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Nr 50

**APPLICATION OF MANY-BODY THEORY
TO THE ONE-ELECTRON PROBLEM OF
ATOMS, MOLECULES AND SOLIDS**

BY

LARS HEDIN



GÖTEBORG 1965



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THE ONE-ELECTRON PROBLEM OF ATOMS,
MOLECULES AND SOLIDS

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Tekn. lic.

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GÖTEBORG.

GÖTEBORG 1965

ELANDERS BOKTRYCKERI AKTIEBOLAG

DOKTORSAVHANDLINGAR
VID
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1965

The present paper is an introduction and summary of a thesis comprising the following two papers:

- A. L. Hedin: New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem. *Physical Review* *139*, A796—A823 (1965).
- B. L. Hedin: Effect of Electron Correlation on Band Structure of Solids. *Arkiv för Fysik* *30*, 231—258 (1965).



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1967

Application of many-body theory to the one-electron problem of atoms, molecules and solids

Then after all, Mal saw a good picture.

William Golding in *The Inheritors*.

1. Introduction

The theory of quantum mechanics is at the base of our theoretical description of nature. In many cases it is unnecessary and pointless to go all the way down to quantum mechanics. For a large portion of modern physics however, the quantum mechanical ideas are indispensable.

The aim of a purely deductive treatment might be stated somewhat as follows. We have to create out of the general abstract theory of quantum mechanics through appropriate specialization and simplification, useful concepts, vivid pictures and simple relations in order to systematize and understand the experimental data and in order to give guidance about areas where it might be profitable to look for new discoveries.

Two important factors in favour of such an a priori approach have developed during the last ten years, namely many-body theory and fast computers. Many-body theory has had a remarkably quick development, and it has now increased our understanding over wide areas of physics. The achievements have however mostly been in the form of general results and not so much in approximation schemes capable of numerical predictions. In the present thesis the emphasis is on the development of a numerically manageable approximation scheme. Specific application is made on the electron gas and on solids, particularly alkali metals. This kind of application is made feasible by the presence of fast computers. The results are encouraging, and there is all reason to expect a rapid future development in this field.

2. A few remarks on many-body theory

The basic equation of quantum mechanics is the Schrödinger equation, which governs the change with time of a physical system. It reads

$$H\psi(t) = i\hbar \frac{\partial}{\partial t} \psi(t), \quad (2.1)$$

where H is the Hamiltonian, i.e. the operator that corresponds to the total energy of the system, and $\psi(t)$ is the state vector describing the properties of the system. When the system is in a stationary state with energy E , the time behaviour of $\psi(t)$ is simply

$$\psi(t) = \exp(-iEt/\hbar)\psi, \quad (2.2)$$

where ψ satisfies the eigenvalue equation

$$H\psi = E\psi. \quad (2.3)$$

We now specialize to the case when the system consists of N electrons moving in a fixed configuration of nuclei. This corresponds to an atom, or to a molecule or solid where the vibrational effects are neglected. The state vector ψ can then be taken as a function of the coordinates of N points

$$\psi(x_1, x_2, \dots, x_N).$$

Except for the hydrogen atom we do not know any analytic solution of Eq. (2.3). Complete numerical solutions are out of the question, except when N is a small number, simply because they require too large a numerical material. To obtain a reasonable accuracy we would for say $N=4$ need at least something of the order of 10^{12} values of ψ !

We thus have to simplify the problem by introducing some approximation. In the Hartree-Fock (HF) approximation, which by far is the most common, ψ has the form of a sum of products, $\pm \varphi_1(x_1)\varphi_2(x_2) \dots \varphi_N(x_N)$, where the functions $\varphi_1, \varphi_2 \dots \varphi_N$ are the same in each product but the coordinates x_1, x_2, \dots, x_N are permuted to make ψ anti-symmetrical. The best choice for the functions ψ_k are those which satisfy the self-consistent equations

$$[\epsilon_k - \hbar(x)]\varphi_k(x) - \int V_{\text{exch}}(x, x')\varphi_k(x')dx' = 0, \quad (2.4)$$

where

$$\begin{aligned}
\hbar(x) &= -\frac{\hbar^2}{2m}\nabla^2 + V(x) \\
V(x) &= \int v(x, x')\rho(x')dx' - \sum Z_n v(x, R_n) = \text{Coulomb potential} \\
v(x, x') &= e^2/|x-x'| = \text{Coulomb interaction} \\
\rho(x) &= \sum_1^N |\varphi_i(x)|^2 = \text{density of electrons} \\
Z_n, R_n &= \text{charge and position of nucleus } n \quad (2.5) \\
V_{\text{exch}}(x, x') &= -v(x, x')\rho(x, x') = \text{exchange potential} \\
\rho(x, x') &= \sum_1^N \varphi_i(x)\varphi_i^*(x') = \text{density matrix.}
\end{aligned}$$

The energy eigenvalues ϵ_k give excitation energies while the total energy is given by a more complicated expression than just the sum of the ϵ_k .

The *HF* approximation gives us an appealingly simple picture of the system. We can think of each electron as described by a wavefunction φ_k , having an energy ϵ_k and contributing with $|\varphi_k(x)|^2$ to the total density $\rho(x)$. The motion of the electron is governed by the Coulomb potential V and a non-local potential V_{exch} , which takes into account some of the effects from the correlation in the motion of the electrons. The *HF* approximation is so widely used that many physicists have almost forgotten that it is an approximation, and actually often a poor one.

The *HF* approximation represents a blind alley from the standpoint of conventional quantum mechanics in the sense that we cannot improve on it without losing the simple physical picture it gives. From the standpoint of many-body theory, on the other hand, the *HF* equation is the lowest order approximation of an exact equation with a very similar structure.

In conventional quantum mechanics we are trying to obtain good approximations for the wavefunction $\psi(x_1, x_2, \dots, x_N)$, and we thus aim at accounting for the simultaneous motion of all the electrons. In many-body theory we instead study propagators or Green's functions, describing what happens if we, say, insert an electron or a test charge at a given point in the system.

We will here discuss only the one-particle Green's function which describes the propagation of a particle from one space-time point

to another in the presence of other particles. The Fourier transform with respect to time of the HF approximation for the one-particle Green's function is

$$G(x, x'; \epsilon) = \sum_k \frac{\varphi_k(x)\varphi_k^*(x')}{\epsilon - \epsilon_k}, \quad (2.6)$$

where the summation over k covers all solutions to Eq. (2.4) not only the N solutions which appear in h and V_{exch} . The exact Green's function is obtained from Eq. (2.6) by replacing the ϵ_k by exact excitation energies and the φ_k by some generalized amplitudes. The equation satisfied by the exact Green's function is

$$[\epsilon - h(x)]G(x, x'; \epsilon) - \int M(x, x''; \epsilon)G(x'', x'; \epsilon)dx'' = \delta(x - x'). \quad (2.7)$$

Here $h(x)$ has the same definition as in Eq. (2.5), except that $\rho(x)$ now stands for the exact density. The self-energy operator M represents all the complicated correlation effects of a many-particle system. If M is written as a power series expansion in the Coulomb interaction v , the first term is the V_{exch} of HF theory. If we knew M completely and solved Eq. (2.7) for G , we would obtain exact information on excitation energies, the electron density and the total energy.

In Eq. (2.3) the Hamiltonian H is well-known but the wavefunction ψ , which contains all information about the system, is an extremely complicated function of a large number of variables. In Eq. (2.7) G contains most of the information we are interested in and still is a function only of a small number of variables. M on the other hand is not given by a simple closed form like H , and in applications we have to use approximations for it. The situation might be put as follows. In Eq. (2.3) we have a well-known operator (H) and an approximate solution (ψ). In Eq. (2.7) we have an approximate operator ($h+M$) and a well-known (if we work hard) solution (G).

The advantage of many-body theory lies to a large extent in a very efficient and simple book-keeping system. Different quantities like say M or the total energy can be given as expansions where each term is represented by a diagram picturing a scattering process. The diagrams which occur in a given expansion are uniquely specified by a few simple topological rules. This has rendered it possible to make partial summations in the expansions and to draw conclusions regarding their analytical properties, which very probably might never have been discovered without the simple diagrammatic rep-

resentation. There has also been developed a functional derivative technique to treat Green's functions, which in some respects is superior to the expansion technique and must be considered a complementary tool.

It should be emphasized that in this section we have only taken up a rather limited aspect of many-body theory. Thus we have not at all considered e.g. temperature effects, while one of the most important achievements of many-body theory is the ease and power by which it incorporates the theory of statistical thermodynamics.

3. Summary of paper A

When we want to proceed beyond general statements to predictions for specific problems we have to develop an approximation scheme. In this paper we have derived a systematic expansion of the self-energy M in terms of a screened interaction W rather than the bare Coulomb interaction v . We can write $W = v\epsilon^{-1} = v(1 - Pv)^{-1}$ where ϵ is the dielectric function and P the polarization function. W represents the effective interaction between two electrons since it by definition equals the sum of the direct (bare) interaction and the indirect interaction via the polarization charges. The latter is taken from linear response theory.

When the polarizability of the system is small, W will differ only little from v . Experience from calculations on atoms indicates that an expansion in v is rapidly convergent in this case. The expansion of M in terms of W can be written, omitting the notation for integral signs and variables

$$\begin{aligned} M &= GW + GWGWG + \dots = \\ &= G(v + vPv + \dots) + GvGvG + \dots \end{aligned} \quad (3.1)$$

The $GvPv$ term gives the direct contribution of second order, while $GvGvG$ gives the exchange contribution of second order. Thus the expansion of M to first order in W contains both the first order and the direct second order terms of the expansion in v .

When the polarizability of the system is large, an expansion in v is poorly convergent or divergent. In this case W is strongly screened and thus much weaker than v . We then expect that the expansion in W should have much better convergence properties than the one in v . To show that the convergence is good enough to be useful is an essential purpose of this paper.

We have not yet specified how G and W should be approximated when we make a certain truncation in the expansion for M . In the scheme developed in this paper we use a self-consistency requirement with a corresponding variational principle. When we truncate the expansion for M at a certain order in $W=v(1-Pv)^{-1}$, the expansion for $P=GG+GGWGG+\dots$ should be truncated at the next lower order. In the equation for G

$$(\epsilon - \hbar - M)G = 1, \quad (3.2)$$

both \hbar and $M=GW+GWGWG+\dots$ then have a well-defined dependence on G for each truncation of M , which gives us the selfconsistency requirement.

An expansion of this kind is numerically useful only when the first order approximation is reasonably accurate. A good test case for the method is the problem of the electron gas since the polarizability is very high in this case. The electron gas has many features in common with a real metal and there is little doubt that if our approximation scheme works for the electron gas it will also work for a metal. As shown in paper B the results for the electron gas are actually also of direct use in the theory of metals.

The discussion of the electron gas forms a large part of paper A. It is rather technical and we will not here take up any of its details. The main conclusion is that the first order approximation for M works reasonably well in its predictions for the total energy, the chemical potential and the excitation spectrum. The higher the density of the electron gas the more accurate is the first order approximation. The prediction for the magnetic susceptibility seems to be fairly reliable at the density of aluminum but its value is doubtful at alkali-metal densities.

The properties of the electron gas have been treated earlier by many different approaches. For high densities its properties are well established. For metallic densities on the other hand there was little possibility, except for the total energy, to judge accuracy and reliability of the rather limited results of earlier calculations.

In paper A we also discuss a certain approximation called *COHSEX* of the first order approximation for M . If we write M in a time-representation rather than an energy-representation, we have

$$M(x, x'; \tau) = i\hbar G(x, x'; \tau) W(x, x'; \tau). \quad (3.3)$$

The Hartree-Fock approximation is obtained from Eq. (3.3) if we neglect polarization, i.e. if we replace $W(x, x'; \tau)$ by $v(x, x')\delta(\tau)$. We now assume that polarization does not broaden the δ -function peak too much, so that the time-variation of $G(\tau)$ within the peak still can be neglected. This leads to the *COHSEX* approximation

$$M(x, x'; \epsilon) = \delta(x - x')V_{COH}(x) - W(x, x'; \epsilon = 0)\rho(x, x'), \quad (3.4)$$

where

$$V_{COH}(x) = \frac{1}{2} \int v(x, x')R(x', x; \epsilon = 0)dx', \quad R = \epsilon^{-1} - 1. \quad (3.5)$$

$R(x', x; \epsilon = 0)$ is the response function giving the induced charge at point x' from the presence of a charge at point x . V_{COH} is the potential a test charge experiences from the electrons it pushes away around it. The index *COH* stands for COulomb Hole, which is the traditional name for this effect. The factor $\frac{1}{2}$ in V_{COH} comes from the mathematics but can also be verified from simple electrostatics. The last term in Eq. (3.4) is the same as the exchange potential of *HF* theory, cf Eq. (2.5), but with v replaced by the static screened potential $W(\epsilon = 0)$. This term can thus be called Screened EXchange.

COHSEX is only a rough approximation for an electron gas but for the Rydberg-like levels of alkali atoms it works quite well. In the limit of high quantum numbers the contribution from exchange is negligible and the Coulomb hole term reduces to the well-known expression

$$V_{COH} = - \frac{\alpha e^2}{2r^4}, \quad (3.6)$$

where α is the polarizability of the ion. Eq. (3.6) was derived already by Born and Heisenberg in 1924.

4. Summary of paper B

Paper B is an application on the theory of solids of the ideas developed in paper A. The problem consists in untangling those contributions which are associated with the ions and the periodic structure from those which are essentially the same as for the electron gas. This raises a series of rather technical questions which cannot be treated in a general way. The treatment given here is made with the small-core metals in mind, but with suitable changes much of it is pertinent also to a larger class of solids.

The question of a proper periodic potential for the calculation of the valence band in a solid, has been much discussed in the literature. In paper B we derive an explicit expression for this potential. It has the following contributions:

- (i) The Hartree-Fock potential from the free ions
- (ii) The Coulomb potential from the valence electrons
- (iii) A correlation contribution

The diagonal elements between Bloch functions of contribution (iii) are electron-gas like. The non-diagonal elements are small. We expect them to give a significant but not drastic effect on band gaps. All these contributions are quite feasible to calculate with a fast computer.

The absolute position of the core levels in a solid can now be measured very accurately by a new technique developed in Uppsala. Appreciable shifts are found for the same ion in different solids. In paper B we have succeeded to separate out the contributions to a core level which occur also in the free ion. The contributions which cause the shift in the solid relative to the free ion are:

- (i) The Coulomb potential from the valence electrons
- (ii) A polarization contribution from the valence electrons
- (iii) A coupling term to other core levels
- (iv) The exchange potential from the valence electrons

Contributions (iii) and (iv) are rather small. Contribution (i) is the largest. When the polarizability is large, as for metals, contribution (ii) is of comparable magnitude to contribution (i). All these contributions are quite feasible to calculate with a fast computer.

Whether we treat the valence band or the core bands we need to know the Coulomb potential from the valence electrons. For many metals the charge density has approximately a muffin-tin form, i.e. it is spherically symmetric inside a sphere around each ion and constant between the spheres. The potential from such a charge distribution is discussed and it is pointed out that we now have a very good knowledge of that potential.

In an appendix we give improved values for the total energy and the Fermi energy of an electron gas, using an extrapolation formula. The values obtained for the Fermi energy should be accurate within a few hundredths of an electronvolt.

Comparisons with experiment are made for the core levels and Fermi level of alkali metals and aluminum. For these simple metals essentially no calculations had to be done and we could instead use results for the electron gas given in paper A. The comparison with experiment came out satisfactory which confirms the analysis made in paper B.

Acknowledgements

This thesis developed out of ideas set forth in two technical reports of the Quantum Chemistry Group in Uppsala. The author is grateful to prof. Stig Lundqvist who was co-author of the first report and with whom he had numerous very inspiring discussions during the years 1960 and 1961. He is also very grateful to the director of the Quantum Chemistry Group prof. Per Olov Löwdin for the interest, encouragement and solicitude he gave the author during the years 1959—1962.

The author wants to thank profs. Lamek Hulthén and Gudmund Borelius of the Royal Institute of Technology in Stockholm for their encouragement and inspiration during the years 1955—1959, and the Swedish Natural Science Research Council for their support during the years 1955—1962.

Most of the work presented in this thesis was carried out during the author's stay at the Solid State Science Division of the Argonne National Laboratory, 1962—1964. He is grateful to the director Oliver C. Simpson for the opportunity of this stay and to Dr John Robinson and other members of the Division for valuable discussions. He is also grateful to several members of the Applied Mathematics Division for advice in programming technique and aid in tracing errors of the programs which were used in calculations for paper A performed on an IBM 704 computer.

Paper B of this thesis was completed at the present Institute and the author is grateful to profs. Stig Lundqvist and Alf Sjölander for their interest and encouragement during that work.

Institute of Theoretical Physics, Göteborg, September 1965.

Lars Hedin

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1965

New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem*

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(Received 8 October 1964; revised manuscript received 2 April 1965)

A set of successively more accurate self-consistent equations for the one-electron Green's function have been derived. They correspond to an expansion in a screened potential rather than the bare Coulomb potential. The first equation is adequate for many purposes. Each equation follows from the demand that a corresponding expression for the total energy be stationary with respect to variations in the Green's function. The main information to be obtained, besides the total energy, is one-particle-like excitation spectra, i.e., spectra characterized by the quantum numbers of a single particle. This includes the low-excitation spectra in metals as well as configurations in atoms, molecules, and solids with one electron outside or one electron missing from a closed-shell structure. In the latter cases we obtain an approximate description by a modified Hartree-Fock equation involving a "Coulomb hole" and a static screened potential in the exchange term. As an example, spectra of some atoms are discussed. To investigate the convergence of successive approximations for the Green's function, extensive calculations have been made for the electron gas at a range of metallic densities. The results are expressed in terms of quasiparticle energies $E(\mathbf{k})$ and quasiparticle interactions $f(\mathbf{k}, \mathbf{k}')$. The very first approximation gives a good value for the magnitude of $E(\mathbf{k})$. To estimate the derivative of $E(\mathbf{k})$ we need both the first- and the second-order terms. The derivative, and thus the specific heat, is found to differ from the free-particle value by only a few percent. Our correction to the specific heat keeps the same sign down to the lowest alkali-metal densities, and is smaller than those obtained recently by Silverstein and by Rice. Our results for the paramagnetic susceptibility are unreliable in the alkali-metal-density region owing to poor convergence of the expansion for f . Besides the proof of a modified Luttinger-Ward-Klein variational principle and a related self-consistency idea, there is not much new in principle in this paper. The emphasis is on the development of a numerically manageable approximation scheme.

1. INTRODUCTION

ONE-PARTICLE equations are widely used to give an approximate description of complicated interacting systems of particles. The Hartree-Fock (HF) equations are used for atoms and molecules, the shell-model equations for nuclei, the Hückel equations for aromatic molecules, and the periodic potential equations for calculation of the energy-band structure of solids. These equations were originally little more than a fairly effective phenomenological model of the system. In the last ten years with the development of formal techniques to treat many-particle systems, much work has been done to connect these equations with an exact theory. Although we now have a wealth of beautiful general theorems, fairly little has been done towards manageable and reliable approximation schemes especially for interacting electrons.

The high-density electron gas is a case that has been examined diligently. Its properties are expressed as series expansions in r_s , where $4\pi r_s^3 a_0^3 / 3 = \Omega / N = 1 / \rho$, with $a_0 =$ Bohr radius $= 0.5292 \times 10^{-8}$ cm. In the metallic density region $r_s = 2-5$, most of the series expansions, however, predict manifestly wrong results.

In this paper the electron-gas problem is reinvestigated, formally and numerically, with the main purpose of estimating the convergence of our expansion in the metallic density region. The application of the method for solids

and particularly for alkali metals will be discussed in another paper.¹

The results of this paper also provide a new approach to, and qualitative conclusions regarding, the general type of excitation spectra, which correspond to a single excited electron outside or a hole in a closed-shell structure. In particular, the alkali atoms and the Born-Heisenberg type of polarization correction are discussed. The treatment is concerned only with a nonrelativistic description of electrons moving in a fixed configuration of nuclei.

In Secs. 2-5 the main results of the formal analysis are presented, detailed derivations being given in the Appendices. In Secs. 6-10 the numerical results for an electron gas are given and the accuracy of our approximations discussed. Section 11 contains a summary of important results.

2. FORMAL FRAMEWORK

The conceptual tool to be used is the one-particle Green's function,²

$$G(1,2) = -(i/\hbar) \langle T(\psi(1)\psi^\dagger(2)) \rangle. \quad (1)$$

Here 1 and 2 each stand for the five coordinates of a

¹ L. Hedin, Arkiv. Fysik (to be published).

² P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959). See also T. Kato, T. Kobayashi and M. Namiki, Progr. Theor. Phys. Suppl. **15**, 3 (1960); A. Klein, *Lectures on the Many-Body Problem*, edited by E. R. Caianiello (Academic Press Inc., New York, 1962), p. 279; P. Nozières, *The Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1964); A. A. Abrikosov, L. P. Gorkov and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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particle: space, spin, and time, $(1) = (\mathbf{r}_1, \zeta_1, t_1) = (\mathbf{x}_1, t_1) = x_1$. T is the Dyson time-ordering operator and ψ is the field operator in the Heisenberg representation. The brackets stand for averaging with respect to the *exact* ground state, rather than the noninteracting ground state of the system.

The Green's function G obeys the equation

$$[\epsilon - h(\mathbf{x}) - V(\mathbf{x})]G(\mathbf{x}, \mathbf{x}'; \epsilon) - \int M(\mathbf{x}, \mathbf{x}''; \epsilon)G(\mathbf{x}'', \mathbf{x}'; \epsilon)d(\mathbf{x}'') = \delta(\mathbf{x}, \mathbf{x}'), \quad (2)$$

where

$$h(\mathbf{x}) = -(\hbar^2/2m)\nabla^2 - \sum_n^{\text{all nuclei}} Z_n v(\mathbf{x}, \mathbf{R}_n),$$

$$V(\mathbf{x}) = \int v(\mathbf{x}, \mathbf{x}')\rho(\mathbf{x}')d(\mathbf{x}'),$$

Z_n and \mathbf{R}_n = charge and position of the n th nucleus,

$$v(\mathbf{x}, \mathbf{x}') = e^2/|\mathbf{x} - \mathbf{x}'|,$$

$$\rho(\mathbf{x}) = \langle \psi^\dagger(\mathbf{x})\psi(\mathbf{x}) \rangle$$

= number density of the electrons

$$= -i\hbar G(\mathbf{x}, t; \mathbf{x}, t + \Delta), \quad (\Delta \rightarrow 0, \Delta > 0),$$

$$G(\mathbf{x}, \mathbf{x}'; \epsilon) = \int G(\mathbf{x}, t; \mathbf{x}', t') \exp\left[\frac{i\epsilon}{\hbar}(t - t')\right] d(t - t').$$

M is the self-energy operator which represents the complicated correlation effects of a many-particle system. A series expansion of M in v gives as first term the HF exchange potential,

$$M^{\text{HF}}(\mathbf{x}, \mathbf{x}'; \epsilon) = -v(\mathbf{x}, \mathbf{x}')\langle \psi^\dagger(\mathbf{x}')\psi(\mathbf{x}) \rangle = i\hbar v(\mathbf{x}, \mathbf{x}')G(\mathbf{x}, t; \mathbf{x}', t + \Delta), \quad (3)$$

which obviously is independent of ϵ .

Later we will write down a set of functionals of G giving successively more accurate approximations of M . Since both V and M are given in terms of G , Eq. (2) represents a self-consistency problem which can also be formulated as a variational problem.

From definition (1) it readily follows that

$$G(\mathbf{x}, \mathbf{x}'; \epsilon) = \sum_s (f_s(\mathbf{x})f_s^*(\mathbf{x}')/(\epsilon - \epsilon_s)),$$

where

$$f_s(\mathbf{x}) = \langle N, 0 | \psi(\mathbf{x}) | N+1, s \rangle; \quad \epsilon_s = E_{N+1, s} - E_{N, 0} - i\Delta \quad \text{when } \epsilon_s \geq \mu, \quad (4)$$

$$f_s(\mathbf{x}) = \langle N-1, s | \psi(\mathbf{x}) | N, 0 \rangle; \quad \epsilon_s = E_{N, 0} - E_{N-1, s} + i\Delta \quad \text{when } \epsilon_s < \mu,$$

and

$$\mu = E_{N+1, 0} - E_{N, 0} = \text{chemical potential} \\ = -(\text{electron affinity}).$$

$|N, 0\rangle$ stands for the ground state of the N -particle system and the sum s runs over *all* states of the $N+1$ and $N-1$ particle systems, the configuration of the nuclei being unchanged.

The amplitudes $f_s(\mathbf{x})$ and the energies ϵ_s are solutions of the eigenvalue equation³

$$[\epsilon - h(\mathbf{x}) - V(\mathbf{x})]f(\mathbf{x}) - \int M(\mathbf{x}, \mathbf{x}''; \epsilon)f(\mathbf{x}'')d(\mathbf{x}'') = 0, \quad (5)$$

in case of a discrete energy value ϵ_s . In the continuous part of the spectrum the solution of (5) in general gives a complex eigenvalue, ϵ . The real part of ϵ represents some average energy of a group of excited states and the imaginary part of ϵ the spread in energy of these states. It is understood that we use the analytical continuation of M into the complex ϵ plane.

The self-consistent solution of Eq. (2) using $M = M^{\text{HF}}$ gives a G built up from the f_s and ϵ_s which are the one-particle functions and energy eigenvalues of the HF approximation. The N smallest values of the ϵ_s correspond to occupied one-electron functions and the remaining to unoccupied or "virtual" functions.

Besides giving information on excitation spectra, the one-particle Green function allows us to calculate the expectation value of any one-particle operator by

$$\langle N | \sum_{i=1}^N 0(x_i) | N \rangle = \int \langle N | \psi^\dagger(\mathbf{x})0(\mathbf{x})\psi(\mathbf{x}) | N \rangle d\mathbf{x} \\ = -i \int \frac{d\epsilon}{2\pi} d(\mathbf{x}) e^{i\epsilon\Delta} 0(\mathbf{x}) G(\mathbf{x}, \mathbf{x}; \epsilon), \quad (6)$$

and also that of the total-energy operator H by

$$\langle N | H | N \rangle = -i \int \frac{d\epsilon}{2\pi} d(\mathbf{x}) d(\mathbf{x}') e^{i\epsilon\Delta} \\ \times \{ \delta(\mathbf{x} - \mathbf{x}') (h(\mathbf{x}') + \frac{1}{2}V(\mathbf{x}')) + \frac{1}{2}M(\mathbf{x}, \mathbf{x}'; \epsilon) \} \\ \times G(\mathbf{x}', \mathbf{x}; \epsilon) + \frac{1}{2} \sum_{nm} Z_n Z_m v(\mathbf{R}_n, \mathbf{R}_m). \quad (7)$$

In Eq. (7) the term involving h gives the expectation value of the kinetic energy plus the electrostatic interaction between electrons and nuclei. The term containing V can be written

$$\frac{1}{2} \int \rho(\mathbf{x}) v(\mathbf{x}, \mathbf{x}') \rho(\mathbf{x}') d\mathbf{x} d\mathbf{x}'. \quad (8)$$

³ This equation was first derived, in a very general form, by J. Schwinger, Proc. Natl. Acad. Sci. U. S. 37, 452 (1951). Its application to many-electron problems has been discussed by G. Pratt, Phys. Rev. 113, 462 (1960); Rev. Mod. Phys. 35, 502 (1963); L. Hedin and S. Lundquist, Quantum Chemistry Group, Uppsala, Sweden, Technical Report T III, 1960 (unpublished); L. Hedin, Quantum Chemistry Group, Uppsala, Sweden, Technical Report No. 84, 1962 (unpublished); Bull. Am. Phys. Soc. 8, 535 (1963).

The MG term gives all exchange and correlation contributions. It is easy to check that Eq. (7) reproduces the HF expression for the energy when G^{HF} and M^{HF} are used.

3. EXPANSION OF M IN TERMS OF A SCREENED POTENTIAL, W

We now turn to our central problem, namely, the development of good approximations for M . The simplest approach is to develop M in a power series of v . It is well known, however, that such an expansion diverges for metals. Even in cases when it is convergent, its convergence rate rapidly becomes poor with increasing polarizability of the system. One common way to handle this problem is to make partial summations to infinite order. The difficulty here is one of knowing what partial summations to choose in order to obtain a systematic theory.

In this paper a new method is developed. We use the Schwinger technique¹ of functional derivatives to generate an expansion in terms of a screened potential⁴ W rather than the bare Coulomb potential v .

The potential W was first introduced by Hubbard⁵:

$$W(1,2) = v(1,2) - \frac{i}{\hbar} \int v(1,3) \langle T(\rho'(3)\rho'(4)) \rangle \times v(4,2) d(3)d(4) = W(2,1), \quad (9)$$

where

$$\rho'(1) = \psi^\dagger(1)\psi(1) - \langle \psi^\dagger(1)\psi(1) \rangle; \quad v(1,2) = v(\mathbf{x}_1, \mathbf{x}_2) \delta(t_1 - t_2).$$

$W(1,2)$ essentially gives the potential at point 1 due to the presence of a test charge at point 2, including the effect of the polarization of the electrons. W represents the effective interaction between two electrons and is

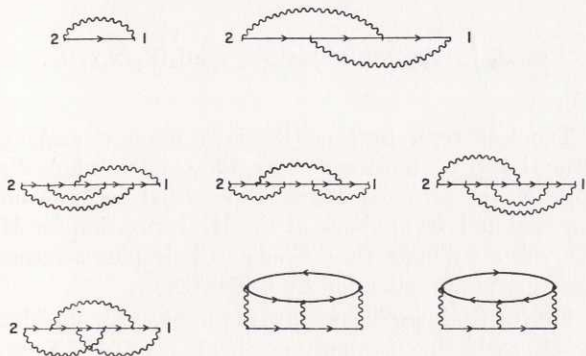


FIG. 1. Diagrams representing the expansion of $M(1,2)$. The one-particle Green's function $G(1,2)$ is represented by an arrow from 2 to 1, and the screened potential $W(1,2)$ by a wiggly line between 1 and 2.

⁴ The feasibility of expanding in a screened interaction has been emphasized by J. C. Phillips, Phys. Rev. **123**, 420 (1961).

⁵ J. Hubbard, Proc. Roy. Soc. **A240**, 539 (1957).

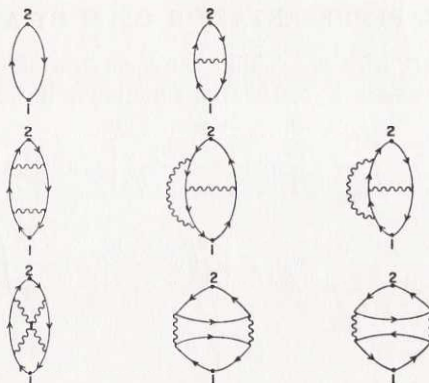


FIG. 2. Diagrams representing the expansion of $P(1,2)$.

much weaker than the bare Coulomb interaction v if the polarizability is large. W is spin-independent.

The first two terms in the expansion of M are

$$M(1,2) = ihG(1,2)W(1^+,2) - \hbar^2 \int G(1,3)G(3,4) \times G(4,2)W(1,4)W(3,2)d(3)d(4) + \dots, \quad (10)$$

where

$$1^+ = \mathbf{x}_1, t_1 + \Delta.$$

The expansion for M is represented by diagrams in Fig. 1. There is only one first-order and one second-order term while there are six third-order terms.

The definition (9) of W is not directly useful since it is in terms of the density-density correlation function rather than the Green's function. Instead we find W from the integral equation

$$W(1,2) = v(1,2) + \int W(1,3)P(3,4)v(4,2)d(3)d(4), \quad (11)$$

where the kernel P can be expanded as

$$P(1,2) = -ihG(1,2)G(2,1) + \hbar^2 \int G(1,3)G(4,1) \times W(3,4)G(2,4)G(3,2)d(3)d(4) + \dots. \quad (12)$$

The expansion for P is represented by diagrams in Fig. 2.

Equations (11) and (12) define W as a functional of G and thus Eq. (10) gives M as a functional of G .⁶ G then has to be obtained self-consistently from Eq. (2). The practical usefulness of this scheme of course depends on how many terms in the expansions of M and P are needed to provide a good approximation. In the following we will try to illuminate that question as much as possible.

⁶ Special cases of such functionals have been proposed by G. Baym and L. P. Kadanoff but no systematic expansion was developed. See G. Baym and L. P. Kadanoff, Phys. Rev. **124**, 287 (1961); G. Baym, Phys. Rev. **127**, 1391 (1962); L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

4. REPRESENTATION OF M BY A "COULOMB HOLE" PLUS SCREENED EXCHANGE

To start with we exhibit the structure of the first-order term in M . From the spectral resolution of G and of the density-density correlation function in W we have

$$M(\mathbf{x}, \mathbf{x}'; \epsilon) = \int_{-\infty}^{\infty} d\tau \sum_s \exp\left[\frac{i\tau}{\hbar}(\epsilon - \epsilon_s)\right] f_s(\mathbf{x}) f_s^*(\mathbf{x}') [\theta(\tau) - \theta(\mu - \epsilon_s)]$$

$$\times \left\{ v(\mathbf{x}, \mathbf{x}') \delta(\tau + \Delta) - \frac{i}{\hbar} \int v(\mathbf{x}, \mathbf{x}'') \sum_t' R_t(\mathbf{x}'') R_t^*(\mathbf{x}''') \exp\left(-\frac{i|\tau|}{\hbar} \epsilon_t\right) v(\mathbf{x}''', \mathbf{x}') d\mathbf{x}'' d\mathbf{x}''' \right\}, \quad (13)$$

$$\theta(\tau) = \begin{cases} 1 & \text{for } \tau > 0 \\ 0 & \text{for } \tau < 0. \end{cases}$$

The term inside the curly brackets is $W(1^+, 2)$. $R_t(\mathbf{x})$ is an oscillator strength function,

$$R_t(\mathbf{x}) = \langle N, t | \psi^\dagger(\mathbf{x}) \psi(\mathbf{x}) | N \rangle, \quad (14)$$

the ordinary oscillator strength being

$$\frac{2m}{\hbar^2} \epsilon_t \left| \int R_t(\mathbf{x}) \mathbf{r} \cdot \mathbf{n} d\mathbf{x} \right|^2, \quad (15)$$

where \mathbf{n} gives the direction of the dipole moment and $\epsilon_t = E_{N,t} - E_N$. The prime on the sum over t in Eq. (13) indicates that the term with $\epsilon_t = 0$ is excluded.

One important use of M is in Eq. (5), which gives the excitation spectra of the $(N \pm 1)$ -particle systems. The energy shift of a level k caused by M is approximately,

$$\int f_k^*(\mathbf{x}) M(\mathbf{x}, \mathbf{x}'; \epsilon_k) f_k(\mathbf{x}') d\mathbf{x} d\mathbf{x}'$$

$$= \int d\tau \sum_s \exp\left[\frac{i\tau}{\hbar}(\epsilon_k - \epsilon_s)\right] [\theta(\tau) - \theta(\mu - \epsilon_s)]$$

$$\times \langle ks | W(\tau) | ks \rangle. \quad (16)$$

Here,

$$\langle ks | W(\tau) | ks \rangle = \int f_k^*(\mathbf{x}) f_s(\mathbf{x}) W(\mathbf{x}, \mathbf{x}'; \tau)$$

$$\times f_s^*(\mathbf{x}') f_k(\mathbf{x}') d\mathbf{x} d\mathbf{x}', \quad (17)$$

is a Coulomb integral when $k = s$, and an exchange integral when $k \neq s$. Generally the Coulomb integral will be much larger than the exchange integrals and the largest exchange integrals will correspond to energies ϵ_s close to ϵ_k . In many cases then the important energy difference, $\epsilon_k - \epsilon_s$, will be small compared to the important energy ϵ_t that appears in W . Assuming that to be the case, we put the factor $\exp[(i\tau/\hbar)(\epsilon - \epsilon_s)]$ in M equal to 1 and obtain,

$$M(\mathbf{x}, \mathbf{x}'; \epsilon) = \frac{1}{2} \delta(\mathbf{x} - \mathbf{x}') W_p(\mathbf{x}, \mathbf{x}'; 0)$$

$$- W(\mathbf{x}, \mathbf{x}'; 0) \langle \psi^\dagger(\mathbf{x}') \psi(\mathbf{x}) \rangle. \quad (18)$$

Here $W_p = W - v$ and we have used the fact that

$$\sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}');$$

$$\sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}') \theta(\mu - \epsilon_s) = \langle \psi^\dagger(\mathbf{x}') \psi(\mathbf{x}) \rangle. \quad (19)$$

The first factor in Eq. (18) gives the contribution of a "Coulomb hole"⁷ since, according to general results of linear response theory,

$$W_p(\mathbf{x}, \mathbf{x}'; 0) = \int v(\mathbf{x}, \mathbf{x}'') \Delta\rho(\mathbf{x}'') d\mathbf{x}''$$

$$= -i \int v(\mathbf{x}, \mathbf{x}'') R(\mathbf{x}'', \mathbf{x}'''; 0) v(\mathbf{x}''', \mathbf{x}') d\mathbf{x}'' d\mathbf{x}''', \quad (20)$$

where $\Delta\rho(\mathbf{x}'')$ is the change in number density at the point \mathbf{x}'' caused by the presence of a point charge at point \mathbf{x}' . $R(\mathbf{x}, \mathbf{x}'; 0)$ is the density-density correlation function. The factor $\frac{1}{2}$ arises mathematically from $\theta(\tau)$ and physically because the force on the electron due to the induced charge is proportional to

$$\text{grad}_{\mathbf{x}} \int v(\mathbf{x}, \mathbf{x}'') \Delta\rho(\mathbf{x}'') d\mathbf{x}'' = \frac{1}{2} \text{grad}_{\mathbf{x}} W_p(\mathbf{x}, \mathbf{x}; 0).$$

The last term in Eq. (18) is a screened exchange potential. If we replace W by v , the Coulomb hole disappears, the screened exchange potential becomes unscreened and we are back at the HF expression for M . We will abbreviate the "Coulomb hole plus screened exchange" approximation by COHSEX.

For the Rydberg-like spectra of one electron outside a closed shell, the assumptions behind COHSEX are readily verified. Let us take sodium as an example. Here the smallest $(N+1)$ -type excitation energy is $\epsilon_1 = E(\text{Na}, 1s^2 2s^2 2p^6 3s) - E(\text{Na}^+, 1s^2 2s^2 2p^6) = -0.378 \text{ Ry}$,

⁷ E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934); E. Wigner, *ibid.* 46, 1002 (1934); Trans. Faraday Soc. 34, 678 (1938).

TABLE I. Quasiparticle energies in rydbergs. (Experimental values without reference are taken from Charlotte Moore's tables.)

| <i>N</i> | | 1 <i>s</i> | 2 <i>s</i> | 2 <i>p</i> | 3 <i>s</i> | 3 <i>p</i> | 3 <i>d</i> | 4 <i>s</i> | 4 <i>p</i> | 5 <i>p</i> |
|----------|-------------------------|------------------------|----------------------|-----------------------|----------------------|-----------------------|----------------------|----------------------|-----------------------|-----------------------|
| 2 | He, HF | -1.8359 ^a | | | | | | | | |
| | He, expt | -1.8073 | | | | | | | | |
| 2 | Li ⁺ , HF | -5.5847 ^a | -0.3934 ^b | -0.2574 ^b | | -0.11354 ^b | | | -0.06356 ^b | -0.04050 ^b |
| | Li ⁺ , expt | -5.5597 | -0.3963 | -0.2629 | | -0.11448 | | | -0.06394 | -0.04075 |
| 10 | Ne, HF | -65.5446 ^c | -3.8606 ^a | -1.7007 ^a | | | | | | |
| | Ne, expt | -63.89 ^c | -3.5628 ^c | -1.5874 | | | | | | |
| 10 | Na ⁺ , HF | -81.5190 ^c | -6.1474 ^a | -3.5944 ^a | -0.372 ^d | -0.2188 ^d | | -0.1406 ^d | -0.1002 ^d | |
| | Na ⁺ , expt | -79.88 ^c | -5.8866 | -3.4810 | -0.3777 | -0.2231 | | -0.1432 | -0.1019 | |
| 10 | Mg ⁺⁺ , HF | | -8.944 ^e | -5.990 ^e | | | | | | |
| | Mg ⁺⁺ , expt | | -8.7359 | -5.8970 | | | | | | |
| 10 | Si ⁴⁺ , HF | | -16.17 ^f | -12.41 ^f | -3.275 ^f | -2.639 ^f | -1.839 ^f | -1.538 ^f | -1.319 ^f | -0.793 ^f |
| | Si ⁴⁺ , expt | | -15.962 | -12.273 | -3.3180 | -2.6655 | -1.8565 | -1.5502 | -1.3279 | -0.7977 |
| 18 | Ar, HF | -237.2202 ^g | | -19.1426 ^g | -2.5545 ^g | -1.1818 ^g | | | | |
| | Ar, expt | -234.6 ^g | | -18.28 ^g | -2.1491 | -1.1627 | | | | |
| 18 | K ⁺ , HF | -267.5042 ^g | | -23.5962 ^g | -3.9275 ^g | -2.3409 ^g | | | | |
| | K ⁺ , expt | -264.8 ^g | | -22.63 ^g | -3.5288 ^g | -2.3387 | | | | |
| 18 | Ca ⁺⁺ , HF | | | | -5.557 ^h | -3.756 ^h | -0.6659 ^h | -0.8295 ^h | -0.6193 ^h | |
| | Ca ⁺⁺ , expt | | | | -5.1634 | -3.7743 | -0.7478 | -0.8725 | -0.6416 | |
| 36 | Kr, HF | | | | | | | -2.303 ^h | -1.06 ^h | |
| | Kr, expt | | | | | | | -2.0386 | -1.0453 | |

^a P. S. Bagus, T. Gilbert, C. C. J. Roothaan, and H. D. Cohen, (to be published).

^b V. Fock and M. Petrashen, *Physik. Z. Sowjetunion* **8**, 547 (1935).

^c P. S. Bagus, University of Chicago thesis, (to be published).

^d V. Fock and M. Petrashen, *Physik. Z. Sowjetunion* **6**, 368 (1934).

^e W. J. Yost, *Phys. Rev.* **58**, 557 (1940).

^f D. R. Hartree, W. Hartree, and M. F. Mannig, *Phys. Rev.* **60**, 857 (1941).

^g D. R. Hartree and W. Hartree, *Proc. Roy. Soc.* **A164**, 167 (1938).

^h B. H. Worsley, *Proc. Roy. Soc.* **A247**, 390 (1958).

while the smallest excitation energy appearing in W is $E(\text{Na}^+, 1s^2 2s^2 2p^5 (2P_{3/2}^0) 3s)$

$$-E(\text{Na}^+, 1s^2 2s^2 2p^6) = 2.414 \text{ Ry.}$$

The average $(\epsilon_1 - \epsilon_s)$ will be numerically smaller than ϵ_1 unless the exchange integrals with the continuum and the core states have great influence.

For higher Rydberg-like states the functions f_s are well outside the closed shell. The exchange term then becomes negligible. We can further make a multipole expansion of the two v 's in the Coulomb hole term. The result is simply

$$M(\mathbf{x}, \mathbf{x}'; \epsilon) = -(\alpha e^2 / 2 |\mathbf{r}|^4) \delta(\mathbf{x}, \mathbf{x}'), \quad (21)$$

where α is the ion-core polarizability. Eq. (21) was first derived by Born and Heisenberg⁸ in 1924. It has been rederived by quantum-mechanical methods,⁹ and widely used¹⁰ to obtain polarizabilities from spectral data.

The Coulomb-hole contribution will lower the energy while screening of the exchange will raise the energy relative to the HF value. *Experimental values of ϵ_s are generally lower than the HF values for $\epsilon_s > \mu$ and higher for $\epsilon_s < \mu$.* To the extent that Eq. (18) remains valid, *this shows that the Coulomb-hole correction dominates for the higher orbitals while the screening of the exchange dominates for the core orbitals.* A comparison between HF values and experimental values is given in Table I.

5. LANDAU FERMI-LIQUID THEORY. THE QUASIPARTICLE INTERACTION IN TERMS OF W

Many important aspects of the theory of metals depend only on the excitation spectrum close to the Fermi surface. This can advantageously be discussed in the framework of Landau's Fermi-liquid theory.¹¹ For simplicity we here treat only the electron gas in a uniform background of positive charge.

Since the electron gas is translationally invariant, $G(1,2)$ and $M(1,2)$ depend only on the difference between 1 and 2. A Fourier transform with respect to space

⁸ M. Born and W. Heisenberg, *Z. Physik* **23**, 388 (1924).

⁹ I. Waller, *Z. Physik* **38**, 635 (1926); J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933); J. H. Van Vleck and N. G. Whitelaw, *ibid.* **44**, 551 (1933); H. Bethe, *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer-Verlag, Berlin, 1933), **24**, 1, 431.

¹⁰ D. R. Bates, *Proc. Roy. Soc.* **A188**, 350 (1947); E. Trefitz and L. Biermann, *Z. Astrophys.* **30**, 275 (1952); A. S. Douglas, *Proc. Cambridge Phil. Soc.* **52**, 687 (1956); K. Bockasten, *Arkiv Fysik* **10**, 567 (1956) and others.

¹¹ L. D. Landau, *Zh. Eksperim. i Teor. Fiz.* **30**, 1058 (1956); **32**, 59 (1959); **35**, 97 (1958) [English transl.: *Soviet Phys.—JETP* **3**, 920 (1956); **5**, 101 (1957); **8**, 70 (1959)]. See also P. Nozières, *Ref. 2*.

and time transforms Eq. (2) into

$$[\epsilon - \epsilon(\mathbf{k})]G(k) - M(k)G(k) = 1; \quad k = (\mathbf{k}, \epsilon); \quad \epsilon(\mathbf{k}) = \hbar^2 \mathbf{k}^2 / 2m. \quad (22)$$

The Fourier transforms are defined as

$$G(k) = \int \exp(i(\mathbf{k}\mathbf{r} + \epsilon\tau/\hbar))G(\mathbf{x}_1, t_1; \mathbf{x}_2, t_2) d\mathbf{r} d\tau; \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2, \quad \tau = t_1 - t_2. \quad (23)$$

$$M(k) = \frac{i}{(2\pi)^4} \int e^{-i\epsilon'\Delta} W(k')G(k-k')dk' - \frac{1}{(2\pi)^8} \int W(k')W(k'')G(k+k')G(k+k'')G(k+k'+k'')dk'dk'' + \dots; \quad (24)$$

$$W(k) = v(k)/(1-v(k)P(k)); \quad v(k) = 4\pi e^2/|\mathbf{k}|^2;$$

$$P(k) = -\frac{2i}{(2\pi)^4} \int G(k')G(k'-k)dk' + \frac{2}{(2\pi)^8} \int G(k')G(k'')G(k''-k)G(k'-k)W(k'-k'')dk'dk'' + \dots.$$

The factor 2 in $P(k)$ comes from the spin summation. The eigenvalue equation, Eq. (5), for the quasiparticle energies becomes

$$E(\mathbf{k}) = \epsilon(\mathbf{k}) + M(\mathbf{k}, E(\mathbf{k})). \quad (25)$$

The chemical potential μ is equal to $E(\mathbf{k}_0)$ where \mathbf{k}_0 , the Fermi momentum, is the same as for the noninteracting gas,¹²

$$|\mathbf{k}_0| = (1/\alpha r_s a_0); \quad \alpha = (4/9\pi)^{1/3} = 0.52106. \quad (26)$$

The derivative of $E(\mathbf{k})$ with respect to $|\mathbf{k}|$ at the Fermi surface is

$$E'(\mathbf{k}) = \epsilon'(\mathbf{k}) + zM'(\mathbf{k}, \mu + \epsilon(\mathbf{k}) - \epsilon(\mathbf{k}_0)) \quad (27)$$

$$z^{-1} = 1 - (\partial M(\mathbf{k}_0, \mu)/\partial \epsilon).$$

Equation (27) was obtained by expanding $M(\mathbf{k}, E(\mathbf{k}))$ as

$$M(\mathbf{k}, \mu + \epsilon(\mathbf{k}) - \epsilon(\mathbf{k}_0)) + (E(\mathbf{k}) - \mu - \epsilon(\mathbf{k}) + \epsilon(\mathbf{k}_0))\partial M/\partial \epsilon + \dots,$$

taking the derivative with respect to \mathbf{k} , and solving for $E'(\mathbf{k})$. The prime on M refers to a total derivative, not a partial derivative. Equation (27) is exact on the Fermi surface but only approximate when $|\mathbf{k}| \neq |\mathbf{k}_0|$. $E'(\mathbf{k})$ gives the level density at the Fermi surface and is simply related to the specific heat C ¹²:

$$C_0/C = E'(\mathbf{k})/\epsilon'(\mathbf{k}). \quad (28)$$

Here C_0 is the noninteracting or Sommerfeld value of C , $C_0 = 16.86 r_s^2 T \mu \text{ cal}/^\circ\text{K}^2 \text{ mole}$. z gives the discontinuity at the Fermi surface in the momentum distribution $n_\sigma(\mathbf{k}) = \langle N | a_{\mathbf{k}, \sigma}^\dagger a_{\mathbf{k}, \sigma} | N \rangle$. Here $a_{\mathbf{k}, \sigma}$ is related to the field operator by the relation

$$\psi(\mathbf{x}) = (1/\Omega^{1/2}) \sum_{\mathbf{k}, \sigma} a_{\mathbf{k}, \sigma} e^{i\mathbf{k}\cdot\mathbf{x}} \chi_\sigma(\zeta).$$

The noninteracting many-particle states of an elec-

tron gas are uniquely specified by their momentum distribution $n_\sigma(\mathbf{k})$. Thus, e.g., the paramagnetic ground state is given by

$$n_\sigma^{(0)}(\mathbf{k}) = \theta(|\mathbf{k}_0| - |\mathbf{k}|). \quad (29)$$

The basic assumption in Landau's theory of a Fermi liquid is that for small excitation energies there exists a one-to-one correspondence between the noninteracting many-particle states and the true states. It has been proven¹³ that the Landau theory is exact to the extent that the interacting many-particle states can be obtained from the noninteracting ones by infinite-order perturbation theory.

The change in energy of the true state corresponding to a change in the distribution function, $n_\sigma(\mathbf{k}) = n_\sigma^{(0)}(\mathbf{k}) + \delta n_\sigma(\mathbf{k})$, of the noninteracting state is

$$\delta E = \sum_{\mathbf{k}, \sigma} E(\mathbf{k}) \delta n_\sigma(\mathbf{k}) + \frac{1}{2} \sum_{\mathbf{k}, \mathbf{k}', \sigma, \sigma'} f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}') \delta n_\sigma(\mathbf{k}) \delta n_{\sigma'}(\mathbf{k}') + \dots \quad (30)$$

Here $E(\mathbf{k})$ is defined by Eq. (25) and f is the quasiparticle interaction. The magnitude of \mathbf{k} and \mathbf{k}' is $|\mathbf{k}_0|$ and f depends only on the angle between them, $f_{\sigma\sigma'}(\theta)$. We split f in two parts,

$$f_{\sigma\sigma'}(\theta) = f_0(\theta) + \delta_{\sigma\sigma'} f_e(\theta). \quad (31)$$

The specific heat and the paramagnetic susceptibilities are obtained from simple integrals involving f . In the former the combination $2f_0 + f_e$ enters and in the latter f_e .¹¹ We can write f as¹¹

$$f(\mathbf{k}, \mathbf{k}') = 2\pi i z_{\mathbf{k}} z_{\mathbf{k}'} {}^0\Gamma^0(\mathbf{k}, \mathbf{k}'), \quad (32)$$

where ${}^0\Gamma^0$ is defined by the integral equation

¹² J. M. Luttinger, Phys. Rev. 119, 1153 (1960).

¹³ P. Nozières and J. M. Luttinger, Phys. Rev. 127, 1423, 1431 (1962).

$${}^0\Gamma^0(k, k') = {}^0I(k, k') + \int {}^0I(k, k'')G^2(k'') {}^0\Gamma^0(k'', k')dk'', \quad (33)$$

$${}^0I(k, k') = \delta M(k) / \delta G(k').$$

In Eqs. (32) and (33) we have for simplicity taken k to

$$f_e(\mathbf{k}, \mathbf{k}') = -\frac{z^2}{\Omega} \left\{ W(\mathbf{k}-\mathbf{k}'; 0) + \frac{i}{(2\pi)^4} \int [2W(\mathbf{k}-\mathbf{k}'; 0)W(k'')G(k+k'')G(k'+k'') + W(k'')W(k''+k-k')G(k+k'')(G(k'-k'')+G(k+k''))]dk'' \right\}, \quad (34)$$

$$f_0(\mathbf{k}, \mathbf{k}') = \frac{z^2}{\Omega} \frac{i}{(2\pi)^4} \int W^2(k'')G(k+k'')(G(k'-k'')+G(k'+k''))dk''.$$

Here $k = (\mathbf{k}, \mu)$ and $k' = (\mathbf{k}', \mu)$. The volume of the system, which appears in the denominator of f , is balanced since the number of terms in the sum in Eq. (30) is of the order of the number of particles. If we indicate the order in W by a superscript, we have that the functional derivative of $M^{(1)}$ gives rise to $f_e^{(1)}$ and $f_0^{(2)}$ while that of $M^{(2)}$ gives the first two terms in $f_e^{(2)}$. The third term in $f_e^{(2)}$ comes from the ${}^0IG^2 {}^0\Gamma^0$ term in Eq. (33). The first-order term in f involves only the static screened potential^{14,15} and corresponds to the COHSEX approximation (Sec. 4) for M . That approximation for M is however not so clear-cut in the case of an electron gas since the ϵ_t spectrum of W starts at zero rather than at a large finite value. The average value of ϵ_t could, on the other hand, be fairly large since the plasmon energy carries a substantial fraction of the oscillator strength.

From Eq. (18) we find that COHSEX for an electron gas is

$$M(\mathbf{k}, \epsilon) = \frac{1}{2} \frac{1}{(2\pi)^3} \int [W(\mathbf{k}', 0) - v(\mathbf{k}')]d\mathbf{k}' - \frac{1}{(2\pi)^3} \int d\mathbf{k}' W(\mathbf{k}', 0) \frac{1}{2\pi i} \int e^{i\epsilon'\Delta} G(\mathbf{k}-\mathbf{k}'; \epsilon')d\epsilon'. \quad (35)$$

The Coulomb hole term is independent of \mathbf{k} and ϵ and thus a constant. The integration over ϵ' in the last term of Eq. (35) gives, closing the contour in the upper half-plane and using the analytic properties of G ,

$$\frac{1}{2\pi i} \int e^{i\epsilon'\Delta} G(\mathbf{k}', \epsilon')d\epsilon' = \frac{1}{\pi} \int_{-\infty}^{\mu} \frac{\text{Im}M(\mathbf{k}', \epsilon')d\epsilon'}{[\epsilon' - \epsilon(\mathbf{k}') - \text{Re}M(\mathbf{k}', \epsilon')]^2 + [\text{Im}M(\mathbf{k}', \epsilon')]^2}. \quad (36)$$

¹⁴ M. Watabe (Ref. 14) has recently treated the Landau theory using this approximation for f . He does not however have the z^2 factor, which is about 0.5 for metallic densities, nor does he take the second-order terms into account.

¹⁵ M. Watabe, Progr. Theoret. Phys. (Kyoto) **29**, 519 (1963).

include a spin index. Since M does not contain the Hartree-like potential, 0I and ${}^0\Gamma^0$ are the "proper operators" marked with a tilde in Nozières' book.

Using the expansion for M given in Eq. (24) and derived in Appendix A, we obtain the following expansion of f in powers of W

If we treat $\text{Im}M$ as a small energy-independent quantity, the integrand in Eq. (36) becomes a δ function and we obtain for the screened exchange term in Eq. (35),

$$-\frac{1}{(2\pi)^3} \int_{|\mathbf{k}-\mathbf{k}'| < |\mathbf{k}_0|} W(\mathbf{k}', 0) \times \left(1 - \frac{\partial M[\mathbf{k}-\mathbf{k}', E(\mathbf{k}-\mathbf{k}')] }{\partial \epsilon} \right)^{-1} d\mathbf{k}'. \quad (37)$$

The last factor in Eq. (37) equals z when $|\mathbf{k}-\mathbf{k}'| = |\mathbf{k}_0|$ and it varies fairly slowly with $|\mathbf{k}-\mathbf{k}'|$. Putting this factor equal to z and using Eq. (27), the specific heat comes out the same as from the linear term in f . The magnitude of M is however about 25% too large at metallic densities. Judging COHSEX from what it gives for the magnitude and derivative of $E(\mathbf{k})$ at the Fermi surface, we conclude that it is a rough but reasonable approximation at metallic densities. From our numerical results, to be discussed later in detail, it is clear that COHSEX becomes better the smaller the value of r_s . For small r_s the factor z poses no problem since here¹⁶ $z = 1 - 0.17r_s$ and thus tends to 1.

An approximation similar to that in COHSEX is useful for estimating higher order diagrams. The expression for $M^{(1)}$ can be written

$$i\hbar G(1,2)W(1^+,2) = [\langle \psi(1)\psi^\dagger(2) \rangle \theta(\tau) - \langle \psi^\dagger(2)\psi(1) \rangle \theta(-\tau)] [v(1^+,2) + W(1^+,2) - v(1^+,2)]; \quad \tau = t_1 - t_2. \quad (38)$$

The approximation in COHSEX consists in neglecting the time-dependence of $\langle \psi\psi^\dagger \rangle$ and $\langle \psi^\dagger\psi \rangle$, or equivalently by replacing

$$W(1^+,2) - v(1^+,2) \rightarrow \delta(\tau) [W(1,2) - v(1,2)]_{\epsilon=0}. \quad (39)$$

$M^{(1)}$ is exceptional in the sense that we have to use 1^+ rather than 1 in $W(1,2)$. When this is not the case we

¹⁶ E. Daniel and S. H. Vosko, Phys. Rev. **120**, 2041 (1960).

can make an approximation in the same spirit as that of COHSEX simply by replacing $W(\tau)$ by $\delta(\tau)W(\epsilon=0)$, or if we work with energy-variables, by replacing $W(\epsilon)$ by $W(0)$.

It should be noted that while the energy dependence of the M operator is very important for an electron gas (see Sec. 9), it is quite negligible for the alkali atoms discussed earlier. Thus if we have an error $\Delta\epsilon$ in the energy argument of M , the correction is only of the order

$$\Delta\epsilon[M(\epsilon)-M^{\text{HF}}]/(\epsilon, \text{ average}). \quad (40)$$

This is easily seen by noting that M^{HF} is energy-independent and that the energy derivative of $[M(\epsilon)-M^{\text{HF}}]$ effectively introduces a factor $(\epsilon, \text{ average})^{-1}$.

6. ELECTRON GAS: SURVEY OF NUMERICAL RESULTS

So far the discussion has been mainly qualitative. We will now see to what extent it is supported by numerical results for the electron gas. Calculations have been made for $r_s=1, 2, 3, 4, 5$, and 6 and in a few cases for smaller and larger r_s values. For G we have used the expression

$$G(\mathbf{k}, \epsilon) = 1/(\epsilon - \epsilon(\mathbf{k}) - \epsilon_0); \\ \epsilon(\mathbf{k}) = (\hbar^2 \mathbf{k}^2 / 2m) + i\Delta \operatorname{sgn}(|\mathbf{k}_0| - |\mathbf{k}|), \quad (41)$$

where ϵ_0 is chosen so that $\mu = \epsilon(\mathbf{k}_0) + \epsilon_0$. From Eq. (24) we see that if the M operator is $M(\mathbf{k}, \epsilon)$ using (41) with $\epsilon_0=0$, it becomes $M(\mathbf{k}, \epsilon - \epsilon_0)$ for $\epsilon_0 \neq 0$. P is independent of ϵ_0 . The equation for μ is $\mu = \epsilon(\mathbf{k}_0) + M(\mathbf{k}_0, \mu - \epsilon_0)$ which combined with the above expression for μ gives,

$$\epsilon_0 = M[\mathbf{k}_0, \epsilon(\mathbf{k}_0)]. \quad (42)$$

It would have been desirable to have used a self-consistent G ,

$$G(\mathbf{k}, \epsilon) = 1/(\epsilon - \epsilon(\mathbf{k}) - M(\mathbf{k}, \epsilon)). \quad (43)$$

This should be possible to do but the size of the numerical enterprise is probably considerably larger than is justified in a first investigation. That (41) is not too bad is shown by the fact that $M(\mathbf{k}, \epsilon(\mathbf{k}))$ is found to have a very weak \mathbf{k} dependence compared to $\epsilon(\mathbf{k})$. On the other hand $\partial M(\mathbf{k}, \epsilon)/\partial \epsilon$ is found to have an appreciable magnitude compared to 1. This might very well effect our quantitative results but can do little to change our qualitative conclusions regarding the convergence of the expansion in W and the smallness of the specific-heat correction.

For M we use the approximation iGW , and for P , the approximation $-iGG$. A quite reliable estimate of the error in the magnitude of M is obtained from a consideration of the total energy of the electron gas. The magnitude of the second-order term in M is also estimated and found to be of the same order as the error in the first-order term.

From the relation $G = G_0 + G_0(M - \epsilon_0)G$ we see that the correction to $M^{(1)} = iGW$ from the use of G_0 instead

of G is approximately $iG_0(M - \epsilon_0)G_0W = iG_0MG_0W + \epsilon_0 \partial M^{(1)}/\partial \epsilon$. This term is appreciably smaller than the uncrossed second-order term appearing in an expansion with $\epsilon_0=0$. The cancellations mentioned by DuBois¹¹ (p. 54 in his paper) involving this term are discussed in Sec. 9.

The first-order term in the quasiparticle interaction f is trivial. The second-order terms have been calculated using $W(\mathbf{k}, 0)$. The contribution to the specific heat coming from f_0 has been evaluated with $W(\mathbf{k}, \epsilon)$. It is found that the $W(\mathbf{k}, 0)$ approximation gives about 70% of the $W(\mathbf{k}, \epsilon)$ approximation at metallic densities. We assume that the error is about the same for the other second-order term in f . The first-order term in f is about three times larger than the second-order terms for $r_s=4$, the ratio being more favorable for smaller r_s . The picture of M that emerges shows a quite large first-order term with a weak \mathbf{k} dependence and a small second-order term with a k dependence of about the same magnitude and opposite sign.^{17,18}

7. ELECTRON GAS: COULOMB HOLE AND CORRELATION HOLE

For the polarization propagator $P(1,2)$ we have used the approximation $-i\hbar G(1,2)G(2,1)$ with G defined by Eq. (41). This gives Lindhard's expression,¹⁹ or as it is often called, the Random Phase Approximation (RPA) for the dielectric constant. To exhibit the properties of this approximation we investigate the Coulomb and correlation holes associated with P .

We define a propagating dielectric function by the relation

$$W(1,2) = \int v(1,3)\epsilon^{-1}(3,2)d(3). \quad (44)$$

From Eqs. (9) and (11) it follows that

$$\epsilon^{-1}(1,2) = \delta(1,2) - \frac{i}{\hbar} \int \langle T(\rho'(1)\rho'(3)) \rangle \\ \times v(3,2)d(3) = (1 - Pv)^{-1}(1,2). \quad (45)$$

The function ϵ^{-1} is closely related to the linear response function ϵ_L^{-1} ,

$$\epsilon_L^{-1}(1,2) = \delta(1,2) - \frac{i}{\hbar} \theta(t_1 - t_2) \\ \times \int \langle [\rho(1), \rho(3)] \rangle v(3,2)d(3), \quad (46)$$

¹⁷ Recent calculations by Rice (Ref. 18) indicate that the energy dependence of W is more important for the first term in $f_e^{(2)}$, Eq. (34), than for the other second-order terms in f . While this makes the convergence properties of the expansion for f worse than anticipated from our results, it does not influence the conclusion regarding a weak \mathbf{k} dependence of M . Our values for the paramagnetic susceptibility on the other hand seem quite unreliable.

¹⁸ T. M. Rice, Ann. Phys. (N. Y.) **31**, 100 (1965).

¹⁹ J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd. **28**, No. 8 (1954); D. F. DuBois, Ann. Phys. (N. Y.) **7**, 174 (1959); **8**, 24 (1959).

which gives the change in the density of the electrons,

$$\rho^{\text{ind}}(1) = \int [\epsilon_L^{-1}(1,2) - \delta(1,2)] \rho^{\text{ext}}(2) d(2), \quad (47)$$

caused by the presence of an external charge density, ρ^{ext} . The Fourier transforms, $\int \exp[(i\epsilon/\hbar)(t_1 - t_2)] dt_1$, of $\epsilon^{-1}(1,2)$ and $\epsilon_L^{-1}(1,2)$ are equal for $\epsilon \geq 0$. The former is an even function of ϵ , while in the latter the real part is even and the imaginary part odd.

From a knowledge of ϵ^{-1} we can calculate the pair correlation function:

$$g(\mathbf{r}) = \rho^{-2} \sum'_{ij} \langle \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j) \rangle \\ = \rho^{-2} [\langle \rho(\mathbf{r}) \rho(\mathbf{0}) \rangle - \rho \delta(\mathbf{r})], \quad (48)$$

where

$$\rho(\mathbf{r}) = \int \psi^\dagger(\mathbf{r}, \zeta) \psi(\mathbf{r}, \zeta) d\zeta, \quad \rho = \langle \rho(\mathbf{r}) \rangle. \quad (49)$$

From the definition of $g(\mathbf{r})$ it readily follows that

$$g(\mathbf{r}) \rightarrow 1 \quad \text{when} \quad \mathbf{r} \rightarrow \infty \\ \int \rho(g(\mathbf{r}) - 1) d\mathbf{r} = -1. \quad (50)$$

The Fourier transform of $g(\mathbf{r})$ is related to $\epsilon(\mathbf{k}, \epsilon)$ by

$$g(\mathbf{k}) = \rho^{-2} \left\{ \frac{1}{2\pi i} \frac{1}{v(\mathbf{k})} \int [1 - \epsilon^{-1}(\mathbf{k}, \epsilon)] d\epsilon - \rho \right\} \\ + (2\pi)^3 \delta(\mathbf{k}). \quad (51)$$

From $\epsilon(\mathbf{k}, \epsilon)$ we can also calculate the linear response value for the change in the electron density around a fixed external point charge. From Eq. (47) we have, taking the external charge to be $-e$ and using the fact that $\epsilon^{-1}(\mathbf{k}, 0) = \epsilon_L^{-1}(\mathbf{k}, 0)$,

$$g_0(\mathbf{r}) = \int [\epsilon^{-1}(1,2) - \delta(1,2)] dt_1 d\zeta_i; \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \quad (52)$$

The Fourier transform of $g_0(\mathbf{r})$ is

$$g_0(\mathbf{k}) = \epsilon^{-1}(\mathbf{k}, 0) - 1. \quad (53)$$

The function $g_0(\mathbf{r})$ gives the *Coulomb hole* discussed in Secs. 4 and 5, while $\rho(g(\mathbf{r}) - 1)$ gives the *correlation hole* surrounding an electron. From a well-correlated wave function for an atom, the correlation hole can be calculated fairly simply from Eq. (48), while the Coulomb hole requires calculations of the type needed to obtain polarizabilities.

We note that *the Coulomb holes for an electron gas and for a system with an energy gap are qualitatively different*. From Eqs. (46) and (52) we have for a system with an

energy gap

$$\int g_0(\mathbf{r}) d\mathbf{r} = 0. \quad (54)$$

For an electron gas, on the other hand, we have from Eq. (53)

$$\int g_0(\mathbf{r}) d\mathbf{r} = g_0(\mathbf{k} = 0) = -1. \quad (55)$$

This relation should hold also for metals.²⁰

The Lindhard expression¹⁹ for the dielectric constant is

$$\epsilon(\mathbf{k}, \epsilon) = 1 - v(\mathbf{k}) P(\mathbf{k}, \epsilon) = 1 + \alpha(\mathbf{k}, \epsilon), \\ \alpha(q, u) = (\alpha r_s / 8\pi) (1/q^3) [H(q + (u/q)) \\ + H(q - (u/q))] = \alpha(q, -u), \quad (56) \\ H(z) = 2z + (1 - z^2) \ln((z + 1)/(z - 1)) = -H(-z), \\ q = (k/2k_0), \quad u = \epsilon(4\hbar^2 k_0^2 / 2m)^{-1}, \\ \alpha = (4/9\pi)^{1/3} = 0.52106.$$

The logarithm is taken from the branch where $|\text{Im} \ln z| < \pi$. To obtain ϵ we have to take $\text{Im} u = \Delta \text{sgn}(\text{Re} u)$ while ϵ_L is obtained by taking $\text{Im} u = \Delta$. For further reference we note that

$$H(z) = 4 \left(\frac{1}{3z} + \frac{1}{15z^3} + \frac{1}{35z^5} + \dots \right); \quad z \rightarrow \infty, \\ H(z) = 4 \left(z - \frac{z^3}{3} - \frac{z^5}{15} - \frac{z^7}{35} - \dots \right) \\ - \pi i (1 - z^2) \text{sgn}(\text{Im} z); \quad z \rightarrow 0,$$

$$\alpha(q, 0) = (\alpha r_s / \pi) 1/q^2, \quad q \rightarrow 0; \\ \alpha(q, 0) = (\alpha r_s / 3\pi) 1/q^4, \quad q \rightarrow \infty; \\ \alpha(0, u) = -(\alpha r_s / 3\pi) 1/u^2; \\ \alpha(q, u) = (\alpha r_s / 3\pi) 1/(q^4 - u^2). \quad |q \pm (u/q)| \rightarrow \infty; \\ \alpha(q, 0) > 0 \quad \text{for all } q;$$

$$\alpha(q, iu) = \frac{\alpha r_s}{4\pi q^2} \left[2 + \frac{w^2 + 1 - q^2}{2q} \ln \frac{w^2 + (1 + q)^2}{w^2 + (1 - q)^2} \right. \\ \left. - 2w \left(\arctan \frac{1 + q}{w} + \arctan \frac{1 - q}{w} \right) \right], \quad w = u/q.$$

The pair correlation function $g(r)$ has been calculated from the RPA expression for $\epsilon^{-1}(q, u)$, $[1 + \alpha(q, u)]^{-1}$, and from the HF expression, $1 - \alpha(q, u)$ and plotted in Fig. 3. The HF expression is obtained by using a HF wave function in Eq. (45). Both the RPA and the HF

²⁰ It is possible that Eq. (54) will remain valid if surface effects are taken into account. The corresponding contribution to M however tends to zero with increasing number of particles.

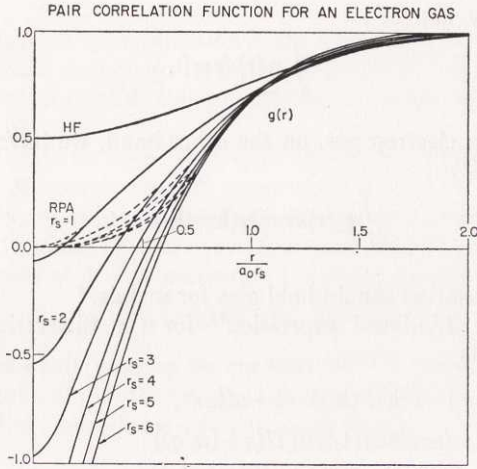


FIG. 3. Pair correlation function for an electron gas.

approximations obey Eq. (50). Since $g(r)$ is a probability it must always be positive but from Fig. 3 we see that the RPA approximation becomes negative^{21,22} for small r . In our calculations however we are not directly interested in $g(r)$ but rather in $r^2g(r)$. In Fig. 4 we see that the influence of the misbehavior of $g(r)$ for small r is suppressed to a large extent by the factor r^2 .

Ueda²³ has calculated $g(r)$ for $r_s = 0.1, 0.5, \text{ and } 1$ using the approximation

$$\epsilon \equiv (1 - P_0v)^{-1} = (1 - P_0v)^{-1} + P_1v, \quad (58)$$

where P_0 is the RPA approximation and P_1 is the next term in the expansion Eq. (12) for P , evaluated with G

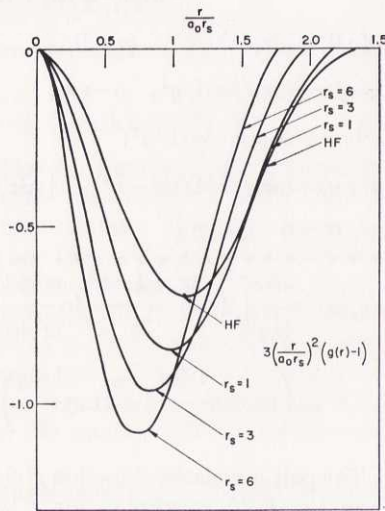


FIG. 4. $3(r/a_0 r_s)^2 \times [g(r) - 1]$. $g(r)$ is the pair correlation function. The area under each curve is equal to -1 .

²¹ A. J. Glick and R. A. Ferrell (Ref. 21) have calculated the RPA approximation of $g(r)$ for $r_s = 2$. They find that $g(0) = -0.15$ while the present calculation gives -0.54 . The quantity $g(0)$ can be written $1 - c \int_0^\infty k^2 f(k) dk$. The reason that their value is in error might be that they fitted $f(k)$ by a Gaussian which underestimates the asymptotic contributions to the integral.

²² A. J. Glick and R. A. Ferrell, *Ann. Physics* **11**, 359 (1960).

²³ S. Ueda, *Progr. Theoret. Phys. (Kyoto)* **26**, 45 (1961).

and W from the RPA approximation. For $r=0$ Eq. (58) gives simply

$$g(0) = 0.5 + 0.5[g^{\text{RPA}}(0) - 0.5], \quad (59)$$

e.g. it gives one half of the RPA correction to HF. Ueda's approximation changes $g(0)$ for $r_s = 1$ and 2 from the RPA values -0.07 and -0.54 to 0.22 ²⁴ and -0.02 and thus Ueda's expression also gives a negative $g(0)$ at metallic densities.

While Eq. (58) is a good approximation for the small values of r_s that Ueda considered, for metallic densities one should rather use

$$\epsilon^{-1} = (1 - P_0v)^{-1} + (1 - P_0v)^{-1} P_1v (1 - P_0v)^{-1}. \quad (60)$$

This expression however can be expected to give an even smaller correction to RPA than does Ueda's. To improve significantly upon RPA it is thus not enough to take $P = P_0 + P_1$ with a simple RPA approximation for G and W .

Considering $P(\mathbf{k}, \epsilon)$ in the limit of small \mathbf{k} , Glick,²⁵ reached the conclusion that one has to take the infinite

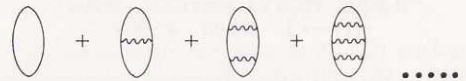


FIG. 5. The ladder-bubble diagrams of Eq. (61).

sum of ladder-bubble diagrams,

$$P = \text{diagrams of Fig. 5}, \quad (61)$$

in order to keep $\text{Im}\epsilon(\mathbf{k}, \epsilon)$ positive for all ϵ . Starting from Ward identities Engelsberg and Schrieffer²⁶ and Lundqvist²⁷ also arrived at Eq. (61) in the cases of electron-phonon and electron-electron interactions, respectively. In Appendices A and B we will argue that the ladder-bubble sum does not give a systematic improvement as far as M and G are concerned. While for the lower metallic densities some infinite summation for P has to be made, for the higher densities it seems more important to explore self-consistent solutions for G to first or perhaps second order in W .

The Coulomb hole $g_0(r)$ has been calculated by Langer and Vosko,²⁸ with the RPA expression for $\epsilon(q, \omega)$. The function $g_0(r)$ is qualitatively similar to $\rho(g(r) - 1)$. It extends over a distance of order $r_s a_0$, obeys Eq. (55) and is finite for $r=0$. The magnitude of $g_0(0)$ is however much larger than ρ , and $g_0(0)$ ranges from -2.20ρ for $r_s = 1.5$ to -6.35ρ for $r_s = 6$. RPA thus predicts that more charge is pushed away, close to the external charge $-e$, than was present at the beginning. This feature

²⁴ Ueda reports a slightly different value, 0.19.

²⁵ A. J. Glick, *Phys. Rev.* **129**, 1399 (1963).

²⁶ S. Engelsberg and J. R. Schrieffer, *Phys. Rev.* **131**, 993 (1963).

²⁷ B. Lundqvist, (unpublished note from Chalmers' University of Technology, Gothenburg, Sweden).

²⁸ J. S. Langer and S. H. Vosko, *J. Phys. Chem. Solids* **12**, 196 (1959).

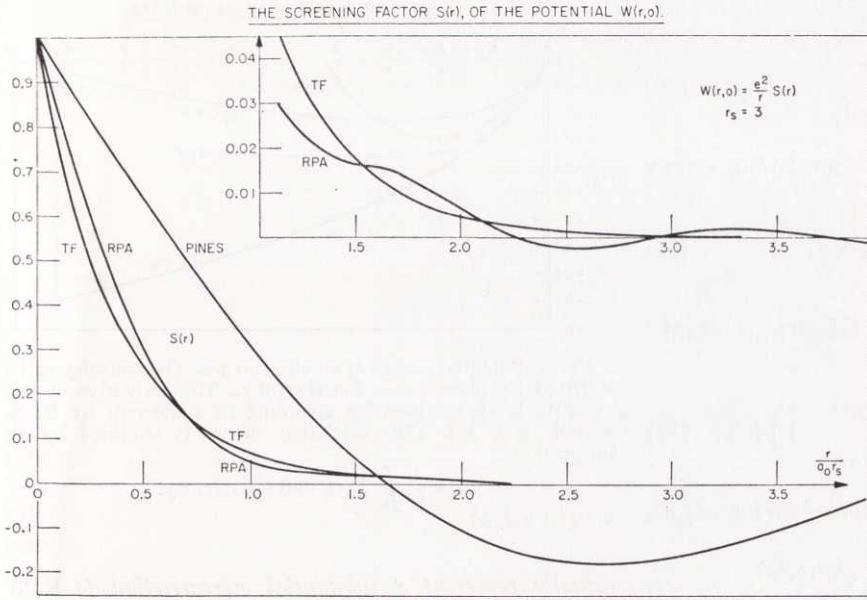


FIG. 6. The screening factor $S(r)$ of the potential $W(r,0)$. $S(r)$ is defined by $W(r,0) = (e^2/r)S(r)$. The curves correspond to $r_s = 3$. The Thomas-Fermi (TF) approximation is $S(r) = e^{-k_e r}$, where $k_e = 0.815r_s^{1/2}k_0$. The Pines' expression (Ref. 30) is given in Eq. (63).

might be true also for the correct $g_0(r)$ since it is defined from a linear response expression.

The behavior of $g_0(r)$ for small r has however relatively small influence on $W(r,0) = (e^2/r)S(r)$,

$$S(r) = -4\pi \int_r^\infty r'(r'-r)g_0(r')dr', \quad (62)$$

as can be seen in Fig. 6 where the Thomas-Fermi (TF) and the RPA results^{29,30} for $S(r)$ are plotted for $r_s = 3$. The TF g_0 tends to infinity for small r but still the TF S threads the RPA S quite well. As a comparison we have also plotted Pines' expression,³¹

$$S(r) = 1 - (2/\pi)Si(x), \quad x = k_e r, \quad k_e = 0.353r_s^{1/2}k_0, \quad (63)$$

$$Si(x) = \int_0^x \frac{\sin t}{t} dt,$$

which is quite different from the two others.

The HF expression for ϵ , namely, $\epsilon^{-1}(q,u) = 1 - \alpha(q,u)$, gives a reasonable result for $r=0$:

$$g_0(0) = -\frac{3}{2}\pi\alpha r_s \rho, \quad (64)$$

but predicts a completely wrong asymptotic behavior,

$$g_0(r) = -3\alpha^2 r_s (a_0 r_s / r) \rho; \quad r \rightarrow \infty, \quad (65)$$

which makes the integral in Eq. (55) divergent.

²⁹ $S(r)$ has also been calculated by March and Murray (Ref. 30) by a rather complicated method. The results for $S(r)$ as obtained from Langer and Vosko's densities (Ref. 28) using Eq. (62) agree within 0.1% with those of March and Murray's for $r_s = 1.5$. Other r_s values cannot be accurately checked since they lie far from those used by Langer and Vosko.

³⁰ N. H. March and A. M. Murray, Proc. Roy. Soc. **A261**, 119 (1961).

³¹ D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 387.

8. ELECTRON GAS: THE TOTAL ENERGY

Our primary interest in this paper is to calculate the electron self energy M . By considering the total energy we can obtain an estimate of the error in $\mu = (h^2 k_0^2 / 2m) + M(\mathbf{k}_0, \mu)$. The relations between ϵ , the energy per particle, and μ are³²

$$\mu = \epsilon - \frac{1}{3}r_s(d\epsilon/dr_s),$$

$$\epsilon = 3r_s^3 \int_{r_s}^\infty \frac{\mu(x)}{x^4} dx. \quad (66)$$

The curve $\epsilon(r_s)$ has its minimum in the neighborhood of $r_s = 4$ and here an error in ϵ gives essentially the same error in μ .

To calculate $\epsilon(r_s)$ we use the virial theorem for an electron gas³³:

$$V + 2T + r_s(d\epsilon/dr_s) = 0, \quad (67)$$

where V and T are the expectation values of the potential and kinetic energies divided by the number of particles. Solving Eq. (67), we have, considering V to be expressed in rydbergs,

$$\epsilon = \frac{1}{r_s^2} \left[A + \int_0^{r_s} xV(x)dx \right] \text{Ry}. \quad (68)$$

From the known behavior³⁴ of ϵ for small r_s we infer that the integration constant A is

$$A = 3/5\alpha^2 = 2.2099. \quad (69)$$

³² F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 343; J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

³³ N. H. March, Phys. Rev. **110**, 604 (1958).

³⁴ M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

For convenience we write $V(r_s)$ as

$$V(r_s) = (1/r_s)(V_{\text{corr}} - B) \quad (70)$$

$$B = 3/2\pi\alpha = 0.9163,$$

which allows us to express the correlation energy $\epsilon_c = \epsilon - \epsilon^{\text{HF}}$ as

$$\epsilon_c = \frac{1}{r_s^2} \int_0^{r_s} V_{\text{corr}}(x) dx \text{ Ry.} \quad (71)$$

V_{corr} can be calculated from the dielectric constant³⁵ $1 + \alpha(q, u)$:

$$V_{\text{corr}} = \frac{4}{\pi\alpha} \int_0^\infty dq \left(\frac{6}{\alpha r_s} \int_0^\infty du \frac{q^2 \alpha(q, iu)}{1 + \alpha(q, iu)} - 1 \right) + B, \quad (72)$$

which, when we use the RPA expression for $\alpha(q, u)$, becomes

$$V_{\text{corr}} = -\frac{24}{\pi\alpha^2 r_s} \int_0^\infty dq \int_0^\infty du \frac{q^2 \alpha^2(q, iu)}{1 + \alpha(q, iu)}. \quad (73)$$

From a general theorem given by Ferrell³⁶ we can deduce a restriction on V_{corr} . Ferrell proved that

$$\partial^2 \epsilon / \partial (e^2)^2 \leq 0 \text{ at constant density,} \quad (74)$$

where e is the electron charge. From the relation $\alpha(\hbar^2/m)(3\pi^2\rho)^{1/3}r_s = e^2$, we see that r_s is proportional to e^2 when the density is kept constant. The factor $1/r_s^2 \text{ Ry} = (1/r_s^2)(me^4/2\hbar^2)$ in Eq. (68) then becomes independent of e^2 and the Ferrell condition, Eq. (74), can be written

$$\frac{d^2}{dr_s^2} \left\{ A + \int_0^{r_s} [V_{\text{corr}}(x) - B] dx \right\} = \frac{d}{dr_s} V_{\text{corr}}(r_s) \leq 0. \quad (75)$$

In Fig. 7 we have plotted different expressions for V_{corr} . The series expansion in r_s is taken from Carr and Maradudin³⁷:

$$\epsilon_c = 0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s - 0.036 r_s, \quad (76)$$

$$V_{\text{corr}} = d(r_s^2 \epsilon_c) / dr_s = r_s (0.1244 \ln r_s - 0.130 + 0.054 r_s \ln r_s - 0.090 r_s).$$

This V_{corr} violates Eq. (75) from $r_s \approx 2$. The RPA expression for V_{corr} satisfies Eq. (75) at least up to $r_s = 100$. The contribution to ϵ_c from exchange of second order in v has been calculated by Gell-Mann and Brueckner.³⁴ They obtain the value 0.046 Ry which gives a contribution of $0.092 r_s$ to V_{corr} . When this is added to RPA, the Ferrell condition becomes violated from $r_s \approx 3$ (see Fig. 7). *The unscreened second-order exchange terms*

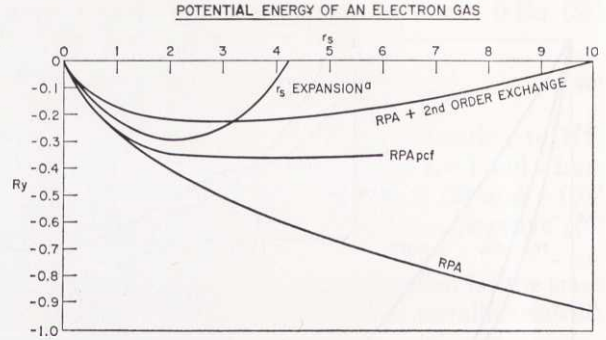


FIG. 7. Potential energy of an electron gas. The quantity $r_s(V) + 0.9163 \text{ Ry}$ plotted as a function of r_s . The derivative of this quantity is always negative according to a theorem by R. A. Ferrell (Ref. 35). The correlation energy is obtained by an integration,

$$\epsilon_c = \frac{1}{r_s^2} \int_0^{r_s} (r_s(V) + 0.9163) dr_s \text{ Ry.}$$

See also Ref. 37.

actually represent a substantial overcorrection to RPA already at $r_s = 1$, as can be seen by comparing with the r_s expansion.

V_{corr} can also be calculated from the pair correlation function $g(r)$,

$$V_{\text{corr}} = \frac{1}{3\pi\alpha} \int_0^\infty x [g^{\text{RPA}}(x) - g^{\text{HF}}(x)] dx; \quad x = 2k_0 r. \quad (77)$$

As a check on the numerical accuracy of g^{RPA} , Eq. (77) was evaluated and found to give the same result as Eq. (73) within a few percent. Since the $g^{\text{RPA}}(r)$ curves violate the condition $g^{\text{RPA}} > 0$, for small r , they were smoothly extrapolated to zero (dashed curves in Fig. 3). *These extrapolated curves were then used in Eq. (77) and the result plotted in Fig. 7 with the label RPA_{pcf}.* Since the correct g lies above g^{RPA} for small r it has to lie below g^{RPA} for some regions of r in order to satisfy the normalization condition. If the correct g were zero for $r = 0$ the RPA_{pcf} V_{corr} would give a rough upper bound to the correct V_{corr} . At metallic densities the dashed curves in Fig. 3 lie so much above the g^{RPA} curves that a further small shift will make relatively little change in V_{corr} . We conclude that, at metallic densities, the RPA_{pcf} V_{corr} is a rough upper bound to the correct V_{corr} .

In Fig. 8 the total energy is plotted as calculated from Eq. (71) using the values for V_{corr} given in Fig. 7. For comparison the HF energy and the energy of the Wigner-type electron lattice³⁸ are also plotted. We note that while the extrapolation of the g curves looks drastic, the difference between the RPA and the RPA_{pcf} curves for the total energy is fairly small even though the energy calculation involves $rg(r)$ and not $r^2g(r)$, cf. Fig. 4 and the discussion of the correlation hole in Sec. 7.

The phase transition where the electrons cease to be

³⁵ P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958).

³⁶ R. A. Ferrell, Phys. Rev. Letters **1**, 443 (1958).

³⁷ W. J. Carr, Jr. and A. A. Maradudin, Phys. Rev. **A133**, 371 (1964).

³⁸ W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961).

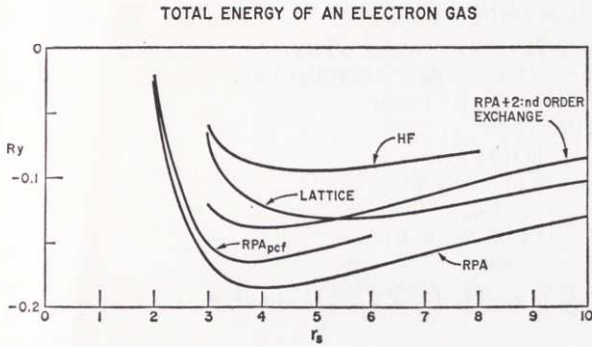


FIG. 8. Total energy of an electron gas. The energy of the electron lattice is taken from Ref. 38.

itinerant and form a lattice has been estimated by de Wette³⁹ to occur between $r_s \approx 47$ and $r_s \approx 100$. From a calculation to finite order in W we expect to find a smooth energy curve, which, if carried to high enough order in W , will cross the energy curve corresponding to electrons on a Wigner lattice. The RPA curve for the total energy lies below the lattice curve at least up to $r_s = 100$. This gives additional evidence, besides the fact that the second-order term in ϵ is positive, that RPA gives a lower bound to the energy. It is indeed hard to imagine that any reasonable curve for V_{corr} which starts out as the series expansion, has a negative slope, and never goes below -0.876 Ry, could lie lower than the RPA curve. The limit -0.876 Ry is set by the fact that the lattice energy goes asymptotically as $-1.792/r_s$ and the HF energy as $-0.916/r_s$.

If we extrapolate the RPA_{pcf} curve for V_{corr} , Fig. 7, with a horizontal line starting at the minimum, the corresponding curve for the total energy will cross the lattice curve at $r_s \approx 11$. This gives further evidence that the RPA_{pcf} curve is an upper bound to the energy. The RPA_{pcf} total energy actually comes quite close to the results of a calculation by Gaskell.⁴⁰ His curve lies 0.003 Ry above and 0.007 Ry below the RPA_{pcf} curve at $r_s = 3$ and $r_s = 5$, respectively. Gaskell made a variational calculation with an antisymmetrized product of pair functions, but due to an additional approximation his results do not quite give a rigorous upper bound for the energy. From all evidence taken together we estimate that *the error in the RPA approximation for the energy ϵ is positive and at most 0.02 Ry.*

We now return to the question of estimating the error in the chemical potential μ . Equation (66) relates the exact ϵ to the exact μ and within the numerical accuracy of our calculations, ± 0.0005 Ry, it holds also for ϵ calculated from Eq. (71) and μ calculated from $M = iGW[P = -iGG, G$ according to Eq. (41)]. If for the error in the energy $\Delta\epsilon$, we use the difference between RPA_{pcf} and RPA, we find that the term $\frac{1}{3}r_s d\Delta\epsilon/dr_s$ is small compared to $\Delta\epsilon$ at metallic densities.

We estimate that *the error in the RPA approximation for the chemical potential μ is positive and at most 0.02 Ry.*

To further investigate the convergence properties of the expansion for M , Eq. (24), we consider the second-order term. While the first-order term is given by a four-dimensional integral, which easily can be reduced to a two-dimensional integral, the second-order term is given by an eight-dimensional integral which is difficult to reduce to less than a seven-dimensional one. As we discussed in Sec. 5, a rough value can however be obtained by using the static potential $W(\mathbf{k}, 0)$ instead of the full potential $W(\mathbf{k}, \epsilon)$. The second-order term then becomes

$$M^{(2)}(k, u) = \frac{1}{\pi^4} \int \frac{d\mathbf{k}_1 d\mathbf{k}_2}{\mathbf{k}_1^2 \mathbf{k}_2^2 \epsilon(\mathbf{k}_1, 0) \epsilon(\mathbf{k}_2, 0) (k^2 - u - 2\mathbf{k}_1 \cdot \mathbf{k}_2)} \text{Ry}, \quad (78)$$

where the integral is taken over the regions

$$\begin{aligned} |\mathbf{k} + \mathbf{k}_1| &\leq 0.5 & |\mathbf{k} + \mathbf{k}_1| &\geq 0.5 \\ |\mathbf{k} + \mathbf{k}_2| &\leq 0.5 & \text{and} & |\mathbf{k} + \mathbf{k}_2| &\geq 0.5 \\ |\mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2| &\geq 0.5 & |\mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2| &\leq 0.5, \end{aligned}$$

and the \mathbf{k} 's are expressed in units of twice the Fermi momentum and u in units of $(4\hbar^2 k_0^2/2m)$. One angular integration is trivial but there still remains a five-dimensional integral. For the particular case of $k=0$, $u=0$, Eq. (78) can however be reduced to a double integral,

$$M^{(2)}(0, 0) = \frac{8}{\pi^2} \int \frac{dk_1 dk_2 \text{sgn}(k_1 - 0.5)}{\epsilon(k_1, 0) \epsilon(k_2, 0) k_1 k_2} \times \ln \left| \frac{2k_1 k_2}{0.25 - k_1^2 - k_2^2} \right| \text{Ry}, \quad (79)$$

over the regions

$$0 \leq k_1 - k_2 \leq 0.5, \quad \text{and} \quad k_1 + k_2 \geq 0.5.$$

This integral was evaluated using a TF-dielectric constant:

$$\epsilon(k, 0) = 1 + (\alpha r_s / \pi)(1/k^2), \quad (80)$$

which is good enough for the present discussion. $M^{(2)}(0, 0)$ was found to vary slowly with r_s at metallic densities, reaching a maximum of 0.014 Ry at $r_s \approx 3$. From values of $(d/dk)M^{(2)}(k, (\hbar^2 k^2/2m))_{k=k_0}$, Sec. 10, we estimate that $\mu^{(2)} = M^{(2)}(k_0, (\hbar^2 k_0^2/2m))$ is about 0.02–0.04 Ry i.e. of about the same size as the error in the first-order contribution $\mu^{(1)}$. It should be realized that while the preceding discussion suggests a very good convergence of the expansion of μ in terms of W , an accurate value of μ cannot be obtained by just adding $\mu^{(2)}$ to μ^{RPA} since the $\mu^{(1)}$ which corresponds to a self-consistent solution for G might well differ from μ^{RPA} by an amount comparable to $\mu^{(2)}$.

In the calculation of the energy we have assumed that

³⁹ F. W. de Wette, Phys. Rev. **135**, A287 (1964).

⁴⁰ T. Gaskell, Proc. Phys. Soc. **77**, 1182 (1961); **80**, 1091 (1962).

TABLE II. Energies of an electron gas in rydbergs.

T_0 = Kinetic Energy in the HF approx. = $(3/5\alpha^2 r_s^2)$ Ry = $(2.2099/r_s^2)$ Ry.
 ϵ_{exch} = Potential Energy in the HF approx. = $-(3/2\pi\alpha r_s)$ Ry = $-(0.9163/r_s)$ Ry.
 $\epsilon_{\text{corr}}^{\text{RPA}}$ = Correlation energy in the RPA = Total energy - HF energy.
 $\epsilon_{\text{corr}}^{\text{a}}$ = $0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s - 0.036 r_s$.
 T = Expectation value of the kinetic energy in the RPA.
 V = Expectation value of the potential energy in the RPA.
 ϵ = Total energy in the RPA = $T + V = T_0 + \epsilon_{\text{exch}} + \epsilon_{\text{corr}}^{\text{RPA}}$.
 ϵ_{Ferr} = Total energy of the Ferro-magnetic state according to RPA.
 $\epsilon_{\text{Latt}}^{\text{b}}$ = Energy of the Wigner type lattice of electrons
 $= -\frac{1.792}{r_s} + \frac{2.65}{r_s^{3/2}} - \frac{0.73}{r_s^2} + \left(\frac{21}{r_s} - \frac{4.8}{r_s^{3/4}} - \frac{1.16}{r_s^{5/4}}\right) e^{-2.06 r_s^{1/2}} - \left(\frac{2.06}{r_s^{5/4}} - \frac{0.66}{r_s^{7/4}}\right) e^{-1.55 r_s^{1/2}}$.
 The energies are accurate to ± 0.0005 Ry.

| r_s | T_0 | ϵ_{exch} | $\epsilon_{\text{corr}}^{\text{RPA}}$ | $\epsilon_{\text{corr}}^{\text{a}}$ | T | V | ϵ | ϵ_{Ferr} | $\epsilon_{\text{Latt}}^{\text{b}}$ |
|-------|--------|--------------------------|---------------------------------------|-------------------------------------|--------|---------|------------|--------------------------|-------------------------------------|
| 1 | 2.2099 | -0.9163 | -0.1578 | -0.132 | 2.3161 | -1.1803 | 1.1358 | 2.2502 | 1.49 |
| 2 | 0.5525 | -0.4582 | -0.1238 | -0.100 | 0.6299 | -0.6594 | -0.0295 | 0.2150 | 0.173 |
| 3 | 0.2455 | -0.3054 | -0.1058 | -0.076 | 0.3083 | -0.4740 | -0.1657 | -0.0695 | -0.067 |
| 4 | 0.1381 | -0.2291 | -0.0938 | -0.054 | 0.1920 | -0.3767 | -0.1847 | -0.1367 | -0.122 |
| 5 | 0.0884 | -0.1833 | -0.0851 | -0.031 | 0.1359 | -0.3158 | -0.1799 | -0.1526 | -0.131 |
| 6 | 0.0614 | -0.1527 | -0.0784 | -0.007 | 0.1040 | -0.2737 | -0.1697 | -0.1534 | -0.130 |
| 7 | 0.0451 | -0.1309 | -0.0730 | +0.018 | 0.0839 | -0.2427 | -0.1588 | -0.1482 | -0.128 |
| 8 | 0.0345 | -0.1145 | -0.0685 | | 0.0703 | -0.2188 | -0.1485 | -0.1413 | -0.118 |
| 9 | 0.0273 | -0.1018 | -0.0647 | | 0.0606 | -0.1998 | -0.1392 | -0.1344 | -0.110 |
| 10 | 0.0221 | -0.0916 | -0.0615 | | 0.0532 | -0.1842 | -0.1310 | -0.1274 | -0.103 |

^a W. J. Carr, Jr., and A. A. Maradudin, Phys. Rev. 133, A371 (1964).

^b W. J. Carr, Jr., R. A. Coldwell-Horsfall, and A. E. Fein, Phys. Rev. 124, 747 (1961).

the ground state is paramagnetic. To obtain the energy of the ferromagnetic state we have to use a Green's function which is zero for, say, spin down and for spin up has a Fermi momentum⁴¹

$$k_0^F = \beta k_0; \quad \beta = 2^{1/3}; \quad k_0 = (\alpha a_0 r_s)^{-1}. \quad (81)$$

As is well known the HF expression for the energy of the ferromagnetic state is, in Rydbergs,

$$\epsilon^F = \beta^2 (3/5\alpha^2 r_s^2) - \beta (3/2\pi\alpha r_s), \quad (82)$$

which lies below the energy of the paramagnetic state for $r_s \geq 5.45$. In RPA we have the simple relation for the correlation energy

$$\epsilon_c^F(r_s) = \frac{1}{2} \epsilon_c^P(r_s \beta^{-4}). \quad (83)$$

To see that we introduce dimensionless variables as in Eq. (56) but with k_0 replaced by k_0^F . From Eq. (24) we then find for the dielectric constant

$$\epsilon^F(q, u; r_s) = \epsilon^P(q, u; r_s \beta^{-4}), \quad (84)$$

and from Eq. (73)

$$V_{\text{corr}}^F(r_s) = \beta V_{\text{corr}}^P(r_s \beta^{-4}). \quad (85)$$

Substituting Eq. (85) into Eq. (71) finally gives Eq. (83). We note that Eq. (84) is not valid if we include higher terms in $P(\mathbf{k}, \epsilon)$, Eq. (24), or if we use a self-consistent G .

Table II gives the values of the energy for the ferro-

magnetic state in the RPA as obtained from Eqs. (82) and (83). We see that ϵ^F lies above ϵ^P (given under the heading ϵ in Table II) and approaches it asymptotically. At $r_s = 10$ the difference between the energies is only 3% of their magnitude. This is a reasonable result since the influence of spin orientation has to vanish when the density tends to zero. The present results do not quite rule out the possibility that the electron gas should become ferromagnetic at some density since we know that the RPA value for $\epsilon^P(r_s)$ lies too low. On the other hand, $\epsilon^F(r_s)$ is also too low but perhaps less so since according to Eq. (83) the error in ϵ_c^F is only half the error in ϵ_c^P . It seems safe to predict that *the electron gas does not become ferromagnetic for $r_s < 7$.*

The numbers in Table II not discussed so far are self explanatory. We only note that the series expansion for ϵ_{corr} rapidly becomes bad for $r_s > 3$ and that our values for $\epsilon_{\text{corr}}^{\text{RPA}}$ do not quite coincide with Hubbard's, his values⁴² being between 0.002 and 0.004 Ry higher than ours.

9. ELECTRON GAS: THE M OPERATOR

The M operator was calculated from the equation

$$M(\mathbf{k}, \epsilon) = \frac{i}{(2\pi)^4} \int \frac{v(\mathbf{k}') d\mathbf{k}'}{\epsilon(\mathbf{k}', \epsilon')} \frac{e^{-i\Delta\epsilon'} d\epsilon'}{\epsilon - \epsilon' - \epsilon(\mathbf{k} - \mathbf{k}')}, \quad (86)$$

cf. Eqs. (24), (41), and (56). The contour for ϵ' runs just below the real axis for $\epsilon' < 0$ and just above for $\epsilon' > 0$.

⁴¹ Superscript $F(P)$ here refers to the ferromagnetic (paramagnetic) state.

⁴² J. Hubbard, Proc. Roy. Soc. A243, 336 (1957).

We first separate out the HF term:

$$W(\mathbf{k}, \epsilon) e^{-i\epsilon\Delta} = \frac{v(\mathbf{k})}{\epsilon(\mathbf{k}, \epsilon)} e^{-i\epsilon\Delta} = v(\mathbf{k}) e^{-i\epsilon\Delta} + v(\mathbf{k}) \left(\frac{1}{\epsilon(\mathbf{k}, \epsilon)} - 1 \right). \quad (87)$$

Since, according to Eq. (57), $(1/\epsilon(q, u)) - 1$ tends to zero as $|u|^{-2}$ for large $|u|$, the convergence factor $e^{-i\epsilon\Delta}$ has been omitted in the last term of Eq. (87). We then separate out the static approximation of the last term in Eq. (87), cf. Sec. 5,

$$W(\mathbf{k}, \epsilon) e^{-i\epsilon\Delta} = v(\mathbf{k}) e^{-i\epsilon\Delta} + v(\mathbf{k}) \left(\frac{1}{\epsilon(\mathbf{k}, 0)} - 1 \right) + v(\mathbf{k}) \left(\frac{1}{\epsilon(\mathbf{k}, \epsilon)} - \frac{1}{\epsilon(\mathbf{k}, 0)} \right). \quad (88)$$

The contributions to $M(q, u)$ from the first two terms of Eq. (88) are easily evaluated by closing the contour for ϵ' in Eq. (86) in the lower half-plane, giving the Coulomb hole plus screened exchange terms,

$$M^c = \frac{4}{\pi\alpha r_s} \int_0^\infty \left(\frac{1}{\epsilon(q', 0)} - 1 \right) dq' - \frac{4}{\pi\alpha r_s} \int_{-1}^1 d\xi \int_0^\infty dq' \frac{\theta(0.25 - q^2 - q'^2 - 2qq'\xi)}{\epsilon(q', 0)} \text{Ry}. \quad (89)$$

To evaluate the contribution from the last term of Eq. (88) we follow Quinn and Ferrell⁴³ and turn the contour of ϵ' in Eq. (86) to run along the imaginary axis. We pick up a contribution from the poles of the Green's function,

$$M^p = \frac{4}{\pi\alpha r_s} \int_{-1}^1 d\xi \int_0^\infty dq' \left(\frac{1}{\epsilon(q', u - \epsilon(\mathbf{q} - \mathbf{q}'))} - \frac{1}{\epsilon(q', 0)} \right) \times [\theta(u - \epsilon(\mathbf{q} - \mathbf{q}')) - \theta(0.25 - \epsilon(\mathbf{q} - \mathbf{q}'))] \text{Ry}; \quad \xi = \mathbf{q} \cdot \mathbf{q}' / (qq'), \quad (90)$$

as well as the contribution from integrating ϵ' along the imaginary axis,

$$M^r = \frac{1}{\pi^2\alpha r_s} \int_0^\infty du' \int_0^\infty dq' \left(\frac{1}{\epsilon(q', iu')} - \frac{1}{\epsilon(q', 0)} \right) \times \frac{1}{qq'} \ln \frac{(u - (q + q')^2) + u'^2}{(u - (q - q')^2) + u'^2} \text{Ry}. \quad (91)$$

We thus have

$$M(q, u) = M^c(q) + M^p(q, u) + M^r(q, u). \quad (92)$$

TABLE III. The Fermi energy for an electron gas, $T+M$, in rydbergs.

| r_s | T | M^{HF} | M^{RPA} | M^a | M^b | M^c |
|-------|--------|-----------------|------------------|---------|---------|---------|
| 1 | 3.6832 | -1.2218 | -1.3965 | -1.8327 | -0.4541 | -1.6267 |
| 2 | 0.9208 | -0.6109 | -0.7491 | -0.9164 | -0.1639 | -0.9137 |
| 3 | 0.4092 | -0.4073 | -0.5259 | -0.6110 | -0.0870 | -0.6577 |
| 4 | 0.2302 | -0.3054 | -0.4112 | -0.4581 | -0.0546 | -0.5224 |
| 5 | 0.1473 | -0.2444 | -0.3406 | -0.3666 | -0.0377 | -0.4375 |
| 6 | 0.1023 | -0.2036 | -0.2926 | -0.3054 | -0.0277 | -0.3787 |
| 7 | 0.0752 | -0.1745 | -0.2575 | -0.2618 | -0.0212 | -0.3354 |
| 8 | 0.0576 | -0.1527 | -0.2308 | -0.2291 | -0.0168 | -0.3019 |
| 9 | 0.0455 | -0.1358 | -0.2097 | -0.2037 | -0.0136 | -0.2753 |
| 10 | 0.0368 | -0.1222 | -0.1925 | -0.1833 | -0.0113 | -0.2535 |

^a The Slater approximation = 1.5 M^{HF} .
^b Screened exchange potential.
^c Screened exchange potential plus Coulomb hole contribution.

M^c and M^r are real and the imaginary part of M comes solely from M^p . For $u=0.25$ ($\epsilon = \hbar^2 k_0^2 / 2m$), M^p is zero as well as its first derivatives with respect to q and u . The real part of $M^p(q, q^2)$ is small. It decreases monotonically from about 0.01 Ry at $q=0$ to 0 at $q=0.5$, except for $r_s=1$ when it has a maximum of 0.02 Ry at $q=0.2$. The imaginary part of $M^p(q, q^2)$ is larger as can be seen from Table IV under the heading M_2 . It decreases monotonically from values of the order 0.1 Ry at $q=0$ to zero at $q=0.5$. The derivatives of $\text{Re}M^p(q, u)$ with respect to u are 10% or less of the derivative of $M(q, u)$ for $0.5 \geq q \geq 0.2$, but increase rapidly for smaller q .

The first term in $M^c(q)$, the Coulomb hole contribution, is independent of q . The second term in $M^c(q)$, the screened exchange contribution, is substantially smaller than the HF exchange term as can be seen from Table III. Comparing M^c with M^{RPA} in Table III, we can see that M^c has too large a magnitude and that the Slater approximation,⁴⁴ which consists of an average of M^{HF} over the Fermi sphere, actually is better.

M^r can conveniently be split into three parts. The first part consists of contributions from integrating u' between 0 and 0.25 in Eq. (91). The second and third parts come from the integration over $u' > 0.25$ and the following division:

$$\frac{1}{\epsilon(q', iu')} - \frac{1}{\epsilon(q', 0)} = \left(\frac{1}{\epsilon(q', iu')} - 1 \right) + \left(1 - \frac{1}{\epsilon(q', 0)} \right). \quad (93)$$

In the third part, i.e., the second term of Eq. (93), the integration over u' can be made analytically,

$$M^{rm}(q, u) = \frac{1}{2\pi^2\alpha r_s} \int_0^\infty dq' \left(1 - \frac{1}{\epsilon(q', 0)} \right) \times \frac{1}{qq'} \left(a \arctan(a) - b \arctan(b) - \frac{1}{2} \ln \frac{1+a^2}{1+b^2} \right) \text{Ry}; \quad a = 4((q+q')^2 - u), \quad b = 4((q-q')^2 - u). \quad (94)$$

⁴³ J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

⁴⁴ J. C. Slater, Phys. Rev. **81**, 385 (1951).

M^{rm} gives the main part of M^r , being about three times as large as each of the first two parts with respect both to magnitude and derivatives. The essential contribution to the first part of M^r comes from $q' < 0.8$, and to the second part from $q' < 2.4$, $u' < 3$, the remaining contributions being small and practically independent of q , u , and r_s .

M^c is easily evaluated since the integration over ξ in Eq. (89) can be made analytically. In evaluating M^r we have the advantage that $\epsilon(q, iu)$ is much more well behaved than $\epsilon(q, u)$. From Eq. (57) we see that $\alpha(q, iu)$ only has three singular points, $u=0$, $q=0$, ± 1 , while $\alpha(q, u)$ is singular along the lines $(q \pm (u/q)) = \pm 1$. The evaluation of M^p involves $\alpha(q, u)$ but fortunately M^p is small and the relative accuracy does not have to be pushed so far.

The integrals were evaluated for

$$\begin{aligned} q=0, & & u=\pm 0.01; \\ q=0.1, 0.2, 0.3, 0.4, & & u=q^2, (q+0.1)^2; \\ q=0.5, 0.6, 0.7, & & u=q^2, (q-0.1)^2. \end{aligned}$$

The results are given in Table IV. The values of M for $u \neq q^2$ are not given directly but in the form

$$z^{-1}(q) = 1 - \Delta M / \Delta \epsilon. \quad (95)$$

For $q=0$ we have given the average of the results for $u = \pm 0.01$. To estimate how well z approximates the limit when $\Delta \epsilon \rightarrow 0$, we compare the values of $\text{Re} z^{-1}$ for $q=0.4, 0.5$, and 0.6 . They agree to about two decimal places which, in conjunction with the fact that $M(q, q^2)$ is almost linear for these q values, shows that $M(q, u)$ can be represented fairly well by a linear expression in q and u for $|q-0.5| < 0.1$ and $|u-0.25| < 0.1$, unless the $M(q, u)$ surface has an anomalous behavior for $u < q^2$, $q < 0.5$ and $u > q^2$, $q \geq 0.5$. To check $\text{Im} z^{-1}$ we note that for u close to 0.25 we have from general arguments¹²

$$M_2(q, u) = C_q (u - 0.25)^2 \text{sgn}(0.25 - u). \quad (96)$$

The values of C_q for $q=0.4$ and 0.6 deviate by about 20% from those for $q=0.5$. We can also check Z at $q=0$ where the calculations were made for three values of u . The values of $\text{Im} z^{-1}$ agree within a few percent while the values for $\text{Re}(z^{-1} - 1)$ deviate from their mean value by 20%, 29% and 65% at $r_s = 1, 4$, and 6 , respectively. We conclude that $M_1(0, u)$ varies very rapidly with u and that our value for $\text{Re} z^{-1}$ is not very reliable when q is small.

To solve Dyson's equation for the quasiparticle energies we expand

$$\begin{aligned} \epsilon = \epsilon(\mathbf{k}) + M(\mathbf{k}, \epsilon - \epsilon_0) &= \epsilon(\mathbf{k}) + M(\mathbf{k}, \epsilon(\mathbf{k})) \\ &+ (\epsilon - \epsilon_0 - \epsilon(\mathbf{k})) [\partial M(\mathbf{k}, \epsilon(\mathbf{k})) / \partial \epsilon], \end{aligned}$$

giving the solution for ϵ

$$\epsilon = \epsilon_0 + \epsilon(\mathbf{k}) + [M(\mathbf{k}, \epsilon(\mathbf{k})) - \epsilon_0] / [1 - \partial M(\mathbf{k}, \epsilon(\mathbf{k})) / \partial \epsilon], \quad (97)$$

where from Eq. (42)

$$\epsilon_0 = M(\mathbf{k}_0, \epsilon(\mathbf{k}_0)) = \mu - \epsilon(\mathbf{k}_0).$$

We note that Eq. (97), owing to the ϵ_0 in the denominator of our G_0 , is different from the corresponding equation used by DuBois⁵¹

$$\epsilon = \epsilon(\mathbf{k}) + M(\mathbf{k}, \epsilon(k))(1 + \partial M / \partial \epsilon).$$

In particular the cancellations mentioned by him between $M^{(1)} \partial M^{(1)} / \partial \epsilon$ and the noncrossed second order term of $M^{(2)}$ are taken into account in Eq. (97), cf. Sec. 6. The real and imaginary parts of the last term in Eq. (97) are given in Table IV under the headings E_1 and E_2 . In Table IV we have also given the screened exchange approximation MS and Pines' approximation MP. We see that the difference between E_1 and MS is substantial; they even have opposite signs for $r_s > 1$. Both E_1 and MS have a weak \mathbf{k} dependence compared to MP. This is also illustrated in Fig. 9.⁴⁵ The almost horizontal curves give $E_1 + \epsilon_0$ and the dashed curves give Pines' approximation. For comparison the kinetic energy $\epsilon(\mathbf{k})$ and the Hartree-Fock approximation for M are also drawn. The infinite slope of the HF curve at $\mathbf{k} = \mathbf{k}_0$ is barely noticeable, owing to the weakness of a logarithmic singularity.

We note that the HF energies deviate from the true

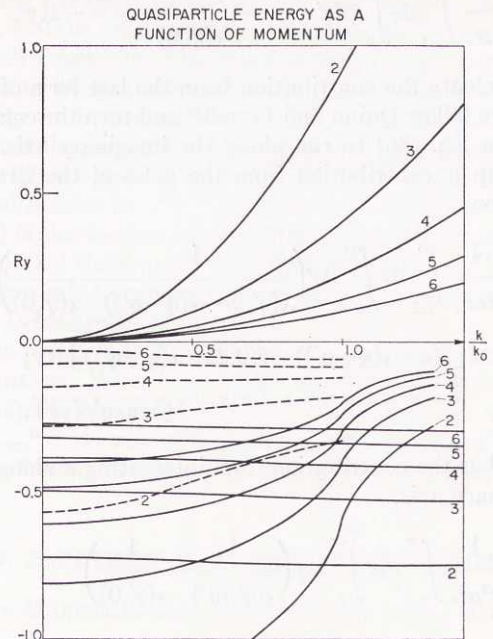


FIG. 9. Quasiparticle energy as a function of momentum. Above the axis: Free-particle part $= (\hbar^2 k^2 / 2m)$. Below the axis: Exchange and correlation part. Dashed curve: Pines' approximation (Ref. 45). Curves with infinite slope at $\mathbf{k} = \mathbf{k}_0$: HF. Almost flat curves: E_1 in Table IV. The r_s value is indicated for each curve.

⁴⁵ D. Pines, Ref. 31, p. 407. The value of β in his Eq. (8.1) is taken as $\beta = 0.375 r_s^{1/2}$. This is the value used by V. Heine, Proc. Roy. Soc. (London) A240, 340 (1957) in his calculation on Al.

TABLE IV. Quasiparticle energy in the momentum representation.

The full quasiparticle energy $= \epsilon(\mathbf{k}) + M(\mathbf{k}_0, \epsilon(\mathbf{k}_0)) + \text{tabulated quantity}$, where $\epsilon(\mathbf{k})$ is the kinetic energy, ($\hbar^2 \mathbf{k}^2 / 2m$). The energies in the table are expressed in rydbergs. The Fermi momentum is $|\mathbf{k}_0|$.

$$M = M(\mathbf{k}, \epsilon(\mathbf{k})) - M(\mathbf{k}_0, \epsilon(\mathbf{k}_0)); M \text{ in the RPA}$$

$$Z^{-1} = 1 - \partial M(\mathbf{k}, \epsilon(\mathbf{k})) / \partial \epsilon; M \text{ in the RPA}$$

$$E = MZ$$

$$MS = M(\mathbf{k}) - M(\mathbf{k}_0); M \text{ from a screened exchange potential}$$

$$MP = M(\mathbf{k}) - M(\mathbf{k}_0); M \text{ from Pines' approximation}^a \text{ with}$$

$\beta = 0.375r_s^{1/2}$. This is essentially the same β value as used by V. Heine^b in his paper on the band structure of Al.

| r_s | | $k/k_0=0$ | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | |
|-------------|-------------|-----------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1 | M_1 | -0.1286 | -0.1232 | -0.1014 | -0.0735 | -0.0428 | 0 | +0.0407 | 0.0459 | |
| | M_2 | 0.2323 | 0.2130 | 0.1608 | 0.0910 | 0.0284 | 0 | -0.0279 | -0.0948 | |
| | Re Z^{-1} | 1.270 | 1.241 | 1.216 | 1.193 | 1.168 | 1.164 | 1.142 | 1.151 | |
| | Im Z^{-1} | 0.186 | 0.150 | 0.108 | 0.064 | 0.021 | 0 | 0.017 | 0.040 | |
| | E_1 | -0.0729 | -0.0774 | -0.0711 | -0.0574 | -0.0362 | 0 | 0.0353 | 0.0370 | |
| | E_2 | 0.1936 | 0.1809 | 0.1386 | 0.0794 | 0.0250 | 0 | -0.0250 | -0.0837 | |
| | MS | -0.2401 | -0.2283 | -0.1940 | -0.1403 | -0.0731 | 0 | 0.0709 | 0.1339 | |
| | MP | -0.7208 | -0.6879 | -0.5860 | -0.4023 | -0.1824 | 0 | | | |
| | 2 | M_1 | 0.0123 | 0.0112 | 0.0086 | 0.0039 | -0.0004 | 0 | 0.0009 | -0.0075 |
| | | M_2 | 0.0976 | 0.0882 | 0.0642 | 0.0349 | 0.0105 | 0 | -0.0105 | -0.0367 |
| Re Z^{-1} | | 1.426 | 1.413 | 1.387 | 1.354 | 1.318 | 1.302 | 1.275 | 1.284 | |
| Im Z^{-1} | | 0.273 | 0.224 | 0.161 | 0.095 | 0.032 | 0 | 0.026 | 0.061 | |
| E_1 | | 0.0210 | 0.0174 | 0.0114 | 0.0047 | -0.0001 | 0 | 0.0005 | -0.0072 | |
| E_2 | | 0.0644 | 0.0597 | 0.0450 | 0.0255 | 0.0080 | 0 | -0.0082 | -0.0282 | |
| MS | | -0.0590 | -0.0561 | -0.0477 | -0.0346 | -0.0182 | 0 | 0.0184 | 0.0359 | |
| MP | | -0.2440 | -0.2276 | -0.1766 | -0.1034 | -0.0489 | 0 | | | |
| 3 | | M_1 | 0.0268 | 0.0253 | 0.0205 | 0.0132 | 0.0056 | 0 | -0.0052 | -0.0147 |
| | | M_2 | 0.0534 | 0.0482 | 0.0350 | 0.0190 | 0.0057 | 0 | -0.0059 | -0.0208 |
| | Re Z^{-1} | 1.521 | 1.537 | 1.525 | 1.492 | 1.455 | 1.429 | 1.400 | 1.407 | |
| | Im Z^{-1} | 0.313 | 0.261 | 0.192 | 0.116 | 0.039 | 0 | 0.033 | 0.078 | |
| | E_1 | 0.0238 | 0.0212 | 0.0161 | 0.0098 | 0.0040 | 0 | -0.0038 | -0.0112 | |
| | E_2 | 0.0302 | 0.0278 | 0.0209 | 0.0120 | 0.0038 | 0 | -0.0041 | -0.0142 | |
| | MS | -0.0230 | -0.0219 | -0.0187 | -0.0137 | -0.0072 | 0 | 0.0075 | 0.0149 | |
| | MP | -0.0998 | -0.0889 | -0.0569 | -0.0344 | -0.0176 | 0 | | | |
| | 4 | M_1 | 0.0262 | 0.0250 | 0.0206 | 0.0139 | 0.0065 | 0 | -0.0064 | -0.0153 |
| | | M_2 | 0.0336 | 0.0304 | 0.0222 | 0.0121 | 0.0037 | 0 | -0.0038 | -0.0137 |
| Re Z^{-1} | | 1.576 | 1.629 | 1.639 | 1.614 | 1.580 | 1.547 | 1.518 | 1.525 | |
| Im Z^{-1} | | 0.334 | 0.282 | 0.211 | 0.130 | 0.044 | 0 | 0.038 | 0.091 | |
| E_1 | | 0.0202 | 0.0180 | 0.0141 | 0.0092 | 0.0042 | 0 | -0.0043 | -0.0105 | |
| E_2 | | 0.0170 | 0.0155 | 0.0117 | 0.0068 | 0.0022 | 0 | -0.0024 | -0.0084 | |
| MS | | -0.0110 | -0.0105 | -0.0090 | -0.0066 | -0.0035 | 0 | 0.0037 | 0.0074 | |
| MP | | -0.0334 | -0.0252 | -0.0126 | -0.0095 | -0.0060 | 0 | | | |
| 5 | | M_1 | 0.0231 | 0.0223 | 0.0186 | 0.0129 | 0.0063 | 0 | -0.0064 | -0.0144 |
| | | M_2 | 0.0230 | 0.0209 | 0.0154 | 0.0085 | 0.0026 | 0 | -0.0027 | -0.0099 |
| | Re Z^{-1} | 1.602 | 1.699 | 1.738 | 1.725 | 1.697 | 1.660 | 1.630 | 1.637 | |
| | Im Z^{-1} | 0.347 | 0.296 | 0.225 | 0.141 | 0.049 | 0 | 0.042 | 0.102 | |
| | E_1 | 0.0167 | 0.0148 | 0.0117 | 0.0078 | 0.0038 | 0 | -0.0040 | -0.0091 | |
| | E_2 | 0.0170 | 0.0097 | 0.0074 | 0.0043 | 0.0014 | 0 | -0.0016 | -0.0055 | |
| | MS | -0.0059 | -0.0057 | -0.0049 | -0.0036 | -0.0019 | 0 | 0.0020 | 0.0040 | |
| | MP | +0.0035 | 0.0090 | 0.0057 | 0.0012 | -0.0008 | 0 | | | |
| | 6 | M_1 | 0.0201 | 0.0195 | 0.0164 | 0.0116 | 0.0058 | 0 | -0.0060 | -0.0132 |
| | | M_2 | 0.0168 | 0.0152 | 0.0113 | 0.0063 | 0.0019 | 0 | -0.0021 | -0.0075 |
| Re Z^{-1} | | 1.609 | 1.753 | 1.825 | 1.827 | 1.807 | 1.766 | 1.738 | 1.745 | |
| Im Z^{-1} | | 0.354 | 0.305 | 0.236 | 0.150 | 0.052 | 0 | 0.046 | 0.112 | |
| E_1 | | 0.0141 | 0.0123 | 0.0096 | 0.0066 | 0.0032 | 0 | -0.0035 | -0.0078 | |
| E_2 | | 0.0073 | 0.0065 | 0.0049 | 0.0029 | 0.0010 | 0 | -0.0011 | -0.0038 | |
| MS | | -0.0034 | -0.0033 | -0.0028 | -0.0021 | -0.0011 | 0 | 0.0012 | 0.0023 | |
| MP | | 0.0264 | 0.0234 | 0.0135 | 0.0061 | 0.0017 | 0 | | | |

^a D. Pines, Ref. 31, p. 407.

^b V. Heine, Proc. Roy. Soc. A240, 340 (1957).

quasiparticle energies in qualitatively the same way for an electron gas as for alkali atoms, though on a largely magnified scale, cf. Sec. 4.

By comparing M with E in Table IV we find that the factor Z has a large influence. For $r_s=1$ we note an anomaly. E_1 drops sharply in going from $q=0$ to $q=0.1$ before it starts rising again. This may be due to either inaccuracies in the Z values or to a discontinuity in the

derivative $\partial E(\mathbf{k})/\partial k_x$. There are however no indications of such a discontinuity in $M(\mathbf{k}, \epsilon(\mathbf{k}))$.

The accuracy of $E(q)$ is not good enough to permit a more detailed statement about its second derivative than the general observation that on the average it is small compared to $\epsilon''(q) = 2(2/\alpha r_s)^2$ Ry. This follows from the fact that $E'(0.5)$ is small compared to $\epsilon'(0.5) = (2/\alpha r_s)^2$ Ry [see Table VI which gives $E'(0.5)/\epsilon'(0.5)$

under the heading $f_e^{(1)}$, f_0 , RPA^(b)], combined with the formula,

$$\frac{1}{0.5} \int_0^{0.5} E''(q)/\epsilon''(0.5) dq = E'(0.5)/\epsilon'(0.5). \quad (98)$$

We have also calculated $M(r, \mu)$ from the formula,

$$M(r, \mu) = \left(\frac{k_0}{\pi}\right)^3 \int e^{i\mathbf{q}\cdot\mathbf{x}} M(q, \mu) d\mathbf{q} = \frac{8e^2 k_0^4}{\pi^3} \frac{1}{x} \int_0^\infty dq \times \int_0^\infty du \left(\frac{1}{\epsilon(q, iu)} - 1\right) \frac{\sin qx}{qx} e^{-(a-0.125)^{1/2} x} \times \cos(a+0.125)^{1/2} x; \quad a = \frac{1}{2}(u^2 + 0.0625)^{1/2}; \quad x = 2k_0 r. \quad (99)$$

The result is given in Fig. 10. Judging from the values of $M(q, \mu)$ at $q=0.4, 0.5,$ and 0.6 it varies considerably faster with q than $M(q, \epsilon(q))$ and $E(q)$. $M'(0.5, \mu)/\epsilon'(0.5)$ equals 0.18, 0.39, and 0.62 for $r_s=1, 3,$ and $6,$ respectively. The variation is however still mild compared to the logarithmic singularity of $M^{HF}(q)$, which can be seen by the suppression of long range oscillations in $M(r, \mu)$. Since $rM(r, \mu)$ extends out to about $r = a_0 r_s$, then $|\mathbf{k}|M(\mathbf{k}, \mu)$ is essentially different from zero only for k smaller than $2\pi/r = (2\pi/a_0 r_s) \cong 3k_0$. Since $E(\mathbf{k})$ varies more slowly with \mathbf{k} than does $M(\mathbf{k}, \mu)$ it is probable that $|\mathbf{k}|E(\mathbf{k})$ extends further out than $3k_0$. In that case the nonlocal potential corresponding to $E(\mathbf{k})$ will have a still smaller range than $M(r, \mu)$ which speaks in favor of using electron-gas results in a local density approximation for a metal.

We conclude this section with a comment on the Coulomb hole plus screened exchange approximation. Returning to Eq. (13) we see that the integral has a factor $\exp[i(\epsilon - \epsilon_s)(\tau/\hbar)][\theta(\tau) - \theta(\mu - \epsilon_s)]$. The Coulomb

hole comes from $\theta(\tau)$ and the screened exchange from $\theta(\mu - \epsilon_s)$ when we put the exponential equal to 1. If we evaluate the contribution to M involving $\theta(\mu - \epsilon_s)$ without approximation, we obtain an energy-dependent screened exchange,

$$M^{ex}(q, u) = -\frac{4}{\pi \alpha r_s} \int_{-1}^1 d\xi \times \int dq' \frac{\theta(0.25 - q^2 - q'^2 - 2qq'\xi)}{\epsilon(q', u - q^2 - q'^2 - 2qq'\xi)} \text{Ry}, \quad (100)$$

which can be compared with the energy-independent screened exchange of Eq. (89). It has been suggested⁴ that the energy dependence should have only a small influence and to check that the integral in Eq. (100) was evaluated for $u = q^2$. Compared to the energy-independent screened exchange the magnitude of $M^{ex}(0.5, 0.25)$ agreed quite well, being 3% and 8% smaller for $r_s=1$ and $6,$ respectively. The slope at $q=0.5$ on the other hand was larger by 4%, 29% and 91% for $r_s=1, 3,$ and $6,$ respectively. The total variation between $q=0$ and $q=0.5$ was larger by 3% and smaller by 27% and 88% for $r_s=1, 3,$ and $6,$ respectively. The two expressions thus agree poorly except for high densities.

10. ELECTRON GAS: THE QUASIPARTICLE INTERACTION

The expansion of the quasiparticle interaction f of the Landau theory of a Fermi liquid is given in Eqs. (31) and (34) up to second order in the screened interaction W . It is convenient to use dimensionless quantities and we redefine f by

$$\delta E_\sigma(\mathbf{k}) = \frac{4\pi e^2}{k_0^2} \frac{1}{(2\pi)^3 \alpha r_s} \sum_{\sigma'} \int f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}') \delta n_{\sigma'}(\mathbf{k}') d\mathbf{k}', \quad (101)$$

where $E_\sigma(\mathbf{k})$ and $\delta n_\sigma(\mathbf{k})$ are defined as in Eq. (30). Writing f as

$$f_{\sigma\sigma'} = f_0 + f_e \delta_{\sigma\sigma'}; \quad f_e = f_e^{(1)} + f_e^{(2)}, \quad (102)$$

we have the following simple expressions⁴⁶ for the specific heat C and the paramagnetic susceptibility χ ,

$$C_0/C = 1 - \int_0^\pi [2f_0(\theta) + f_e(\theta)] \cos\theta \sin\theta d\theta, \quad (103)$$

$$\chi_0/\chi = C_0/C + \int_0^\pi f_e(\theta) \sin\theta d\theta,$$

where C_0 and χ_0 are the values for a noninteracting or Sommerfeld electron gas and θ is the angle between \mathbf{k} and \mathbf{k}' . Both \mathbf{k} and \mathbf{k}' have the magnitude $|\mathbf{k}_0|$.

⁴⁶ See e.g., P. Nozières in Ref. 2.

SELF-ENERGY OPERATOR AS A NONLOCAL POTENTIAL

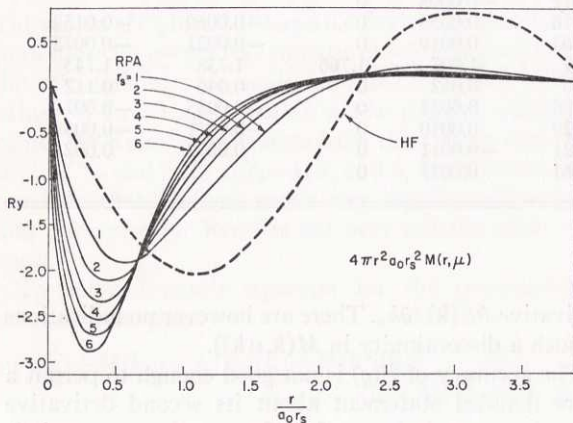


Fig. 10. Self-energy operator as a nonlocal potential. We have multiplied $M(r, \mu)$ by a factor $4\pi r^2 a_0 r_s^2$ from the volume element $4\pi r^2 dr = 4\pi r^2 a_0 r_s dx$, and by an extra r_s to make the HF curve r_s independent.

With our present definition of f , Eq. (101), using Green's functions according to Eq. (41) and dimensionless integration variables according to Eq. (56) we have

$$f_e^{(1)} = -V(\kappa, 0),$$

$$f_e^{(2)} = -\frac{i}{\pi^2} \int \frac{V(q_1, u_1) dq_1 du_1}{u_1 - q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} \left[\frac{2V(\kappa, 0)}{u_1 - q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} - \frac{V(\mathbf{q}_1 + \boldsymbol{\kappa}, u_1)}{u_1 + q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} + \frac{V(\mathbf{q}_1 - \boldsymbol{\kappa}, u_1)}{u_1 - q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} \right], \quad (104)$$

$$f_0 = \frac{i}{\pi^2} \int \frac{V^2(q_1, u_1) dq_1 du_1}{u_1 - q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} \times \left[\frac{1}{u_1 - q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} - \frac{1}{u_1 + q_1^2 - 2\mathbf{q}' \cdot \mathbf{q}_1} \right],$$

where we have omitted the z^2 factors and used the notation

$$V(q, u) = (\lambda/4q^2 \epsilon(q, u)); \quad \lambda = \alpha r_s / \pi = r_s / 6.03;$$

$$\boldsymbol{\kappa} = \mathbf{q} - \mathbf{q}' = (\mathbf{k} - \mathbf{k}') / (2k_0); \quad (105)$$

$$\kappa^2 = \frac{1}{2}(1 - \cos\theta) = \sin^2(\theta/2).$$

As discussed in Sec. 5, we can obtain rough approximations by replacing $W(\mathbf{k}, \epsilon)$ by $W(\mathbf{k}, 0)$ or, in the present notation, replacing $V(q, u)$ by $V(q, 0)$. The expressions for $f_e^{(2)}$ and f_0 then become,

$$f_e^{(2)} = \frac{1}{\pi} \int V(q_1, 0) dq_1 \left[\frac{2V(\kappa, 0)\eta_1}{\boldsymbol{\kappa} \cdot \mathbf{q}_1} - \frac{V(\mathbf{q}_1 + \boldsymbol{\kappa}, 0)\eta_2}{(\boldsymbol{\kappa} + \mathbf{q}_1) \cdot \mathbf{q}_1} \right],$$

$$f_0 = -\frac{1}{\pi} \int V^2(q_1, 0) dq_1 \left(\frac{\eta_1}{\boldsymbol{\kappa} \cdot \mathbf{q}_1} - \frac{\eta_2}{(\boldsymbol{\kappa} + \mathbf{q}_1) \cdot \mathbf{q}_1} \right), \quad (106)$$

$$\eta_1 = \theta(0.25 - (\mathbf{q} + \mathbf{q}_1)^2) - \theta(0.25 - (\mathbf{q}' + \mathbf{q}_1)^2),$$

$$\eta_2 = \theta(0.25 - (\mathbf{q} + \mathbf{q}_1)^2) - \theta((\mathbf{q}' + \mathbf{q}_1)^2 - 0.25).$$

Using the G defined in Eq. (41) we have from Eqs. (27) and (28)

$$C_0/C = 1 + z \left[\frac{d}{dk} M(\mathbf{k}, \epsilon(\mathbf{k})) \right] / \left(\frac{d}{dk} \epsilon(\mathbf{k}) \right). \quad (107)$$

Neglecting the z factors, the contributions to C_0/C in Eq. (107) are identical with those in Eq. (103) according to the following correspondences:

$$f_e^{(1)}, \text{ Eq. (104)} \rightarrow M^e, \text{ Eq. (89)},$$

$$f_0, \text{ Eq. (104)} \rightarrow M^r, \text{ Eq. (91)}, \quad (108)$$

$$f_e^{(2)}, \text{ Eq. (106)} \rightarrow M^{(2)}, \text{ Eq. (78)}.$$

The first and third correspondences are easily checked by straightforward differentiation of M^e and $M^{(2)}$. To prove the second correspondence we write the expres-

sions for M^r in the form

$$M^r(\mathbf{k}, \epsilon(\mathbf{k})) = \frac{2}{(2\pi)^4} \int d\mathbf{k}'' \int_0^\infty dw \frac{\epsilon(\mathbf{k} + \mathbf{k}'') - \epsilon(\mathbf{k})}{(\epsilon(\mathbf{k} + \mathbf{k}'') - \epsilon(\mathbf{k}))^2 + w^2} \times (W(\mathbf{k}'', iw) - W(\mathbf{k}'', 0)). \quad (109)$$

We then perform a partial integration with respect to w , ($dW/dw = W^2 dP/dw$),

$$M^r(\mathbf{k}, \epsilon(\mathbf{k})) = \frac{16}{(2\pi)^7} \int d\mathbf{k}'' \int_0^\infty dw \times \arctan \frac{\epsilon(\mathbf{k} + \mathbf{k}'') - \epsilon(\mathbf{k})}{w} W^2(\mathbf{k}'', iw) \times \int d\mathbf{k}' \frac{(\epsilon(\mathbf{k}' + \mathbf{k}'') - \epsilon(\mathbf{k}')) w \theta(k_0 - |\mathbf{k}'|)}{\{[\epsilon(\mathbf{k}' + \mathbf{k}'') - \epsilon(\mathbf{k}')]^2 + w^2\}^2}. \quad (110)$$

The last integral in Eq. (110) can be written⁴⁷

$$-\frac{m}{2\hbar^2 k_0} \frac{w}{\mathbf{k} \cdot \mathbf{k}''} \int \frac{\mathbf{k} \cdot \mathbf{k}' \delta(|\mathbf{k}'| - k_0) d\mathbf{k}'}{[\epsilon(\mathbf{k}' + \mathbf{k}'') - \epsilon(\mathbf{k}')]^2 + w^2}. \quad (111)$$

When we form $d/dk = (\mathbf{k}/k_0) \cdot d/d\mathbf{k}$ of $M^r(\mathbf{k}, \epsilon(\mathbf{k}))$, the factor $(\mathbf{k} \cdot \mathbf{k}'')^{-1}$ drops out and it is relatively easy to check that we arrive at the same expression for C_0/C as when f_0 of Eq. (104) is used in Eq. (103). It is easily realized that we have the correspondence f_0 , Eq. (106) $\rightarrow M^r$, Eq. (110) with $W(\mathbf{k}, 0)$ instead of $W(\mathbf{k}, iw)$.

Thus the RPA result for the specific heat is reproduced by $f_e^{(1)}$ and f_0 apart from a factor z . It seems probable, although we have not been able to prove it, that if we use Eq. (43) instead of Eq. (41) for G , the iGW expression for M will give exactly the same result for C_0/C as $f_e^{(1)}$ and f_0 [cf. the discussion in connection with Eqs. (35) to (37)].

The numerical results for $f_e^{(1)}$, Eq. (104) and $f_e^{(2)}$, f_0 , Eq. (106) are given in Table V and Fig. 11. The f 's are multiplied by $\sin\theta$ to make it easier to estimate their contributions in Eq. (103). The z^2 -factor is not included in Table V and Fig. 11. Since we have numerical results for $M^r[\mathbf{k}, \epsilon(\mathbf{k})]$ we can evaluate the contribution to $C_0/C - 1$ from f_0 , Eq. (104) and compare with the contribution from the static approximation for f_0 , Eq. (106). These contributions are given in Table VI under the headings (f_0 , RPA) and (f_0 , static). We expect similar differences between the contributions from $f_e^{(2)}$ according to Eqs. (104) and (106). The static approximation for the second-order terms in f is thus fairly rough and seems to somewhat underestimate them.

⁴⁷ We use the identity

$$\int \nabla f(\mathbf{k}) \theta(|\mathbf{k}_0| - |\mathbf{k}|) d\mathbf{k} = \int (\mathbf{k}/|\mathbf{k}|) f(\mathbf{k}) \delta(|\mathbf{k}_0| - |\mathbf{k}|) d\mathbf{k}.$$

TABLE V. Quasiparticle interactions multiplied by $\sin\theta$.

| θ | $r_s=1$ | | | $r_s=2$ | | | $r_s=3$ | | |
|--------------------------|-------------|---------|-------------|-------------|---------|-------------|-------------|---------|-------------|
| | $f_e^{(1)}$ | f_0 | $f_e^{(2)}$ | $f_e^{(1)}$ | f_0 | $f_e^{(2)}$ | $f_e^{(1)}$ | f_0 | $f_e^{(2)}$ |
| $\frac{\pi}{8} \times 0$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | -0.0788 | -0.0009 | -0.0187 | -0.0869 | -0.0032 | -0.0264 | -0.0900 | -0.0069 | -0.0285 |
| 2 | -0.0969 | -0.0018 | -0.0188 | -0.1274 | -0.0067 | -0.0322 | -0.1424 | -0.0141 | -0.0367 |
| 3 | -0.0842 | -0.0030 | -0.0112 | -0.1271 | -0.0106 | -0.0217 | -0.1531 | -0.0220 | -0.0250 |
| 4 | -0.0656 | -0.0043 | -0.0038 | -0.1081 | -0.0152 | -0.0066 | -0.1379 | -0.0304 | -0.0044 |
| 5 | -0.0473 | -0.0062 | 0.0019 | -0.0824 | -0.0201 | 0.0070 | -0.1095 | -0.0383 | 0.0156 |
| 6 | -0.0307 | -0.0084 | 0.0055 | -0.0553 | -0.0241 | 0.0159 | -0.0755 | -0.0429 | 0.0286 |
| 7 | -0.0151 | -0.0095 | 0.0063 | -0.0278 | -0.0231 | 0.0171 | -0.0386 | -0.0374 | 0.0289 |
| 7+ | | -0.0091 | 0.0057 | | -0.0202 | 0.0148 | | -0.0318 | 0.0246 |
| 7+ | | -0.0066 | 0.0041 | | -0.0139 | 0.0105 | | -0.0211 | 0.0171 |
| 7+ | | -0.0042 | 0.0025 | | -0.0085 | 0.0065 | | -0.0127 | 0.0104 |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| θ | $r_s=4$ | | | $r_s=5$ | | | $r_s=6$ | | |
| | $f_e^{(1)}$ | f_0 | $f_e^{(2)}$ | $f_e^{(1)}$ | f_0 | $f_e^{(2)}$ | $f_e^{(1)}$ | f_0 | $f_e^{(2)}$ |
| $\frac{\pi}{8} \times 0$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | -0.0917 | -0.0116 | -0.0273 | -0.0927 | -0.0173 | -0.0241 | -0.0933 | -0.0238 | -0.0192 |
| 2 | -0.1512 | -0.0237 | -0.0354 | -0.1571 | -0.0350 | -0.0299 | -0.1613 | -0.0480 | -0.0214 |
| 3 | -0.1706 | -0.0363 | -0.0220 | -0.1832 | -0.0530 | -0.0141 | -0.1926 | -0.0718 | -0.0024 |
| 4 | -0.1510 | -0.0488 | 0.0027 | -0.1770 | -0.0699 | 0.0141 | -0.1905 | -0.0932 | 0.0290 |
| 5 | -0.1311 | -0.0594 | 0.0276 | -0.1486 | -0.0827 | 0.0425 | -0.1632 | -0.1078 | 0.0510 |
| 6 | -0.0924 | -0.0634 | 0.0432 | -0.1067 | -0.0852 | 0.0593 | -0.1190 | -0.1080 | 0.0767 |
| 7 | -0.0480 | -0.0522 | 0.0412 | -0.0561 | -0.0673 | 0.0538 | -0.0633 | -0.0826 | 0.0667 |
| 7+ | | -0.0430 | 0.0347 | | -0.0544 | 0.0445 | | -0.0647 | 0.0549 |
| 7+ | | -0.0281 | 0.0236 | | -0.0349 | 0.0299 | | -0.0417 | 0.0360 |
| 7+ | | -0.0167 | 0.0143 | | -0.0206 | 0.0179 | | -0.0244 | 0.0215 |
| 8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

From Table V and Fig. 11 we see that *the first-order term in f is appreciably larger than the second-order terms for the higher metallic densities*. The convergence of the expansion for f , however, does not seem to be as good as that for μ .

From the results for $f_e^{(2)}$ and for $M^{(2)}(0,0)$ we can estimate the magnitude of $M^{(2)}[\mathbf{k}, \epsilon(\mathbf{k})]$ at $\mathbf{k}=\mathbf{k}_0$. The derivative of $M^{(2)}[\mathbf{k}, \epsilon(\mathbf{k})]$ relative to that of $\epsilon(\mathbf{k})$ at $\mathbf{k}=\mathbf{k}_0$ is roughly given by the value of $(f_e^{(2)}, \text{static})$ in Table VI. Taking into account that $M^{(2)}[\mathbf{k}, \epsilon(\mathbf{k})]$ should flatten out at small \mathbf{k} by introducing an extra factor of 0.5, we arrive at the estimate of $M^{(2)}[\mathbf{k}_0, \epsilon(\mathbf{k}_0)]$ which was given in Sec. 8, namely 0.04–0.02 Ry for r_s varying from 3 to 6. For smaller r_s , $M^{(2)}$ becomes larger and the ratio $M^{(2)}/M^{(1)}$ smaller.

The influence of the errors in the second order terms of f is suppressed since they should cancel each other to a large extent. This can be seen in Table VI by comparing the columns $(f_0, f_e^{(2)}, \text{static})$ with $(f_e^{(1)}, \text{RPA})$ or $(f_e, f_0, \text{static})$.

In Fig. 12^{48–50} the results for the specific heat are plotted. The series expansion in r_s , given by DuBois,⁵¹ starts to deviate from our result already at $r_s=0.5$ and

for $r_s>1$ it is obviously wrong. Pines' result, which is given by $f_e^{(1)}$ with $W(r, \epsilon) = (e^2/r)S(r)$ and $S(r)$ according to Eq. (63), is qualitatively similar to ours but exaggerates the difference between C and C_0 . Silverstein⁵² has recently tried to include the second-order term in M by an interpolation procedure similar to that used by Nozières and Pines⁵³ for the correlation energy. Silverstein expressed $C_0/C-1$ as an integral over the momentum transfer q , using RPA for small q and unscreened perturbation theory up to second order for large q . His results are however more negative than the RPA results (compare the last two columns in Table VI) even though the second-order terms give a positive contribution to $C_0/C-1$. This probably is due to his use of a series expansion in q for the RPA part of his integrand rather than the complete RPA expression. Silverstein's result⁵⁴ for χ_0/χ minus his result for C_0/C are given in the last column of Table VII. They agree roughly with our results from $f_e^{(1)}$ without the z^2 factor.

Since $f_e^{(1)}$ gives the largest contribution to the specific heat as well as to the paramagnetic susceptibility, it is of interest to examine how sensitive the results are to the precise form of $f_e^{(1)}$. The series expansion of the RPA expression for $\epsilon(\kappa, 0)$ is easily

⁴⁸ D. Pines, Ref. 31, p. 408, Eq. (8.4). ($\beta=0.353r_s^{1/2}$).

⁴⁹ D. F. DuBois, Ann. Phys. 8, 24 (1959).

⁵⁰ S. D. Silverstein, Phys. Rev. 128, 631 (1962).

⁵¹ D. F. DuBois, Ann. Phys. (N. Y.) 8, 24 (1959).

⁵² S. D. Silverstein, Phys. Rev. 128, 631 (1962).

⁵³ P. Nozières and D. Pines, Phys. Rev. 111, 442 (1958).

⁵⁴ S. D. Silverstein, Phys. Rev. 130, 1703 (1963).

TABLE VI. Different contributions to $(C_0/C)-1$.

| r_s | $f_e^{(1)}$ RPA | f_0 RPA | f_0 static | $f_e^{(2)}$ static | $f_0, f_e^{(2)}$ static | f_e, f_0 static | $f_e^{(1)}$ TF | f_e, f_0 static ^a | $f_e^{(1)}, f_0$ RPA ^b | Silverstein |
|-------|--------------------|--------------|-----------------|-----------------------|----------------------------|----------------------|-------------------|-----------------------------------|--------------------------------------|-------------|
| 1 | 0.0489 | -0.0157 | -0.0127 | 0.0184 | 0.0058 | 0.0547 | 0.0495 | 0.0404 | 0.0285 | 0.029 |
| 2 | 0.0498 | -0.0419 | -0.0304 | 0.0351 | 0.0047 | 0.0545 | 0.0518 | 0.0322 | 0.0061 | -0.039 |
| 3 | 0.0451 | -0.0712 | -0.0482 | 0.0477 | -0.0005 | 0.0446 | 0.0493 | 0.0218 | -0.0183 | -0.080 |
| 4 | 0.0392 | -0.1017 | -0.0649 | 0.0576 | -0.0073 | 0.0319 | 0.0460 | 0.0133 | -0.0404 | -0.125 |
| 5 | 0.0332 | -0.1326 | -0.0808 | 0.0657 | -0.0151 | 0.0181 | 0.0429 | 0.0066 | -0.0599 | -0.179 |
| 6 | 0.0275 | -0.1635 | -0.0954 | 0.0726 | -0.0228 | 0.0047 | 0.0396 | 0.0015 | -0.0770 | -0.232 |

^a Including the renormalization factor z^2 .

^b Including the renormalization factor z .

obtained from Eq. (57), and is

$$\epsilon(\kappa, 0) = 1 + (\lambda/\kappa^2)(1 - (\kappa^2/3) - (\kappa^4/15) - (\kappa^6/35) - \dots); \quad |\kappa| < 1 \quad (112)$$

$$\epsilon(1, 0) = 1 + \frac{1}{2}\lambda.$$

The first two terms in $\epsilon(\kappa, 0)$ give the TF approximation,

$$f_e^{(1)} = -(\lambda/4(\kappa^2 + \lambda)); \quad \kappa^2 = \sin^2(\theta/2), \quad (113)$$

while the first three terms give the same expressions as Eq. (113) but with λ replaced by $\lambda/(1 - \frac{1}{3}\lambda)$. Using Eq. (113) for f gives

$$\begin{aligned} C_0/C &= 1 - \lambda - \lambda(\lambda + \frac{1}{2}) \ln(\lambda/(1 + \lambda)), \\ \chi_0/\chi &= 1 - \lambda - \lambda^2 \ln(\lambda/(1 + \lambda)). \end{aligned} \quad (114)$$

By comparing $(f_e^{(1)}, \text{TF})$ and $(f_e^{(1)}, \text{RPA})$ in Table VI and $(f_e^{(1)}, \text{TF})$ and $f_e^{(1)}$ in Table VII, we see that the TF expression Eq. (114) gives a quite reasonable result.

Eq. (114) can also be compared with the high-density results^{55,56}

$$\begin{aligned} C_0/C &= 1 - \lambda - \lambda/2 \ln \lambda, \\ \chi_0/\chi &= 1 - \lambda - \lambda^2/2(\ln \lambda - 1.534). \end{aligned} \quad (115)$$

Thus in the high-density limit the lowest order term in f correctly reproduces the $\lambda \ln \lambda$ and λ terms. It may be noted that while the HF expression for C_0/C diverges, the HF expression for χ_0/χ , namely, $1 - \lambda$, gives a reasonable high-density description. Numerically the expressions for χ_0/χ according to Eqs. (114) and (115) are not too different at high densities. At $r_s = 1$ they are, respectively, 0.888 and 0.879.

Osaka⁵⁷ has recently calculated C_0/C in what is stated to be the RPA. His result is identical¹⁵ with that of Eq. (114) when λ is replaced by $\lambda/(1 - \lambda/3)$. He used a rela-

TABLE VII. Different contributions to $\chi_0/\chi - C_0/C$.

| r_s | $f_e^{(1)}$ | $f_e^{(2)}$ | f_e | f_e^a | $f_e^{(1)}, \text{TF}$ | Silverstein |
|-------|-------------|-------------|---------|---------|------------------------|-------------|
| 1 | -0.1686 | -0.0149 | -0.1835 | -0.1355 | -0.1617 | -0.157 |
| 2 | -0.2459 | -0.0177 | -0.2636 | -0.1566 | -0.2305 | -0.228 |
| 3 | -0.2980 | -0.0070 | -0.3050 | -0.1494 | -0.2741 | -0.301 |
| 4 | -0.3367 | 0.0141 | -0.3226 | -0.1347 | -0.3049 | -0.350 |
| 5 | -0.3670 | 0.0431 | -0.3240 | -0.1176 | -0.3280 | -0.384 |
| 6 | -0.3915 | 0.0784 | -0.3131 | -0.1004 | -0.3460 | -0.360 |

^a Including the renormalization factor z^2 .

⁵⁵ M. Gell-Mann, Phys. Rev. 106, 369 (1957).

⁵⁶ K. Sawada, Phys. Rev. 112, 328 (1958).

⁵⁷ Y. Osaka, J. Phys. Soc. Japan 17, 547 (1962).

tion between specific heat and polarization propagator which was derived from Eq. (A1) in his paper. Equation (A1) is however not quite correct since the μ factors should not be there.

Watabe¹⁵ has recently made an analysis of the influence of Coulomb correlations on metallic properties using the Landau Fermi-liquid Theory. He approximates f by $f_e^{(1)}$, [cf. Eqs. (104) and (105)] neglecting higher order terms and the z^2 factor. For $\epsilon(\kappa, 0)$, he takes the limiting expression⁵⁸ for small κ

$$\epsilon(\kappa, 0) = 1 + (\lambda\gamma/\kappa^2), \quad (116a)$$

$$\gamma^{-1} = \chi_0/\chi + 2 \int_0^\pi f_0(\theta) \sin \theta d\theta. \quad (116b)$$

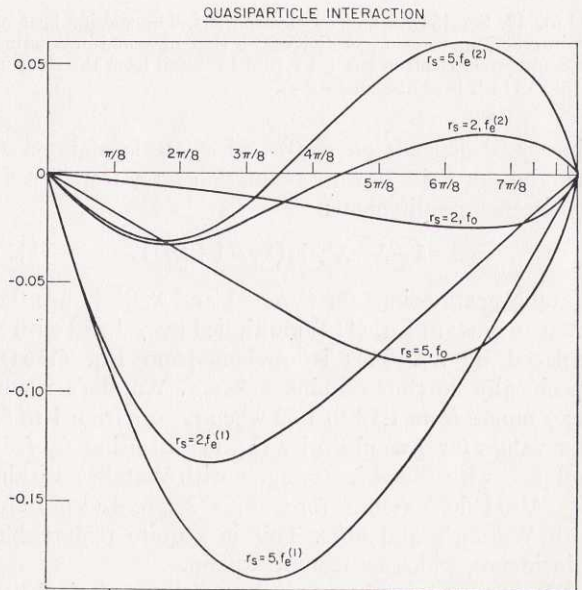


FIG. 11. Quasi-particle interaction. The quasi-particle interaction f is here defined by

$$\delta E_\sigma(\mathbf{k}) = \left(\frac{4\pi e^2}{k_0^2} \frac{1}{(2\pi)^3} \frac{\pi}{c v_s} \right) \sum_{\sigma'} \int f_{\sigma\sigma'}(\mathbf{k}, \mathbf{k}') \delta n_{\sigma'}(\mathbf{k}') d\mathbf{k}',$$

$f_{\sigma\sigma'} = f_0 + (f_e^{(1)} + f_e^{(2)}) \delta_{\sigma\sigma'}$. f depends only on the angle θ between \mathbf{k} and \mathbf{k}' . In this figure, f times $\sin \theta$ is plotted against θ . $f_e^{(1)}$ is a first-order term in W , and f_0 and $f_e^{(2)}$ are of second order in W . The z^2 factor is not included in f .

⁵⁸ V. P. Silin, Zh. Eksperim. i Teor. Fiz. 33, 495 (1957) [English transl.: Soviet Phys.—JETP 6, 387 (1958)]; S. Misawa, Progr. Theoret. Phys. (Kyoto) 27, 840 (1962).

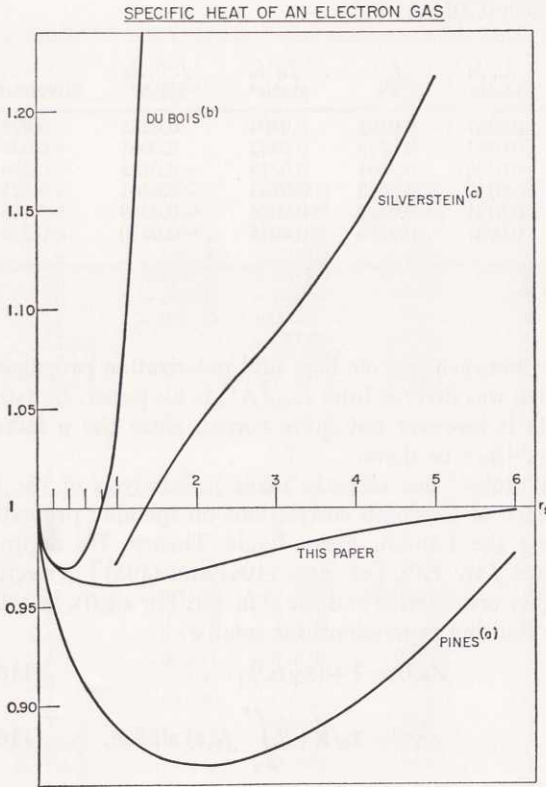


FIG. 12. Specific heat of an electron gas. The specific heat of an interacting electron gas divided by that of a non-interacting or Sommerfeld electron gas ($[1 + (\text{third column from the right in Table VI})^{-1}]$) is plotted against r_s .

Since $f_e^{(1)}$ depends on $\epsilon(\kappa, 0)$ and $\epsilon(\kappa, 0)$ depends on f , Watabe can write down an equation for γ from a self-consistency requirement:

$$\gamma^{-1} = 1 - \lambda - \lambda^2 \gamma \ln(\lambda \gamma / (1 + \lambda \gamma)). \quad (117)$$

Watabe's expressions for $C_0/C - 1$ and $\chi_0/\chi - 1$ are the same as those in Eq. (114) multiplied by γ^{-1} and with λ replaced by $\lambda \gamma$. This is obvious from Eq. (116a). Specifically he thus obtains $\chi/\chi_0 = \gamma$. Watabe's result for γ ranges from 1.12 to 1.32 when r_s goes from 1 to 5. Our values for γ as given by Eq. (116b) using f_0 , $f_e^{(1)}$ and $f_e^{(2)}$ with the z^2 factor agree with Watabe's within 1%. Also Glick's result²⁵ for γ at $r_s = 2$ agrees accurately with Watabe's and ours. This is a quite remarkable coincidence, which we cannot explain.

We now make a few remarks on the analytical behavior of the different contributions to $f_{\sigma\sigma'}(\theta)$. $f_e^{(1)}(\theta)$ varies between -0.25 and $-0.25(\lambda/(1+\lambda/2))$. The slope of $f_e^{(1)}(\theta)$ is zero at $\theta = 0$ and $\theta = \pi$. $f_0(\theta)$ and $f_e^{(2)}(\theta)$ start out with finite values at $\theta = 0$ and go to infinity at $\theta = \pi$ as $\ln(1 + \cos\theta)$. The coefficients of the \ln term have opposite signs and roughly the same magnitude. We thus have a singular attraction between quasiparticles of opposite momenta and opposite spin giving a tendency towards a superconducting state. This effect does *not* come from the logarithmic singularity in $\epsilon(\kappa, 0)$. The

same effect has been noted earlier in case of a dilute Fermi gas,⁵⁹ and is there supposed to disappear when higher order terms are taken into account. To see if this attraction might be strong enough to make a spherical Fermi surface unstable, we considered the following distortion,

$$1 + \delta > k/k_0 > 1, \quad \theta < \eta: \quad \delta n_+(k, \theta) = 1$$

$$1 + \delta > k/k_0 > 1, \quad \theta > \pi - \eta: \quad \delta n_-(k, \theta) = 1$$

$$1 > k/k_0 > 1 - \frac{1}{4}\eta^2\delta:$$

$$\delta n_+(k, \theta) = \delta n_-(k, \theta) = -1, \quad \delta \rightarrow 0, \quad \eta \rightarrow 0.$$

The lowering in energy from f relative to the increase in energy from E then becomes $a\eta^2 \ln \eta$ where a , the coefficient of the singular term in f , ranges between 0.015 and 0.038 when r_s goes from 1 to 6. The attraction is thus far too weak to be of any importance.

It should be pointed out that it is not clear if there should be a z^2 factor in f when we use an approximation G_0 instead of the self-consistent G . To see this we use the results from Appendix B and write

$$E = \sum_k^{occ} [\epsilon(\mathbf{k}) + V_{\text{eff}}(\mathbf{k})] + \Delta E,$$

$$\Delta E = \frac{i}{(2\pi)^4} \Omega \int [\phi(k'; G) + e^{i\epsilon\Delta} \quad (118)$$

$$\times \text{Tr}(V_{\text{eff}}G + G_0^{-1}G - 1 - \ln G_0^{-1}G)] dk'_{(s)},$$

$$G_0(\mathbf{k}, \epsilon) = (\epsilon - \epsilon(\mathbf{k}) - V_{\text{eff}}(\mathbf{k}))^{-1}; \quad \epsilon(\mathbf{k}) = (\hbar^2 k^2 / 2m).$$

Suppose now that we approximate G by G_0 in ΔE , which since ΔE is stationary might not be too serious. We then have

$$E = \sum \epsilon(\mathbf{k}) + \frac{i}{(2\pi)^4} \Omega \int \phi(k'; G) dk'_{(s)}. \quad (119)$$

Since

$$\delta G_0(k) / \delta n_{k'} = 2\pi i \delta(\mathbf{k} - \mathbf{k}') \delta(\epsilon - \epsilon(\mathbf{k}) - V_{\text{eff}}(\mathbf{k})) \quad (120)$$

we have that

$$\begin{aligned} E(\mathbf{k}) &= \delta E / \delta n_{\mathbf{k}} = \epsilon(\mathbf{k}) + M(\mathbf{k}, \epsilon(\mathbf{k}) + V_{\text{eff}}(\mathbf{k})), \\ f(\mathbf{k}, \mathbf{k}') &= \delta E(\mathbf{k}) / \delta n_{\mathbf{k}'} = 2\pi i {}^0 I(k, k'); \\ \epsilon &= \epsilon' = \epsilon(\mathbf{k}_F) + V_{\text{eff}}(\mathbf{k}_F). \end{aligned} \quad (121)$$

Suppose on the other hand that we start from

$$E(\mathbf{k}) = \epsilon(\mathbf{k}) + M(\mathbf{k}, E(\mathbf{k})), \quad (122)$$

where M is a functional of G_0 . We then have for f

$$f(\mathbf{k}, \mathbf{k}') = 2\pi i z {}^0 I(k, k'); \quad \epsilon = \epsilon' = \epsilon(\mathbf{k}_F) + V_{\text{eff}}(\mathbf{k}_F). \quad (123)$$

The equations for f , (121) and (123), may be compared to Eq. (32). We thus get different results depending on

⁵⁹ See A. A. Abrikosov *et al.*, (Ref. 2), p. 36.

which of several exact formulas we put the approximation G_0 in. It seems hard to resolve this ambiguity without a numerical comparison with a calculation involving some energy-dependent M in the denominator of G .

11. SUMMARY

The main results from the formal analysis are (1) A set of self-consistent equations for the one-electron Green's function involving a screened potential W (Sec. 3 and Appendix A). (2) A variational formulation for each self-consistent equation (Appendix B). (3) A specific approximation for the first-order equation. This approximation has been named COHSEX and it involves a "Coulomb hole" and a screened exchange term (Sec. 4). (4) An expansion of the quasiparticle interaction $f(\mathbf{k}, \mathbf{k}')$ of the Landau Fermi-liquid theory in terms of the screened potential W (Sec. 5). (5) An explicit verification that for the first- and second-order terms in W , the quasiparticle energy $E(\mathbf{k})$ and the quasiparticle interaction $f(\mathbf{k}, \mathbf{k}')$ give the same result for the specific heat of an electron gas (Sec. 10).

The numerical results are primarily intended to illustrate the convergence properties of the self-consistent equations for the Green function. Without actually solving the self-consistency problem, we have been able to draw some important conclusions. These derive mainly from calculations for the electron gas but also partly from analysis of spectral data for atoms. Qualitative conclusions regarding the electron gas are expected to hold also for metals. The main conclusions are: (1) For an electron outside a closed-shell structure, COHSEX is expected to work well (Sec. 4). (2) The magnitude of the quasiparticle energy $E(\mathbf{k})$ for an electron gas is given quite well by the first-order equation (Sec. 8). To obtain a good representation of the \mathbf{k} dependence of $E(\mathbf{k})$, we have to go to the second-order equation (Sec. 10). (3) The expansion for the quasiparticle interaction has much poorer convergence than that for $E(\mathbf{k})$. In particular it seems unreliable at the alkali-metal densities (Sec. 10). (4) The \mathbf{k} dependence of $E(\mathbf{k})$ is very small at the Fermi surface (Secs. 9 and 10). (5) The quantitative results for $f(\mathbf{k}, \mathbf{k}')$ and \mathbf{k} dependence of $E(\mathbf{k})$ will probably be appreciably changed by carrying through a self-consistent solution. This might best be done by parametrizing the spectral function for the Green function and using the variational formulation. (6) The energy-dependence of the self-energy $M(\mathbf{k}, \epsilon)$ is appreciable and cannot be neglected (Sec. 9). (7) The results largely confirm the values of the correlation energy for an electron gas obtained by Nozières and Pines⁵³ and by Gaskell.⁴⁰ In addition we give a discussion of the possible errors involved (Sec. 8). (8) The electron gas does not seem to become ferromagnetic for $r_s < 7$. For higher r_s the difference between the ferromagnetic and paramagnetic energies is very small and no prediction could be made (Sec. 8).

ACKNOWLEDGMENT

The author is grateful for many stimulating discussions with members of the Solid State Science Division. In particular he wishes to thank Dr. John Robinson for a critical reading of the manuscript.

APPENDIX A. EXPANSION OF THE SELF-ENERGY M AND THE POLARIZATION PROPAGATOR P IN TERMS OF THE SCREENED INTERACTION W

The results in this Appendix up to Eq. (A25) are well known to the "Green's-function people". The present derivation, however, utilizes only the Schrödinger equation. It constitutes a "low-brow" version of those parts of the "high-brow" Green's-function theory that we need here.

We write the Schrödinger representation of the Hamiltonian for the system to be considered as

$$H = H_0 + H_1,$$

$$H_0 = \int \psi^\dagger(\mathbf{x}) h(\mathbf{x}) \psi(\mathbf{x}) d\mathbf{x}$$

$$+ \frac{1}{2} \int \psi^\dagger(\mathbf{x}) \psi^\dagger(\mathbf{x}') v(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') \psi(\mathbf{x}) d\mathbf{x} d\mathbf{x}', \quad (\text{A1})$$

$$H_1 = \int \rho(\mathbf{x}) w(\mathbf{x}, t) d\mathbf{x}, \quad \rho(\mathbf{x}) = \psi^\dagger(\mathbf{x}) \psi(\mathbf{x}),$$

where h and v are defined as in Eq. (2). We use the notation $(1) = x_1 = (\mathbf{x}_1, t_1) = (\mathbf{r}_1, \zeta_1, t_1)$. The potential $w(\mathbf{x}, t)$ is to be put equal to zero in the final formulas. Let the time-evolution operator for the state vectors in the Schrödinger representation be $V(t, t')$ when $w \neq 0$, and $U(t, t')$ when $w = 0$. The Schrödinger equation then gives

$$V(t, t') = U(t, t') - i/\hbar \int_{t'}^t U(t, t'') H_1(t'') V(t'', t') dt''. \quad (\text{A2})$$

The functional derivative of V with respect to w is

$$(\delta V(t, t') / \delta w(\mathbf{x}_2, t_2)) = -(i/\hbar) \times \text{sgn}(t - t') V(t, t_2) \rho(\mathbf{x}_2) V(t_2, t'), \quad (\text{A3})$$

if t_2 is inside the time interval determined by t and t' , otherwise $\delta V / \delta w$ is zero. We define the Heisenberg representation of the field operator by

$$\psi(\mathbf{x}, t) = V(-T_0, t) \psi(\mathbf{x}) V(t, -T_0), \quad (\text{A4})$$

where T_0 is large and positive. Schrödinger's equation then gives

$$i\hbar(\partial \psi(\mathbf{x}, t) / \partial t) = V(-T_0, t) \times [\psi(\mathbf{x}), H_0 + H_1] V(t, -T_0). \quad (\text{A5})$$

By evaluating the commutator in Eq. (A5), we obtain

$$\left[i\hbar \frac{\partial}{\partial t} - h(\mathbf{x}) - w(\mathbf{x}, t) \right] \psi(\mathbf{x}, t) - \int v(\mathbf{x}, \mathbf{x}') \psi^\dagger(\mathbf{x}', t) \psi(\mathbf{x}', t) d\mathbf{x}' \psi(\mathbf{x}, t) = 0. \quad (\text{A6})$$

Using the facts that $d\theta(t)/dt = \delta(t)$ and $\psi(\mathbf{x})\psi^\dagger(\mathbf{x}') + \psi^\dagger(\mathbf{x}')\psi(\mathbf{x}) = \delta(\mathbf{x}, \mathbf{x}')$, we obtain from Eq. (A6)

$$\left[i\hbar \frac{\partial}{\partial t} - h(\mathbf{x}) - w(\mathbf{x}, t) \right] T(\psi(\mathbf{x}, t)\psi^\dagger(\mathbf{x}', t')) - \int v(\mathbf{x}, \mathbf{x}'') T(\psi^\dagger(\mathbf{x}'', t)\psi(\mathbf{x}'', t)\psi(\mathbf{x}, t)\psi^\dagger(\mathbf{x}', t')) d\mathbf{x}'' = i\hbar \delta(\mathbf{x}, \mathbf{x}') \delta(t, t'), \quad (\text{A7})$$

where T is the Dyson time-ordering operator. The product of four field operators in Eq. (A7) can be generated by a functional derivative. Using Eq. (A3) we have

$$(\delta/\delta w(3))V(T_0, -T_0)T(\psi(1)\psi^\dagger(2)) = -\frac{i}{\hbar}V(T_0, -T_0)T(\psi^\dagger(3)\psi(3)\psi(1)\psi^\dagger(2)), \quad (\text{A8})$$

assuming t_3 to be in the interval $T_0, -T_0$. We define the one-particle Green's function by

$$G(1,2) = -\frac{i}{\hbar} \frac{\langle N | U(-T_0, T_0) V(T_0, -T_0) T(\psi(1)\psi^\dagger(2)) | N \rangle}{\langle N | U(-T_0, T_0) V(T_0, -T_0) | N \rangle}, \quad (\text{A9})$$

where $|N\rangle$ is some state of the N -particle system with $w=0$. The definition Eq. (A9) coincides with Eq. (1) when $w=0$, and $|N\rangle$ is the ground state. From Eqs. (A7), (A8), and (A9) we have

$$\left(i\hbar \frac{\partial}{\partial t_1} - h(1) - V(1) \right) G(1,2) - i\hbar \int v(1^+, 3) \frac{\delta}{\delta w(3)} G(1,2) d(3) = \delta(1,2), \quad (\text{A10})$$

where

$$V(1) = w(1) + \int v(1^+, 3) \frac{\langle N | U(-T_0, T_0) V(T_0, -T_0) \psi^\dagger(3)\psi(3) | N \rangle}{\langle N | U(-T_0, T_0) V(T_0, -T_0) | N \rangle} d(3), \quad (\text{A11})$$

$$1^+ = (\mathbf{x}_1, t_1 + \Delta) \quad \text{and} \quad v(1,2) = v(\mathbf{x}_1, \mathbf{x}_2) \delta(t_1 - t_2).$$

The second term in Eq. (A11) comes from the functional derivative of the denominator in Eq. (A9). If we had defined the Green's function without that denominator, we would have had $\langle N | U(-T_0, T_0) V(T_0, -T_0) | N \rangle \times \delta(1,2)$ instead of $\delta(1,2)$ in Eq. (A10). That, however, would have spoiled a simple definition of the inverse of the Green's function, [cf. Eqs. (A14) and (A15) below]. We note that it is important to use $v(1^+, 3)$ rather than $v(1, 3)$ in Eq. (A10) in order to correctly reproduce the four operators in Eq. (A7). In Eq. (A11), on the other hand, we can replace $v(1^+, 3)$ by $v(1, 3)$. From Eqs. (A9) and (A11) we have

$$V(1) = w(1) - i\hbar \int v(1, 3) G(3, 3^+) d(3). \quad (\text{A12})$$

T_0 is to be taken large enough so that all times of interest in $G(1,2)$ lie in the interval $(-T_0, T_0)$. Equation (A10) can be derived from Schwinger's dynamical principle, cf., e.g. the first or the second paper in Ref. 2. *The present derivation of the basic Eq. (A10) has however the virtue of being very elementary and fairly short.*

We define the self-energy operator or mass opera-

tor M by

$$\left(i\hbar \frac{\partial}{\partial t_1} - h(1) - V(1) \right) G(1,2) - \int M(1,3) G(3,2) d(3) = \delta(1,2). \quad (\text{A13})$$

From the definition of the inverse Green's function

$$\int G(1,3) G^{-1}(3,2) d(3) = \delta(1,2), \quad (\text{A14})$$

follows the identity

$$\frac{\delta G(1,2)}{\delta w(3)} = - \int G(1,4) \frac{\delta G^{-1}(4,5)}{\delta w(3)} G(5,2) d(4) d(5). \quad (\text{A15})$$

Using Eqs. (A10), (A13), and (A15) we can write M as

$$M(1,2) = -i\hbar \int v(1^+, 3) G(1,4) \frac{\delta G^{-1}(4,2)}{\delta w(3)} d(3) d(4). \quad (\text{A16})$$

We define the screened interaction W by

$$W(1,2) = \int v(1,3) \frac{\delta V(2)}{\delta w(3)} d(3). \quad (A17)$$

From Eqs. (A3) and (A11) it is easily seen that this definition gives the same result as Eq. (9), remembering that w has to be put equal to zero when the functional derivative has been taken. Using Eqs. (A12), (A15), and (A17) we can write W as

$$W(1,2) = v(1,2) + i\hbar \int v(1,3)v(2,4)G(4,5) \times \frac{\delta G^{-1}(5,6)}{\delta w(3)} G(6,4^+) d(3)d(4)d(5)d(6). \quad (A18)$$

Using the identity

$$\frac{\delta}{\delta w(1)} = \int \frac{\delta V(2)}{\delta w(1)} \frac{\delta}{\delta V(2)} d(2), \quad (A19)$$

W can be written

$$W(1,2) = v(1,2) + \int W(1,3)P(3,4)v(4,2)d(3)d(4), \quad (A20)$$

where

$$P(3,4) = i\hbar \int G(4,5)G(6,4^+) \frac{\delta G^{-1}(5,6)}{\delta V(3)} d(5)d(6). \quad (A21)$$

Introducing the vertex function Γ ,

$$\Gamma(1,2; 3) = -(\delta G^{-1}(1,2)/\delta V(3)) = \delta(1,2)\delta(1,3) + (\delta M(1,2)/\delta V(3)), \quad (A22)$$

we finally obtain the following expressions for M and P :

$$M(1,2) = i\hbar \int W(1^+,3)G(1,4)\Gamma(4,2; 3)d(3)d(4), \quad (A23)$$

$$P(1,2) = -i\hbar \int G(2,3)G(4,2^+)\Gamma(3,4; 1)d(3)d(4). \quad (A24)$$

The functional derivatives of G and W can be written

$$\frac{\delta G(1,2)}{\delta V(3)} = \int G(1,4)G(5,2)\Gamma(4,5; 3)d(4)d(5), \quad (A25)$$

$$\frac{\delta W(1,2)}{\delta V(3)} = \int W(1,4)W(5,2) \frac{\delta P(4,5)}{\delta V(3)} d(4)d(5). \quad (A26)$$

Equation (A25) follows immediately from Eqs. (A15) and (A22). To prove Eq. (A26) we write W in the form $W = v(1 - Pv)^{-1}$ and use an identity similar to that of Eq. (A15). From Eqs. (A22) to (A26) we can now generate series expansions in W .

The contribution to Γ of zero order in W is

$$\Gamma^{(0)}(1,2; 3) = \delta(1,2)\delta(1,3). \quad (A27)$$

The lowest order contributions to M and P are thus

$$M^{(1)}(1,2) = i\hbar G(1,2)W(1^+,2), \quad (A28)$$

$$P^{(0)}(1,2) = -i\hbar G(1,2^+)G(2,1).$$

To obtain the first-order contribution to Γ from Eq. (A22) it is sufficient to take the functional derivative only of the explicit G in $M^{(1)}$,

$$\Gamma^{(1)}(1,2; 3) = i\hbar G(1,3)G(3,2)W(1^+,2). \quad (A29)$$

This gives for M and P

$$M^{(2)}(1,2) = (i\hbar)^2 \int W(1^+,3)G(1,4)G(4,3)G(3,2)W(4^+,2)d(3)d(4), \quad (A30)$$

$$P^{(1)}(1,2) = -(i\hbar)^2 \int G(2,3)G(4,2^+)W(3^+,4)G(3,1)G(1,4)d(3)d(4).$$

The second-order contribution to Γ arises both from $M^{(1)}$ and $M^{(2)}$. From $M^{(1)}$ we have

$$\Gamma^{(2)'}(1,2; 3) = i\hbar W(1^+,2) \int G(1,4)G(5,2)\Gamma^{(1)}(4,5; 3)d(4)d(5) + i\hbar G(1,2) \int W(1^+,4)W(5,2)(-i\hbar)(G(5,4)G(4,3)G(3,5)^+ + G(5,3)G(3,4)G(4,5^+))d(4)d(5), \quad (A31)$$

and from $M^{(2)}$

$$\Gamma^{(2)''}(1,2; 3) = (i\hbar)^2 \int W(1^+,4)W(5^+,2)(G(1,3)G(3,5)G(5,4)G(4,2) + G(1,5)G(5,3)G(3,4)G(4,2) + G(1,5)G(5,4)G(4,3)G(3,2))d(4)d(5). \quad (A32)$$

The third-order contribution to Γ contains 49 terms, 6 from G and 6 from W in $M^{(1)}$, 3 from the G 's and 4 from the W 's in $M^{(2)}$ and 30 from the G 's in $M^{(3)}$.

We can obviously continue in this way and generate as many terms as we wish. We can also generate infinite partial summations in W . Thus if we, e.g., decide to approximate M by $M^{(1)}$ in Eq. (A22) and to consider only the functional derivative of the explicit G , we obtain the following integral equation for Γ ,

$$\Gamma(1,2;3) = \delta(1,2)\delta(1,3) + i\hbar \int W(1^+,2) \times G(1,4)G(5,2)\Gamma(4,5;3)d(4)d(5). \quad (A33)$$

Eq. (A33) generates for P the ladder-bubble sum given in Eq. (61). When we insert this Γ into Eq. (A23) we obtain for M only one diagram in each order. Thus we include the first but not the second and the third of the third-order diagrams of Fig. 1. This does not seem to be a systematic improvement on M . If at all an infinite summation should be made, a wider class of diagrams should be included. This conclusion is supported also by our results in Appendix B.

APPENDIX B. VARIATIONAL PRINCIPLES

We start by treating the case of an electron gas. The results are then generalized to the case of an arbitrary system. Klein⁶⁰ has proved that when we express the energy difference between the interacting and noninteracting ground states as a certain functional $\Delta E(G)$ of the one-particle Green's function G , this functional is stationary with respect to small changes of G relative to the true G . We write ΔE as⁶¹

$$\Delta E(G) = i \frac{\Omega}{(2\pi)^4} \int \{ \Phi(k'; G) + e^{i\epsilon'\Delta} \text{Tr}[G_0^{-1}(k')G(k') - 1 - \ln G_0^{-1}(k')G(k')] \} dk'_{(s)}, \quad (B1)$$

where the functional Φ has the property

$$\int \delta\Phi(k'; G) / \delta G(k) dk'_{(s)} = -M(k; G)e^{i\epsilon'\Delta}. \quad (B2)$$

Here Ω is the volume of the system. The variable k includes spin, momentum and energy, while in $k_{(s)}$ spin is left out. Tr stands for spin summation. The functional $M(k; G)$ becomes the true $M(k)$ when G equals the true G . From Eqs. (B1) and (B2) we see that the demand that $\delta\Delta E(G) / \delta G(k)$ be zero for all k gives

$$-M(k; G) + G_0^{-1}(k) - G^{-1}(k) = 0, \quad (B3)$$

or

$$(\epsilon - \epsilon(k) - M(k; G))G(k) = 1.$$

Since Eq. (B3) is satisfied for the true G , ΔE is stationary. Klein expressed Φ as an infinite sum of "skeleton" diagrams ordered after increasing powers of the bare interaction v . If we replace this Φ by some truncated expression Φ' , we obtain truncated functionals $\Delta E'$ and M' from Eqs. (B1) and (B2). The functional $\Delta E'$ is stationary if and only if G is a self-consistent solution of Eq. (B3), M replaced by M' .

We will now develop expressions for Φ , that give an $M(k; G)$ expanded in the screened potential W . Equation (B3) then gives the self-consistent equations for G that we derived in Appendix A and discussed in Sec. 3. We start by writing down the expectation value of the potential energy, Eq. (7):

$$\langle V \rangle = -\frac{i}{2} \frac{\Omega}{(2\pi)^4} \int e^{i\epsilon\Delta} M(k)G(k)dk. \quad (B4)$$

The Fourier transforms of M and P , Eqs. (A23) and (A24), are

$$M(k) = \frac{i}{(2\pi)^4} \int e^{-i\epsilon'\Delta'} W(k')G(k-k')\Gamma(k,k')dk', \quad (B5)$$

$$P(k') = -\frac{i}{(2\pi)^4} \int e^{i\epsilon\Delta} G(k)G(k-k')\Gamma(k,k')dk, \quad (B6)$$

where the vertex function $\Gamma(1,2;3)$ has been regarded as a function of $x_1 - x_2$ and $x_3 - x_1$ in taking the Fourier transform. We note that the $P(k)$ of Eq. (B6) has to be integrated over spin to give the $P(k)$ of Eq. (24). Comparing Eqs. (B4), (B5), and (B6) we see that

$$\langle V \rangle = \frac{i}{2} \frac{\Omega}{(2\pi)^4} \int P(k')W(k')dk', \quad (B7)$$

where for $P(k')$ we have used a slightly modified expression,

$$P(k') = -\frac{i}{(2\pi)^4} \int e^{i\epsilon\Delta} e^{-i\epsilon'\Delta'} \times G(k)G(k-k')\Gamma(k,k')dk, \quad \Delta > \Delta'. \quad (B8)$$

We have to choose Δ' smaller than Δ since the limit $\Delta' \rightarrow 0$ is taken before $\Delta \rightarrow 0$ in Eq. (B4). This modification of $P(k)$ only influences its asymptotic behavior at large ϵ . It corresponds to redefining the explicit G 's in P as $G^{\text{new}}(k) = e^{i\epsilon\Delta} G(k)$ or $G^{\text{new}}(1,2) = G(1,2^+)$. We can consider the G 's appearing in Γ and W as so modified without changing Eq. (B7). The expression for $\langle V \rangle$ can be written

$$\langle V \rangle = \frac{i}{2} \frac{\Omega}{(2\pi)^4} \int \frac{v(k) \text{Tr}P(k)}{1 - v(k) \text{Tr}P(k)} dk_{(s)}. \quad (B9)$$

Equation (B9) gives a modification of the usual rela-

⁶⁰ A. Klein, Phys. Rev. 121, 950 (1961).

⁶¹ See P. Nozières, (Ref. 1), pp. 221-229.

tion³⁴ between $\langle V \rangle$ and the inverse dielectric function, the infinite constant being taken care of by the redefinition of the Green function.

The energy shift ΔE is obtained from $\langle V \rangle$ by the well-known expression

$$\Delta E = \int_0^1 \frac{d\lambda}{\lambda} \langle V \rangle, \quad (\text{B10})$$

where all v 's in $\langle V \rangle$ are replaced λv . If we neglect the λ dependence of P we have, from Eqs. (B9) and (B10),

$$\Delta E = -\frac{i}{2} \frac{\Omega}{(2\pi)^4} \int \ln(1-v(k) \text{Tr}P(k)) dk_{(s)}. \quad (\text{B11})$$

Since the imaginary part of the dielectric function always has the same sign we have no trouble with the branches of the logarithm. The modification of P , Eq. (B8), occurs only when Pv is small compared to 1 and thus has no influence in this question. By taking the functional derivative of the Φ corresponding to Eq. (B11) we can find out what more terms are needed in Φ to make it satisfy Eq. (B2). The expression for Φ which gives M up to $(n+1)$ st order in W is

$$\Phi^{(n)}(k; G) = -\frac{1}{2} \left\{ \ln \left[1 - v(k) \sum_{m=0}^n \text{Tr}P^{(m)}(k) \right] + W(k) \sum_{m=0}^n \frac{m}{m+1} \text{Tr}P^{(m)}(k) \right\}, \quad (\text{B12})$$

where W is defined from $P = \sum_0^n P^{(m)}$. To verify this we form the functional derivative of Eq. (B12),

$$\int \frac{\delta \Phi^{(n)}(k'; G)}{\delta G(k)} dk'_{(s)} = \frac{1}{2} \int \sum_{m=0}^n \frac{1}{m+1} \times \left[W(k') \frac{\delta P^{(m)}(k')}{\delta G(k)} - m P^{(m)}(k') \frac{\delta W(k')}{\delta G(k)} \right] dk'. \quad (\text{B13})$$

$$\Delta E(G) = -\frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \frac{d\epsilon}{2\pi} \frac{d\epsilon'}{2\pi} e^{i\epsilon\Delta} e^{i\epsilon'\Delta} G(\mathbf{x}, \mathbf{x}; \epsilon) G(\mathbf{x}', \mathbf{x}'; \epsilon') v(\mathbf{x}, \mathbf{x}') - \frac{i}{2} \int \frac{d\epsilon}{2\pi} \left[\text{Tr} \left(\ln(1 - P(\epsilon)v) + W(\epsilon) \sum_{n=1}^{\infty} \frac{n}{n+1} P^{(n)}(\epsilon) \right) \right] + i \int \frac{d\epsilon}{2\pi} e^{i\epsilon\Delta} \text{Tr}(G_0^{-1}(\epsilon)G(\epsilon) - 1 - \ln G_0^{-1}(\epsilon)G(\epsilon)). \quad (\text{B14})$$

Here the quantities inside the trace are considered as matrices labelled by $(\mathbf{x}, \mathbf{x}')$ where \mathbf{x} includes position and spin. The unperturbed state is taken with full interaction between electrons and nuclei. On account of the cyclical property of a trace we can take derivatives of the matrices as if they were scalars. The proof that Eq. (B14) gives the correct energy shift and the correct equation for G follows similar lines as that for the electron gas.

Equation (B14) is however rather inconvenient since G_0 is very different from G as soon as the nuclear charge Z is larger than, say, 2. It is easy to realize that all

The functional derivatives of the mW 's in $P^{(m)}$ cancel the last term in Eq. (B13), while the functional derivatives of the $2(m+1)$ explicit G 's in $P^{(m)}$ give $-M^{(m+1)}$. A look at the details shows that $W\delta P^{(0)}/\delta G$ would not have given $M^{(1)}$ if we had had normal G 's instead of modified G 's in $P^{(0)}$. We have actually checked Eq. (B12) only for $n=0, 1$, and 2, but from the structure of the theory we conjecture that Eq. (B12) is valid for arbitrary n .

There are a few comments that can be made in connection with the important Eq. (B12). We note that there is a *definite coupling between $P^{(n)}$ and $M^{(n+1)}$* . We can thus not expand P to say first order and obtain an equation with M also of first order. It is further *not possible to sum just the ladder bubbles of Eq. (61)*. This is clear if we look at $P^{(2)}$, Fig. 2, where there is a mutual cancellation between the W derivatives of the first three diagrams. Each of these gives one third the sum of the first three diagrams in $M^{(3)}$, Fig. 1. The last three diagrams in $P^{(2)}$ on the other hand cancel their W derivatives individually and are in one-to-one correspondence with the last three diagrams of $M^{(3)}$.

So far we only know that the Φ of Eq. (B12) obeys Eq. (B2). We have also to check that Eq. (B1) is satisfied. It is enough to prove that $\lambda(d\Delta E/d\lambda) = \langle V \rangle$ since $\Delta E = 0$ for $\lambda = 0$. Comparing Eqs. (B12), (B9), and (B1) we see that $\lambda(d/d\lambda)$ applied on the explicit λv of the logarithm in Eq. (B12) gives $\langle V \rangle$. The remaining λ 's appear in connection with W and G . It is easy to see by comparing with Eq. (B13) and the discussion following that equation that these terms vanish.

The generalization of the electron-gas results to a non-uniform system is fairly simple. In the general case we have to take account also of the $V(\mathbf{x})$ term of Eq. (7), which vanishes identically for an electron gas in a uniform positive background. Glancing at Eqs. (7), (B1), and (B12) we write

occupied functions in G_0 will then be closely the same as those of an ion with charge Z . Thus, e.g., in case of a metal, what must become conduction electrons in G will in G_0 look like tightly bound core electrons. To improve the situation we split the Hamiltonian into an unperturbed part

$$H_0 = \int \psi^\dagger(\mathbf{x}) h(\mathbf{x}) \psi(\mathbf{x}) dx + \int \psi^\dagger(\mathbf{x}) V_{\text{eff}}(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') dx dx', \quad (\text{B15})$$

and a perturbation

$$H_1 = \lambda \left\{ \frac{1}{2} \int \psi^\dagger(\mathbf{x}) \psi^\dagger(\mathbf{x}') v(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') \psi(\mathbf{x}) d\mathbf{x} d\mathbf{x}' - \int \psi^\dagger(\mathbf{x}) V_{\text{eff}}(\mathbf{x}, \mathbf{x}') \psi(\mathbf{x}') d\mathbf{x} d\mathbf{x}' + \frac{1}{2} \sum'_{nm} Z_n Z_m v(\mathbf{R}_n, \mathbf{R}_m) \right\}. \quad (\text{B16})$$

V_{eff} can be chosen quite arbitrary but we may think of a Hartree potential plus Coulomb-hole and screened-exchange potentials. The $\Delta E(G)$ corresponding to H_1 of Eq. (16) is given by Eq. (B14) plus two additional terms,

$$\Delta E(G) = \text{Eq. (B14)} + i \int \frac{d\epsilon}{2\pi} e^{i\epsilon\Delta} \text{Tr}(V_{\text{eff}} G(\epsilon)) + \frac{1}{2} \sum'_{nm} Z_n Z_m v(\mathbf{R}_n, \mathbf{R}_m). \quad (\text{B17})$$

The G_0 of Eq. (B14) now of course corresponds to Eq. (B15). It is easily checked that Eq. (B17) gives the correct energy shift and equation for G .

The unperturbed energy corresponding to Eq. (B15) is simply the sum of the N smallest eigenvalues of the one-electron operator $h + V_{\text{eff}}$. While this generally is not a good approximation of the true energy, it is on the other hand not very far off. *The importance of the split into $H_0 + H_1$ lies however in the fact that G_0 has now become quite realistic.* Specifically, if we approximate G by G_0 in Eq. (B17) we find that the $V_{\text{eff}} G$ term cancels against the same term in E_0 and that the last integral in Eq. (B14) vanishes. The GGv term is the Coulomb energy and the $\ln(1 - Pv)$ term gives in the lowest approximation the HF exchange energy. If we want, we can gradually improve V_{eff} to make G_0 more closely like G . This is, however, only possible up to a certain point since V_{eff} is energy-independent.

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LARS HEDIN

Effect of electron correlation on band structure of solids



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Effect of electron correlation on band structure of solids

By LARS HEDIN

ABSTRACT

Starting from a recently developed approximation method for the one-particle Green's function the effect of electron correlation on band structure of solids is analysed. The analysis suggests that conventional band calculations, which essentially neglect valence-valence exchange, should give reasonable results except for the absolute positions of the bands. All core bands are found to shift upwards with approximately the same amount, while the highest band shifts downwards. The magnitudes of the shifts are larger, the larger the polarizability of the electrons in the highest occupied band.

For metals with a small core, such as alkali metals and aluminum, the results from a conventional band calculation can be roughly corrected using properties of the electron gas. The theoretical results for core band positions and for the Fermi level compare reasonably well with experimental results from the electron spectroscopic method developed in Uppsala and from photo emission of electrons.

The approximations proceed in two steps. First we derive formulae which involve an expansion in a screened potential W , and inversion of the dielectric function by regarding its nondiagonal elements in momentum space as perturbations. These approximations should be relevant to a fairly wide class of solids, which, however, does not include transition metals and rare earth metals. In the next step we make specific approximations of the different terms. These approximations are primarily intended for simple metals, but could, *mutatis mutandis*, be used also in other situations.

The crystal potential for the valence electrons, that we arrive at, consists of the Hartree-Fock potential from the free ions, the ordinary Hartree potential from the valence electrons and a correlation contribution, which is electron-gas like. The correlation contribution has a form which is simple enough to make it useful for numerical calculations. The influence on band gaps is expected to be significant but not drastic.

1. Introduction

The concept energy band structure is based on a one-particle equation. The equations used are akin to the Hartree-Fock equation. The energy eigenvalues are interpreted as giving the one-particle-like excitation energies in the same manner as in a Hartree-Fock approximation according to Koopmans' theorem.

It is known since long that if a Hartree-Fock theory were carried through consistently for a metal it would give a quite erroneous excitation spectrum [1], and also that the results for semiconductors would probably be quite poor.

The anomaly arises from valence-valence electron exchange. In band calculations one accordingly either neglects valence-valence exchange or treats it with the Slater [2] free electron average. The Slater approximation in many cases gives almost a constant contribution, and can never give the Hartree-Fock type anomaly. Band calculations differ from Hartree-Fock calculations also in the respect that one mostly does not try to obtain self-consistency, and that often also valence-core exchange is neglected. At present a large number of band calculations have been made. The results are qualitatively and often quantitatively in good agreement with experimental data.

The theoretical basis for band calculations is actually not as poor as the foregoing description might indicate. On good physical ground it can be expected that the effective interaction between electrons is screened, and that a screened interaction should appear in the exchange term, which makes its behaviour quite reasonable [3]. Through Pines' work [4] in the early fifties these ideas were for the first time put on a semi-quantitative basis, although many fundamental questions such as the sharpness of the Fermi surface remained unsolved. With the development of many body theory during the last decade the fundamental questions connected with band theory have been largely clarified. Explicit proposals have also been made for improved one-particle equations [5]. The main drawback in these treatments is the lack of a systematic approximation scheme and of numerical estimates.

In a recent paper [6] a systematic self-consistent theory based on a variational theorem was developed. Extensive calculations for the electron gas were made. Even though these calculations were not fully self-consistent, the main results should be reliable. The most important result was that the momentum dependence of the elementary excitations in an interacting electron gas differed from that of noninteracting electrons by only a few percent. More refined calculations however seem necessary to obtain accurate values of this small correction term. It was also found possible to locate the Fermi level fairly well. From these results it is already clear that the accepted procedure in band calculations of treating valence-valence exchange as a constant is essentially correct for free-electron-like metals. The main purpose of this paper is to separate out the electron-gas-like contributions and to estimate the correction terms arising from the periodicity of the lattice structure.

In section 2 we give a brief discussion of the Green's function formalism. The main purpose of that section is to prove that the solutions of the homogeneous part of the equation for the Green's function give the quasi-particle energies. Most of this section can be omitted by those who are ready to accept its conclusion from physical intuition.

In section 3 the polarization propagator P is analysed. The Fourier transform of P is separated into a diagonal part, and a nondiagonal part which is treated as a perturbation. The magnitude of the perturbation is discussed, and judged to be small.

In sections 4 and 5 we proceed to the main task of this paper, the analysis of the valence and core bands. In section 6 we analyse the electrostatic part of the crystal potential for the case that the charge density has a "muffin-tin" form.

In section 7 we give numerical results for Li , Na , K and Al . In section 8 we discuss accuracy, selfconsistency and possibilities of more refined calculations.

We also look at the second order exchange terms and make a comparison with the quantum defect method.

In an appendix we give improved values for the total energy and the Fermi energy of an electron gas, using an extrapolation formula. The values obtained for the chemical potential should be accurate within a few hundredths of an electron volt. In a second appendix we estimate some small coupling terms between core and valence electrons.

2. Qualitative discussion of the quasi-particle equation

For definitions and the basic properties of the one-particle Green's function we refer to section 2 of ref. 6. Here we recapitulate only a few important formulae. The one-particle Green's function has the spectral resolution

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_s \frac{f_s(\mathbf{x}) f_s^*(\mathbf{x}')}{\varepsilon - \varepsilon_s}, \quad (2.1)$$

and obeys the equation

$$[\varepsilon - h(\mathbf{x})] G(\mathbf{x}, \mathbf{x}'; \varepsilon) - \int M(\mathbf{x}, \mathbf{x}''; \varepsilon) G(\mathbf{x}'', \mathbf{x}'; \varepsilon) d\mathbf{x}'' = \delta(\mathbf{x} - \mathbf{x}'), \quad (2.2)$$

where

$$h(\mathbf{x}) = -\frac{\hbar^2}{2m} \nabla^2 - \sum_n \frac{z_n e^2}{|\mathbf{r} - \mathbf{R}_n|} + \int \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') d\mathbf{r}'. \quad (2.3)$$

The symbol \mathbf{x} stands for three space coordinates and a spin coordinate, $\mathbf{x} = \mathbf{r}, \zeta$. M is the non-local energy-dependent self-energy operator, which contains all correlation effects. The energies ε_s give the one-particle-like excitation spectrum. Now consider the homogeneous equation corresponding to Eq. (2.2)

$$[\varepsilon - h(\mathbf{x})] f(\mathbf{x}) - \int M(\mathbf{x}, \mathbf{x}'; \varepsilon) f(\mathbf{x}') d\mathbf{x}' = 0. \quad (2.4)$$

It is simple to prove that $\varepsilon = \varepsilon_s$ and $f = f_s$ is a solution in the case when ε_s is a discrete eigenvalue. For solids the ε_s are in general not discrete. The eigenvalues ε of Eq. (2.4) are then complex and give the energies of quasi-particles. We now proceed to show this.

We first notice that for a perfect lattice

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = G(\mathbf{x} + \mathbf{R}, \mathbf{x}' + \mathbf{R}; \varepsilon), \quad (2.5)$$

where \mathbf{R} is a lattice vector. We can thus expand G in terms of one-particle Bloch functions

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_{\mathbf{k}, n, n'} G_{nn'}(\mathbf{k}, \varepsilon) \varphi_{n\mathbf{k}}(\mathbf{x}) \varphi_{n'\mathbf{k}}^*(\mathbf{x}'). \quad (2.6)$$

Here \mathbf{k} is restricted to the first Brillouin zone and n is a zone index. Equation (2.2) may now be replaced by a matrix equation

$$(\varepsilon - h - M)G = 1, \quad (2.7)$$

where the matrices are labeled by the zone indices. We have one such equation for each value of \mathbf{k} . The explicit form of G is

$$G_{nn'}(\mathbf{k}, \varepsilon) = \sum_s \frac{\langle N | a_{n\mathbf{k}} | N+1, s \rangle \langle N+1, s | a_{n'\mathbf{k}}^+ | N \rangle}{\varepsilon - \varepsilon_s} + \sum_s \frac{\langle N | a_{n'\mathbf{k}}^+ | N-1, s \rangle \langle N-1, s | a_{n\mathbf{k}} | N \rangle}{\varepsilon - \varepsilon_s}, \quad (2.8)$$

where the operators $a_{n\mathbf{k}}$ refer to a representation of the field operator with the Bloch functions $\varphi_{n\mathbf{k}}$ as a basis. If the states are taken as simple Slater determinants, matrix elements like $\langle N | a_{n\mathbf{k}} | N+1, s \rangle$ are different from zero only for one value of s , namely $s=n, \mathbf{k}$. In this case we thus have

$$G_{nn'}(\mathbf{k}, \varepsilon) = \frac{\delta_{nn'}}{\varepsilon - \varepsilon_{n\mathbf{k}}}. \quad (2.9)$$

For interacting particles matrix elements like $\langle N | a_{n\mathbf{k}} | N+1, s \rangle$ will be different from zero for many states s . If we regard the matrix element as a function of ε_s , we expect this function, by an argument similar to that used for an electron gas, to be sharply peaked, at least when the maximum occurs for an ε_s close to the chemical potential μ . The analytical continuation of $G_{nn'}(\mathbf{k}, \varepsilon)$ should then have a complex pole slightly off the real axis just as in the electron gas case. We next want to construct a solution for G , valid when ε is close to a given value ε^* , which we take as one of the eigenvalues of Eq. (2.4). We then have

$$\left[\varepsilon - h - M(\varepsilon^*) - (\varepsilon - \varepsilon^*) \frac{\partial M(\varepsilon^*)}{\partial \varepsilon} \right] G(\varepsilon) = 1. \quad (2.10)$$

From the solutions of the homogeneous equation

$$\left[\varepsilon_i - h - M(\varepsilon^*) - (\varepsilon_i - \varepsilon^*) \frac{\partial M(\varepsilon^*)}{\partial \varepsilon} \right] f_i(\mathbf{x}) = 0, \quad (2.11)$$

we construct the expression

$$\sum_i \frac{f_i(\mathbf{x}) g_i^*(\mathbf{x}')}{\varepsilon - \varepsilon_i}, \quad (2.12)$$

where g_i is not yet specified. One solution to Eq. (2.11) is obviously $\varepsilon_i = \varepsilon^*$. Here and in the following we restrict ourselves to Bloch functions of a definite \mathbf{k} . Equation (2.12) is a solution for G in Eq. (2.10) if

$$\sum_i \left[1 - \frac{\partial M(\varepsilon^*)}{\partial \varepsilon} \right] f_i(\mathbf{x}) g_i^*(\mathbf{x}') = \delta(\mathbf{x} - \mathbf{x}'). \quad (2.13)$$

Eq. (2.13) is true if the g_i are chosen as the biorthogonal set to $[1 - (\partial M / \partial \varepsilon)] f_i$, which is possible if the f_i are linearly independent and form a complete set of Bloch functions of momentum \mathbf{k} . In case the antihermitian part of M and $\partial M / \partial \varepsilon$ is neglected, as can be done in the interesting cases when we are close to the Fermi surface, one can prove that the expression for G becomes

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_i \frac{f_i(\mathbf{x}) f_i^*(\mathbf{x}')}{\varepsilon - \varepsilon_i} \left[\left\langle f_i \left| 1 - \frac{\partial M(\varepsilon^*)}{\partial \varepsilon} \right| f_i \right\rangle \right]^{-1}, \quad (2.14)$$

where the f_i are assumed normalized to 1. We note that in Eqs. (2.12) and (2.14) the ε_i are discrete but complex eigenvalues. We have thus proved that the eigenvalues of Eq. (2.4) are identical to complex poles of G and thus give quasi-particle energies. This result is rather clear from physical intuition, but it seemed worth while also to verify it from the mathematical machinery. It should be pointed out that this result cannot be obtained by simply saying that we consider a finite crystal with discrete levels. The Green's function which we introduce in this case will namely be completely insignificant, since it will oscillate extremely rapidly when the energy varies.

3. Analysis of the RPA polarization propagator

We follow a previous work [6] and expand the self-energy M in terms of a screened potential W . The expression for W involves the polarization propagator P

$$W = v(1 - Pv)^{-1} = v\varepsilon^{-1}. \quad (3.1)$$

Here v is the bare Coulomb interaction, e^2/r , and ε is the dielectric function. We approximate P by

$$P(1, 2) = -i\hbar G(1, 2) G(2, 1). \quad (3.2)$$

For G we take

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_k \frac{\varphi_k(\mathbf{x}) \varphi_k^*(\mathbf{x}')}{\varepsilon - \varepsilon_k}, \quad (3.3)$$

where the $\varphi_k = \Omega^{-\frac{1}{2}} e^{i\mathbf{k}\mathbf{r}} u_k(\mathbf{x})$ and ε_k are chosen to give a reasonable approximation of the band functions and energies. Ω stands for the total volume of the solid. For core bands k stands for a \mathbf{k} -vector in the first Brillouin zone and a band index, while for the valence band and higher bands k stands for a \mathbf{k} -vector in the extended zone scheme. With this convention u_k is close to a free ion function for the core bands, and close to 1 in the outer part of the unit cell for most states in the other bands. The Fourier transform of Eq. (3.2) with respect to time gives

$$P(\mathbf{r}, \mathbf{r}'; \varepsilon) = - \sum_{k'}^{\text{occ}} \sum_k^{\text{unocc}} \frac{2(\varepsilon_k - \varepsilon_{k'})}{(\varepsilon_k - \varepsilon_{k'})^2 - \varepsilon^2} |kk'\rangle \langle kk'|, \quad (3.4)$$

where

$$|kk'\rangle = \int \varphi_k(\mathbf{x}) \varphi_{k'}^*(\mathbf{x}) d\zeta. \quad (3.5)$$

The integration over the spin variable ζ , forces k and k' to have the same spin. Eq. (3.4) gives the analogue of the Lindhard [7] or RPA dielectric function, which has been discussed by Ehrenreich and Cohen [8].

We define the Fourier transform of P with respect to \mathbf{r} and \mathbf{r}' by

$$P(\mathbf{q}, \mathbf{q}'; \varepsilon) = \frac{1}{\Omega} \int e^{i\mathbf{q}\mathbf{r}} P(\mathbf{r}, \mathbf{r}'; \varepsilon) e^{-i\mathbf{q}'\mathbf{r}'} d\mathbf{r} d\mathbf{r}'. \quad (3.6)$$

On account of the periodicity of the lattice, $P(\mathbf{q}, \mathbf{q}'; \varepsilon)$ is zero unless \mathbf{q} and \mathbf{q}' differ by a reciprocal lattice vector.

We separate P in the following two ways

$$P = P^c + P^v = P_0 + P_1. \quad (3.7)$$

P^c is that part of Eq. (3.4) where k' runs over the core states, and P^c is thus similar to the polarization propagator of a free ion. P^v is that part of Eq. (3.4) where k' runs over the occupied valence states, and P^v is thus similar to the polarization propagator of an electron gas. P_0 is that part of P which is diagonal in the momentum-representation, and P_1 is thus the non-diagonal part. The different separations of P are used in expansions of W such as

$$W = W_0 + W_0 P_1 W_0 + W_0 P_1 W_0 P_1 W_0 + \dots, \quad (3.8)$$

where

$$W_0 = v(1 - P_0 v)^{-1}. \quad (3.9)$$

We first investigate P^v . The quantity to evaluate in Eq. (3.6) is

$$\int_{\Omega} e^{i\mathbf{q}\mathbf{r}} \varphi_{\mathbf{k}}(\mathbf{r}) \varphi_{\mathbf{k}'}^*(\mathbf{r}) d\mathbf{r} = \delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}} + \sum_{\mathbf{K}} \Delta(\mathbf{k}, \mathbf{q}; \mathbf{K}) \delta_{\mathbf{k}, \mathbf{k}+\mathbf{q}-\mathbf{K}}, \quad (3.10)$$

where

$$\Delta(\mathbf{k}, \mathbf{q}; \mathbf{K}) = \frac{1}{\Omega_0} \int_{\Omega_0} e^{i\mathbf{K}\mathbf{r}} (u_{\mathbf{k}}(\mathbf{r}) u_{\mathbf{k}+\mathbf{q}-\mathbf{K}}^*(\mathbf{r}) - 1) d\mathbf{r}. \quad (3.11)$$

Here \mathbf{K} is a reciprocal lattice vector, and Ω_0 the volume of a unit cell, $\Omega_0 = \Omega/N$. From the orthonormality of the $\varphi_{\mathbf{k}}$ we have

$$\Delta(\mathbf{k}, \mathbf{0}; \mathbf{K}) = 0. \quad (3.12)$$

For the valence band and higher bands of free-electron-like metals the $u_{\mathbf{k}}$ are close to 1 except in the core region or when \mathbf{k} is close to a zone boundary. Disregarding the latter case we see from Eq. (3.11) that a generous estimate of Δ is

$$\Delta \approx \text{volume of ion core} / \text{volume of unit cell}. \quad (3.13)$$

If the distortion close to zone boundaries occurs only in a small fraction of \mathbf{k} -space it will have little influence on P^v since the Δ 's occur in integrals over \mathbf{k} -space, cf Eqs (3.14) and (3.15). From the equations we have written down it is easy to find the expression for P^v . The diagonal and non-diagonal parts are given by

$$P_0^v(\mathbf{q}, \varepsilon) = -\frac{1}{\Omega} \sum_{\mathbf{k}'}^{\text{occ.val.}} \sum_{\mathbf{k}}^{\text{unocc.}} \frac{2(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^2 - \varepsilon^2} \times \left\{ \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}} |1 + \Delta(\mathbf{k}, \mathbf{q}; \mathbf{0})|^2 + \sum_{\mathbf{K} \neq \mathbf{0}} |\Delta(\mathbf{k}, \mathbf{q}; \mathbf{K})|^2 \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}-\mathbf{K}} \right\}, \quad (3.14)$$

$$P_1^v(\mathbf{q} + \mathbf{K}_1, \mathbf{q} + \mathbf{K}_2; \varepsilon) = -\frac{1}{\Omega} \sum_{\mathbf{k}'}^{\text{occ.val.}} \sum_{\mathbf{k}}^{\text{unocc.}} \frac{2(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^2 - \varepsilon^2} \times \left\{ \Delta(\mathbf{k}, \mathbf{q} + \mathbf{K}_1; \mathbf{K}_1 - \mathbf{K}_2) \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}+\mathbf{K}_2} + \Delta^*(\mathbf{k}, \mathbf{q} + \mathbf{K}_2, \mathbf{K}_2 - \mathbf{K}_1) \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}+\mathbf{K}_1} + \sum_{\mathbf{K}} \Delta(\mathbf{k}, \mathbf{q} + \mathbf{K}_1; \mathbf{K}_1 - \mathbf{K}) \Delta^*(\mathbf{k}, \mathbf{q} + \mathbf{K}_2; \mathbf{K}_2 - \mathbf{K}) \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}+\mathbf{K}} \right\}. \quad (3.15)$$

To investigate the convergence of the sum over \mathbf{K} in Eqs (3.14) and (3.15) we write Δ as

$$\Delta^*(\mathbf{k}, \mathbf{q}; \mathbf{K}) = \frac{\hbar \mathbf{q} \langle \mathbf{k} | e^{-i\mathbf{q}\mathbf{r}} \mathbf{P} | \mathbf{k} + \mathbf{q} - \mathbf{K} \rangle}{m \varepsilon_{\mathbf{k}+\mathbf{q}-\mathbf{K}} - \varepsilon_{\mathbf{k}} + \frac{\hbar^2 \mathbf{q}^2}{2m}}, \quad (3.16)$$

where \mathbf{P} is the momentum operator, and the matrix element is taken between Bloch functions. Eq. (3.16) follows by taking a matrix element of the commutator $[H_{\text{eff}}, e^{-i\mathbf{q}\mathbf{r}}]$, where H_{eff} is the one-particle Hamiltonian corresponding to the Bloch functions $\varphi_{\mathbf{k}}$ and energies $\varepsilon_{\mathbf{k}}$. For large \mathbf{K} we see that Δ is at most of the order

$$\Delta(\mathbf{k}, \mathbf{q}; \mathbf{K}) \cong \frac{2k'q}{K^2}, \quad (3.17)$$

where we have replaced $\mathbf{k} + \mathbf{q} - \mathbf{K}$ by the \mathbf{k}' appearing in Eq. (3.14). We now decouple $|\Delta|^2$ in Eq. (3.14) from the summation over \mathbf{k}' by replacing k' in Eq. (3.17) by its maximum value, k_F . If we further replace $\varepsilon_{\mathbf{k}}$ and $\varepsilon_{\mathbf{k}'}$ by free particle energies, the last term in Eq. (3.14) becomes

$$\sum_{\mathbf{K} \neq \mathbf{0}} P^{\text{el.gas}}(\mathbf{q} - \mathbf{K}, \varepsilon) \frac{4k_F^2 q^2}{K^4}.$$

Since for the electron gas $P(q, \varepsilon) \approx (1/q)^2$ for large q we see that the last term in Eq. (3.14) converges as rapidly as K^{-6} . The same is true for Eq. (3.15). Since Δ is a small quantity, we neglect the last term in Eq. (3.14) as being of order Δ^2 . We then have a result for P_0^v which differs from that for the electron gas in only two respects. We have an additional factor $|1 + \Delta|^2$ and the $\varepsilon_{\mathbf{k}}$ have the effect of the periodic lattice.

Since $P_0^v(q; \varepsilon)$ appears only in the combination

$$1 - \frac{4\pi e^2}{q^2} P_0^v(q; \varepsilon),$$

it is its behaviour for small q that is of most interest. In the single *OPW* approximation, i.e. keeping only 1 orthogonalized plane wave, we obtain for Δ

$$\Delta(\mathbf{k}, \mathbf{q}; \mathbf{0}) \cong -\frac{1}{2} \sum_c |\alpha_c(\mathbf{k} + \mathbf{q}) - \alpha_c(\mathbf{k})|^2, \quad (3.18)$$

where $\alpha_c(\mathbf{k}) = 1/\Omega_0^{\frac{1}{2}} \int u_c^*(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} d\mathbf{r}$, $u_c(\mathbf{r}) =$ core function, and we have kept only the term of lowest order in q . We note that one has to take normalization of the *OPW*'s properly into account in order not to have a spurious non-zero result for $\Delta(\mathbf{k}, \mathbf{0}; \mathbf{0})$. According to this estimate, Δ is indeed very small in the region of q -space that is of interest, namely $q \lesssim 2k_F$. We have also calculated Δ from Callaway's wavefunctions for sodium [10] and find that for $k \rightarrow 0$, $q \rightarrow 0$, $\Delta(\mathbf{k}, \mathbf{q}; \mathbf{0}) = -0.0083(q/k_F)^2$, where k_F is the Fermi momentum.

We next turn to the estimation of P_0^c . If we assume a negligible overlap between core functions on different atoms, we find from Eq. (3.4) that $P^c(\mathbf{r}, \mathbf{r}'; \varepsilon)$ can be written as a sum of non-overlapping polarization propagators. We compare one of these with the expression for the polarization propagator of a free ion in the so called uncoupled Hartree-Fock approximation [9], which is known to work reasonably well for closed shell systems. The core-functions φ_k , are closely the same in both cases. The sum over k in Eq. (3.4) runs over all functions orthogonal to the core functions except the occupied functions in the valence band. The functions φ_k in the two cases differ in the core region mainly from the use of different boundary conditions, since the potentials are roughly the same. The energies ε_k and $\varepsilon_{k'}$ are certainly different in the solid compared to the free ion, but the shifts are small compared to the differences $\varepsilon_k - \varepsilon_{k'}$ between core and valence levels. Since the boundary conditions are applied well outside the core region we find that P^c in one lattice cell is roughly the same as the P of a free ion. The missing terms "occ val" in the sum over k in Eq. (3.4) have little influence since the oscillator strength of P^c considered as a function of energy is peaked at roughly [highest core energy], and only has a small tail in the region of the missing terms. The error introduced is of the order of a few percent. We thus have

$$P_0^c(\mathbf{q}, \varepsilon) \cong \frac{1}{\Omega_0} \int e^{i\mathbf{q}\mathbf{r}} P^{\text{ion}}(\mathbf{r}, \mathbf{r}'; \varepsilon) e^{-i\mathbf{q}'\mathbf{r}'} d\mathbf{r} d\mathbf{r}'. \quad (3.19)$$

For those ε where $P_0^v \neq 0$, P_0^c is little different from its static value, and we can put $\varepsilon = 0$ in Eq. (3.19). The q -dependence of P_0^c is also much weaker than that of P_0^v in the region of interest, $q \lesssim 2k$. We approximate P_0^c by its limit when $q \rightarrow 0$, $\varepsilon \rightarrow 0$

$$\lim_{q \rightarrow 0} -v(q) P_0^c(q, 0) = \frac{4\pi}{\Omega_0} \alpha_D, \quad (3.20)$$

where α_D is the dipolar polarizability of a free ion in the uncoupled Hartree-Fock approximation. If we had had a lattice only of ions and with no valence electrons, the static dielectric constant would have been

$$\varepsilon_s = 1 + \frac{4\pi}{\Omega_0} \alpha_D. \quad (3.21)$$

We thus arrive at the following approximation for the diagonal part of the dielectric function

$$\varepsilon_s \left[1 - \frac{v(q)}{\varepsilon_s} P_0^v(q, \varepsilon) \right], \quad (3.22)$$

where P_0^v is given by Eq. (3.14).

4. Discussion of the valence band

The main effects of the periodic lattice are embodied in the crystal potential appearing in the $h(\mathbf{x})$ of Eq. (2.3). The selfenergy operator M is certainly modified compared to the electron gas case, but the corrections are only of order Δ . For simple metals the correction is small, but even for semiconductors like *Si* and *Ge*, it should not be too large, and an expansion in Δ should still be a proper procedure.

In this section we will only discuss the first order term of M in its W -expansion. The second order term is also mainly free-electron like, and since it is small the corrections arising from the presence of a periodic lattice are not very important. The influence of M on band gaps is discussed in sec. 8.

The first order term of M can be written

$$M(\mathbf{x}, \mathbf{x}', \varepsilon) = \frac{i}{2\pi} \int e^{-i\varepsilon'\delta} W(\mathbf{x}, \mathbf{x}'; \varepsilon') G(\mathbf{x}, \mathbf{x}'; \varepsilon - \varepsilon') d\varepsilon', \quad (4.1)$$

where δ is a small positive quantity. To calculate the quasi-particle energy E_k , we only need the expectation value of M . Approximating E_k by ε_k in the energy argument of M , which our experience from the electron gas case tells us is a reasonable thing to do, we have from Eqs. (3.3) and (4.1)

$$M(k) = \int \varphi_k^*(\mathbf{x}) M(\mathbf{x}, \mathbf{x}'; \varepsilon_k) \varphi_k(\mathbf{x}') d\mathbf{x} d\mathbf{x}' = \frac{i}{2\pi} \int e^{-i\varepsilon\delta} \sum_{k'} \frac{\langle kk' | W(\varepsilon) | kk' \rangle}{\varepsilon_k - \varepsilon_{k'} - \varepsilon} d\varepsilon. \quad (4.2)$$

In the last section we split off a core part of the polarization propagator, Eq. (3.7). It is also convenient to split off a core part of the Green's function

$$G^c(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_k^{\text{core}} \frac{\varphi_k(\mathbf{x}) \varphi_k^*(\mathbf{x}')}{\varepsilon - \varepsilon_k}. \quad (4.3)$$

Writing $P = P_0 + P_1^v + P_1^c$, $W = W_0 + W_0(P_1^v + P_1^c)W_0$ (neglecting the third order terms), and $G = G^c + (G - G^c)$, we obtain

$$\begin{aligned} M(k) &= M_I + M_{II} + M_{III} + M_{IV} \\ M_I &= G^c W \cong \text{core-valence exchange} \\ M_{II} &= (G - G^c) W_0 = \text{electron-gas-like result} \\ M_{III} &= (G - G^c) W_0 P_1^v W_0 = O(\Delta^2) \\ M_{IV} &= (G - G^c) W_0 P_1^c W_0 = O(\alpha\Delta). \end{aligned} \quad (4.4)$$

To see that the first term gives essentially the ordinary core-valence exchange contribution, we separate it out explicitly

$$M_{\text{I}} = - \sum_{k'}^{\text{core}} \langle kk' | v | kk' \rangle + \frac{i}{2\pi} \int \sum_{k'}^{\text{core}} \frac{\langle kk' | W(\varepsilon) - v | kk' \rangle}{\varepsilon_k - \varepsilon_{k'} - \varepsilon} d\varepsilon. \quad (4.5)$$

We have to show that the last term in Eq. (4.5) is small. To do that we replace W by $W^v + W^v P^c W^v$, where W^v is defined from $v(1 - P^v v)^{-1}$, and thus is not diagonal in momentum space. From the energies involved in P^v one realizes that $W^v(\varepsilon) - v$ rapidly approaches zero when ε becomes larger than the Fermi energy. When the energy difference between valence and core bands, $\varepsilon_k - \varepsilon_{k'}$, which appears in the denominator of Eq. (4.5), is much larger than the Fermi energy, which often is the case, one can expect that the integral should give a contribution roughly $\varepsilon_F / |\varepsilon_k - \varepsilon_{k'}|$ smaller than the first term in Eq. (4.5). Explicit estimates made in appendix B support that conclusion. We then have a remaining contribution involving the matrix element $\langle kk' | W^v P^c W^v | kk' \rangle$, which approximately can be replaced by $\langle kk' | v P^c v | kk' \rangle$. This contribution to $G^c W$ is of the order of a core-valence exchange matrix element squared, divided by a core-valence energy difference, and thus is very small compared to the first term in Eq. (4.5), which itself is rather small.

We next consider the second term in Eq. (4.4). Straight-forward calculations give

$$M_{\text{II}} = \frac{i}{(2\pi)^4} \int e^{-i\varepsilon\delta} \frac{W_0(\mathbf{q}, \varepsilon)}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon} |1 + \Delta(\mathbf{k}, \mathbf{q}; \mathbf{0})|^2 d\varepsilon d\mathbf{q} \\ + \frac{i}{(2\pi)^4} \sum_{\mathbf{K} \neq \mathbf{0}} \int e^{-i\varepsilon\delta} \frac{W_0(\mathbf{q}, \varepsilon)}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}-\mathbf{K}} - \varepsilon} |\Delta(\mathbf{k}, \mathbf{q}; \mathbf{K})|^2 d\varepsilon d\mathbf{q}. \quad (4.6)$$

The explicit expression for W_0 is

$$W_0(\mathbf{q}, \varepsilon) = \frac{v(\mathbf{q})}{\varepsilon_s} \left(1 - \frac{v(\mathbf{q})}{\varepsilon_s} P_0^v(\mathbf{q}, \varepsilon) \right)^{-1}, \quad v(\mathbf{q}) = \frac{4\pi e^2}{q^2}, \quad (4.7)$$

where P_0^v is given by Eq. (3.14) and ε_s by Eq. (3.21). This contribution to M reduces to the electron gas result if we put $\varepsilon_s = 1$, $\Delta = 0$ and $\varepsilon_k = \hbar^2 k^2 / 2m$. If we put $\varepsilon_s = 1$ and neglect the Δ^2 -terms in Eqs (4.6) and (3.14), we have a result which is formally very similar to that derived by Bassani, Robinson, Goodman and Schrieffer [5]. The present result is however not limited to an *OPW* scheme, and the Δ 's can be estimated from any type of calculation for the wavefunctions. A Wigner-Seitz method with a spherical approximation of the cell should give accurate enough results for the small quantity Δ . We also note that if we apply Bassani, Robinson, Goodman and Schrieffer's formula as it stands we will get $\Delta(k, 0; 0) \neq 0$, which, from Eq. (3.12), we know is incorrect.

The last two terms in Eq. (4.4) can be written, neglecting a small contribution involving $P_1 \Delta^2$

$$\begin{aligned}
 M_{\text{III}} + M_{\text{IV}} = & \frac{i}{(2\pi)^4} \int \sum_{\mathbf{K} \neq 0} \frac{W_0(\mathbf{q}, \varepsilon) W_0(\mathbf{q} + \mathbf{K}, \varepsilon)}{\varepsilon_{\mathbf{K}} - \varepsilon_{\mathbf{K} + \mathbf{q}} - \varepsilon} d\mathbf{q} d\varepsilon \\
 & \times \{P_1(\mathbf{q}, \mathbf{q} + \mathbf{K}; \varepsilon) \Delta(\mathbf{k}, \mathbf{q} + \mathbf{K}; \mathbf{K}) + P_1(\mathbf{q} + \mathbf{K}, \mathbf{q}; \varepsilon) \Delta^*(\mathbf{k}, \mathbf{q} + \mathbf{K}; \mathbf{K})\}. \quad (4.8)
 \end{aligned}$$

Since P_1^c is linear in Δ it gives a contribution of order Δ^2 in Eq. (4.8), while P_1^c gives a contribution of order $\alpha\Delta$, where α is the polarizability of the free ion. Both contributions should generally be small, but can be estimated in particular cases.

If we consistently neglect all Δ^2 -terms, that is Eq. (4.8) and the last term in Eqs. (3.14) and (4.6), we are left with an expression, which is similar in structure to the electron gas result. The differences consist in that the $\varepsilon_{\mathbf{k}}$ have the effect of the lattice, and in $v(q)$ being replaced by $v(q) |1 + \Delta(\mathbf{k}, \mathbf{q}; 0)|^2 / \varepsilon_s = v(q) / \varepsilon_s^*$. From Schwartz' inequality one can show that $|1 + \Delta(\mathbf{k}, \mathbf{q}; 0)|$ is always smaller than 1 so that ε_s^* is larger than ε_s . The effect of bandstructure can be roughly taken into account by replacing $v(q)$ by $v(q) / \varepsilon_s^*$ and $\varepsilon_{\mathbf{k}}$ by $(1/m^*) \hbar^2 k^2 / 2m$. This amounts to rescaling the electron gas value of M as

$$M^*(r_s) = \frac{m^*}{\varepsilon_s^{*2}} M(r_s^*), \quad r_s^* = \frac{m^* r_s}{\varepsilon_s^*}. \quad (4.9)$$

The use of an effective mass m^* is probably not of much significance for free-electron-like metals, since we know from electron gas calculations, that the integration over \mathbf{q} in Eq. (4.6) extends far enough to have a smoothing effect on the deviations of $\varepsilon_{\mathbf{k}}$ from $\hbar^2 k^2 / 2m$. For a degenerate semiconductor, on the other hand, it is appropriate for approximately parabolic bands to use an effective mass [11]. In this case the "core" should include also the valence band, and r_s^* can become smaller than 1, since ε_s is generally large while m^* is small.

5. Discussion of the core bands

The core functions are essentially unchanged in going from the ion to the solid. The core energies, on the other hand, change appreciably. The larger part of this change comes from the electrostatic potential of the valence electrons, but also polarization effects are quite important. The reason why the wavefunctions do not change much is that both the electrostatic and the polarization potentials are slowly varying in the core region. The situation is analogous to differences between ion and atom, but the changes are less marked than between ion and solid since in the solid the valence electron is confined to the unit cell while in the atom it extends much further out. To see the order of the different effects we quote some figures for the 1s energy level in the lithium ion and atom, given in Ry.

$$\begin{array}{ll}
 \text{Ion: } \varepsilon_{\text{HF}} = -5.585 & \text{Atom: } \varepsilon_{\text{HF}} = -4.956 \\
 \varepsilon_{\text{expr}} = -5.560 & \varepsilon_{\text{expr}} = -4.767
 \end{array}$$

The difference $\varepsilon_{\text{HF}}(\text{atom}) - \varepsilon_{\text{HF}}(\text{ion}) = 0.629$ gives essentially the change from the Hartree potential of the 2s electron. The difference $\varepsilon_{\text{expr}}(\text{atom}) - \varepsilon_{\text{HF}}(\text{atom}) = 0.189$ gives the polarization contribution, which is seen to be quite appreciable, and much larger than the polarization contribution in the ion, $\varepsilon_{\text{expr}}(\text{ion}) - \varepsilon_{\text{HF}}(\text{ion}) = 0.025$.

In performing the formal analysis it is convenient to split $M(k)$ into the following five terms

$$\begin{aligned}
 M(k) &= M_{\text{I}} + M_{\text{II}} + M_{\text{III}} + M_{\text{IV}} + M_{\text{V}}, \\
 M_{\text{I}} &= - \sum_{k'}^{\text{occ}} \langle kk' | v | kk' \rangle \\
 M_{\text{II}} &= \frac{i}{2\pi} \int \sum_{k' \notin B_k} \frac{\langle kk' | W^v(\varepsilon) - v | kk' \rangle}{\varepsilon_k - \varepsilon_{k'} - \varepsilon} d\varepsilon \\
 M_{\text{III}} &= \frac{i}{2\pi} \int \sum_{k' \in B_k} \frac{\langle kk' | W^v(\varepsilon) - v | kk' \rangle}{\varepsilon_k - \varepsilon_{k'} - \varepsilon} d\varepsilon \\
 M_{\text{IV}} &= \frac{i}{2\pi} \int \sum_{k' \in B_k} \frac{\langle kk' | W^v(\varepsilon) P^c(\varepsilon) W^v(\varepsilon) | kk' \rangle}{\varepsilon_k - \varepsilon_{k'} - \varepsilon} d\varepsilon \\
 M_{\text{V}} &= \frac{i}{2\pi} \int \sum_{k' \notin B_k} \frac{\langle kk' | W^v(\varepsilon) P^c(\varepsilon) W^v(\varepsilon) | kk' \rangle}{\varepsilon_k - \varepsilon_{k'} - \varepsilon} d\varepsilon. \tag{5.1}
 \end{aligned}$$

W^v is an electron-gas-like screened interaction defined by $W^v = v(1 - P^v v)^{-1}$. The symbols $k' \in B_k$ and $k' \notin B_k$ indicate that k' is in the same band as k respectively not in the same band as k . We will show that the different terms in Eq. (5.1) have the following significance:

M_{I} : core-core + core-valence exchange

M_{II} : dominant polarization contribution

M_{III} : small, but not quite negligible

M_{IV} : second order energy of free ion

M_{V} : second order energy of free ion.

The statement regarding M_{I} is by definition true. We note that there is negligible coupling between different lattice cells for all contributions to M in Eq. (5.1). To see this we write M_{I} as

$$M_{\text{I}} = - \frac{1}{N} \sum_{k'}^{\text{occ}} \sum_{\mathbf{R}} e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}} \iint_{\Omega_0} \varphi_k(\mathbf{x}) \varphi_{k'}^*(\mathbf{x}) \frac{e^2}{|\mathbf{r}-\mathbf{r}'+\mathbf{R}|} \varphi_{k'}^*(\mathbf{x}') \varphi_{k'}(\mathbf{x}') d\mathbf{x} d\mathbf{x}'. \tag{5.2}$$

In Eq. (5.2) we have normalized φ_k to 1 in the unit cell,

$$\varphi_k = \Omega_0^{-\frac{1}{2}} e^{i\mathbf{k}\mathbf{r}} u_k(\mathbf{r}).$$

The $\varphi_{k'}(\mathbf{x})$ appearing in the integral are very close to atomic functions when k' is in a core band. If we neglect the dependence on \mathbf{k}' in each band, which

is a very good approximation, we obtain a factor $\sum_{\mathbf{k}'} e^{-i\mathbf{k}'\mathbf{R}} = N\delta_{\mathbf{R},0}$ and thus we have no interatomic exchange coupling. To investigate the $\mathbf{R} \neq 0$ terms in Eq. (5.2) when k' is in the valence band, we expand the Coulomb potential in a multipole series. The first non-vanishing term is the dipolar one, since φ_k and $\varphi_{k'}$ are closely orthogonal in the unit cell. The dipole matrix elements are small compared to the nearest neighbor distance, and explicit estimates show that the contributions to M_{I} from the nearest neighbors are extremely small. Rapid convergence in the summation over \mathbf{R} is assured by the summation over \mathbf{k}' , due to the phase-factors in Eq. (5.2). Similar arguments may be carried through for the contributions $M_{\text{II}}-M_{\text{V}}$.

To treat M_{II} we note that the bandwidths of core bands are very much smaller than the Fermi energy. We thus can write M_{II} as

$$M_{\text{II}} = -\frac{1}{2} \sum_{\mathbf{k}' \in B_k} \langle k\mathbf{k}' | W^v(0) - v | k\mathbf{k}' \rangle. \quad (5.3)$$

We expand $W^v - v$ as

$$W^v - v = (W_0^v - v) + W_0^v P_1^v W_0^v. \quad (5.4)$$

The contribution to Eq. (5.3) from the first term in Eq. (5.4) can be written

$$M_{\text{IIa}} = -\frac{1}{2} \sum_{c'} \langle cc' | W_0^v - v | cc' \rangle, \quad (5.5)$$

where c and c' now stand for atomic functions normalized to 1, and c' is summed over atomic states with the same spin as c . Thus c' takes on only one value when c is an s -function, and three values when c is a p -function. We write $W_0^v - v$ in coordinate space as

$$(W_0^v - v)_{(\mathbf{r}-\mathbf{r}')} = \int e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} A(\mathbf{q}) d\mathbf{q}$$

$$A(\mathbf{q}) = \frac{v(q)}{(2\pi)^3} [(1 - P_0^v(\mathbf{q}, 0)v(q))^{-1} - 1], \quad v(q) = \frac{4\pi e^2}{q^2}. \quad (5.6)$$

Since the functions c and c' are localized to the core region, only small values of $\mathbf{r}-\mathbf{r}'$ will contribute in Eq. (5.6), and we can make a series expansion in powers of $\mathbf{r}-\mathbf{r}'$ (cf. fig. 6 in ref. 6). We obtain

$$M_{\text{IIa}} = -\frac{1}{2} \left\{ \int A(\mathbf{q}) d\mathbf{q} - \frac{1}{3} \langle c | r^2 | c \rangle \int q^2 A(\mathbf{q}) d\mathbf{q} + \dots \right\}, \quad (5.7)$$

where we have used the fact that, because c and c' have the same angular momentum, $\langle c | \mathbf{r} | c' \rangle = 0$. If we approximate P_0^v by its electron gas value we have

$$M_{\text{IIa}} \cong -M_{\text{COH}} + \frac{1}{6} \langle c | r^2 | c \rangle 4\pi e^2 g_0(0) + \dots, \quad (5.8)$$

where M_{COH} is the Coulomb hole energy and $g_0(\mathbf{r})$ the Coulomb hole function given in Eqs (89) and (52) of ref. 6. The numerical values of M_{COH} are given in ref. 6, and of $g_0(\mathbf{r})$ in a work by Langer and Vosko [12]. We note that $g_0(0)$ as defined in Eq. (52) of ref. 6 is a negative number. Since M_{COH} is a negative number, the first term in Eq. (5.8) is positive, while the second is negative.

From the second term in Eq. (5.4) we have the contribution

$$M_{\text{IIb}} = -\frac{1}{2} \sum_{c'} \langle cc' | W_0^v P_1^v W_0^v | cc' \rangle. \quad (5.9)$$

Neglecting the second order term in Δ , we write P_1^v , Eq. (3.15), as

$$P_1^v(\mathbf{r}, \mathbf{r}'; 0) = \frac{1}{\Omega} \sum_{\mathbf{k}'}^{\text{occ val}} \sum_{\mathbf{k}''}^{\text{unocc}} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{2\delta_{\mathbf{k}', \mathbf{k}''+\mathbf{k}}}{\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}''}} e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')} \\ \times \{ (u_{\mathbf{k}''}(\mathbf{r}) u_{\mathbf{k}'+\mathbf{k}}^*(\mathbf{r}) - 1) - \Delta(\mathbf{k}'', \mathbf{k}; \mathbf{0}) + (u_{\mathbf{k}''}^*(\mathbf{r}') u_{\mathbf{k}'+\mathbf{k}}(\mathbf{r}') - 1) - \Delta^*(\mathbf{k}'', \mathbf{k}; \mathbf{0}) \}. \quad (5.10)$$

In deriving in Eq. (5.10) we have used the fact that

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} = \Omega_0 \delta(\mathbf{r}), \quad (5.11)$$

when \mathbf{r} is in lattice cell zero. We obtain for M_{IIb}

$$M_{\text{IIb}} = -\frac{1}{2} \frac{1}{\Omega} \sum_{\mathbf{k}'}^{\text{occ val}} \sum_{\mathbf{k}''}^{\text{unocc}} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{2\delta_{\mathbf{k}', \mathbf{k}''+\mathbf{k}}}{\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}''}} \sum_{c'} \\ \times \{ \langle cc' | W_0^v | \varphi_{\mathbf{k}''} \varphi_{\mathbf{k}'+\mathbf{k}} - \Omega_0^{-1} e^{-i\mathbf{k}\mathbf{r}} \rangle \langle e^{-i\mathbf{k}\mathbf{r}} | W_0^v | cc' \rangle \Omega_0 \\ + \langle cc' | W_0^v | e^{-i\mathbf{k}\mathbf{r}} \rangle \langle \varphi_{\mathbf{k}''} \varphi_{\mathbf{k}'+\mathbf{k}}^* - \Omega_0^{-1} e^{-i\mathbf{k}\mathbf{r}} | W_0^v | cc' \rangle \Omega_0 \\ - | \langle cc' | W_0^v | e^{-i\mathbf{k}\mathbf{r}} \rangle |^2 (\Delta(\mathbf{k}'', \mathbf{k}; \mathbf{0}) + \Delta^*(\mathbf{k}'', \mathbf{k}; \mathbf{0})) \}. \quad (5.12)$$

In Eq. (5.12) we have normalized $\varphi_{\mathbf{k}}$ to 1 in the unit cell.

We make the approximation

$$\langle e^{-i\mathbf{k}\mathbf{r}} | W_0^v | cc' \rangle = W_0^v(\mathbf{k}, 0) \langle c' | e^{i\mathbf{k}\mathbf{r}} | c \rangle \cong \delta_{cc'} W_0^v(\mathbf{k}, 0), \quad (5.13)$$

which comes from neglecting terms of order $(\mathbf{k}\mathbf{r})^2$ in an expansion of $e^{i\mathbf{k}\mathbf{r}}$, and thus should be quite good. To obtain an order of magnitude estimate of Eq. (5.12) we neglect the \mathbf{k}'' dependence in the matrixelement and in Δ . We then have

$$M_{\text{IIb}} = - \int \frac{d\mathbf{k}}{(2\pi)^3} P_0^v(\mathbf{k}, 0) W_0^v(\mathbf{k}, 0) \\ \times \text{Re} \{ \Omega_0 \langle cc | W_0^v | \varphi_{\mathbf{k}_0} \varphi_{\mathbf{k}_0+\mathbf{k}}^* - \Omega_0^{-1} e^{-i\mathbf{k}\mathbf{r}} \rangle - W_0^v(\mathbf{k}, 0) \Delta(\mathbf{k}_0, \mathbf{k}; \mathbf{0}) \}, \quad (5.14)$$

Table 1

| r_s | $g_0(0)$ | Ω_0 | A |
|-------|----------|------------|------|
| 1.5 | -.1558 | 14.14 | 2.20 |
| 3 | -.03341 | 113.1 | 3.78 |
| 4.5 | -.01343 | 381.7 | 5.13 |
| 6 | -.007007 | 904.8 | 6.34 |

where we have replaced \mathbf{k}' by the Fermi momentum \mathbf{k}_0 in the matrixelement and in Δ , and neglected the Δ 's in P_0^v of Eq. (3.14). We further use electron gas values for P and W , and put $\mathbf{k}=0$ in the matrix element and equal to \mathbf{k}_0 in Δ . This procedure is likely to overestimate Δ . Our estimate of the magnitude of M_{IIb} becomes

$$\begin{aligned}
 M_{\text{IIb}} &\cong A \langle cc | W_0^v | \varphi_{\mathbf{k}_0}, \varphi_{\mathbf{k}_0}^* - \Omega_0^{-1} \rangle + B \Delta(\mathbf{k}_0, \mathbf{k}_0; 0) \\
 A &= -\Omega_0 \int \frac{d\mathbf{k}}{(2\pi)^3} \left(\frac{1}{\varepsilon(\mathbf{k}, 0)} - 1 \right) = -\Omega_0 g_0(0) \\
 B &= \int \frac{d\mathbf{k}}{(2\pi)^3} W_0(\mathbf{k}, 0) \left(\frac{1}{\varepsilon(\mathbf{k}, 0)} - 1 \right). \tag{5.15}
 \end{aligned}$$

In table 1 we give values of $g_0(0)$ and A as obtained from ref. 12. The values are given in atomic units. The matrixelement multiplying A in Eq. (5.15) is small for two reasons. The first reason is that W_0 is a strongly screened potential. The second reason is that $|\varphi_{\mathbf{k}_0}|^2 - (1/\Omega_0)$ is oscillating in sign. Numerical estimates give values of a few thousandths of a Ry. The contribution to M_{IIb} is thus of the order of 0.01 Ry or less. The quantity B equals $2M_{\text{COH}}$ if we replace W_0 by v . The effect of screening makes B smaller than M_{COH} . The estimate Eq. (5.15) for M_{IIb} can easily be calculated in particular cases.

The term M_{III} can be expected to be small for the reason that $W^v - v$ is different from zero only for a fraction $\varepsilon_F/|\varepsilon_{k'} - \varepsilon_k|$ of the energy integration, cf the discussion after Eq. (4.5). The actual magnitude is estimated in appendix B, using a simplified expression for the dielectric constant. The largest shift ≈ 0.7 eV, was found to occur for the aluminum $2s$ level.

In the same manner as for the term M_{II} , we obtain

$$M_{\text{IV}} = -\frac{1}{2} \sum_{c'} \langle cc' | W^v(0) P^c(0) W^v(0) | cc' \rangle. \tag{5.16}$$

We approximate W^v by the diagonal part W_0^v . Comparing with Eqs. (5.6) and (5.7) we see that we can make the expansion

$$W_0^v(0) = \frac{e^2}{r} + \text{const.} + O(r^2). \tag{5.17}$$

Since the functions occurring in P^c are orthogonal, the constant will make no contribution. If we neglect the term of order r^2 , the contribution Eq. (5.16) becomes essentially the same as a second order perturbation correction to the level k of a free ion. In contribution M_V we can replace W^v by v when $|\varepsilon_k - \varepsilon_{k'}|$ is large compared to the Fermi energy. Also in this case we are then back to essentially a free ion contribution. The terms M_{IV} and M_V exhaust all direct second order contributions to the free ion level, calculated in a perturbation scheme based on the Hartree-Fock Hamiltonian. The first order terms are zero. The second order exchange contributions to the ion level also come out of the M -operator as discussed in section 8. We will give a detailed demonstration of this in an other paper treating correlation in atoms.

Summarizing the different contributions to a core level, we have

$$E_k = \varepsilon_k^{\text{ion}}(\text{expr}) + V_v^{\text{Coul}} + V_{cv}^{\text{exch}} + M_{II} + M_{III}, \quad (5.18)$$

where the first term is the experimental value for the level in the free ion. The second and third terms are the Coulomb and exchange interactions with the valence electrons. The shift of the level in the solid relative to the free ion comes mainly from V_v^{Coul} and the polarization term M_{II} , for which an approximation formula is given in Eq. (5.8). M_{III} is small but not quite negligible. Its dominant contribution, as shown in appendix B, comes from a coupling between different core levels via the potential $W^v - v$. In the end, after a fairly complicated analysis, we have thus arrived at a formula of quite a simple structure, namely Eq. (5.18).

6. Electrostatic potential from a "muffin-tin" charge density

To calculate the energy difference between core bands and higher bands, the difference in electrostatic potential between the center of the cell and the outer parts has to be known. In this section we will investigate that problem assuming the charge density to have a "muffin-tin" form, which is a good approximation for many metals. By a "muffin-tin" form we mean that the charge density in the Wigner-Seitz cell is spherically symmetric inside some sphere, and equals a constant ρ in the remaining part of the cell. We will take the spherical region as the inscribed sphere, and call it S . We take the origin of the coordinate system to lie in the center of S .

In the approximation of a "muffin-tin" charge density the potential in S from the charge distribution outside S can be obtained by taking the electron charge density to equal ρ everywhere outside S . We will call this potential V_L .

The potential V_L has been calculated and used by Heine [13]. It was recalculated by Behringer [14], who found an error in Heine's calculation, and the potential was used by Segall [15]. Since then there has however appeared an extensive tabulation of Hund's potential for a simple cubic lattice [16], from which V_L can easily be obtained for all cubic lattices.

We have recalculated V_L for a face-centered cubic lattice, and found it to be quite small. We have also calculated the average of the potential over the cell-

corners, i.e. the constant V_c that appears in a "muffin-tin" potential. A few remarks are made on where the zero point for the potential should be placed.

Hund's potential ϕ is the potential from unit positive point charges on a simple cubic lattice in a compensating background of uniform negative charge. The unit for the potential is e^2/a , where a is the lattice constant. The zero point of the potential is chosen according to Ewald's convention, i.e. the average value of the potential is taken as zero. In this section we will express potentials in units of $e^2/(2r_s)$, and distances in units of r_s , where r_s has its usual definition, $4\pi r_s^3/3 = \Omega_0 = \text{volume of unit cell}$.

The potential Ψ from unit point charges on a fcc lattice in a compensating uniform background is related to ϕ by

$$\Psi(\mathbf{r}) = -2 \left(\frac{3}{16\pi} \right)^{\frac{1}{2}} [\phi(\mathbf{r}) + \phi(\mathbf{r} + \mathbf{a}_1) + \phi(\mathbf{r} + \mathbf{a}_2) + \phi(\mathbf{r} + \mathbf{a}_3)], \quad (6.1)$$

where

$$2 \left(\frac{3}{16\pi} \right)^{\frac{1}{2}} = 0.781592, \quad \mathbf{a}_1 = (a/2)(1, 1, 0)$$

$$\mathbf{a}_2 = (a/2)(1, 0, 1)$$

$$\mathbf{a}_3 = (a/2)(0, 1, 1).$$

We have inserted a minus sign since the potential is to act on electrons. Two values of Ψ , to which we will refer several times, are

$$\lim_{r \rightarrow 0} \left(\Psi(\mathbf{r}) + \frac{2}{r} \right) = 3.58349$$

$$\Psi(P_2) = 0.85172. \quad (6.2)$$

P_2 is the point $(a/2, 0, 0)$, where Heine chose Ψ to be zero.

The potential V_L can, apart from a constant, be written

$$V_L = \Psi - V, \quad (6.3)$$

where

$$V(r) = 3 - r^2 - \frac{2}{r}. \quad (6.4)$$

Eq. (6.3) is valid for the case that $\varrho = \varrho_0 = 1/\Omega_0$, where Ω_0 is the volume of the unit cell. When $\varrho \neq \varrho_0$, V_L should be multiplied by ϱ/ϱ_0 . $V(r)$ is the potential from a uniform electron density ϱ_0 inside a sphere of radius r_s , and from a positive unit point charge at the origin.

The zero point of the crystal potential depends on the surface conditions of the crystal. To fix a position for the zero point we use the condition

$$V_L(0) = 0. \quad (6.5)$$

This means that we have to subtract 0.58349 from the Ψ defined by Eq. (6.1).

The values of V_L for three directions of high symmetry are given in Table 2

Table 2. Values of V_L for a fcc lattice.

| r/r_i | (1, 1, 0) | (1, 1, 1) | (1, 0, 0) | Average |
|---------|-----------|-----------|-----------|---------|
| 0 | .00000 | .00000 | .00000 | .00000 |
| 1/6 | +.00003 | -.00009 | .00016 | +.00002 |
| 2/6 | -.00037 | -.00091 | .00131 | -.00015 |
| 3/6 | -.00251 | -.00296 | .00680 | -.00050 |
| 4/6 | -.01070 | -.00540 | .02211 | -.00150 |
| 5/6 | -.03536 | -.00548 | .05493 | -.00533 |
| 6/6 | -.09906 | +.00736 | .12008 | -.01574 |

for equally spaced values of r between 0 and $r_i = 0.9047 r_s$, where r_i is the radius of the sphere S . The average in column 5 of Table 2 is formed from the second, third and fourth columns with the weights 12/26, 8/26 and 6/26 respectively. The values for the (1, 1, 0) direction were obtained directly from the tabulated values of Hund's potential, while for the other directions a linear interpolation was made. The accuracy of Hund's potential is stated [16] to be $\pm \frac{1}{2} 10^{-4}$ or better, and the positive value in the second column is probably spurious. To have V_L expressed in Rydbergs (13.605 eV) for the case of aluminum, the values in Table 2 should be multiplied by 1.163, according to Heine's estimate [13] of the charge density in the cell corners. For alkali metals V_L should be much smaller, because r_s is larger and because there is only 1 valence electron per atom, instead of 3 as for aluminum. The crystal potential is uniquely defined through the choice of zero point for Ψ specified by Eq. (6.5). In the region S it equals $V_L +$ (potential from actual charge distribution in S) + (potential from a uniform charge distribution of density ρ in the region between the spheres with radii r_i and r_s). In the region between S and the cell boundaries the crystal potential equals Ψ .

We will now calculate the average V_c of the crystal potential over the region between S and the cell boundaries

$$V_c = [\Omega_0 - 4\pi r_i^3/3]^{-1} \left(\int_{\Omega_0} \Psi d\mathbf{r} - \int_S \Psi d\mathbf{r} \right). \quad (6.6)$$

This can easily be done since, with the present definition of Ψ , we have

$$\int_{\Omega_0} \Psi d\mathbf{r} = -0.58349 \Omega_0. \quad (6.7)$$

We obtain using for V_L the values given in the last column of Table 2, $V_c = 0.0700$. For aluminum with Heine's choice of zero point for the crystal potential we have that $V_c = 1.163 (0.0700 + 0.5835 - 0.8517) \text{ Ry} = -0.2305 \text{ Ry}$, cf. Eq. (6.2), while Segall under these conditions obtained -0.273 Ry . The constant 1.163 appears in the text after Table 2.

The choice of zero point for the crystal potential is of importance for the position of the Fermi level. Perhaps the simplest choice, which is still reasonably realistic, consists in taking the crystal to be composed of an integral number of Wigner-Seitz cells all having the same charge distribution. This should provide

a sound starting point for calculating the dipole layer, which has to develop at the surface.

The average of the potential from an integral number of Wigner-Seitz cells of point charges in a uniform background is [17]

$$V_{av} = -\frac{2\pi e^2}{3\Omega_0^2} \int_{\Omega_0} r^2 d\mathbf{r}. \quad (6.8)$$

The proof of Eq. (6.8) given in ref. 17 does not seem convincing to the author. A straight-forward proof by direct integration can however be made. We follow ref. 17 and transform the integral in Eq. (6.8) by Gauss' theorem

$$V_{av} = -\frac{2\pi e^2}{3\Omega_0^2} \frac{1}{3} \int (x^2, y^2, z^2) \cdot dS. \quad (6.9)$$

Evaluation of the surface integrals for a fcc and bcc lattice gives

$$V_{av} = \begin{cases} -\frac{\pi}{2^{1/3} \gamma r_s} \text{Ry} = -0.6139 \frac{1}{r_s} \text{Ry, fcc} \\ -\frac{19\pi}{48 \gamma r_s} \text{Ry} = -0.6123 \frac{1}{r_s} \text{Ry, bcc} \end{cases} \quad (6.10)$$

$$\gamma = (8\pi/3)^{1/3} = 2.03098.$$

Our result for the fcc lattice is the same as that given for the hcp lattice by Hughes and Callaway [18]. Our result for the bcc lattice however differs from that given by Callaway and Glasser [17]

$$V_{av} = -\frac{2\pi\sqrt{221}}{75 \gamma r_s} \text{Ry} = -0.6132 \frac{1}{r_s} \text{Ry, bcc.}$$

The present choice of the zero point for the crystal potential is lower than that defined through Eq. (6.5) by $0.6139 - 0.5835 = 0.0304$ for a fcc lattice, and by $0.6123 - 0.5837 = 0.0286$ for a bcc lattice. The differences are thus rather small. The difference between Heine's choice of zero point and that given by Eq. (6.5) is on the other hand appreciable, $0.8517 - 0.5835 = 0.2682$.

7. Numerical results for *Li*, *Na*, *K* and *Al*

The results in this section are obtained from combining results of energy band calculations [15, 19], results for the electron gas [6, 12], values of free ion polarizabilities [9] and experimental values for free ion core levels [20]. We have calculated and compared with experiment the position of Fermi levels and core levels.

We first treat the Fermi level. The complete expression for the quasi-particle energy is according to Eq. (2.4)

$$E_k = \langle \varphi_k | \hbar + M(E_k) | \varphi_k \rangle. \quad (7.1)$$

We have evaluated Eq. (7.1) on the basis of calculations made by Ham [19] on *Li*, *Na*, and *K* and by Segall [15] on *Al*. Both authors used a "muffin-tin" potential. Ham's potential inside the inscribed sphere was essentially equal to the Hartree-Fock potential of the free ion. In principle his potential also contains some correlation effects of the ion, but these are probably insignificant, as we will argue in sec. 8. The flat portion of the "muffin-tin" potential was taken as the average of $(-2/r)$ Ry between spheres of radii r_i and r_s . Ham's potential can thus be written

$$V^{\text{Ham}} = \begin{cases} V_{\text{ion core}} & r < r_i \\ -\frac{2.125}{r_s} \text{Ry} & r > r_i. \end{cases} \quad (7.2)$$

The parts in $h+M$ that were not included in Ham's potential we treat as a perturbation. They are the Coulomb potential from the valence electrons and from ions in other cells than the one considered, and also $M - M_I$, where M_I is the core-valence exchange given in Eq. (4.4).

The potential which we should have according to sec. 6 using the proper values for a bcc lattice, is

$$V = \begin{cases} \frac{1}{r_s} \left(3 - \left(\frac{r}{r_s} \right)^2 \right) \text{Ry} + V_{\text{ion core}} & r < r_i \\ \frac{0.036}{r_s} \text{Ry} & r > r_i, \end{cases} \quad (7.3)$$

where we have taken a "muffin-tin" form for the potential, put $V_L = 0$ and assumed the valence-electrons to have a uniform density. The average value over the unit cell of the difference between V and V^{Ham} is

$$V_v^{\text{Coul}} = \frac{2.417}{r_s} \text{Ry}. \quad (7.4)$$

This value is quite close to what one obtains in a simple Wigner-Seitz sphere approximation, namely $2.4/r_s$ Ry.

The contribution to M of first order in the screened potential W is given Eq. (4.4). We neglect the contributions M_{III} and M_{IV} . M_I is already taken into account by Ham. For M_{II} we take the electron gas value given in appendix A, rescaled according to Eq. (4.9), with $m^* = 1$ and ϵ_s from the free ion polarizabilities tabulated by Dalgarno [9]. Higher order contributions to M , which are essentially free-electron-like, can be considered included in M_{II} . We thus arrive at the simple formula for the Fermi level

$$\mu = \mu^{\text{BS}} + V_v^{\text{Coul}} + \epsilon_s^{-2} M^{\text{el. gas}}(r_s/\epsilon_s), \quad (7.5)$$

where μ^{BS} stands for Ham's value of μ .

Segall's calculation was made on the basis of Heine's elaborate potential [13], which includes the Coulomb potential from the valence electrons. For *Al* the term V_v^{Coul} has thus to be left out in Eq. (7.5). The results from Eq. (7.5) are given in Table 3. To see the effect of scaling M , we have also given the un-

Table 3. Fermi levels of some metals in Ry.

| | Li | Na | K | Al |
|---|-------|-------|-------|---------|
| r_s | 3.248 | 3.931 | 4.862 | 2.065 |
| ϵ_s | 1.015 | 1.057 | 1.142 | 1.041 |
| $M(r_s)$ | -.471 | -.398 | -.330 | -.706 |
| $M(r_s/\epsilon_s)/\epsilon_s^2$ | -.463 | -.374 | -.285 | -.675 |
| V_v^{Coul} | +.743 | +.615 | +.497 | (2.418) |
| μ^{BS} | -.429 | -.365 | -.320 | +.401 |
| μ from $M(r_s/\epsilon_s)/\epsilon_s^2$ | -.149 | -.124 | -.108 | -.274 |
| μ_{expr} | -.168 | -.168 | -.166 | -.323 |

Table 4. Core levels of some metals in Ry.

| | Li, 1s | Na, 2s | Na, 2p | K, 3s | K, 3p | Al, 2s | Al, 2p |
|---------------------------------------|--------|--------|--------|--------|--------|---------|--------|
| $\epsilon_{\text{HF}}^{\text{ion}}$ | -5.585 | -6.147 | -3.594 | -3.928 | -2.341 | -12.304 | -8.946 |
| $\epsilon_{\text{expr}}^{\text{ion}}$ | -5.560 | -5.887 | -3.481 | -3.529 | -2.339 | -12.089 | -8.830 |
| $-M_{\text{COH}}$ | .541 | .474 | .474 | .408 | .408 | .734 | .734 |
| $g_0(0)$ | -.056 | -.064 | -.072 | -.094 | -.121 | -.021 | -.023 |
| V_v^{Coul} | .924 | .763 | .763 | .617 | .617 | 2.581 | 2.600 |
| $\mu - \epsilon_c$, calc | 4.00 | 4.59 | 2.19 | 2.49 | 1.33 | 8.52 | 5.25 |
| $\mu - \epsilon_c$, expr | 4.03 | 4.67 | 2.28 | 2.51 | 1.33 | 8.48 | 5.35 |

scaled values of $M(r_s)$. The experimental values are taken from the work function [21]. The agreement is astonishingly good considering the uncertainty in the choice of zero point for the crystal potential, cf. sec. 6. It should be noted that the choice $\Psi(P_2)=0$ used by Segall for Al gives a potential which lies $(0.273 + 1.163 \cdot 0.070) = 0.354$ Ry lower than with the choice $V_L(0)=0$ that was used for the alkali metals. Since agreement with experiment is still reasonably good, this indicates that Al should have a quite large value of the surface dipole moment. Bardeen [22] has made a rough calculation of the distortion of the charge-distribution at the crystal surface which was essentially based on the condition $V_L(0)=0$. He finds for Na, that μ is lowered by about 0.03 Ry, which considerably improves on the agreement in Table 3.

The result of our analysis for the core levels is given in Eq. (5.18). We neglect the terms M_{III} and $V_{\text{cv}}^{\text{exch}}$, and approximate M_{II} by Eq. (5.8). We thus have

$$E_k = \epsilon_k^{\text{ion}}(\text{expr}) + V_v^{\text{Coul}} - M_{\text{COH}} + \frac{2\pi}{3} e^2 g_0(0) \langle r^2 \rangle. \quad (7.6)$$

We have looked at some of the core-valence exchange terms for the alkali metals and found them to be only a few hundredths of a Ry. M_{III} has been

estimated in Appendix B. It has found to be negligible except for the *Al* 2*s*-level, where it was about 0.05 Ry. V_v^{Coul} was taken as $3/r_s$ Ry for the alkali-metals. This assumes a uniform charge density of the valence electrons, and neglects the *r*-dependence in the potential. The effect of the *r*-dependence is to lower V_v^{Coul} , and the effect of the non-uniformity of the charge-density, especially from the first maximum in the wavefunction, is to raise V_v^{Coul} , but none of these effects could be of much importance. For *Al* V_v^{Coul} was calculated from the potential of the valence electrons inside the Wigner-Seitz sphere, given by Heine [13]. Such a calculation assumes the choice of zero point for the crystal potential given by $V_L(0)=0$, and thus 0.354 Ry has to be subtracted to make the result conform with the potential used in the calculation of μ . M_{COH} was taken from ref. 6, $g_0(0)$ from ref. 12 and $\langle r^2 \rangle$ was calculated from ion wave functions. The results are given in Table 4, where for comparison the values of the ion levels in the Hartree-Fock approximation are also given. The values of μ are taken from the row " μ from $M(r_s/\epsilon_s)/\epsilon_s^2$ " in Table 3. The experimental data are taken from results obtained with the electron spectroscopic method [23] developed in Uppsala. If we include the M_{III} term, the value for the 2*s*-level in *Al* becomes 8.47 instead of 8.52.

The agreement between theory and experiment in Table 4 is gratifying, and suggests that we have succeeded to account for the major effects. The uncertainty in $M_{\text{II}} \approx -M_{\text{COH}} + g_0(0) \dots$ should be about 0.02 Ry and the left out core-valence interaction should also be of about that size. The temperature effect, which has not been taken into account, is also of the order of a few hundredths of a Rydberg.

8. Discussion

In section 7 we discussed the accuracy of the different terms in the simple approximations given by Eqs. (7.5) and (7.6). The results seem to confirm that the sorting out of small contributions, made in sections 4 and 5, was essentially correct. In particular an expansion in terms of Δ , defined by Eq. (3.11), seems to be appropriate.

The approximations given by Eqs. (7.5) and (7.6) have a simple physical and mathematical structure, and it is easy to see qualitatively what will happen when we consider other solids. Calculations for other solids than those considered here, and more refined calculations for the simple solids should be worthwhile.

So far we have not taken up the problems of self-consistency, and of the effects of M on band gaps. This problem might be treated by setting up a secular equation based on simple APW's from a "muffin-tin" potential. The non-diagonal elements of M will be linear in Δ , and for simple metals they should be of the order of a few hundredths of a Ry. It is thus possible that they could compete with the other non-diagonal elements.

To obtain a reasonable and still tractable approximation of the non-diagonal elements of M , the following simplifications could be made.

(1) The dielectric function appearing in W could be replaced by an expression such as the one used in Appendix B. The energy integration in M can then be performed analytically.

(2) The energies $\varepsilon_{k'}$ in Eq. (4.2) could be replaced by free particle energies, since the effects of band structure will be smoothed out by the integration over k' .

(3) The Bloch waves $\varphi_{k'}$ appearing in Eq. (4.2) could, for the same reason, be replaced by, say, simple APW's.

We have confined the numerical estimates to the positions of the Fermi level and the core levels. We will also give a qualitative discussion of the implications of the work on the electron gas in ref. 6, on some other properties.

(i) Level density at the Fermi surface. The correction should amount to only a few percent, which is insignificant considering the uncertainties in the magnitude of the correction from electron-phonon interaction and in the experimental values.

(ii) Bandwidth for a metal. The results from the first order term in M indicate that the correction should be only a few tenths of an eV. Judging from the change in the derivative of M at the Fermi surface when the second order term is included, the correction to the bandwidth should be even smaller and change sign.

(iii) Tail of the soft X-ray absorption curve. Part of the tail may be attributed to the imaginary part of the quasi-particle energy at $k=0$. The value obtained from the first order term in M varies between 0.5 and 1 eV, which is of about the same size as the observed tails.

(iv) Paramagnetic susceptibility. The values obtained for the electron gas, do not seem accurate enough to make a comparison with experiment.

The situation indicates the need of improved calculations for the electron gas, particularly regarding the paramagnetic susceptibility. In this case further investigations of the contributions from the periodic potential are also needed.

Only a few core levels have been investigated. The reason is that relatively few experimental values for the free ion core levels are available. On this point there is a need for calculations beyond the Hartree-Fock approximation. Ordinary second order perturbation theory should be sufficient. Such calculations are now in progress at this institute. The direct second order contributions are identical to the terms M_{IV} and M_V of Eq. (5.1) with W^v replaced by v . The remaining second order contributions, which are of exchange type, are given by the second order term in M with W replaced by v . They are quite important particularly for s -levels, where they may become almost one half of the direct terms.

The explicit expression for the second order contribution to M is

$$M^{(2)}(k) = -\frac{1}{(2\pi)^3} \sum_{k_1 k_2 k_3} \int \frac{\langle k k_1 | W(\varepsilon_1) | k_3 k_2 \rangle \langle k_1 k_2 | W(\varepsilon_2) | k k_3 \rangle d\varepsilon_1 d\varepsilon_2}{(\varepsilon_1 + \varepsilon_k - \varepsilon_{k_1}) (\varepsilon_1 + \varepsilon_2 + \varepsilon_k - \varepsilon_{k_2}) (\varepsilon_2 + \varepsilon_k - \varepsilon_{k_3})}. \quad (8.1)$$

If we approximate $W(\varepsilon)$ by $W(0)$, which corresponds to the approximation COHSEX in ref. 6, Eq. (8.1) becomes

$$M^{(2)}(k) = \sum_{k_1 k_2 k_3} \frac{\langle k k_1 | W(0) | k_3 k_2 \rangle \langle k_1 k_2 | W(0) | k k_3 \rangle}{\varepsilon_{k_1} + \varepsilon_{k_3} - \varepsilon_{k_2} - \varepsilon_k} (\theta(k_1) - \theta(k_2)) (\theta(k_3) - \theta(k_2)), \quad (8.2)$$

where $\theta(k) = 1, \quad k \text{ occ}$
 $0, \quad k \text{ unocc.}$

The dominant contribution arises when k_1 and k_3 are in band k . The state k_2 has then to lie in the unoccupied region. For the same reason as in sec. 5, $W(0)$ can be replaced by v , and we are back to essentially a free ion contribution.

Many band calculations are made with an empirical ion-potential, chosen to reproduce the one-particle-like spectrum of the atom up to the ionization limit. The potential suggested by the present treatment is the Hartree-Fock potential of the free ion. This potential reproduces the atomic spectrum with an accuracy [6], that is higher than we now can hope to attain in band calculations. The effect of correlation in this spectral region is thus not very important. The empirical potential has the drawback that it is arbitrary to a large extent, since it is required to reproduce only a fairly narrow region of the energy spectrum. The region in space where the potential is most important is different in the solid compared to the atom, since the atomic wavefunctions extend much further out than the unit cell. The energy region covered by the wavefunctions in the solid starts at a lower value than in the atom and extends above the ionization limit. For these reasons it seems more reliable to use a HF ion potential than an empirical potential. This should be quite feasible to do with, say, the quantum defect method, where the "defect" is then taken from HF data, or with the augmented plane wave method.

There has been expressed some uncertainty [24] about the importance of including the Born-Heisenberg polarization potential, $-\alpha e^2/2r^4$. We have however made estimates which show that the true polarization potential does not take on the $1/r^4$ form until at a rather large distance from the core, while it is much weaker in the region of space that is of interest in a solid, namely within a Wigner-Seitz cell. We hope to obtain more detailed information in this question from the perturbation calculations now in progress for free ions.

The Born-Heisenberg polarization potential does not appear in the present type of analysis, where instead the dynamical effect of the ions appears as a rescaling of electron gas results with a static dielectric constant. This leads to a raising rather than a lowering of the band.

There has also been uncertainty about the influence of the $1/r^4$ potential on the cohesive properties of solids. We will return to this question in a later paper, where we will show that no such potential will appear, and also that the shifts of the core levels in a solid have no influence at all on the cohesive energy.

ACKNOWLEDGEMENT

Part of this work was performed under the auspices of the U.S. Atomic Energy Commission during the author's stay at the Solid State Science Division of the Argonne National Laboratory. He is grateful to Dr. O. C. Simpson for the opportunity of this stay and to Dr. J. Robinson for valuable discussions.

He also wishes to thank Drs S. Lundqvist and A. Sjölander at this Institute for their active interest and encouragement.

Institute of Theoretical Physics, Sven Hultins gata, Göteborg, May 1965

APPENDIX A

In this appendix we will try to make as good an estimate as possible of the correlation energy of an electron gas, based on the information available. We will make the assumption that the series expansion given by Carr and Maradudin [25] is reliable up to $r_s = 1$. We will then extrapolate the quantity V_{corr} used in ref. 6. From general principles we know that V_{corr} has a negative derivative, cf. sec. 8 in ref. 6, and we assume that its slope will not become larger than in the RPA approximation, which thus is taken as a sort of lower bound.

The quantity V_{corr} is related to the total energy per particle, ε , and the chemical potential, μ , by the relations

$$\begin{aligned} \varepsilon_c &= \frac{1}{r_s^2} \int_0^{r_s} V_{\text{corr}}(x) dx, \\ \varepsilon &= \frac{3}{5} \alpha^2 r_s^2 - \frac{3}{2\pi\alpha r_s} + \varepsilon_c, \quad \alpha = \left(\frac{4}{9\pi}\right)^{\frac{1}{3}} = 0.52106, \\ \mu &= \varepsilon - \frac{r_s}{3} \frac{d\varepsilon}{dr_s}, \end{aligned} \quad (\text{A.1})$$

where $(3/4\pi r_s^3) =$ number density and the energies are expressed in Rydbergs ($1 \text{ Ry} = 13.605 \text{ eV}$).

The formula adopted for the extrapolation is

$$V_{\text{corr}}(x) = V_{\text{corr}}(1) + \frac{1}{c} V'_{\text{corr}}(1) (1 - e^{-c(x-1)}). \quad (\text{A.2})$$

If we specify c , ε_c and μ are uniquely determined from the boundary conditions

$$\begin{aligned} \varepsilon_c(1) &= - \cdot 132 \\ V_{\text{corr}}(1) &= - \cdot 220 \\ V'_{\text{corr}}(1) &= - \cdot 125, \end{aligned} \quad (\text{A.3})$$

which are taken from Carr and Maradudin's expression. We used three values for c , namely 0.2, 0.4 and 0.6. The value $c = 0.2$ gives a V_{corr} which runs more or less parallel to the RPA curve, while $c = 0.6$ gives a curve which quickly flattens out to a horizontal line. The results are given in table 5. The quantity M is defined from

$$\mu = \left(\frac{1}{\alpha^2 r_s^2} + M \right) \text{Ry}, \quad (\text{A.4})$$

where the first term is the contribution from the kinetic energy. We see that M is quite insensitive to the value of the parameter in the formula we use. The values used in section 7 are taken from the column $c = 0.4$.

Table 5

| r_s | $c = 0.2$ | | | $c = 0.4$ | | | $c = 0.6$ | | |
|-------|-------------------|--------------|--------|-------------------|--------------|--------|-------------------|--------------|--------|
| | V_{corr} | ϵ_c | M | V_{corr} | ϵ_c | M | V_{corr} | ϵ_c | M |
| 1 | -.220 | -.132 | -1.368 | -.220 | -.132 | -1.368 | -.220 | -.132 | -1.368 |
| 2 | -.330 | -.103 | -.727 | -.323 | -.102 | -.727 | -.314 | -.101 | -.727 |
| 3 | -.426 | -.088 | -.506 | -.392 | -.085 | -.506 | -.366 | -.083 | -.505 |
| 4 | -.502 | -.079 | -.395 | -.438 | -.074 | -.392 | -.394 | -.070 | -.390 |
| 5 | -.564 | -.072 | -.326 | -.469 | -.066 | -.322 | -.409 | -.061 | -.319 |
| 6 | -.615 | -.066 | -.280 | -.490 | -.059 | -.274 | -.418 | -.054 | -.270 |

APPENDIX B

In this appendix we will estimate the terms

$$A = \frac{i}{2\pi} \sum_{k' \notin B_k} \int \frac{\langle k k' | W^v(\epsilon) - v | k k' \rangle}{\epsilon_k - \epsilon_{k'} - \epsilon} d\epsilon, \quad (\text{B.1})$$

which appear in Eq. (4.5) and contribution M_{III} in Eq. (5.1). In the former case k' runs over the core states and k is in the valence band, and in the latter case k is in a core band and k' runs over all states except those in band k .

We will approximate W^v by an electron gas value, using the simple formula for the dielectric function

$$\frac{1}{\epsilon(q, u)} = 1 + \frac{\omega_p^2}{u^2 - \omega_1^2}, \quad \omega_1 = \omega_p + q^2. \quad (\text{B.2})$$

Here we have used the dimensionless variables q and u defined by

$$\begin{aligned} k &= 2 k_0 q \\ \epsilon &= 4 \frac{\hbar^2 k_0^2}{2m} u, \end{aligned} \quad (\text{B.3})$$

where k_0 is the Fermi momentum, $k_0 = (\alpha r_s a_0)^{-1}$. In terms of these the plasmon energy becomes, $\omega_p = (\alpha r_s / 3\pi)^{\frac{1}{2}}$. This approximation for the dielectric constant is chosen so that $\text{Im} \epsilon(q, u)^{-1}$ gives a δ -function line in the (q, u) plane and satisfies the sum rule

$$\int_0^\infty u \text{Im} \epsilon(q, u)^{-1} du = -\frac{\pi}{2} \omega_p^2. \quad (\text{B.4})$$

The form of the function $\omega_1(q)$ is left arbitrary by the condition Eq. (B.4). It has been taken as a simple function satisfying the correct limiting conditions $\omega_1(0) = \omega_p$ and $\lim_{q \rightarrow \infty} \omega_1(q) = q^2$. Calculations performed by B. Lundqvist

at this institute show, that this approximation gives the self-energy operator M with an accuracy of a few percent.

A straightforward but lengthy analysis gives

$$\begin{aligned}
 A &\cong \frac{4}{r_s^3} \sum_{k'} A_{kk'} f_{k'} \text{ Ry} \\
 A_{kk'} &= \frac{1}{(2l+1)} |\langle k|r|k'\rangle|^2 \begin{cases} l+1 & \text{when } l'=l+1 \\ l & \text{when } l'=l-1 \end{cases} \\
 f_{k'} &= \begin{cases} (\varepsilon_p^{\frac{1}{2}} + (\varepsilon_p + I)^{\frac{1}{2}})^{-1} & \text{when } \varepsilon'_k < \varepsilon_k \\ \varepsilon_p^{\frac{1}{2}}/I & \text{when } \varepsilon_k < \varepsilon_{k'} < \mu \\ -(\varepsilon_p^{\frac{1}{2}} + (\varepsilon_p + I)^{\frac{1}{2}})^{-1} & \text{when } \mu < \varepsilon_{k'} \end{cases} \\
 I &= |\varepsilon_{k'} - \varepsilon_k|, \quad \varepsilon_p = \left(\frac{\alpha r_s}{3\pi}\right)^{\frac{2}{3}} \frac{4}{(\alpha r_s)^2} \text{ Ry}. \quad (\text{B.5})
 \end{aligned}$$

Here l and l' are the angular momenta associated with the states k and k' . The energies are in Ry. The integration in the matrixelement covers the unit cell, and the functions k and k' are normalized to 1 over this region. The angular integrations are already performed and only the radial part of the wavefunctions enter. The distance from the center of the cell, r , is expressed in units of the Bohr radius. In deriving Eq. (B.5) we made a series expansion of W , stopping at the first non-vanishing term. This should be allowable, since either k or k' is a core state. For the valence states $A_{kk'}$ has to be multiplied by the square of the coefficient for the particular angular momentum part of the wavefunction, which is involved.

From Eq. (B.5) we see that the conditions which favour a large value of A are

- (i) high electron density \rightarrow small r_s ,
- (ii) large matrix elements,
- (iii) small band separations compared to the plasmon energy.

We will look in detail on the coupling between the $2s$ and $2p$ states of aluminum. The relevant data are

$$\begin{aligned}
 r_{2s, 2p}^2 &= .357 \quad r_s = 2.065 \\
 I &= 3.36 \\
 \varepsilon_p &= 1.17 \quad \frac{4}{r_s^3} = .454.
 \end{aligned}$$

The shift in the $2s$ level becomes

$$\Delta E_{2s} = .454 \frac{.357 \cdot 1.17^{\frac{1}{2}}}{3.36} = 0.052 \text{ Ry},$$

and in the $2p$ level

$$\Delta E_{2p} = .454 \frac{1}{3} \frac{.357}{1.17^{\frac{1}{2}} + (1.17 + 3.36)^{\frac{1}{2}}} = 0.017 \text{ Ry}.$$

The other terms are much smaller, mainly because of the dipole matrixelements. The alkali metals are somewhat worse with respect to conditions (ii) and (iii), but much better with respect to (i). The shift for them are smaller than those for *Al* by about a factor 5.

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Tryckt den 6 oktober 1965

Uppsala 1965. Almqvist & Wiksells Boktryckeri AB

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