mathbf{k}_1 + \mathbf{k}| > k_F}} \sum_{\substack{k_2 < k_F \\ |\mathbf{k}_2 - \mathbf{k}| > k_F}} \frac{1}{\mathbf{k} \cdot (\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k})} \text{ Ry/electron}, \tag{40}$$

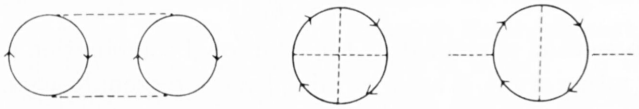
which is just the direct part (as opposed to the exchange part) of the second-order perturbation term (Macke 1950).

5. Allowance for the exchange correction

At the end of the previous section it was shown that in the short-range limit (38) reduces to the direct part of the second-order perturbation term. This is unsatisfactory because it is known that in this limit half of the direct term is cancelled by the exchange part of the second-order perturbation, since only correlations between electrons with opposite spins are important in this limit. Thus the simple theory based upon taking into account only the polarization part shown in figure 1 (*a*) must be corrected to obtain a theory which is correct in the short-range limit; this correction will be discussed in the present section.

The exchange part of the second-order perturbation term corresponds to the diagram shown in figure 3 (*b*). One would automatically include the contribution of this diagram if one included in the calculation of $\mathscr{V}^*$ not only the contribution of the polarization part of figure 1(*a*), but also the contribution of the next simplest

polarization part, that shown in figure 3 (*c*). Unfortunately, however, the contribution of this polarization part is very difficult to compute, and one can therefore only allow for the exchange correction in an approximate way.



(*a*) (*b*) (*c*)

FIGURE 3

The simplest way in which one could allow for the exchange term would be to calculate the contribution to the correlation energy from the exchange part of the second-order perturbation term, and add this energy to the correlation energy calculated from (38). The exchange part of the second-order perturbation term is given by the expression

$$\epsilon^{(2)}_{\text{exch.}} = 32\pi^2 \sum_{\mathbf{k}} \sum_{\substack{\mathbf{k}_1 \\ k_1<k_F \\ |\mathbf{k}_1+\mathbf{k}|>k_F}} \sum_{\substack{\mathbf{k}_2 \\ k_2<k_F \\ |\mathbf{k}_2-\mathbf{k}|>k_F}} \frac{1}{k^2} \frac{1}{(\mathbf{k}+\mathbf{k}_1-\mathbf{k}_2)^2} \frac{1}{\mathbf{k}.(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k})} \text{ Ry} \tag{41}$$

(Macke 1950); the magnitude of this energy, which is independent of the gas density, has been calculated by Brueckner & Gell-Mann (1957) using a Monte Carlo method and is found to be $0{\cdot}046 \pm 0{\cdot}002$ Ry per electron. Although this method would be simple, it would also be rather inaccurate. This is because, although the expression (41) has no divergence for small k, nevertheless, a large part of the contribution to the k sum comes from small k; however, for small k the screening of the interaction which is not taken into account in (41) is important. For this reason, simply to add the energy $\epsilon^{(2)}_{\text{exch.}}$ would considerably overestimate the importance of the exchange correction and lead to too low a value of the correlation energy.

The method used to correct for the exchange effects was to make an approximate estimate of the contribution of $\mathscr{S}^*$ of the polarization part shown in figure 3 (*c*) and of certain higher-order terms of the same type. This method has the advantage that since it is $\mathscr{S}^*$ itself which is corrected the effect of the screening is automatically taken into account. The results obtained using this method are, however, only accurate to the extent to which the method of estimating the contribution of the diagram 3 (*c*) is accurate. It is shown in § 6 that owing to this cause one overestimates the correlation energy by about 0·004 Ry per electron.

From a study of the terms involved (see Appendix for further discussion) it was concluded that the contribution to $\mathscr{S}^*$ of the diagram of figure 3 (*c*) together with certain higher-order terms could be approximately represented by replacing the $\mathscr{S}^*(\mathbf{k}, \omega)$ calculated in § 3 by

$$\mathscr{S}^*(\mathbf{k}, \omega) = \frac{\mathscr{S}^*_0(\mathbf{k}, \omega)}{1 + f(\mathbf{k})\, \mathscr{S}^*_0(\mathbf{k}, \omega)}, \tag{42}$$

where $f(\mathbf{k})$ is the function

$$f(\mathbf{k}) = \frac{1}{2} \frac{k^2}{k^2 + k_F^2}, \tag{43}$$

and $\mathscr{S}^*_0(\mathbf{k}, \omega)$ is the $\mathscr{S}^*(\mathbf{k}, \omega)$ calculated in § 3. If the expression (42) for $\mathscr{S}^*$ is substituted into (12), then it is found that in (14) one must replace the Σ and A in the

denominator of the integrand of the first term by Σ' and A', where Σ' and A' are the same as Σ and A but are multiplied by a factor

$$1-\frac{1}{2}\frac{k^2}{k^2+k_F^2}. \tag{44}$$

Although the method of estimating the additional contribution to $\mathscr{V}^*$ from the diagram 3 (*c*) is rather crude, it has a certain physical reasonableness. For the effect of multiplying the Σ and A in the denominator of (14) by the factor (44) is equivalent to replacing the factor $v(k) = 4\pi e^2/k^2$ which they contain by a factor

$$\frac{4\pi e^2}{k^2}-\frac{1}{2}\frac{4\pi e^2}{k^2+k_F^2}. \tag{45}$$

However, the effect of the exchange terms is to reduce the correlation effects between electrons with parallel spins because they are not permitted to approach one another more closely than a distance of the order r_s by the exclusion principle. This is roughly equivalent to saying that the correlation effects due to the interaction of electrons with parallel spins at short distances are much reduced. But the introduction of (45) in place of $v(k) = 4\pi e^2/k^2$ is equivalent to this since half the interactions of an electron are with electrons of opposite spin, and these are cut off in (45) on the short-range side at about the right distance.

Further, if one replaces Σ and A by Σ' and A' in (12) and expands in powers of Σ' and A' for large x, one now obtains in the short-range limit instead of (40) the short-range part of

$$64\pi^2\sum_{\mathbf{k}}\frac{1}{k^2}\left(\frac{1}{k^2}-\frac{1}{2}\frac{1}{k^2+k_F^2}\right)\sum_{\substack{\mathbf{k}_1\\ k_1<k_F\\ |\mathbf{k}_1+\mathbf{k}|>k_F}}\sum_{\substack{\mathbf{k}_2\\ k_2<k_F\\ |\mathbf{k}_2-\mathbf{k}|>k_F}}\frac{1}{\mathbf{k}.(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k})}\ \text{Ry/electron}, \tag{46}$$

which in the limit of large k is one-half of (40), as it should be. Furthermore, comparing (46) with (40), it is seen that the present method estimates the exchange part of the second-order perturbation term to be

$$32\pi^2\sum_{\mathbf{k}}\frac{1}{k^2}\frac{1}{k^2+k_F^2}\sum_{\substack{\mathbf{k}_1\\ k_1<k_F\\ |\mathbf{k}_1+\mathbf{k}|>k_F}}\sum_{\substack{\mathbf{k}_2\\ k_2<k_F\\ |\mathbf{k}_2-\mathbf{k}|>k_F}}\frac{1}{\mathbf{k}.(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k})}\ \text{Ry/electron}, \tag{47}$$

which is to be compared with the exact expression (41). If one calculates the value of the expression (47) and compares it with the 0·046 Ry per electron of the expression (41) some idea of how good the approximation (42) is can be obtained. In fact, calculation shows that (47) has the value 0·036 Ry per electron, which is rather smaller than Brueckner and Gell-Mann's estimate of (41). It can be concluded that the approximation (42) underestimates the effect of the exchange term by about 20 %.

If one replaces Σ and A by Σ' and A' in (14) then it is found that (38) has to be replaced by

$$-\frac{3}{4\pi}E_F\int_0^\infty x^2\,\mathrm{d}x\int_0^\infty \mathrm{d}y\left\{\frac{\Sigma}{\Sigma'}\tan^{-1}\frac{\Sigma'}{1-A'}-\Sigma\right\}, \tag{48}$$

where Σ' and A' are given by (26) and (27) except that they are to be multiplied by a factor

$$1-\frac{1}{2}\frac{x^2}{1+x^2}. \tag{49}$$

6. Numerical results

The integrals in equations (38) and (48) have been evaluated numerically for values of ξ corresponding to gas densities $r_s = 2, 3, 4$ and 5 (in B.U.), making use of the Ferranti Mark I* Computer at the Atomic Weapons Research Establishment, Aldermaston. The results are quoted in the first and third lines of table 1. In the last line of this table the differences between the correlation energies calculated from (38) and (48) are quoted. These differences represent the contributions to the correlation energy of the exchange effects when screening is taken into account. Comparison of these contributions with the value 0·046 Ry per electron of the expression (41) shows the importance of taking the screening into account when correcting for the exchange effects. Since in the preceding section it was shown that the approximation (42) underestimated the exchange effects by about 20 %, it is to be expected that the estimates of the correlation energy are too big by about 20 % of the energies in the last line of table 1, i.e. are overestimates by about 0·004 Ry per electron.

Table 1. Correlation energies (Ry per electron)

gas density, r	2·0	3·0	4·0	5·0
$\epsilon_{\text{corr.}}$ calculated from (48)	−0·099	−0·086	−0·074	−0·067
$\epsilon_{\text{corr.}}$ calculated by Bohm & Pines	−0·093	−0·081	−0·072	−0·066
$\epsilon_{\text{corr.}}$ calculated from (38)	−0·121	−0·104	−0·090	−0·081
exchange correction	0·022	0·018	0·016	0·014

It will be seen that the correlation energies calculated from (48) are in good agreement with those calculated by Bohm & Pines (Pines 1955), the latter being quoted in the second line of table 1.

Not only is it possible to compare the total correlation energies obtained here with those obtained by Bohm & Pines, but one can also compare the contributions arising from the long- and short-range parts of the interaction and from the intermediate region between these. This is possible because one can in the present method, as in Bohm & Pines's method, determine the contribution to the correlation energy arising from a single Fourier component of the Coulomb interaction.

Consider a general interaction whose Fourier expansion is

$$v(\mathbf{x}-\mathbf{x}') = \sum_{\mathbf{k}} v(\mathbf{k})\, e^{i\mathbf{k}.(\mathbf{x}-\mathbf{x}')}. \tag{50}$$

Then the total correlation energy will be given by (12). However, $\mathscr{S}^*(\mathbf{k}, \omega)$ contains a factor $v(\mathbf{k})$; if, therefore, one were to omit a given $v(\mathbf{k})$ from the expansion (50), then the corresponding contribution to the $\mathbf{k}$ integration in the first term of (12) would drop out. Thus the contribution of this Fourier component of the interaction to the correlation energy through the first term of (12) is

$$\frac{i\hbar}{4\pi n}\int_0^\lambda \frac{d\lambda}{\lambda}\int d\omega\, \frac{\mathscr{S}^*(\mathbf{k}, \omega)}{1-\mathscr{S}^*(\mathbf{k}, \omega)}. \tag{51}$$

Similarly, one can find the contribution of this Fourier component of the interaction to the second and third terms of (12). In this way it can be shown that the

contribution of those Fourier components of the interaction whose length is between xk_F and $(x+\mathrm{d}x)\,k_F$ to the correlation energy is given by

$$\frac{3}{4\pi}E_F I(x)\,\mathrm{d}x = -\frac{3}{4\pi}E_F\int_0^\infty \mathrm{d}y\left(\frac{\Sigma}{\Sigma'}\tan^{-1}\frac{\Sigma'}{1-A'}-\Sigma\right)x^2\,\mathrm{d}x. \tag{52}$$

In figure 4 plotted $I(x)$ has been plotted together with the corresponding quantity in Bohm & Pines's theory, $I_{BP}(x)$, for a gas density $r_s = 4$. $I_{BP}(x)$ was calculated from the expressions

$$\frac{3}{4\pi}E_F I_{BP}(x)\,\mathrm{d}x = \left[-\frac{1}{3n}\sum_i\frac{p_i^2}{2m}-\frac{2\pi e^2}{k^2}+\frac{\hbar\omega_p}{2}\left\{1+\frac{k^2}{2nm^2\omega_p^2}\sum_i p_i^2+\frac{\hbar^2k^4}{8m^2\omega_p^2}\right\}\right]\frac{4\pi k^2\,\mathrm{d}k}{(2\pi)^3}$$

$$+\frac{0{\cdot}916}{r_s}\left[\frac{4}{3}+\frac{k}{k_F}-\frac{1}{16}\left(\frac{k}{k_F}\right)^3\right]\mathrm{d}k \qquad \text{for} \quad x<\beta;$$

$$=\frac{4\pi k^2\,\mathrm{d}k}{8\pi^2}\frac{32\pi^2}{k^4}\sum_{\substack{\mathbf{k}_1\\ k_1<k_F\\ |\mathbf{k}_1+\mathbf{k}|>k_F}}\ \sum_{\substack{\mathbf{k}_2\\ k_2<k_F\\ |\mathbf{k}_2-\mathbf{k}|>k_F}}\frac{1}{\mathbf{k}.(\mathbf{k}_1-\mathbf{k}_2+\mathbf{k})} \text{ for } x>\beta. \tag{53}$$

which give the contributions to the correlation energy of Fourier components of the interaction with lengths between xk_F and $(x+\mathrm{d}x)k_F$ in Bohm & Pines's theory; the notation used on the right-hand sides of these expressions is that of Bohm & Pines (1953).

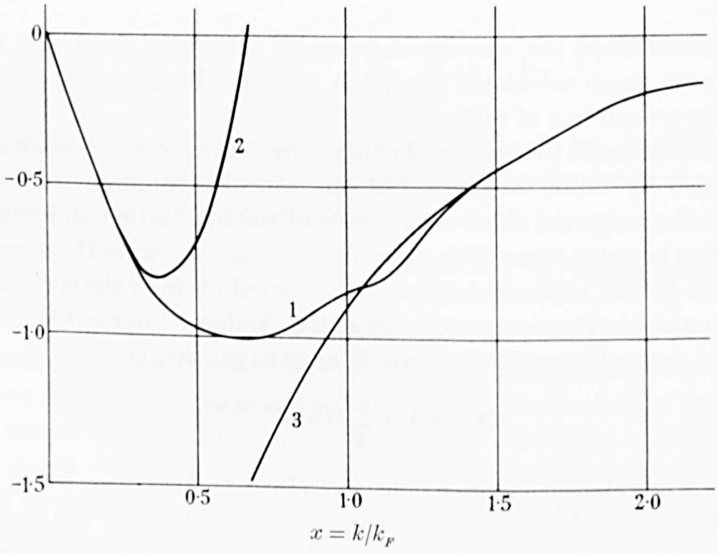


FIGURE 4. Graph showing the contributions of various Fourier components of the interaction to the correlation energy in the present and in Bohm & Pines's theory. 1, $I(x)$: 2, $I_{BP}(x)$, long-range part: 3, $I_{BP}(x)$, short-range part.

It will be seen that at $k = \beta k_F$ there is a discontinuity in $I_{BP}(x)$ due to the fact that the two methods of calculation used by Bohm & Pines for the long- and short-range parts of the interaction do not agree at the cut-off. On the other hand, the curve $I(x)$ shows no such discontinuity because the treatment given here applies

throughout the whole range of k, giving a description of collective motion at one end of the range and of particle motion at the other end. It will be noticed that the curve $I(x)$ shows a point of inflexion at $k \approx k_F$; we have not yet been able to give any simple explanation of this effect.

7. Summary and conclusions

In the present paper the following results have been obtained:

(i) The correlation energy of a free-electron gas has been expressed in terms of $\mathscr{V}(\mathbf{k}, \omega)$, the Fourier transform of the modified interaction discussed in I, and the integral equation giving $\mathscr{V}(\mathbf{k}, \omega)$ in terms of $\mathscr{V}^*(\mathbf{k}, \omega)$ has been solved.

(ii) The quantity $\mathscr{V}^*(\mathbf{k}, \omega)$ has been calculated in the lowest order for the ground state of an electron gas.

(iii) It has been shown that in the long-range limit the results obtained in this lowest-order calculation agree with Bohm & Pines's plasma oscillation theory, and the singularity which represents the plasma oscillations in the present theory has been identified.

(iv) It has been shown that in the short-range limit these lowest-order calculations are inadequate because they fail to give the exchange part of the second-order perturbation term; failure to allow for this term can lead to significant errors.

(v) An approximate method of correcting the theory to allow for these exchange terms has been suggested and applied to calculate the correlation energy at several gas densities; the error due to the approximations in this calculation is estimated to be about 0·004 Ry per electron. The results have been compared to Bohm & Pines and are to be in good agreement with them as regards total correlation energies.

I should like to thank Dr J. Corner and the staff of the Theoretical Physics Division at the Atomic Weapons Research Establishment, Aldermaston for permission to use the Ferranti Mark I* Computer and for their general assistance in this part of the work.

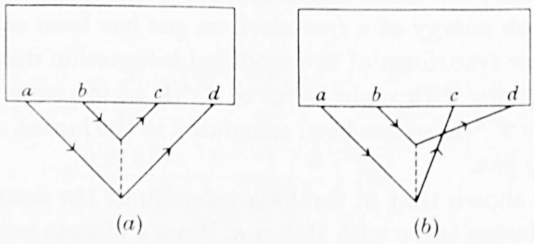
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Appendix

In this appendix the rough intuitive arguments which lie behind the adoption of the approximation (42) for $\mathscr{V}^*$ are briefly outlined. It is first convenient to introduce the idea of exchange conjugate diagrams. Let us compare the diagrams shown in figures 5 (*a*) and 5 (*b*); in each of these diagrams one interaction line and its vertices have been shown explicitly; the parts of the diagram not shown explicitly are supposed to be identical. Then the only difference between these diagrams is that the outcoming lines from the interaction shown have been crossed over in one

diagram relative to the other. This corresponds physically to the fact that the two diagrams represent essentially the same physical process except that in one of them the scattering shown is an exchange scattering process. Such diagrams will therefore be called exchange conjugates of one another. In general one can obtain exchange conjugates of any particular diagram by crossing over the outcoming particle lines at any number of interactions.



(*a*) (*b*)

FIGURE 5

If one writes down the contribution of a diagram G to the S matrix of energy shift in the form of an integral over the particle momenta attached to the particle lines of the diagram, then one can obtain the corresponding integrals giving the contributions of its exchange conjugate diagrams by simple substitutions. For if in the integral giving the contribution of G a certain interaction line gives a factor $v(\mathbf{k})$, then the integral representing the contribution of the diagram obtained from G by exchange conjugation at this interaction line is the same as that giving the contribution of G except that $v(\mathbf{k})$ must be replaced by $v(\mathbf{k}+\mathbf{k}_1-\mathbf{k}_2)$, where $\mathbf{k}_1$ and $\mathbf{k}_2$ are the momenta of the incoming particle lines at the interaction line, and one must multiply by a factor (-2) or $(-\frac{1}{2})$ to allow for the change in the number of closed particle loops which results from exchange conjugation (the factor 2 or $\frac{1}{2}$ arises from spin summations since on carrying out the spin summation each particle loop yields a factor 2).



(*a*) (*b*)

FIGURE 6

Consider now the polarization part shown in figure 6 (*a*), consisting of n polarization parts of the type shown in figure 1 (*a*) strung together. If one exchanges conjugates at all the interaction lines one obtains the polarization part shown in figure 6 (*b*) and $(n-1)$ interaction lines crossing the loop; this is a proper polarization part contributing to $\mathscr{V}^*$. Now according to the preceding paragraph, the integral representing the contribution of this polarization part will be the same as that representing the contribution of diagram 6 (*a*) except that we must replace the $v(\mathbf{k})$ corresponding to the interaction lines of the latter by $v(\mathbf{k}+\mathbf{k}_1-\mathbf{k}_2)$ and must multiply by $(-\frac{1}{2})^{n-1}$. If one now makes the essential approximation of replacing

the $v(\mathbf{k}+\mathbf{k}_1-\mathbf{k}_2)$ by $4\pi e^2/(k^2+k_F^2)$ everywhere, arguing that $|\mathbf{k}_1-\mathbf{k}_2| \approx k_F$ and therefore

$$v(\mathbf{k}+\mathbf{k}_1-\mathbf{k}_2) = \frac{4\pi e^2}{|\mathbf{k}+\mathbf{k}_1-\mathbf{k}_2|^2} \approx \frac{4\pi e^2}{k^2+k_F^2} \equiv v'(\mathbf{k});$$

on the average, then since the contribution to $\mathscr{G}(\mathbf{k},\omega)$ of the diagram 6(*a*) is

$$[\mathscr{G}_0^*(\mathbf{k},\omega)]^n,$$

where $\mathscr{G}_0^*(\mathbf{k},\omega)$ is that corresponding to the diagram 1(*a*) which was calculated in §3, the contribution of diagram 6(*b*) to $\mathscr{G}^*(\mathbf{k},\omega)$ will be

$$\mathscr{G}_0^*(\mathbf{k},\omega)\left[-\frac{1}{2}\frac{v'(\mathbf{k})}{v(\mathbf{k})}\mathscr{G}_0^*(\mathbf{k},\omega)\right]^{n-1} = \mathscr{G}_0^*(\mathbf{k},\omega)\left[-f(\mathbf{k})\mathscr{G}_0^*\right]^{n-1},$$

where

$$\frac{1}{2}\frac{v'(\mathbf{k})}{v(\mathbf{k})} = \frac{1}{2}\frac{k^2}{k^2+k_F^2} \equiv f(\mathbf{k}).$$

Summing over $n = 0, 1, 2, \ldots$, one finds that the total contribution of diagrams of the type 6(*b*) to $\mathscr{G}^*(\mathbf{k},\omega)$ is

$$\mathscr{G}_0^*(\mathbf{k},\omega)\sum_{n=0}^{\infty}[-f(\mathbf{k})\,\mathscr{G}_0^*(\mathbf{k},\omega)]^n = \frac{\mathscr{G}_0^*(\mathbf{k},\omega)}{1+f(\mathbf{k})\,\mathscr{G}_0^*(\mathbf{k},\omega)},$$

which is the result (42). It will be noticed that the simplest diagram of the type 6(*b*) is that shown in figure 3(*c*), which has therefore been included.

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The description of collective motions in terms of many-body perturbation theory

III. The extension of the theory to the non-uniform gas

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The theory previously developed and applied to calculate the correlation energy of a free-electron gas is extended in this paper to calculate the energy of an electron gas in a potential field. Two new features arise: (i) the introduction of a self-consistent field which is a generalization of the ordinary Hartree field; (ii) the occurrence of 'local field correction' effects. It is shown that the energy of the gas can be expressed in terms of the eigenvalues of a certain homogeneous integral equation and a stationary principle for these eigenvalues is given. The theory is applied to crystals and an approximate expression for the correlation energy of a metal is derived neglecting Lorentz–Lorenz corrections effects.

1. Introduction

In two previous papers (Hubbard 1957, 1958), which will be referred to as I and II, it was shown how a theory of the electron gas equivalent to Bohm & Pines's plasma oscillation theory (Bohm & Pines 1953) could be derived directly from the perturbation theory solution of the many-body problem by making use of a diagrammatic method of analysis of the perturbation series. For simplicity in these papers only the case of the free-electron gas, i.e. an electron gas moving in a constant external potential, was treated. However, in the main application of the theory, to the electronic motion in solids, the electrons move in the periodic field of the ion cores. It is, therefore, desirable to generalize the theory of papers I and II to this case. This generalization is straightforward and will be carried through in the present paper.

The theory of the first part of paper I (§§ 1 to 4) did not involve any assumption concerning the spatial uniformity of the gas and can therefore be taken over as it stands. In § 5 of I it was shown that if the gas density were assumed to be uniform certain diagrams could be neglected. These were diagrams containing some part which was connected to the rest of the diagram by only a single interaction line; such diagrams will be said to be H-reducible. In the case of a non-uniform gas these H-reducible diagrams give a contribution to the energy. However, it will be shown in the present paper that if a suitable self-consistent field, which is a generalization of the ordinary Hartree field (Hartree 1928), is introduced then these diagrams can again be eliminated from consideration. When this is done the theory of paper I goes through as before.

In this way one is led quite naturally to introduce a Hartree-like field. This is what would be expected in the non-uniform case, for the piling up of the electrons around the ion cores leads to additional strong electrostatic fields which are represented by the Hartree field. It will be seen that the theory leads to the introduction

of a Hartree-like rather than a Hartree–Fock field. This is because in the present theory exchange and correlation effects are treated together and the latter cannot be represented by a self-consistent field of the ordinary type. That sensible results concerning the behaviour of electron gases can only be obtained when exchange and correlation effects are treated together is well known.

In paper II extensive use was made of the uniformity of the electron gas to introduce the Fourier transform of the modified interaction and related quantities, and in particular to solve the integral equation for the modified interaction. In the non-uniform case this is no longer possible. It will be shown, however, that it is possible to solve the integral equation in the present case by the introduction of the eigenfunctions of a certain homogeneous integral equation. It is further shown that the correlation energy can be expressed in terms of the eigenvalues of this latter equation. The necessity to introduce the eigenfunctions of this equation instead of the plane waves used in the uniform case is connected with the need to introduce a local field correction in calculating the dielectric properties of crystalline solids. A stationary principle for the eigenvalues of the integral equation is given.

The program described above is carried though in §§ 2, 3 and 4 of this paper. In § 2 the way in which the theory of I is modified by the introduction of a self-consistent potential is described, and in § 3 it is shown how by the introduction of a suitable self-consistent field the H-reducible diagrams can be eliminated. In § 4 the solution of the integral equation and the calculation of the energy are described.

In § 5 the special results which are obtained when the electrons move in a periodic potential field are discussed, and it is shown how an approximate expression for the correlation energy may be derived making use of the stationary principle; the approximation essentially neglects local field correction effects.

2. The introduction of the self-consistent field

At the very outset of the theory developed in I the Hamiltonian of the system was written in the form

$$H = H_0 + H', \tag{1}$$

where

$$H_0 = \sum_i \frac{p_i^2}{2m} + \sum_i U(\mathbf{x}_i), \tag{2}$$

in which $\mathbf{p}_i$ is the momentum and $U(\mathbf{x}_i)$ the potential energy in an external field of the ith particle and

$$H' = \sum_{i \neq j} v(\mathbf{x}_i - \mathbf{x}_j) \tag{3}$$

is the interaction Hamiltonian of the particles. H_0 was then treated as the unperturbed Hamiltonian of the system and H' as the perturbation.

To introduce the self-consistent field one splits up the Hamiltonian H in a different manner from (1). Let the self-consistent field be $V(\mathbf{x})$ and let

$$V = \sum_i V(\mathbf{x}_i). \tag{4}$$

Then one writes instead of (1)

$$H = \bar{H}_0 + \bar{H}' = (H_0 + V) + (H' - V) \tag{5}$$

and now treats $\bar{H}_0 = H_0 + V$ as the unperturbed Hamiltonian and $\bar{H}' = H' - V$ as the perturbation.

When this is done the theory developed in I goes through as before except for the following changes:

(i) In I the $u_i(\mathbf{x})$ and E_i, which are the solutions of the eigenvalue equation

$$[p^2/2m + U(\mathbf{x})]\, u_i(\mathbf{x}) = E_i u_i(\mathbf{x}), \tag{6}$$

were introduced. Since the unperturbed Hamiltonian is now $\bar{H}_0$ instead of H_0 one introduces in the present case the solutions $u_i'(\mathbf{x})$ and E_i' of the eigenvalue equation

$$[p^2/2m + U(\mathbf{x}) + V(\mathbf{x})]\, u_i'(\mathbf{x}) = E_i' u_i'(\mathbf{x}) \tag{7}$$

and the corresponding creation and destruction operators $\bar{\eta}_i'$ and η_i'. The main difference which this makes is that the density $\rho(\mathbf{x})$ and the propagator $S(x', x)$ are now given by the equations

$$\rho(\mathbf{x}) = \sum_i^{\text{occ.}} |\, u_i'(\mathbf{x})\,|^2, \tag{8}$$

$$S(x', x) = \epsilon(t' - t) \sum^{\text{unocc.}} u_i'(\mathbf{x}')\, \bar{u}_i'(\mathbf{x}) \exp\{(\mathrm{i}/\hbar)\, E_i'(t - t')\}$$

$$- \epsilon(t - t') \sum_i^{\text{occ.}} u_i'(\mathbf{x}')\, \bar{u}_i'(\mathbf{x}) \exp\{(\mathrm{i}/\hbar)\, E_i'(t - t')\}. \tag{9}$$

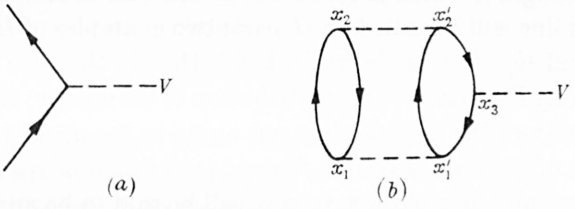


FIGURE 1

(ii) The perturbation H' when written in the notation of field theory now becomes

$$\bar{H}' = \frac{1}{2}\int \bar{\psi}(\mathbf{x}')\, \psi(\mathbf{x}')\, v(\mathbf{x} - \mathbf{x}')\, \bar{\psi}(\mathbf{x})\, \psi(\mathbf{x})\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}' - \tfrac{1}{2} N v(0) - \int \bar{\psi}(\mathbf{x})\, V(\mathbf{x})\, \psi(\mathbf{x})\, \mathrm{d}\mathbf{x}, \tag{10}$$

the last term arising from the introduction of the self-consistent field. If one now makes a diagrammatic analysis of the perturbation series using the perturbation (10) one finds that the additional term in (10) gives rise to a new type of vertex on the diagrams. Whereas the first term of (10) gives rise to the interaction lines with vertices at each end, the last term of (10) gives rise to single vertices with one incoming particle line and one outgoing particle line; these will be drawn in the way shown in figure 1 (*a*), and will be referred to as V-lines. When calculating the contribution to the energy or the S-matrix of any diagram one introduces into the integrand a factor $-(1/\mathrm{i}\hbar)\, V(\mathbf{x}_i)$ for every V-line whose vertex is labelled x_i and an integration over $x_i = (\mathbf{x}_i, t_i)$; the order of a diagram is the sum of the number of interaction and V-lines in the diagram.

An example of a diagram with a V-line is shown in figure 1 (b); the contribution to ΔE of this diagram is given by the expression

$$\frac{1}{3!}\left(\frac{1}{\mathrm{i}\hbar}\right)^3 \int \mathrm{d}x_1 \mathrm{d}x_1' \mathrm{d}x_2 \mathrm{d}x_2' \mathrm{d}x_3 \mathrm{i}\hbar\delta(t_1)\, v(x_1 - x_1')\, v(x_2 - x_2')\, V(x_3) \times S(x_2, x_1)\, S(x_1, x_2)\, S(x_2' x_1')\, S(x_3, x_2')\, S(x_1', x_3). \tag{11}$$

3. The elimination of H-parts

In this section it will be indicated how by the introduction of a suitable self-consistent field it is possible to eliminate from further consideration all those diagrams containing what will be called H-parts. It will be assumed that a self-consistent field has been introduced in the manner described in the preceding section, and attention will be restricted to vacuum diagrams, i.e. diagrams contributing to the energy shift ΔE.

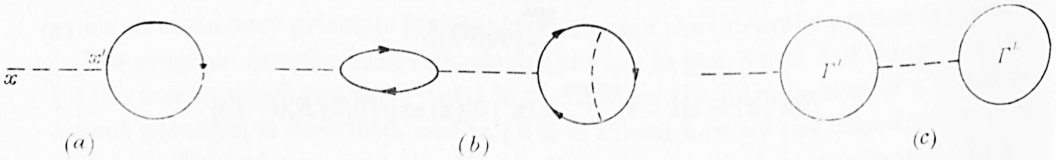


Figure 2

Any part of a diagram which is connected to the rest of the diagram by only a single interaction line will be called an H-part; two examples of H-parts are shown in figures 2 (a) and (b). It was shown in I, § 5, that in the case of a uniform gas diagrams containing H-parts gave no contribution to the energy; the proof depended upon the uniformity of the gas and does not apply in the present case.

If an H-part is of the form shown in figure 2 (c), i.e. can be resolved into a polarization part and some other H-part, then it will be said to be an improper H-part, otherwise it will be called a proper H-part. Clearly every improper H-part can be uniquely resolved into a proper H-part and some polarization part.

Denoting the integral representing the contribution to ΔE of a vacuum diagram G by $\Delta E(G)$ as in I, an H-part Γ contained in a diagram gives a factor of the form

$$H'(x_i, \Gamma) = \int v(x_i - x_i')\, H''(x_i', \Gamma)\, \mathrm{d}x_i' \tag{12}$$

in the integrand of $\Delta E(G)$ when the integrations at the vertices of the H-part have been performed, where x_i is the point at which the H-part is connected to the rest of the diagram. Because the theory contains no preferred origin of time, $H'(x, \Gamma)$ and $H''(x, \Gamma)$ are independent of t and may be written $H'(\mathbf{x}, \Gamma)$ and $H''(\mathbf{x}, \Gamma)$. As an example, for the H-part shown in figure 2 (a) $H''(\mathbf{x}) = \rho(\mathbf{x})$ and

$$H'(\mathbf{x}) = \int v(\mathbf{x} - \mathbf{x}')\, \rho(\mathbf{x}')\, \mathrm{d}\mathbf{x}'. \tag{13}$$

An H-part Γ attached to a diagram G at a point x_i gives a factor $H'(\mathbf{x}_i, \Gamma)$ in the integrand of $\Delta E(G)$ when the integrations at the vertices of the H-part have been

carried out, whilst a V-line attached at the same point would give a factor $-V(\mathbf{x}_i)$ in the integrand. This suggests that it might be possible to choose the self-consistent field $V(\mathbf{x})$, which is at our disposal, in such a way as to make the subdiagram shown in figure 3 (*a*) cancel against the sum of all the subdiagrams of the type shown in figure 3 (*b*) where Γ is a proper H-part. In fact, a detailed counting of diagrams, described in the appendix, shows that the choice

$$V(\mathbf{x}) = \sum_{\Gamma} \frac{2^{n(\Gamma)}}{g(\Gamma)} H'(\mathbf{x}, \Gamma), \tag{14}$$

where the sum is over all proper H-parts, makes the total contribution to ΔE of all diagrams containing H-parts and V-lines cancel out except for the symmetrical diagrams of the type shown in figure 3 (*c*) in which Γ is a proper H-part; their contribution to ΔE does not cancel exactly and half of it must be subtracted from ΔE. In (14) $n(\Gamma)$ is the order of the H-part Γ, defined to be the number of interaction lines contained in Γ apart from that connecting it to the rest of the diagram, whilst $g(\Gamma)$ is the g-factor of Γ defined to be the number of permutations of the interaction lines of Γ which leave it topologically unchanged.

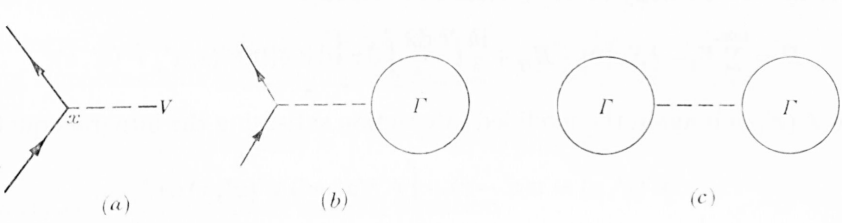


FIGURE 3

Thus, by making the choice (14) for the self-consistent field one can eliminate from consideration all the diagrams containing H-parts except those of the type shown in figure 3 (*c*). When the contribution to ΔE of these latter diagrams has been allowed for, only diagrams of the same type as those considered in the free-electron gas case, i.e. without H-parts, need be considered. It can be shown that the total contribution to ΔE of the diagrams of the type shown in figure 3 (*c*) is

$$E_H = -\sum_{\Gamma} \frac{2^{2n(\Gamma)-1}}{[g(\Gamma)]^2} \int H''(\mathbf{x}, \Gamma)\, v(\mathbf{x}-\mathbf{x}')\, H''(\mathbf{x}', \Gamma)\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}'. \tag{15}$$

The calculation of $V(\mathbf{x})$ from (14) is of the nature of a self-consistent calculation since the quantities $H'(\mathbf{x}, \Gamma)$ depend upon the density $\rho(\mathbf{x})$ and propagator $S(x', x)$ which in turn depend upon the $u_i'(\mathbf{x})$ and E_i' (see equations (8), (9)), which in turn depend upon $V(\mathbf{x})$ through (7). The simplest proper H-part is that shown in figure 2 (*a*) whose contribution to $V(\mathbf{x})$ is

$$\int v(\mathbf{x}-\mathbf{x}')\, \rho(\mathbf{x}')\, \mathrm{d}\mathbf{x}'. \tag{16}$$

Thus, if all other H-parts were neglected our self-consistent field would be the symmetrized Hartree field, and one may regard the self-consistent field introduced

here as a generalization of the ordinary Hartree field. The contribution of the diagram of figure 2 (*a*) to E_H is given by

$$-\frac{1}{2}\int \rho(\mathbf{x})\, v(\mathbf{x}-\mathbf{x}')\, \rho(\mathbf{x}')\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}', \tag{17}$$

which is just the term which has to be subtracted from the sum of energy parameters in an ordinary Hartree calculation when calculating the total energy of the system.

In the rest of this paper it will be assumed that a suitable self-consistent field has been introduced in the manner described in this and the previous section so that we need not concern ourselves with diagrams containing H-parts.

4. The solution of the integral equation

When a self-consistent field has been introduced and the H-parts have been eliminated, the theory of the introduction of the modified interaction and the elimination of the polarization parts goes through as in the free-electron case except that one has the additional contribution of equation (15) to the energy. The expression for the total energy of the system now becomes

$$E = \sum_i^{\text{occ.}} E_i - \tfrac{1}{2}Nv(0) + E_H + \frac{\mathrm{i}\hbar}{2}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}x \int \mathrm{d}x'\, \delta(t)\, \mathscr{V}(x,x')\, \overline{\mathscr{V}}(x',x), \tag{18}$$

where $\mathscr{V}(x',x)$ is again the modified interaction satisfying the integral equation

$$\mathscr{V}(x',x) = v(x'-x) + \int \mathscr{V}^*(x',x'')\, \mathscr{V}(x'',x)\, \mathrm{d}x'' \tag{19}$$

and $\mathscr{V}^*(x',x)$ can be expressed as sum over proper polarization parts

$$\mathscr{V}^*(x',x) = \sum_\Gamma W(x',x;\Gamma). \tag{20}$$

It should be noticed that one has to use the propagator (9) calculated in terms of the self-consistent wave functions in calculating the contributions to $\mathscr{V}^*$.

In the free-electron case (see II) $\mathscr{V}^*$ was calculated directly from (20) and $\mathscr{V}$ was obtained by solving the integral equation (19) by Fourier transformation, this being possible because in the free-electron case $\mathscr{V}^*$ was a function of the difference of its arguments only. In the non-uniform case this is no longer so and a different method of solving (19) has to be adopted. This method will now be described.

It is convenient to solve not the equation (19) but an equivalent equation. If (19) is multiplied by $\overline{\mathscr{V}}(x,x'')$ and integrated over x'' one obtains the equation

$$F(x',x) = \mathscr{V}^*(x',x) + \int \mathscr{V}^*(x',x'')\, F(x'',x)\, \mathrm{d}x'', \tag{21}$$

where

$$F(x',x) = \int \mathscr{V}(x',x'')\, \overline{\mathscr{V}}(x'',x)\, \mathrm{d}x'' \tag{22}$$

and use has been made of the relation (I, (69))

$$\mathscr{V}^*(x',x) = \int \overline{\mathscr{V}}(x',x'')\, v(x''-x)\, \mathrm{d}x''. \tag{23}$$

The integral appearing in (18) can at once be expressed in terms of the function F

$$\frac{i\hbar}{2}\int_0^\lambda \frac{d\lambda}{\lambda}\int dx \int dx'\, \delta(t)\, \mathcal{G}(x,x')\, \mathcal{G}(x',x) = \frac{i\hbar}{2}\int_0^\lambda \frac{d\lambda}{\lambda}\int dx\, \delta(t)\, F(x,x). \tag{24}$$

Although the kernel of the integral equation (21) does not depend upon the difference of its whole arguments, it does depend upon the difference of its time arguments. One may, therefore, obtain a partial solution by introducing the Fourier transform with respect to time of F and the other quantities

$$F(x',x) = \frac{1}{2\pi}\int d\omega\, F(\mathbf{x}',\mathbf{x},\omega)\, e^{i\omega(t'-t)}, \tag{25}$$

with a similar definition for $\mathcal{G}^*(\mathbf{x}',\mathbf{x},\omega)$. One then has to solve the integral equations

$$F(\mathbf{x}',\mathbf{x},\omega) = \mathcal{G}^*(\mathbf{x}',\mathbf{x},\omega) + \int \mathcal{G}^*(\mathbf{x}',\mathbf{x}'',\omega)\, F(\mathbf{x}'',\mathbf{x},\omega)\, d\mathbf{x}'', \tag{26}$$

whilst the right-hand side of (24) can be rewritten

$$\frac{i\hbar}{4\pi}\int_0^\lambda \frac{d\lambda}{\lambda}\int d\omega\, d\mathbf{x}\, F(\mathbf{x},\mathbf{x},\omega). \tag{27}$$

The integral equation (23) may be solved by the introduction of the eigenvalues $\mu_i(\omega)$ and eigenfunctions $\phi_i(\mathbf{x},\omega)$ of the homogeneous integral equation

$$\mu_i(\omega)\, \phi_i(\mathbf{x},\omega) = \int \mathcal{G}^*(\mathbf{x},\mathbf{x}',\omega)\, \phi_i(\mathbf{x}',\omega)\, d\mathbf{x}' \tag{28}$$

and also those of the associated integral equation

$$\mu_i(\omega)\, \chi_i(\mathbf{x},\omega) = \int \mathcal{G}^*(\mathbf{x}',\mathbf{x},\omega)\, \chi_i(\mathbf{x}',\omega)\, d\mathbf{x}'. \tag{29}$$

It can be shown that if $\mu_i(\omega)$ is an r-fold degenerate eigenvalue of (28), i.e. an eigenvalue of (28) to which there belong r linearly independent eigenfunctions, then $\mu_i(\omega)$ is also an r-fold degenerate eigenvalue of (29). Furthermore, if one denotes the eigenfunctions of (28) belonging to the eigenvalue $\mu_i(\omega)$ of (28) by $\phi_i^\alpha(\mathbf{x},\omega)$, where the superscript α distinguishes between the various linearly independent eigenfunctions belonging to the eigenvalue $\mu_i(\omega)$, and the corresponding eigenfunctions of (29) belonging to this same eigenvalue by $\chi_i^\alpha(\mathbf{x},\omega)$, then it can be shown (see, for example, Lovitt 1924) that

$$\int \chi_i^\alpha(\mathbf{x},\omega)\, \phi_j^\beta(\mathbf{x},\omega)\, d\mathbf{x} = 0 \quad \text{if} \quad i \neq j, \tag{30}$$

so that by forming suitable linear combinations of the ϕ_i^α and χ_i^α one can obtain the general orthonormality relation

$$\int \chi_i^\alpha(\mathbf{x},\omega)\, \phi_j^\beta(\mathbf{x},\omega)\, d\mathbf{x} = \delta_{ij}\delta_{\alpha\beta}. \tag{31}$$

To solve the integral equation (26) one now expands $F(\mathbf{x}',\mathbf{x},\omega)$ according to

$$F(\mathbf{x}',\mathbf{x},\omega) = \sum_{i,j}\sum_{\alpha\beta} F_{ij}^{\alpha\beta}(\omega)\, \phi_i^\alpha(\mathbf{x}',\omega)\, \chi_j^\beta(\mathbf{x},\omega). \tag{32}$$

If (32) is substituted into (26) one can obtain after simple manipulation using the orthonormality relations (31) and equation (28) the result

$$F_{ji}^{\alpha\beta}(\omega) = \mu_i(\omega)\,\delta_{\alpha\beta}\delta_{ij} + \mu_i(\omega)\,F_{ij}^{\alpha\beta}(\omega), \tag{33}$$

which has the immediate solution

$$F_{ij}^{\alpha\beta}(\omega) = \frac{\mu_i(\omega)}{1-\mu_i(\omega)}\,\delta_{ij}\delta_{\alpha\beta}. \tag{34}$$

Putting (32) into (27), using the orthonormality relations (31) and substituting the solution (34) for the $F_{ij}^{\alpha\beta}(\omega)$, one obtains in place of (27) the expression

$$\frac{\mathrm{i}\hbar}{4\pi}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}\omega \sum_i \frac{h_i(\omega)\,\mu_i(\omega)}{1-\mu_i(\omega)}\,, \tag{35}$$

where $h_i(\omega)$ is the degeneracy of the eigenvalue $\mu_i(\omega)$ of (28). Thus, the total energy of the system, and hence the correlation energy can be expressed in terms of the eigenvalues of the integral equation (28).

In the free-particle case the eigenvalues of (28) are plane waves $\mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{x}}$ the corresponding eigenvalue being $\mathscr{V}^*(\mathbf{k},\omega)$; putting these eigenvalues into (35) reproduces equation (12) of II.

There is a well-known stationary principle for the eigenvalues of the integral equation (28). If $\phi(\mathbf{x}) = \phi_i(\mathbf{x},\omega)$ and $\chi(\mathbf{x}) = \chi_i(\mathbf{x},\omega)$, then

$$\mu_i(\omega) = \frac{\int \chi(\mathbf{x})\,\mathscr{V}^*(\mathbf{x},\mathbf{x}',\omega)\,\phi(\mathbf{x}')\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'}{\int \chi(\mathbf{x})\,\phi(\mathbf{x})\,\mathrm{d}\mathbf{x}} \tag{36}$$

and the right-hand side of this equation is stationary against small variations in $\phi(\mathbf{x})$ and $\chi(\mathbf{x})$. Thus, if $\phi(\mathbf{x})$ is an approximation to $\phi_i(\mathbf{x},\omega)$ and $\chi(\mathbf{x})$ is an approximation to the corresponding $\chi_i(\mathbf{x},\omega)$, then the right-hand side of (36) gives an approximation to $\mu_i(\omega)$ correct to the second order.

5. The application of the theory to crystals

In a crystalline solid the electrons move in a periodic potential field. Because of this periodicity the eigenfunctions $u_i'(\mathbf{x})$ of (7) will be of Bloch form from which it can be deduced that the propagator $S(x',x)$ of (9) has the property

$$S(\mathbf{x}'+\mathbf{X},t';\,\mathbf{x}+\mathbf{X},t) = S(\mathbf{x}',t';\,\mathbf{x},t), \tag{37}$$

where $\mathbf{X}$ is any lattice vector, from which it can be further deduced that the kernel $\mathscr{V}^*(\mathbf{x}',\mathbf{x},\omega)$ of the integral equation (28) has the same property. It follows at once that the eigenfunctions $\phi(\mathbf{x},\omega)$ also have the Bloch form and that the corresponding eigenvalues $\mu_i(\omega)$ have a band structure. One may accordingly label these eigenvalues $\mu_{\mathbf{k}n}(\omega)$ where $\mathbf{k}$ is a vector lying in the Brillouin zone and n is a subscript which labels the various bands; alternatively one may introduce an 'extended zone scheme' and label the eigenvalues $\mu_{\mathbf{k}}(\omega)$. One can then write result (35) as

$$\frac{\mathrm{i}\hbar}{4\pi}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}\omega\,\mathrm{d}\mathbf{k}\,\frac{\mu_{\mathbf{k}}(\omega)}{1-\mu_{\mathbf{k}}(\omega)}\,. \tag{38}$$

The fact that the eigenfunctions of (28) have the Bloch form

$$\phi(\mathbf{x},\omega) = \mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{x}}\tau_{\mathbf{k}}(\mathbf{x},\omega), \quad \tau_{\mathbf{k}}(\mathbf{x},\omega)\,\text{periodic}, \tag{39}$$

can be readily interpreted physically. An analogous situation occurs in the theory of dielectrics. When an external electric field is applied to a crystal the polarization produced generates an electric field in the interior of the crystal which has a periodic modulation; the average of this field over the modulations is the field normally measured in the crystal. Because this latter average field differs from the actual periodic field existing in the crystal, one has to make a correction in calculating the dielectric properties of the crystal; this correction constitutes part of what is usually known as the local field correction. It is hoped to show in a further paper that there is a close connexion between the present theory and the theory of the dielectric properties. Thus, the fact that in the non-uniform crystalline case one is involved in solving the integral equation (28) whose solutions are of Bloch form is connected with the necessity to introduce the Lorentz–Lorenz correction in calculating the dielectric properties of crystals; this correction does not occur in the free-electron gas case.

If one neglects the Lorentz–Lorenz correction effects then the eigenfunctions $\phi_{\mathbf{k}}(\mathbf{x},\omega)$ and $\psi_{\mathbf{k}}(\mathbf{x},\omega)$ can be approximated to by plane waves

$$\phi_{\mathbf{k}}(\mathbf{x},\omega) \approx \mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{x}}, \quad \psi_{\mathbf{k}}(\mathbf{x},\omega) \approx \mathrm{e}^{-\mathrm{i}\mathbf{k}.\mathbf{x}}. \tag{40}$$

If these approximations are substituted into the stationary principle (36) then one obtains the approximation

$$\mu_{\mathbf{k}}(\omega) = \mathscr{K}^*(-\mathbf{k},\mathbf{k},\omega) \tag{41}$$

to the eigenvalue $\mu_{\mathbf{k}}(\omega)$, where $\mathscr{K}^*(\mathbf{k}',\mathbf{k},\omega)$ is the Fourier transform of $\mathscr{K}^*(\mathbf{x}',\mathbf{x},\omega)$ with respect to $\mathbf{x}$ and $\mathbf{x}'$. If the approximation (41) is substituted into (38) one obtains the expression

$$\frac{\mathrm{i}\hbar}{4\pi}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\,\mathrm{d}\omega\,\mathrm{d}\mathbf{k}\,\frac{\mathscr{K}^*(-\mathbf{k},\mathbf{k},\omega)}{1-\mathscr{K}^*(-\mathbf{k},\mathbf{k},\omega)}, \tag{42}$$

which is exactly the same as the result obtained in the free-electron case (the first term of equation (12) of paper II) except that the $\mathscr{K}^*(\mathbf{k},\omega)$ of the free-electron case is replaced by $\mathscr{K}^*(-\mathbf{k},\mathbf{k},\omega)$. Writing

$$\mu_{\mathbf{k}}(\omega) = \mathscr{K}^*(-\mathbf{k},\mathbf{k},\omega) = A(\mathbf{k},\omega) + \mathrm{i}\Sigma(\mathbf{k},\omega), \tag{43}$$

where $A(\mathbf{k},\omega)$ is the real part and $\Sigma(\mathbf{k},\omega)$ is the imaginary part of $\mathscr{K}^*(-\mathbf{k},\mathbf{k},\omega)$, (42) can be rewritten

$$-\frac{\hbar}{4\pi}\int_0^\lambda \frac{\mathrm{d}\lambda}{\lambda}\int \mathrm{d}\mathbf{k}\,\mathrm{d}\omega\,\frac{\Sigma(\mathbf{k},\omega)}{[1-A(\mathbf{k},\omega)]^2+\Sigma^2(\mathbf{k},\omega)}, \tag{44}$$

a form identical with the free-electron result. Thus, if the local field correction effects are neglected the results in the non-uniform case can be written in a form exactly similar to the free-electron gas case.

Consider now the calculation of the quantities $A(\mathbf{k},\omega)$ and $\Sigma(\mathbf{k},\omega)$ in the non-uniform case. The quantity $\mathscr{V}^*(x',x)$ can again be calculated directly from (20) retaining only the leading term corresponding to the simplest of all polarization diagrams, that shown in figure 4.



FIGURE 4

The $\overline{W}$ corresponding to this polarization part is given as in the free-electron case by

$$\overline{W}(x',x) = -(1/\mathrm{i}\hbar)\,S(x',x)\,S(x,x'), \tag{45}$$

where $S(x',x)$ is now the propagator given by (9). The calculation of $A(\mathbf{k},\omega)$ and $\Sigma(\mathbf{k},\omega)$ from (9), (45) and (43) is similar to the free-electron gas calculation performed in § 3 of II and yields the results

$$A(\mathbf{k},\omega) = \frac{8\pi e^2}{\hbar k^2}\sum_{i,j}\frac{N_i\,|\,M_{ij}(\mathbf{k})\,|^2\,(E'_j-E'_i)}{\hbar^2\omega^2-(E'_j-E'_i)^2}, \tag{46}$$

$$\Sigma(\mathbf{k},\omega) = -\frac{8\pi^2e^2}{\hbar k^2}\sum_{i,j}N_i(1-N_j)\,|\,M_{ij}(\mathbf{k})\,|^2\left[\delta\left(\omega+\frac{E'_j-E'_i}{\hbar}\right)+\delta\left(\omega+\frac{E'_i-E'_j}{\hbar}\right)\right], \tag{47}$$

where the N_i are the occupation numbers of the single particle states $u'_i(\mathbf{x})$ in the unperturbed wave function and

$$M_{ij}(\mathbf{k}) = \int \overline{u}'_j(\mathbf{x})\,\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}\,u'_i(\mathbf{x})\,\mathrm{d}\mathbf{x}. \tag{48}$$

It will be seen that as in the free-electron case the $A(\mathbf{k},\omega)$ agrees with the real part of the dielectric constant calculated neglecting the local field correction (Hubbard 1955), whilst the imaginary part again differs in that the sum of the two δ-functions appears instead of their difference.

Comparing with the analysis given in § 4 of II it will be seen that in the integral (44) one will again obtain a large contribution to the energy from the region of the line $A(\mathbf{k},\omega)=1$ if $\Sigma(\mathbf{k},\omega)$ is small in this region, corresponding to the presence of collective motion with a frequency given by that at which the real part of the dielectric constant vanishes. In those cases where $\Sigma(\mathbf{k},\omega)$ is large at the collective oscillation frequency it will not be possible clearly to recognize plasma oscillations as such, but the present theory gives an adequate account of the correlation energy even in this heavy damping case.

6. Summary of results

In the present paper the free-electron gas theory developed in two previous papers has been extended to non-uniform gases, and in particular to electron gases in crystalline fields. The following results have been obtained.

(i) In the non-uniform case certain diagrams containing 'H-parts' which give no contribution in the free-electron gas case have to be taken into consideration. It has been shown, however, how they may again be eliminated by the introduction of a self-consistent field which is a generalization of the ordinary Hartree field.

(ii) The solution of the integral equation connecting $\mathscr{V}$ and $\mathscr{V}^*$ cannot be obtained so simply as in the free-electron gas. It has been shown that in the non-uniform case it can be solved with the help of the eigenfunctions of a certain homogeneous integral equation, and that the correlation energy can be expressed in terms of the eigenvalues of this equation. A stationary principle for these eigenvalues has been given. The connexion of this integral equation with the Lorentz–Lorenz correction occurring in the theory of dielectrics has been indicated.

(iii) It has been shown that in the case of an electron gas moving in a crystalline potential the eigenvalues of the integral equation have a band spectrum. The eigenvalues of the integral equation have been approximately calculated in this case neglecting the Lorentz–Lorenz correction and it has been shown that with this approximation the theory can be written in a form exactly analogous to the free-electron gas theory.

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Appendix

It is convenient to divide all vacuum diagrams into four classes:

(i) class A contains all vacuum diagrams which contain no H-parts or V-lines;

(ii) class B contains all vacuum diagrams of the type shown in figure 5 (*a*), i.e. which consist of two proper H-parts connected by an interaction line;

(iii) class C contains all diagrams of the type shown in figure 5 (*b*), i.e. which consists of a proper H-part joined to a V-line;

(iv) class D contains all other vacuum diagrams; every diagram of this class is of the form shown in figure 5 (*c*), i.e. consists of a 'core' Γ to which are attached two or more proper H-parts or V-lines. The contributions to ΔE of the diagrams of classes B, C and D will be considered in detail.

Class D contains a subclass D' which consists of all those diagrams of class D which involve no H-parts but only V-lines. If Γ is any structure belonging to class D, then by replacing all the proper H-parts contained in Γ by V-lines one can obtain a unique structure Γ'' belonging to class D'. All those structures of class D which reduce in this way to a given structure Γ'' of class D', together with the structure Γ'' itself form a subclass of class D which we will denote by $T(\Gamma'')$; every structure of class D belongs to one and only one of these classes $T(\Gamma'')$.

Let Γ'' now be a structure belonging to class D' and let G' be a diagram with the structure Γ'' and such that in G' the V-lines are connected to the points $x_1, x_2, \ldots, x_p$ of G'. Suppose now that Γ is some structure of the class $T(\Gamma'')$ obtainable from Γ'' by replacing the V-lines joined to the points $x_1, x_2, \ldots, x_p$ by the proper H-parts $\Gamma_{i_1}, \Gamma_{i_2}, \ldots, \Gamma_{i_p}$, where $\Gamma_1, \Gamma_2, \ldots$, are the set of all proper H-parts, and we have introduced the convention of saying that a V-line has been replaced by the special

'H-part' Γ_0 if in fact it is unaltered in going from the structure Γ' to Γ. Let G be some diagram with structure Γ; then when the integrations at the vertices of the proper H-parts of G have been performed $\Delta E(G)$ is given by the same integral which gives $\Delta E(G')$ except that:

(i) it has been multiplied by a factor $(n')!/n!$, where n and n' are the orders of the structures Γ and Γ';

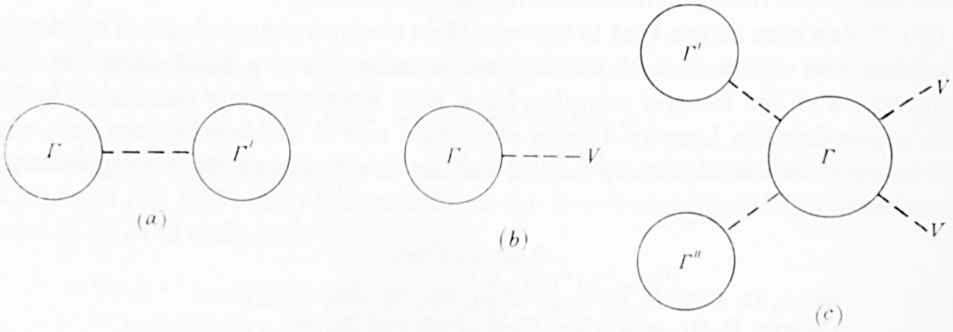


FIGURE 5

(ii) that every factor $-V(\mathbf{x}_\alpha)$ in the integrand of $\Delta E(G')$ has been replaced by a factor $H'(\mathbf{x}_\alpha, \Gamma_{i_\alpha})$, where one is to take $H'(\mathbf{x}, \Gamma_0) = -V(\mathbf{x})$. This result can be written formally

$$\Delta E(G) = \frac{n'!}{n!}\,\Delta E(G'; H'(\mathbf{x}_1, \Gamma_{i_1}), \ldots, H'(\mathbf{x}_p, \Gamma_{i_p})), \tag{A 1}$$

where the expression on the right stands for the integral for $\Delta E(G')$ with the modifications indicated above. From (A 1) it follows that

$$\Delta E(\Gamma) = \frac{2^{n-n'}g(\Gamma')}{g(\Gamma)}\,\Delta E(\Gamma'; H'(\mathbf{x}, \Gamma_{i_1}), \ldots, H'(\mathbf{x}, \Gamma_{i_p})), \tag{A 2}$$

where $\Delta E(\Gamma)$ denotes the contribution of all those diagrams with the structure Γ (see I, equation (25)). It can be shown that in the case of diagrams of class D that

$$g(\Gamma) = g(\Gamma')\,g(\Gamma_{i_1})\,g(\Gamma_{i_2}), \ldots, g(\Gamma_{i_p}). \tag{A 3}$$

Since the expression on the right-hand side of (A 2) depends linearly upon the $H'(\mathbf{x}_\alpha, \Gamma_{i_\alpha})$ it follows that (A 2) can be written

$$\Delta E(\Gamma) = \Delta E(\Gamma''; H(\mathbf{x}, \Gamma_{i_1}), \ldots, H(\mathbf{x}_p, \Gamma_{i_p})), \tag{A 4}$$

where

$$H(\mathbf{x}, \Gamma_i) = \frac{2^{n(\Gamma_i)}}{g(\Gamma_i)}\,H'(\mathbf{x}, \Gamma_{i_p}) \tag{A 5}$$

and $n = n' + n(\Gamma_{i_1}) + n(\Gamma_{i_2}) + \ldots$ has been used.

Consider now the total contribution to ΔE of all the structures of the class $T(\Gamma')$. Since all these structures are obtainable by replacing the V-lines of Γ' in all possible ways by proper H-parts or V-lines, it follows from (A 4) that this total contribution is given by

$$\sum_{\Gamma_{i_1}} \sum_{\Gamma_{i_2}} \cdots \sum_{\Gamma_{i_p}} \Delta E(\Gamma''; H(\mathbf{x}_1, \Gamma_{i_1}), \ldots, H(\mathbf{x}_p, \Gamma_{i_p})), \tag{A 6}$$

where the sums run over all proper H-parts together with the special H-part Γ_0. Since each of the terms on the right-hand side depends linearly upon the $H(\mathbf{x}_\alpha, \Gamma_{i_\alpha})$, it follows that the quantity (A 6) can be written

$$\Delta E(\Gamma'; H(\mathbf{x}), \ldots, H(\mathbf{x})), \tag{A 7}$$

where

$$H(\mathbf{x}) = \sum_{\Gamma_i} H(\mathbf{x}, \Gamma_i) = -V(\mathbf{x}) + \sum_{\Gamma}^{\text{proper}} \frac{2^{n(\Gamma)}}{g(\Gamma)} H'(\mathbf{x}, \Gamma). \tag{A 8}$$

However, the choice (14) for $V(\mathbf{x})$ makes $H(\mathbf{x})$ vanish and therefore the total contribution of the class $T(\Gamma')$. However, the choice (14) for $V(\mathbf{x})$ is independent of the class $T(\Gamma')$ and therefore makes the total contribution to ΔE of each of the classes $T(\Gamma')$ vanish and therefore the total contribution of all the diagrams of class D.

Consider now the diagrams of class B. Let Γ be some structure of class B consisting of two proper H-parts Γ' and Γ'' joined by an interaction line. Then it can be shown that the contribution to ΔE of all those diagrams with the structure Γ is given by

$$\frac{2^{n(\Gamma')+n(\Gamma'')}}{g(\Gamma)} \int H''(\mathbf{x}, \Gamma')\, v(\mathbf{x}-\mathbf{x}')\, H''(\mathbf{x}', \Gamma'')\, \mathrm{d}\mathbf{x}'\, \mathrm{d}\mathbf{x}''. \tag{A 9}$$

In this case $g(\Gamma) = g(\Gamma')g(\Gamma'')$ if Γ' and Γ'' are different, but if they are the same $g(\Gamma) = 2[g(\Gamma')]^2$. It follows that the total contribution of all diagrams of class B which is obtained by summing (A 9) over all proper H-parts Γ' and Γ'' is given by

$$\begin{aligned}
&\sum_{\Gamma'} \sum_{\Gamma''} \frac{2^{n(\Gamma')+n(\Gamma'')}}{g(\Gamma')g(\Gamma'')} \int H''(\mathbf{x}, \Gamma')\, v(\mathbf{x}-\mathbf{x}')\, H''(\mathbf{x}', \Gamma'')\, \mathrm{d}\mathbf{x}'\, \mathrm{d}\mathbf{x}'' \\
&\qquad + \sum_{\Gamma} \frac{2^{2n(\Gamma)-1}}{[g(\Gamma)]^2} \int H''(\mathbf{x}, \Gamma)\, v(\mathbf{x}-\mathbf{x}')\, H''(\mathbf{x}', \Gamma)\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}' \\
&= \sum_{\Gamma'} \frac{2^{n(\Gamma')}}{g(\Gamma')} \int H''(\mathbf{x}, \Gamma')\, V(\mathbf{x})\, \mathrm{d}\mathbf{x} - \sum_{\Gamma} \frac{2^{2n(\Gamma)-1}}{[g(\Gamma)]^2} \int H''(\mathbf{x}, \Gamma)\, V(\mathbf{x}-\mathbf{x}')\, H''(\mathbf{x}', \Gamma)\, \mathrm{d}\mathbf{x}\, \mathrm{d}\mathbf{x}',
\end{aligned} \tag{A 10}$$

using (14).

Finally, the contribution of all the diagrams of class C can be shown to be

$$-\sum_{\Gamma'} \frac{2^{n(\Gamma')}}{g(\Gamma')} \int H''(\mathbf{x}, \Gamma')\, V(\mathbf{x})\, \mathrm{d}\mathbf{x}, \tag{A 11}$$

where the sum runs over all proper H-parts Γ'. Combining (A 10) and (A 11), the total contribution to ΔE of all vacuum diagrams is the sum of that of the diagrams of class A, i.e. those with no H-parts or V-lines, and the contribution given in equation (15) which is the sum of (A 10) and (A 11).

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