CORRELATION ENERGY OF AN ELECTRON GAS

by

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SYNOPSIS OF ACADEMIC CAREER

After a four year course in "Applied Physics" at the Royal College of Science and Technology, I received the Associateship of the College with First Class Honours in 1956. At this time I became interested in plasma physics especially those connected with gas discharges. I continued my studies at the College in the Electrical Engineering Department, and in 1957 I received the Postgraduate Diploma for Advanced Study in Electrical Engineering ("Microwaves"). Later that year I began my research at St. Andrews under the supervision of Dr. C. G. Kuper, being primarily interested in theoretical aspects of the collective behaviour of particles.

DECLARATION

I hereby declare that this special study has been carried out and the thesis composed by myself and that this thesis has not been accepted in fulfillment of the requirements of any other degree or professional qualification.

SUMMARY

Methods of calculating the correlation energy of an electron gas are examined. The first section reviews those developed for the uniform electron gas. The second part is devoted to the non-uniform gas problem. Possible application of these theories to electrons in metals is discussed.

CONTENTS

PART I - THE UNIFORM GAS

PART II - THE NON-UNIFORM GAS

NOTE ON UNITS AND SYMBOLS

It is convenient to express the correlation energy of a solid in rydbergs/electron, a rydberg being defined :

$$1 \text{ rydberg} = \frac{me^4}{2\hbar^2}$$

$$= \text{Energy of the first Bohr orbit}$$

$$= \underline{13.6 \text{ e.v.}}$$

or alternatively in terms of the units used in cohesive energy calculations :

1 ryd/atom = 312 k. cal/mol

The inter-electron spacing is expressed in units of the radius of the first Bohr orbit a_o i.e.

$$\frac{4}{3} \pi(r_s a_o)^3 = \frac{1}{n}$$

where n is the number of electrons per unit volume, and r_s the inter-electron spacing in units of a_o,

where $$a_o = \frac{\hbar^2}{me^2}$$

$$= \underline{0.5292 \text{ Å}}$$

Some of the symbols used are :-

P - Fermi momentum

E_F - Fermi energy

E_G - Energy gap

q - momentum transfer

k_c - maximum wave vector for which collective behaviour exists.

β - $\frac{k_c}{P}$

ϵ_1 - real part of the dielectric constant

ϵ_2 - imaginary part of the dielectric constant

λ - coupling constant $= \frac{4\pi e^2}{q^2 V}$

V - volume of the system

ω_p - classical plasma frequency $= \left(\frac{4\pi n e^2}{m}\right)^{\frac{1}{2}}$

ρ_k - Fourier transform of the density fluctuations

a_k^*, a_k - creation and destruction operators respectively for an electron of momentum k

c_{kq}^*, c_{kq} - creation and destruction operators for electron hole pairs.

m^* - effective mass ratio

f_{on} - oscillator strength associated with the transition from state o to state n

$\delta_{kk'}$ - Dirac delta function

PART I

UNIFORM GAS

I - INTRODUCTION

One of the major problems of metal physics is the calculation of the cohesive energy. This may be defined as the difference in energy at $0^{O}K$ between the combined energy of the atoms of the metal and the sum of the energies of the atoms when taken separately. Early attempts at calculating the cohesive energy using an independent particle model failed, because of the neglect of the Pauli Principle and electron interactions.

Calculating the energy of an electron gas by the Hartree, Fock$^{(I)}$ approximation one uses a wave function constructed by taking a Slater determinant of free electron wave functions

$$\Psi = \frac{I}{\sqrt{n!}} \left| \begin{array}{cccc} \phi_i(x_i) & \phi_2(x_i) & \phi_3(x_i) & ------ \\ \phi_2(x_i) & \phi_2(x_2) & \phi_2(x_3) & ------ \\ \vdots & \vdots & \vdots & \end{array} \right| \qquad (I.I)$$

This wave function does not give the correct cohesive energy for a metal, for, although it includes the Pauli Principle, it omits any interaction between the electrons. The energy arising from this interaction was termed <u>CORRELATION ENERGY</u> by WIGNER$^{(2)}$: i.e. the correlation energy of an electron gas is the difference between the true energy and that obtained by the HARTREE, FOCK approximation.

We shall first consider the hypothetical case of a uniform electron gas at high density. Here it is normally assumed that the gas is an infinite one and is at 0°K. The positive ions are smeared out to form a uniform background of positive charge which cancels the effect of the average electron charge density. The potential of the ions is in fact replaced by an infinite constant and its effect is found to cancel in all physical processes.

Any attempt to include the electron interaction by standard perturbation theory leads to a divergent answer. This is entirely due to the long range nature of the Coulomb field. It is well known however, that these divergences are cancelled by polarization effects, any out of balance in the charge distribution being quickly screened. A physical example of this is the skin effect found in metals.

Failure of standard perturbative methods can be simply demonstrated. The Hamiltonian for the free electron gas may be written :

$$H = \sum_{i} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} \frac{e^2}{r_{ij}} \qquad (I.2)$$

$$= H_{ke} + H_{int}$$

The ground state energy of the gas E_o is,

$$E_o = e_f + e_x + e_{corr} \qquad (I.3)$$

where e_f is the Fermi energy/electron $= \frac{3}{5}\,\frac{\hbar^2 p^2}{2m} \Big/ \frac{me^4}{2\hbar^2}$

$$= \frac{2.21}{r_s^{\,2}} \text{ rydbergs}$$

and e_x = first order interaction energy.

e_{corr} = correlation energy i.e. the energy arising from the sum of the higher order perturbation terms.

$$e_x = \frac{1}{2} \sum_{ij} \left[(ij \mid H_{int} \mid ij) - (ij \mid H_{int} \mid ji) \right] \qquad \text{(I.4)}$$

The first term is the electrostatic energy which is assumed to be cancelled by the interaction with the positive charge background. The second term, the exchange interaction, vanishes unless the interacting pair have parallel spins. Fourier transforming the potential in a box of unit volume

$$e_x = -4\pi e^2 \left[\frac{1}{(2\pi)^3}\right]^2 \int \frac{dk_i\, dk_j}{|k_i - k_j|^2} \qquad \text{(I.5)}$$

$$= -\frac{0.916}{r_s} \text{ rydbergs/electron}$$

$[e_f + e_x]$ is obtained from the Hartree-Fock theory

The second order perturbation term is not quite as straightforward

$$\Delta E = \sum_n \frac{|\langle n \mid H_{int} \mid 0 \rangle|^2}{|E_n - E_0|} \qquad \text{(I.6)}$$

Here there are two terms since the electrons may have parallel or anti-parallel spins. These will be referred to as the direct and exchange contributions respectively.

In these virtual processes two electrons in the Fermi Sea with initial momenta $\underline{k}_i$ and $-\underline{k}_2$ undergo a collision with momentum transfer q, emerging into unoccupied states $(\underline{k}_i + \underline{q})$ and $(-\underline{k}_2 - \underline{q})$ above the Fermi surface and then return to their initial states.

The direct contribution is : (momentum in units of P)

$$\epsilon_a^{(2)} = -\frac{3}{8\pi^5}\int d\underset{\sim}{q}\int_{\substack{|\underset{\sim}{k}_1|<1\\|\underset{\sim}{k}_1+\underset{\sim}{q}|>1}} d\underset{\sim}{k}_1\int_{\substack{|\underset{\sim}{k}_2|<1\\|\underset{\sim}{k}_2+\underset{\sim}{q}|>1}} d\underset{\sim}{k}_2\;\frac{1}{q^4}\cdot\frac{1}{\left[q^2+\underset{\sim}{q}\cdot(\underset{\sim}{k}_1+\underset{\sim}{k}_2)\right]} \tag{1.7}$$

and the exchange term:

$$\epsilon_b^{(2)} = \frac{3}{16\pi^5}\int d\underset{\sim}{q}\int_{\substack{|\underset{\sim}{k}_1|<1\\|\underset{\sim}{k}_1+\underset{\sim}{q}|>1}} d\underset{\sim}{k}_1\int_{\substack{|\underset{\sim}{k}_2|<1\\|\underset{\sim}{k}_2+\underset{\sim}{q}|>1}} d\underset{\sim}{k}_2\;\frac{1}{q^2\left[\underset{\sim}{q}+\underset{\sim}{k}_1+\underset{\sim}{k}_2\right]^2}\cdot\frac{1}{\left[q^2+\underset{\sim}{q}\cdot(\underset{\sim}{k}_1+\underset{\sim}{k}_2)\right]} \tag{1.8}$$

In $e_a^{(2)}$ there is a factor $\frac{1}{q^2}$ for each collision [Fourier transform of the Coulomb potential] while in $e_b^{(2)}$ one factor is the other $\frac{I}{(\underset{\sim}{k}_1 + \underset{\sim}{k}_2 + \underset{\sim}{q})^2}$ in which exchange occurs.

If the summations are now performed it can be readily seen that the direct contribution gives a divergent result.

For low momentum transfers the q^2 in $[q^2 + \underset{\sim}{q}\cdot(\underset{\sim}{k}_1 + \underset{\sim}{k}_2)]^{-1}$ can be neglected. The following summation has then to be performed

$$\epsilon_a^{(2)} \sim \sum_k \frac{k^2}{k^5} \rightarrow \int \frac{d\underset{\sim}{k}}{k^3} \rightarrow \int \frac{dk}{k}$$

which has a logarithmic divergence for q → o

The exchange contribution on the other hand has no such divergence since there is a factor $\frac{1}{q^2}$ less, hence,

$$\epsilon_b^{(2)} \sim \sum_k \frac{1}{k} \rightarrow \int \frac{d\underset{\sim}{k}}{k} \rightarrow \int k\, dk$$

Closer examination of the higher order perturbation terms reveals that these are also divergent.

The occurrence of this divergence could have been anticipated from a classical viewpoint. In a gas of charged particles i.e. a plasma, two collective effects take place, Debye screening and plasma oscillations. The screening effect is due to the polarization of the medium by the charged particles, and prevents the action of the coulomb interaction at distances appreciably greater than the screening distance. Plasma oscillations are due to electrostatic forces in the system which act if any local charge excess or deficiency exists. Both of these effects involve the co-operative action of many particles and hence cannot be treated by standard perturbation theory. The Debye screening does in fact remove the divergence discussed earlier.

These considerations can be put on a quantum mechanical footing by the Thomas-Fermi statistical method.(3) One might think that introduction of statistics would have considerable influence on the classical argument. However, this is not so, because these phenomena involve distances long compared with the wavelength associated with the electrons. In the Thomas-Fermi method of treating the many body problem, it is assumed that the electrons are effectively free at each point. If a charge q is introduced into a neutral plasma then a change in the electron density $\delta\rho$ occurs and an effective potential ϕ is set up. These

These are related through Poisson's equation, i.e.

$$\nabla^2\phi + 4\pi e\,\delta\rho = 4\pi q \qquad (I.9)$$

$\delta\rho$ can be readily shown to be,

$$\delta\rho = \frac{1}{3\pi^2}\left[\frac{2m}{\hbar^2}\left(E_F + e\phi\right)\right]^{3/2} - n \approx \frac{3}{2}\frac{n}{E_F}e\phi$$

Inserting this into equation (I.9) and solving for ϕ one finds,

$$\phi = \frac{q}{r}\exp\left(-\frac{r}{\lambda_{FT}}\right) \qquad (I.10)$$

where

$$\lambda_{FT} = \left(\frac{E_F}{6\pi n e^2}\right)^{\frac{1}{2}}$$

Hence, as in the classical Debye - Huckel theory$^{(4)}$ one finds that the long range coulomb potential is screened within a distance λ_{FT}. It will be shown later however, that this approach overestimates the screening power of the electron gas.

2 - COLLECTIVE DESCRIPTION OF ELECTRON INTERACTIONS

The presence of individual and collective excitations can be readily illustrated by a simple examination of the density fluctuations ρ_k of the electron gas. Re-writing the electron Hamiltonian as :

$$H = \sum_i \frac{p_i^2}{2m} + 2\pi e^2 \sum_{k \neq 0} \frac{1}{k^2}[\rho_k^* \rho_k - n] \tag{2.1}$$

where $\rho_k = \int \rho(x) \exp\left(-i\underset{\sim}{k}\cdot\underset{\sim}{x}\right) dx = \sum_i \exp\left(-i\underset{\sim}{k}\cdot\underset{\sim}{x}\right)$

Since ρ_k commutes with the potential energy we may write :

$$\dot{\rho}_k = \frac{1}{i\hbar}\left[\rho_k, H\right]$$

Hence the equation of motion for ρ_k is :

$$\ddot{\rho}_k = -\sum_i \left(\frac{k\cdot p_i}{m} + \frac{\hbar k^2}{2m}\right) \exp\left(-i\underset{\sim}{k}\cdot\underset{\sim}{x}_i\right) - \sum_q \frac{4\pi e^2}{mq^2}\, \underset{\sim}{k}\cdot\underset{\sim}{q}\, \rho_{k-q}\, \rho_q \tag{2.2}$$

Separating the term q = k and transposing it to the left hand side, equation 2.2 becomes :

$$\ddot{\rho}_k + \omega_p^2 \rho_k = -\sum_i \left(\frac{k\cdot p_i}{m} + \frac{\hbar k^2}{2m}\right) \exp\left(-i\underset{\sim}{k}\cdot\underset{\sim}{x}_i\right) - \sum_{q \neq k} \frac{4\pi e^2}{mq^2}\, \underset{\sim}{q}\cdot\underset{\sim}{k}\, \rho_{k-q}\, \rho_q \tag{2.3}$$

where $\omega_p^2 = \frac{4\pi n e^2}{m}$, ω_p being the plasma frequency.

Hence ρ_k performs simple harmonic motion at a frequency ω_p providing the terms on the right hand side of equation 2.3 can be neglected.

This corresponds to the physical picture of electrons moving in a completely collective manner. Under what conditions is this picture valid ? The second term may be neglected if the electrons are distributed at random, since there will be contributions from many electrons to $\rho_{k-k'}$. The phase factors appearing in the exponential being distributed at random, tend to cancel one another. Bohm and Pines$^{(5)}$ call this the Random Phase Approximation. The first term may be approximated to $k^2 V^2{}_o \rho_k$ where V_o is the velocity of an electron at the top of the Fermi distribution.

The condition for plasma oscillations then is

$\frac{k^2 V^2}{\omega_p^2} \ll 1$ or k less than some critical vector k_c

Hence one may expect the electron gas to exhibit collective behaviour for $k < k_c$ and individual particle motion for $k > k_c$. The latter may be regarded as statistical fluctuations coming from the thermal motion of weakly interacting electrons. The Debye screening length λ_s is of the order of $\frac{1}{k_c}$.

The basic problem is to develop a theory which is capable of treating the collective and individual effects together. Bohm and Pines$^{(6)}$ found that in a particular co-ordinate system, the plasma oscillations could be described by a set of equivalent harmonic oscillators, which only contribute a zero point energy to the system, leaving an effective Hamiltonian

$$H = \sum_{i} \frac{p_i^2}{2m} + \sum_{k>k_c} \frac{2\pi e^2}{k^2} \left[\rho_k^* \rho_k - n\right] \qquad (2.4)$$

for the individual motion of the electrons. They employ an extended Hamiltonian,

$$H = \sum_{i} \frac{p_i^2}{2m} + \sum_{k} \frac{2\pi e^2}{k^2} \left[\rho_k^* \rho_k - n\right] + \sum_{k<k_c} \left[\frac{\pi_k^* \pi_k}{2} + \pi_k^* \sqrt{\frac{4\pi e^2}{k^2}}\, \rho_k\right] \qquad (2.5)$$

where they have introduced n' field co-ordinates Q_k and their conjugate momenta Π_k which commute with the co-ordinates of the individual particles.

ie, $[\Pi_k, Q_k{}'] = -i\hbar \delta_{kk'}$, $[\Pi_{k}, P_i] = 0$ $[\Pi_k x_i] = 0$

$[Q_k, P_i] = 0$ $[Q_k, x_i] = 0$

These co-ordinates represent the collective excitations of the electron gas and their number n' is given by the number of wave vectors between 0 and k_c i.e.

$$n' = \frac{k_c^3}{6\pi^2}$$

In order to conserve the number of degrees of freedom of the system they are compelled to introduce an associated set of subsidiary conditions,

$$\Pi_k \Psi = 0 \qquad (k < k_c) \qquad (2.6)$$

Where Ψ is the extended wave function. By carrying out a canonical transformation of the form,

$$O_{\text{new}} = \exp\left(-\frac{is}{\hbar}\right) \; O_{\text{old}} \; \exp\left(\frac{is}{\hbar}\right)$$

Taking $$s = \sum_{k < k_c} \sqrt{\frac{4\pi e^2}{k^2}} \; Q_k \, \rho_k \tag{2.7}$$

the extended Hamiltonian becomes,

$$H = \sum_i \frac{p_i^2}{2m} + H_{sr} + \sum_{k<k_c} \left[\frac{\Pi_k^* \Pi_k}{2} + \omega_p^2 \frac{Q_k^* Q_k}{2} - \frac{2\pi n e^2}{k^2} \right]$$

$$+ \; H_{int} + U \tag{2.8}$$

where $$H_{sr} = \sum_{\substack{k > k_c \\ i \neq j}} \frac{2\pi e^2}{k^2} \exp[i\underset{\sim}{k}.(\underset{\sim}{x}_i - \underset{\sim}{x}_j)] \tag{2.9}$$

H_{int} is the contribution from a linear interaction between the electrons and the plasmons.

$$H_{int} = i \sum_{k<k_c} \left(\frac{k.P_i}{m} + \frac{\hbar k^2}{2m} \right) \sqrt{\frac{4\pi e^2}{k^2}} \; Q_k \exp[-i\underset{\sim}{k}\underset{\sim}{x}_i] \tag{2.10}$$

and U, an electron interaction term which is bi-linear in the plasmon co-ordinates,

$$U = \frac{2\pi e^2}{m} \sum_{\substack{kq,i \\ k \neq q}} Q_k^* \; Q_q \sqrt{\frac{1}{k^2 q^2}} \; \underset{\sim}{q} \cdot \underset{\sim}{k} \exp\left[i(\underset{\sim}{k} - \underset{\sim}{q}) \cdot \underset{\sim}{x}_i\right] \tag{2.11}$$

If the terms H_{int} and U are neglected then we have a system of electrons interacting via a screened Coulomb potential of range k_c^{-1} and a set of n' plasmons. The neglect of U corresponds to the Random Phase Approximation, while H_{int} corresponds to the first term on the right hand side of equation (2.3). Considering H_{sr} to be a small perturbation Bohm and Pines find that the coupling introduced between the electrons and plasmons by H_{int} may be measured by a constant,

$$g^2 = \left[\left(\frac{k.p_i}{m\omega_p} \right) \right] \underset{k < k_c}{\text{average over}} = \frac{\beta^2}{2r_s}$$

where $\beta = \frac{k_c}{k}$, and r_s is the inter-electron spacing measured in units of the Bohr radius a_o.

Hence for sufficiently small values of β, H_{int} represents a weak coupling between the electrons and plasmons which may be treated by perturbations methods, U being an even weaker term. The ground state energy of the electron gas is calculated by assuming a wave function $\Psi = \psi_{osc}\,\phi_o$ for the system. ϕ_{osc} is a product of simple harmonic oscillator wave functions and ϕ_o is a Slater determinant for the free electron gas.

The energy of each electron is,

$$E = \frac{3}{5} P + \sum_{k<k_c} \frac{1}{n} \left(\frac{\hbar\omega_p}{2} - \frac{2\pi n e^2}{k^2} \right) + (H_{sr})_{av} \qquad (2.12)$$

The first term is the kinetic energy, the second, the difference between the zero point oscillations of the plasmons and the self-energy of the charge distribution they have replaced. The last term is the exchange energy associated with H_{sr}.

The second term is readily evaluated and is :-

$$\frac{1}{n}\sum_{k<k_c}\left(\frac{\hbar\omega_p}{2} - \frac{2\pi n e^2}{k^2}\right) = 0.866\,\frac{\beta^3}{r_s^{3/2}} - 1.22\,\frac{\beta}{r_s} \tag{2.13}$$

Excluding the contribution of the short range portion of H_{sr}, Bohm and Pines minimize the energy of the electrons with respect to β. After including a contribution from H_{int} they find $\beta = 0.4 r_s^{\frac{1}{2}}$. This cut-off is very much lower than that obtained by the Fermi-Thomas method ($\beta = 0.815\, r_s^{1/2}$)

H_{sr} is calculated from conventional second order perturbation theory

$$H_{sr}^{corr} = 0.1244 \ \text{In}\ \beta - 0.0508 - O(\beta^2) \tag{2.14}$$

Adding this to the second order exchange energy $e_b^{(2)}$, (see equation 1.8) calculated by Gell-Mann and Brueckner$^{(7)}$ by a Monte Carlo process to be 0.046 rydbergs, one finds the correlation energy:

$$E_{corr} = 0.1244 \ln\beta - 0.0048 + 0.866\,\frac{\beta^3}{r_s^{3/2}} + 1.22\,\frac{\beta}{r_s} \tag{2.15}$$

Substituting $\beta = 0.4r_s^{1/2}$

$$E_{corr} = [0.0622 \ln r_s - 0.140 + O(r_s)]\text{ryd/electron} \quad (2.16)$$

This result agrees with the result obtained earlier by Wigner and also with experiment, showing the physical concepts to be correct. The method, however lacks mathematical rigour. The Random Phase Approximation which neglects the coupling between the excitations corresponding to different momentum transfers is not substantiated though later work does in fact show that it is exact in the high density limit. Inclusion of the electron plasmon coupling term H_{int} by perturbation theoretic methods is questioned by Sawada et al.(8) The determination of the cut-off for plasmon behaviour is one of weak points of the Bohm-Pines theory being evaluated by minimizing the energy given by part of the transformed Hamiltonian neglecting all the remaining terms dependent on β. They are forced to exclude the short range term H_{sr} which would give a divergent result. This procedure must be questioned since the actual correlation energy is independent of β. It is not possible to separate a small part of the Hamiltonian giving a β dependent energy and to minimize it with respect to β neglecting the variation of larger terms.

Their approach is rather artificial and is by far inferior to the linked cluster expansion method used by Gell-Mann Brueckner, which gives an exact and mathematically rigorous, answer for the uniform gas at high density.

3 - LINKED CLUSTER PERTURBATION METHOD

To avoid the divergence which appears in each order we may apply the adiabatic process, replacing the singular potential by a soft one and making the adiabatic parameter tend to zero. The original potential is recovered after the summation has been done. Here it is assumed that the energy levels remain discrete and do not cross. This assumption has been shown to be correct for the uniform electron gas by Luttinger and Ward(9)

As before $H = H_o + H_c$

where H_o = unperturbed Hamiltonian of the electrons

and H_c = coulomb interaction term

Assuming ϕ_o to be the unperturbed wave function and Ψ_o the lowest eigenfunction of H then :

$$H_o \phi_o = E_o \phi_o \qquad (3.1)$$

and $$H \Psi_o = (E_o + \Delta E)\Psi_o \qquad (3.2)$$

Ψ_o is derived from ϕ_o by adiabatically switching on the interaction H_c over the time interval $-\infty$ to 0. Goldstone(10) proves the adiabatic theorem in the following way for the case of a discrete set of eigenstates with a unique ground state.

He first defines the operators,

$$H_I(t) = \exp(iH_o t)\, H_c \exp(-iH_o t) \exp(\alpha t) \qquad (3.3)$$

and $$U_\alpha = \Sigma_{n=o}^{\infty} (-i)^n \;\; {}_{o>t_1>t_2>t_n} \; H_I(t_1)\, H_1(t_2) - - - - H_1(t_n)dt_1 - - - dt_n \tag{3.4}$$

As $\alpha \rightarrow 0$ the unitary operator U_α describes the adiabatic process

$$\Psi_o(t=o) = \lim_{\alpha \rightarrow o} \frac{U_\alpha(o, -\infty)\, \phi_o}{(\phi_o \,|\, U_\alpha \,|\, \phi_o)} \tag{3.5}$$

U and the scattering or S matrix are simply related,

$$S = \lim_{\alpha \rightarrow o} \lim_{\substack{t_1 \rightarrow \infty \\ t_2 \rightarrow -\infty}} U_\alpha(t_1, t_2) \tag{3.6}$$

(see for instance Akhiezer and Berestetsky P.230)

Hence $E = (\phi_o \,|\, H_1 \,|\, \Psi_o)$

$$= \lim_{\alpha \rightarrow o} \frac{(\phi_o \,|\, H_1 U_\alpha \,|\, \phi_o)}{(\phi_o \,|\, U_\alpha \,|\, \phi_o)} \tag{3.7}$$

Processes involved in this matrix element may be represented by graphs of the form,

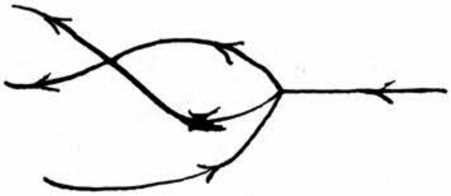


Figure I

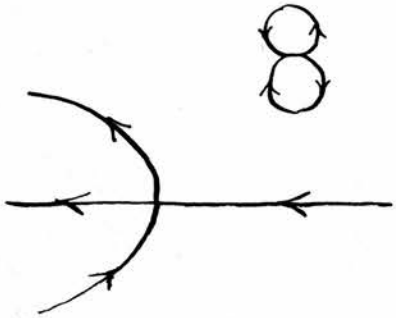


Figure 2

where a line directed to the right represents an electron excited above the Fermi surface, and one to the left, a hole below the surface. These diagrams can either be linked or unlinked as in Figure 2. It follows that $U_\alpha \phi_o$ is given by rules applying to the sume of linked graphs multiplied by a factor consisting only of unlinked parts. This factor is $(\phi_o \mid U_\alpha \mid \phi_o)$. Thus Ψ_o as defined in equation (3.5) is given by taking the limit $\alpha \rightarrow o$ in the sum of the linked graphs only.

$$\text{Hence} \quad \Psi_o = \sum_1 \left(\frac{I}{E_o - H_o} \cdot H_1\right)^n \phi_o \qquad (3.8)$$

and the energy shift is,

$$E = \sum_1 \left(\phi_o \middle| H_1 \left(\frac{I}{E_o - H_o} H_1\right)^n \middle| \phi_o\right) \qquad (3.9)$$

where Σ_1 stands for the summation over all connected diagrams leading from ϕ_o to ϕ_o ie. those having no external lines. Equations 3.8 and 3.9 are the linked cluster perturbation formulae. They differ from the usual bound state formula by having E_o in the denominator instead of $(E_o + \Delta E)$. This difference is compensated by the different enumeration of terms, summing over linked graphs and by ignoring the Pauli Exclusion Principle.

Bohm and Pines show that the correlation energy of an electron gas at high density may be expressed as :

$$e_{corr} = 0.0622 \ \ln r_s + C$$

where the constant C has been determined approximately. As pointed out earlier, each term in the perturbation series diverges.

Macke(12) realised, that if he summed the linked perturbation series to infinity, the divergences would cancel and produce a convergent result. Unfortunately he failed to sum all the pertinent diagrams. The full summation was carried out by Gell-Mann and Brueckner using techniques developed by Feynman(13) and Dyson(14) for use in quantum electrodynamics.

The most divergent processes occur in the linked diagrams where a single momentum transfer q is passed from virtual electron-hole pair to electron-hole pair. These processes may be conveniently illustrated by graphs, the third order term is shown in Figure 3.

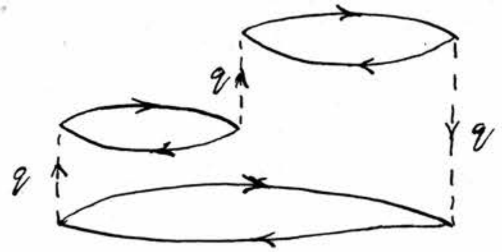


Figure 3

The number of possible diagrams in each order of perturbation is equal to the number of distinct ways of ordering the vertices in time. For the n^{th} order diagram this is $= \frac{n!}{n}$ Macke sums the first diagram in each order of the perturbation series. Selection of linked diagrams of the type shown in Figure 3 is exactly equivalent to the Random Phase Approximation of Bohm and Pines.

Exchange may take place at any of the vertices. Each time this occurs, however, the divergence is reduced by a factor $\frac{1}{q^2}$ which becomes $\frac{I}{(q + k_i + k_2)}2$ (see equation 1.8)

The only exchange term to contribute to the constant C is the second order one. Higher exchange terms contribute to higher powers of r_s and can be neglected in this approximation.

The summation of the direct interaction perturbation terms to all orders, allowing for all possible time sequences presents some difficulty. Gell-Mann, Brueckner carry out the time sequence sum by introducing a Feynman propagator function,

$$F(t_1) = \int dk_1 \exp[- t_1(\underline{k}_i \cdot \underline{q} + \frac{q^2}{2})] \tag{3.10}$$

Each term in the perturbation series can then be written in the form:

$$A_n = \frac{1}{n} \int dt_1 - - - - dt_n F(t_1) - - - F(t_n) \quad (t_1 - - - t_n) \tag{3.11}$$

By transforming the δ function,

i.e. $$\delta(t_i - - - t_n) = \frac{q}{2\pi} \int_{-\infty}^{\infty} du \exp (iq(t_i \quad t_2 - - - t_n)) \tag{3.12}$$

A_n can be written $$A_n = \frac{q}{2\pi n} [Q_q(u)]^n \tag{3.13}$$

where $$Q_q(u) = \int \underline{dk} \int_{-\infty}^{\infty} dt \exp [-t(\underset{\sim}{k} \cdot \underset{\sim}{q} + \frac{q^2}{2})] \exp(iqtu) \tag{3.14}$$

Carrying out the sum over n they find the Contribution from the direct scattering to be :

$$E_{\text{corr}}^{\text{dir scatt}} = \frac{3}{8\pi^5} \cdot \frac{1}{2\pi} \int_{-\infty}^{\infty} du \int \frac{dq}{q^3} \left(\frac{\pi^2 q^2}{\alpha r_s} \right)^2 \left[\ln\left(1 + \frac{\alpha r_s Q_q(u)}{\pi^2 q^2} \right) - \frac{\alpha r_s Q_q(u)}{\pi^2 q^2} \right] \quad (3.15)$$

In the q integral, only small values of q contribute, since it converges rapidly as q → ∞.

The first term on the right hand side of equation (3.15) can be rewritten as,

$$\int_0^{\infty} F(q) \, \frac{dq}{q} = \int_0^{\infty} \left[F(q) - F_2(q) \right] \frac{dq}{q} + \int_0^{\infty} F_2(q) \, \frac{dq}{q} \quad (3.16)$$

where $F_2(q)$ is the second order direct contribution to the correlation energy. The leading q dependence in the first two terms of equation (3.16) now cancels for large q, the difference going as $\frac{1}{q^2}$ at high density. Since the contribution to the integral comes from small q it is possible to select an arbitrary cut-off which Gell-Mann, Brueckner make q = 1. It is now possible to approximate the integrals for small q. Equation (3.16) can now be written as :

$$\int_0^1 F(q \to 0) \frac{dq}{q} - \lim_{\beta \to 0} \left[\int_0^1 F_2(q \to 0) \frac{dq}{q} - \int_\beta^{\infty} F_2(q) \frac{dq}{q} \right] \quad (3.17)$$

the logarithmic divergence at the lower limit in the last two integrals cancelling. The small q form of F(q) is obtained by taking the small q limit of $Q_q(u)$

$$Q_{q}(u) = \int d\underset{\sim}{k} \; \frac{\frac{q^2}{2} + \underset{\sim}{q}\cdot\underset{\sim}{k}}{\left(\frac{q^2}{2} + \underset{\sim}{q}\cdot\underset{\sim}{k}\right)^2 + q^2u^2} \tag{3.18}$$

As q tends to zero this can be approximated to,

$$Q_{q}(u) = 4\pi\left[\, I - u\tan^{-1}\left(\frac{I}{u}\right)\,\right] \tag{3.19}$$

$$= 4\pi R(u)$$

Hence

$$E_{corr}^{\substack{direct\\ scatt.}} = \frac{3}{8\pi^5}\cdot\frac{1}{2\pi}\int_{-\infty}^{\infty} du \,.\, 4\pi\int_0^1 \frac{dq}{q}\left(\frac{\pi^2q^2}{\alpha r_s}\right)^2\left[\ln\left(1 + \frac{4\alpha r_s R}{\pi q^2}\right) - \frac{4\pi\alpha r_s R}{\pi q^2}\right] + \delta \tag{3.20}$$

where $\alpha = \left(\frac{4}{9\pi}\right)^{1/3}$

and δ represents the last two terms in equation (3.16).

Evaluating the integrals and neglecting terms which vanish as $r_s \to 0$, Gell-Mann and Brueckner find,

$$E_{corr}^{scatt} = 0.0622 \ln r_s - 0.142 \text{ ryd/electron} \tag{3.21}$$

Adding the second order exchange energy, which they evaluate by a Monte-Carlo method to be 0.046 ryd., the correlation energy is:

$$E_{corr} = [0.0622 \ln r_s - 0.096] \text{ ryd/electron} \tag{3.22}$$

This method is more mathematically rigorous than the Bohm-Pines approach. Their summation is however only convergent for large momentum transfers. They assume with no justification that their result could be extended into the region of low momentum transfer. This approach is vindicated by Sawada and others who derive the result in a manner which avoids the perturbation expansion.

4 - ANALOGY WITH THE MESON PAIR THEORY

Gell-Mann and Brueckner show that one can use a propagator for pairs between interactions. The pair created with momentum transfer q propagates from one interaction to the next, changing itself into another pair with the same momentum difference between electron and hole. The pair in fact appears to propagate as a single particle. Sawada(15) noted the similarity of this problem with that of an infinitely heavy particle interacting with a neutral scalar meson field through a product potential, a problem solved earlier by Wentzel(16). Using his method Sawada re-derives the Gell-Mann, Brueckner result showing that their assumptions are indeed valid. Later Wentzel(17) gave the result in a more elegant form. It is convenient to write the Hamiltonian in second quantization. Here the quiescent Fermi sea can be identified with the vacuum state in quantum electrodynamics. Simple excited states, in the form of electron-hole pairs, are produced from the vacuum state by operating on it with the creation and destruction operators a^* and a. These operators are obtained by expanding the wave function Ψ of the electrons in plane waves :

$$\text{i.e} \quad \Psi(r) = \sum_k a_k \exp(ikr) \tag{4.1}$$

The Coulomb interaction term

$$H_c = \frac{1}{2}\iint \Psi^*(r')\,\Psi(r')\,v(r-r')\,\Psi^*(r)\,\Psi(r)\,dr\,dr' \tag{4.2}$$

then becomes:

$$H_c = \sum_{\substack{k_1,k_2\\k_3,k_4}} a^*_{k_1} a_{k_2} a^*_{k_3} a_{k_4} \quad \frac{1}{r-r'} \exp[iq\,(r-r')]\, dr\, dr' \tag{4.3}$$

where q is the momentum transfer $= k_2 - k_1 = k_4 - k_3$

Hence $$H_c = \sum_{\substack{k_1,k_2\\k_3,k_4}} \frac{2\pi e^2}{q^2} a^*_{k_1} a_{k_2} a^*_{k_3} a_{k_4} \tag{4.4}$$

$$q = k_2 - k_1 = k_4 - k_3$$

In physical terms a^*_k is a creation operator and a_k, a destruction operator for an electron of momentum k. These operators anti-commute, i.e.,

$$[a_k, a^*_{k'}] = \delta_{kk'} \; ; \; [a^*_k, a^*_{k'}] = [a_k, a_{k'}] = 0$$

The Hamiltonian expressed in second quantization is,

$$H = \sum_k e_k a^*_k a_k + \frac{1}{2} \sum_{\substack{k_1,k_2\\q}} \lambda_q (a^*_{-k_1} a_{-k_1-q} + a^*_{k_1+q} a_{k_1}) \times (a^*_{k_2} a_{k_2-q} + a^*_{-k_2-q} a_{-k_2}) \tag{4.5}$$

$$= H_k + H_c$$

where $\lambda_q = \frac{4\pi e^2}{q^2 V}$; the summations over k, and q being subject to the conditions $|\underset{\sim}{k}| < P$ and $|\underset{\sim}{k} + \underset{\sim}{q}| > P$

Writing $$A_q = \sum_k (c_{k,q} + c^*_{-k,\,-q}) \; ; \; c_{kq} = a^*_k a_{k-q}$$

$$H_c = \sum_q \lambda_q A^*_q A_q \tag{4.6}$$

Wentzel following Sawada adopts the approximation commutation rules:

$$[H_c, c^{*}_{kq}] = \lambda_q A^{*}_q \quad ; \quad [H_c, c_{kq}] = -\lambda_q A_q$$

$$[H_k, c^{*}_{kq}] = \omega_{kq} c^{*}_{kq} \quad ; \quad [H_k, c_{kq}] = -\omega_{kq} c_{kq}$$

where $\omega_{kq} = [E_{k+q} - E_k]$

Since H_k only enters Sawada's calculation via these commutators, it is possible to replace H_k by

$$H_k = \sum_{kq} \omega_{kq} c^{*}_{kq} c_{kq} \tag{4.7}$$

which yields the same commutators.

The problem then becomes exactly equivalent to the meson pair theory, each electron-hole pair being effectively treated like a boson.

Introducing the canonical field variables,

$$\phi_{kq} = \left(\frac{I}{2\omega_{kq}}\right)^{1/2} [c_{kq} + c^{*}_{-k-q}] \tag{4.8}$$

and $$\Pi_{kq} = i\left(\frac{\omega_{kq}}{2}\right)^{1/2} [c^{*}_{kq} - c_{-k-q}] \tag{4.9}$$

where $\phi_{kq} = \phi^{*}_{-k-q}$ and $\Pi_{kq} = \Pi^{*}_{-k-q}$ for reality

The Hamiltonian expressed in terms of these field variables is:

$$H = \frac{I}{2} \sum_{kq} (\Pi^{*}_{kq} \Pi_{kq} + \omega^{2}_{kq} \phi^{*}_{kq} \phi_{kq} \quad - \omega_{kq})$$

$$\sum_{qk_1 k_2} \lambda_q (\omega_{k_1 q} \, \omega_{k_2 q})^{1/2} \; \phi^{*}_{k_1 q} \, \phi_{k_2 q} \qquad (4.10)$$

i.e. the problem has been reduced to a system of linearly coupled oscillators. The secular determinant is :

$$\phi_q(\sigma^2) = I + 2\lambda_q \sum_k \left(\frac{\omega_{kq}}{\omega^2_{kq} - \sigma^2} \right) = 0 \qquad (4.11)$$

The roots σ of this equation are the excitation energies of the one pair states and the correlation energy, the zero point energy of the normal vibrations.

$$E_o = \frac{1}{2} \sum_{kq} (\sigma_{kq} - \omega_{kq}) + \text{constant} \qquad (4.12)$$

The secular determinant may be written as

$$\Delta(\sigma^2) = \prod_k (\sigma^2 - \sigma^2_{kq}) \qquad (4.13)$$

In the limit of the coupling constant $\lambda \to 0$

$$\Delta_o(\sigma) = \prod_k (\sigma^2 - \omega^2_{kq}) \qquad (4.14)$$

$\phi_q(\sigma^2)$ expressed in terms of poles and zeros in the complex plane is therefore :

$$\phi_q(\sigma^2) = \frac{\Delta(\sigma^2)}{\Delta_o(\sigma^2)} \qquad (4.15)$$

Now

$$\sum_{kq}[f(\sigma^2_{kq}) - f(\omega^2_{kq})\ ] = \frac{1}{2\pi i}\oint d\sigma^2 f(\sigma^2)\sum_{kq}\left(\frac{1}{\sigma^2-\sigma^2_{kq}} - \frac{1}{\sigma^2-\omega^2_{kq}}\right)$$

$$= \frac{1}{2\pi i}\oint d\sigma^2\ f(\sigma^2)\sum_{q}\frac{d[\ln\ \phi_q\ (\sigma^2)]}{d\sigma^2} \qquad (4.16)$$

where the closed contour in the complex σ plane is taken to encircle all zeros σ^2_{kq} and poles ω^2_{kq}.

Integrating by parts,

$$\sum_{k}[\ f(\sigma^2_{kq}) - f(\omega^2_{kq})\ ] = -\frac{1}{2\pi i}\oint\sum_{q} d\sigma^2\ f'(\sigma^2)\ln\phi(\sigma^2) \qquad (4.17)$$

Hence the direct scattering contribution to the correlation energy is :

$$E_o = -\frac{\hbar}{4\pi i}\oint d\sigma\sum_{q}\ln\ \phi_q(\sigma^2) + \text{ constant} \qquad (4.18)$$

The constant is the self energy of the electrons.

Going to the continuum limit i.e. V → ∞ and replacing $\sum_{k}$ by an integral subject to the conditions $|\underset{\sim}{k}| < P$ and $|\underset{\sim}{k} + \underset{\sim}{q}| > P$, the function $\phi_q(\sigma^2)$ becomes discontinuous along part of the real axis. The integral breaks into two parts, one corresponding to the scattering states and the other to the plasmon pole.

The total correlation energy is obtained by integrating round contour C_1 (see figure 4).

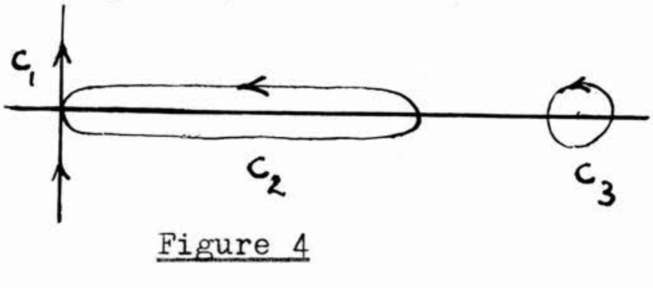


Figure 4

Here it is convenient to calculate the contribution of the scattering states and the plasmons separately.

The scattering contribution is found by carrying out the contour integral C_2 which is found to be,

$$E^{scatt}_{corr} = -\sum_q \frac{\lambda_q}{2} \sum_k + \sum_q \lambda_q \sum_k \frac{1}{[\eta - \eta^*]} \ln \left[\frac{1+\eta_q(k)}{1+\eta_q^*(k)}\right] \qquad (4.19)$$

where $\eta_q(k) = \lambda_q \sum_k \left[\frac{1}{(\omega_{kq} - \sigma)} - \frac{1}{(\omega_{kq} + \sigma - i\epsilon)}\right]$

and $\eta^*_q(k) =$ complex conjugate

Hence $$E^{scatt}_{corr} = -\sum_q \frac{\lambda_q}{2} \sum_k \quad \sum_q \frac{\lambda_q}{2} \sum_k \frac{1}{\lambda\left[\sum_{k'} \pi \delta(\omega_{k'q} - \sigma)\right]}$$

$$\times \tan^{-1} \left\{ \frac{\lambda \sum_{k'} \delta(\omega_{k'q} - \sigma)}{1 + \lambda \sum_{k'} \left[\frac{1}{\omega_{k'q} - \sigma} - \frac{1}{\omega_{k'q} + \sigma - i\epsilon}\right]} \right\} \qquad (4.20)$$

This contribution has been calculated by Sawada et al to be,

$$E^{scatt}_{corr} = (0.0622 \ln r_s - 0.273) \text{ ryd/electron} \qquad (4.21)$$

The plasmon contribution is found from the residue of the pole at $\hbar\omega_{pl}$.

Onsager calculates this to be 0.131 rydbergs (see Sawada et al (8) for details.) Adding the second order exchange term to the scattering and plasmon contributions the correlation energy is :

$$E_{corr} = [0.0622 \ \ln r_s - 0.096] \text{ ryd/electron}$$

which is exactly the Gell-Mann, Brueckner result. This shows that they include the contributions of the plasmons and displays the equivalence of the Wentzel, Sawada, and Gell-Mann, Brueckner techniques. Sawada et al show that plasmons are simply pair excitations with fixed momentum transfer summed with a certain phase relation.

5 - DIELECTRIC APPROACH

If an external potential $V(x)$ is applied to a medium, then an effective potential $U(x)$ composed of the external potential together with the potential change produced by the charges within the medium, will be experienced by the medium. $V(x)$ and $U(x)$ are related by

$$U(x) = \int K(x,x') \, V(x') \, dx' \qquad (5.1)$$

$K(x,x')$ is simply the inverse of the dielectric constant of the medium.

Hubbard(18) shows by summing a similar series to that of Gell-Mann and Brueckner that the Coulomb potential in an electron gas becomes

$$V_{eff}(k,w) = \frac{v(k)}{[I - V^{*}(k,w)]} \qquad (5.2)$$

$[I - V^{*}(k,w)]$ being the dielectric constant

This is of the form :

$$V_{eff}(k,w) = \frac{e^2}{(k^2 + a^2)} \qquad (5.3)$$

Taking the inverse transform, this becomes,

$$V_{eff}(r) = \frac{e^2}{r} \exp(-ar) \qquad (5.4)$$

Hence the polarizibility of the electron gas reduces the Coulomb potential to a Yukawa type potential. The parameter 'a' can be identified as the inverse of the Thomas-Fermi screening length. It is this screening action which prevents the Infra-red divergence which is apparent in the second order perturbation term.

Nozieres and Pines (19) have shown that the Sellmeyer formula for the dielectric constant,

$$\epsilon = I + 4\pi\alpha$$

where $4\pi\alpha$ is the Kramers-Heisenberg complex polarizibility, is applicable to a metal in spite of its high polarizibility. Hence we can identify Hubbards $V^{*}(k,w)$ with the polarizibility of the electron gas.

The dielectric approach is perhaps the most important, from the experimental point of view, for it is through measuring the longitudinal dielectric constant of the solid that an estimate of the correlation energy can be obtained.

Lindhard (20) pointed out that the imaginary part of can be calculated from the scattering of high energy electrons in passing through thin metal films. The probability/unit time ($\frac{dw}{dt}$) that a particle transfers momentum k to the electronic system is (21):

$$\frac{dw}{dt} = \frac{8\pi e^2}{k^2}\,\omega\;\mathrm{Im}\left[\frac{I}{\epsilon(k,\omega)}\right] \tag{5.5}$$

Having obtained $\mathfrak{Im}\left(\frac{I}{\epsilon}\right)$ the interaction energy

$$E_{int} = (\Psi_o \,|\, H_c \,|\, \Psi_o) \tag{5.6}$$

where Ψ_n 's are the exact wave functions for the system, can be calculated since,

$$E_{int} = \sum_{K}\left[\frac{\hbar}{2\pi}\int dw\;\mathrm{Im}\frac{I}{\epsilon(kw)} - \frac{2\pi ne^2}{k^2}\right] \tag{5.7}$$

The ground state energy may then be obtained from E_{int} using the relation :

$$E_0(e^2) = E_0(0) + \int_0^{e^2} \frac{dg'}{g'} E_{int}(g') \qquad (5.8)$$

(See Sawada(15) for proof.)

where $g' = e^2$, the coupling constant

Integrating over g'

$$E_0(e^2) = E_0(0) + \sum_k \left\{ \frac{\hbar}{2\pi} \int_0^\infty \tan^{-1}\frac{\epsilon_2}{\epsilon_1}\, d\Omega - \frac{2\pi n e^2}{k^2} \right\} \qquad (5.9)$$

where $\epsilon_1 = I + 4\pi\alpha_1$ = real part of the dielectric constant

and $\epsilon_2 = 4\pi\alpha_2$ = imaginary " " " "

Nozieres and Pines find for the free electron gas that,

$$4\pi\alpha_1 = \frac{8\pi e^2}{\hbar k^2} \sum_n \frac{|(\rho_k)_{on}|^2 \omega_{no}}{(\omega_{no}^2 - \Omega^2)} \qquad (5.10)$$

and

$$4\pi\alpha_2 = \frac{4\pi^2 e^2}{\hbar k^2} \sum_n |(\rho_k)_{on}|^2 \delta(\Omega - \omega_{no}) \qquad (5.11)$$

where

$$(\rho_k)_{no} = \langle \Psi_n | \rho_k | \Psi_0 \rangle$$

Assuming free electron wave functions :

$$4\pi\alpha_1 = \frac{8\pi e^2}{q^2} \sum_{\substack{|\underset{\sim}{k}| < p \\ |\underset{\sim}{k}+\underset{\sim}{q}| > p}} \frac{E(k+q) - E(k)}{\left[E(k+q) - E(k)\right]^2 - \Omega^2} \qquad (5.12)$$

and

$$4\pi\alpha_2 = \frac{4\pi^2 e^2}{\hbar q^2} \sum_{\substack{|\underset{\sim}{k}| < p \\ |\underset{\sim}{k}+\underset{\sim}{q}| > p}} \delta\left(\Omega - \frac{E(k+q) - E(k)}{\hbar}\right) \qquad (5.13)$$

Inserting these expressions into equation 5.9 produces the Gell-Mann, Brueckner result, showing the compatibility of this method.

The success of a simple dielectric formulation in the Gell-Mann, Brueckner limit arises from the fact that here the important momentum transfers corresponds to wavelengths which are large compared to the interparticle spacing.

Another approach worth mentioning here is the electron self-energy method developed by Quinn and Ferrel(22). A single electron near the surface of the Fermi sea is singled out and the polarization of the gas around it studied in detail. This single electron together with its polarization cloud may be thought of as a quasi-particle. The energy of this clothed particle is given by the difference between the self energy of the particle in the medium and in a vacuum ; somewhat analogous to the mass renormalization found in quantum electrodynamics.

They calculate the Greens function or polarization propagator of the electron gas, by considering the inelastic scattering of a fast incident electron. This procedure is equivalent to Hubbard's summation of linked diagrams for the effective potential existing between the electrons. Quinn and Ferrel also give an alternative derivation using Lindhard's(20) expression for the dielectric constant :

$$\epsilon(k,\omega) = 1 - \frac{3}{64\beta^2 z^2}\left[\frac{(u-z)^2-1}{2z}\ ln\left(\frac{u-1-z}{u+1-z}\right)\right.$$

$$\left. + \frac{(u+z)^2-1}{2z}\ ln\left(\frac{u+1+z}{u-1+z}\right) - 2\right]$$

where $u = \frac{\omega m}{kP}$; $z = \frac{k}{2P}$ and $\beta = \frac{P^2}{2m\omega_P}$

For the case $\omega = 0$ and k small this may be approximated to :

$$\epsilon(k,0) = 1 + \frac{4P}{\pi k^2}$$

and for ω large and k small.

$$\epsilon(k, \omega) = 1 - \frac{4p^3}{3\pi\omega^2}$$

From the work of Feynman it can be readily shown that the self energy of a particle, in terms of the dielectric constant is,

$$S.E.(k) = \frac{e^2}{4\pi^3} \oint \frac{d^3k_1\, d\omega}{k_1^2\, \epsilon(k,\omega)} \times \frac{i}{\left[E(k) - E(k-k_1)(1-i\delta) - \omega\right]}$$

while the self energy in a vacuum is

$$SE_0(k) = \frac{e^2}{4\pi^3} \oint \frac{d^3k_1\, d\omega}{k_1^2} \times \frac{i}{\left[E(k) - E(k-k_1)(1-i\delta) - \omega\right]}$$

The change in self energy due to the presence of the dielectric medium is

$$\Delta E(k) = S.E.(k) - S.E_0(k)$$

On evaluating the integrals one finds that the exchange contribution appears from the residue associated with a pole in the integration the line integral producing the direct term. The result obtained is identical with that obtained by Gell-Mann, Brueckner.

One pleasing thing about this method is that there is no artificial separation of the direct and exchange terms. Another advantage of the formulation is that it is possible to replace the dielectric constant of the uniform gas by that pertaining to a real metal. Hence the method is quite attractive though no new result has been obtained.

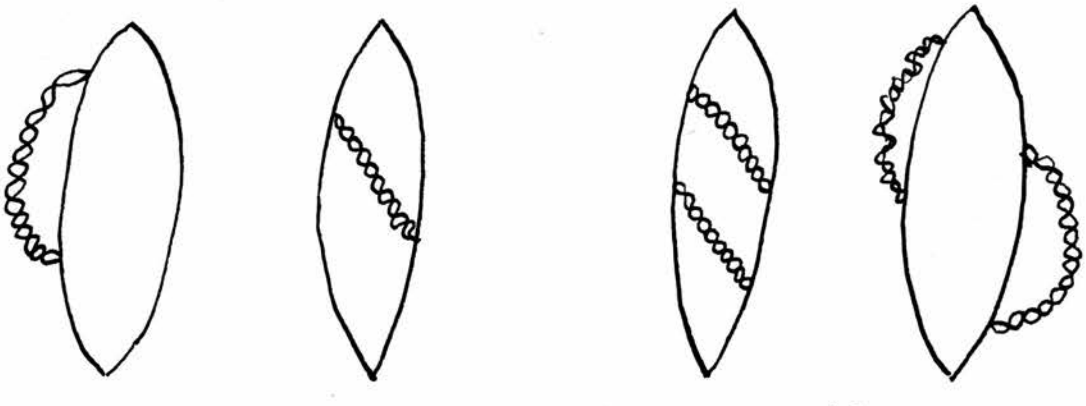
6 - EXTENSION OF THE UNIFORM ELECTRON GAS THEORY BEYOND THE RANDOM PHASE APPROXIMATION

Dubois(23) has extended the theory of an electon gas beyond the 'Random Phase Approximation' using the Gell-Mann, Brueckner propagator technique. He does this by including higher order graphs, replacing $Q_q(u)$ in the Gell-Mann, Brueckner expression for the correlation energy (see equation 3.15) by :

$$Q_{r_s}(q,u) = Q_q^{(0)}(u) + Q_q^{(1a)}(u) + Q_q^{(1b)}(u) + Q_q^{(2)}(u) + ----$$

$$= \sum_i Q_q^{(i)}(u) \qquad (6.1)$$

$Q_q^o(u)$ represents the terms obtained under the Random Phase Approximation. Some of the higher terms are shown graphically in Figure 5.



(1a) (1b) (2)

Figure 5

The generalized expression for the direct part of the correlation energy is :

$$\epsilon_{corr}^{direct} = \frac{3}{8\pi^5}\cdot\frac{1}{2\pi}\int_{-\infty}^{\infty} du \int \frac{d\underset{\sim}{q}}{q^3}\left(\frac{\pi^2 q^2}{\alpha r_s}\right)^2 \left[\ln\left(1+\frac{\alpha r_s \sum_i Q_q^{(i)}(u)}{\pi^2 q^2}\right) - \frac{\alpha r_s \sum_i Q_q^{(i)}(u)}{\pi^2 q^2}\right] \tag{6.2}$$

Including the first two Q functions,

$$Q_q^{(1a)}(u) = -\frac{\alpha r_s}{2\pi^2}\cdot\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} du_1 \int_{-\infty}^{\infty} du_2 \int d^3k_1 \int d^3k_2 \tag{6.3}$$

$$\times\ S_F(k_1+q, u_1+u)\, S_F(k_1, u_1)\, P_{r_s}(k_1-k_2, u_1-u_2)\, S_F(k_2+q, u_2+u)\, S_F(k_2, u_2)$$

and

$$Q_q^{(1b)}(u) = -\frac{\alpha r_s}{2\pi^2}\left(\frac{1}{2\pi^2}\right)\int_{-\infty}^{\infty} du_1 \int_{-\infty}^{\infty} du_2 \int d^3k_1 \int d^3k_2$$

$$\times\ S_F(k_1+q, u_1+u)\, S_F(k_1, u_1)\, P_{r_s}(k_1-k_2, u_1-u_2)\, S_F(k_1+q, u_1+u)$$

$$\times\ S_F(k_2+q, u_2+u) \tag{6.4}$$

where $S_F(k,w)$ is the Feynman particles propagator

$$S_F(k,u) = -\frac{i\hbar}{(2\pi)^4}\left[\frac{P}{u-u(k)} - i\pi\,\delta[u-u(k)]\,\alpha\right]$$

α - the adiabatic switching parameter.

and

$$P_{r_s}(k, u) = \frac{1}{\left[k^2 + \frac{\alpha r_s}{\pi^2} Q_{r_s}(k, u)\right]}$$

Dubois calculates the correlation energy to be :

$$E_{corr} = [0.0622 \ln r_s - 0.096 + 0.0049\, r_s \ln r_s + B\, r_s] \text{ ryd/electron.}$$

7 - RANGE OF VALIDITY OF THE LINKED CLUSTER EXPANSION

All methods evolved for estimating the correlation energy of the electron gas have included some kind of approximation. It is clearly desirable to have some check on the range of validity of the expansions. An estimate can be made using the fact that the lowest eigenvalue of a Hermitian operator, containing a parameter linearly, has a negative second derivative with respect to the parameter. This result may be derived from the virial theorem in classical mechanics.(24) Here it will be derived by a quantum mechanical method.

The wave equation corresponding to this problem is :

$$H(\lambda)\,\Psi(\lambda) = E(\lambda)\,\Psi(\lambda) \tag{7.1}$$

where H is a linear function of the coupling constant λ Differentiation of equation with respect to λ gives

$$H'\,\Psi + H\,\Psi' = E'\,\Psi + E\,\Psi' \tag{7.2}$$

which on substitution into :

$$E''(\lambda) = \langle\Psi'|H'|\Psi\rangle + \langle\Psi|H'|\Psi'\rangle \tag{7.3}$$

yields the result,

$$E''(\lambda) = -2\langle\Psi'|H|\Psi'\rangle + 2E\langle\Psi'|\Psi\rangle + E'\left[\langle\Psi'|\Psi\rangle + \langle\Psi|\Psi'\rangle\right] \tag{7.4}$$

The coefficient of $E'(\lambda)$ is zero by normalization, so that the final answer is :

$$E''(\lambda) = -2\langle\Psi'|\Psi'\rangle\left[\frac{\langle\Psi'|H|\Psi'\rangle}{\langle\Psi'|\Psi'\rangle} - E\right] \tag{7.5}$$

Since Ψ minimizes the energy, the first term on the right hand side of equation 7.5, cannot be less than E, from which it follows that :

$$E''(\lambda) \lesssim 0 \tag{7.6}$$

Thus the second derivative of the ground state energy of the electron gas with respect to the coupling constant e^2 cannot be positive.

Ferrel$^{(25)}$ has applied this theorem to the Gell-Mann, Brueckner expansion. He finds it convenient to fix the density by making $r_s = 1$ and to vary the coupling constant from e^2 to λe^2. One then obtains the energy of the electrons in terms of the coupling constant by replacing r_s by λ and by multiplying by λ^2. Hence:

$$E(\lambda) = \left[2.21 - 0.916\lambda + 0.0622\lambda^2 \ln\lambda - 0.096\lambda^2\right] \text{ryd}/\text{electron} \tag{7.7}$$

Differentiating this twice and applying equation 7.6 one finds that :

$$\lambda \lesssim 1.05$$

Alternatively, we may conclude that the Gell-Mann, Brueckner result is valid only for $r_s \lessapprox 1$. Ferrel estimates that for the density corresponding to $r_s \sim 3$, the error is at least 40 %

Applying this technique to the result derived by Dubois one finds that his theory is valid for $r_s \lessapprox 2$. Since the highest electron density found in metals is in aluminium where $r_s \sim 2.0$, it is apparent that we still await a theory which is applicable to realistic densities.

8 - CORRELATION ENERGY AT LOW AND INTERMEDIATE DENSITIES

As yet, no satisfactory method has been produced for calculating the correlation energy of an electron gas at intermediate density i.e. $2 < r_s < 5.5$ There are however, some interpolation formulae in existence which are in fair agreement with experiment. These will be discussed briefly in this section along with a short comment on the low density case.

The low density case will be considered first. Here the potential energy is very much greater than the kinetic energy, quite the reverse of the high density case. This is generally referred to as the 'strong coupling' case on account of the strong interaction between the particles. For densities corresponding to $r_s \sim 20$, the potential energy is so great that the electrons are forced to form a lattice. Here of course, the Random Phase Approximation is not valid. The correlation energy may again be expressed as a series expansion :

$$E_{corr} = \left(\frac{A}{r_s} + \frac{B}{r_s^{3/2}} + \cdots \right) \tag{8.1}$$

The first term represents the difference between the potential energy of the electrons and the exchange energy, while the second reprdsents their zero point energy. The constant A may be determined by carrying out an Ewald sum for the lattice. The binding energy is found(20) to be $-\frac{1.8}{r_s}$ ryd/electron.

Subtracting the first order exchange energy $-\frac{0.916}{r_s}$ on finally obtains :

$$E_{corr}^{low\ density} = -\frac{0.88}{r_s}\ ryd/electron \tag{8.2}$$

for the correlation energy of a low density electron gas.

On the basis of the Lindemann(27) formula for the melting of a solid Nozieres and Pines estimate that the expression is valid only for $r_s > 20$, the electronic solid being unstable for higher densities.

Wigner(28) combines this with his high density result and obtains an expression for intermediate densities:

$$E_{corr} = \frac{-0.88}{(r_s \quad 7.8)}\quad ryd/electron \tag{8.3}$$

This expression is in remarkably good agreement with the experimental results obtained for the alkali metals (see Table I)

Determination of the constant B in equation requires precise knowledge of the spectrum of oscillations of the electron gas. For a rough estimate of the zero point energy one can consider an Einstein model of the lattice in which each electron vibrates independently with a frequency $\frac{\omega_p}{\sqrt{3}}$ where

$$\omega_p = \left(\frac{4\pi ne^2}{m}\right)^{\frac{1}{2}}$$

is the classical plasma frequency. Since there are two transverse and one longitudinal modes, one finds that the constant B, representing the zero point energy is 3 ryd/electron. These lattice waves obey the Kohn$^{(29)}$ sum rule

$$\sum_{i=1}^{3} \omega_i^2 = \omega_p^2$$

An alternative solution to the problem, still compatible with this sum rule would be to assume longitudinal phonons only. In this case B = 1.73 ryd/electron. Ferrel$^{(30)}$ estimates the correction to the Einstein model and finds

$$E_{corr}(r_s) = \left\{ -\frac{0.88}{r_s} + \frac{2.82}{r_s^{3/2}} \right\} \text{ryd/elect} \qquad (8.4)$$

Using the high density result of Gell-Mann, Brueckner and his own low density result, he proposes an interpolation formula

$$E_{corr}(r_s) = \left\{ -0.0186 - \frac{0.094}{r_s} + \frac{0.029}{r_s^2} \right\} \text{ryd/elect} \qquad (8.5)$$

for the region $0.85 \lesssim r_s \lesssim 7.0$

As one goes from high to low density, half of the direct term is cancelled by the exchange part of the second order perturbation term. One can show$^{(31)}$ that the probability density $\rho(r_{ij})$ for finding any electron at r_i and any other at r_j is given by

$$\rho(r_{ij}) = \left\{ 1 - \frac{9}{2}\left[\frac{pr\cos pr - \sin pr}{(pr)^3} \right]^2 \right\} \qquad (8.6)$$

where ρ is the Fermi momentum

If one plots the probability of finding an electron at a distance r from any particular electron r_s against $\frac{r}{r_s}$ one obtains:

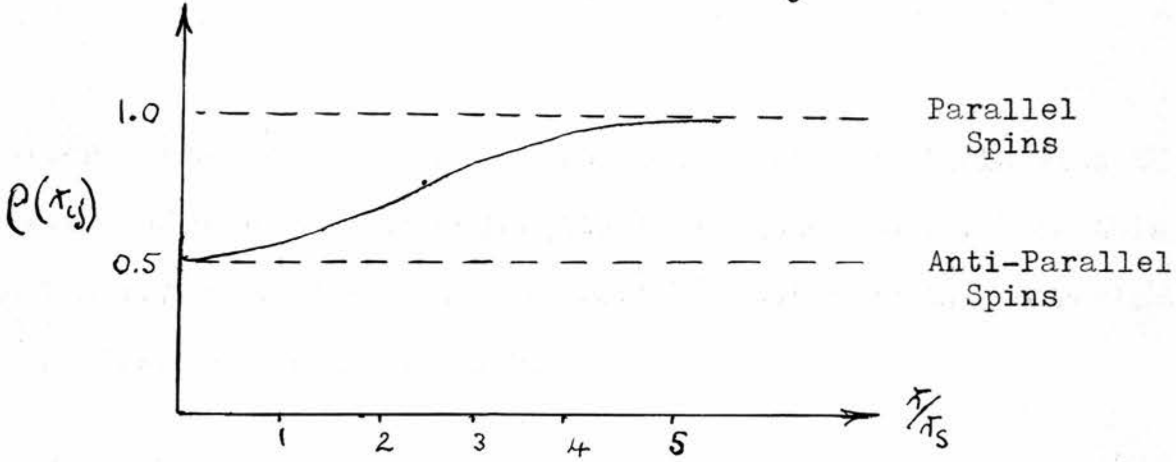


Figure 6

Electrons with anti-parallel spins are not correlated because they are unaffected by the Pauli Principle. Moreover, at long distances $\left(\frac{r}{r_s} > 4\right)$, electrons with parallel spins are not correlated. This is due to the fact that the Pauli Principle is purely quantum mechanical and cannot be effective for distances greater than the wavelength that can be associated with the electrons. Using this fact Nozieres and Pines$^{(32)}$ propose a rather crude approximation in which they assume the Random Phase Approximation result for $\beta \lessapprox 0.47 r_s^{1/2}$ and retain only the contribution to the second order perturbation term from electrons with anti-parallel spins for $\beta \gtrsim 0.47 r_s^{1/2}$

The interpolation formula thus produced is:

$$E_{corr}(r_s) = \left\{ 0.0622 \ln r_s - 0.159 \right\} \text{ryd}/\text{electron} \tag{8.7}$$

Hubbard $^{(18)}$ also modifies his exact high density in a similar manner. He does so by multiplying the real and imaginary parts of the dielectric constant, A and Σ by an empirical factor

$$\left\{ 1 - \frac{1}{2} \frac{k^2}{(k^2 + p^2)} \right\}$$

This is equivalent to replacing the Coulomb potential $v(k) = \frac{4\pi e^2}{k^2}$ by

$$\frac{4\pi e^2}{k^2} \left[1 - \frac{1}{2} \frac{k^2}{(k^2 + p^2)} \right]$$

In this way the correlation affects of electrons with parallel spins at short distances are much reduced. Hubbard finds that his answer is in close agreement with that of Pines. An advantage of this method over that of Pines is that it provides a smooth continuous expression for the correlation energy. Pines and Hubbard estimate that their expressions should give the correlation energy to within ± 20% in the intermediate region.

9 - CRITIQUE OF THE VARIOUS METHODS

First and foremost the restrictions common to all methods will be considered. The system of interacting particles are are enclosed in a box. Both the number of particles n and the volume V of the box are assumed to be so large that all effects which vanish in the limit $V, n \rightarrow \infty$, $\frac{n}{V}$ remaining constant, can be neglected. The theories are limited to systems in their ground state i.e. at zero temperature. This restriction prevents one from considering the interaction of virtual with real electron hole pairs, though there is no reason why the methods cannot be extended to incorporate these. The problem is greatly simplified by assuming two body interactions between the particles, the total interaction being a sum over two particle interactions. This approach has been applied, with great success, to the theory of nuclear structure and of liquids. So far, the positive background has been smeared out, all periodic effects due to the lattice being ignored.

All high density methods employ the "Random Phase Approximation", all coupling between excitations corresponding to different momentum transfers q and q' are neglected. Wentzel shows that this is in fact the only approximation required to obtain the high density result. Convergence of the perturbative expansion is assumed, though as will be shown in Part II, this is only true in special cases.

The Bohm, Pines method describes the physics of the plasma in a neat and concise way. It does however, introduce some approximations which are quite unnecessary in obtaining the high density result. A momentum cut-off is introduced above which the gas exhibits collective behaviour and below independent particle motion. This cut-off they estimate to be $\frac{q_{max}}{p} = 0.40 \; r_s^{\frac{1}{2}}$ which is much lower than the value obtained using the Linked Cluster Expansion ($0.47 \; r_s^{\frac{1}{2}}$). Hence an important part of the plasmon contribution is omitted since this goes as β^3. The derivation of this cut-off by Bohm, Pines is somewhat suspect since it is evaluated by minimizing the energy given by part of their transformed extended Hamiltonian (see equation 2.8) assuming that the other terms arising from the Hamiltonian, dependent on β can be neglected. The terms arising from equation 2.9 are however by no means negligible, so that their approach can at most be only a semi-quantitative one. Much of the discrepancy between the Bohm, Pines and Linked Cluster Expansion methods originates from this approximation.

Bohm and Pines introduce an extra $\frac{k_c^3}{6\pi^2}$ field co-ordinates to represent the plasmon modes. In order to preserve the total number of degrees of freedom, they are forced to introduce an equal number of constraints or subsidiary conditions. The actual techniques employed by Bohm and Pines in obtaining their expression for the correlation energy leads to certain violation of the subsidiary conditions though no real serious error appears to be incurred. (see Bohm, Huang, and Pines)(33) These subsidiary conditions do in fact define the ground state of the electron gas. The particle wave functions used, consist of a Slater determinant of plane waves slightly modified by the short range correlation introduced by H_{sr} and H_{rp}, and do not satisfy the subsidiary conditions. Modifications to the wave function involve the introduction of slight correlations in electron positions of the type that would reduce the long range density fluctuations. The effect on the potential energy coming from H_{sr} is negligible for this involves the short wavelength fluctuations. Hence the only way H_{sr} can be affected is through coupling with the long wavelength density fluctuations. This coupling is in fact small, so that the subsidiary conditions have little effect on H_{sr}. The kinetic energy is also unaffected for it involves only slowly varying density fluctuations. Neglect of the subsidiary conditions is therefore not thought to be a serious omission in the Bohm, Pines theory and appears to be only a point of mathematical rigour.

As we have seen, it is possible to avoid the divergences without resorting to an artificial separation of collective and individual particle motion as used by Bohm and Pines.

This can be done by an adiabatic process in which the singular potential is replaced by a soft one, making the adiabatic parameter tend to zero and recovering the original potential after the summation has been completed. In this procedure it is assumed that the levels in the unperturbed system go over to discrete levels in the perturbed system when the interaction is switched on. Luttinger and Ward have shown this to be so for a uniform gas of electrons at high density, though some caution must be exercised in other cases as will be shown in Part II. Using the linked cluster expansion Gell-Mann and Brueckner obtain a finite answer by summing the perturbation series to infinity the divergence for small momentum transfer q being shown to be spurious. The Random Phase Approximation of Bohm and Pines is implicit in their method by the choice of diagrams. They find however, that the perturbation series converges only for large q and assume that this result can be extended into the region of divergence.

This assumption of Gell-Mann, Brueckner is substantiated by Sawada who rederives their result without resorting to perturbatio theory. He considers the same diagrams neglecting interactions between holes and excited electrons. Subsequent reformulation of Sawada's method by Wentzel treats electron-hole pairs as bosons. This paper together with that of Sawada et al gives a most mathematically and exact approach within the RPA formalism.

Possible extension of this theory to non-uniform gases will be discussed in Part II.

In its original form, the Linked Cluster Expansion method did not exhibit the collective effects associated with the electron gas. Doubt existed as to whether the plasmon contribution had in fact been included. Brout and Sawada et al point out how the plasmon solutions are inherent in the Gell-Mann, Brueckner and Sawada theories.

The work of Dubois is a natural extension of the work of Gell-Mann, Brueckner. Application of Ferrel's check on the range of validity shows that his expression is valid for $r_s \lessapprox 2$. He calculates the contribution of $Q^{(1a)}$ and $Q^{(1b)}$ but does not derive an expression for $Q^{(2)}$. Dubois points out that for the purposes of calculating the ground state energy in this approximation, the effect of $Q^{(2)}$, being additive, may be calculated by third order perturbation theory. Suhl and Werthamer(34) have calculated $Q^{(2)}$ in terms of the Nozieres and Pines dielectric constant. Extension beyond this approximation to obtain an expression valid for metallic densities is unlikely as the mathematics associated with the higher order diagrams become exceedingly complex.

Thermodynamic methods using Grand Partition Functions developed by several authors,(35) have not been discussed since nothing new appears to emerge from them, being simply other ways of formulating the Linked Cluster Expansion. If one takes the Partition Function

$$Z = \text{trace} \ \exp(-\beta H)$$

where β is equivalent to the coupling constant, and expand the exponential then one just reverts to the linked cluster perturbation series.

The dielectric approach has been developed neglecting local field corrections, i.e. the effects of localized charges. In the high density case where one has almost free electrons the Sellmeyer formula for the dielectric constant $\epsilon = I + 4\pi\alpha$ is assumed to hold. This breaks down when $I \gg 4\pi\alpha$. Here local field corrections arise but they are small on account of the low polarizability. Local field effects can be expected to be important in the intermediate region.

The Lorentz expression,

$$\frac{3(\epsilon - I)}{(\epsilon + 2)} = 4\pi\alpha$$

should be used at low density where the electrons are spatially ordered. Here of course, the Random Phase Approximation does not hold. The ground state energy has been shown to be dependent on the complex dielectric constant and may be calculated from $\mathcal{Im}\left(\frac{1}{\epsilon}\right)$ derived from a characteristic energy loss experiment. Application of the Kramers, Kronig relations,

$$[\,\epsilon(k,\omega) \;-\; I\,] = \frac{1}{i\pi}\oint_{-\infty}^{\infty} \frac{\epsilon(k,\omega')}{(\omega'-\omega)}\,d\omega'$$

$$\left[\,\frac{1}{\epsilon(k,\omega)} - 1\,\right] = \frac{1}{i\pi}\oint_{-\infty}^{\infty} \frac{\frac{1}{\epsilon(k,\omega')}}{(\omega'-\omega)}\,d\omega'$$

permit calculation of the $\Re(\frac{1}{\epsilon})$ from the measurement of Im $(\frac{1}{\epsilon})$ The correlation energy can then be obtained by direct substitution into equation

Since the Linked Cluster Expansion is valid only up to $r_s \sim I$ and its extension by Dubois to $r_s \lesssim 2$, some form of interpolation between the high and low density limits is required to estimate the correlation energy of the electrons in metals. Values of r_s found in metals range from 2 (Aluminium) to 5.6 (Caesium) Interpolation methods developed by Ferrel, Wigner and Pines appear to be in fair agreement with experimental results. (see Table I).

TABLE I

COHESIVE ENERGY OF THE ALKALI METALS

E_{HF} is the cohesive energy calculated in the Hartree Fock approximation, E_{exp} is the experimental value, and E_{Wigner} etc is the cohesive energy calculated incorporating the respective expression for the correlation energy. All energies are given in rydbergs.

Metal	r_s	E_{ion}^{*}	E_{HF}	E_{WIGNER}	E_{FERREL}	$E_{PINES}^{\dagger}$	E_{EXP}^{*}
Li	3.22	-0.280	-0.055	-0.135	-0.100	-0.132	-0.117
Na	3.96	-0.230	-0.022	-0.098	-0.062	-0.095	-0.084
K	4.87	-0.166	-0.014	-0.083	-0.052	-0.080	-0.073
Rb	5.18	-0.153	-0.011	-0.079	-0.048	-0.076	-0.061
Cs	5.57	-0.140	-0.009	-0.076	-0.045	-0.072	-0.060

* Taken from H Brooks Phys. Rev. <u>91</u> 1027

† Taken from D Pines Solid State Physics <u>I</u> 367 (Academic Press 1955)

Unfortunately we cannot compare Hubbard's method as he is forced to evaluate his integrals numerically. He does so for $r_s = 2, 3, 4, 5$, so that it is not possible to compare his result with the others as above, though his answer will not differ much from that of Pines. An additional check on the interpolation procedure is provided by Ferrel's condition that $E''(\lambda) \leqslant 0$. When comparing the experimental values with those derived from interpolation methods, it should be remembered that these formulae have been derived from the theory of a uniform gas. The discrepancy between theory and experiment may well be due to local field effects which become important in this region. Methods of assessing the effect of the ion lattice on the correlation energy will be discussed in the next section.

PART II

NON-UNIFORM GAS

10 - CHARACTERISTIC ENERGY LOSS OF ELECTRONS IN PASSING THROUGH METAL FILMS

The dielectric formulation discussed in Part I is particularly well suited to the non-uniform gas problem, as the maximum amount of information about the electrons in the solid is contained in Im $\left(\frac{1}{\epsilon(k,\omega)}\right)$. Normally this is measured by observing the scattering of electrons in the kilovolt energy range in passing through foil of the order of a few hundred Angstroms thick. $\epsilon(k,\omega)$, the exact dielectric constant of the valence electrons in the solid, is defined for the momentum transfer k and energy transfer $\hbar\omega$ involved in a single inelastic event.

It can be readily shown$^{(21)}$ that the probability/unit time, $\frac{dw}{dt}$, that a particle transfers momentum k and energy to an electron gas is,

$$\frac{dW}{dt} = \frac{2\pi}{\hbar}\left(\frac{4\pi e^2}{k^2}\right)^2 \omega \sum_n \left|(\rho_k)_{no}\right|^2 \delta\left(\omega_{no} - \omega\right) \qquad (10.1)$$

where $(\rho_k)_{no}$ is the matrix element of the density fluctuations. By introducing a test charge and examining its effect on the electron gas one can define and calculate the dielectric constant. Nozieres and Pines do this and find that,

$$\frac{1}{\epsilon(k,\omega)} = 1 - \frac{4\pi e^2}{\hbar k^2} \sum_n \left|(\rho_k)_{no}\right|^2 \left\{\frac{1}{\omega_{no} - \omega - i\eta} + \frac{1}{\omega_{no} + \omega + i\eta}\right\} \qquad (10.2)$$

Combining equations 10.1 and 10.2 one then obtains the connection between the energy loss and the dielectric constant,

$$\frac{dW}{dt} = \frac{8\pi e^2}{k^2}\,\omega\,\mathcal{I}m\left(\frac{1}{\epsilon(k,\omega)}\right) \tag{10.3}$$

From energy loss experiments one can therefore determine $\epsilon(k,\omega)$ and hence the correlation energy (see Chapter 5) Limitations of equation (10.3) have of course, to be borne in mind.

The characteristic energy loss spectrum of a metal can be expected to contain two groups of individual particle energy losses, a strong low energy peak associated with the intraband transitions, cutting off at $\frac{kP}{m}$ and a series of broad peaks associated with interband transitions. These transitions are, however, heavily screened. The major energy absorption comes from the excitation of plasmons associated with the zero of $\epsilon(k,\omega)$. The plasmon dispersion relation is,

$$1 = \frac{4\pi e^2}{m}\sum_{\nu}\frac{f_{o\nu}}{\omega_0^2 - \omega_{\nu o}^2} \tag{10.4}$$

If the majority of the transitions associated with $f_{o\nu}$ are such that $\omega_{\nu o} \ll \omega_p$ then the plasmon frequency ω_0 in a solid is,

$$\omega_0^2 = \omega_p^2 + \frac{4\pi e^2}{m}\sum_{\nu}\frac{f_{o\nu}\,\omega_{\nu o}^2}{\omega_p^2} \tag{10.5}$$

being almost equal to the classical free electron value. One would expect this to be applicable to most non-transition metals, since here, valence electron plasmons are of the order of 15 e.v. while most $f_{o\nu}$'s are only a few electron volts. Hence one would expect non-transition metals with a small energy gap, to exhibit the same characteristic energy loss spectrum as a free electron gas. This prediction is found to be in good agreement with experiment.

The plasmon excitations are formed in the wake of the exciting particle in a similar manner to the production of Cerenkov radiation. Since the plasma oscillations are quantized (plasmons), the observed discrete energy losses will appear as multiples of the basic plasmon energy. Such discrete energy losses were first observed by Ruthemann(36) and Lang(37) and recent work has been reviewed by Marton et al(38) Good agreement between the classical result for a free electron gas and experiment is obtained for some metals as can be seen from Table II.

<u>TABLE II.</u> (energies in e.V.) (data taken from reference 39)

Metal	Be	Mg	Aℓ	Ge	Pb
$\Delta E_{obs.}$	19	10	15	17	13
$\hbar\omega_p$	19	11	16	16	13

These figures have been calculated by assuming that the valence electrons are completely free and that the core electrons take no part in the interaction.

Distinction between individual electron behaviour and the collective mode is less clear in the transition metals. Here the individual core excitation energies are comparable with the plasmon energy. As a result, the plasmons are damped and there is a shift in the plasmon energy. This is illustrated in recent measurements by Powell.(40) A possible phenomenological model has been put forward by Wilson.(41) As he correctly points out, most metals have optical absorption levels which occur at similar energies as the plasmons; it is therefore possible that a fast electron may excite an optical transition as well as a plasmon. This may well be the reason for the discrepancy between theory and experiment as found in the case of copper, where the calculated plasmon energy is 11 e.v. while that observed is 20 e.v. Wilson suggests that there is an optical transition band stretching from 11 e.v. to at least 20 e.v.

In order to calculate the dielectric constant one must also measure the angular distribution of the characteristic energy losses, since from this one can derive the dispersion relation. This can be readily shown from the Bohm, Pines dispersion relation for the free electron gas, which can be obtained from equation (4.11) by a simple transformation and is,

$$1 = \frac{4\pi e^2}{m} \sum_i \frac{1}{\left[\left(\omega - \frac{k \cdot p_i}{m}\right)^2 - \frac{\hbar^2 k^4}{4m}\right]} \qquad (10.6)$$

Expanding the denominator one can approximately write,

$$\omega^2 \approx \omega_p^2 + \frac{6}{5} \frac{E_F k^2}{m} \qquad (10.7)$$

where E_F is the Fermi energy.

Let us now consider an electron of energy $E = \frac{p^2}{2m}$ which emits a plasmon of energy $\hbar\omega_p$ and in so doing, is scattered through an angle θ

By the conservation of energy and momentum.

$$\theta \sim \frac{\hbar k}{p}$$

Substituting in equation (10.7) for k gives

$$-\theta^2 + \left(\frac{5m\hbar^2}{6E_F p^2}\right)\omega^2 = \frac{5m\hbar^2}{6E_F p^2}\omega_p^2 \qquad (10.8)$$

This is the equation of a hyperbola with a focus on the ω axis An angular distribution of this type was first observed by Watanabe,(42) who, by careful measurement of the curve, obtained a reasonable value for the dispersion relation. Good agreement between his measurement and that predicted by the free electron theory is obtained for Al and Be.

11 - PRELIMINARY CONSIDERATIONS FOR A NON-UNIFORM GAS THEORY

In this section it will be shown how the foregoing picture of the uniform electron gas developed in Part I is modified in the presence of a periodic field such as that existing in solids. The inclusion of this periodic potential leads to a band structure in momentum representation, allowing two types of excitations for the solid (a) intraband transitions and (b) interband transitions. The latter are associated with the periodic nature of the potential and one would expect that these could alter the free electron result. The periodic potential may alter the shape of the band from the simple free electron parabola $E(k) = \frac{\hbar^2 k^2}{2m}$. If the effect on the band shape is regular then this may be incorporated into the correlation theory by introducing an effective mass m$\overset{*}{m}$ in place of the real mass m. How the theory is altered by the energy gap is harder to predict, though it is evident that the logarithmic term in the correlation energy expression remains.

Application of a modified theory of the electron gas may be possible for simple valence solids such as the light alkali metals and alkaline earths. Here there is a distinct separation between the valence electrons and the core electrons. The problem may then be treated as one in which the valence electrons are moving in the potential of the periodic array of nuclei and of the core electrons. It is assumed that one can neglect core-valence exchange and correlations, which is equivalent to saying that the core polarizibility is very small. Nozieres and Pines$^{(19)}$ have shown that this is a reasonable approximation.

The potential due to the core electrons and nuclei can be well described by a Hartree potential V(r) so that the Hamiltonian of the valence electrons may be written

$$H = \sum_{i} \left[\frac{p_i^2}{2m} + V(r_i) \right] + \frac{I}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{e^2}{r_{ij}} \tag{11.1}$$

$$= H_o + H_c$$

H_o can now be treated as the unperturbed Hamiltonian with eigenstates Ψ_n which are the usual Bloch wave functions. The valence electron-electron interaction term may then be treated as a perturbation on H_o.

As before the system is assumed to be at absolute zero so that all particles are in their ground states. The metal is also assumed to possess a perfect lattice the effect of dislocations etc, being ignored. The wave function for the system $\Psi(x)$ may be expanded in terms of the Bloch wave functions ϕ_{nk} having energy E_{nk}

$$\Psi(x) = \sum_{n,k} a_{nk} \; \phi_{nk} \tag{11.2}$$

Hence for a gas of non interacting Bloch electrons, the energy of the system expressed in second quantized form is:

$$H_0 = \left\langle \Psi^* \right| \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \left| \Psi \right\rangle$$

$$= \sum_{\substack{nk \\ n'k'}} a_k^* a_k \int \psi_{nk}^* \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi_{n'k'} \, d\tau \qquad (11.3)$$

$$H_0 = \sum_{\underset{\sim}{n}\underset{\sim}{k}} a_k^* a_k \, E_{\underset{\sim}{n}\underset{\sim}{k}} \qquad (11.4)$$

where the a_k^* and a_k are creation and destruction operators for Bloch electrons.

The Coulomb term H_c is :

$$H_c = \frac{1}{2} \int \Psi^*(r)\, \Psi(r')\, v(r - r')\, \Psi^*(r')\, \Psi(r)\; d\underset{\sim}{r}\, d\underset{\sim}{r}' \qquad (11.5)$$

On substitution for Ψ

$$H_c = \sum_{\substack{k_1, k_2, k_3, k_4 \\ k_1 - k_2 = k_4 - k_3 = q}} \frac{2\pi e^2}{q^2}\, a_{k_1}^* a_{k_2} a_{k_3}^* a_{k_4} \qquad (11.6)$$

Hence to extend the Gell-Mann, Brueckner type of approach to non uniform gases, one replaces the free electron energies by Bloch energies. The perturbation series, however, becomes rather cumbersome, and it is no longer possible to sum it except in some special cases. It is not essential to expand in terms of Bloch waves. As an alternative procedure we can retain the kinetic energy as the unperturbed term and treat both the electron-electron and electron-core interactions as perturbation terms. The perturbation series now contains three types of terms, electron-electron, electron-ion, and ion-ion interaction terms. The first group give the Gell-Mann, Brueckner result while the others represent corrections due to the presence of the ions. Both methods have been used on the problem and the relative merits of each will be discussed in detail.

12 - ELECTRON-ION PLASMA APPROACH

The problem of calculating the correlation energy of an electron gas in the presence of a periodic field can be greatly simplified by replacing the rigid lattice by an ion plasma. This method has been applied by Silverman and Weiss(43) and others with a fair measure of success. In their model, the positively charged ions are smeared out and replaced by point charges whose magnitudes are determined by the valency of the atoms.

Silverman and Weiss extend the Wentzel formulation to include the electron-ion interaction term H_I. Their Hamiltonian is of the form:

$$H = H_o + H_c + H_I \tag{12.1}$$

Where $H_o + H_c$ are the Wentzel terms:

$$H_I = \frac{I}{2} \sum_{k,q} V^i_q \, c_{kq} + \frac{I}{2} \sum_{k,q} V^i_{-q} \, c_{-k,-q} \tag{12.2}$$

The summations extend over all k and q, V^i_q being the $q^{\underline{th}}$ Fourier component of the electron-ion potential. Imposing the restriction that $|\underset{\sim}{k}| < \rho$ and $|\underset{\sim}{k} + \underset{\sim}{q}| > P$, H_I becomes:

$$H_I = \frac{I}{2} \sum_{k,q} [V^i_q \, (c_{kq} + c^*_{-k-q}) + c.c.] \tag{12.3}$$

Introducing Wentzel's canonical field variables ϕ_{kq} and Π_{kq}, the Hamiltonian reduces to:

$$H = \frac{1}{2} \sum_{k,q} (\Pi^{*}_{kq}\Pi_{kq} + \omega^{2}_{kq} \phi^{*}_{kq}\phi_{kq} - \omega_{kq})$$

$$+ \sum_{q} \lambda_{q} \sum_{k,k'} (\omega_{kq} \omega_{k'q})^{\frac{1}{2}} \phi^{*}_{kq} \phi_{k'q}$$

$$+ \frac{1}{2} \sum_{k,q} (2\omega_{kq})^{-\frac{1}{2}} (V^{i}_{q} \phi_{kq} + c.c.) \qquad (12.4)$$

Silverman and Weiss then diagonalize the Hamiltonian by transforming to a new set of co-ordinates Q and P which are related to ϕ and Π by the equations:

$$\phi_{k} = \sum_{k} d_{kk'} Q_{k'} + b_{k}$$

$$\Pi_{k} = \sum_{k'} d_{kk'} P_{k'}$$

where $d_{kk'}$ and b_{k} are constants which satisfy the relations:

$$\delta_{kk'} = \sum_{k''} d_{kk''} d^{*}_{k'k''} \quad \text{and} \quad \sum_{k} \omega_{k}^{\frac{1}{2}} b_{k} = \frac{2^{\frac{1}{2}} V_{q}^{i*} \sum_{k} \frac{1}{\omega_{kq}}}{\left(1 + 2\lambda_{q} \sum_{k} \frac{1}{\omega_{kq}}\right)}$$

b_{k} is chosen in such a way as to eliminate terms linear in Q. H then becomes:

$$H = \frac{1}{2} \sum_{k,q} \left(P^{*}_{kq} P_{kq} + \Omega^{2}_{kq} Q^{*}_{kq} Q_{kq} - \omega_{kq}\right) \qquad (12.5)$$

$$- \sum_{q} \frac{|V_{q}^{i}|^{2} \sum_{|k|<p} \frac{1}{\omega_{kq}}}{\left(1 + 2\lambda_{q} \sum_{|\underset{\sim}{k}|<p} \frac{1}{\omega_{kq}}\right)}$$

The second term represents the shift in the ground state energy due to the introduction of the point charges. To evaluate this contribution to the energy, Silverman and Weiss assume that the charge impurities are distributed at random. Averaging in a manner similar to Kohn and Luttinger(44) they find:

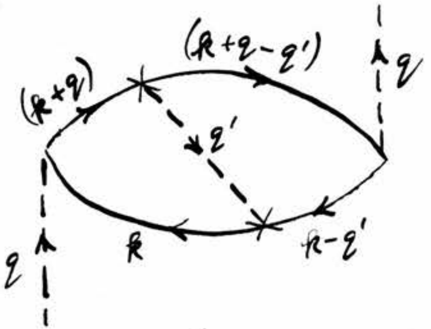
$$|V_q^i|^2 = \frac{16\pi^2 z^2 e^4 n_i}{V q^4}$$

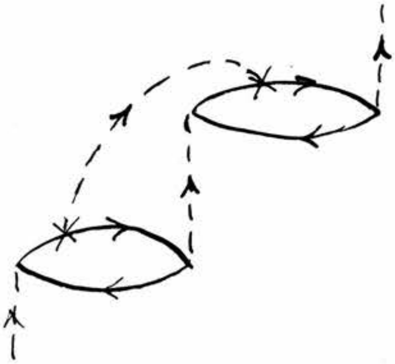
where n_i is the number of charge impurities and z the charge on each impurity or ion. Evaluating the correction to the Wentzel ground state one finds:

$$\Delta E = -\frac{2z^2}{(\pi\alpha)^{\frac{1}{2}}} \cdot \left(\frac{n_i}{n}\right) \cdot \frac{1}{r_s^{\frac{1}{2}}} \qquad (12.6)$$

where $\alpha = (\frac{4}{9\pi})^{\frac{1}{3}}$ and n the number of electrons.

This result may be obtained by a variety of less elegant methods. Perhaps the most obvious way of tackling the problem is to treat the electron-ion along with electron-electron interaction as a perturbation. The perturbation expansion then contains three sub-series, terms which include processes with H_c only, others with H_i, and those having a mixture of H_c and H_i. Wentzel has already summed the contribution of the first group. Those containing H_i only, corresponding to the ion-ion interaction are neglected, since they are in no way connected with the correlation energy. Silverman and Weiss sum the electron-ion terms, which may be represented by graphs of the form:





(cross represents electron-ion interaction)

Figure 7

Figure 8

From these graphs it is evident that the energy must be at least quadratic in the electron-ion matrix element in order that the system may return to its vacuum state. Possible graphs fall into two groups, those in which H_i connects an electron and a hole as shown in Figure 7 and others such as in Figure 8. The latter can be ignored since these contribute a lower divergence and may be neglected in the high density limit. Summing the relevant diagrams leads to similar results to that obtained by diagonalizing the Hamiltonian.

Silverman and Weiss suggest that the power series expansion for the correlation energy of a non uniform gas should contain a parameter $\left(\frac{n_c}{n}\right)$ as well as r_s.

13 - CALCULATION OF THE CORRELATION ENERGY IN THE PRESENCE OF A RIGID LATTICE

The electron-ion plasma approach, discussed in the previous section, while being simple, does not yield any information on the effects of the periodicity of the lattice. In this section the effects of a perfect rigid lattice at 0°K on the correlation energy will be considered, first in the weak binding and later in the tight binding approximation.

(a) Weak Binding Approximation

In Part I, Section 5, it has been shown how the correlation energy can be calculated from the dielectric constant of the electron gas. The Nozieres, Pines(21) formulae for the polarization can be simply adapted to the non-uniform case by replacing the free electron wave functions by Bloch wave functions. The expressions for the real and imaginary parts of the polarization are :

$$4\pi\alpha_1 = \frac{4\pi e^2}{m}\sum_{\nu}\frac{f_{o\nu}}{\left|\omega_{\nu o}^2 - \Omega^2\right|} \tag{13.1}$$

$$4\pi\alpha_2 = \frac{2\pi^2 e^2}{m}\sum_{\nu}\frac{f_{o\nu}}{\omega_{\nu o}}\,\delta\left(\Omega - \omega_{\nu o}\right) \tag{13.2}$$

where the Bloch function oscillator strengths

$$f_{0\nu} = \frac{2m}{\hbar k^2}\,\omega_{\nu 0}\left|(\rho_k)_{0\nu}\right|^2 \tag{13.3}$$

obey the sume rule $\sum_{\nu} f_{0\nu} = n$

The summations in equation 13.1 and 13.2 extend over intraband and interband transitions. For an isotropic metal and in the long wave limit i.e. $|\underset{\sim}{k}| \to 0$

$$f_{0n}^{intra}(0) = \frac{m}{3\hbar^2}\sum_{\alpha}\frac{\partial^2 E}{\partial k_\alpha^2} = \frac{1}{3}\sum_{\alpha}\left(\frac{m}{m^*}\right)_{\alpha\alpha} \tag{13.4}$$

and $$f_{0n}^{inter}(0) = \frac{2}{3m}\sum_{\alpha}\frac{\left|(p_{i\alpha})_{0n'}\right|^2}{\hbar\,\omega_{n'0}} \tag{13.5}$$

where $\left(\frac{1}{m^*}\right)_{\alpha\beta}$ is the effective mass tensor
and k an arbitrary wave vector inside the Brillouin zone.

Inserting these expressions into equations 13.1 and 13.2 one finds that the polarizibility and hence the dielectric constant and correlation energy are only slightly affected by the presence of the periodic ion field. The correlation energy is to a first approximation, modified by a factor $\left(\frac{m}{m^*}\right)$

Falk$^{(45)}$ has also formulated this problem via the dielectric approach. He assumes Bloch wave functions for the electrons of the form:

$$\Psi_s(k r) = u_s(k, r) \exp(i \underset{\sim}{k} \cdot \underset{\sim}{r}) \tag{13.6}$$

and expands the $u_s(k, r)$'s in a Fourier series in the reciprocal lattice vector K

$$u_s(k, r) = \sum_K \chi_s(k, K) \exp(-i \underset{\sim}{K} \cdot \underset{\sim}{r}) \tag{13.7}$$

He then determines the dielectric constant of the medium and finds:

$$\epsilon(k, K, \omega) = \delta_{K0} + \alpha(k, K, \omega) \tag{13.8}$$

where $\alpha(k - K', K - K', \omega)$

$$\approx \frac{k - K}{|k - K|^2} \cdot \frac{16\pi e^2}{n} \sum_{ss'} \int_0^{\rho} \frac{dk'}{(2\pi)^3}$$

$$\times \frac{1}{\omega^2} \cdot \frac{\hbar^2}{m} \sum_{K''} K'' \chi^*_{s'}(k', K'') \chi_s(k', K'')$$

$$\times (1 - \delta_{ss'}) \sum_{K'''} \chi^*_{s'}(k' - K', K''') \chi_s(k - K, K''') \tag{13.9}$$

Close inspection of the form of α reveals that this and hence $\epsilon(k, \omega)$ has a simple pole when $k = K \neq K'$ and a simple zero for $k = K' \neq K$. These poles and zeros simply correspond to Bragg's law.

Falk finds for the inverse of the dielectric constant $\frac{1}{\epsilon(k, K, \omega)}$ in the weak binding limit:

$$\frac{1}{\epsilon(k,K,\omega)} = \delta_{K0} \cdot \frac{1}{1+\beta(k,0,\omega)} - (1-\delta_{K0})\frac{|k|}{|k-K|} \cdot \frac{\beta(k,K,\omega)}{\left[1+\beta(k,0,\omega)\right]} \qquad (13.10$$

where

$$\beta(k-K', K-K', \omega) = \frac{|k-K|}{|k-K'|}\,\alpha(k-K', K-K', \omega)$$

The first term in equation 13.10 corresponds to the free electron gas result slightly modified by the periodic field while the second term results from the modification of the energy v momentum relation near the Brillouin zone boundary.

Inserting this result for the dielectric constant into Hubbard's formulation, Falk finds the correlation energy to be: (excluding the exchange term)

$$E_{corr} = -\frac{i\hbar}{2}\int \frac{dk}{(2\pi)^3} \cdot \frac{d\omega}{2\pi}\, \frac{\beta(k,0,\omega)}{\sum_K \beta(k,K,\omega)} \ln\left[1 + \sum_K \beta(k,K,\omega)\right] \qquad (13.1$$

Comparing this result with equation 3.15 of Part I we can see that this is a simple generalization of the free electron result

Hubbard(46) uses a similar approach, modifying his free electron model(18) by incorporating the effect of the ion cores by a Hartree field $V = \sum_i V(x_i)$. He then writes the Hamiltonian in the form

$$H = (H_o + V) + (H' - V)$$

where H' is the normal Coulomb term $(H_o + V)$ is treated as the unperturbed Hamiltonian and $(H' - V)$ as the perturbation. The theory is then similar to that derived for the uniform gas. However, this method produces an answer as complicated as Falk's. Hartree equations for the electrons in the lattice have to be solved and also the effective interaction which is expressed as an integral equation.

(b) Tight Binding Approximation

Callaway(47) using the Gell-Mann, Brueckner technique, has calculated the correlation energy of a semiconductor. He assumes a simple band structure model in which there is an energy gap E_g above the Fermi surface, and electrons having an effective mass $m m^*$. All other effects of crystal structure are ignored. Callaway considers two limiting cases, (a) that of the large energy gap corresponding to an insulator, and (b) the small energy gap, the semiconducting case.

The second order perturbation term in Gell-Mann, Brueckner notation becomes after inclusion of the energy gap E_g and effective mass $m^* m$:

$$E_2 = -\frac{3m^*}{8\pi^5}\int dq \int dk_1 \int dk_2 \frac{1}{\left[q^2 + \underline{q}\cdot(\underline{k}_1 + \underline{k}_2) + \epsilon_G\right]}\left[\frac{1}{q^4} - \frac{1}{2q^2(k_1+k_2+q)^2}\right] \qquad (13.12)$$

$$\text{where} \quad \epsilon_G = \frac{E_G}{2E_F}$$

In the insulator case we need only consider this term, for two reasons. The first is that the divergence obtained for the free electron gas is no longer present and therefore it is unnecessary to sum the perturbation series. This is due to the presence of E_g in the energy denominator, which, being independent of the momentum transfer q, makes the contribution independent of r_s. The second reason for the neglect of higher or perturbation terms is that their contribution is small since an energy denominator containing E_g is obtained for each virtual pair interaction.

Callaway evaluates the second order contribution using Macke's$^{(12)}$ co-ordinate system and Monte Carlo methods. He finds it to be:

$$E_2 = -0.526\, m^* \frac{E_F}{E_G} \ \text{ryd}/\text{electron} \qquad (13.13$$

where E_f is the Fermi energy.

As Callaway points out however, we cannot really identify this with the true correlation energy of an insulator since it vanishes in the limit of very large E_g. This is contrary to what one would expect, for the correlation energy arises from the inability of the Hartree-Fock method to localize the electrons sufficiently. In the tight binding case of an insulator, the electrons are well localized on individual atoms so that the correlation energy should be non zero in the limit of a large energy gap. The limits within which one can apply this result, are therefore in doubt.

Callaway then calculates the correlation energy of a semiconductor, corresponding to the case of small E_g. He does this using the method of Gell-Mann, Brueckner modifying the Feynman propagator to include the energy gap. Inclusion of the effective mass of the electrons is trivial. The result consists of a series in E_g and r_s, the zero order term being the correlation of the free electron gas :

$$E_c(E_G) = E_c(0) + \left[0.100 \left(\frac{m^*}{r_S} \right)^{\frac{1}{2}} - 0.079\, m^* \right] \frac{E_G}{E_F} \text{ ryd/electron} \qquad (13.1$$

where $E_c(o) = m^* [0.0622 \ln m^* r_S - 0.096]$ ryd/elect

Extension of this method to the electrons in metals, where the Fermi surface and Brillouin zone boundaries do not coincide, is rather difficult, since each virtual excitation can be either intraband or interband. It is the summation of these processes that presents the problem. We can however, modify Callaway's method for the insulator, to suit the case of a metal, by assuming a band structure of the form shown in Figure 9, where the breadth of the valence band is less than the energy gap.

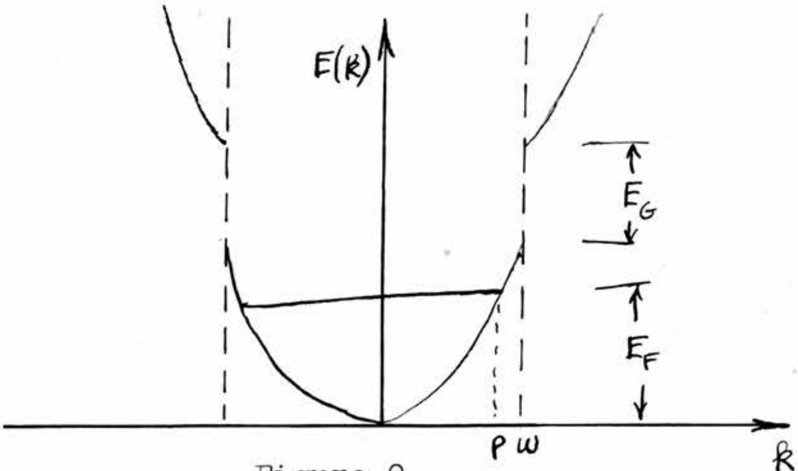


Figure 9

The second order direct interaction perturbation term, using the above band structure, is approximately:

$$\Delta E^{(2a)}_{corr} = -\frac{3m^*}{8\pi^5}\sum_{q}\frac{1}{q^4}\left[\sum_{\substack{k_1,k_2<1\\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>1,\ <\frac{\omega}{\rho}\\ |\underset{\sim}{k}_2+\underset{\sim}{q}|>1,\ <\frac{\omega}{\rho}}}\frac{1}{\left[q^2+\underset{\sim}{q}\cdot(\underset{\sim}{k}_1+\underset{\sim}{k}_2)\right]}+2\sum_{\substack{k_1k_2<1\\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>\frac{\omega}{\rho}\\ |\underset{\sim}{k}_2+\underset{\sim}{q}|>1,\ <\frac{\omega}{\rho}}}\frac{1}{\epsilon_G}+\sum_{\substack{k_1k_2<1\\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>\frac{\omega}{\rho}\\ |\underset{\sim}{k}_2+\underset{\sim}{q}|>\frac{\omega}{\rho}}}\frac{1}{2\epsilon_G}\right] \qquad (13.15)$$

while the corresponding Gell-Mann, Brueckner term is:

$$\Delta E^{(2a)}_{\text{corr G.B.}} = -\frac{3}{8\pi^5}\sum_{q}\frac{1}{q^4}\sum_{\substack{k_1 k_2 < 1 \\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>1 \\ |\underset{\sim}{k}_2+\underset{\sim}{q}|>1}} \frac{1}{\left[q^2+\underset{\sim}{q}\cdot(\underset{\sim}{k}_1+\underset{\sim}{k}_2)\right]} \tag{13.16}$$

Subtracting equation 13.16 from 13.15 one obtains the correction to the Gell-Mann, Brueckner result i.e.

$$\Delta E_{\text{correction}} = \left[\Delta E^{(2a)}_{\text{corr}} - \Delta E^{(2a)}_{\text{corr G.B.}}\right] \tag{13.17}$$

If the effective mass ratio m^* is assumed to be unity then :

$$\Delta E^{\text{ion}}_{\text{direct corr}} = -\frac{3}{8\pi^5}\sum_{q}\frac{1}{q^4}\left[-\sum_{\substack{k_1,k_2<1 \\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>\frac{\omega}{p} \\ |\underset{\sim}{k}_2+\underset{\sim}{q}|>\frac{\omega}{p}}}\frac{1}{\left[q^2+\underset{\sim}{q}\cdot(\underset{\sim}{k}_1+\underset{\sim}{k}_2)\right]} + 4\sum_{\substack{k_1k_2<1 \\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>\frac{\omega}{p} \\ |\underset{\sim}{k}_2+\underset{\sim}{k}|>1<\frac{\omega}{p}}}\frac{1}{\epsilon_G} + \sum_{\substack{k_1,k_2<1 \\ |\underset{\sim}{k}_1+\underset{\sim}{q}|>\frac{\omega}{p} \\ |k_2+q|>\frac{\omega}{p}}}\frac{1}{\epsilon_G}\right] \tag{13.18}$$

In the first term of equation 12.18 both excited electrons must cross the energy gap so that one can approximate this to :

$$\sum_{\substack{k_1\ k_2<1 \\ |k_1+q|>\frac{\omega}{p} \\ |k_2+q|>\frac{\omega}{p}}}\frac{1}{\epsilon_G}$$

Hence.

$$\Delta E^{\text{ion}}_{\text{direct corr}} = -\frac{3}{8\pi^5}\sum_{q}\frac{1}{q^4}\left\{4\sum_{\substack{k_1k_2<1 \\ |k_1+q|>\omega/p \\ |\underset{\sim}{k}_2+\underset{\sim}{k}|>1<\frac{\omega}{p}}}\frac{1}{\epsilon_G}\right\} \tag{13.19}$$

Evaluating the volumes of integration using Macke's co-ordinate system and expanding in terms of the parameter $\delta = \frac{\omega - \rho}{\rho}$ one finds that the correction is to the first approximation:

$$\Delta E^{\text{ion}}_{\text{dir corr}} = -\frac{12}{\pi^2}\,\delta\left(\frac{E_F}{E_G}\right)\int_0^1\left[\frac{2}{q} - 1 - \frac{q}{6} + \frac{q^2}{12}\right]dq \qquad (13.20$$

Hence this näive approach still possesses an infra-red divergence even though the Gell-Mann, Brueckner term has been subtracted. This could have been anticipated as one part of the non-uniform second order perturbation term allows an interband transition for one excited electron and an intra-band transition for the other, the divergence arising from the latter as in the uniform gas case. The correction can however be calculated by applying a cut-off to the integral. This would normally beobtained by summing the whole perturbation series. However, the error incurred using the rigorous free electron gas cut-off, $\beta = 0.47\, r_s^{\frac{1}{2}}$ would be slight.

The second order exchange term cannot be similarly calculated on account of the momentum transfer factor $\frac{1}{|q + k_1 + k_2|^2}$

It can however be worked out using Monte Carlo methods. Callaway has shown for the case of an insulator, that this contribution is small compared to the second order direct term. Hence one feels justified in neglecting the correction of the exchange term in this approximation for a metal.

This method can at most, give us a qualitative answer, since in the calculation one is forced to assume unit effective mass and a spherical Fermi sea. The range of validity is also in doubt though one might expect the result to be applicable in cases where the energy gap is two or three times the breadth of the valence band.

14 - DIAGONALIZATION OF THE HAMILTONIAN BY A CANONICAL TRANSFORMATION

One method of extending the range of validity of the theory is by including higher order linked cluster and electron-ion terms. These can be more readily included if the Wentzel Hamiltonian is first diagonalized. Silverman and Weiss do this, but in such a way that they need not know the exact form of the transformation. If it is known, one can obtain the wave function corresponding to the Wentzel Hamiltonian by operating with it on the vacuum state wave function. This wave function can be considered as the unperturbed wave function and higher terms in the Hamiltonian may then be treated as perturbations. Such a procedure is satisfactory for the electron-ion interaction but not for the higher order electron-electron terms for these have been shown to possess subsidiary divergences of the form $r_s \ln r_s$. It may be possible however, to sum the perturbation series produced by expanding in terms of the Wentzel rather than the free electron wave functions. Hence it would appear worthwhile attempting to calculate the required transformation. The un-physical, though often instructive, one dimensional case is considered first.

One Dimensional Case

The transformation required to diagonalize the Hamiltonian of a one dimensional electron gas is a relatively simple one.

Taking the Hamiltonian in the Wentzel form, the qth. term is :

$$H_q = \sum_k \left[\pi_k^* \pi_k + \omega^2 \phi_k^* \phi_k - \omega_k + \lambda\omega \sum_\ell \phi_k^* \phi_\ell \right] \tag{14.1}$$

Applying the cyclic transformation :

$$\Phi_k = \sum_m \frac{1}{\sqrt{n}} \exp\left(\frac{2\pi \iota k m}{n} \right) \phi_m \tag{14.2}$$

one finds the Hamiltonian assumes the form:

$$H_q = \sum_k \left(\pi_k^* \pi_k + \Omega^2 \Phi_k^* \Phi_k - \omega_k \right) \tag{14.3}$$

Two solutions are obtained for Ω, one corresponding to the scattering states, the other to the plasmons.

Three Dimensional Case

In the three dimensional case the Hamiltonian is :

$$H_q = \sum_k \left[\pi_k^* \pi_k + \omega_k^2 \phi_k^* \phi_k - \omega_k + \lambda \sum_\ell \sqrt{\omega_k \omega_\ell}\, \phi_k^* \phi_\ell \right] \tag{14.4}$$

A possible canonical transformation capable of diagonalizing equation 14.4 is :

$$T = \exp\left[\alpha_{k\ell}\,\pi_k\,\phi_\ell\right]$$

where $\alpha_{k\ell}$ is anti - hermitian for reality

i.e. $\alpha_{k\ell} = - \alpha^{*}_{\ell k}$

This leaves the $\Pi_k\Pi_k$ term unaffected, operating on the ϕ's only.

ϕ_ℓ transform to $\Phi_\ell = T^{-1}\phi_\ell T$

Expanding the exponentials one finds :

$$\Phi_\ell = \phi_\ell - \frac{i}{\hbar}\left[S,\phi_\ell\right] - \frac{1}{2\hbar^2}\left[S\left[S\,\phi_\ell\right]\right] + \frac{i}{3\hbar^2}\left[S\left[S\left[S\,\phi_\ell\right]\right]\right] - - -$$

ie
$$\Phi_\ell = \sum_k \left[\exp\left(-\alpha_{k\ell}\right)\right]\phi_k \qquad (14.5)$$

Applying this to equation 14.4 and equating diagonal and non-diagonal parts one obtains the equations for the matrix elements :

$$\sum_m \Omega_m^2\, B^{-1}_{km}\, B_{mk} = \omega_k^2 \qquad (14.6)$$

$$\frac{1}{2}\sum_m \Omega_m^2\, B^{-1}_{mk}\, B_{m\ell} = \lambda\sqrt{\omega_k\omega_\ell} \qquad (14.7)$$

where
$$B_{k\ell} = \exp\left[\alpha_{k\ell}\right]$$

Solution of these equations gives α_{kl} and hence the required transform.

Fukuda(48) has also attempted to calculate this unitary transformation. He assumes that the ground state wave function can be expressed:

$$\Psi_0 = a V \phi_0 \tag{14.8}$$

where a is a normalization constant, V an operator containing electron creation operators only, and ϕ_0 is the vacuum state wave function. Taking V to be of the general form :

$$V = \exp\left(\sum_{kk'} K_{kk'} c_k^* c_{k'}^* \right) \tag{14.9}$$

he then calculates $K_{kk'}$ by a variational method. Fukuda shows that the transformation does in principle work, though the mathematics become rather involved, and it remains to be seen whether the higher matrix elements can in fact be calculated in this way.

15 - LIMITATIONS OF THE LINKED CLUSTER EXPANSION METHOD WHEN APPLIED TO THE NON-UNIFORM GAS PROBLEM

One must exercise some degree of caution in applying the Linked Cluster Expansion method to electron gas systems such as those found in metals. This method assumes that when the interaction between the electrons is switched on, the levels in the unperturbed system retain their identity in the perturbed system i.e. they remain discrete. This has been shown by Luttinger and Ward(9) to be so, for a system of fermions of spin $\frac{1}{2}$, in which both the energies and the perturbing potential are spherically symmetric, indicating that the Brueckner, Goldstone series is convergent for this particular case.

Kohn and Luttinger(49), on the other hand, prove that the series is no longer convergent for the non-spherical case such as one has in a metal. Here the interaction potential (Coulomb) is indeed spherically symmetric but the Fermi surface has only the symmetry of the lattice. The energy levels lose their identity in the perturbed system and the Brueckner, Goldstone series is found to have a zero radius of convergence. As long as the volume of the system V is large but finite, the true energy levels regarded as functions of the coupling constant , have sharp bends but do not cross. In the limit $V \rightarrow \infty$, the terms which ensure that the levels do not cross are lost as they are of order V^{-1}. Hence, for a finite value of λ, the state which grows smoothly out of the original ground state is no longer the lowest.

Instead of switching the interaction in adiabatically as Goldstone does, Kohn and Luttinger calculate the energy of the ground state at a temperature T, take the limit $V \rightarrow \infty$ first and then let the temperature tend to zero. The Brueckner, Goldstone formula is obtained if the order of the limiting procedures is reversed. This is the only fundamental difference between the two methods.

They calculate the energy using the Grand Partition Function method developed by Montroll and Ward and others(35). Due to the finite temperature, contributions of two types of diagrams have to be considered. One group is composed of the Brueckner, Goldstone graphs which have been considered earlier. The second and third order diagrams are shown below :

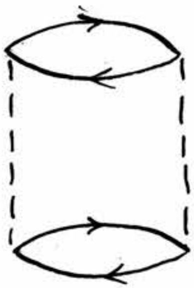


Figure 10(a)

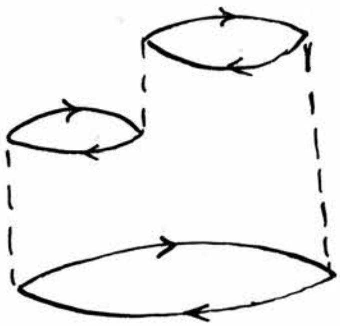


Figure 10(b)

The second group consists of anomalous diagrams which arise from the finite temperature. The second and third order diagrams are shown below in order that they may be compared with the Brueckner, Goldstone counterparts.

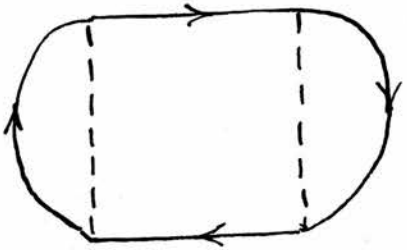


Figure 11(a)

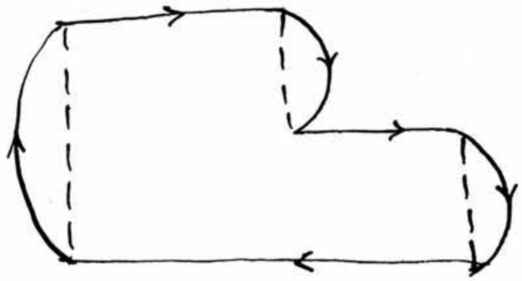


Figure 11(b)

The anomalous diagrams are those in which some electrons and holes are forced by momentum conservation, to be in the same state. This is only possible at a finite temperature. Kohn and Luttinger find that the contribution of these diagrams remains finite after they take the limit $T \rightarrow 0$. In order to illustrate their point, they evaluate the second order term. (The first order term is unchanged since the first non vanishing anomalous diagram is of second order). The anomalous diagrams reduce the contribution of the second order term indicating that there is a lower state than the Brueckner, Goldstone one for this particular case. This correction is found to vanish only if the interaction potential and the unperturbed energies are spherically symmetric, partially confirming the findings of Luttinger and Ward.

Wentzel(50) has interpreted the meaning of the Kohn and Luttinger term geometrically. He points out that, since the new term involves the diagonal part of the interaction only it should be possible to derive the result more simply by omitting the off-diagonal terms of the Hamiltonian. He assumes an expression for the ground state energy of the form :

$$E(\lambda) = \int_{\rho(\lambda)} \epsilon_k \, d^3k + \frac{1}{2}\lambda \int_{\rho(\lambda)} d^3k \int_{\rho(\lambda)} v_{kk'} \, d^3k' \tag{15.1}$$

where $\int_{\rho(\lambda)} d^3k$ denotes integration over the non-spherical Fermi sea. Since the Fermi sea is defined as that surface over which E is a minimum one can write :

$$\mu(\lambda) = \epsilon_k + \lambda \int_{\rho(\lambda)} v_{kk'} \, d^3k' \tag{15.2}$$

Differentiating equation (15.1) with respect to λ and using the fact that $\int_{\rho(\lambda)} d^3k$ equal to the total number of states below the Fermi surface, is a constant, one finds :

$$\frac{\partial}{\partial\lambda}\left(E(\lambda)\right) = \frac{1}{2} \int_{\rho(\lambda)} d^3k \int_{\rho(\lambda)} v_{kk'} \, d^3k' \tag{15.3}$$

The Kohn, Luttinger term is $\left(\frac{\partial^2 E}{\partial \lambda^2}\right)_{\lambda=0}$

which is obviously zero in the spherical case.

In the linked cluster expansion, it has been assumed that the system is at 0°K. The vacuum state is then considered to be that in which all the states up to the Fermi surface are filled and those above, empty. This presupposes that the Fermi surface is a sharp, well defined entity. Luttinger(51) has shown that this assumption is quite wrong. This view is shared by Van Hove(52), who, on the basis of recent work, casts doubt on the existence of a sharp surface even for weak repulsive forces.

The chief reasons for this are that the coulomb interactions between the electrons in metals are of the same order of magnitude as their kinetic energies and the correlation energy is comparable to the binding energy. Therefore we cannot expect the momenta of the individual electrons to be good quantum numbers and consequently the Fermi surface cannot be sharp.

In the unperturbed system the occupation number n_k may be written :

$$n_k = \begin{matrix} 1 & \text{for} & \epsilon_k < \rho \\ 0 & \text{for} & \epsilon_k > \rho \end{matrix}$$

or alternatively in terms of a contour integral :

$$n_k = \frac{1}{2\pi i} \int_{\rho - i\infty}^{\rho + i\infty} \frac{\exp\left(y_0^+\right)}{\left(y - \epsilon_k\right)} \, dy \qquad (15.4)$$

If an interaction is present n_k may be written :

$$n_k = \frac{1}{2\pi i}\int_{P-i\infty}^{P+i\infty} \frac{\exp(y_0^+)}{[y - \epsilon_k - G_k(y)]}\,dy \tag{15.5}$$

where $\frac{1}{[y - \epsilon_k - G_k(y)]}$ is the propagator of the system and $G_k(y)$ is the proper self energy part of the propagator. This describes how the propagation of a particle is affected by the presence of others with which it interacts. It is determined by summing polarization graphs of the type considered by Quinn and Ferrel$^{(22)}$.

The analytic properties of $G_k(y)$ are :

1) $G_k(y)$ is analytic everywhere except on the real axis.

2) $\mathrm{Lim}\ G_k(y \pm i\beta) = K_k(y) \mp iJ_k(y)$ where $J_k(y) \geq 0$

3) $J_k(x) = C_k(y - P)^2$: $C_k > 0$ as $y \to P$

The last property comes about in the following way. The contribution of the diagram shown in Figure 12 to $G_k(y)$ is :

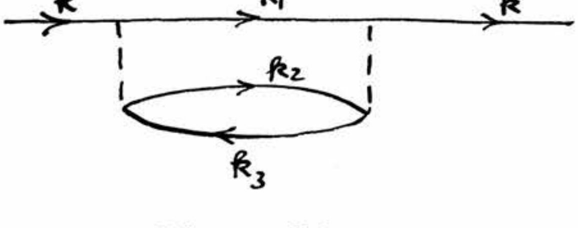


Figure 12

$$G_k^{(1)}(y) = \sum_{\substack{k_1 k_2 k_3 \\ k_1 k_2 > P \\ k_3 < P}} \frac{|\langle k_2 k_3 | v | k k_1 \rangle|^2}{\left[y - \left(\epsilon_{k_1} + \epsilon_{k_2} - \epsilon_{k_3}\right)\right]} \tag{15.6}$$

This contribution has an imaginary part $\delta\left[\, y - \left(\epsilon_{k_1} + \epsilon_{k_2} - \epsilon_{k_3}\right)\right]$ Since k_1, k_2 represent electrons with energies greater than the Fermi momentum P and k_3, a hole with energy less than P,

$$\left(\epsilon_{k_1} + \epsilon_{k_2} - \epsilon_{k_3}\right) \geq P \tag{15.7}$$

Hence for y near P, one obtains a contribution from a very small portion of phase space and it is for this reason that

$$J_k(x) \propto (y - P)^2$$

The true Fermi surface is given by :

$$P - \epsilon_k - K_k(P) = 0 \tag{15.8}$$

and the single particle energy E_k by the solution of the equation :

$$E_k - \epsilon_k - K_k(E) = 0 \tag{15.9}$$

For electrons in a lattice, one must average over the band index before the Fermi surface and single particle energies are known. Luttinger and Migdal$^{(53)}$ have shown that the Fermi surface as well as being smeared out at 0°k, possesses a finite discontinuity at the Fermi surface. These effects, however should produce negligible effects on the correlation energy for De Hass- Van Alphen measurements(54) have shown that the Fermi surface is sharp to one part in 10^4.

16 - CONCLUSIONS

As we have seen from the work of Bohm and Pines, the electron gas in a metal behaves in a plasma-like way. Any slight deviation from neutrality creates forces which try to cancel the space charge. If there is little damping, over compensation takes place and the system oscillates longtitudinally as in a sound wave. This condition is known as plasma oscillation. The positions of the electrons are correlated by this plasma behaviour and by scattering type interactions. Localization of the electrons leads to a contribution to the electron energy over and above that derived from the Hartree, Fock theory and has been called correlation energy. Addition of this energy term produces more binding and reasonable agreement with experimental results. (See Table I). Unfortunately this comparison can only be made using interpolation results derived from calculations made in the high and low density limits.

The formulation of the high density uniform gas case by Wentzel gives perhaps the most lucid account of the problem. Brout(55) and Sawada et al(8) point out the existence of the plasmon contribution in the linked cluster expansion. The low density case can be reduced to the problem of calculating the energy of an electron in an electron lattice. Methods for treating the uniform gas have however, been adequately discussed at the end of Part I and this section will be confined to analysis of the various methods developed for the non-uniform gas.

In theory, the uniform gas methods can be simply extended to the non-uniform case by replacing the free electron wave functions by Bloch functions. Expressions become complicated, and it is no longer possible to sum the perturbation series. Approximate methods of dealing with the problem have however been evolved.

The approach developed by Silverman and Weiss, in which the electron-ion system is regarded as a two component plasma is rather interesting. The ions are treated as a gas of charged impurities mingling with the electrons. One immediate drawback of the method is that it does not incorporate any effects associated with the periodicity of the lattice. It may be of use in the theory of liquid metals, though here it should be remembered that only the long range order is destroyed, band structure, arising from the short range order being still very much in evidence. For the alkali metals, having I valence electron/atom = I, the Silverman and Weiss formula reduces to:

$$\Delta E^{ion}_{corr} = -\frac{2}{(\pi\alpha)^{1/2}} r_s^{-1/2} \text{ ryd/electron}$$

where $\alpha = \left(\frac{4}{9\pi}\right)^{1/3}$

This represents the correction to the Gell-Mann, Brueckner high density result and appears to be rather large. One would however, be inclined to look for a substantial correction, as the effect of the charged impurities is to bunch the electrons, localizing them to a greater degree and thus increasing the correlation energy.

The dielectric formulation is perhaps the most useful since the correlation energy can then be estimated directly from energy loss experiments. The Nozieres, Pines free electron formula is simply modified by inserting Block wave functions into the expressions for the polarizability. Falk's expression is just a simple generalization of the free electron case, but the energy cannot be readily calculated from it, though it does show how the periodic field modifies the free electron gas expression. His result agrees with that of Nozieres and Pines and confirms that interband transitions do not make an important contribution to the correlation energy in the weak binding limit. Hubbard's(46) solution of this problem, obtained from the extension of his uniform theory, also becomes rather intractable. The Hartree equations for the electrons in the lattice have to be solved and secondly the effective interaction expressed as an integral equation when the screening is modified by the ionic field. These equations have yet to be solved and it looks as though computer techniques are necessary.

In order to obtain a quantitative answer one is forced to make sweeping assumptions, such as those made by Callaway, His work on the correlation energy of an insulator must be regarded with suspicion since his expression goes to zero as $E_g \to \infty$, quite the reverse of what one would expect. Consequently the range, over which the extension of his theory to metals is applicable, is in doubt, though one would expect it to hold for the case where the energy gap is two or three times the breadth of the valence band. The extension to metals provides an answer dependent on the parameters, effective mass m^*, ratio of valence bandwidth to energy gap, and position of the Fermi level relative to the Brillouin zone boundary. A complete theory of the non-uniform gas should embody all these parameters. This expression may be applied to a metal such as aluminium which has a valence bandwidth of 15 e.v., an energy gap 4 e.v. and $m^* = I$. It should be remembered however, that this result has been calculated for the high density case so that it is not possible to compare it with experiment.

Kohn and Luttinger's work shows that a simple extension of the linked Cluster expansion to the non-uniform case in which the Fermi surface is non-spherical, such as that in a metal, is not valid, the series being convergent only for spherical symmetry.

Van Hove has indicated how terms which cannot be represented by a power series may be found in the ground state energy, even for the case of very weak repulsive forces. These terms are however, found to be exponentially small, so that in a case such as this, one would expect the linked cluster expansion to give a reasonable asymptotic representation. The Fermi surface at $0^{o}K$ is defined by Luttinger, as the locus of the discontinuity in the momentum distribution curve and is generally distorted by the electron-electron interactions. This distortion is, however slight, as can be seen from De Hass Van Alphen results, which show that the surface is sharp to one part in 10^{4}.

It can be argued that the error incurred by applying a modified form of the linked cluster expansion to metals such as sodium, will be slight, since here the Fermi surface is almost isotropic. The periodic field will influence states very close to the Brillouin zone boundary in k space, though only a small fraction of the total number in the Fermi distribution will be affected, even in polyvalent metals such as Mg and Al. Interband transitions may alter the properties of the quasi-particles and their interactions. Their mean lifetime decreases quadratically(56) as they approach the Fermi surface while their energy varies linearly. Hence it can be concluded that the effect of the periodic potential on the correlation energy should be small, properties such as electron transport and specific heat, which depend on the states near the Fermi surface being more likely to be affected.

Further work must be done to incorporate higher order exchange terms and the rescattering of real excited particles (non zero temperatures). The effect of the smearing out of the Fermi surface should be investigated more closely. The question of the existence and sharpness of the Fermi surface may be studied as Kohn suggests, by examining the singularities of the dielectric constant. One possible way of developing a theory for the intermediate region ($2 < r_s < 5.5$) is to determine the wave function for the Wentzel Hamiltonian, as has been attempted here. Once this has been determined, one can expand in terms of this wave function rather than in plane waves. The subsidiary divergences in the perturbation expansion which are known to exist i.e. $r_s \ln r_s$ can be treated in a manner analogous to the Gell-Mann, Brueckner method. Higher order exchange terms must also be incorporated.

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