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SUMMARY

The case of an inhomogeneous electron gas within which the density variation is significant over a spatial range of the order of a Fermi wavelength is considered in this report. It is seen that for most systems of physical interest this sort of non-uniformity is a result of diffraction effects. This is a fundamentally different phenomenon than can reasonably be treated by the density gradient method of Kohn for slowly varying inhomogeneous electron gases. Several sample cases are treated.

The first considerations are directed towards the problem of a weak periodic potential in an interacting electron gas. The momentum-dependent self-energy is calculated for an electron propagating in the many-body medium of an electron gas plus a periodic lattice pseudo-potential. This is the equivalent of a quasi-particle energy spectrum and thus an orthogonalized plane wave energy band. It does not appear that the lattice drastically changes qualitative aspects of plane wave many-body theory.

A dielectric formulation for a general inhomogeneous electron gas is presented. By introducing a new image technique, the dielectric function within the random phase approximation, which is valid in the surface region of an electron gas, is obtained.

A Green's function formalism is developed for treating the static dielectric screening of a point impurity in an electron gas.

The surface dielectric function is used with the impurity screening formalism to treat the problem of impurity screening in the surface region. This is an idealized model of ionic adsorption on metal surfaces. Screening charge densities resulting from volume polarization effects are calculated. From these results, it is seen why unjustifiable application of classical image forces in previous adsorption theories has fortunately produced reasonable results.

A new method for obtaining the appropriate plasmon contribution to the electron self-energy in the surface region is developed. With these results, the electron gas surface potentials calculated by Loucks and Cutler are then improved.

I. INTRODUCTION

The striking success of the single-electron theory of metals has provided large amounts of quantitative information pertaining to electron behavior in real metals. The initial philosophy upon which the single-electron theory was based concerns an electron in an N-electron metal feeling a static periodic potential provided by the ionic cores of the nuclei and inner-shell electrons, plus the time-averaged, self-consistent potential of all other N-1 conduction electrons. The resulting energy eigenfunctions for such a system are Bloch functions which reflect the symmetry of the particular lattice in question. The fact that the pseudo-momentum of an electron is a good quantum number solely as a result of the particular translational invariance present is made manifest in the Bloch function representation. In a periodic potential, the translational invariance is that of the translation group of the crystal only. Thus in the reciprocal lattice of the crystal, momentum is a good quantum number only within an additive reciprocal lattice vector and, consequently, crystal momentum is the conserved quantity usually associated with translational invariance. This situation has given rise to an energy band theory in the reduced zone scheme and has required the introduction of a variable called the band index to keep track of the fact that crystal momentum and not mechanical momentum is conserved. The Fermion nature of an electron is considered in this picture by allowing only two electrons to occupy any Bloch state, the factor of 2 arising from the two different eigenstates of spin. The ground state of the system is obtained by having electrons occupy the N/2 lowest Bloch states. In this picture, which is called the Hartree approximation, there are absolutely no correlations between electrons either of a dynamically or statistically imposed nature. The original N-particle Hamiltonian has been decoupled and reduced to a sum of N-single-particle Hamiltonians. The wave function for the system is a product of N-non-interacting wave functions.

The next advance in single-electron theory was the inclusion of exchange effects. It was realized that some correlation existed between electrons of parallel spin as a result of the exclusion principle. Electrons in the same spin state tend to stay away from each other. Thus, when evaluating the time-average, single-electron interaction with all other N-1 electrons, there is a deficiency of parallel spin electrons around the given electron. This means that the repulsive interaction is lessened and thus the total energy of the system is reduced, in fact, by a sufficient amount to allow for binding, although not by the quantitatively correct amount. Decoupling the N-particle Hamiltonian in this way and writing the full wave-function as a Slater determinant is known as the Hartree-Fock approximation.

These single-particle approximations have been quite useful in gaining much understanding of the behavior of metals. Single-electron energy band theory has for the most part successfully explained the characteristic optical spectrum of solids. Fermi surface experiments are in relatively good agreement with single-electron theory. Single-electron transport theory in solids has been successful. And so the list could go on.

However, there is a wide class of phenomena which is either not in agreement with single-electron theory or categorically has no hope of being interpreted in terms of single-electron theory. Examples of disparity between single-electron theory and experiment can be found in some calculated density of states at the Fermi surface, electron specific heats, electron effective masses, and bandwidths. Phenomena which cannot be treated within the context of single-electron theory include total energies of metals, all plasma effects, screening effects, and many electron surface effects. It is this class of phenomena which are treated in this document, the many-body effects, in hopes that an effective coupling between single-electron theory and many-body theory can provide adequate representation of nature.

Wigner (ref. 1) was the first person to offer a semi-quantitative analysis of dynamical correlations between electrons of anti-parallel spin. He realized that electron-electron repulsion tends to keep anti-parallel spin electrons apart so when one calculates total energies of a metallic or electron gas system, one should use wavefunctions which consider this correlation effect. Since the exact wavefunction keeps all electrons apart, they do not feel their mutual repulsion so strongly as when in a configuration corresponding to uncorrelated wavefunctions. This reduction in energy, the difference between the exact ground-state energy and the Hartree-Fock ground-state energy, he called the correlation energy. Within an approximation which becomes exact in an unphysical, low-electron-density region, Wigner then made probably the first many-body calculation.

The problem of electron correlation and many-body effects then lay dormant for many years until the landmark work of Bohm and Pines (ref. 2). They modelled a metal in the following manner. Assume the periodic potential to be sufficiently weak, such that an adequate first approximation is to assume the ion core charge density uniformly smeared over the unit cell. The resulting picture is that of an electron gas sloshing around in a uniform potential in a manner quite analogous to a classical plasma. This has often been referred to as jellium. To consider e-e interactions proceed as follows. The e-e Coulomb repulsion is written as a Fourier series. The $q = 0$ (infinite wavelength) Fourier component of the repulsion exactly cancels the infinite wavelength attraction of the smeared-out ion charge. Problems arise because the unscreened Coulomb $1/r$ interaction is long-range. Thus the low q components of the e-e interactions give rise to divergences in momentum integrals. Bohm and Pines realized that, in truth, the e-e interaction is really screened and, beyond some characteristic length of the order of a Thomas-Fermi screening length, an electron reacts with other electrons in some average way. They envisioned the electron gas sloshing around as a cooperative phenomenon which could be expressed in terms of a Fourier sum of density fluctuations about the mean electronic density. These density fluctuations were just the plasma oscillations of the electron gas. Since the plasma oscillations extend over a large region of space, the low-q components of the e-e interaction could be seen to affect the long wavelength density fluctuations. Thus, if one could separate the full interacting electron Hamiltonian into a plasma part and an electron part, then the divergent-appearing, low-q portion of the e-e interaction would go into the plasma Hamiltonian and no divergence problems would appear in the quasi-electron part which uses the high-q portion of the unscreened interaction. To carry out this procedure, they performed a series of appropriate canonical transformations on the interacting electron Hamiltonian and obtained a Hamiltonian which was conveniently separable into a plasma part, an electron-like part, and a weak coupling between the two which could usually be treated in perturbation theory. The plasma part was just a sum of harmonic oscillators which could then be quantized in the appropriate manner for a Bose field and the resulting quanta were then called plasmons. The characteristic plasma frequency for electrons of a density found in metal conduction bands was seen to be of the order of 10 eV, much higher in energy than could be excited by e-plasmon interactions or thermal effects. Thus the only effect of the low-q portion of the e-e interaction on the total energy of the system was the addition of a plasmon zero point energy $1/2\, h\,\omega_p$. In any event, the recognition of the electron gas as a field in which density fluctuations could occur and the subsequent recognition of the many-body cooperative phenomena giving rise to plasmons spurred a wave of new work on electron correlation effects in electron gases and real metals. It should be noted that, in the Bohm-Pines (BP) theory, first use of the approximation, which has been the blessing and nemesis of many-body theorists, the random phase approximation (RPA), was made. Unfortunately this approximation, the nature of which will be discussed later, makes the BP and most many-body theories rigorously valid only for electron gas densities much higher than those found in conduction bands.

The pioneering work of Bohm and Pines (BP) led Gell-Mann and Brueckner (G-MB) to the most significant breakthrough in modern many-body theory (ref. 3). The idea of the electron gas as a field in which quantized density fluctuations could be induced by a particle propagating in this field was totally reminiscent of the non-relativistic specialization of the field theoretic ideas developed in quantum electrodynamics. In quantum electrodynamics, success in the usage of perturbation series generated in a propagator formalism and pictorially represented with Feynman diagrams had been realized. What was the difference between an electron, which in physical reality cannot be imagined as decoupled from the electromagnetic field, propagating in the electromagnetic field and inducing density fluctuations and an electron coupled to the field of the many-body medium within which it propagates and induces fluctuations? Mathematically, as well as physically, the distinction was small. For the Fermi gas, the following picture thus evolved. Initially, with no e-e interactions, we can define a Fermi sphere in momentum space which is the equivalent of the field theoretic vacuum state. Turning on e-e interactions results in the excitation of two high-momentum propagating electrons above the Fermi sphere and two low-momentum holes propagating beneath the Fermi sphere. The electron-hole pairs can then annihilate, create new e-h pairs, and undergo complicated exchange processes, or a whole host of various processes. Gell-Mann and Brueckner set up an infinite order perturbation series to describe the effects of the e-e interaction. Each term in the perturbation expansion could be represented by a Feynman diagram. They reckoned that one could approximate the exact series by considering only the most divergent diagram in any order of the perturbation expansion. Through this assumption they were able to choose a particular set of diagrams, the bubble or ring diagrams to be discussed later, the infinite series of which was exactly summable. Thus the stigma of a perturbation theory treatment was removed. As it turned out, by choosing the particular, most divergent diagrams that they did, they obtained exactly the BP result for the correlation energy. Hence, it can be seen that the RPA is made by choosing the ring diagrams only. It is within the context of a diagrammatic analysis that we chose to understand and use the RPA. One limiting feature of the G-MB theory was that it did not explicitly display the existence of the plasma poles. However, the theory did open the road for the vast usage of field theoretic and Green's function techniques which have proved to be the forte of subsequent many-body theory.

Sawada (ref. 4) and Sawada, Brueckner, Fukuda, and Brout (ref. 5) provided an elegant formulation of the G-MB theory in terms of the equation-of-motion method. This work was stimulated by Sawada et al who realized the mathematical similarity between the G-MB electron gas pair theory and the theory of scaler-pair meson fields. In their formulation of the electron gas problem they showed that the G-MB theory, in fact, had the plasma pole implicit within it.

DuBois (ref. 6) presented extensive work on the formal field theoretic aspects of the electron gas. He showed that great and almost impossible effort was required to extend most aspects of the RPA to the region of metallic density when done through a systematic application of perturbation theory. Much work was done on the plasmon aspects of the electron gas. The connection between the propagator for a density fluctuation and the wave number and frequency-dependent dielectric function was given. Thus, if one can calculate a dielectric function or equivalently a polarizability for the electron gas, then the formal apparatus for calculating other physically relevant quantities, such as self-energies, correlation energies, and plasmon damping "constants," exists.

Another tack was taken by Hubbard (ref. 7) as he tried, in an approximate manner, to make the RPA applicable for electron gases of metallic density. For many properties, the RPA and Hubbard-corrected RPA give quite similar numerical results. In any event, Hubbard's work seems to be the best correction to the RPA presently available.

Ehrenreich and Cohen (ref. 8) presented an elegant piece of work which demonstrated the equivalence between a linearized, self-consistent field theory and the RPA with Hartree factorization of two particle operators. They obtain simple expressions for the dielectric functions.

More recently Hedin (ref. 9) considered the electron gas from a slightly different point of view. A Green's function theory is developed in which perturbation expansions are done with a screened rather than bare Coulomb interaction. As expected, this greatly improves convergence problems. He also provides large quantities of numerical tabulations of relevant electron gas properties.

Hedin, Lundqvist, and Lundqvist (ref. 10) have used a novel approach to evaluate electron and hole self-energies resulting from a coupling between virtual electrons or holes and virtual plasmons. Although DuBois (ref. 6) warned that this procedure has no physical validity, the author of reference 10 seemed to show the existence of a new, many-body resonance, a coupled hole-plasmon state, which may have been observed and which, if it in fact exists, explains a sizable quantity of anomalous density of state data for such materials as nickel.

The preceding review of published work has been given to set the stage for the problems of central interest in the present thesis. In all of the aforementioned theories, the jellium model has been treated; that is, an electron gas in which complete translational invariance exists. This approach is the reasonable first attack on the problem of many-body effects in metals. However, in real metals there are many different occurrences which destroy the assumed homogeneity of space. The obvious first observation is that the ion core potential is not smeared out over the unit cell; a periodic potential is present instead. This aspect of nature should be considered before the final many-body theory answer is realized. A second class of phenomena concerns the existence of impurities or imperfections in the metal or electron gas. The third major class of problems might be regarded as a subclass of the imperfection group, problems arising from the presence of a surface or boundary in an electron gas. It is these three types of problems which will be treated here. As will be seen in the historical review and subsequent chapters, there are many mathematical and physical problems which arise in this type of many-body problem and, for the most part, both the theory and mathematical apparatus for dealing with these problems remain in their infancy.

Some brief considerations of the work which has been done with the lattice in an electron gas are now presented.

In the self-consistent field theory of Ehrenreich and Cohen (E-C) (ref. 8), they consider lattice effects in an electron gas by doing expansions in a Bloch wave rather than plane wave basis. They obtain a dielectric function which can be split up into terms involving intra-band and inter-band transitions from which suitable approximations on each part can be made.

Falk (ref. 11) has presented a calculation on the influence of a lattice upon the dielectric properties of an electron gas. Again, expansions are done in a Bloch-wave basis. By considering the most divergent portions of integrals, he obtains relatively simple formal expressions for dielectric functions and correlation energies.

Further work along these lines was done by Pratt (ref. 12) in an attempt to introduce self-energy effects into band theory. He obtains single-particle Schrodinger-type equations which include periodicity and many-body effects but which are almost impossible to solve self-consistently, at least from the practical point of view.

The most well known attempt to put a lattice into an electron gas is the projected wave-field approach of Bassani, Robinson, Goodman, and Schrieffer (ref. 13). Essentially what they do is the following. The exact wave functions are expanded in a few orthogonalized plane waves (OPW). They then define two electron fields, one corresponding to the plane wave portion of the OPW's and the other corresponding to the projection onto the core states. Each field is quantized independent of the other and a weak coupling between the two fields might then exist. From this point of view they obtain formal energy spectra for quasi-particles which contain both periodicity and self-energy effects.

Sham and Kohn (ref. 14) made reference to lattice effects when they presented one of their works on inhomogeneous electron gases. Although their theory is quite formal, applicable mathematical techniques are provided.

The author (ref. 15) has investigated this problem from a point of view which in many ways is similar to that of the authors of reference 13. However, the mathematical aspects are carried further towards completion and contact with physical pictures is maintained. This is discussed in detail in section III of this document.

The second interesting class of translational invariance spoilers are impurities in an otherwise homogeneous electron gas. The simplest example of an impurity in such a gas is an atom. If one assumes a liberal point of view, it can be seen that an atom is nothing but an electron gas with a point impurity immersed in it -- the nucleus. Although nuclear physicists reject the idea that their life's work is concerned with the study of a piece of "dirt," for present purposes this is a sufficiently acceptable outlook. The electron gas tries to screen the nucleus, Friedel oscillations are set up, and thus shell structures result, or so it was thought.

This was the point of view taken by Baraff and Borowitz (ref. 16) and DuBois and Kivelson (ref. 17) as they tried to improve upon Thomas-Fermi atoms by systematically using many-body theory ideas and density gradient expansions in hopes of generating shell structure. As they learned, for subtle reasons this is a theoretically impossible task.

In a totally new approach to the inhomogeneous electron gas problem, Kohn and Sham (ref. 18) were able to obtain almost perfect shell structure radial charge densities for atoms when treated as a many-body screening problem.

The next class of impurity problems is that of a point impurity immersed in a metal. For the most part, the case of substitutional rather than interstitial impurities is considered in this document. Langer and Vosko (ref. 19) presented the first calculation on many-body impurity screening effects. Essentially they considered the impurity to be a source which interacts with the electron field, thus causing an energy shift in single-particle energies. This energy shift is then related to screening charge densities in a self-consistent manner through Poisson's equation. They provide extensive numerical computations of screening charge densities calculated within the RPA and Hubbard approximation. As expected in a correct treatment, long-range Friedel quantum density oscillations are found which decay in amplitude as r^{-3} and oscillate with a spatial frequency of twice the Fermi momentum. This result will be important in later sections of this thesis.

A purely Green's function treatment of point Coulomb impurities was offered by Layzer (ref. 20). He shows the relationship between the purely diagrammatic self-consistent field approach of Langer and Vosko and the Green's function method.

An extremely novel method of tackling the impurity problem came from Sziklas (ref. 21). He combined the Bohm-Pines plasma theory with the E-C self-consistent field theory to show that, under certain conditions, the screening charge around an impurity could be regarded as a bound state plasmon, a trapped density fluctuation. The primarily s-state plasmon would be expected to have a discrete hydrogenic-like excitation spectrum which in principle would be observable. It is a shame that this idea has not been further developed.

The more traditional approach to the impurity problem in a metal is based in large upon the work of Friedel (ref. 22). If screening is regarded as a scattering process, describable in a phase shift analysis, then his famous sum rule gives the required relation between various phase shifts to guarantee self-consistency in the screening charge density.

Although the tight-binding impurity theory of Koster and Slater (ref. 23) does not on the surface appear to use many-body screening effects as a basic ingredient, in fact it does so implicitly. By considering an impurity so localized that it only gives non-vanishing matrix elements between Wannier functions centered on the impurity site, it is implicitly required that the impurity be rapidly screened. This formalism has enabled Sokoloff (ref. 24) to treat such problems as magnetic impurities in terms of band wave-functions following the lines of Anderson's theory (ref. 25). By using the various matrix elements as adjustable parameters, many-body screening effects are introduced phenomenologically.

Clogston (ref. 26) presented a method of relating the Koster-Slater matrix elements to the Friedel sum rule such that self-consistency was obtained.

Recently Sham (ref. 27) has attacked the impurity problem from a many-body theory point of view with a direct application to semi-conductor or insulator impurities. However, most of the formalism is quite useful in the metal impurity.

The author has considered the metal impurity problem from the point of view outlined in the Thomas-Fermi atom theories (ref. 28). He discovered several hidden assumptions which are required but rarely stated in order to obtain the standard RPA screening charge densities. Certain aspects of this work are discussed in section IV of this technical report.

By far, the most significant work on the problem of inhomogeneous electron gases has emananted from Kohn and others working with him, namely, Hohenberg, Sham, and Majumdar (refs. 29-31). The original basis of this work is found in a presumably general theory which states that all properties of an inhomogeneous electron gas can be expressed in terms of a unique, universal functional of the electron density at a point (ref. 29). Of course no method has yet been devised to obtain this functional, but the theory has given cause for more work using density as the basic variable. Thus slowly varying or small departures from the mean electron density are treated in a formalism based upon perturbation-like expansions in powers and orders of the density gradient. In general, polarizabilities or dielectric functions calculated for the uniform gas are used in some sort of perturbation treatment. Another innovation has been to use a WKB basis as a starting point for expressing non-uniform potentials and densities (ref. 30). Good preliminary success has been obtained.

Kohn and Majumdar also investigated the conditions required for an impurity to be screened by formation of a localized bound state pulled out of the band of continuum states or by formation of a virtual bound state within the occupied portion of the band. Although striking in some of its successes in treating slowly varying inhomogeneities, it is the author's feeling that this approach cannot be justifiably extended to the cases of lattice or surface effects for the following reasons, which are similar to the reasons for the failure of the many-body Thomas-Fermi atom theory. There are two fundamentally different origins of density variations in an electron gas. In the case of a slowly varying potential, the number of non-interacting electrons with positive kinetic energies roughly follows the contours of the potential variation. In this case it is possible to make a one-to-one correspondence between the total energy and the density. This is the type of situation for which the HK theory is intended (ref. 29). On the other hand, for the lattice- or surface-induced inhomogeneities, the density variations are caused by interferences set up between electrons when each non-interacting electron is forced to satisfy the Bloch or surface boundary condition, or, in other words, phase correlations give rise to rapidly varying total density changes. In this case, there is no exclusion of low kinetic energy electrons in the region of low total density so a one-to-one correspondence between density and energy does not necessarily exist. If this conjecture is valid, then the "density as a basic variable theory" cannot, in its present form, be expected to be applicable to lattice- or surface-induced inhomogeneities. It should be pointed out in passing that this is precisely why a systematic usage of gradient expansion techniques failed in the atom theories, for in atoms the Friedel oscillations or shell structure occur basically as a result of forcing a boundary condition on the non-interacting electron wavefunctions, that of having zero amplitude at the origin. This is not a real many-body effect but instead a property of the wave nature of electrons which would be impossible to describe in terms of many-body interactions. Further considerations along these lines should be forthcoming.

The methods of Kohn have been further carried on by Grover (ref. 32). Essentially he does a density matrix formulation using a WKB basis to symbolize the inhomogeneous nature of the system.

The third class of inhomogeneity effects in an electron gas, and probably the most neglected in spite of their importance, is that of surface effects. Perhaps the plethora of phenomenological surface theories have led people to conclude erroneously that surface theory is progressing at a satisfactory rate. One must be careful not to fall into the tempting trap of believing that reproduction of numbers in agreement with experiment constitutes understanding. With a few exceptions, this has been the curse of surface physics and has led to its retarded theoretical growth.

An amazing feature pertaining to surface effects is that, almost in toto, electronic surface properties are manifestations of pure many-body effects. For instance, it is well known that the surface dipole barrier contributes only a very small percentage, say 10 percent, to the surface barrier, that barrier which allows for the binding of a metal. If we assume an idealized model with no surface dipole, then in the Hartree approximation, where any attractive potential would be electrostatic, a metal does not exist. Consequently, the total surface barrier arises from exchange and correlation effects which are of purely quantum mechanical origin. On the metal side of the surface, an electron is propagating through the many-body field within which it can undergo exchange processes or induce density fluctuations and thus self-energy processes resulting in a lowering of its energy whereas, on the vacuum side, the electron is completely decoupled from such a field and thus is found to be at a higher energy. Any "theory" which does not recognize this picture of a surface is categorically in conflict with standard principles of physics as stated through Maxwell's equations, the Pauli Exclusion principle, the correspondence principle, and the principle of complementarity.

With regards to the surface problem, one of the immediately relevant objects of interest is knowledge as to the form of the average total potential (exchange and correlation) as one approaches the surface from deep within the metal. The first work along these lines was done by Bardeen (ref. 33). He showed that using a sine wave basis with a mathematical nodal surface somewhere outside the physical surface was a good approximation to the traditionally desired basis consisting of decaying exponentials outside the physical surface. Essentially the justification is as follows. The sine waves depart from decaying exponential behavior only in the region where the wave function amplitude becomes very small. Since it really doesn't matter how nothing is described, the most convenient way available should be used as resulting errors will be negligible. With this in mind, Bardeen calculated the values for the exchange energy at two points in the surface region, and then formed a smoothly oscillating curve which merged into the image potential far outside the metal and which joined onto the interior potential deep within the metal.

Several years later, Juretschke (ref. 34) performed numerical calculations of the exchange integral for a continuous distribution of points in the surface region. The resulting potential approached the interior potential within the metal and oscillated with increasing amplitude as the surface was approached, thus giving a functional form for the surface barrier. An especially clear physical picture of the origin of the reduced exchange energy attraction in the surface region in terms of squashed exchange holes is given.

Loucks and Cutler (ref. 35) added further sophistications to the Juretschke picture by realizing that a screened Coulomb exchange potential should be used. Furthermore they included correlation effects in an approximate manner within the context of the BP plasma oscillation theory. Further work along this line has been completed by the author and constitutes section VII of this document.

One of the more dramatic and consequently interesting electronic surface phenomena is the existence of a collective mode of oscillation with a characteristic frequency of the bulk plasma frequency divided by the square root of 2. Most of the work which has been done on surface plasmons stems from the original work of Ritchie (ref. 36) and Stern and Ferrell (ref. 37). Very simple derivations and explanations of the surface plasmon are given. Essentially the surface plasmon results from the collective oscillations of the induced polarization charge in the surface region which is screening out the fact that there is a surface. Since the effective electron density in the surface region is less than in the interior, it is to be expected that the relevant plasma frequency would be reduced.

Ritchie and Marusak have presented detailed calculations of the surface plasmon dispersion relation (ref. 38).

In section IV of this work, it is shown that in a calculation of the dielectric function appropriate to the surface region of an electron gas, there exists a pole at precisely the surface plasma frequency. Of course, this is required in a proper treatment.

The existence of the surface plasmon should be of more than peripheral interest to solid-state theorists. There have been several cases in which optical properties of solids were obtained by a Kramers-Kronig analysis of optical reflectance data which disagreed with photo-emission data. Assignments of certain interband transitions have been given as a result of the reflectance data, only to find out later that the strong absorption was caused by the excitation of a surface plasmon and not an interband transition. Such transitions, of course, were not observed in the photo-emission studies.

Fedders (ref. 39) has produced a paper in which he considers electron gas surface effects from a dielectric and Green's function point of view. This work seems to be a big step in the right direction, although it occassionally dips into the realm of notational obscurity.

The last type of surface effect to be considered is dielectric screening both of a dynamic and static nature. Heine (ref. 40) has suggested the importance of the role of screening in Auger-effect experiments at a solid surface.

The author (ref. 41) has done a simplified theory of hydrogen-like atom adsorption on electron gas surfaces to illustrate the importance of static screening of surface impurities on observable properties of the composite system.

The case of the polarizability of a two-dimensional electron gas, such as is found in the idealized model of an n-type inversion layer of a Si-SiO_2-metal system, has been investigated by Stern (ref. 42). He then calculates the two-dimensional screened potential around an impurity and estimates charge densities which are not in conflict with those obtained by the author (ref. 43). Further elucidation of the author's work in this area forms the basis of section VI.

Finally mention should be made of the work of Bennett and Duke (ref. 44) on bimetallic interface phenomena. Based on much of the inhomogeneous electron gas work cited in this introduction, they have attempted to obtain a description of the resulting electronic configuration, from the dielectric point of view, when two different dielectric materials are placed in intimate contact with one another.

With the recording of this necessary background material, the intent of this report can now be legitimately stated. Basically the general effects in an electron gas with limited translational invariance constitute the subject of interest. It is felt that the best way to handle this problem is through several specific examples rather than a general formalism. That this is the point of view adopted is motivated by the feeling that each specific problem, be it the lattice, impurity, or surface problem, has its own unique individualistic traits which allow for different simplifying mathematical assumptions, while still remaining within the framework of a single field theory. However, in no way is it meant to imply that each problem is distinctly different from the physical point of view. This, in fact, is a major point, viz., that physics is physics and the artificial barriers set up to distinguish band theory from many-body theory from impurity theory from surface physics are, in fact, artificial. Nature does not distinguish between fields so why should one who is trying to describe nature make such a separation? The report is best summarized by making recourse to a descriptive outline of the structure of the work.

Since the general mathematical structure of the entire work is to be done within the context of a field theoretic or Green's function point of view, perhaps the most general point of view presently available, section II, is devoted to generalities. A summary of how the quantized field notion follows from the interacting Schrodinger equation is given. The concept of Green's functions as particle propagators is developed and the relevance of the Green's function to physical observables is noted. The notation used throughout the report is established. The self-energy of a particle propagating in a polarizable field is then discussed.

The first problem to be treated is the effect of a weak periodic potential in an electron gas. In section III, the self-energy of an electron in the many-body medium of the electron gas, plus periodic potential, is obtained. The resulting energy spectrum is the equivalent of an OPW energy band, self-consistently corrected for many-body effects.

The central importance of the wave number and frequency-dependent dielectric function to many-body effects is recognized in section IV. Following the self-consistent field theory derivation, a dielectric function for a general, non-uniform electron gas whose non-interacting single electron wave functions can be expanded in an arbitrary sum of plane waves is derived. In keeping with the spirit of the self-consistent field theory, the linearized version of this expression is retained. A new image technique which enables calculation of a dielectric function in the surface region of a bounded electron gas from the derived general expression is developed. It is interesting to note that the inverse dielectric function has a pole at the surface plasmon frequency as it should.

The theory of impurity screening in the interior of the electron gas, based upon the Thomas-Fermi atom theories, is developed in section V. It is shown that to obtain the standard "correct" results, several hidden assumptions must be made.

Section VI is concerned with the static dielectric screening of a point impurity at the surface. This is of interest for this is precisely that which occurs when ions are adsorbed on metal surfaces. Screening charge densities are calculated, the results of which show why some of the phenomenological theories of adsorption have achieved as good successes as they have. Suggestions for new surface experiments are then offered.

A new approach to the many-body aspects of the surface potential is then presented in section VII. The new potentials are compared with previous calculations and comments are made.

Finally in section VIII, general conclusions of this study are made.

II. FIELD THEORY AND GREEN'S FUNCTION FORMALISM

At the risk of belaboring the formal aspects of this report, a brief review of the Green's function formalism and a statement of the notation used throughout the document are included at this point.

For the interested reader, the book by Schultz is by far one of the best of the currently available introductory texts to many-body theory (ref. 45). Nozieres's book (ref. 46) also provides a good introduction, but really serves its most important function to the "professional" many-body theorist. Also worthy of mention is the excellent book by Kadanoff and Baym which gives a "layman's" version of Martin-Schwinger theory plus much more (ref. 47).

It might at first be asked: Why do things within a field theoretic context? The answer is this: The central feature of the types of processes being considered is the method in which a particle interacts with a density fluctuation in the many-body medium which is induced as a result of the presence of the particle. Since this is a natural field theoretic problem, the motivation is clear.

The usual prescription for obtaining a quantized field theory from a particle theory is as follows. The particle equation, in this case, the Schrodinger equation, is taken to be the field equation. Through a variational procedure one obtains a Lagrangian density. The canonically conjugate momenta to the field are given by relations of the form:

$$\pi(\vec{x},t) = \frac{\partial L(\psi,\dot{\psi})}{\partial\dot{\psi}(\vec{x},t)}$$

Thus, a field Hamiltonian through a Legendre transformation of the Lagrangian can be defined. Quantum mechanics is introduced by requiring that the field variable and momenta satisfy commutation or anti-commutation relations appropriate to the spin of the field. It might be expected that if the field equation were written as an inhomogeneous differential equation, then a Green's function method would be used to provide formal solutions.

How the equations of motion for the electron field Green's functions follow from a statement of the Schrodinger equation for a single electron coupled to all other electrons through two body interactions becomes a matter of interest. The time-dependent Schrodinger equation is written:

$$\left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2}\right)\psi(\vec{r}_1,t) = \int d^3r_2 v(\vec{r}_1-\vec{r}_2)\,\psi^\dagger(\vec{r}_2,t)\psi(\vec{r}_2,t)\psi(\vec{r}_1,t) \quad (1)$$

In Eq. (1), $v(\vec{r}_1-\vec{r}_2)$ is the generalized interaction term which includes e-e interactions and could include single-electron interactions with a source, such as in the impurity problem, if one so desires. $\psi^\dagger$ is the adjoint of ψ. Usually the system of natural units in which $\hbar = c = m = 1$ is used, the standard unit system being restored only when necessary for computational purposes. Unit quantization volume will also be used. Occasionally the four-dimensional notation $(\vec{r}_1;t_1) = (1)$ in configuration space and $(\vec{p};\omega) = (p) = (\vec{p}, p^o)$ in momentum space is used.

To transcribe Eq. (1) into a quantized field equation for a spin 1/2 field, it is required that the ψ's, now to be regarded as field creation and annihilation operators, satisfy the anti-commutation relations:

$$\begin{aligned} \left\{\psi(1), \psi^\dagger(1')\right\} &= \delta^{(4)}(1-1') \\ \left\{\psi(1), \psi(1')\right\} &= 0 \\ \left\{\psi^+(1), \psi^+(1')\right\} &= 0, \end{aligned} \tag{2}$$

in which $\psi(1)$ destroys a particle at the space-time point $(\vec{r}_1, t_1)$ and $\psi^\dagger(1)$ creates a particle at $(\vec{r}_1, t_1)$.

Various Green's functions are defined in terms of these single-particle operators and the exact, interacting ground state of the many-body system. For example, the single particle Green's function is defined as

$$G_1(\vec{r}, t; \vec{r}', t') = i \left\langle T \left[\psi(\vec{r};t) \quad \psi^\dagger(\vec{r}';t') \right] \right\rangle \tag{3}$$

and has the following meaning. It is a measure of the probability that if an electron is created in the interacting system at $(\vec{r}';t')$ it will later be found at $(\vec{r};t)$. The operator T is called a time-ordering operator which requires the earlier of the two times t, t' to be at the extreme right. Essentially the expectation value of the operator $\psi\psi^\dagger$ is taken with respect to the exact, time-dependent ground state. In a similar manner, two-particle Green's functions are defined as

$$\begin{aligned} &G_2(\vec{r}_1\, t_1, \vec{r}_2 t_2; \vec{r}_1'\, t_1'. \vec{r}_2'\, t_2') \\ &= - \left\langle T \left[\psi(\vec{r}_1 t_1)\, \psi(\vec{r}_2 t_2)\, \psi^\dagger(\vec{r}_2' t_2')\, \psi^\dagger(r_1' t_1') \right] \right\rangle \end{aligned} \tag{4}$$

Now it can be seen how to obtain a differential equation for a single-particle Green's function from Eq. (1). If Eq. (1) is multiplied on the right by $\psi^\dagger(\vec{r}_1', t')$ and the expectation value of the time-ordered product is taken with respect to the exact ground state of the system, then the result is:

$$\left\langle T\left[\left(i\frac{\partial}{\partial t_1} + \frac{\nabla^2}{2}\right)\psi(\vec{r}_1, t_1)\, \psi^\dagger(\vec{r}_1', t_1')\right]\right\rangle$$

$$= \left\langle T\left[\int d^3r_2\, v(\vec{r}_1 - \vec{r}_2)\, \psi^+(\vec{r}_2, t_2^{\,+})\psi(\vec{r}_2, t_2)\psi(\vec{r}_1, t_1)\psi^\dagger(\vec{r}_1', t_1')\right]\right\rangle,$$

which by virtue of the fact that T commutes with the purely spacelike operators, can be written as

$$\left\langle T\left[i\frac{\partial}{\partial t_1}\psi(\vec{r}_1, t_1)\, \psi^\dagger(\vec{r}_1', t_1')\right]\right\rangle + \frac{\nabla^2}{2}\left\langle T\left[\psi(\vec{r}_1, t_1)\psi^\dagger(\vec{r}_1', t_1')\right]\right\rangle \qquad (5)$$

$$= \int d^3r_2\, v(\vec{r}_1 - \vec{r}_2)\left\langle T\left[\psi^\dagger(\vec{r}_2, t_2^+)\,\psi(\vec{r}_2, t_2)\psi(\vec{r}_1, t_1)\psi^\dagger(r_1', t_1')\right]\right\rangle$$

An ambiguity arises with respect to the first expression because the time derivative also plays a role in the time ordering, giving rise to a singular point when 1 = 1'. If the time ordering is carried out using the anticommutation of Eq. (2), it can be seen that

$$\left\langle T\left[i\frac{\partial}{\partial t_1}\psi(\vec{r}_1, t_1)\psi^\dagger(\vec{r}_1', t_1')\right]\right\rangle = i\frac{\partial}{\partial t_1}\left\langle T\left[\psi(\vec{r}_1, t_1,)\psi^\dagger(\vec{r}_1', t_1')\right]\right\rangle \qquad (6)$$

$$- \delta^{(3)}(\vec{r}_1 - \vec{r}_1')\, \delta(t_1 - t_1').$$

Furthermore, the field operators in the two-body term can be rearranged to take the form of the two-body Green's function (Eq. (4)). The double combinations of field operators already are in the form of a single-particle Green's function as in Eq. (3). Combining Eqs. (3) through (6) yields:

$$\left(i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2}\right)G_1(1, 1') - i\int d^3r_2\, v(\vec{r}_1 - \vec{r}_2)\, G_2(1, 2; 1', 2') \qquad (7)$$

$$= \delta^{(3)}(\vec{r}_1 - \vec{r}_1')\, \delta(t_1 - t_1')$$

which is the equation of motion for a single-particle Green's function coupled to a two-particle Green's function. One must either approximate the two-particle function or write its differential equation which couples G_2 with G_1 and G_3. The last alternative is rarely done. Equation (7) expresses the manner in which single-particle propagation is coupled to and affected by the presence of all other electrons.

Oftentimes it is more convenient to rewrite Eq. (7) as a purely single-particle Green's function equation by introducing a new integral operator, called the mass operator. In this new form, Eq. (7) becomes

$$(i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2})\, G_1(1,1') - \int d^3r_1''\, \Sigma(1,1'')\, G_1(1'',1') = \delta(1 - 1'). \tag{8}$$

The price to be paid for this simplification is that now Eq. (8) is most likely a non-linear equation and Σ is a complicated, non-local integral operator.

Equation (8) is particularly easy to solve in the case of homogeneous systems. In this case, absolute position has no significance, only relative separations. Thus, the Green's function and mass operator become functions of one variable only in the manner of $G_1(1,1') \rightarrow G_1(1 - 1')$. If the Fourier transform of Eq. (8) is taken with respect to $(1 - 1')$ for the free-field case in which $\Sigma(1,1'') = 0$, the free-particle propagator is:

$$G_o(\vec{p}, \omega) = \frac{1}{\omega - \frac{p^2}{2} \pm i\eta} \tag{9}$$

where η is an infinitesimal constant, specifying the contour of integration. A formal integral equation, known as the Dyson equation, can be built up from the Fourier transform of the full Eq. (8). The momentum space integral equation for the full interacting propagator is given by

$$G(\vec{p}, \omega) = G_o(\vec{p}, \omega) + G_o(\vec{p}, \omega)\, \Sigma(\vec{p}, \omega)\, G(\vec{p}, \omega), \tag{10}$$

which is formally solved as

$$G(\vec{p}, \omega) = \frac{G_o(\vec{p}, \omega)}{1 - G_o(\vec{p}, \omega)\, \Sigma(\vec{p}, \omega)} \tag{11}$$

The energy eigenvalues of the interacting system are ascertained by the poles of the full Green's function of Eq. (11). Direct substitution of Eqs. (9) in (11) gives the eigenvalue condition:

$$\omega(\vec{p}) = \frac{p^2}{2} + \Sigma(\vec{p}, \omega)$$

which is a complicated transcendental equation caused by the dependence of Σ on ω.

The usefulness of the Green's function method is seen in the following. The expectation value of any single-particle operator with respect to the exact interacting system is given by

$$\langle O \rangle = \frac{1}{2\pi i} \oint d\omega \int d^3r\, O(\vec{r})\, G_1(\vec{r},0;\, \vec{r},0^+) \tag{12}$$

where the + sign signifies that the time variable in the creation operator is taken at an infinitesimally later time than in the annihilation operator. The contour in the complex energy plane is chosen such that it encloses the poles of all occupied states. In particular, the charge density at a point is given by

$$\eta(\vec{r}) = \frac{e}{2\pi i} \oint d\omega\, G_1(\vec{r}, 0; \vec{r}, 0^+). \tag{13}$$

In general, the type of self-energy processes represented by the mass operator Σ being considered are those resulting from a particle of momentum $\vec{p}$ propagating in the many-body field which induces a virtual density fluctuation of momentum $\vec{q}$, thus reducing the particle's momentum to $\vec{p} - \vec{q}$. The particle and density fluctuation propagates until either a new density fluctuation is excited or the original density fluctuation and particle recombine. These processes are best visualized in terms of Feynman diagrams as shown in Figure 1. In these pictures, a single straight line represents the free-particle propagator $G_o(p)$, a double straight line represents the exact propagator $G(p)$, the wiggly line represents a propagator for the effective interaction called

$$D\,(q) = \frac{v(\vec{q})}{\epsilon\,(q)},$$

and the circle is called the vertex function representing non-linear complications which result as the particle and interaction lines recombine.

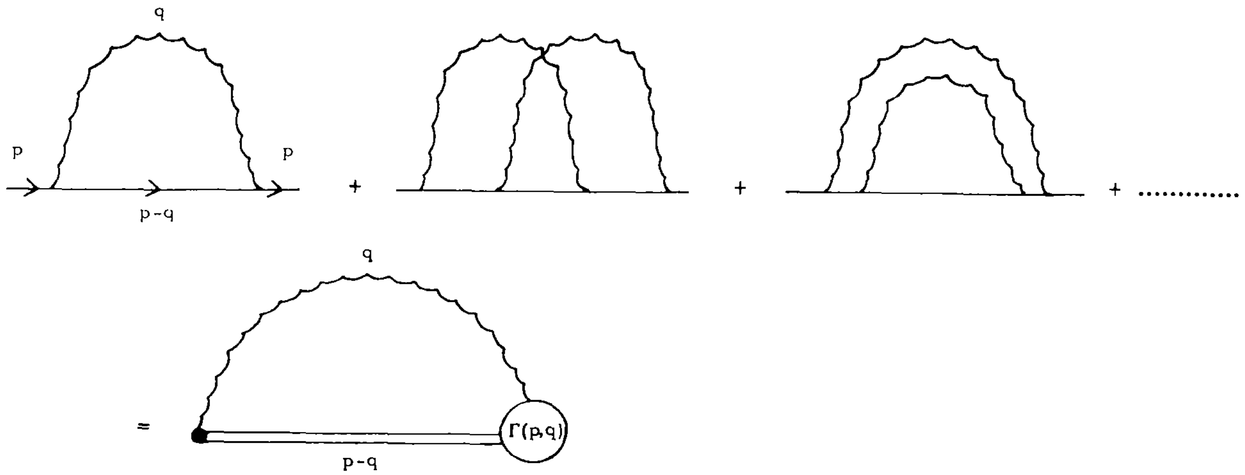

Figure 1. -- Typical diagrams contributing to the self-energy of a Fermion propagating in the many-body field.

It can be shown that the sum of all proper self-energy processes of the form shown in Figure 1 can be exactly summed to yield the single diagrammatic representation also shown which is expressible as an integral:

$$\Sigma(\vec{p}, p^o) = i \int_{|\vec{p} - \vec{q}| > p_F} \frac{d^4 q}{(2\pi)^4} G(p - q)\, \Gamma(p, q)\, D(q) \,. \tag{14}$$

The restriction on the allowed values of q guarantees that the Pauli principle is not violated in the intermediate electron state.

Equation (14) can be rewritten in the form:

$$\Sigma(\vec{p}, p^o) = V_{exch}(\vec{p}) + i \int \frac{d^4 q}{(2\pi)^4} G(p - q)\, \Gamma(p, q)\, D_F(q) \left(v(\vec{q})\right)^2 \tag{15}$$

with the density fluctuation propagator identified as

$$D_F(q) = \frac{1}{v(\vec{q})} \left(\frac{1}{\epsilon(q)} - 1 \right) .$$

Equation (15) follows from the fact that a Green's function, or in the field theoretic language, a propagator for Poisson's equation can be identified which is the differential equation whose solution is the screened 1/r potential. In Eq. (15), the interaction propagator has been split into two parts. The first is a generalized exchange term; the second involves the creation and propagation of a density fluctuation through the system. As will be seen later, the density fluctuations arise from exciting states within the electron hole continuum or exciting collective plasmons. The evaluation of Eq. (14) for various systems will be one of the major undertakings in this thesis.

It should also be pointed out that a Coulomb potential can be written as a Fourier integral:

$$\frac{e^2}{r} = \int \frac{d^3 q}{(2\pi)^3} v(\vec{q})\, e^{i\vec{q}\cdot\vec{r}}$$

with the Fourier coefficient

$$v(\vec{q}) = \frac{4\pi e^2}{q^2}$$

In the theory of the free electron gas, abundant usage of a dimensionless parameter r_s prevails. This parameter is uniquely determined by the electron gas density through the following relation:

$$\text{No. electrons/vol} = 1/\tfrac{4}{3}\pi r^3 \quad \text{and} \quad r_s = r/a_o$$

where a_o is the Bohr radius. For metallic densities $1.8 \lesssim r_s \leq 5$. The RPA is strictly valid only when $r_s \lesssim 1.8$. Various formulas for free electron gas quantities of interest appear below as functions of fundamental constants and as functions of r_s.

Number density:

$$n = \frac{3}{4\pi a_o^3 r_s^3} = \frac{1.61}{r_s^3}\ \text{Å}^{-3}$$

Plasma frequency:

$$\hbar\omega_p = \hbar\left(\frac{4\pi n e^2}{m}\right)^{1/2} = \left(\frac{12}{r_s^3}\right)^{1/2}\ \text{Ry}$$

Fermi wavenumber:

$$k_F = \frac{1}{(\frac{4}{9}\pi)^{1/3} a_o r_s} = \frac{3.64}{r_s}\ \text{Å}^{-1}$$

$$\lambda_F = \frac{2\pi}{k_F} = 1.72\, r_s\ \text{Å}$$

$$\langle E \rangle = \frac{3}{5}\frac{k_F^2}{2m} = \frac{2.21}{r_s^2}\ \text{Ry}$$

Thomas-Fermi screening length:

$$k_{T\text{-}F} = \left(\frac{6\pi n e^2}{E_F}\right)^{1/2} = \frac{2.22}{r_s^{1/2}}\ \text{Å}^{-1}$$

Since many-body theory is usually tried out on materials with simple band structures, typically the alkalis, beryllium, and aluminum, numerical values for the fundamental electron gas properties are displayed below:

Property \ Material	Be	Al	Li	Na	k
r_s	1.88	2.07	3.22	3.96	4.87
$n\ (\mathring{A}^{-3})$	0.243	0.182	0.048	0.026	0.0139
$h\omega_p\ (R_y)$	1.35	1.17	0.6	0.44	0.321
$k_F\ (\mathring{A}^{-1})$	1.94	1.76	1.13	0.92	0.747
$\langle E \rangle\ (R_y)$	0.626	0.515	0.213	0.141	0.093
$k_{T-F}(\mathring{A}^{-1})$	1.62	1.54	1.24	1.11	1.01

At this point all the formal apparatus required to understand the following sections has been cited.

III. FIELD THEORY OF AN INTERACTING ELECTRON GAS IN A PERIODIC POTENTIAL

Generalities

Since the investigations undertaken in this report provide basic understanding of real physical phenomena occurring in real metals, it is at once necessary to see what effects the presence of a periodic potential have on many-body effects, since this is a very critical inhomogeneity. Frequent objections arise from the fact that most many-body calculations are done using a plane wave basis to describe the originally non-interacting electrons. One then seeks the adiabatic transform of plane wave electrons when the e-e interactions are turned on. But so-called non-interacting single electron "eigenstates" in metals are Bloch functions and not plane waves so one should seek the adiabatically transformed Bloch state if one is dealing with many-body effects in real solids. As mentioned in section I, this problem has been considered to some extent by others (refs. 11-14).

The theory to be presented in this section contains some ideas which lie implicit in references 11 through 14 and are here made explicit in physically understandable terms. The basic underlying concept used is the following. The system of concern has two different sorts of interaction terms in the full many-body Hamiltonian--electron-electron interactions and electron-lattice interactions. The electron correlation part is treated first, obtaining Green's functions for single quasi-particles which include a self-energy term resulting from propagation through the polarizable field of the Fermi sea. Then the dressed electron is allowed to propagate through the periodic pseudo-potential and the self-energy of a quasi-particle in a periodic potential is obtained.

The correlation effects are evaluated in the plane wave approximation. This is a reasonable assumption though for the following reasons. First, the procedure of Bassani, Robinson, Goodman, and Schrieffer (ref. 13) could be followed by expanding electron states in an orthogonalized plane wave (OPW) basis and then considering many-body effects on the OPW electrons. This, of course, makes the mathematical aspects of the many-body part of the problem much simpler than if an attempt to compute correlation effects on augmented plane wave (APW) electrons had been made. From a physical point of view, the plane wave approximation can be seen to be sensible. In the core region, far within the APW sphere, that region in which electrons do not have plane wave behavior, the electrons have high kinetic energies and thus go through the core very quickly. Consequently most of the electron's time is spent in the region in which it behaves like a plane wave and, for the most part, the electrons will feel correlation effects as if they were plane wave electrons. In the core region, the high energy electron will not have its behavior disturbed much by the relatively weak correlation interaction so there is really little need to carry through atomic-like core effects, which are well treated in the Hartree-Fock approximation, in calculating many-body correlation effects; that is, many-body effects are important only where core effects are small so an effective separation of the two can be made. This sort of argument could be expressed quantitatively along the lines of the Cohen-Heine cancellation theorem (ref. 48). It is worthwhile to realize that high energy electrons don't correlate very much relative to the plane wave portion of the electron, thus permitting treatment of many-body effects before the lattice effects.

The structure of this section is as follows. In the next subsection, Theoretical Considerations, general field theoretic considerations are given to the problem of a particle moving in two fields -- the electron gas and the periodic potential. Expressions are obtained for the single quasi-particle self-energies and thus for OPW energy bands with many-body effects included. In the last subsection, Discussions and Conclusions, a discussion of the physical origin and implications of these results is given.

Theoretical Considerations

Consider the full electron Hamiltonian for a perfect real metal with interacting electrons:

$$H = \sum_{i,j=1}^{N} \left\{ - \frac{\nabla_i^2}{2} + \frac{1}{N} V(\vec{r}_i + \vec{R}_j) \right\} + \sum_{i<j} v(\vec{r}_i - \vec{r}_j)$$

where

$V(\vec{r}_i + \vec{R}_j)$ is the periodic lattice potential and

$$v(\vec{r}_i - \vec{r}_j) = \frac{e^2}{|\vec{r}_i - \vec{r}_j|} = \sum_q \left(\frac{4\pi e^2}{q^2} \right) e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}$$

is the electron-electron interaction. Zero temperature is assumed and electron-phonon interactions are neglected.

Consider now the following part of the full Hamiltonian:

$$H_o = \sum_{i=1}^{N} - \frac{\nabla_i^2}{2} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$= \sum_{i=1}^{N} - \frac{\nabla_i^2}{2} + \sum_{q \neq 0} \left(\frac{4\pi e^2}{q^2} \right) e^{i\vec{q} \cdot (\vec{r}_i - \vec{r}_j)}$$

which is needed to describe the dominant many-body effects. The starting point is the kinetic energy operator whose eigenfunctions are plane waves. This allows defining of a spherical Fermi surface which is equivalent to the vacuum state in field theory. Since all the momentum eigenstates are filled beneath the Fermi surface, there can be no particle propagation in momentum space unless a passive electron is excited above the Fermi sphere. Then the elementary excitation with momentum greater than the Fermi momentum, called an electron, can propagate freely, scatter off of a source, or interact with a field. Likewise, the positively charged elementary excitation called a hole, with momentum less than the Fermi momentum, can undergo the same sort of processes.

Next the modification upon propagating electrons with $p > p_f$, passive electrons with $p < p_f$, and propagating holes with $p < p_f$ which result from turning on electron-electron interactions should be studied. Two passive electrons within the Fermi sphere interact through the q'th Fourier component of the e-e interaction, giving two virtual electron-hole pairs. This is shown in Figure 2. These propagating electrons and holes can then interact with the polarizable Fermi sea or with the lattice potential.

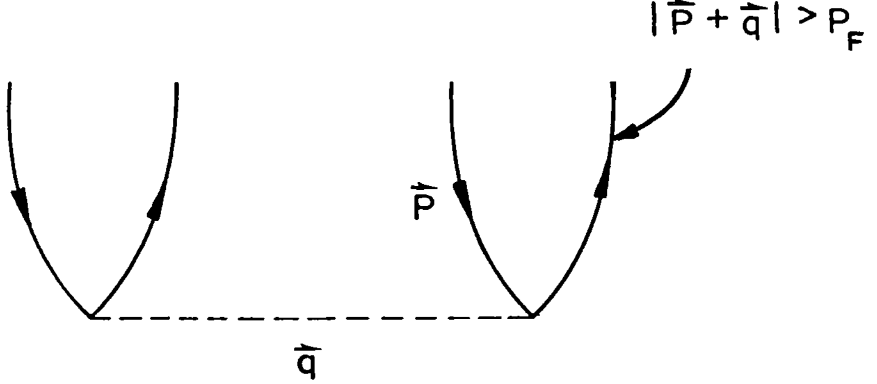

Figure 2. -- Interaction of two electrons beneath the Fermi sphere resulting in the formation of two electron-hole pairs.

Consider first self-energy processes within the Fermi sea. The propagating Fermions can have their lines modified by processes such as those which were shown in Figure 1. The first object of interest in our calculation is the self-energy resulting from e-e interactions as given in Eqs. (1) and (4):

$$\Sigma_e(\vec{p}, p^o) = i \int_{|\vec{p}-\vec{q}| > P_F} \frac{d^4q}{(2\pi)^4} G_e(\vec{p}-\vec{q}; p^o - q^o)\, \Gamma(p, q)\, D(q) , \tag{16}$$

with the meaning of relevant quantities well discussed in Section II. In order to obtain calculable end results, approximations on the quantities appearing within the integral of Eq. (16) must always be made. The first of these is to set the vertex function $\Gamma(p,q) = 1$. This is one of the linearizing approximations. It is hard to check the validity of this assumption quantitatively because few people have been able to find manageable methods of going beyond this zero-order interaction. It might be hoped that since $\Sigma_e(p)$ is expected to be a small correction to the single-electron spectrum, corrections to $\Gamma = 1$ would be of a higher order smallness and thus not too significant.

As an example of the type of corrections resulting from higher order vertex functions, consider the following. It is known from BCS theory of super-conductivity (ref. 49) that small corrections to the zero-order electron-phonon vertex function give rise to the superconducting instability; that is to say, vastly different qualitative changes can occur as a result of small modifications to the vertex function. Since metals which have quite normal properties are being considered here, there are few qualitative disparities between intuitive theory and experimental observations. Thus it appears that the zero-order vertex function is a justifiable approximation since small corrections can lead to qualitative changes which are not required.

With regards to the exact interaction propagator D(q), there exist various standard approximation schemes for obtaining dielectric functions, each with associated good and bad points. The Thomas-Fermi function has a simple functional form which is good from the computational point of view, but has no dynamical properties and hence describes static screening only. This is unrealistic. The Hartree-Fock dielectric function has the virtue of describing dynamic screening within the context of a very familiar model, but has the unrealistic property of a vanishing density of states at the Fermi surface which is the region in momentum space where most many-body effects occur. The random phase approximation (RPA) provides an exact dielectric function, but only for electron densities much higher than those found in real metal conduction bands. The Hubbard-modified RPA function is nearly equivalent to an interpolation between exact high and low density dielectric functions (ref. 50) and thus should provide a reasonable approximation to the exact interaction propagator.

To obtain the propagator for the physical electron in terms of non-interacting electrons, the Dyson equation is formally solved:

$$G_e(p - q) = \frac{G_o(p - q)}{1 - G_o(p - q)\, \Sigma_e(p - q)} \tag{17}$$

In Eq. (17), the free particle non-interacting Green's function

$$G_o(\vec{p} - \vec{q};\ p^o - q^o) = \frac{1}{p^o - q^o - (|\vec{p} - \vec{q}|)^2/2m \pm i\eta}$$

is used to describe electrons (holes) if $|\vec{p} - \vec{q}|$ is larger (smaller) than the Fermi momentum.

It is useful at this point to illustrate the types of processes which are usually considered (at least within the RPA or Hubbard-modified RPA (ref. 7) to give the most divergent contributions to the self-energy loops in Figure 1. Some of these are shown in Figure 3. In Figure 3a, the propagating particle

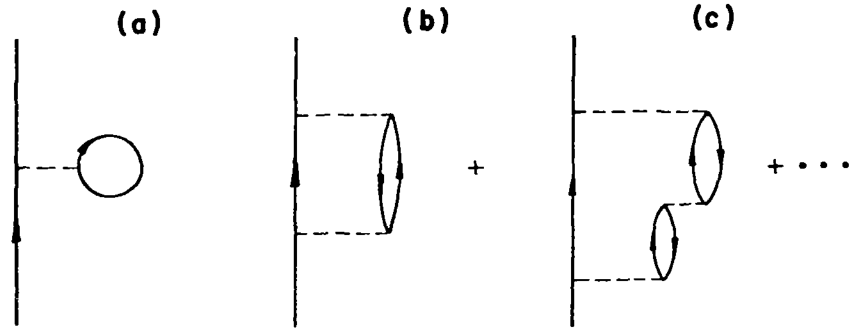

Figure 3 -- Lowest order Hartree and RPA self-energy diagrams.

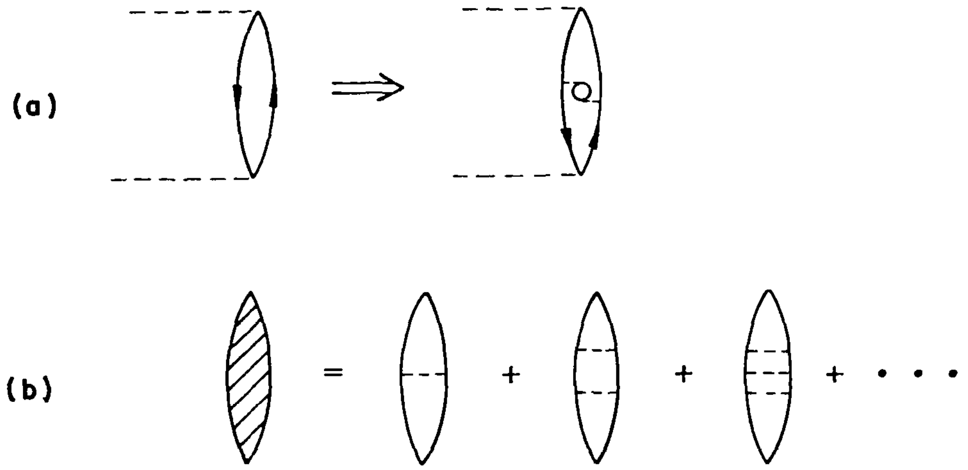

Figure 4 -- a Hubbard modification of a bubble diagram.
b Multiple scattering modification of a bubble.

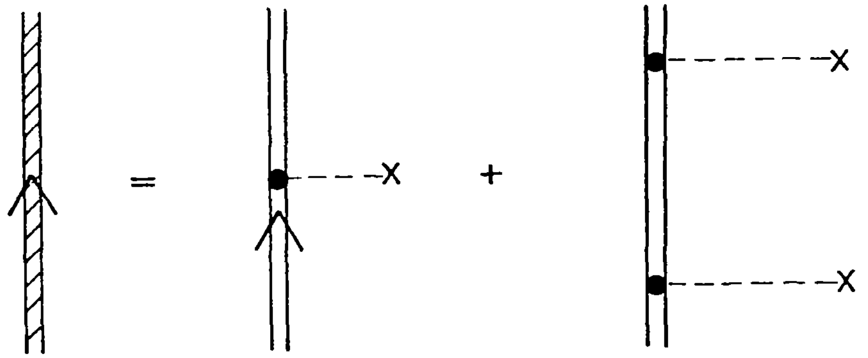

Figure 5 -- Graphical illustration of the dressed electron propagator in a periodic potential.

interacts with a passive particle, but not strongly enough to excite it out of the Fermi sea, so the passive particle must go back where it started from within the Fermi sphere to prevent violation of the exclusion principle. Thus the propagating particle simply scatters off the Hartree potential of the Fermi sea electrons. In Figures 3b and 3c, the propagating particle interacts strongly enough with a passive electron to excite it above the Fermi surface thus leaving behind a lower momentum hole. The pairs propagate and eventually annihilate by creating a new pair or by interacting with the initial pair.

Here the relevance of the Hubbard correction to the RPA with regard to the periodic lattice problem should be noted. Hubbard has suggested that the RPA, an inherently high density approximation, comes closer to the truth for metallic densities if one allows the propagating electron and hole forming the pair to interact; that is, the motions of the electron and hole are correlated. He thus replaces uncorrelated bubble diagrams by the diagram shown in Figure 4a in which the electron and hole interact once through a Thomas-Fermi screened interaction. Recently Crowell, Anderson, and Ritchie (ref. 51) have investigated this problem in relation to positron annihilation theory and have found that relatively good agreement with experiment could be obtained if instead of a single screened interaction, a multiple scattering ladder series was used to describe the electron-hole attraction. It is significant that the series converged extremely rapidly, requiring only three or four multiple scatterings within a single bubble.

In the case of the periodic lattice, another effect is present which may tend to cancel the electron-hole attraction. The lattice core potential is attractive for the electron and repulsive for the hole. Thus once a pair is formed via the e-e interactions, the electron and hole will feel an effective repulsion as a result of the core. At worst this will minimize the need for a Hubbard-type correction. Although no calculations as to the quantitative importance of this effect are offered, some conjectures may be made. It is indeed possible that, under certain conditions, a balance between the effective lattice induced e-h repulsion and the direct e-h attraction could be obtained. Under these circumstances the electron-hole pair would have quite a long lifetime and could be recognized as some sort of many-body excitation resembling a virtual exciton. One manifestation of such an entity might be an effective dipole potential around the ion cores giving rise to a mild discontinuity in the usual muffin tins. For the time being this is left as an interesting problem to contemplate and as a partial argument for using uncorrelated bubbles in real metals.

Next one might ask how the physical Fermion lines appearing in a diagram describing a many-body process would be modified if these quasi-particles were put into the field of a weak periodic pseudo-potential.

The periodic pseudo-potential can be written as

$$\sum_{\vec{R}_j} \frac{1}{N} V(\vec{r}_i + \vec{R}_j) = \frac{1}{N} \sum_{\vec{R}_j, \vec{q}} W(|\vec{q}|)\, e^{i\vec{q}\cdot\vec{r}_i}\, e^{i\vec{q}\cdot\vec{R}_j}$$

$$= \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{r}_i}\, W(|\vec{q}|)\, S(\vec{q}) = V(r_i) \qquad (18)$$

where $W(|\vec{q}|)$ is the spherically symmetric OPW form factor, $S(q) = \sum_{\vec{K}} \delta(\vec{q} + \vec{K})$ is the lattice structure factor, and K is a reciprocal vector (ref. 52). In other words, the Fourier transform of the electron-lattice interaction is given as

$$V(\vec{q}) = W(|\vec{q}|)\, S(\vec{q}). \qquad (19)$$

A quasi-particle propagating in this field will not have a true self-energy because the lattice potential plays the role of a distribution of sources and sinks rather than a polarizable medium through which the particle propagates. However, one can still define a mathematical object which serves the same function as a self-energy operator. This object expresses the way in which the propagation of a quasi-particle is modified by the static lattice "field". In Figure 5 are shown diagrams corresponding to the simplest interactions. If the particle lines interacting with the lattice field were those for bare electrons, then consideration of the two events shown in Figure 5 would be sufficient to generate OPW bands (ref. 52). The first figure describes the effects of the $q = 0$ component of the OPW form factor which has been canceled by the $q = 0$ component of the electron-electron interaction. The second event is a quasi-particle of momentum $\vec{p} - \vec{q}$ scattering into an intermediate, unoccupied state $\vec{p} - \vec{q} + \vec{q}\,'$, and then returning to its original state in a manner quite similar to the self-energy process shown in Figure 1. An effective lattice self-energy or level shift operator is then identified by

$$\Sigma_L(\vec{p} - \vec{q};\ p^o - q^o) = \int \frac{d^3q'}{(2\pi)^3}\, V(-\vec{q}\,')\, G_e(\vec{p} - \vec{q} + \vec{q}\,';\ p^o - q^o)\, V(\vec{q}\,')$$

$$|\vec{p} - \vec{q} + \vec{q}\,'| > p_F \qquad (20)$$

in analogy with Eq. (16) where $G_e(\vec{p} - \vec{q} + \vec{q}\,';\ p^o - q^o)$ is the propagating physical electron Green's function given in Eq. (17). Substituting the periodic potential given by Eq. (19) into Eq. (20) and performing the integrals yields

$$\Sigma_L (p - q) = \sum_{\substack{K \\ |\vec{p} - \vec{q} + \vec{K}| > p_F}} \left| W(\vec{K}) \right|^2 G_e (\vec{p} - \vec{q} + \vec{K};\, p^o - q^o) \tag{21}$$

Furthermore, considerations in this report are limited to points in the first Brillouin zone away from edges and corners so that, at most, only two OPW's need be considered.

The formal procedure of writing and solving a multiple scattering t matrix or ladder sum for a quasi-particle Green's function modified by the effective lattice self-energy Σ_L can be used to obtain

$$G_L (p - q) = \frac{Ge\ (p - q)}{1 - G_e\ (p - q)\ \Sigma_L\ (p - q)} \tag{22}$$

Using Eqs. (17) and (21) in the above yields:

$$\begin{aligned} G_L(p - q) = {} & 1\Big/\Big[\Big(p^o - q^o - E_o\ (\vec{p} - \vec{q}) - \Sigma_e \big(\vec{p} - \vec{q};\, p^o - q^o\big)\Big) \\ & - \left| W(\vec{K}) \right|^2 \Big/ \Big(p^o - q^o - E_o\ (\vec{p} - \vec{q} + \vec{K}) \\ & - \Sigma_e \big(\vec{p} - \vec{q} + \vec{K};\, p^o - q^o\big)\Big)\Big] . \end{aligned} \tag{23}$$

If Γ (p, q) is set = 1 as discussed earlier, this Green's function describing a quasi-particle propagating in a periodic potential is placed into the original self-energy expression, a slight amount of rearrangement is done, the electron self-energy, valid for all values of p, is:

$$\begin{aligned} \Sigma_{Tot}(\vec{p};p^o) = {} & i \int_{\substack{|\vec{p} - \vec{q}| > p_F \\ |\vec{p} - \vec{q} + \vec{K}| > p_F}} \frac{d^4 q}{(2\pi)^4}\ D\ (\vec{q};\, q^o) \\ & \Big[p^o - q^o - E_o\ (\vec{p} - \vec{q} + \vec{K}) - \Sigma_e\ (\vec{p} - \vec{q} + \vec{K};\, p^o - q^o) \Big] \Big/ \\ & \Big[\Big(p^o - q^o - E_o\ (\vec{p} - \vec{q}) - \Sigma_e \big(\vec{p} - \vec{q};\, p^o - q^o\big)\Big) \\ & \times \big(p^o - q^o - E_o\ (\vec{p} - \vec{q} + \vec{K}) - \Sigma_e\ (\vec{p} - \vec{q} + \vec{K};\, p^o - q^o)\big) \\ & - \left| W(\vec{K}) \right|^2 \Big] . \end{aligned} \tag{24}$$

The positions of the poles of the integral are determined by the solution of the secular determinant:

$$\begin{vmatrix} p^{o} - q^{o} - E_{o}(\vec{p} - \vec{q}) - \mathrm{Re}\,\Sigma_{e}(\vec{p} - \vec{q};\, p^{o} - q^{o}) & W(\vec{K}) \\ W(\vec{K}) & p^{o} - q^{o} - E_{o}(\vec{p} - \vec{q} + \vec{K}) - \mathrm{Re}\,\Sigma_{e}(\vec{p} - \vec{q} + K;\, p^{o} - q^{o}) \end{vmatrix} = 0$$

with $\mathrm{Re}\Sigma_e$ the real part of the polarization self-energy operator. It is known that Σ_e is very nearly constant with variations in momentum (ref. 9). Thus:

$$\Sigma_{e}(\vec{p} - \vec{q};\, p^{o} - q^{o}) \approx \Sigma_{e}(\vec{p} - \vec{q} + \vec{K};\, p^{o} - q^{o})$$

It can be shown that this assumption implies that there is a correlation hole around each electron, within which the charge density variation has the usual $j_1(k_c r)$ spherical Bessel function form. *Equating the self-energies yields:*

$$\begin{aligned} -q^{o} &= \frac{1}{2}\left(E_{o}(\vec{p} - \vec{q}) + E_{o}(\vec{p} - \vec{q} + \vec{K}) - 2p^{o} + 2\,\mathrm{Re}\,\Sigma_{e}(p - q)\right) \\ &\quad \pm\left(\frac{1}{4}\left(E_{o}(\vec{p} - \vec{q}) - E_{o}(\vec{p} - \vec{q} + \vec{K}) + \Sigma_{e}(\vec{p} - \vec{q};\, p^{o} - q^{o})\right.\right. \qquad (25) \\ &\quad \left.\left. - \Sigma_{e}(\vec{p} - \vec{q} + \vec{K};\, p^{o} - q^{o})\right)^{2} + |W(\vec{K})|^{2}\right)^{1/2} \\ &= -\alpha \end{aligned}$$

To be completely rigorous, the cut representing the continuous distribution of poles of the interaction propagator D(q) should also be considered. However, in a spectral decomposition, the two poles for q^o will be quite sharp and not obscured by the background. The effects of the D(q) cut can be absorbed in an effective renormalization constant, called Z_2, which usually satisfies $0.75 \lesssim Z_2 \lesssim 1$ in electron gas problems (ref. 9). This renormalization decreases the magnitude of the residues at the two principal poles since some of the spectral weight now appears in the cut.

To perform the q^o integral of Eq. (24), the contour shown in Figure 6 was chosen. The pole corresponding to the state in the second zone is marked with a broken x. If work is done in an extended zone scheme, this pole is on another Riemann sheet. Since in the reduced zone scheme all poles are on the same sheet, the higher zone poles must be included by introducing band indices. The q^o part of the integral is of the form:

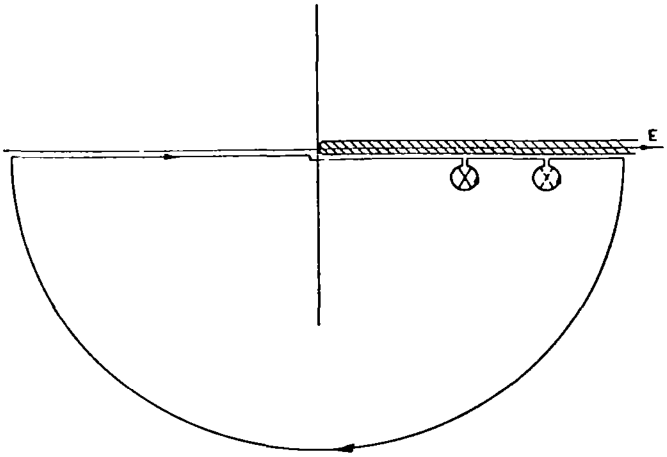

Figure 6 - Contour for Complex Integration

$$\int dq^o \frac{f(q^o)}{g(q^o)} = Z_2 \sum_{n=1,2} 2\pi i \frac{f(q^o)}{g'(q^o)} \Bigg|_{q^o = \alpha n} \tag{26}$$

where $\alpha n = q^o$ is the solution for intermediate states in the n'th band of the hopelessly non-linear Eq. (25). Referring to the denominator of Eq. (24) and setting the Σ's equal gives:

$$\begin{aligned} g(q^o) = \; & \Sigma_e^2 (p - q) - \Sigma_e (p - q) (2 p^o - 2 q^o - E_o (\vec{p} - \vec{q}) \\ & - E_o (\vec{p} - \vec{q} + \vec{K})) + (p^o - q^o)^2 - (p^o - q^o) (E_o(\vec{p} - \vec{q} + \vec{K}) \\ & + E_o (\vec{p} - \vec{q}) + E_o (\vec{p} - \vec{q}) E_o (\vec{p} - \vec{q} + \vec{K}) - |W(\vec{K})|^2. \end{aligned} \tag{27}$$

Consequently:

$$\begin{aligned} g'(q^o) = & \Big\{ \Big[E_o (\vec{p} - \vec{q}) + E_o (\vec{p} - \vec{q} + \vec{K}) \Big] - 2 (p^o - q^o) \\ & + 2 \Sigma_e (\vec{p} - \vec{q}; p^o - q^o) \Big\} \times \left(\frac{\partial \Sigma_e(\vec{p} - \vec{q}; p^o - q^o)}{\partial q^o} + 1 \right) \end{aligned} \tag{28}$$

If the following expansion is made:

$$\frac{\partial \Sigma_e (\vec{p} - \vec{q}; p^o - q^o)}{\partial q^o} \simeq \frac{\partial}{\partial q^o} \Big[\Sigma_e(\vec{p} - \vec{q}; - q^o \Big] - p^o \frac{\partial \Sigma_e(\vec{p} - \vec{q}; - q^o)}{\partial q^o} + \dots) \tag{29}$$

and one of the Ward (ref. 53) identities is used:

$$\Lambda\ (-q^o) = 1 - \frac{\partial\, \Sigma_e\ (-q^o)}{\partial\ q^o},$$

then Eq. (29) takes the form:

$$\frac{\partial\, \Sigma_e\ (\vec{p} - \vec{q};\ p^o - q^o)}{\partial\ q^o} = 1 - \Lambda(q^o) - p^o \frac{\partial}{\partial\, q^o} \Big(1 - \Lambda(-q^o)\Big). \tag{30}$$

Taking the vertex function $\Lambda(q^o) = 1$, the usual first approximate which is equivalent to linearization:

$$\begin{aligned} g'(q^o) \simeq \Big(&-(E_o(\vec{p} - \vec{q}) + E_o(\vec{p} - \vec{q} + \vec{K}) - 2\,(p^o - q^o) \\ &+ 2\Sigma_e\ (\vec{p} - \vec{q};\ p^o - q^o)\Big). \end{aligned} \tag{31}$$

Now, in a similar manner, if the expansion, Ward's identity, and the unit vertex function for treating difficult Σ_e's in Eq. (25) are used, then $g'\ (q^o = a_n)$ becomes simply:

$$g'(a_n) = \pm\, 2\left(\frac{1}{4}\Big(E_o(\vec{p} - \vec{q}) - E_o(\vec{p} - \vec{q} + \vec{K})\Big)^2 + |\,W(K)|^2\right)^{1/2} \tag{32}$$

Thus through the complex integration of Eq. (26) the total self-energy operator, Eq. (24), becomes

$$\begin{aligned} \Sigma_{Tot}(\vec{p};\, p^o) = -\frac{1}{2}\, Z_2 \sum_{n=1,\,2} \int_{\substack{|\vec{p} - \vec{q}\,| > p_F \\ |\vec{p} - \vec{q} + \vec{K}\,| > p_F}} &\frac{d^3 q}{(2\pi)^3}\, D(\vec{q};\, a_n)\Big(p^o - a_n - E_o(\vec{p} - \vec{q} + \vec{K}) \\ &- \Sigma_e(\vec{p} - \vec{q} + \vec{K};\ p^o)\Big) \left[\left(\frac{1}{4}(E_o(\vec{p} - \vec{q}) - E_o(\vec{p} - \vec{q} + \vec{K})\right)^2 \right. \\ &\left. + \,|\,W(\vec{K})|^2\Big)^{1/2}\right]^{-1}. \end{aligned} \tag{33}$$

Putting Eq. (25) for α_n into the numerator gives the result:

$$\Sigma_{Tot}(\vec{p};p^o) = -\frac{1}{2} Z_2 \int_{|\vec{p}-\vec{q}| > p_F \cdot} \frac{d^3q}{(2\pi)^3} \left[D(\vec{q};\alpha_1) - D(\vec{q};\alpha_2) \right]$$

$$- \frac{1}{4} Z_2 \int_{\substack{|\vec{p}-\vec{q}| > p_F \\ |\vec{p}-\vec{q}+\vec{K}| > p_F}} \frac{d^3q}{(2\pi)^3} \left[D(\vec{q};\alpha_1) + D(\vec{q};\alpha_2) \right] . \tag{34}$$

$$\left[\frac{E_o(\vec{p}-\vec{q}+\vec{K}) - E_o(\vec{p}-\vec{q})}{\left[\frac{1}{4}\left(E_o(\vec{p}-\vec{q}) - E_o(\vec{p}-\vec{q}+\vec{K})\right)^2 + |W(\vec{K})|^2\right]^{1/2}} \right]$$

Note that the only place in which p^o appears in the right hand side of Eq. (34) is through Eq. (25) determining the value of α_n used in the interaction propagator $D(\vec{q};\alpha_n)$. The energy spectrum is given by

$$E(\vec{p}) = E_{OPW}(\vec{p}) + \Sigma_{Tot}(\vec{p};E)$$

with the first iteration

$$E(\vec{p}) \simeq E_{OPW}(\vec{p}) + \Sigma_{Tot}(\vec{p};\frac{\vec{p}\cdot\vec{p}}{2m}). \tag{35}$$

These are amazingly simple and quite understandable results considering the vast complexity of the system investigated. The meaning, interpretation, and discussion of the present results appear in the following section.

Discussion and Conclusions

Through a rather involved mathematical excursion, a very simple general expression for the self-energy of an electron in the many-body potential of an interacting electron gas, plus a periodic lattice potential, has evolved. The result is quite general, subject to the folliwing conditions. Since the RPA has yet to be invoked, this not necessarily a high density theory. To perform numerical calculations would require an explicit expression for the interaction propagator $D(q) = v(\vec{q})/\epsilon(q)$. If plane wave many-body theory can give a good $\epsilon(q)$, then Eqs. (34) and (35) can give a correspondingly good self-energy if there exists a periodic potential, at least for materials and points in the Brillouin zone which have been previously treated by two non-interacting OPW electrons. First attempts will be made by using the RPA or Hubbard-corrected RPA to see how significant many-body interactions really are (ref. 54). It would also be interesting to split up the density fluctuation propagator into a plasmon and pair propagator as was done by Hedin et al (ref. 10) and see how the lattice affects the plasmon part of the self-energy.

A look at Eq. (34) prompts the following comments as to the structure of this end result. The first simple integral is just one-half the self-energy for an electron gas with no periodic lattice except for two modifications. First, the interaction propagator is taken at the energy α_n of Eq. (25) rather than at the free electron energy because the lattice shifts the free electron energies. Second, the fact that work is being done in the reduced zone scheme is made manifest by admixture with the α_2 pole. The second integral provides the dominant lattice contribution. In the empty lattice test where $W(\vec{K}) = 0$, α = the free electron energy and the second integral becomes one-half the free electron self-energy with the modification from the admixture with the α_2 pole. However, this contribution exactly cancels the α_2 term in the first integral so the required limiting expression is precisely obtained. That Eq. (34) gives the required value in the limit adds confidence to its overall validity.

The origin of the lattice contribution can be explained as follows. Initially an unperturbed Fermi sphere exists. Two passive electrons interact as shown in Figure 2 and are excited above the Fermi sphere. If they have interacted through a large enough momentum transfer $\vec{q}$, then one of the virtual electrons may have enough momentum to satisfy the Bragg condition $2(\vec{p} + \vec{q}) \cdot \vec{K} = K^2$. If one of the virtual physical electrons (i.e., corrected for many-body effects) is Bragg-reflected, then the remaining hole will not have any electron to annihilate with and thus will have a longer lifetime to make its influence felt. The same is true for the reflected electron.

Consequently both the electron and hole will remain in high energy states for longer times than are advantageous for reduction of the total energy. Thus the dominant important lattice effect of Bragg reflections serves to decrease the absolute value of the self-energy. Since the self-energy is a negative quantity, the lattice increases the exact total energy of the system relative to the free electron total energy when evaluated at α_n.

It is worthwhile commenting upon the procedure to be used for obtaining numerical results based on the theory presented herein. To calculate many-body OPW bands, pick a particular symmetry line and point on this line. This determines the value of p used to calculate α_n given in Eq. (25). Knowing the symmetry line of the particular lattice considered, one can then obtain tabulated values for the OPW form factor W(K)(ref. 52). Using the numerical tabulations of Hedin, one can also obtain values for Σ_e required in

Eq. (25). Expressions for $D(\vec{q};\alpha)$ exist in the literature within the various approximation schemes for the dielectric function as previously discussed (ref. 6). Thus everything needed to perform numerical integration of Eq. (34) exists. Sample calculations to see exactly the lattice effects on the many-body theory* are in order.

Calculations of some experimentally relevant quantities such as electron specific heats, density of states at the Fermi surface, and bandwidths, or equivalently, effective masses are also in order. It will be interesting to see what percentage of the electron effective mass, usually attributed to single-electron interactions with the periodic potential, actually arise from many-body interactions in a periodic potential.

An important point to be picked up from this work is the following. Electronic behavior in solids is determined in large by three distinctly different phenomena which can be treated separately. The first of these is concerned with high kinetic energies of electrons in the core region. One can project out of the true wavefunctions the wiggly portion which is well treated in an atomic-like Hartree-Fock approximation. The second point is concerned with the possibilities of Bragg reflections at zone faces. This is dealt with by taking linear combinations of the wavefunction which remain after projecting out the high-energy components. The last point is related to the many-body effects which, for the most part, affect the low-energy or plane-wave components of the exact wavefunction. By doing each problem separately and as exactly as possible and then combining the results in a self-consistent manner, one can finally arrive at potentially useful results which should provide a better understanding of real electronic behavior in real metals.

Thus, the first plateau in this study of inhomogeneous electron gases has been attained. An expression has been obtained for the momentum-dependent self-energy of an electron in an interacting electron gas with a periodic pseudo-potential. Although the importance of this correction to single electron energy band theory may be of significance, as will be seen in the near future, it appears that the lattice offers no quantitatively new feature which needs to be included for present purposes. It is thus concluded that lattice effects may be of significance in the many-body corrections to energy band theory, a quite precise theory, but are not of first order importance in the inhomogeneous electron gas effects to be treated in the following sections.

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*P. deCicco (personal communication)

IV. DIELECTRIC FORMULATION IN AN ARBITRARY, NON-INTERACTING ELECTRON BASIS

Generalities

As has been stressed previously, the central rallying point of many-body effects can be considered to be the time-dependent linear response function of the electron gas to a driving force. This response function is usually presented in the form of a dielectric function, susceptibility, or polarizability. The simplest derivation of the RPA dielectric function for a homogeneous electron gas has been through the self-consistent field theory of Ehrenreich and Cohen (ref. 8), further elucidated by Brout and Carruthers (ref. 54).

A general derivation of the RPA dielectric function for an inhomogeneous electron gas, within which the originally non-interacting electron wave functions are expandable in a plane wave basis, is now presented. In the limit in which each wavefunction is the "sum" of only one plane wave, the homogeneous case, the derived dielectric function reduces to the ordinary RPA result. With the aid of a new image technique, the general inhomogeneous electron gas dielectric function takes on a simple form in the surface region also. With this imaging technique, the inverse dielectric function appropriate in the surface region displays a pole at the surface plasma frequency.

Theoretical Considerations

Following EC, the Liouville equation describing the time evolution of the single particle density matrix is considered:

$$i \frac{\partial \rho}{\partial t} = \left[H, \rho \right]. \tag{36}$$

The Hamiltonian for the system is written as

$$H = H_o + V(r,t) \tag{37}$$

with

$$H_o = KE + V_o(r)$$

defining the complete set of non-interacting electron eigenfunctions $| \psi_{\vec{k}} \rangle$ which are assumed to be plane wave expandable. The exact eigenfunctions satisfy

$$H_o | \psi_{\vec{k}} \rangle = E(k) \, | \psi_{\vec{k}} \rangle \tag{38}$$

with

$$|\psi_{\vec{k}}\rangle = \sum_{\vec{k}'} \Gamma_{\vec{k},\vec{k}'} e^{i\vec{k}' \cdot \vec{r}} = \sum_{\vec{k}'} \Gamma_{\vec{k},\vec{k}'} |\vec{k}'\rangle$$

and Γ the coefficient matrix. The self-consistent potential $V(r, t)$ is determined by the applied field plus the possibly time-dependent induced screening charge. The operator ρ, representing the single-particle density matrix, is expanded as

$$\rho = \rho_o + \rho_1 \tag{39}$$

such that

$$\rho_o | \psi_{\vec{k}}\rangle = f_o (E_{\vec{k}}) | \psi_{\vec{k}}\rangle \tag{40}$$

where f_o is the Fermi function.

Considering that the non-interacting Liouville equation is

$$i \frac{\partial \rho_o}{\partial t} = \left[H_o, \rho_o \right] \tag{41}$$

and linearizing by neglecting the term

$$\left[V(\vec{r}, t), \rho_1 \right]$$

in the full commutator of Eq. (36), allows determination of the equation of motion for ρ_1, the measure of departure from the equilibrium distribution. Substitution of Eqs. (37), (39), and (41) into the linearized Eq. (36) yields:

$$i \frac{\partial \rho_1}{\partial t} = \left[H_o, \rho_1 \right] + \left[V(\vec{r}, t), \rho_o \right] . \tag{42}$$

Taking matrix elements of Eq. (42) between the time-independent states

$$|\psi_{\vec{k}}\rangle$$

and

$$|\psi_{\vec{k}+\vec{q}}\rangle$$

and utilizing Eqs. (38) and (40), then yields:

$$i \frac{\partial}{\partial t} \left\langle \psi_{\vec{k}} \right| \rho_1 \left| \psi_{\vec{k}+\vec{q}} \right\rangle = (E(\vec{k}) - E(\vec{k}+q)) \left\langle \psi_{\vec{k}} \right| \rho_1 \left| \psi_{\vec{k}+\vec{q}} \right\rangle$$

$$+ \left(f_o (E_{\vec{k}+\vec{q}}) - f_o (E_{\vec{k}}) \right) \left\langle \psi_{\vec{k}} \right| V(\vec{r},t) \left| \psi_{\vec{k}+\vec{q}} \right\rangle . \tag{43}$$

In keeping with the sign convention of EC, the self-consistent potential is written as

$$V(\vec{r},t) = \sum_{\vec{q}} V(\vec{q},t)\, e^{-i\vec{q}\cdot\vec{r}}.$$

and is related to the charge density through Poisson's equation:

$$\nabla^2 V = -4\pi e^2 n$$

or in momentum space,

$$V(\vec{q},t) = \frac{4\pi e^2}{q^2}\, n_{\vec{q}} \tag{44}$$

with

$$n(\vec{r}) = \sum_{q} n_{\vec{q}}\, e^{-i\vec{q}\cdot\vec{r}}. \tag{45}$$

The expectation value of a single particle operator is given by

$$\langle O \rangle = \mathrm{Tr}\ (\rho O)$$

where ρ is the density matrix and Tr is the operation of taking the trace. In the present case, the density increment operator is of interest,

$$\rho_1 = \delta(\vec{x}_{op} - \vec{r}).$$

The trace is written as the sum of diagonal elements of the matrix of the operator between the exact single-particle states $|\psi_{\vec{k}}\rangle$. Following this procedure, the density increment is:

$$n(\vec{r}) = \sum_{k'} \left\langle \psi_{\vec{k}'} \right| \delta(\vec{x}_{op} - \vec{r})\, \rho_1 \left| \psi_{\vec{k}'} \right\rangle . \tag{46}$$

Now inserting the exact eigenfunction representation of the unit operator

$$1 = \sum_{\vec{k}} | \psi_{\vec{k}} \rangle \langle \psi_{\vec{k}} |$$

into Eq. (46) yields:

$$n(\vec{r}) = \sum_{\vec{k},\vec{k}'} \langle \psi_{\vec{k}'} | \delta(\vec{x}_{op} - \vec{r}) | \psi_{\vec{k}} \rangle \langle \psi_{\vec{k}} | \rho_1 | \psi_{\vec{k}'} \rangle . \qquad (47)$$

If a complete set of eigenfunctions of the position operator is introduced:

$$1 = \int d^3y \, | \vec{y} \rangle \langle \vec{y} | ,$$

then Eq. (47) becomes:

$$n(\vec{r}) = \int d^3y \sum_{\vec{k},\vec{k}'} \langle \psi_{\vec{k}'} | \vec{y} \rangle \delta(\vec{y} - \vec{r}) \langle \vec{y} | \psi_{\vec{k}} \rangle \langle \psi_{\vec{k}} | \rho_1 | \psi_{\vec{k}'} \rangle \qquad (48)$$

with the transformation functions

$$\langle \vec{y} | \psi_{\vec{k}} \rangle = \sum_{\vec{k}'''} \Gamma_{\vec{k},\vec{k}'''} e^{i \vec{k}''' . \vec{y}} ,$$

$$\langle \psi_{\vec{k}'} | \vec{y} \rangle = \sum_{\vec{k}''} \Gamma_{\vec{k}',\vec{k}''} e^{-i \vec{k}'' . \vec{y}} . \qquad (49)$$

Performing the $\vec{y}$ integration and using the transformation functions allows Eq. (48) to take the form:

$$n(\vec{r}) = \sum_{\substack{\vec{k},\vec{k}' \\ \vec{k}'',\vec{k}'''}} \Gamma^{*}_{\vec{k}',\vec{k}''} \Gamma_{\vec{k},\vec{k}'''} e^{i(\vec{k}''' - \vec{k}'') . \vec{r}} \langle \psi_{\vec{k}} | \rho_1 | \psi_{\vec{k}'} \rangle . \qquad (50)$$

If one calls $\vec{k}' = \vec{k} + \vec{q}$ and replaces the sum on $\vec{k}'$ by a sum on $\vec{q}$, then:

$$n(\vec{r}) = \sum_{\vec{q}} e^{-i\vec{q}\cdot\vec{r}} \sum_{\substack{\vec{k},\vec{k}'' \\ \vec{k}'''}} \Gamma^{*}_{\vec{k}+\vec{q},\vec{k}''} \, \Gamma_{\vec{k},\vec{k}'''} \, e^{i(\vec{k}''' - \vec{k}'' + \vec{q})\cdot\vec{r}}$$

$$\left\langle \psi_{\vec{k}} \,|\, \rho_1 \,|\, \psi_{\vec{k}+\vec{q}} \right\rangle . \tag{51}$$

In order that Eq. (45) and (51) be compatible, it is required that $\vec{k}''' - \vec{k}'' + \vec{q} = 0$. Thus the Fourier coefficient of the density increment is

$$n(\vec{q}) = \sum_{\vec{k},\vec{k}''} \Gamma^{*}_{\vec{k}+\vec{q},\vec{k}''} \, \Gamma_{\vec{k},k''-\vec{q}} \left\langle \psi_{\vec{k}} \,|\, \rho_1 \,|\psi_{\vec{k}+\vec{q}} \right\rangle . \tag{52}$$

Returning to Eq. (43), it if it assumed that the time dependence of ρ_1 goes as

$$\rho_1 \sim e^{-i\omega t},$$

and if the excitation frequency is defined as

$$E(\vec{k}+\vec{q}) - E(\vec{k}) = \omega_{\vec{q}}(\vec{k}),$$

then

$$\left\langle \psi_{\vec{k}} \,|\, \rho_1 \,|\, \psi_{\vec{k}+\vec{q}} \right\rangle = \frac{(f_o(E_{\vec{k}+\vec{q}}) - f_o(E_{\vec{k}}))}{\omega + \omega_{\vec{q}}(\vec{k})}$$

$$\times \left\langle \psi_{\vec{k}} \,|\, V(\vec{r}) \,|\, \psi_{\vec{k}+\vec{q}} \right\rangle . \tag{53}$$

The matrix element of the self-consistent potential is written as

$$\left\langle \psi_{\vec{k}} \,|\, V(\vec{r}) \,|\, \psi_{\vec{k}+\vec{q}} \right\rangle = \sum_{\substack{\vec{k}'^{v},\vec{k}^{v} \\ \vec{q}'}} \Gamma^{*}_{\vec{k},\vec{k}'^{v}} \, \Gamma_{\vec{k}+\vec{q},\vec{k}'^{v}} \, V(\vec{q}')$$

$$\left\langle \vec{k}'^{v} \,\middle|\, e^{-i\vec{q}'\cdot\vec{r}} \,\middle|\, \vec{k}^{v} \right\rangle . \tag{54}$$

Since the plane wave matrix element is $\delta(\vec{k}^{v} - \vec{q}' - \vec{k}'^{v})$, Eq. (54) becomes:

$$\left\langle \psi_{\vec{k}} \middle| V(\vec{r}) \middle| \psi_{\vec{k}+\vec{q}} \right\rangle = \sum_{\vec{k}'^{v},\vec{q}'} \Gamma^{*}_{\vec{k},\vec{k}'^{v}} \, \Gamma_{\vec{k}+\vec{q},\vec{k}'^{v}+\vec{q}'} \, V(\vec{q}'). \tag{55}$$

Combining Eqs. (52), (53), and (55), and changing variables $\vec{k}'' \rightarrow \vec{k}'$ and $\vec{k}^{iv'} \rightarrow \vec{k}''$ yields:

$$n_{\vec{q}} = \sum_{\vec{k}} \frac{f_o(E_{\vec{k}+\vec{q}}) - f_o(E_{k})}{\omega + \omega_q(\vec{k})} \left\{ \sum_{\substack{\vec{k}',\vec{k}'' \\ \vec{q}'}} \Gamma^{*}_{\vec{k}+\vec{q},\vec{k}'} \, \Gamma_{\vec{k},\vec{k}'-\vec{q}} \right. \\ \left. \times \, \Gamma^{*}_{\vec{k},\vec{k}''} \, \Gamma_{\vec{k}+\vec{q},\vec{k}''+\vec{q}'} \, V(\vec{q}') \right\} \tag{56}$$

Classical electrodynamics is now used to obtain an expression relating the dielectric function with the polarization charge. The polarization is related to the induced charge through

$$\vec{\nabla} \cdot \vec{P} = en$$

or in momentum space

$$-i\vec{q} \cdot \vec{P}_{\vec{q}} = en_{\vec{q}}.$$

The polarization is also given by

$$\vec{P}_{\vec{q}} = \frac{\epsilon(\vec{q},\omega) - 1}{4\pi} \vec{E}_{\vec{q}}$$

with

$$e\vec{E}_{\vec{q}} = -i\vec{q} \, V(\vec{q},t).$$

Solving for the dielectric function:

$$\epsilon(\vec{q},\omega) = 1 + v(q) \frac{n_{\vec{q}}}{V(\vec{q},t)} . \tag{57}$$

If Eq. (56) is linearized, as in the spirit of the EC theory, by including only the q' = q term, then Eq. (57) is:

$$\epsilon(\vec{q},\omega) = 1 + v(q) \sum_{\vec{k}} \frac{f_o(E_{\vec{k}+\vec{q}}) - f_o(E_{\vec{k}})}{\omega + \omega_{\vec{q}}(\vec{k})} \tag{58}$$

$$\times \left\{ \sum_{\vec{k}',\vec{k}''} \Gamma^*_{\vec{k}+\vec{q},\vec{k}'} \Gamma_{\vec{k},\vec{k}'-\vec{q}} \Gamma^*_{k,k''} \Gamma_{\vec{k}+\vec{q},\vec{k}''+\vec{q}} \right\}$$

This is a completely general result for the linear dielectric function of any inhomogeneous electron gas, in which the non-interacting electron wave-functions are expandable in a plane wave basis. If the bracketed term were unity, then Eq. (58) would be the precise expression for the RPA dielectric function in a uniform electron gas. The utility of Eq. (58) depends upon the simplicity of the original non-interacting basis. Clearly if the Γ matrix is complicated, requiring the superposition of many plane waves, then the resulting ϵ, if calculable, will be very complicated.

In the following section, it will be shown that Eq. (58), together with an image technique, can produce a relatively simple expression for the RPA dielectric function in an electron gas with a surface.

Surface Dielectric Function

One of the more interesting and experimentally relevant examples of an inhomogeneous electron gas occurs in the surface region of a metal. As is always the case in these sorts of problems, the destruction of translational invariance reduces the symmetry of the problem to the point where any quantitative theory can be attempted on highly idealized models which accentuate only the most dominant features of the physical system.

The problem of surface properties of electron gases has always been handled within the context of the following model (refs. 33-35, 39). A potential well with a perfectly reflecting infinite surface barrier perpendicular to the z direction is assumed. This allows one to work with the following non-interacting wave-functions:

$$\psi(\vec{r}) = \left(\frac{2}{\Omega}\right)^{1/2} \sin k_z z \; e^{i\vec{k}_t \cdot \vec{r}_t} \qquad z \geq 0 \tag{59}$$

$$\psi(\vec{r}) = 0 \qquad z \leq 0 \; .$$

In general, people like to think of decaying exponential wave-functions for $z \leq 0$. However, if one considers the nodal plane $z = 0$ as a mathematical surface somewhere outside the physical surface, then the charge density given by the Eq. (59) wavefunctions

$$n_o(\vec{r}) = \frac{4}{(2\pi)^3} \int_0^{p_F} \sin^2 k_z z \, d^3k$$

$$= n_{int} \left[1 - 3 \left(\frac{\sin(2p_F r \cos\theta) - (2p_F r \cos\theta) \cos(2p_F r \cos\theta)}{(2p_F r \cos\theta)^3} \right) \right] \qquad (60)$$

is not significantly different from that obtained with decaying exponentials and the physical surface at $z = \xi$, $\xi > 0$. As Bardeen has suggested,

$$\xi \sim O(1 \text{Å}).$$

The coordinate system used in Eq. (60) is illustrated in Figure 7. In Figure 8, Eq. (60) is drawn for various radial lines into the electron gas. Note that if

$$p_F r \cos\theta$$

was taken as the ordinate, then a single universal curve would be applicable, that one for $\theta = 0$ in Figure 8.

To proceed an expression for the dielectric function of this model is needed. The coefficient matrix Γ is obtained by taking the Fourier transform of the Eq. (59) wavefunctions. Thus:

$$\Gamma_{\vec{k},\vec{k}'} = \lim_{L \to \infty} 2^{\frac{1}{2}} \int_0^L dz \int_{L/2}^{L/2} d^2 r_t \sin k_z z \, e^{i\vec{k}_t \cdot \vec{r}_t} \, e^{-i\vec{k}' \cdot \vec{r}}$$

becoming

$$\Gamma_{\vec{k},\vec{k}'} = \frac{k_z}{k_z^2 - k'^2_z} \qquad (61)$$

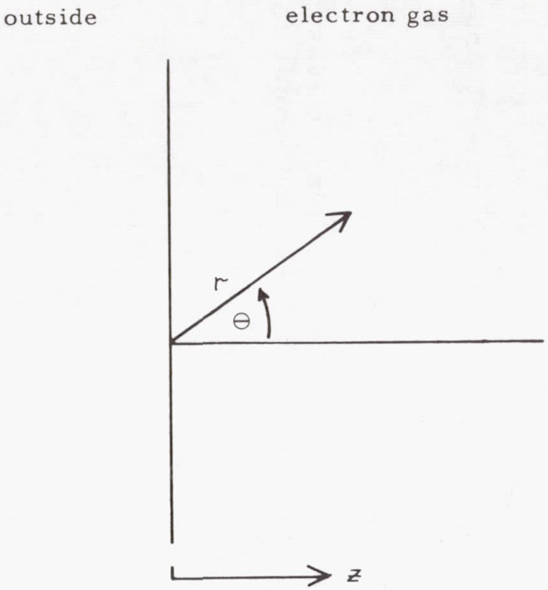

Figure 7. -- Coordinate system used to describe electron gas surface effects.

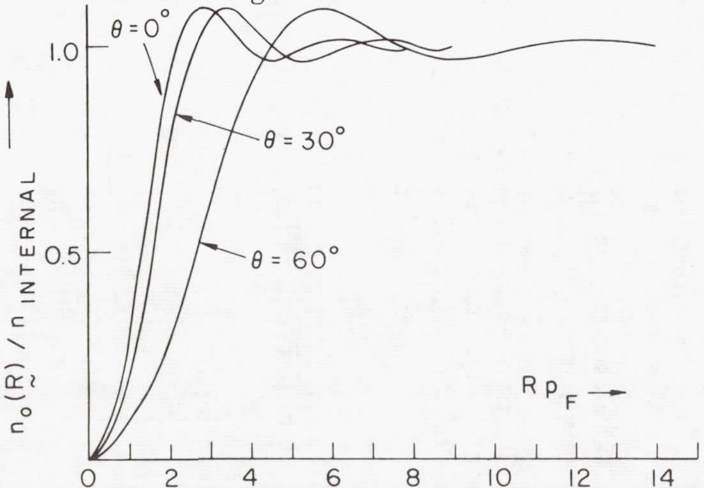

Figure 8. -- Unperturbed charge density as a function of position near an electron gas surface.

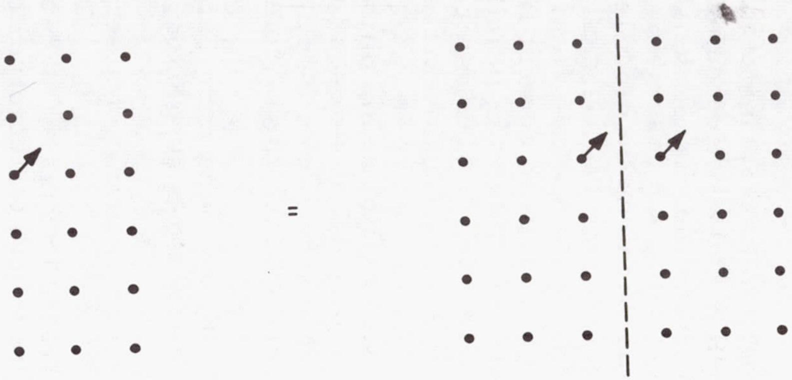

Figure 9a. -- Model for describing the lattice response of a surface atom in terms of the response of an atom in an infinite area.

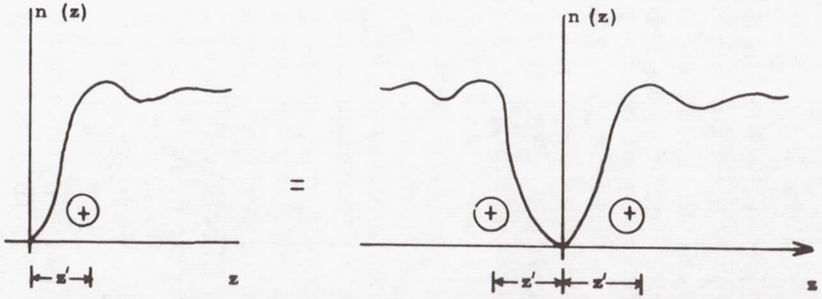

Figure 9b. -- Model for describing the dielectric response of an electron gas with a surface in terms of the response of an infinite electron gas.

which indeed is more complicated than one desires for use in Eq. (58). Thus the motivation for finding a simpler technique definitely exists.

Goodman (ref. 55) has devised an image technique for describing the lattice dynamics of surface atoms. How this approach can be modified to describe electronic surface properties will now be described. Briefly what Goodman does is the following. He realizes that a surface atom in the semi-infinite lattice responds to a point impulsive displacement from its equilibrium position in a manner which can be related to the infinite lattice response. In Figure 9a the situation is illustrated. The figure shows that the response of the semi-infinite lattice to an initial surface atom displacement is exactly the same as the response of the infinite lattice to an equivalent displacement of two atoms on either side of the mathematical surface such that initially there is no net force across the surface plane. It is clearly much easier to calculate response functions for the infinite lattice since one does not get into the problems of complicated Fourier transforms as in Eq. (61).

Goodman's thinking is also applicable to the surface electron gas response or dielectric function. Consider Figure 9b which displays the electron gas analog. This picture suggests that the response of a semi-infinite electron gas to some perturbation a distance z' into the gas is exactly that of an infinite gas with the same perturbations at z' and -z' such that no electric field lines cross the mathematical surface. Although an example in which the charge density has a node at z = 0 has been drawn, this is not a necessary condition. The image technique is applicable wherever the mathematical surface is defined. The charge density will always be continuous at z = 0, but only in a few cases will the derivatives be so. This makes for complicated Fourier transforms or Γ matrices, but does not vitiate the theoretical validity of the model.

The beauty of the infinite gas with a nodal plane at z = 0, as shown in the right hand side of Figure 9b is that the sine wavefunctions

$$\psi_{\vec{k}}(\vec{r}) = \left(\frac{2}{\Omega}\right)^{1/2} \sin k_z z \; e^{i\vec{k}_t \cdot \vec{r}_t} , \tag{62}$$

valid for all space, are easily built up from a small sum of plane waves, two to be exact. The Γ coefficients needed in Eq. (58) take the simple form

$$\Gamma^{*}_{\vec{k}+\vec{q},\vec{k}'} = -\frac{1}{\sqrt{2}i}\left(\delta_{k_z+q_z,k'_z} - \delta_{k_z+q_z,\,-k'_z}\right)\delta_{\vec{k}_t+\vec{q}_t,\vec{k}'_t} \tag{63}$$

$$\Gamma^{\vec{k},\vec{k}'\,-\vec{q}} = \frac{1}{\sqrt{2}i}\left(\delta_{k_z,k'_z-q} - \delta_{k_z,\,-k'_z+q_z}\right)\delta_{\vec{k}_t,\vec{k}'_t\,-\vec{q}_t}$$

$$\Gamma^{*\,\vec{k},\vec{k}''} = -\frac{1}{\sqrt{2}i}\left(\delta_{k_z,k''_z} - \delta_{k_z,\,-k''_z}\right)\delta_{\vec{k}_t,\vec{k}''_t}$$

$$\Gamma_{\vec{k},\vec{k}''} = \frac{1}{\sqrt{2}i}\left(\delta_{k_z,k''_z} - \delta_{k_z,\,-k''_z}\right)\delta_{\vec{k}_t,\vec{k}''_t}$$

where, as usual, the subscript t signifies vector momentum transverse to the surface. It is important to realize that Kronecker delta functions are used and always implied in future sections since, at times, sloppiness in the mathematical treatment of the Dirac delta function limit becomes evident. When these coefficients are used and the $\vec{k}'$ and $\vec{k}''$ sums in Eq. (58) are performed, the bracketed term becomes:

$$\left\{\quad\right\} = \frac{1}{2}\left(1-\delta_{k_z,\,-k_z}\right)\left(1-\delta_{k_z,\,-k_z}\right. \\ \left. -\delta_{k_z+q_z,\,-k_z-q_z} + \delta_{q_z,\,-q_z}\right) \tag{64}$$

Equation (64) lends itself to physical interpretation. All the

$$\delta_{k_z,\,-k_z}$$

terms just eliminate the infinite wavelength component of the electron gas, a necessary requirement if one imposes the constraint of a nodal plane somewhere. This restriction adds mathematical rigor to the present model but offers no computational problem. Similarly the third delta function requires one to avoid the point $k_z = -q_z$ when integrating on $\vec{k}$. Since this point, for any given $\vec{q}$, is non-singular, one can formally perform the k integration as

$$\int_{\substack{a \\ k_z \neq -q_z}}^{b} d^3k\, f(\vec{k}) = \lim_{\epsilon\to 0}\int d^2k_t \left\{\int_{-q_z+\epsilon}^{b_z} dk_z \right. \\ \left. + \int_{a}^{-q_z-\epsilon} dk_z\right\} f(\vec{k}) \to \int_a^b d^3k\, f(\vec{k}). \tag{65}$$

This is valid since f(k) is smoothly and not piece-wise continuous at $k_z = -q_z$ and non-singular. Thus Eq. (62) is simply

$$\Big\{ \quad \Big\} = \frac{1}{2}\left(1 + \delta_{q_z, -q_z}\right).$$

The $q_z = 0$ delta function introduces a coupling between the spherically symmetric dielectric function and the surface boundary condition as is better illustrated by writing the dielectric function in its final form:

$$\epsilon(\vec{q},\omega) = 1 - \frac{v(q)}{2} \sum_{\vec{k}} \frac{(f_o(E_{\vec{k}+\vec{q}}) - f_o(E_{\vec{k}})}{\omega + \omega_q(\vec{k})} - \frac{v(q)}{2}\, \delta_{q_z,0} \sum_{\vec{k}} \frac{(f_o(E_{\vec{k}+\vec{q}}) - f_o(E_{\vec{k}})}{\omega + \omega_{\vec{q}}(\vec{k})} \tag{66}$$

which, by some simple manipulations involving a different way of expressing the Pauli principle constraints, can also be written as

$$\epsilon(\vec{q},\omega) = 1 - \frac{v(q)}{2} \sum_{\substack{k < p_F \\ |\vec{k}+\vec{q}| > p_F}} \left(\frac{1}{\omega - \omega_{\vec{q}}(\vec{k}) + i\eta} - \frac{1}{\omega + \omega_{\vec{q}}(\vec{k}) - i\eta} \right) (1 + \delta_{q_z,0}) = 1 - 4\pi\alpha(\vec{q}) \tag{67}$$

introducing the notation for the polarizability.

The zeroes of $\epsilon(\vec{q},\omega)$ ascertain the eigenvalues of the electron-hole pair continuum of excitations and also the collective plasmon state. In the long wavelength limit, as $q \rightarrow 0$, it is easy to show that Eq. (67) gives the plasma frequency since

$$0 = 1 - \lim_{q\rightarrow 0} \frac{v(q)}{2} \sum_{\substack{k < p_F \\ |\vec{k}+\vec{q}| > p_F}} \left(\frac{2\omega_{\vec{q}}(\vec{k})}{\omega^2 - \omega_{\vec{q}}^2(\vec{k})} \right) (1 + \delta_{q_z,0}).$$

As $q \to 0$,

$$\omega_{\vec{q}}(\vec{k}) = \frac{\vec{q}\cdot\vec{k}}{m} + \frac{q^2}{2m} \approx 0$$

in the denominator. In the numerator, the $\vec{q} \cdot \vec{k}$ term gives zero when integrated over k. Thus, going to an integral, the surviving term is

$$0 = 1 - \lim_{q\to 0} \frac{v(q)}{2} \int_{\substack{k < p_F \\ |\vec{k}+\vec{q}| > p_F}} \frac{d^3k}{(2\pi)^3} \left(\frac{q^2}{2m}\right) \frac{1}{\omega^2} (1 + \delta_{q_z, 0}). \tag{68}$$

With $v(q) = 4\pi e^2/q^2$, the k integral giving the number density, and $\lim_{q\to 0} (1 + \delta_{q_z, 0}) \to 2$,

$$0 = 1 - \frac{4\pi e^2}{2q^2}\, n\, 2\, \frac{q^2}{2m}\, \frac{2}{\omega^2}$$

and thus

$$\omega_{Pl} = \left(\frac{4\pi n e^2}{m}\right)^{1/2} \tag{69}$$

which is the standard volume plasma frequency.

Now a method for transcribing these results, by use of the image technique, into a form suitable for surface calculations will be presented. As was shown in Figure 9b, the response of the semi-infinite electron gas to some driving force is equivalent to the response of the infinite gas to the same driving force and its image. On a microscopic scale, considering the driving force to be the e-e interactions, Figure 9c shows the physical situation. The response of an electron at a' to an electron at b' in the surface problem is mathematically equivalent to the response of an electron a to electron b and its image c in the infinite sine wave electron gas. Thus, if one wishes to know the response of electron a to electron b at the surface where z = 0, then the imaging technique says that one wants the response of a to 2b, that is, a responds as if the surface electron charge were twice the standard electron charge. Conversely, if one wants to know how the surface electrons respond to all other electrons in the bulk, then this situation is the equivalent of a surface electron of charge e responding to interior electrons of charge e/2. If this

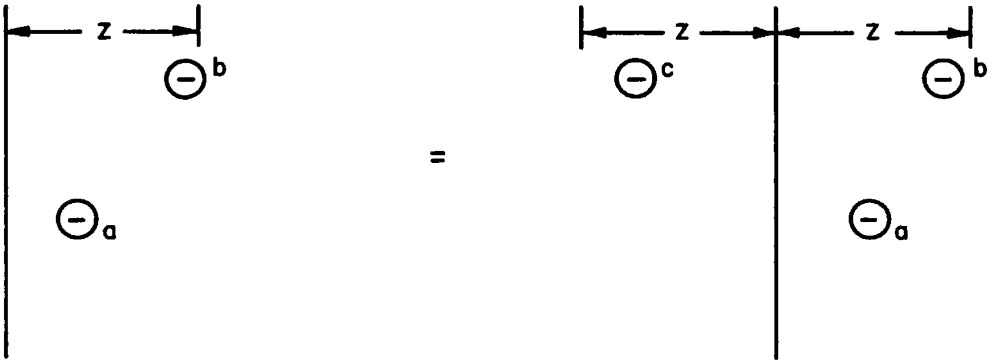

Figure 9c.--Example of equivalent force fields in the semi-infinite and infinite electron gas.

modification is introduced into Eq. (69) for the plasma frequency, that is,

$$e^2 \rightarrow e^2/2,$$

then the pole for the collective oscillations of the surface electrons appears at

$$\omega_s = \frac{\omega_{Pl}}{\sqrt{2}} ,$$

a result which has been known for a long time, but not derived in this manner (refs. 36-39, 56). The main reason for demonstrating the surface plasmon now is to show that the theory developed so far is consistent with already existing theory. Consideration of the surface plasmon in relation to correlation effects upon the surface barrier will be covered in section VIII.

It should also be noted that ϵ in the surface problem is really quite Z-dependent. This fact has been hidden in the sense that we are looking only at the z = 0 case which simplified nicely. The problem of z dependences is contained in the position of electrons b and c in Figure 9c. However, even in the general case, the z dependence will not be drastic. The poles corresponding to the pair continuum will be shifted an amount less than the level spacing, a negligible effect. The principal influence will be felt in the collective oscillations. As one goes into the metal, the bulk plasma oscillations will begin to appear. There will formally still exist two poles at the surface and bulk plasma frequency, but the residue at the surface plasmon pole rapidly decreases as the metal is entered and consequently the residue of the volume pole rapidly rises from zero at z = 0 to unity.

One final specific example, which will be the topic of section VI, should be mentioned. The problem of static dielectric screening of a point impurity in the surface region is ideally suited for the theory just developed. A glance at Figure 9b shows that the screening of an impurity of charge e at $z = 0$ in the semi-infinite electron gas is exactly the same as the screening of an impurity of charge 2e at $z = 0$ in the full electron gas, an amazingly simple but correct outlook on a potentially complicated problem when viewed from too hasty a position.

Now specific calculations using this formalism may be carried on. In the next section, the notions of impurity screening are developed, this being the simplest case of an inhomogeneous electron gas. Then in section VI, the surface dielectric formalism of this section and the impurity formalism of section V are coupled such that a surface impurity theory is produced. Finally in section VII, a many-body theory is developed in terms of the surface dielectric function, which yields surface many-body corrections to the surface potential theory of Loucks and Cutler (ref. 35).

V. IMPURITY SCREENING THEORY

Early in the lifetime of modern many-body theory, the problem of static RPA impurity screening was treated by Langer and Vosko, LV (ref. 19). In this section, a Green's function formalism, based upon the Thomas-Fermi atom theories of Baraff and Borowitz, BB (ref. 16) and DuBois and Kivelson, DK (ref. 17), is developed. It is seen that to obtain the standard accepted results, certain approximations must be made which are never discussed in the literature. The formalism established in this section is then used in the following sections to describe surface impurity screening effects.

Basically, the area of interest concerns a point positively charged impurity atom or ion immersed in an electron gas. This impurity then polarizes the gas as the free electrons move about to screen the effects of the impurity. A cloud of polarization charge is thus built up around the impurity. The present aim is to obtain an expression for the induced charge density as a function of distance from the impurity site. This is the simplest inhomogeneous electron gas problem, the inhomogeneity arising from the fact that the static impurity destroys the translational invariance. Thus the role of absolute as well as relative electron position becomes important.

The starting point is the equation of motion for the single particle Green's function, given by Eq. (8) and rewritten here:

$$\left(i \frac{\partial}{\partial t_1} + h\,(1)\right) G_1\,(1,\,1') - \int d2\, \Sigma\,(1,\,2)\, G_1\,(2,\,1') = \delta\,(1 - 1') \qquad (70)$$

where h (1) is the kinetic energy operator.

Equation (70) may be expressed as a pair of equations

$$\int K(1,\,2)\, d2\, G_1\,(2,\,1') = \delta\,(1 - 1') \qquad (71)$$

and

$$K\,(1,\,2) = \left(i \frac{\partial}{\partial t_1} + h\,(1)\right) \delta\,(1 - 2) + i \sum\,(1,\,2). \qquad (72)$$

In these equations, the mass operator Σ contains all the information about e-e and electron-impurity interactions. The next step is to Fourier transform. It is here that one sees the difficulties which arise as a result of the impurity field. If one transforms Eq. (70) with respect to relative coordinates

$$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$$

and the time interval $t_1 - t_2$ keeping the remaining

$$R = \frac{\vec{r}_1 + \vec{r}_2}{2}$$

fixed, then Eq. (71) becomes

$$\int K(1, 2)\, d2\, G_1(2, 1')\, e^{-i\, p.\vec{r}_{12}}\, e^{i\omega(t_1 - t_2)}\, d^3 r_{12}\, d(t_1 - t_2) = 1. \tag{73}$$

It is desirable to express this integral in terms of the individual Fourier transforms of K and G_1 with respect to 1 - 1'. This is a problem since K itself is position-dependent. However BB and DBK have provided a formal method for doing this by working in a mixed representation, that is, a representation in which K and G are partially momentum - and partially spatially-dependent. The mixed representation transforms of interest are defined as

$$K(\vec{R}, \vec{P}) = \int d^3 r_{12}\, dt_{12}\, K(1, 2)\, e^{-i\vec{p}.\vec{r}_{12}}\, e^{i\omega t_{12}} \tag{74}$$

and

$$G(\vec{R}, \vec{P}) = \int d^3 r_{12}\, dt_{12}\, G(1, 2)\, e^{-ip.r_{12}}\, e^{i\omega t_{12}} \tag{75}$$

The K operator can be evaluated by substitution of Eq. (72) in Eq. (74), producing:

$$\begin{aligned} K(\vec{R}, \vec{P}) = {} & \int d^3 r_{12}\, dt_{12} \left[E - h\left(\vec{R} + \tfrac{1}{2}\vec{r}_{12}\right)\right] \delta(\vec{r}_{12})\, \delta(t_{12})\, e^{-i\vec{p}.\vec{r}_{12}}\, e^{i\omega t_{12}} \\ & + i \int d^3 r_{12}\, dt_{12}\, \Sigma\left(\vec{R} + \tfrac{1}{2}\vec{r}_{12}, \vec{R} - \tfrac{1}{2}\vec{r}_{12}; t_{12}\right) e^{-i\vec{p}.\vec{r}_{12}}\, e^{i\omega t_{12}} \end{aligned} \tag{76}$$

which integrates to

$$K(\vec{R}, \vec{P}) = E - h(\vec{p}) + i \int d^3 r_{12}\, \Sigma\left(\vec{R} + \tfrac{1}{2}\vec{r}_{12}, \vec{R} - \tfrac{1}{2}\vec{r}_{12}; E\right) e^{-i\vec{p}.\vec{r}_{12}} \tag{77}$$

To go further, one must consider the structure of the mass operator. Sham and Kohn (ref. 14) have introduced a mass operator for a possibly non-uniform electron gas which splits up the inhomogeneity effects into an average local potential and a short-range, non-local potential reflecting the detailed structure of the inhomogeneous gas:

$$\begin{aligned}\Sigma\left(\vec{R}+\tfrac{1}{2}\vec{r}_{12},\ \vec{R}-\tfrac{1}{2}\vec{r}_{12};\ E\right) = {} & \phi\left(\vec{R}+\tfrac{1}{2}\vec{r}_{12}\right)\,\delta\left(\vec{r}_{12}\right) \\ & + M\left(\vec{R}+\tfrac{1}{2}\vec{r}_{12},\ \vec{R}\right. \\ & \left. -\tfrac{1}{2}\vec{r}_{12};\ E-\phi(\vec{R})\right).\end{aligned} \qquad (78)$$

In this expression, ϕ is the electrostatic potential at the average position R which an electron feels as it moves from $\vec{r}_1$ to $\vec{r}_2$. $\phi(R)$ does not depend on the details of how $\phi(\vec{R}+\vec{r})$ varies within the short interval $\vec{r}_1$ to $\vec{r}_2$. M is a short range function which tells how an electron with the shifted energy $E - \phi(\vec{R})$, the average energy in the interval $\vec{r}_1$ to $\vec{r}_2$, picks up the details of the density variation. Stated another way, it tells the chances that, if an electron is known to initially be at

$$R - \tfrac{1}{2}\vec{r}_{12},$$

it will end up at

$$\vec{R} + \tfrac{1}{2}\vec{r}_{12}.$$

It is a measure of the correlated motion of an electron through an envrionment of non-uniform density electrons. If this function were an instantaneous spatial average of two particle correlations between particles at

$$\vec{R} + \tfrac{1}{2}\vec{r}_{12}$$

and

$$\vec{R} - \tfrac{1}{2}\vec{r}_{12} \quad ,$$

then in the Hartree approximation, M would be a constant. Work will be done within this pseudo-Hartree factorization of single-particle, self-correlation effects. Essentially this approximation is equivalent to the linearizing assumptions which LV used to do a screening calculation. If the induced charge density is much smaller than the initial unperturbed density, then the inhomogeneity effects, as measured by M in Eq. (78), should be very small and the linear or pseudo-Hartree approximation thus valid.

Inserting Eq. (78) in (77) and doing the r_{12} integral with M = constant yields:

$$K(\vec{R},\vec{p}) = E - h(\vec{p}) - \phi(\vec{R}) \tag{79}$$

which sort of looks like an inverse mixed representation Green's function.

To relate K with the physically relevant Green's function G, BB have shown that there is a differential operator θ, defined below, that connects G and K (ref. 16). Their result is stated as follows:

$$\theta\left[K(\vec{R}, \vec{p}\omega), G(R, \vec{p}\omega)\right]$$

$$= \lim_{\substack{\vec{R}' \to \vec{R} \\ \vec{p}' \to \vec{p}}} \exp\left\{\frac{i\hbar}{2}\left(\nabla_{\vec{R}} \cdot \nabla_{\vec{p}'} - \nabla_{\vec{R}'} \cdot \nabla_{\vec{p}}\right)\right\} K(\vec{R},\vec{p}\omega)G(\vec{R}',\vec{p}'\omega) = 1. \tag{80}$$

As has been shown by BB and DBK, it is difficult to use the θ operator in anything beyond the zero-order term in the formal expansion of the exponential operator. It should also be pointed out that the method of gradient expansion of the charge density for doing inhomogeneous electron gas problems, introduced in a somewhat phenomenological sense by Kohn et al (refs. 29-31), would have the preceding line of reasoning as its formal justification. Also worthy of note is the fact that treating inhomogeneity corrections in the manner of gradient expansions will not produce Friedel oscillations in the induced electron density which screens the field producing the density gradient. This is why the BB and BKD corrections to the Thomas-Fermi atom cannot, even in a formal sense, reproduce shell structure of the atom. Kohn and Sham (ref. 30) have made an effort to get around this problem by using WKB wavefunctions which necessitate a classical turning point and thus partial reflection at points in the inhomogeneous medium. Consequently interferences are set up in the inhomogeneous gas which is screening the field producing the inhomogeneity. The direct result of this phenomenon is the presence of Friedel oscillations.

Returning to Eq. (80), one notes that to zero order in homogeneity corrections, G is related to K in a simple manner:

$$G(\vec{R},\vec{p}\,\omega) = \frac{1}{K(\vec{R},\vec{p}\omega)} \quad .$$

Relative to Eq. (79) this appears to be almost the standard result if one were not in the mixed representation and if account had not been taken of the "extraneous coordinate" present in a non-uniform system. Work will always be done in the zero-order in the realization that this linearizing approximation can, in principle, be corrected by considering higher order terms in the θ operator. However, it is believed that θ represents an asymptotic expansion which unphysically diverges in higher than zero-order terms.

To extract physical quantities such as electron number densities, the following relations are needed. In analogy with Eq. (13), the mixed representation charge density is given by

$$n(\vec{R},\vec{p}) = \frac{1}{2\pi i} \oint d\omega\, G(R,\vec{p}\omega) \quad . \tag{81}$$

True physical charge density in coordinate space is given by

$$n(\vec{R}) = \frac{1}{(2\pi)^3} \int_{p<p_F} d^3p\, n(\vec{R},\vec{p}) \tag{82}$$

so it is seen that $n(\vec{R},\vec{p})$ is similar to a charge density in momentum space. If one uses a formal identity to write the Green's function as

$$G(\vec{R}, p\omega) = \frac{1}{\omega - h(\vec{p})} + \frac{1}{\omega - h(\vec{p})}\, \phi(\vec{R})\, \frac{1}{\omega - h(\vec{p}) - \phi(\vec{R})} \quad , \tag{83}$$

then one can see that the first term on the right-hand side gives the initial charge density when put in Eqs. (81) and (82) whereas the second term gives the screening charge density:

$$\begin{aligned} \delta n(\vec{R}) &= \frac{1}{2\pi i\,(2\pi)^3} \oint d\omega \int_{p<p_F} d^3p'\, \frac{1}{\omega - h(\vec{p})}\, \phi(\vec{R})\, \frac{1}{\omega - h(\vec{p}) - \phi(\vec{R})} \\ &= \frac{1}{2\pi i\,(2\pi)^6} \oint d\omega \int_{p<p_F} d^3p \int_{p'>p_F} d^3p'\, \frac{1}{\omega - h(\vec{p})}\, \phi(\vec{R})\, \frac{\delta(\vec{p} - \vec{p}' - \vec{q})}{\omega - h(\vec{p}') - \phi(\vec{R})} \end{aligned} \tag{84}$$

where $\vec{q}$ is the momentum transfer in the scattering event described below. The screening process may be envisioned in the following manner. An incident electron of momentum $\vec{p}$ comes upon the impurity and scatters off of it transferring momentum $\vec{q}$. The outgoing momentum is $\vec{p}'$. The electron can scatter directly off the impurity, or through intermediate state many-body processes involving excitation of electron-hole pairs. Within the RPA, the lowest order impurity scattering processes are shown in Figure 10. The sum of all possible RPA processes is equivalent to a single scattering from a screened potential. Thus one can write:

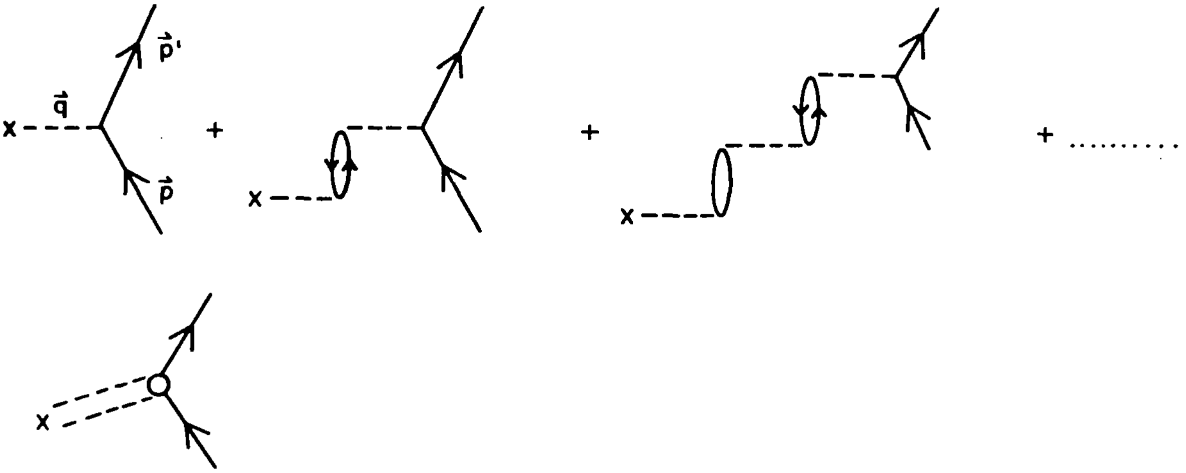

Figure 10.--Representative diagrams included in static RPA screening of an impurity.

$$\phi(\vec{R}) = \int \frac{d^3q}{(2\pi)^3} \left(\frac{4\pi e^2}{q^2} \right) \frac{1}{\epsilon(q,0)} \; e^{i\vec{q}\cdot\vec{R}} \quad . \tag{85}$$

Scatterings which involve more than a single momentum transfer to or from the source, such as those shown in Figure 11, are not considered, as is the customary procedure (ref. 57). If one approximates the outgoing propagator as a free-particle Green's function and puts Eq. (85) into Eq. (84), then

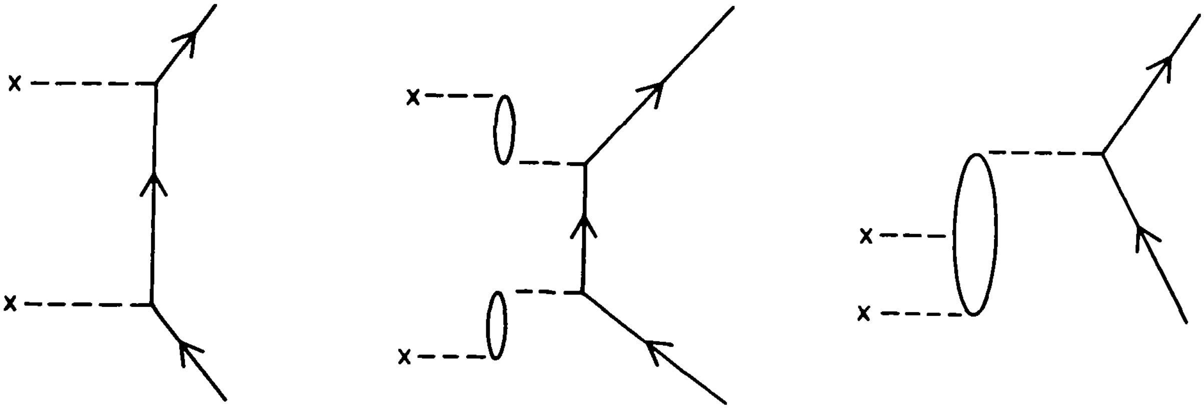

Figure 11.--Representative diagrams not included in static RPA screening of an impurity.

$$\delta n(\vec{R}) = \frac{1}{2\pi i(2\pi)^9} \oint d\omega \, d^3p \, d^3p' \, d^3q \frac{1}{\omega - \frac{p^2}{2}} \frac{v(q)}{\epsilon(q,0)} \frac{\delta(\vec{p} - \vec{p}' - \vec{q})}{\omega - \frac{p'^2}{2}} e^{i\vec{q}\cdot\vec{R}} \tag{86}$$

with the Pauli principle restrictions implied. Doing the p' and ω integrations results in

$$\delta n(\vec{R}) = \frac{1}{(2\pi)^6} \int\limits_{\substack{p<p_F \\ |\vec{p}+\vec{q}|>p_F}} d^3q \, d^3p \, \frac{v(q)}{\epsilon(q,0)} \, e^{i\vec{q}\cdot\vec{R}} \frac{1}{\frac{\vec{p}\cdot\vec{q}}{m} + \frac{q^2}{2m}} \quad . \tag{87}$$

The p integration is done according to standard procedure (ref. 6) and yields an integrand which is simply related to ϵ. Hence:

$$\delta n(\vec{R}) = \frac{p_F^3}{(2\pi)^3} \int_0^\infty d^3q \left(\frac{1}{\epsilon(q,0)} - 1 \right) e^{i\vec{q}\cdot R} \tag{88}$$

where now q and R are given in units of Fermi momentum. Equation (88) is further simplified to a one-dimensional integral by performing the straightforward angular integrations. Thus:

$$\delta n(R) = \frac{p_F^3}{2\pi^2} \int_0^\infty dq \, \frac{q \sin qR}{R} \left(\frac{1}{\epsilon(q,0)} - 1 \right) \tag{89}$$

which is the result first obtained by Langer and Vosko (ref. 19). The charge density is given in units of

$$p_F^3 \quad .$$

Numerical examples appear in section VI, when bulk impurity screening is compared with surface impurity screening.

The derivation of simple RPA screening has been covered for two reasons. The first was to see what really was hidden in the standard derivations. One thing which is never cited is the assumption equivalent to using the zero order θ operator. If one is interested, the formal machinery to compute higher order corrections exists. Another interesting observation is the equivalence of the pseudo-Hartree approximation to the non-local part of the mass operator and the assumptions implicit in a linear screening theory.

The second reason for going through a Green's function screening theory in which expansion is made in terms of screened rather than bare Coulomb potentials is that the present formalism is more general than the LV self-consistent field approach. A wider class of problems can be treated within the context of a single formalism developed here. In the next section the case of a surface impurity will be treated.

VI. IMPURITY SCREENING IN THE SURFACE REGION OF AN ELECTRON GAS

Generalities

Since the theoretical ideas necessary for considering two different sorts of inhomogeneity problems, namely, surfaces and impurities, have been developed thus far, it seems natural to attempt a coupling between the two, that is, impurities in the surface region.

This problem should be of great interest for various reasons. First, it is of intrinsic interest in the general theory of inhomogeneous electron gases. A more practical reason is that this model system is precisely a model for ionic adsorption on metal surfaces. The role of ion screening in the surface region has only recently been gaining recognition (refs. 40-44), although a thorough theory has yet to be produced. This topic is further developed in this section. Previous adsorption theories have treated the metal or electron gas in a very phenomenological sense; that is, it has been assumed that the ion-metal interaction would have basically the same functional form as a classical image force, even at short distances where field penetration and bulk screening occur (ref. 58). This section will show why these theories have been so successful in spite of their lack of rigor in treating the metal or electron gas.

Theoretical Considerations

The idea to be contemplated is this. A point impurity of charge Ze is placed on the surface of a semi-infinite electron gas. As was pointed out in Section IV (Dielectric Function), the response of the semi-infinite gas to an impurity of charge Ze placed at $z = 0$ is exactly the same as the response of the infinite sine wave electron gas to an impurity of charge 2Ze at $z = 0$. The dielectric function for the infinite sine wave gas is known, so such things as screening charge densities could be calculated.

For various computational reasons, one is better off working in the coordinate representation initially since it is not yet clear how momentum conservation holds in this coupled inhomogeneity problem. The starting point is the configuration space analog of the Dyson equation, Eq. (10), for the exact, interacting electron Green's function in the presence of an impurity.

$$G(\vec{r},\vec{r}\,';t) = G_o(\vec{r},\vec{r}\,';t) + \int d^3\vec{r}\,''\, G_o(\vec{r},\vec{r}\,'';t)\, V(\vec{r}\,'')\, G(\vec{r}\,'',\vec{r}\,';t) \,. \quad (90)$$

As mentioned in Section V, when computing charge densities, the first term on the right-hand side gives the unperturbed charge density whereas the second term gives the screening charge. If, as in the case of the bulk impurity, one considers screening to occur within the context of a scattering event, and if one considers processes involving only a single momentum transfer from the bare impurity, then G can be replaced by G_o within the integral of Eq. (90). The screening charge density is thus determined through knowledge of

$$\lim_{\substack{\vec{r}\to\vec{r}\,'\\ t\to 0}} \delta G(\vec{r},\vec{r}\,';t) = \int d^3r'' \; G_o(\vec{r},\vec{r}\,'';t)\; V(\vec{r}\,'')\; G_o(\vec{r}\,'',\vec{r}\,';t) \; . \tag{91}$$

The screened impurity potential is given by

$$V(\vec{r}\,'') = \int \frac{d^3q}{(2\pi)^3}\, 2\left(\frac{4\pi e^2}{q^2}\right) \frac{1}{\epsilon_s(\vec{q},0)}\, e^{i\vec{q}\cdot\vec{r}\,''} \tag{92}$$

where the factor of 2 comes from the image method and $\epsilon_s(\vec{q},0)$ is the sine wave dielectric function, Eq. (66), whose z dependence is discussed later in this section. For completeness, the formula for $\epsilon_s(\vec{q},0)$ when the integrals of Eq. (60) are carried out is cited:

$$\epsilon_s(\vec{q},0) = 1 + \frac{p_F}{a_o q^2}\left[1 + \frac{1}{p_F q}\left(p_F^2 - \frac{q^2}{4}\right) \ln\left|\frac{q+2p_F}{q-2p_F}\right|\right](1+\delta_{q_z,0}) \; . \tag{93}$$

In the above equation, a_o = the Bohr radius.

The non-interacting Green's function is written in an eigenfunction expansion as

$$G_o(\vec{r},\vec{r}\,'') = \sum_{\vec{k}} \frac{|\psi_{\vec{k}}\rangle\langle\psi_{\vec{k}}|}{E - E(\vec{k})} \tag{94}$$

Using the eigenfunctions given by Eq. (62), Eq. (94) becomes

$$G_o(\vec{r},\vec{r}\,'') = 2 \sum_{\vec{k}} \frac{\sin k_z z \, \sin k_z z' \, e^{i\vec{k}_t \cdot (\vec{r}_t - \vec{r}_t\,')}}{E - E(k)} \tag{95}$$

If one writes the sine wave product in $G_o(\vec{r}\,'',\vec{r}\,')$ as a sum of products of exponentials and combines Eqs. (91), (92), and (95), the result is

$$\delta G(\vec{r},\vec{r}) = \frac{2}{(2\pi)^9} \int d^3q\, d^3k\, d^3k' \left\{ \frac{v(q)}{\epsilon_s(\vec{q},0)} e^{i(\vec{k}_t - \vec{k}_t{}')\cdot\vec{r}_t} \right.$$

$$\times \sin k_z z \sin k_z' z \int d^3r'\, e^{i(\vec{k}_t' + \vec{q}_t - \vec{k}_t)\cdot\vec{r}_t{}'}\, e^{iq_z z'}$$

$$\times \left(e^{i(k_z + k_z')z'} - e^{i(k_z - k_z')z'} - e^{-i(k_z - k_z')z'} \right.$$

$$\left.\left. + e^{-i(k_z + k_z')z'} \right) \times \frac{1}{E - E(k)} \frac{1}{E - E(k')} \right\} \quad . \qquad (96)$$

Owing to the perfect symmetry or asymmetry of all the functions of k_z and k_z' in the integrand, it can be shown that appropriate variable transformations of the form $k_z \rightarrow -k_z$ in each of the four z' exponentials can be made. These simplify things greatly. When this straightforward procedure is followed, all four r' integrals take exactly the same form and give a result

$$\int d^3r' f(\vec{r}') \rightarrow 4\ \delta(\vec{k}' + \vec{q} - \vec{k})$$

which guarantees momentum conservation at the vertex. Thus, Eq. (96) reduces to

$$\delta G(\vec{r},\vec{r}) = \frac{4}{(2\pi)^9} \int d^3q\, d^3k\, d^3k'\, \frac{v(q)}{\epsilon_s(\vec{q},0)} e^{i(\vec{k}_t - \vec{k}_t{}')\cdot\vec{r}_t} \qquad (97)$$

$$\times \sin k_z z \sin k_z' z\ \delta(\vec{k}' + \vec{q} - \vec{k}) \frac{1}{E - E(k)} \frac{1}{E - E(k')} \quad .$$

The product of sines is written as

$$\sin k_z z \sin k_z' z = \frac{1}{4} \left(e^{i(k_z - k_z')z} + e^{-i(k_z - k_z')z} \right. \qquad (98)$$

$$\left. - e^{i(k_z + k_z')z} - e^{-i(k_z + k_z')z} \right).$$

In the physical system considered, an inversion symmetry about the z = 0 plane exists. Thus the theory is invariant with respect to the transformation

$z \rightarrow -z$, provided one keeps only the symmetric part of any oscillatory exponential in the end results. Thus the sine function can be written in an equivalent form:

$$\sin k_z z \, \sin k_z' z = \frac{1}{2}\left(e^{i(k_z - k_z')\, z} - e^{-i(k_z + k_z')\, z}\right) . \tag{99}$$

At this point, since an interest in charge densities given by Eq. (13) exists, the energy integral is performed. This step, together with Eq. (99) put into Eq. (97), gives:

$$\delta n(\vec{r}) = \frac{2}{(2\pi)^9} \int d^3q \, d^3k \, d^3k' \left\{ \frac{v(q)}{\epsilon_s(\vec{q}, o)} \; e^{i(\vec{k} - \vec{k}')\cdot \vec{r}} \right. \\ \left. \times \left(1 - e^{-2ik_z z}\right) \delta(\vec{k}' - \vec{k} + \vec{q}) \frac{1}{E(k) - E(k')} \right\} . \tag{100}$$

Performing the k' integration to use up the delta function yields:

$$\delta n(\vec{r}) = \frac{2}{(2\pi)^6} \int d^3q \frac{v(q)}{\epsilon_s(\vec{q}, o)} \; e^{i\vec{q}\cdot\vec{r}} \int\limits_{\substack{k < p_F \\ |\vec{k} - \vec{q}| \, > p_F}} \frac{d^3k}{\vec{k}\cdot\vec{q} - q^2/2} \\ - \frac{2}{(2\pi)^6} \int d^3q \frac{v(q)}{\epsilon_s(\vec{q}, o)} \; e^{i\vec{q}\cdot\vec{r}} \int\limits_{\substack{k < p_F \\ |\vec{k} - \vec{q}| \;\; p_F}} \frac{d^3k \; e^{-2ik_z z}}{\vec{k}\cdot\vec{q} - q^2/2} . \tag{101}$$

Considerable insight into the problem can be gained by contemplating the structure of Eq. (101), which is an exact result so far. The first term is exactly the result of Langer and Vosko except for the fact that the non-spherically symmetric dielectric function appropriate to the sine wave electrons is being used. This term will present no computational problem. The second term has an extra oscillatory term in it as a result of pure surface effects on the incident and scattered electrons. One might hope that some physical simplifications will allow evaluation of this expression in the interesting asymptotic regions of z small and large. Note that the second integral has virtually no hope of being exactly evaluated since the standard methods of treating the Pauli principle restrictions can be meaningfully invoked only for spherically symmetric k integrals. However, one can still proceed with his exact treatment, even if only in a formal sense. The idea is to remain exact for as long as possible before contaminating the theory with approximations needed to obtain numbers.

There exists a form of the mean value theorem which now is of use (ref. 59). Theorem: If there is an integral of the form

$$I = \int_a^b f(x)\, g(x)\, dx,$$

with f(x) and g(x) well behaved, then it can be proved that there exists a ξ with $a \leq \xi \leq b$, such that

$$\int_a^b f(x)\, g(x)\, dx = f(\xi) \int_a^b g(x)\, dx.$$

For this particular case, one takes $f(x) = e^{-2ik_z z}$. Thus Eq. (101) can be written

$$\delta n(\vec{r}) = \frac{2}{(2\pi)^6} \int d^3q \frac{v(q)}{\epsilon_s(\vec{q}, o)} e^{i\vec{q}\cdot\vec{r}} (1 - e^{-2i\xi z}) \int \frac{d^3k}{\vec{q}\cdot\vec{k} - q^2/2} \quad (102)$$

The k integration, as in Eq. (87), is simply related to the spherically symmetric RPA dielectric function by $v(q)\, I\,(q,k) = \epsilon(q,0) - 1$. Performing this integral yields:

$$\delta n(\vec{r}) = \frac{2}{(2\pi)^3} \int d^3q \frac{1}{\epsilon_s(\vec{q})} e^{i\vec{q}\cdot\vec{r}} (\epsilon(q) - 1)(1 - e^{-2i\xi z}), \quad (103)$$

which is still an exact result.

Now the more difficult aspects of the theory must be faced. Two problems are present. First, there is no simple way of determining ξ and, second, ξ depends parametrically on both q and z. Fortunately the physics of the situation can help some. In reference to Eq. (101), it was mentioned that the oscillatory term of the second integral was a result of the surface boundary conditions. This effect is washed out within the order of a Fermi wavelength. Mathematically this can be demonstrated easily. For large z, the exponential oscillates rapidly in momentum space, and thus the integral on $k_z \to 0$ by virtue of the Riemann-Lebesque lemma:

Lemma:

$$\text{If} \int f(k)\, dk < \infty ,$$

then

$$\lim_{z \to \text{large}} \int f(k)\, e^{izk}\, dk \to 0.$$

Thus the exact long-range screening charge density is given by

$$\delta n_{l.r.}(\vec{r}) = \frac{2}{(2\pi)^3} \int d^3q \frac{1}{\epsilon_s(\vec{q})} (\epsilon(q) - 1)\, e^{i\vec{q} \cdot \vec{r}} . \tag{104}$$

It is fortunate that the long-range part can be obtained in an asymptotically exact form for this enables us to determine the effect of the surface on impurity Friedel oscillations with no approximations.

The short-range behavior is another problem. In any approximation scheme, the most important condition to be maintained is that at the surface z = o, the screening charge density is zero, for in a linear dielectric response model there certainly can be no induced charge where originally there was no charge. Again, in reference to Eq. (101), one might expect that in the near region things would not be too dependent on the accuracy of ξ; that is, for z small, the exponential varies slowly relative to other factors in the integrand. Thus an average value of k_z within the integration range

$$(0 < k_z < p_F),$$

say,

$$\frac{1}{\sqrt{2}}\, p_F$$

is arbitrarily assigned to ξ. This is a good approximation as $z \to 0$ and hopefully is an adequate one for intermediate ranges where $z = \theta(p_F)$. With this, the first approximation, and the replacement of the exponent by the symmetric cosine as discussed previously, Eq. (103) in the near region, takes the form:

$$\delta n_{s.r}(\vec{r}) = \frac{2}{(2\pi)^3}(1 - \cos\left(\sqrt{2}p_F z\right) \int d^3q \frac{1}{\epsilon_s(\vec{q})} (\epsilon(q) - 1)\, e^{i\vec{q}\cdot\vec{r}} \qquad (104)$$

or with an elementary trigonometric identity:

$$\delta n_{s.r}(\vec{r}) = \frac{2}{(2\pi)^3} \sin^2\left(\frac{p_F z}{\sqrt{2}}\right) \int d^3q \frac{1}{\epsilon_s(\vec{q})} (\epsilon(q) - 1)\, e^{i\vec{q}\cdot\vec{r}} . \qquad (105)$$

Equation (105) is easily interpreted. The first thing to notice is that the surface boundary condition at $z = 0$ is satisfied. Second, one can see through the structure of this result. The terms within the integral are just the same terms as in the long-range part (Eq. (104)). These terms reflect the many-body impurity Friedel oscillations modified by the surface dielectric function. However, in the surface region, z = small, surface boundary condition density oscillations must play a role. Hence, the presence of the multiplicative "surface sine" term is expected. The resulting charge density configuration has the form of sine wave screened impurity Friedel oscillations superposed on surface density oscillations, a not unreasonable result and incidentally the sort of result Kohn and Sham (ref. 30) contemplated in problems of impurity screening in inhomogeneous electron gases.

One word of explanation as to the nature and motivation for the present method of approximation is in order. Although it may be true that the asymptotic results could have been surmised without going through the formal development since Eq. (101), it is felt that the formalism has been useful for various reasons. Equation (103) is an exact result. Although the author has not been able to conceive of a truly convincing general approximation for the quantity ξ, he feels that there probably is a reasonable procedure such as a modified stationary phase or steepest descent method by which ξ could be obtained. If this procedure could be discovered, then the present theory up to Eq. (103), which is the end point of the theory, would be immediately applicable with no modifications. Another possible way of determining an approximate value of ξ would be to convince one's self that ξ is not very q-dependent, but is only a function of p_F. Then one could take the volume integral of $\delta n(\vec{r})$, set it equal to 1, and see what value of ξ is needed to guarantee self-consistency. This is left as an excercise for the future.

The non-isotropic surface dielectric function will now be treated. From Eq. (66), it is seen that $\epsilon_s(\vec{q})$ can be written as

$$\epsilon_s(\vec{q}) = \frac{1}{2}\epsilon(q) + \frac{1}{2}\epsilon(q)\,\delta_{q_z,0} \qquad (106)$$

However, it must be remembered that this is the dielectric function at $z = 0$ only. In effect, the above should really be written as

$$\epsilon_s(\vec{q}) = \epsilon_s(\vec{q};\ z = 0).$$

As z increases, the dielectric function must approach the volume limit,

$$\lim_{z \to \text{large}} \epsilon_s(\vec{q};z) = \epsilon(q).$$

Folowing lines similar to Stern (ref. 42), one calls upon an ansatz for dealing with the z dependence by allowing the surface effects to decay exponentially into the metal while the volume effects increase in the same manner. With the ansatz, Eq. (106) becomes:

$$\epsilon_s(\vec{q};z) = \frac{1}{2}\epsilon(q) + \frac{1}{2}\epsilon(q)\,(1 - e^{-qz}) + \frac{1}{2}\epsilon(q)\,e^{-qz}\,\delta_{q_z,0} \tag{107}$$

which upon rearrangement is

$$\epsilon_s(\vec{q};z) = \epsilon(q) + \frac{1}{2}\epsilon(q)\,e^{-qz}\,(\delta_{q_z,\,0} - 1). \tag{108}$$

Equation (108) clearly satisfies both the small- and large-z-limiting conditions.

The inverse dielectric function when taken inside an integral on q, that of Eq. (103), is of concern. Using the operator identity

$$\frac{1}{a+b} = \frac{1}{a} - \frac{1}{a}\,b\,\frac{1}{a+b}$$

for $\epsilon_s^{-1}(\vec{q};z)$ in Eq. (103) with $a = \epsilon(q)$ and $b = \frac{1}{2}\epsilon(q)e^{-qz}\,(\delta_{q_z,0} - 1)$ yields:

$$\begin{aligned} \frac{1}{\epsilon_s(\vec{q};z)} &= \frac{1}{\epsilon(q)} - \frac{e^{-qz}\,\delta_{q_z,0}}{\epsilon(q)}\,\frac{1}{2 + e^{-qz}(\delta_{q_z,0} - 1)} \\ &\quad + \frac{e^{-qz}}{\epsilon(q)}\,\frac{1}{2 + e^{-qz}(\delta_{q_z,0} - 1)} \end{aligned} \tag{109}$$

which can formally be written as

$$\frac{1}{\epsilon_s(\vec{q};z)} = \frac{1}{\epsilon(q)} + \frac{e^{-qz}}{\epsilon(q)}\left(\frac{1}{2 - e^{-qz}}\right)\Bigg|_{q_z \neq 0.} \tag{110}$$

Equation (110) is a valid representation of Eq. (109), only when $\epsilon_s^{-1}(\vec{q};z)$ appears within an integral, as it does in the present case. With arguments as given in section IV, it is seen that the $q_z \neq 0$ restriction on the second term provides no difficulties since the integrand is well behaved for $q_z = 0$. Consequently, one obtains the simple form for the inverse dielectric function:

$$\frac{1}{\epsilon_s(\vec{q};z)} = \frac{1}{\epsilon(q)}\left(\frac{2}{2 - e^{-qz}}\right). \tag{111}$$

With Eq. (111), the expression for the surface impurity screening charge density (Eq. (103)) becomes:

$$\delta n(\vec{r}) = 2\int\frac{d^3q}{(2\pi)^3}\left(\frac{1}{\epsilon(q)} - 1\right)\left(\frac{2}{2 - e^{-qz}}\right)e^{i\vec{q}\cdot\vec{r}}\left(1 - e^{-2i\xi z}\right). \tag{112}$$

If all length and momentum variables are now written in units of Fermi momentum, and the angular integrals are performed, then the asymptotic limits of the screening charge density become:

$$\delta n_{s.r.}(\vec{r}) = \frac{p_F^3}{\pi^2}\sin^2\left(\frac{z}{\sqrt{2}}\right)\int_0^\infty dq\left(\frac{1}{\epsilon(q)} - 1\right)q\,\frac{\sin qr}{r}\left(\frac{2}{2 - e^{-qz}}\right) \tag{113}$$

and

$$\delta n_{l.r.}(\vec{r}) = \frac{p_F^3}{\pi^2}\int_0^\infty dq\left(\frac{1}{\epsilon(q)} - 1\right)q\,\frac{\sin qr}{r}\left(\frac{2}{2 - e^{-qz}}\right). \tag{114}$$

These terms represent the Langer and Vosko result with two modifications. The multiplicative sine factor merely says that surface density oscillations must be superimposed on the impurity quantum density oscillations. The z dependent term within the integrand is also a departure from Langer and Vosko's result. This is the term which couples what happens to the spherically symmetric response as a result of the constraints in the z direction.

In the next section, the numerical evaluation of these integrals is presented, the results discussed, and experimental suggestions made.

Numerical Results and Discussion

Equations (113) and (114) have been evaluated numerically for several different electron gas densities along various radial lines emanating from the impurity. The results are displayed graphically in Figures 12 through 15 for values of $r_s = 1.5$, 2, 3, and 4.

Much can be said about these results of screening charge as a function of vector position from the impurity. One should first observe that these results are quite understandable. At $R = 0$, for any θ, the initial charge density is zero because of the infinite barrier. Thus, in the linearized model, there will be no polarization charge where initially there was no charge. As the weakly screened field penetrates into the gas, polarization charge builds up as the unperturbed electron density increases. Further into the electron gas past the point where the maximum screening charge density is seen, the screening becomes more effective and the polarization charge density decreases. Long-range Friedel oscillations, plotted on an expanded scale in the insets, are also present, although their structure is more complicated than volume impurity oscillations. This results from the fact that a phenomenon involving interferences between two diffraction patterns of different symmetries, that of the surface and that of the impurity, is being considered.

For a quantitative comparison with volume effects, the results obtained by Langer and Vosko for an impurity in a homogeneous electron gas of density $r_s = 3$ are also plotted in Figure 14. It can be seen that the surface impurity screening is of a much longer range than the volume impurity screening, as it must be. In the surface problem, the low-density region cannot provide enough electronic charge to do much screening. Hence the screening charge is less than in the volume case. To make up for this deficiency, as the relatively unscreened surface impurity field penetrates the metal, it must induce a larger long-range polarization charge than in the volume case, so that the impurity may be totally screened at large distances. Consequently the surface impurity charge density curves cross over the volume curves.

As was mentioned, the structure of the oscillatory curves is more complicated for the surface impurity, at least in the intermediate region $4 \lesssim Rp_F \lesssim 10$, where chaotic things are happening. As this chaos settles, the longer range Friedel oscillations, say for $Rp_F \gtrsim 10$, become well behaved in the sense of volume oscillations. Still there are significantly

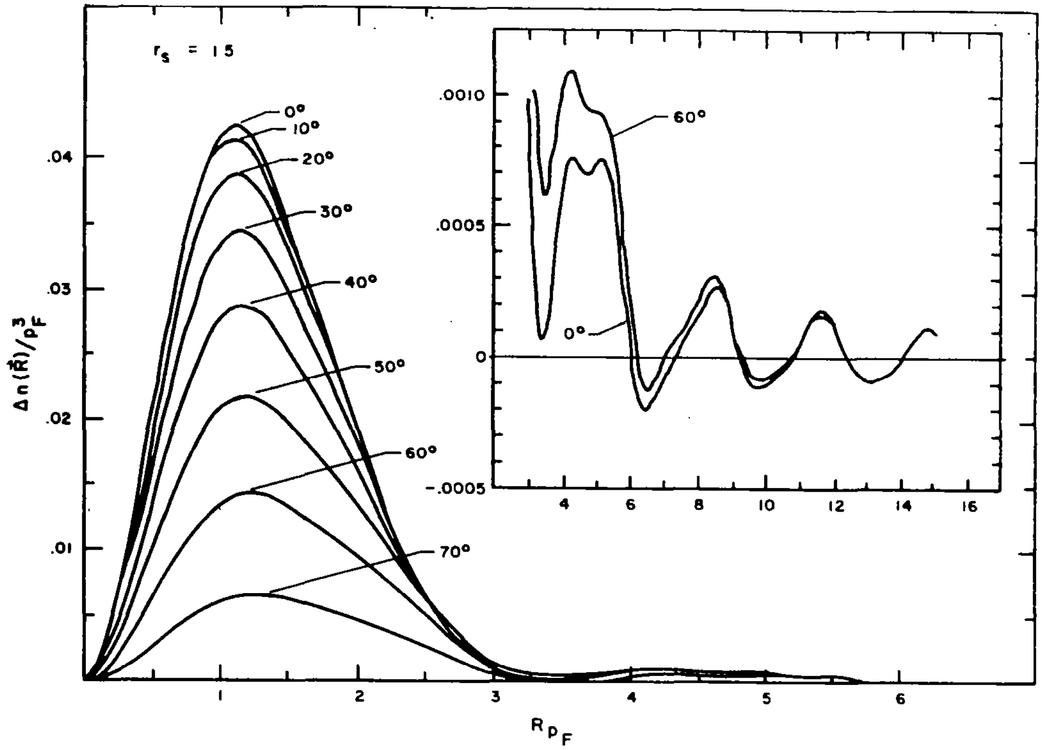

Figure 12 - Surface impurity screening charge density, r_s=1.5.

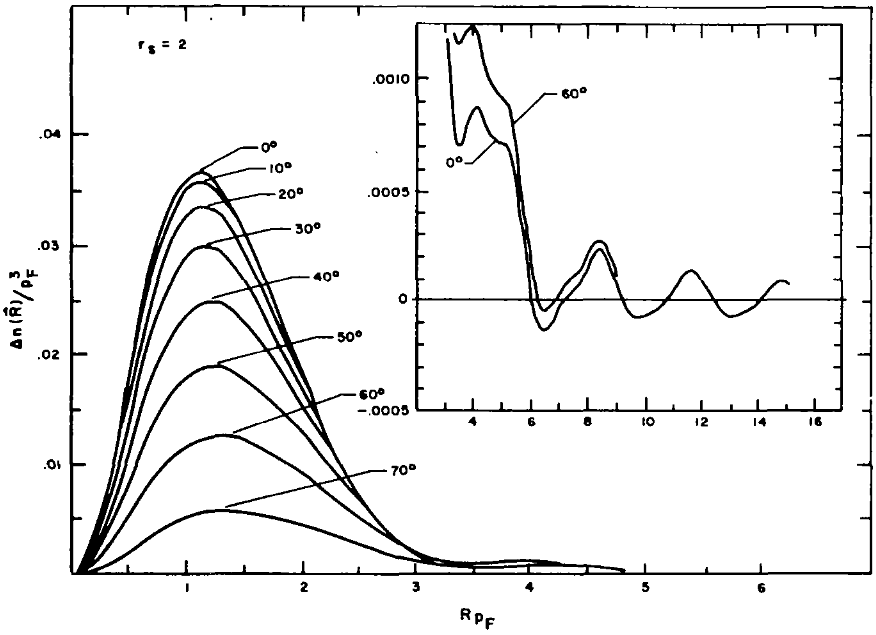

Figure 13 - Surface impurity screening charge density, r_s=2.0.

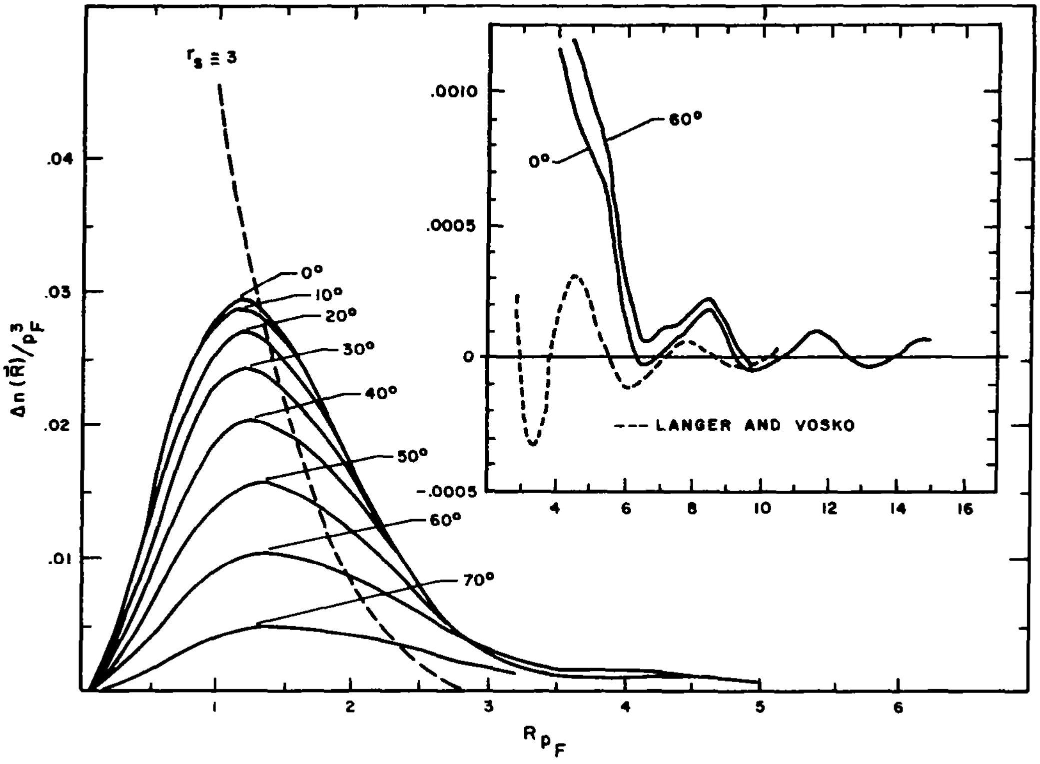

Figure 14 - Surface impurity screening charge density, $r_s=3.0$.

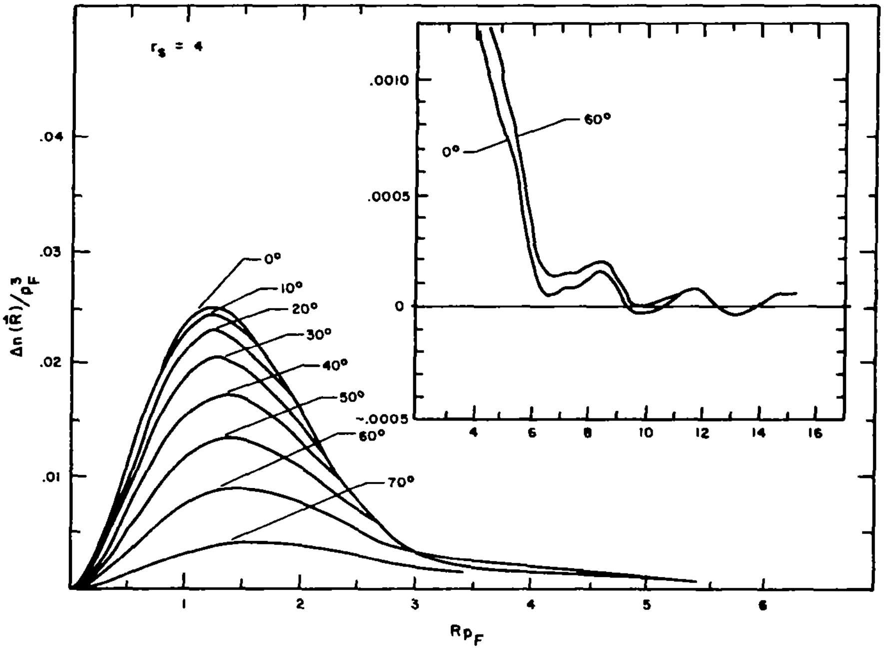

Figure 15 - Surface impurity screening charge density, $r_s=4.0$.

longer range effects for the surface impurity than the volume impurity as suggested in the preliminary theory of surface impurities (ref. 43). This observation could be of experimental interest for a number of reasons.

First, standard magnetic resonance and Knight shift experiments are measuring effects occurring within the skin depth of metals. Since the conduction band electron polarization around ion cores or impurities in the outer skin is different than in the bulk, measurable events, such as impurity-impurity interactions, may be different than those inferred from standard theories using the customary long-range polarization charge density

$$\delta n \simeq (\cos 2p_F R \;/\; R^3.$$

Second, the existence of polarization properties different on the surface than in the bulk should offer encouragement for devising new resonance-type surface experiments to replace the rather dreary assemblage of presently existing experiments. It should also be noted that in the case of an adsorbed partial monolayer, a distribution of surface impurities, there may be significant impurity-impurity interactions caused by the intermediary of the polarizable electron gas. Put another way, the long-range surface Friedel oscillations, for large angles, of one impurity may interact with the oscillations from a nearby impurity, thus giving rise to an effective interaction which could not be inferred without considering the many-body screening effects. It can be seen that the problem is much more subtle than would be guessed from the various oversimplified theories which exist.

With regard to the numerical results, a few more comments are in order. As anticipated, it can be seen that the screening charge increases more slowly as the transverse component of the radial line increases, since the unperturbed electron density doing the screening increases more slowly.

The following structure can also be observed in all the curves. A maximum in the screening charge density is seen at $Rp_F \sim 1.1$ and a second rise in charge density at $Rp_F \sim 5\text{-}6$ corresponding to the first Friedel oscillation. However, the amount of screening charge in the first lobe decreases as the electron gas density decreases. For instance, if $r_s = 1.5$, then

$$\Delta n(R p_F = 1.1) = 0.0425 \text{ for } \theta = 0$$

whereas if

$$r_s = 4, \; \Delta n\,(Rp_F = 1.1) = 0.025.$$

This means that in the lower density gas, more of the screening, and thus induced charge, appears further into the metal. For this reason, the classical image charge is not applicable for honestly describing surface impurity effects because the screening charge exists in the metal and not on the surface. This, of course, is a manifestation of the fact that the electron gas or real metal is not a perfect conductor as must be assumed if the concept of an image charge is to contain any real meaning. In the case of a perfect conductor, $r_s = 0$. The total screening charge will appear within the first lobe with a maximum at $Rp_F \sim 1.1$. But since

$$p_F = \frac{3.64}{r_s}, \lim_{r_s \to 0} R \sim r_s \to 0.$$

Hence the screening charge appears either at the impurity site with $R = 0$ or in the $\theta = 90$-deg curve, in either case at $z = 0$. This is then a true surface polarization charge which is a consequence of the necessary conditions for having a perfect conductor. As the density is decreased to real metal densities, then screening effects and their consequences must be considered from the volume polarization point of view. The fortuitous success people have had using the image force and surface polarization concepts in absolutely no way says that the approach is correct.

The present results may be applied to existing theories of ionic adsorption in the following manner. Essentially one is interested in the dipole moment formed by the point ion core or impurity and the resulting polarization charge since the change in electron work function is given by

$$\Delta \phi_e = 2\pi \sigma M$$

where σ is the density of dipoles and M is the dipole strength. As stated in Eq. 23-1/2 of the author's atom-metal interaction theory (ref. 8), the dipole strength is $M_o = q(s + \epsilon(s))$ where q = the ion charge, s = the ion-surface separation which could be taken to be the ionic radius, and "$\epsilon(s)$ is some effective location for the polarization charge of the positive ion core and has a numerical value greater than s for small s." The assignment of the value of the ionic radius for s is dubious at best. However, since this seems to be a convenient way of assigning parameters to the size of the adsorbate, the idea is introduced.

A value for $\epsilon(s)$ can be obtained from the calculated screening charge densities as follows. Approximate calculations of the dipole component of the polarization charge distribution

$$M = q\langle z\rangle = \int z\, \delta n(\vec{R})\, R^2 dR\, d\Omega \qquad (115)$$

have shown that a reasonable representation of the calculation is given by

$$\langle z\rangle \approx \frac{3.5}{p_F} = .96 r_s \text{ Å}. \qquad (116)$$

Thus it is apparent that the strength of the effective dipole moment of an ion on a real metal surface is quite dependent upon the substrate properties, the free electron density. This observation has not previously been subjected to quantitative analysis, and, with only a few exceptions, has not even been qualitatively recognized. To apply these ideas in real calculations, one must obtain the density of s- and p-like conduction band electrons, those electrons which participate in the screening. If one is dealing with noble or transition metals in which there is great hybridization between the free electron-like s and p bands and the tight-binding d bands, one must not include the electron densities coming from the d bands since the d electrons do not contribute much to the true screening charge density.

In a typical system of experimental interest, such as cesium on tungsten, sample parameters for theoretical calculations might be

$$s = r_i = 1.3\text{Å}$$

and

$$2 < r_s < 3.$$

With this choice of fundamental atomic and metallic parameters, the dipole length would be:

$$\frac{M_o}{q} = (r_i + .96\ r_s) \simeq 4\ \text{Å}. \tag{117}$$

This is in accord with work function data. The point to be made here is that, in the calculations of reference 58, it had to be assumed that the dipole length was at least 4 Å or the atom-metal separation at least 2 Å in order that meaningful results might be obtained. This separation, however, is quite a bit greater than 1.3 Å which must be used in an image force picture. Now it can be seen why the 4-Å dipole length assumed is the correct value and not the 2.5-Å value required in a classical image force model. The general rule is this: If the ion-metal separation becomes as small as a Fermi wavelength, then the average position of the screening charge will be deeper into the metal than the ion-metal separation. In this case, perfect conductor image forces have little quantitative significance. With the simple approximate relation given by Eq. (116), it is imagined that more realistic data correlation with relevant properties of both the ion and metal systems will now be possible.

One final point to be made is concerned with the general trend of work function changes with s and p electron densities. From Eq. (116), it would appear that the work function change would be greatest for an ion adsorbed on a metal with the lowest electron density (r_s largest). However, another competing trend must be considered. In general, the bare work function of a metal decreases with decreasing electron density. Thus, the position of the shifted and broadened atomic level will overlap more of the occupied portion of the conduction band. Consequently, the atom-metal bond will become more metallic and thus less ionic in character (ref. 58). In this case, the effective charge on the adsorbate is reduced and the actual dipole moment $M = q_{eff}(r_i + \langle z \rangle)$ will decrease.

There are thus two competing trends. As the electron density is decreased, $\langle z \rangle$ increases but q_{eff} decreases. Hence there exists an optimal electron gas density for the greatest work function change using a particular adsorbate to specify the value of r_i. Put another way, it may be that cesium would produce the greatest work function change in one metal wheras potassium would produce the greatest change in some other metal, solely as a result of the different electron gas densities in the two metals.

It is hoped that considerations along the lines outlined in this section will be taken by workers doing numerical calculations of electronic surface properties for it seems that if such considerations are not given, then there can be little correspondence between what is calculated and what is occurring in physical reality.

VII. INFLUENCE OF MANY-BODY EFFECTS ON THE SURFACE POTENTIAL

Generalities

A perhaps mysterious claim was mentioned in the introductory section in which an allusion to the necessary connection between the surface potential barrier and many-body effects was made. A demonstration of this assertion and how existing theoretical treatments of the surface barrier can be improved upon by using the theoretical ideas set forth in the preceding sections will be presented in this section.

Basically, the idea of a surface barrier infers that deep within a metal an electron propagates through a partially non-local potential generated by the many-body medium of the electron gas, plus the periodic pseudo-potential of the lattice. As shown in section III, the periodic lattice does not drastically alter the many-body effects. As the electron travels about, it undergoes energy-reducing processes of the exchange and self-energy type. For the most part, these terms do not depend upon position because of the translational invariance of the system. However, thinking in Thomas-Fermi terms, one would expect that if the electron gas density varied, then the exchange and correlation effects, depending directly upon the electron gas density, would also vary. In the simplest possible illustrative example, consider the average Hartree Fock free electron exchange energy = $-0.916/r_s$. As the density decreases, r_s increases and thus the reduction in total energy caused by exchange decreases. Hohenberg and Kohn (ref. 29) have given a general theorem which proves that the energy and density are uniquely related. Although it is the author's opinion that the given proof of this theorem does not apply to the density variations in the surface region, he believes that the physical idea is basically sound. As the propagating electron comes into the surface region, the electron density of the field within which it is propagating decreases. Thus one would expect the energy lowering exchange and self-energy effects to be less pronounced. Consequently, the electron "potential energy" (a loose definition of that part of the total energy not including kinetic energies) increases in the surface region. However, the electrons are in energy eigenstates so the kinetic energy must go negative, corresponding to the classically forbidden region. Therefore binding occurs as a result of the many-body effective potential barrier. An interesting item to contemplate in this line of thinking is the following. Since the barrier is caused by many-body effects, such as self-energy processes, the barrier height depends on the momentum of the particular electron incident upon it; that is, an electron on the Fermi surface which is normally incident upon the metal surface sees the outside vacuum potential at a height ϕ_e, the electron work function. However, an electron with kinetic energy $p_F^2/2m - \epsilon$ normally incident does not see a height $\phi_e + \epsilon$ because its momentum is different. The momentum-dependent energy reducing many-body effects it induces are different. Consequently, when referring to such phenomenological constructs as electron work functions, one should use a relation of the form $\phi_e = \phi_e(\vec{p})$ with the condition $\phi_e(p_F \hat{i}_z) = \phi_{usual}$ where the true barrier, minus the Fermi energy which a normally incident Fermi surface electron sees, has been arbitrarily set equal to the phenomenological barrier minus the Fermi energy. This sort of phenomenon might have quantitative significance if one derived the correct Richardson-type equation for thermionic emission. In the derivation it is necessary to do phase space integrals of the form

$$\int d^3p \; e^{-\phi/kT} \; f(\vec{p}, T)$$

which should be of the form

$$\int d^3p \; e^{-\phi(\vec{p})/kT} \; f(\vec{p}, T) \; .$$

From the relative success of the standard Richardson equation in interpreting experimental data, it is probable that these corrections are not of first order importance. However, as the quality of the experimental situation improves, these observations may be of more than academic interest.

There are other far-reaching motivations for studying the nature of the surface barrier. Periodic deviations in the Schottky effect have been theoretically studied by Cutler and Gibbons (ref. 61). They demonstrate the strong dependence of these deviations on the reflection coefficient for a metal electron incident upon the surface barrier. It is well known from elementary quantum mechanics that the reflection coefficient is extremely sensitive to the form of the barrier and its higher order derivatives. D'Haenens and Coomes (ref. 62) have displayed the problems one gets into by oversimplifying the nature of the surface barrier. In attempting to explain their experimental data, they use a Sommerfeld box model for the metal with no regard to many-body effects. Using a perfectly square barrier to represent the surface, they require bandwidths which are roughly twice as large as in reality in order to achieve agreement with experiment. This of course is an entirely unacceptable situation and the idea of the square barrier must be discarded in calculations requiring reflection coefficients. An adequate replacement is required.

Still another field of research should be concerned with the nature of the surface potential barrier, the field of photoemission studies. Spicer and co-workers (ref. 63) have developed experimental techniques for doing photo studies to a high degree of accuracy. From measurements of energy distributions of emitted electrons, they infer bulk density of states and attempt to explain certain optical properties of solids. Decimal point accuracy assignments are given to particular interband transitions, based on a simple theoretical model for the photoemission process. It seems that a more complete study of the surface barrier and its effect upon an incident photo-excited electron would help to understand further the work of Spicer.

This problem was considered initially by Bardeen (ref. 33). Juretschke (ref. 34) performed a calculation of the unscreened exchange potential as a function of the distance from the surface which demonstrated both the existence of the barrier and the fact that the potential is not monotonic but has oscillatory structure. Loucks and Cutler (ref. 35) refined this calculation by using an exchange potential shielded by a spherically symmetric screening function and including rudimentary correlation effects within the context of the plasma oscillation theory. Here the Loucks and Cutler theory is extended by considering collective effects more appropriate for an electron gas with a surface, although still in a fairly rudimentary manner. However, a formalism is set up which would enable one to do a more exact calculation if this is felt necessary. As mentioned earlier, because of the present state of the art on the experimental side of the fence, such undue effort does not seem justified.

Theoretical Considerations

The objective of this section was to calculate the self-energy for a propagating electron in an electron gas with a surface. The difference between the self-energy in the surface region and that deep within the interior gives a contribution to the surface potential barrier.

The physical picture can be stated in the following manner. Initially one starts with a propagating plane wave electron. If it happens to enter the surface region, the density fluctuations it induces will be different from those in the interior. Consequently, in the case of electrons with kinetic energies less than the Fermi energy plus phenomenological work function, scattering occurs back into the metal. The nature of the surface is seen through this picture: an incident plane wave electron scatters off of a density fluctuation it induces in a much different manner than in the bulk. The scattering is such that an incident electron of momentum k_z will have outgoing momentum of $-k_z$ as a result of scattering from the surface potential, $V_s(z)$. Thus the sine wave functions previously used in surface calculations are really scattering states, the sum of an incident plus scattered wave. An attempt to calculate the form of $V_s(z)$, the effective potential induced by an incident plane wave, will now be made.

The method utilized in the calculation is now outlined. As discussed in section II, the self-energy of an electron propagating in the many-body field can be written as

$$\Sigma(\vec{p}, p^0) = i \int \frac{d^4q}{(2\pi)^4} G(p-q) \Gamma(p,q) D(q) \tag{118}$$

with

$$D(q) = \frac{v(\vec{q})}{\epsilon(\vec{q}, q^o)} .$$

An equivalent statement of Eq. (118) is:

$$\Sigma(\vec{p}, p^o) = i \int \frac{d^4q}{(2\pi)^4} G(p-q)\,\Gamma\,(p,q)\,v(\vec{q}) + i \int \frac{d^4q}{(2\pi)^4} G(p-q)\,\Gamma\,(p,q)\,v(\vec{q}) \left(\frac{1}{\epsilon(\vec{q}, q^o)} - 1 \right), \tag{119}$$

within which one could introduce the density fluctuation propagator:

$$S(q) = \frac{1}{v(q)} \left(\frac{1}{\epsilon(\vec{q}, q^o)} - 1 \right) . \tag{120}$$

In the first integral of Eq. (119), if one sets $G = G_o$ and $\Gamma = 1$, then this is just the unscreened Hartree-Fock exchange contribution to the self-energy. The second term in Eq. (119) involving the propagation of the density fluctuation can also be split up into two parts -- one involving density fluctuations arising from excitation of virtual electron-hole pairs and the other involving the excitation of a virtual plasmon. The procedure for effecting this division is discussed by DuBois (ref. 6). Here his end result is simply quoted. It says that

$$S(q) = \frac{e^2}{v(q)} \int \frac{d^3k}{(2\pi)^3} \frac{2[E_o(\vec{k} + \vec{q}) - E_o(\vec{k})]}{\omega^2 - [E_o(\vec{k} + \vec{q}) - E_o(\vec{q})]^2} \frac{1}{|\epsilon[\vec{q}; E_o(\vec{k} + \vec{q}) - E_o(\vec{k})]^2} - \frac{1}{\partial\epsilon(\vec{q}; \omega_{\vec{q}}) / \partial\omega} \frac{2\omega_{\vec{q}}\,\theta(q_c - |\vec{q}|)}{\omega^2 - (\omega_{\vec{q}} - i\delta)^2} . \tag{121}$$

The first term, which takes into account pair excitation, gives rise to modified short-range interaction effects. The point of view is adopted that if term number one was dealt with in a rigorous manner, then one could derive the screened exchange self-energy. Then, if one devised a method of modifying the bulk theory to a surface theory, the end result of a proper treatment of the Hartree-Fock plus screening terms would give the screened exchange potential calculated by Loucks and Cutler (ref. 35).

Within the context of this point of view, the only thing left to consider in the self-energy is the second term of Eq. (121) which is related to the plasmon part of a density fluctuation. In this term, the θ step function is introduced to indicate that the plasmon is a well-defined excitation only for momenta less than some critical momentum q_c where the relatively flat plasma dispersion curve merges with the pair continuum shown in Figure 16.

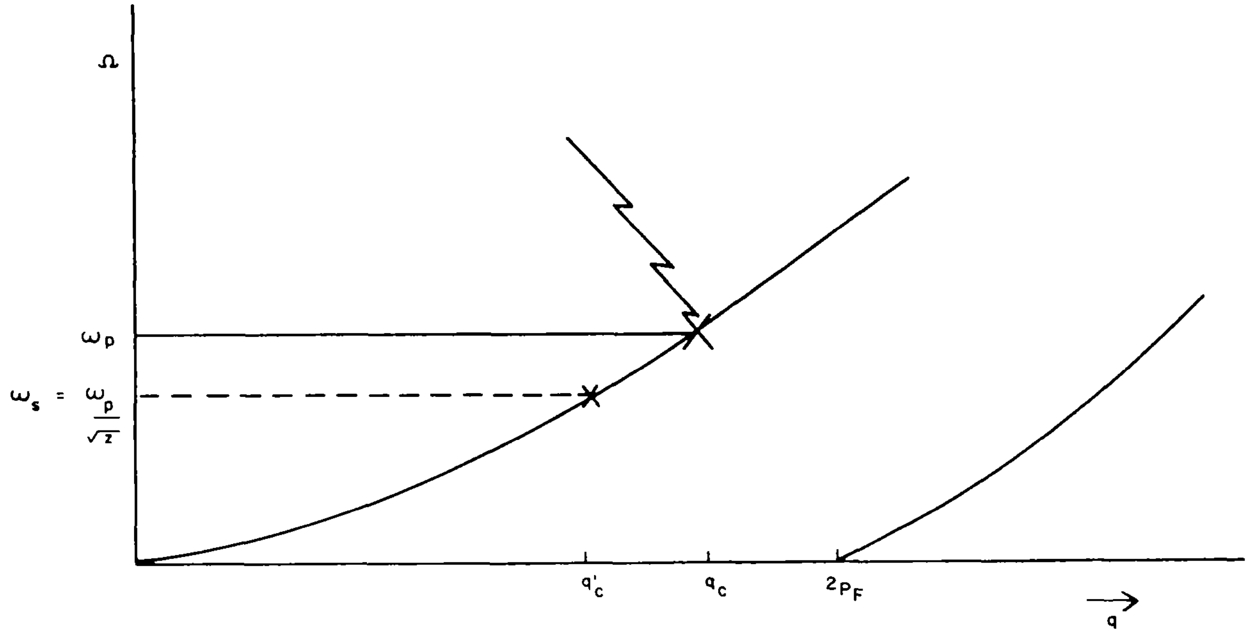

Figure 16. Elementary excitation spectrum in an electron gas.

It will be convenient to introduce a parameter $\beta \equiv q_c/p_F$.

It might be expected that since the $q = 0$ collective oscillations in the surface region have a frequency $\omega_s = \omega_p/\sqrt{2}$ as compared to ω_p in the interior, a difference in plasma self-energy effects between the volume and surface region could be categorized by properly taking this effect into account. The problem is that in the surface region, the surface plasmon has its momentum parallel to the surface only. Thus, in the surface region, $\lim_{q_t \to 0} \omega_s(\vec{q}) = \omega_p/\sqrt{2}$, whereas the collective oscillations with momentum normal to the surface go as $\lim_{q_z \to 0} \omega(\vec{q}) = \omega_p$. To perform the surface calculation with absolute correctness involves using a non-spherically symmetric plasmon dispersion relation to account for the fact that surface plasmons propagate parallel to the surface only. In the present approximate treatment, it may be assumed that the dispersion relation is symmetric in the sense that an electron in the surface region excites a virtual plasmon of frequency $\omega_p/\sqrt{2}$ independent of angle, whereas an electron in the bulk excites one at ω_p. This is an improvement upon the Loucks and Cutler treatment in which the relevant plasmon contribution was taken at a frequency of ω_p independent of position.

With these assumptions, one can now proceed with the mathematical aspects of the theory. The plasmon part of the self-energy of Eq. (119) can be written as

$$\Sigma_p (\vec{P}, p^o) = i \int \frac{d^4q}{(2\pi)^4} \left| g_{\vec{q}} \right|^2 D_p(q)\, G(p-q) \tag{122}$$

if, by use of Eq. (121) in (119), one identifies:

$$D_p(q) = \frac{2\omega_{\vec{q}}}{\omega^2 - \omega_{\vec{q}}^2 + i\eta} \tag{123}$$

which is a standard Boson propagator for the plasmon where

$$\left| g_{\vec{q}} \right|^2 = \frac{v(\vec{q})}{\partial \epsilon\, (\vec{q}, \omega_{\vec{q}}) / \partial \omega} \tag{124}$$

is an effective coupling between the propagating electron and virtual plasmon. The mathematical aspects of this problem, a propagating Fermion emitting a virtual Boson in a self-energy process, are identical with many other problems in physics such as the polaron problem (ref. 64), He^3 coupled to phonon modes (ref. 65), and hole coupling to plasmons (ref. 10).

In the long wavelength limit, the dielectric function is given by

$$\epsilon\, (\vec{q}, \omega_{\vec{q}}) \simeq 1 - \frac{\omega_s^2}{\omega_{\vec{q}}^2}$$

Furthermore, it is a reasonably good approximation to take the surface plasmon as being dispersionless; that is, $\omega_{\vec{q}} = \omega_s$ = constant. With these assumptions, Eq. (124) becomes:

$$\left| g_{\vec{q}} \right|^2 = \frac{2\pi e^2 \omega_s}{|\vec{q}|^2} \tag{125}$$

Equations (123) and (124) in Eq. (122) give:

$$\Sigma_{\text{surf}} = -i\, 4\pi e^2 \omega_s \int \frac{d^4q}{(2\pi)^4} \frac{1}{\vec{q}^{\,2}} \frac{1}{\omega^2 - \omega_s^2 + i\eta}\, G(p-q) \tag{126}$$

The next item on the agenda is to consider the appropriate Green's function for the incident electron G(p-q). This can be formally written as

$$G(p-q) = \frac{1}{\omega - E^{o}_{\vec{p}-\vec{q}} + i\eta} \tag{127}$$

with the following explanation. If one takes E^{o}_{p-q} to be the energy of an electron deep in the metal, and if one then sets the exchange potential at $z = 0$ as the zero, then

$$E^{o}_{\vec{p}-\vec{q}} = \frac{(\vec{p}-\vec{q})^2}{2m} + \left\{ V_{int} - V_x(0) \right\}$$

results. In this expression V_{int} is the total internal potential which includes both screened exchange and correlation effects. On the other hand, $V_x(0)$ is only the screened exchange part of the surface potential since it is precisely the correlation energy part which is to be calculated. Note that V_{int} and V_x are negative numbers. For brevity,

$$\Sigma_{int} = V_{int} - V_x(0)$$

may be written.

Some further approximations may now be introduced. These approximations will limit the accuracy of the calculations to within a factor of 2 or so. But this is sufficiently accurate to learn whether a more detailed calculation is worthwhile. The approximations are this. First, one can assume that $q << p$ in E^{o}_{p-q}. Since one is only considering $q < q_c$ for plasmons, the first assumption does not completely tax the credibility gap. Next assume that the dominant processes occur for electrons near the Fermi surface and thus replace $p \rightarrow p_F$. With these assumptions, the electron Green's function becomes

$$G(p-q) \approx \frac{1}{\omega - \frac{p_F^2}{2m} - \Sigma_{int} + i\eta} \tag{128}$$

where Σ_{int} is also taken as a constant independent of momentum.

Equation (126) can now be written as

$$\Sigma_{surf} = i\,4\pi e^2 \omega_s^2 \int_{q<q_c} \frac{d^3q\, d\omega}{(2\pi)^4} \frac{1}{q^2} \frac{1}{(\omega + \omega_s)} \frac{1}{(\omega - \omega_s)} \frac{1}{\omega - \frac{p_F^2}{2m} - \Sigma_{int}} \tag{129}$$

The energy integral is performed around the contour shown in Figure 17 which encloses the poles at

$$\omega = +\omega_s, \frac{p_F^2}{2m} + \Sigma_{int}$$

but not $\omega = -\omega_s$. Equation (129) then reduces to

$$\Sigma_{surf} = -2\pi e^2 \frac{\omega_s}{\omega_s + \Sigma_{int} + \frac{p_F^2}{2m}} \int_{q< q_c'} \frac{d^3q}{(2\pi)^3} \frac{1}{q^2} \tag{130}$$

which is simply

$$\Sigma_{surf} = -\frac{e^2}{\pi} k_F \beta_s \frac{\omega_s}{\omega_s + \Sigma_{int} + \frac{p_F^2}{2m}} . \tag{131}$$

For the case of the dispersionless plasmon β_s, the surface plasmon cutoff is related to β the volume cutoff by

$$\beta_s = 2^{-1/4} \beta = .84\beta$$

If a similar derivation were performed for the plasmon contribution to the self-energy deep within the metal, one would obtain:

$$\Sigma_{plasma} = -\frac{e^2}{\pi} k_F \beta, \tag{132}$$

the standard result. As an aside, it is encouraging to see that the field theoretic approach, coupled with the approximations that have been made, is equivalent to the Bohm-Pines theory. In the next section it is discussed

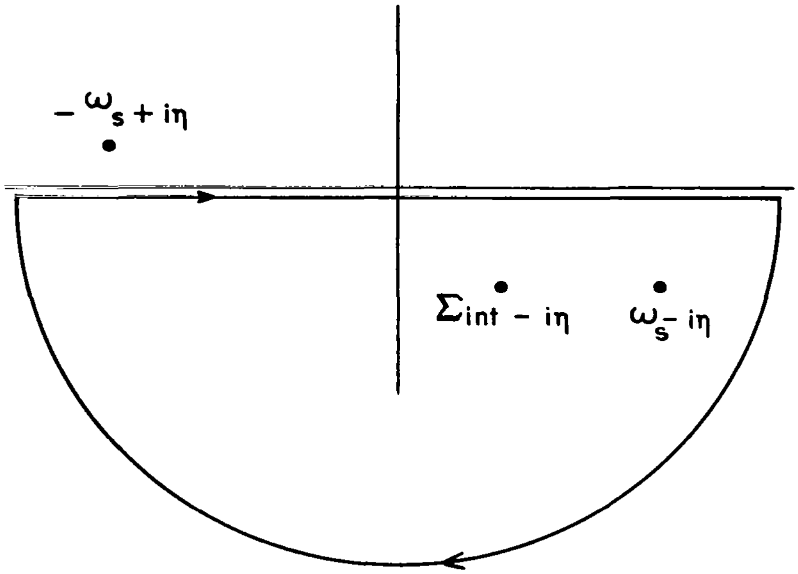

Figure 17. Integration contour in complex energy plane.

how these results are used in calculating surface potentials, and numerical results, which are the Loucks and Cutler calculation with the surface plasmon correction, are presented. The relevance of this correction to the experimental situation is also covered.

Numerical Results and Discussion

As has been previously stressed, the theory presented in this section has been directed towards obtaining corrections to the Loucks and Cutler results by considering modifications to bulk correlation energy processes appropriate in the surface region. Mathematically these modifications came in two different ways. First, it was assumed that a propagating electron couples to virtual surface plasmons of frequency $\omega_p / \sqrt{2}$ rather than ω_p in an isotropic manner. Although this is not rigorous, the end result given in Eq. (129) would be rather insensitive to a fractional change such as $1/\sqrt{2}$ in the resonant frequency. Second, a new Green's function, Eq. (129), was used to describe an electron coming into the surface region from within the metal.

At this point one may wonder how the z dependence of the self-energy was handled, since it does not appear in Eq. (131), nor in the derivation leading to it. The explanation is this. What has just been calculated is the self-energy appropriate to the $z = 0$ plane only. A calculation for a general point $z = 0$ could be done by using the image technique, but the labor involved would be forbidding. However, since interest lies essentially in the form of the effective potential as a function of z, the following approximation scheme is adopted. First, it is assumed that the oscillatory structure of a fully calculated $\Sigma(z)$ would parallel the structure of the Loucks and Cutler potential energy curves. Within this approximation, one can incorporate the present results into their calculated curves essentially by a rescaling of the energy in the following manner. In Figure 18 their results are reproduced. These curves represent one-electron potentials which include screened exchange plus a z-independent correlation energy. The z-dependence arises only from variations of the screened exchange.

If one considers the theory developed in this section, then the following modification to Loucks' and Cutler's work is required. At z = 0, the plasmon self-energy part of the "potential" differs from the interior value by a factor

$$\frac{0.84\,\omega_s}{\omega_s + \Sigma_{int} + \frac{p_F^2}{2m}}$$

In other words for any β, at z = 0 the Loucks and Cutler result should have added to it:

$$\Delta\Sigma = \Sigma_{surf} - \Sigma_{int} = \frac{+\,e^2 k_F \beta}{\pi}\left[\frac{.16\,\omega_s - \Sigma_{int} - \frac{p_F^2}{2m}}{\omega_s + \Sigma_{int} + \frac{p_F^2}{2m}}\right] \qquad (133)$$

Thus, the procedure followed here is to take one of their particular curves. The interior potential determines the V = V(∞) ordinate. At z = 0, rescaling is performed in the sense that $V(0) = V_{LC}(0) + \Delta\Sigma$ is required. Then with this new scale, values of V(z) for z arbitrary can be read from their result. These steps have been performed and the results drawn in Figure 19 with electron densities taken at the value for Na. A number of interesting observations can be made when comparing the original Loucks-Cutler curves of Figure 18 with the surface-corrected ones. First, it should be noted that for all practical purposes, both sets of curves with $\beta \leq 0.6$ coincide. This is reasonable though for two reasons. Plasmon contributions to total energies are being considered. The lower β is, the fewer plasma modes there are. Thus one would expect low-β systems to have the smallest plasmon self-energies and consequently the smallest discrepancy between the original Loucks-Cutler treatment and the present one. Another measure of the importance of the plasmon self-energy term is how it stands in proportion to other energy-reducing terms, in particular, the screened exchange term. As Loucks and Cutler show, the magnitude of the screened exchange decreases with increasing β. Thus as β gets larger, the plasmon self-energy process becomes as important as the screened exchange. As a result, one would expect corrections to the surface plasmon self-energy diagrams to become more important. Hence, two distinctly

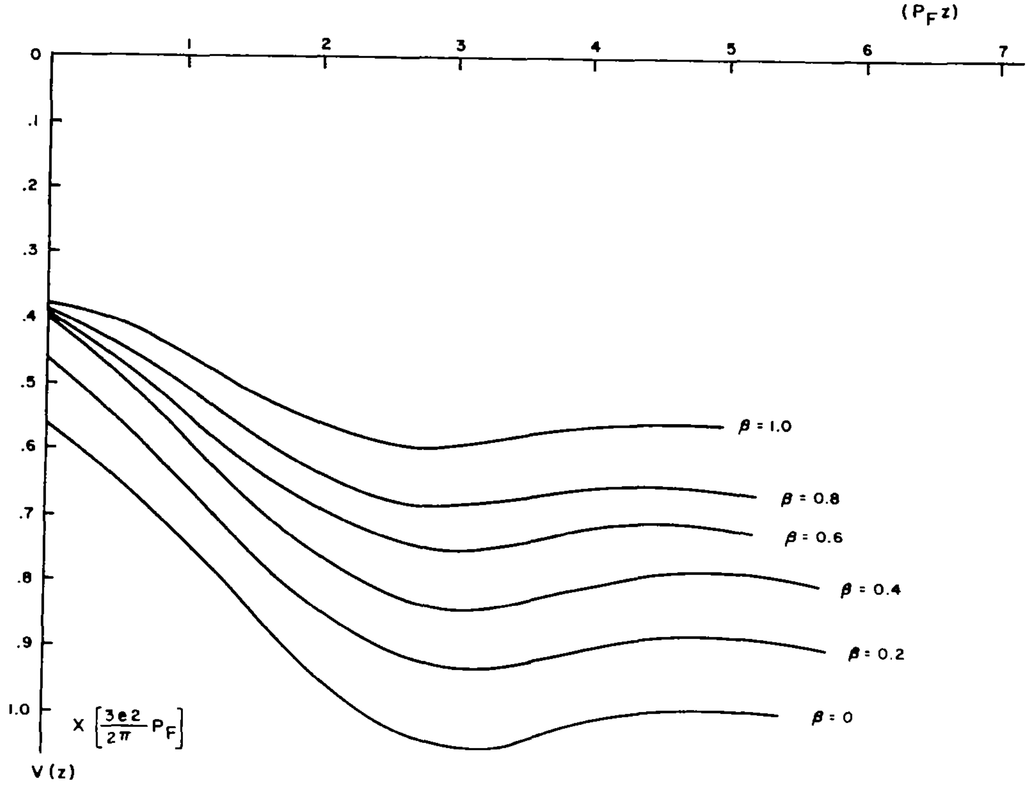

Figure 18 - Electron gas surface potential calculated by Loucks and Cutler.

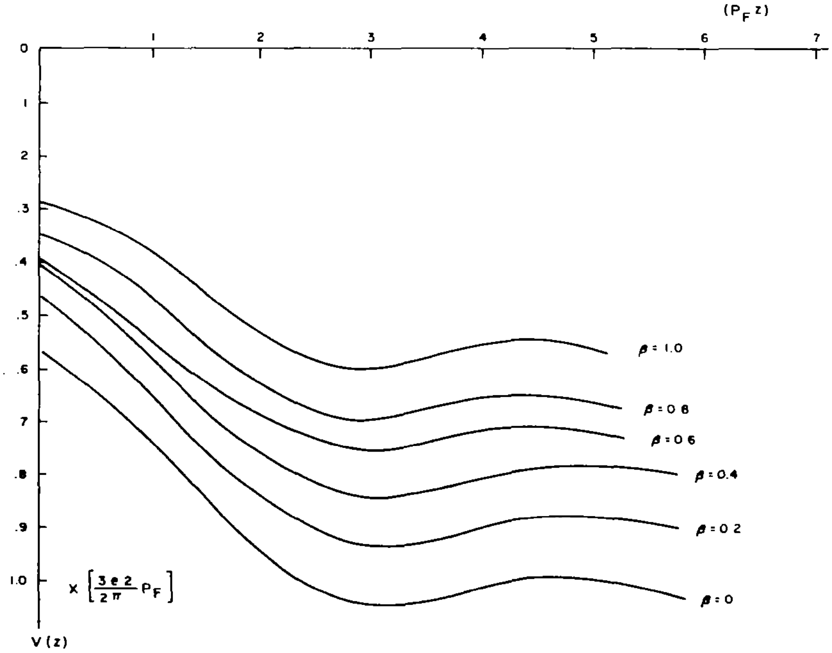

Figure 19 - Electron gas surface potential calculated in present thesis.

different reasons exist for anticipating the surface plasmon correlation energies, as calculated in this section, to be more pronounced in the domain of higher β's. Comparing Figures 18 and 19, one can see that what was expected did actually take place. The height of the repulsive barrier at $z = 0$ for $\beta = 0.8$ and 1.0 is significantly greater in the present theory than in that of Loucks and Cutler. But this is reasonable for several reasons also. In the first place, the correlation energy, which is always attractive at reasonable electron densities, becomes less attractive as the electron density is reduced. Thus one would expect an appropriate correlation energy contribution in the surface region, the region of reduced electron density, to be smaller than in the interior. The present calculations bear this out. On the other hand, in the original Loucks-Cutler calculations, this type of correction is applied to the screened exchange energy but not to the correlation energy. Thus, as β increases, their surface potential curves become quite flat, not becoming increasingly repulsive fast enough as the surface region is entered from the interior. Since the value of β for Na seems to be ~ 0.8, the surface correlation effects are pronounced and consideration must be given to those effects before a theory of real world physical systems hopes to be reasonably complete.

One final observation is concerned with the possible reflection coefficients at these potential barriers. Since the original Loucks-Cutler curves had a relatively small slope, the reflection coefficient would be smaller than in the present curves. This change in the gradient might be of some importance when one constructs simple, analytical approximate surface potential functions based on the results shown in Figures 18 and 19 (ref. 66).

VIII. CONCLUSIONS

Thus far this document has shown a fairly quantitative understanding of selected examples of inhomogenous interacting electron gases. In fact, most of the problems that have been undertaken have been exactly soluble, at least in the asymptotic sense and within the RPA or some more appropriate plane wave many-body theory approximation. This would seem to be just opposite what would be expected when one looks at the difficulties the Kohn school has had in obtaining practical solutions to inhomogenous electron gas problems.

As might be expected, there is, of course, good reason why the type of problems dealt with in this report have been amenable to rather neat solutions in spite of their initially ominous appearance. The fundamental problem with non-translationally invariant systems has been that, in general, nothing could be said about the meaningful conserved quantity usually associated with momentum in an invariant system. Thus, when Kohn starts theorizing on a slowly varying electron gas, the closest he can come to anything resembling states which are superpositions of momentum eigenstates, are WKB wave functions. The inhomogeneous nature of the electron gas is thus reflected in the different single particle WKB energy eigenfunctions. However, these functions are difficult in momentum space so he cannot Fourier transform his configuration space problem into momentum space and take advantage of any conservation laws which greatly reduce the computational complexity of the problem. But all is not bleak because the problems which he deals with are those in which the change in total electron density relative to the average density is very small over a distance of the order of a Fermi wavelength. Consequently he can avail himself of very truncated Taylor or density-gradient expansions to take care of the spatial variations. As the density change becomes more rapid, higher order terms in the expansions must be maintained in order that there remain any correspondence between calculated results and physical reality. When this situation prevails, the Kohn approach, with density as a basic variable, becomes of decreasing utility for obtaining results which will be evaluated numerically and compared with experimental situations.

But, as if there were some overall justice in nature, those examples of inhomogeneous electron gases which do vary significantly in the distance of a Fermi wavelength have other characteristics which make them calculable also. A little reflection by the reader will show that most of the physically relevant, rapidly varying gases come about as a result of a localized boundary condition. Take for instance the cases investigated in this report. First, the periodic potential which certainly induces a rapid density variation puts certain boundary conditions on the non-interacting energy eigenfunctions: that they be Bloch functions. As discussed in the Introduction, there still is a conserved momentum-like quantity associated with this boundary condition, the crystal momentum. Thus it is possible to Fourier transform this many-body problem to momentum space provided one remembers to allow for inter-band as well as intra-band transitions in any scattering events. Crystal momentum conserving delta functions appear and the problem thus becomes computationally manageable.

Similar things happen in the impurity problem. The existence of an impurity potential which is singular at the origin requires all the single electron wavefunctions to readjust themselves, such that they have zero amplitude at the impurity. The self-consistent, many-body formalism of this report was just a fancy way of seeing to it that this boundary condition was satisfied.

In the case of the model surface problem, the infinite barrier places the zero amplitude boundary condition on non-interacting electron wavefunctions. In the cases considered here, sine waves satisfy this boundary condition. But sine waves are zero momentum eigenfunctions, so once again we see that there is something we can say about momentum conservation in this non-invariant system. As has been seen, this fact enables us to go to momentum space where we can pick up a delta function, thus making calculations feasible.

The following observations suggest a general rule. In all cases of rapid density variation, the cause has been some natural condition which imposes boundary conditions on single-electron wavefunctions. The density variation, and thus long-range Friedel density oscillation, whether around an impurity or surface, is just a manifestation of the non-interacting electrons interfering in a manner which washes out the effects of the boundary conditions in a distance of order of Fermi wavelengths. The Friedel oscillations are not caused by any strange many-body effect, but only by a classical wave diffraction effect. In any event, for most rapidly varying density phenomena in nature, the cause can be seen to be a boundary condition which all electrons must satisfy, regardless of their energies. Perhaps this is the kernel of the idea: if one has a non-momentum or energy-dependent boundary condition, then one can usually obtain a set of single-electron basis functions satisfying this condition, for which something can be said about momentum eigenvalues. If this is the case, then it is possible to work in momentum space. As we have seen, for the lattice and surface problem, the eigenfunctions might be small sums of plane waves. Then the only problem when doing many-body theory in this basis is to keep track of interferences between various plane wave components of a single electron wave function. This might be a minor nuisance but some conservation laws are available for use.

On the other hand, the slowly varying density variations considered by Kohn are usually man-made. The boundary conditions they impose are energy-dependent. Such things as applied fields, stresses, and minor deformations on the atomic level are well treated within his formalism. In these sorts of problems it is realistic to think in terms of local microscopically uniform systems, along the philosophy of Thomas-Fermi theory, and develop a calculational scheme based on density-gradient expansions. But in these sorts of problems there is a one-to-one correspondence between the non-uniform, slowly varying potential producing the inhomogeneous gas and the non-uniform density, whereas in the diffraction-produced inhomogeneous electron gases, such is not the case. Thus it seems that the slowly and rapidly varying inhomogeneous electron gases are of fundamentally different origins and thus should be considered from fundamentally different theoretical viewpoints.

The rule of thumb is that in a rapidly varying system, there is a significant boundary condition to be faced. Somehow one should get a reasonable single-electron basis set satisfying this boundary condition. There will always be something definite and simple that can be said about the momentum spectrum of this non-interacting basis. Then one should go to momentum space and keep track of all many-body interaction interference terms since interference effects are at the heart of this type of inhomogeneous electron gas. For the slowly varying case, one should forget momentum conservation and work within the density-gradient expansion formalism of Kohn. Fortunately, most of the physically interesting systems fall into one or the other of these categorizations.

The author feels that the realization of this point of view and the illustration of it by several specific examples constitute the major achievement and positive contribution of this report. The specific conclusions of each illustrative example have been stated in their respective sections so there is little need to repeat them here.

From a point of apparent chaos, the problem of many-body effects in rapidly varying inhomogeneous electron gases has been reduced to one which is conceptually little more difficult than the case of homogeneous electron gases, although a bit more troublesome from the computational point of view. This is because interferences between various components of a single electron wavefunction must be properly catalogued.

It is the hope of the author that the procedures developed and expounded here will be of use in future refinements of electron gas theory which will ultimately lead to the accurate, quantitative predictions of observable properties of real metals.

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