

PERTURBATION IN AN ELECTRON GAS

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A Thesis

Presented to

the Faculty of the Department of Physics

University of Houston

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

Chei-mei Chou Li

January, 1966

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## ABSTRACT

A first order perturbation method is used for treating localized defects in metals in a self-consistent way. The calculations are performed under the Hartree approximation using both the ordinary Coulomb interactions between electrons appropriate for the one electron approximation and the effective short-range potential resulting from the Bohm-Pines plasma theory of metals. The results of the above approximations are tested for self-consistency by the application of the Friedel sum rule. The results are then compared with the statistical approximation of the Thomas-Fermi method. It is found that they are very similar.

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## CHAPTER I

### INTRODUCTION

Many of the interesting properties of solids have their origin in imperfections which interrupt the periodicity of the lattice upon which the solid is based. These imperfections can be dislocation, interstitial atoms, missing atoms, etc. The effect of a given imperfection on electrons in a solid has been considered by many authors, such as Slater and Koster,<sup>1</sup> Du Pre<sup>2</sup> and Roth.<sup>3</sup>

Thomas and Fermi<sup>4</sup> developed a statistical model for treating the problem of the self-consistent field. Our present work is concerned with the application of first order perturbation theory to the one electron method of treating a many electron system. From this theory we obtain a method for finding a self-consistent potential in terms of a given unscreened perturbation. The approach is that originally suggested by Bardeen<sup>5</sup> in his treatment of the electrical conductivity of monovalent metals. We solve this problem using Hartree's<sup>6</sup> approximation for both the ordinary Coulomb interaction and the effective short-range interaction resulting from the Bohm-Pines<sup>7,8,9,10</sup> plasma theory of metals.

As a test of the self-consistency of a given potential, Friedel<sup>11</sup> developed a sum rule involving the phase shifts that arise in scattering from the potential. This rule is applied to determine the range of densities for which our theory is valid. The results of

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this work indicate that neither the statistical treatment nor the perturbation treatment are valid approximations for real metals, at least for point impurities.

## CHAPTER II

### THE SELF-CONSISTENT FIELD METHOD

#### The Thomas-Fermi Approximation

The general treatment of the Thomas-Fermi approximation starts from the minimum energy principle.<sup>4,12</sup> We assume the conduction electron and the ion system to be represented by a Lorentz plasma, that is, a uniform cloud of electron moving in a background of fixed positive charge. The Thomas-Fermi approximation follows from equating the electronic kinetic energy to that given by statistical mechanics, namely

$$T = c \int \rho(\vec{r})^{5/3} dV, \quad (2-1)$$

where  $C$  is a constant of proportionality and  $\rho(\vec{r})$  is the electronic charge density. If the potential due to the uniform background of positive charge is  $V_N$ , the total energy of the electron gas with unscreened perturbation  $\delta V_0$  is

$$E = c \int \rho(\vec{r})^{5/3} dV + \int V_N \rho(\vec{r}) dV + \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} dV dV' + \int \delta V_0 \rho(\vec{r}) dV. \quad (2-2)$$

If  $\rho(\vec{r})$  is the correct charge distribution, the energy minimum principle states that  $E$  should be stationary under arbitrary

variation of  $f(\bar{r})$ . Since total charge is conserved, however, we must consider only those variations for which

$$\text{const} = \int f(\bar{r}) dV. \quad (2-3)$$

We then have

$$\frac{5}{3} c f^{2/3} + V_N + \frac{1}{2} \int \frac{f(\bar{r}')}{|\bar{r} - \bar{r}'|} dV' + \delta V_0 = \lambda, \quad (2-4)$$

where  $\lambda$  is a Lagrangian multiplier resulting from the constraint (2-3).

When an unscreened perturbation  $\delta V_0$  is introduced, the charge density changes from its unperturbed value  $f_0$  to a perturbed value

$$f(\bar{r}) = f_0 + \delta f(\bar{r}). \quad (2-5)$$

Upon substitution of (2-5) into (2-4), the quantity  $V_N$  is seen to be cancelled by the potential due to the unperturbed electron gas, and there results

$$\frac{5}{3} c f^{2/3} + \delta U + \delta V_0 = \lambda, \quad (2-6)$$

where

$$\delta U = \frac{1}{2} \int \frac{\delta f(\bar{r}')}{|\bar{r} - \bar{r}'|} dV'$$

is the electrostatic energy due to the change in charge density,  $\delta f$ .

If  $\delta V_0$  vanishes, that is, no perturbation is introduced,  $\lambda$  is seen to be exactly the Fermi energy  $E_0$ . We write the screened perturbation as

$$\delta V = \delta U + \delta V_0, \quad (2-7)$$

and hence

$$f(\vec{r}) = \left[ \frac{3}{5c} (\epsilon_0 - \delta V) \right]^{3/2}. \quad (2-8)$$

Under the assumption  $\delta V \ll E_0$ , we expand (2-8) and retain only the terms linear in  $\frac{\delta V}{E_0}$ . We then have

$$\delta f \cong -\frac{3}{2} \frac{f_0}{E_0} \delta V. \quad (2-9)$$

The change in electronic charge density  $\delta f$  can be related to  $\delta U$  through Poisson's equation which in fact insures self-consistency. Then  $\nabla^2 \delta U = -4\pi e \delta f$ . This expression, with the help of (2-9), becomes

$$\left. \begin{aligned} (\nabla^2 - \beta^2) \delta U &= \beta^2 \delta V_0 \\ \beta^2 &= 6\pi e \frac{f_0}{E_0} \end{aligned} \right\}. \quad (2-10)$$

Equation (2-10) is recognized as a form of the inhomogeneous Helmholtz equation, which has well known solutions.

The effect of the introduction of a charge  $q$  will be a redistribution of the electron gas. Whether the electronic charge density decreases or increases in the vicinity of the charge depends upon whether  $q$  is positive or negative. The electron gas, in fact, "screens" the charge  $q$ , so that the net field at large distance is zero. This

screening, however, will be negligible for points sufficiently close to charge  $q$ . The boundary conditions on  $\delta V(\bar{r})$  are therefore

$$\left. \begin{aligned} \delta V(\bar{r}) &\longrightarrow 0 & \text{as } r &\longrightarrow \infty \\ \delta V(\bar{r}) &\longrightarrow \frac{q}{r} & \text{as } r &\longrightarrow 0 \end{aligned} \right\}. \quad (2-11)$$

Equation (2-10) has the particular solution

$$\delta U = -\frac{\beta^2}{4\pi} \int G_p(\bar{r}, \bar{r}') \delta V_0(\bar{r}') dV' \quad (2-12)$$

with the Green's function  $G_p(\bar{r}, \bar{r}')$  satisfying

$$(\nabla^2 - \beta^2) G_p(\bar{r}, \bar{r}') = -4\pi \delta(\bar{r} - \bar{r}'). \quad (2-13)$$

The appropriate Green's function which satisfies (2-13) and the boundary condition (2-11) is easily seen to be

$$G_p(\bar{r}, \bar{r}') = \frac{1}{|\bar{r} - \bar{r}'|} e^{-\beta|\bar{r} - \bar{r}'|}. \quad (2-14)$$

For any given unscreened perturbation  $\delta V_0$ , the shielding potential  $\delta U$  in the Thomas-Fermi approximation is given by the evaluation of (2-12). To this end it is useful to expand the Green's function in spherical harmonics,<sup>13</sup> i.e.

$$G_p(\bar{r}, \bar{r}') = -4\pi\beta \sum_{l=0}^{\infty} \sum_{m=-l}^l j_l(i\beta r_2) h_l^{(1)}(i\beta r_1) Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi). \quad (2-15)$$

The function  $j_l(\rho)$  is the spherical Bessel function of order  $l$  and has the asymptotic behavior

$$j_l(\rho) \xrightarrow{\rho \rightarrow 0} \frac{2^l l!}{(2l+1)!} \rho^l$$

$$j_l(\rho) \xrightarrow{\rho \rightarrow \infty} \frac{1}{\rho} \sin\left(\rho - \frac{l}{2}\pi\right),$$

while the function  $h_l^{(1)}(\rho)$  is the spherical Hankel function of the first kind and behaves as

$$h_l^{(1)}(\rho) \xrightarrow{\rho \rightarrow 0} \frac{(2l)!}{i 2^l l!} \rho^{-(l+1)}$$

$$h_l^{(1)}(\rho) \xrightarrow{\rho \rightarrow \infty} \frac{1}{\rho} \exp\left\{i\left[\rho - \frac{\pi}{2}(2l+1)\right]\right\}.$$

If  $\delta V_0$  has spherical symmetry only the term  $l=0$  in (2-15) contributes, and (2-12) reduces to the result

$$\begin{aligned} \delta U = & -\frac{\beta}{r} \left[ e^{-\beta r} \int_0^r r' \delta V_0(r') \sinh \beta r' dr' \right. \\ & \left. + \sinh \beta r \int_r^\infty r' \delta V_0(r') e^{-\beta r'} dr' \right]. \end{aligned} \quad (2-16)$$

For  $\delta V_0 = \frac{ze^2}{r}$ , corresponding to a point impurity of charge  $ze$ , equation (2-16) is easily evaluated and gives

$$\delta V = \frac{ze^2}{r} e^{-\beta r}. \quad (2-17)$$

This special case of (2-17) is exactly the result of Mott,<sup>14</sup> who made the earliest attempts to treat impurities in metals in a self consistent way. From equation (2-17), it is seen that  $\beta$  is a constant characterized only by the density of conduction electrons and  $\frac{1}{\beta}$  is a measure of the screening distance. Mott's development assumed that the conduction electrons could be represented by a gas of uniform density and that the Fermi level was not altered by perturbation. This last assumption is reasonable since the Fermi energy is determined solely by the density, and the effects of the perturbation are negligibly small outside a radius  $\frac{1}{\beta}$ . Hence the density is essentially unchanged over the major part of the metal. For example, if we assume that the electron gas is that of the valence electrons in a monovalent metal, then in terms of the atomic radius  $r_0$ , that is the radius of a sphere containing one electron, we have

$$\rho_0 = \frac{3e}{4\pi r_0^3},$$

and

$$E_0 = \frac{\hbar^2}{2m} \left( \frac{9\pi}{4} \right)^{2/3} \frac{1}{r_0^2},$$

so that

$$\frac{1}{\beta} = \frac{1}{3} \left( \frac{9\pi}{4} \right)^{1/3} (a_0 r_0)^{1/2},$$

where  $a_0 = \frac{\hbar^2}{me^2}$  is the Bohr radius. If  $r_0$  is measured in atomic units, this gives

$$\frac{1}{\beta} = 0.64 r_0^{1/2} \text{ atomic units.}$$

For sodium  $r_0$  is about 4 atomic units, so that

$$\frac{1}{\beta} = 0.68 \text{ \AA},$$

which is smaller than the average inter-electronic distance.

It is instructive to write the differential equation (2-10) in another form, which is convenient for comparison with later results.

Through Fourier transformation,

$$\delta u(\bar{q}) = - \frac{\beta^2}{\beta^2 + q^2} \delta V_0(\bar{q}), \tag{2-18}$$

which combined with the definition of the total perturbed potential gives

$$\delta V(\bar{q}) = \frac{\delta V_0(\bar{q})}{1 + \frac{\beta^2}{q^2}}, \tag{2-19}$$

where

$$\delta V_0(\bar{q}) = \frac{1}{(2\pi)^3} \int \delta V_0(\bar{r}) e^{-i\bar{q} \cdot \bar{r}} dV. \tag{2-20}$$

By this technique, we see that an alternate but equivalent solution of (2-10) is

$$\delta V(\bar{r}) = \int \delta V(\bar{q}) e^{i\bar{q} \cdot \bar{r}} dV_q. \tag{2-21}$$

The results (2-19) and (2-21) will be compared with the quantum mechanical solution to the problem obtained by perturbation theory.

This is the problem to which we now turn.

### Perturbation on the Continuous Spectrum

Since we shall be interested in the effect of  $\delta V$  on a set of conduction electrons in a metal, we now investigate the formalism of perturbation theory with a continuous spectrum.

Consider a system with a continuous spectrum  $E_{\bar{k}}$  and eigenfunctions  $\Psi_{\bar{k}}(\bar{r})$  subject to the perturbation  $\delta V(\bar{r})$ . Let  $\Psi_{\bar{k}}$  and  $\Psi_{\bar{k}}$  be such that

$$\Psi_{\bar{k}} \xrightarrow{\delta V \rightarrow 0} \Psi_{\bar{k}},$$

where  $\Psi_{\bar{k}}$  is an eigenfunction of the unperturbed Hamiltonian. If the  $\Psi_{\bar{k}}$  comprise a complete set, we may write

$$\Psi_{\bar{k}} = \Psi_{\bar{k}} e^{-\frac{i}{\hbar} E_{\bar{k}} t} + \sum_{\bar{k}''} b(\bar{k}'', \bar{k}) e^{-\frac{i}{\hbar} E_{\bar{k}''} t}. \quad (2-22)$$

$\Psi_{\bar{k}}$  and  $\Psi_{\bar{k}}$  satisfy the Schrödinger equation,

$$\left. \begin{aligned} H_0 \Psi_{\bar{k}} &= i\hbar \frac{\partial \Psi_{\bar{k}}}{\partial t} \\ H \Psi_{\bar{k}} &= i\hbar \frac{\partial \Psi_{\bar{k}}}{\partial t} \end{aligned} \right\} \quad (2-23)$$

where  $H_0$  is the unperturbed Hamiltonian operator, and  $H = H_0 + \delta V$

Substitution of (2-22) into (2-23) yields

$$\begin{aligned}
 & \delta V \psi_{\bar{k}} e^{-\frac{i}{\hbar} E_{\bar{k}} t} - i\hbar \sum_{\bar{k}''} \frac{db(\bar{k}', \bar{k})}{dt} \psi_{\bar{k}''} e^{-\frac{i}{\hbar} E_{\bar{k}''} t} \\
 & + \sum_{\bar{k}''} b(\bar{k}', \bar{k}) \delta V \psi_{\bar{k}''} e^{-\frac{i}{\hbar} E_{\bar{k}''} t} = 0.
 \end{aligned} \tag{2-24}$$

If  $\delta V$  can be considered as being turned on at  $t=0$ , that is, when  $t \rightarrow 0$   $b(\bar{k}, \bar{k}) \rightarrow 1$  and  $b(\bar{k}', \bar{k}) \rightarrow 0$ , first order perturbation theory gives<sup>15</sup>

$$\frac{db(\bar{k}', \bar{k})}{dt} = \frac{i}{\hbar} \langle \bar{k}' | \delta V | \bar{k} \rangle e^{-\frac{i}{\hbar} (E_{\bar{k}} - E_{\bar{k}'}) t}. \tag{2-25}$$

Upon integrating equation (2-25) from  $t=0$  to  $t=t$ , one obtains

$$b(\bar{k}', \bar{k}) = -\frac{\langle \bar{k}' | \delta V | \bar{k} \rangle}{E_{\bar{k}} - E_{\bar{k}'}} [1 - e^{-\frac{i}{\hbar} (E_{\bar{k}} - E_{\bar{k}'}) t}], \tag{2-26}$$

where the matrix  $\langle \bar{k}' | \delta V | \bar{k} \rangle$  is defined as

$$\langle \bar{k}' | \delta V | \bar{k} \rangle = \int \psi_{\bar{k}'}^* \delta V \psi_{\bar{k}} dV. \tag{2-27}$$

Therefore, so far as the first order perturbation theory is concerned, the perturbed wave function  $\Psi_{\bar{k}}$  is

$$\begin{aligned}\Psi_{\bar{R}} &= \Psi_{\bar{R}} e^{-\frac{i}{\hbar} E_{\bar{R}} t} + \sum_{\bar{K}} \frac{\langle \bar{K}' | S | \bar{R} \rangle}{E_{\bar{R}} - E_{\bar{K}'}} \left[ 1 - e^{-\frac{i}{\hbar} (E_{\bar{R}} - E_{\bar{K}'}) t} \right] \Psi_{\bar{K}'} e^{-\frac{i}{\hbar} E_{\bar{K}'} t} \\ &= \left\{ \Psi_{\bar{R}} + \sum_{\bar{K}} \frac{\langle \bar{K}' | S | \bar{R} \rangle}{E_{\bar{R}} - E_{\bar{K}'}} \left[ 1 - e^{-\frac{i}{\hbar} (E_{\bar{R}} - E_{\bar{K}'}) t} \right] \Psi_{\bar{K}'} \right\} e^{-\frac{i}{\hbar} E_{\bar{R}} t} \quad (2-28)\end{aligned}$$

Since we are considering perturbation on the continuous spectrum, we may express  $\sum_{\bar{K}}$  as an integration over the states of the whole energy range, i.e.

$$\sum_{\bar{K}} = \int g(E_{\bar{K}'}) dE_{\bar{K}'},$$

where  $g(E_{\bar{K}'})$  is the density of eigenstates between  $E_{\bar{K}'}$  and  $E_{\bar{K}'} + dE_{\bar{K}'}$ . We also choose to regard  $E_{\bar{R}}$  as a complex variable. Therefore (2-28) becomes

$$\Psi_{\bar{R}} = \left\{ \Psi_{\bar{R}} + \int dE_{\bar{K}'} g(E_{\bar{K}'}) \frac{\langle \bar{K}' | S | \bar{R} \rangle}{E_{\bar{R}} - E_{\bar{K}'}} \left[ 1 - e^{-\frac{i}{\hbar} (E_{\bar{R}} - E_{\bar{K}'}) t} \right] \right\} e^{-\frac{i}{\hbar} E_{\bar{R}} t} \quad (2-29)$$

The integral (2-29) is taken along the real axis, and is well defined.

We can displace slightly the path of integration into lower half plane without changing the value of integral, since there is no singularity on the real axis.

Now consider this integral as to be composed of two parts,

$$\int dE_{\mathbf{R}'} g(E_{\mathbf{R}'}) \psi_{\mathbf{R}'} \frac{\langle \mathbf{R}' | S | \mathbf{R} \rangle}{E_{\mathbf{R}} - E_{\mathbf{R}'}}$$

and

$$\int dE_{\mathbf{R}'} g(E_{\mathbf{R}'}) \psi_{\mathbf{R}'} \frac{\langle \mathbf{R}' | S | \mathbf{R} \rangle}{E_{\mathbf{R}} - E_{\mathbf{R}'}} e^{-\frac{i}{\hbar}(E_{\mathbf{R}} - E_{\mathbf{R}'})t}$$

Since the imaginary part of  $E_{\mathbf{R}'}$  is negative on the path of integration, the second integral approaches zero as  $t$  approaches infinity. In the first integral, we may again make the real axis the contour of integration provided we add an infinitely small negative number to  $E_{\mathbf{R}'}$  to insure that we pass below the singular point. Thus we obtain the limiting form of the perturbed wave function for large time as

$$\Psi_{\mathbf{R}} = \left[ \psi_{\mathbf{R}} + \sum_{\mathbf{R}'} \frac{\langle \mathbf{R}' | S | \mathbf{R} \rangle}{E_{\mathbf{R}} - E_{\mathbf{R}'} + i\epsilon} \psi_{\mathbf{R}'} \right] e^{-\frac{i}{\hbar}E_{\mathbf{R}}t}, \quad (2-30)$$

### Perturbation in the Hartree Approximation

We now consider perturbations on the conduction electrons in an electron gas in the Hartree approximation.<sup>4,6</sup> This problem was first considered by Bardeen<sup>5</sup> in his investigation of the electrical

conductivity of monovalent metals. He assumed that the wave functions of the electron in the undistorted crystal were plane waves, and used these to calculate the charge distribution. This requires that the periodic part of the actual wave functions vary slowly throughout the major part of the volume. The calculations of Wigner and Seitz,<sup>16</sup> and of Slater<sup>17</sup> show that this assumption is valid for sodium, and it probably holds reasonably well for other monovalent metals. Recently Walker<sup>12</sup> has approached the problem using a similar method. Our treatment follows that of Bardeen and Walker.

The Hartree equation for the conduction electrons may be written in the form

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V + U\right)\psi_{\vec{k}}(\vec{r}) = E_{\vec{k}}\psi_{\vec{k}}(\vec{r}).$$

The potential  $V$  is that due to the interaction of the conductive electrons and the positive background of the plasma model, and  $U$  is an operator that accounts for the interaction of the electrons among themselves. The potential  $U$  has the form

$$U(\vec{r}) = -e \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} dV' \quad (2-31)$$

with

$$\rho(\vec{r}) = -e \sum_{\vec{k}' < k_0} \psi_{\vec{k}'}^+(\vec{r}) \psi_{\vec{k}'}(\vec{r}). \quad (2-32)$$

The summation here goes over all occupied states, that is over all

states having an energy less than Fermi energy  $E_0 = \frac{\hbar^2}{2m} k_0^2$ . Strictly speaking, the state  $\bar{k} = \bar{k}'$  should be omitted, since it represents the self-interaction of the electrons. This does not alter the conclusions which follow because the eigenfunctions for the electrons extend throughout the plasma and the interaction energy of such an electron with itself is negligible.

Suppose now an unscreened perturbation  $\delta V_0$  is introduced which alters the charge density  $\rho(\bar{r})$  and hence  $U$ . The total perturbation is then

$$\delta V = \delta V_0 + \delta U. \quad (2-33)$$

The screening effect is included in  $\delta U$ , which may be written as

$$\delta U = -e \int \frac{\delta \rho(\bar{r}')}{|\bar{r} - \bar{r}'|} dv'. \quad (2-34)$$

The problem is to determine  $\delta \rho$ , and then  $\delta U$  using perturbation theory so that  $\delta V$  is self-consistent. To this end, we write

$$\begin{aligned} \delta \rho(\bar{r}) &= -e \delta \sum_{\bar{k}'} \psi_{\bar{k}'}^* \psi_{\bar{k}'} \\ &= -e \sum_{\bar{k}'} \left[ \delta \psi_{\bar{k}'}^* \psi_{\bar{k}'} + \psi_{\bar{k}'}^* \delta \psi_{\bar{k}'} \right], \end{aligned} \quad (2-35)$$

and express the difference in the perturbed and unperturbed wave functions following (2-22), as

$$\delta \Psi_{\vec{k}} = \sum_{\vec{k}'} b(\vec{k}', \vec{k}) \Psi_{\vec{k}'} \quad (2-36)$$

with

$$b(\vec{k}', \vec{k}) = \frac{\langle \vec{k}' | S V | \vec{k} \rangle}{E_{\vec{k}'} - E_{\vec{k}} + i\epsilon} \quad (2-37)$$

Substitution of (2-36) and (2-37) into (2-35) yields

$$\delta \rho = -e \sum_{\vec{k} < k_0} \sum_{\vec{k}'} [b^*(\vec{k}', \vec{k}) \Psi_{\vec{k}'}^* \Psi_{\vec{k}} + b(\vec{k}', \vec{k}) \Psi_{\vec{k}'} \Psi_{\vec{k}}^*] \quad (2-38)$$

Here  $\sum_{\vec{k} < k_0}$  is the sum over all states from the lowest state up to the Fermi level, while  $\sum_{\vec{k}'}$  is the sum over all possible states. The symmetry property of  $E_{\vec{k}}$

$$E_{\vec{k}} = E_{-\vec{k}} \quad , \quad (2-39)$$

allows the conclusion

$$\sum_{\vec{k} < k_0} \sum_{\vec{k}'} b^*(\vec{k}', \vec{k}) \Psi_{\vec{k}'}^* \Psi_{\vec{k}} = \sum_{\vec{k} < k_0} \sum_{\vec{k}'} b^*(\vec{k}, -\vec{k}') \Psi_{\vec{k}'}^* \Psi_{-\vec{k}'} \quad (2-40)$$

From substitution of (2-40) into (2-38), we obtain

$$\delta P = -e \sum_{k < k_0} \sum_{k''} \left\{ b^*(-\bar{k}'', -\bar{k}') + b(\bar{k}'', \bar{k}') \right\} \Psi_{\bar{k}''} \Psi_{\bar{k}'}^* \quad (2-41)$$

In order to carry out the integrations in (2-34), we make use of the explicit form of the electronic wave function

$$\Psi_{\bar{k}}(\bar{r}) = \frac{1}{(2\pi)^{3/2}} e^{i\bar{k} \cdot \bar{r}}, \quad (2-42)$$

with the normalization volume taken as one cm.<sup>3</sup>. Equation (2-34) may then be rewritten as

$$\begin{aligned} \delta U \Psi_{\bar{k}}(\bar{r}) &= e^2 \sum_{k < k_0} \sum_{k''} \frac{1}{(2\pi)^3} \left[ b^*(-\bar{k}'', -\bar{k}') + b(\bar{k}'', \bar{k}') \right] \Psi_{\bar{k}}(\bar{r}) \int \frac{e^{i(\bar{k}' - \bar{k}'') \cdot \bar{r}'}}{|\bar{r} - \bar{r}'|} dV' \\ &= \frac{4\pi e^2}{(2\pi)^{3/2}} \sum_{k < k_0} \sum_{k''} \left[ b^*(-\bar{k}'', -\bar{k}') + b(\bar{k}'', \bar{k}') \right] \frac{\Psi_{\bar{k}' - \bar{k}''}^*(\bar{r}) \Psi_{\bar{k}}(\bar{r})}{|\bar{k}'' - \bar{k}'|^2}. \end{aligned} \quad (2-43)$$

The relation

$$\int \frac{e^{i(\bar{k}' - \bar{k}'') \cdot \bar{r}'}}{|\bar{r} - \bar{r}'|} dV' = \frac{4\pi}{|\bar{k}'' - \bar{k}'|^2} e^{i(\bar{k}' - \bar{k}'') \cdot \bar{r}} \quad (2-44)$$

has been used in obtaining (2-43).

The matrix element of  $\delta U$  may now be calculated and gives

$$\begin{aligned}
\langle \bar{k} + \bar{q} | \delta V | \bar{k} \rangle &= \int \psi_{\bar{k} + \bar{q}}^* \delta V \psi_{\bar{k}} dV \\
&= \frac{4\pi e^2}{(2\pi)^6} \sum_{\bar{k}' < \bar{k}_0} \sum_{\bar{k}''} \frac{[b^*(-\bar{k}', -\bar{k}') + b(\bar{k}'', \bar{k}')]}{|\bar{k}'' - \bar{k}'|^2} \int e^{i(\bar{k}' - \bar{k}'' + \bar{q}) \cdot \bar{r}} dV \\
&= \frac{4\pi e^2}{(2\pi)^3} \sum_{\bar{k}' < \bar{k}_0} \frac{[b^*(-\bar{k}' - \bar{q}, -\bar{k}') + b(\bar{k}' + \bar{q}, \bar{k}')] }{q^2}. \quad (2-45)
\end{aligned}$$

In arriving at (2-45) we have made use of the Dirac delta function in the form

$$\delta(\bar{k}) = \frac{1}{(2\pi)^3} \int e^{i\bar{k} \cdot \bar{r}} dV. \quad (2-46)$$

Since the operator  $\delta V$  is Hermitian, it has the property

$$\langle \bar{k}' | \delta V | \bar{k} \rangle^* = \langle -\bar{k}' | \delta V | -\bar{k} \rangle, \quad (2-47)$$

and we may write

$$b^*(-\bar{k}' - \bar{q}, -\bar{k}') = \frac{\langle \bar{k}' + \bar{q} | \delta V | \bar{k}' \rangle}{E_{\bar{k}'} - E_{\bar{k}' + \bar{q}} - i\epsilon}. \quad (2-48)$$

Making use of (2-37) and (2-48) we have

$$\langle \bar{k} + \bar{q} | \delta V | \bar{k} \rangle = \frac{e^2}{2\pi^2} \sum_{\bar{k}'} \frac{\langle \bar{k}' + \bar{q} | \delta V | \bar{k}' \rangle}{q^2} \left[ \frac{1}{E_{\bar{k}'} - E_{\bar{k}' + \bar{q}} + i\epsilon} + \frac{1}{E_{\bar{k}'} - E_{\bar{k}' + \bar{q}} - i\epsilon} \right]. \quad (2-49)$$

We now apply the identity

$$\lim_{\epsilon \rightarrow 0} \frac{1}{x \pm i\epsilon} = P \frac{1}{x} \mp i\pi \delta(x) \quad (2-50)$$

in which the symbol  $P$  indicates that the Cauchy principal part is to be taken in integration, that is

$$P \int_{-\infty}^{\infty} f(x) dx = \lim_{\epsilon \rightarrow 0} \left[ \int_{-\infty}^{-\epsilon} f(x) dx + \int_{\epsilon}^{\infty} f(x) dx \right].$$

From this definition we obtain the matrix element  $\delta U(\bar{q})$ ,

$$\begin{aligned} \delta U(\bar{q}) &= \langle \bar{k} + \bar{q} | \delta U | \bar{k} \rangle \\ &= \frac{e^2}{\pi^2} P \sum_{k' < k_0} \frac{\langle \bar{k}' + \bar{q} | \delta V | \bar{k}' \rangle}{q^2 \left( E_{\bar{k}'} - E_{\bar{k}' + \bar{q}} \right)}. \end{aligned} \quad (2-51)$$

Since (2-7) is the condition for self-consistency, the matrix of the required potential is given by

$$\langle \bar{k} + \bar{q} | \delta V | \bar{k} \rangle = \langle \bar{k} + \bar{q} | \delta V_0 | \bar{k} \rangle + \frac{e^2}{\pi^2} P \sum_{k' < k_0} \frac{\langle \bar{k}' + \bar{q} | \delta V | \bar{k}' \rangle}{q^2 \left( E_{\bar{k}'} - E_{\bar{k}' + \bar{q}} \right)} \quad (2-52)$$

This equation has the form of an inhomogeneous Fredholm integral equation of the first kind. Its solution for this particular case is trivial. The matrix of  $\delta V$  is independent of  $\bar{k}$ , and is dependent

only on  $\bar{q}$ , the difference between initial and final wave vectors.

Therefore the solution can be immediately obtained and is

$$\delta V(\bar{q}) = \delta V_0(\bar{q}) + \frac{e^2}{\pi^2 q^2} \delta V(\bar{q}) P \sum_{k' < k_0} \frac{1}{E_{k'} - E_{k'+\bar{q}}} \quad (2-53)$$

The sum in this equation has been calculated by Bardeen, who finds

$$\frac{e^2}{\pi^2 q^2} P \sum_{k' < k_0} \frac{1}{E_{k'} - E_{k'+\bar{q}}} = -\frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right), \quad (2-54)$$

with

$$\beta^2 = 6\pi e \frac{p_0}{E_0}$$

and

$$f_H(x) = \frac{1}{2} + \frac{1-x^2}{4x} \log \left| \frac{1+x}{1-x} \right|. \quad (2-55)$$

Therefore,  $\delta V(\bar{q})$ , the matrix of the self-consistent potential is determined, and has the value

$$\delta V(\bar{q}) = \frac{\delta V_0(\bar{q})}{1 + \frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right)} \quad (2-56)$$

$\delta V(\bar{r})$  is found by Fourier inversion to be

$$\delta V(\bar{r}) = \int \frac{\delta V_0(\bar{q})}{1 + \frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right)} e^{i\bar{q} \cdot \bar{r}} dV_q \quad (2-57)$$

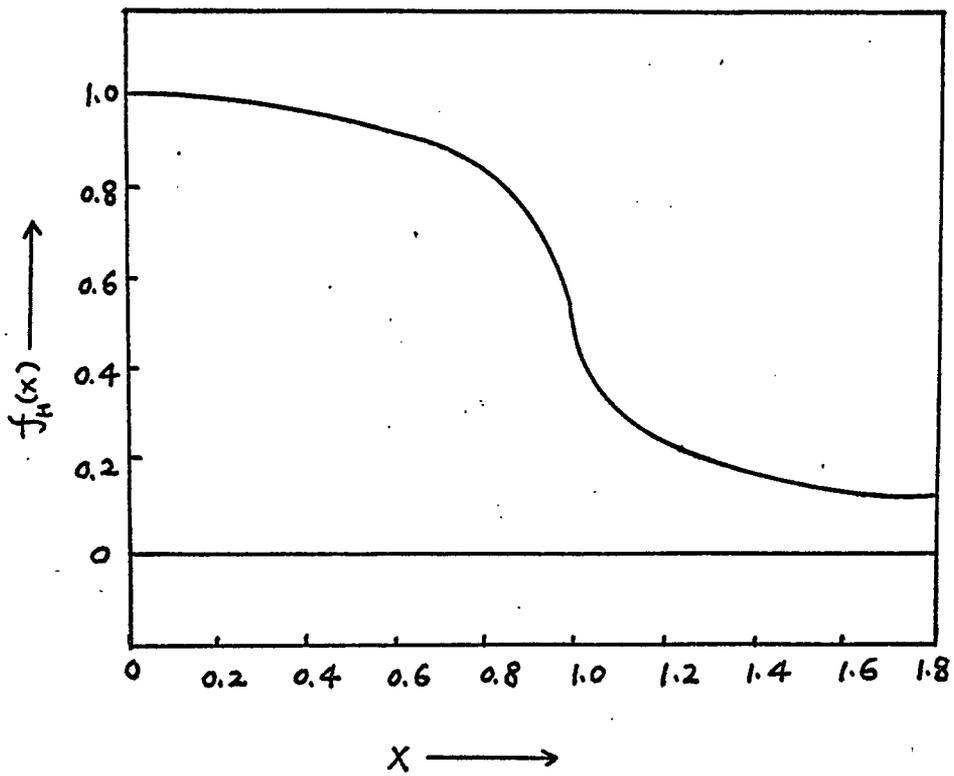
Comparison of equation (2-19) and (2-56) shows that the results of the perturbation theory reduce to that of the Thomas-Fermi approximation with the replacement  $f_H \rightarrow 1$ . Figure I shows the behavior of function  $f_H(x)$ .

### Plasma Oscillation in Metals

During recent years a theory of the interaction of electrons in metals has been developed which offers a simple justification of the independent particle approximation. This is the collective coordinate theory of Bohm and Pines.<sup>4,7-10</sup> The essence of the result of this theory may be interpreted in the following way. Suppose as a result of a chance fluctuation in the thermal motion, the electron charge density in some region is below the average density. Then the positive background charge attracts neighboring electrons to restore charge neutrality. But the attracted electrons acquire momentum and more electrons accumulate in the region than is necessary to neutralize the positive charge. The excess charge thus created repels electrons outward again, and so oscillations of the electron gas are set up. These are in fact plasma oscillations.

Because of the plasma oscillation, an electron can no longer interact independently with another electron. This is reasonable since, if one displaces an electron from an equilibrium position, the resulting electron cloud will produce a screening effect. This correlation in the motion of the electrons has been carefully studied by Bohm and

FIGURE I



$$f_H(x) \xrightarrow{x \rightarrow 0} 1 - \frac{1}{3}x^2$$

$$f_H(1) = \frac{1}{2}$$

$$f_H'(1) = -\infty$$

$$f_H(x) \xrightarrow{x \rightarrow \infty} \frac{1}{3x^2}.$$

Pines. They found that the potential energy between two electrons a distance  $|\bar{r}_i - \bar{r}_j|$  apart was no longer of the Coulomb form, but effectively was given by

$$V(\bar{r}_i - \bar{r}_j) = \sum_{k < k_c} \frac{4\pi e^2}{k^2} e^{i\bar{k} \cdot (\bar{r}_i - \bar{r}_j)}, \quad (2-58)$$

where  $k_c = 0.35 r_0^{-1/2} k_0$  is that value which minimized the total energy of the system.

The sum in (2-58) may be evaluated in the limit of large normalization volume and there results

$$\begin{aligned} V(\bar{r}_i - \bar{r}_j) &= \sum_{k < k_c} \frac{4\pi e^2}{k^2} e^{i\bar{k} \cdot (\bar{r}_i - \bar{r}_j)} \\ &= \frac{e^2}{|\bar{r}_i - \bar{r}_j|} F(k_c |\bar{r}_i - \bar{r}_j|), \end{aligned} \quad (2-59)$$

where

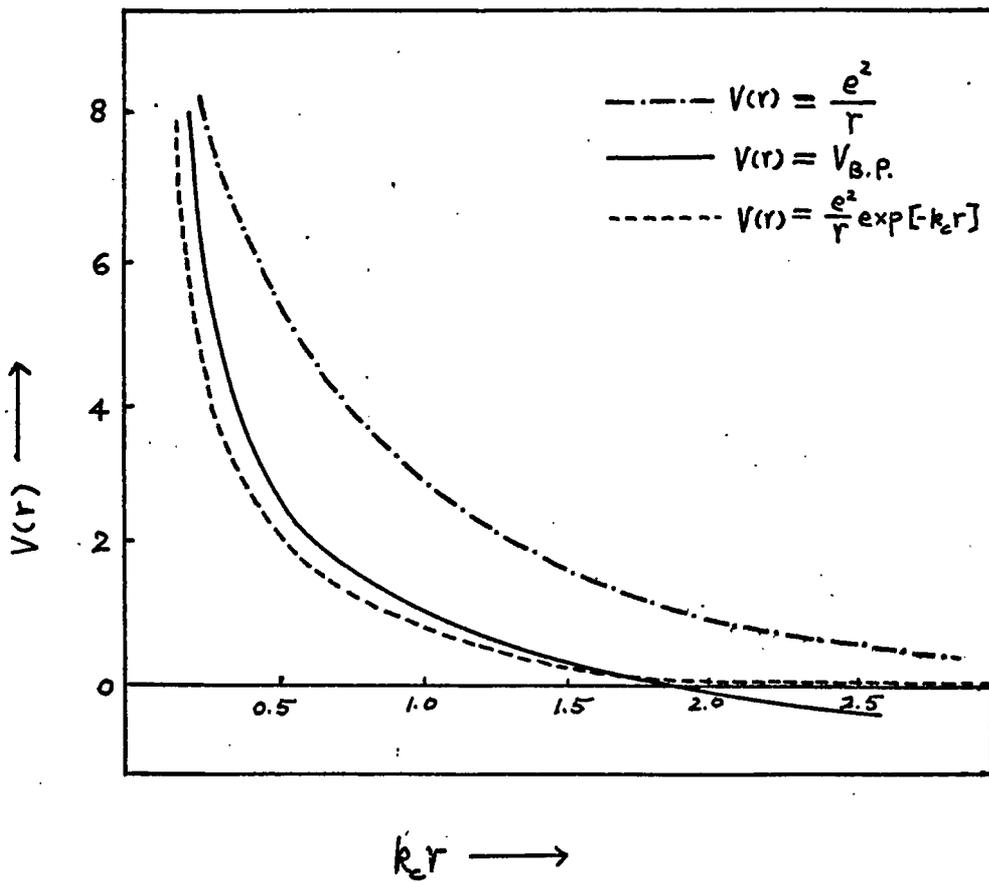
$$F(z) = 1 - \frac{z}{\pi} S_i(z), \quad (2-60)$$

with

$$S_i(z) = \int_0^z \frac{\sin t}{t} dt. \quad (2-61)$$

A sketch of  $V(\bar{r})$  is shown in Figure II.

FIGURE II



Perturbation Theory with Bohm-Pines Short-Range Interaction

In the Bohm-Pines plasma theory<sup>10</sup> the potential of two electrons a distance  $|\bar{r}_i - \bar{r}_j|$  apart due to the short-range interaction is effectively

$$\sum_{k < k_c} \frac{4\pi e^2}{k^2} e^{i\bar{k} \cdot (\bar{r}_i - \bar{r}_j)}$$

Using a similar analysis to that described in section 3 of this chapter, but replacing the Coulomb interaction by Bohm-Pines result, one may obtain the self-consistent potential  $\delta V(\bar{q})$  as

$$\delta V_{B.P.}(\bar{q}) = \delta V_0(\bar{q}), \quad \text{for } \bar{q} \leq \bar{k}_c; \quad \left. \right\} \quad (2-62)$$

and

$$\delta V_{B.P.}(\bar{q}) = \frac{\delta V_0(\bar{q})}{1 + \frac{\beta^2}{q^2} f_H\left(\frac{q}{2\hbar_0}\right)}, \quad \text{for } \bar{q} > \bar{k}_c,$$

where  $f_H(x)$  and  $\beta$  are the same as defined earlier in this chapter. The analysis leading to this result is similar to the previous analysis and will not be repeated here.

The asymptotic behavior of  $\delta V_{B.P.}(\bar{q})$  shows that

$$\delta V_{B.P.}(\bar{q}) \xrightarrow{q \rightarrow 0} \infty$$

which indicates that  $\delta V(\bar{r})$  must behave for large  $r$  as  $r^{-n}$  with  $n \leq 3$ . This is in conflict with the fact that the impurity must be shielded. The reason for this contradiction is that we have

considered only the Bohm-Pines short-range interaction which tends to pile the electrons around the impurity. We have neglected all exchange effects which give rise to a repulsion between electrons of like spins. If we consider "exchange" terms, it becomes very difficult to solve the resulting integral equation corresponding to that given by equation (2-52). The results of the treatment by Bohm and Pines indicates that there would be little difference between this calculation and that given by the simple Hartree theory. For these reasons, we consider only the Hartree theory for purposes of numerical calculations.

#### The Condition for Self-Consistency

The meaning of a self-consistent potential is that the potential in which a system of electrons is assumed to move must be such as to produce wave functions for the electrons which gives rise to the same potential. Therefore the potential  $\delta V(\vec{r})$  obtaining by Fourier transformation

$$\delta V(\vec{r}) = \int \delta V(\vec{q}) e^{i\vec{q} \cdot \vec{r}} dV_{\vec{q}}$$

should be self-consistent at least in the first order approximation. To obtain an exactly self-consistent potential, it would be necessary to solve the Schroedinger equation for electrons of all energies less than Fermi energy. Then a new potential  $\delta V(\vec{r})$  could be evaluated from the resulting wave functions. Since the electronic wave functions

extend throughout space and the necessary integrals would be difficult to determine with any precision, this is an almost impossible task. Instead, can we perform a test to verify the self-consistency of an assumed potential? Friedel<sup>11</sup> has given an affirmative answer in his "sum rule" which results from the following simple argument.

Friedel replaced the periodic boundary conditions by a perfectly reflecting spherical surface of a large radius  $R$ . The wave function for the unperturbed electrons are spherical Bessel functions which have the limiting behavior

$$j_l(kr) \xrightarrow{r \rightarrow \infty} \frac{1}{kr} \sin(kr - \frac{l}{2}\pi).$$

Similarly the wave functions for electrons after being scattered by a potential are

$$R_l(kr) \xrightarrow{r \rightarrow \infty} \frac{1}{kr} \sin(kr - \frac{l}{2}\pi + \delta_l).$$

Here  $k$  is the wave vector,  $l$  is the angular momentum quantum number, and  $\delta_l$  is the phase shift resulting from the scattering.

Since it has been assumed that there is a perfectly reflecting boundary surface at  $R$ , the wave functions should vanish there. This gives the allowed values of  $k$  for the unperturbed system. These values are

$$kR - \frac{l}{2}\pi = m\pi,$$

and for the perturbed system

$$kR - \frac{l}{2}\pi + \delta_l = n\pi.$$

Thus the change in wave vector for two consecutive allowed values of  $k$  are

$$\Delta k R = \pi,$$

and

$$\Delta k R + \Delta k \frac{\partial \delta_l}{\partial k} = \pi$$

respectively. Therefore the number of states per increment of  $k$  introduced by the perturbation is  $\frac{1}{\pi} \frac{\partial \delta_l}{\partial k}$  for each  $l$ .

The total change of the number of states up to some value  $k$  is

$$\Delta N = \frac{1}{\pi} \int_0^k \frac{\partial \delta_l}{\partial k} dk = \frac{1}{\pi} [\delta_l(k) - \delta_l(0)]. \quad (2-63)$$

Suppose the perturbation introduced is due to a change  $Z e$ . In order that this be shielded at  $R \rightarrow \infty$ , there must be introduced enough states to hold  $Z$  electrons below the Fermi level. Since each angular momentum eigenstate has an orbital degeneracy of  $(2l+1)$ , and since each state can hold two electrons because of spin, the total number of states introduced below Fermi-energy is

$$Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) [\delta_l(k_0) - \delta_l(0)]. \quad (2-64)$$

This is the Friedel sum rule, and must be satisfied by a self-consistent potential.

It should be pointed out that the behavior of the phase shift for vanishingly small energy is such that<sup>18</sup>

$$\delta_l(0) = n_l \pi, \quad (2-65)$$

where  $n_l$  is the number of bound states of orbital angular momentum  $l$ . Hence for the case of a weak attraction potential possessing no bound states or for an arbitrary repulsive potential, the sum rule is

$$Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \delta_l(k_0) . \quad (2-66)$$

Recently Rawls and Schulz<sup>19</sup> have suggested a classical treatment for the calculation of selected energy levels in a Yukawa potential that utilizes the Bohr theory. They also obtained an expression for the number of bound states of given angular momentum. Since our screened potential is similar to the Yukawa type, we may use their treatment to estimate the maximum  $r_0$  for which no bound state appears. For  $r_0 > (r_0)_{max.}$ , the potential is strong enough to produce bound states. This implies that the first order perturbation theory is no longer valid for this potential. Thus our estimate of  $(r_0)_{max.}$  is an upper bound in the validity of our calculations.

Rawls and Schulz found that the smallest value of  $\beta$  for which no bound state of zero angular momentum corresponding to the principal quantum number  $n$  can occur is given by

$$\beta = 0.736 \frac{Z}{n^2} . \quad (2-67)$$

Taking  $\beta$  to be that resulting from the statistical treatment of section 1, that is

$$\beta = \left( 6\pi e \frac{f_0}{E_0} \right)^{\frac{1}{2}} = 1.56 r_0^{-\frac{1}{2}} ,$$

we find that the maximum atomic radius for producing no bound states is

$$(\gamma_0)_{\max.} = \left(\frac{2.1}{Z}\right)^2 \quad (2-68)$$

From equation (2-68), we may expect that for  $Z = +1$ ,  $\gamma_0 < 4.41 \text{ A.U.}$

and for  $Z = +2$ ,  $\gamma_0 < 1.21 \text{ A.U.}$  our theory should be valid.

CHAPTER III

NUMERICAL PROCEDURES

A point impurity of charge  $ze$  gives rise to the unscreened potential  $\delta V_0(\vec{r})$  whose matrix is

$$\delta V_0(\vec{q}) = \frac{4\pi ze^2}{q^2} . \quad (3-1)$$

Substitution of (3-1) into (2-56) yields

$$\delta V(\vec{q}) = \frac{\frac{4\pi ze^2}{q^2}}{1 + \frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right)} . \quad (3-2)$$

We then obtain the self-consistent potential  $\delta V(\vec{r})$  as

$$\delta V(\vec{r}) = \frac{2e^2}{\pi r} \int_0^\infty \frac{1}{1 + \frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right)} \cdot \frac{\sin qr}{q} dq . \quad (3-3)$$

Since the function  $f_H(x)$  defined by equation (2-55) has the asymptotic behavior

$$f_H(x) \xrightarrow{x \rightarrow \infty} \frac{1}{3x^2} ,$$

we choose a value  $q_{\max}$  such that

$$\frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right) \approx \frac{4\beta^2 k_0^2}{3q^4} \ll 1 .$$

Then we may rewrite equation (3-3) as

$$\delta V(\bar{r}) \approx \frac{2e^2}{\pi r} \left[ \int_0^{q_{\max}} F(q) \sin qr \, dq + \int_{q_{\max}}^{\infty} \frac{\sin qr}{q} \, dq \right], \quad (3-4)$$

with

$$F(q) = \frac{1}{q \left[ 1 + \frac{\beta^2}{q^2} f_H\left(\frac{q}{2k_0}\right) \right]}. \quad (3-5)$$

To evaluate  $\delta V(\bar{r})$ , many numerical integrations must be performed.

The first part of  $\delta V(\bar{r})$ , in equation (3-4) has the form

$$g(r) = \int_a^b F(q) \sin qr \, dq.$$

Ordinary techniques of numerical integration, particularly for large value of  $r$ , are difficult to apply due to the rapid oscillation of  $\sin qr$ . Filon<sup>20</sup> has given a method of performing integrations of this type by a generalization of Simpson's rule. If the range of integration is divided into  $2n$  intervals of equal length  $h$ , Filon has shown that the integral may be approximated by

$$g(r) = h \left\{ \alpha [F(a) \cos ka - F(b) \cos kb] + \beta S_{2p} + \gamma S_{2p-1} \right\}. \quad (3-6)$$

with

$$\alpha = \frac{1}{\theta} + \frac{\cos \theta \sin \theta}{\theta^2} - \frac{2 \sin^2 \theta}{\theta^3}$$

$$\beta = 2 \left[ \frac{(1 + \cos^2 \theta)}{\theta^2} - \frac{2 \sin \theta \cos \theta}{\theta^3} \right]$$

$$\Upsilon = 4 \left[ \frac{\sin \theta}{\theta^3} - \frac{\cos \theta}{\theta^2} \right]$$

$$S_{2p} = \sum_{p=0}^n F(a+2ph) \sin [k(a+2ph)] - F(a) \sin ka - F(b) \sin kb$$

$$S_{2p-1} = \sum_{p=0}^n F(a+\overline{2p-1}h) \sin [k(a+\overline{2p-1}h)]$$

$$\theta = hk .$$

The error involved in the use of this integration formula is approximately the same as the error inherent in the evaluation of

$$\int_a^b F(q) dq$$

by Simpson's rule.

The second part of the integration in (3-4) can be rewritten as

$$\begin{aligned} \int_{q_{\max}}^{\infty} \frac{\sin qr}{q} dq &= \frac{\pi}{2} - \int_0^{q_{\max}} \frac{\sin qr}{q} dq , \\ &= \frac{\pi}{2} - S_i(q_{\max} r) , \end{aligned}$$

where  $S_i(z)$  is the ordinary sine integral.

In this way, a tentative self-consistent potential was calculated by means of equation (3-4). Using this potential the scattering phase shifts were determined, and from them the Friedel sum obtained. The departure of this sum from its required value is a measure of the lack of self-consistency.

The required phase shifts were obtained by ordinary methods as described by Schiff,<sup>15</sup> namely

$$\tan \delta_2 = \frac{k j_2'(z) - d_2(z) j_2(z)}{k n_2'(z) - d_2(z) n_2(z)} \Big|_{z=ka}$$

where  $d_2$  is the ratio of the wave function to its derivative for energy corresponding to  $k$ , and  $a$  is the radius for which the scattering potential is sufficiently small. For the numerical evaluation of the phase shifts, a computer program written by Mayes<sup>21</sup> was used. A description of this program can be found in Mayes' thesis.

Our calculations were carried out for four cases, namely for  $Z = +1, +2, -1$  and  $-2$ . Figure III shows plots of the phase shift sum against atomic radius  $\gamma_0$ . From these data one may ascertain the range of  $\gamma_0$  for which self-consistency approximately holds. Since for these four cases the region of self-consistency is around  $\gamma_0 = 0.5 \text{ A.U.}$ , one concludes that the perturbation treatment is not valid for real metals at least for point impurities. This follows since the range of  $\gamma_0$  for typical metals is from  $2.66 \text{ A.U.}$  to  $5.72 \text{ A.U.}$  Figure IV shows a plot of the self-consistent potential for  $Z = +1$  and  $\gamma_0 = 0.5 \text{ A.U.}$ , that value of  $\gamma_0$  producing self-consistency. We have also given a plot of  $2e^{-\beta r}$  on this figure to show the comparison of the results from statistical and quantum mechanical treatments. It is seen that these are very similar to each other. Table I gives

a list of  $\gamma$  and  $\gamma * V$  for  $Z = +1$  and  $\gamma_0 = 0.5 A.U.$

From these data we may observe a significant fact, namely the long range oscillation of the perturbing potential surrounding a localized impurity. This phenomena can be explained on the basis of Walker's<sup>12</sup> expression for the displaced charge density which behaves asymptotically as

$$\Delta \rho \xrightarrow[r \rightarrow \infty]{} \frac{-e\alpha}{2\pi^2 r^3} \cos(2k_0 r + \phi)$$

with

$$\alpha \cos \phi = \frac{1}{2} \sum_{\ell} (-)^{\ell} (2\ell+1) \sin 2\delta_{\ell}(k_0)$$

$$\alpha \sin \phi = \sum_{\ell} (-)^{\ell} (2\ell+1) \cos 2\delta_{\ell}(k_0)$$

It is clear that an asymptotically oscillating charge density gives rise to a similarly oscillating potential.

FIGURE III

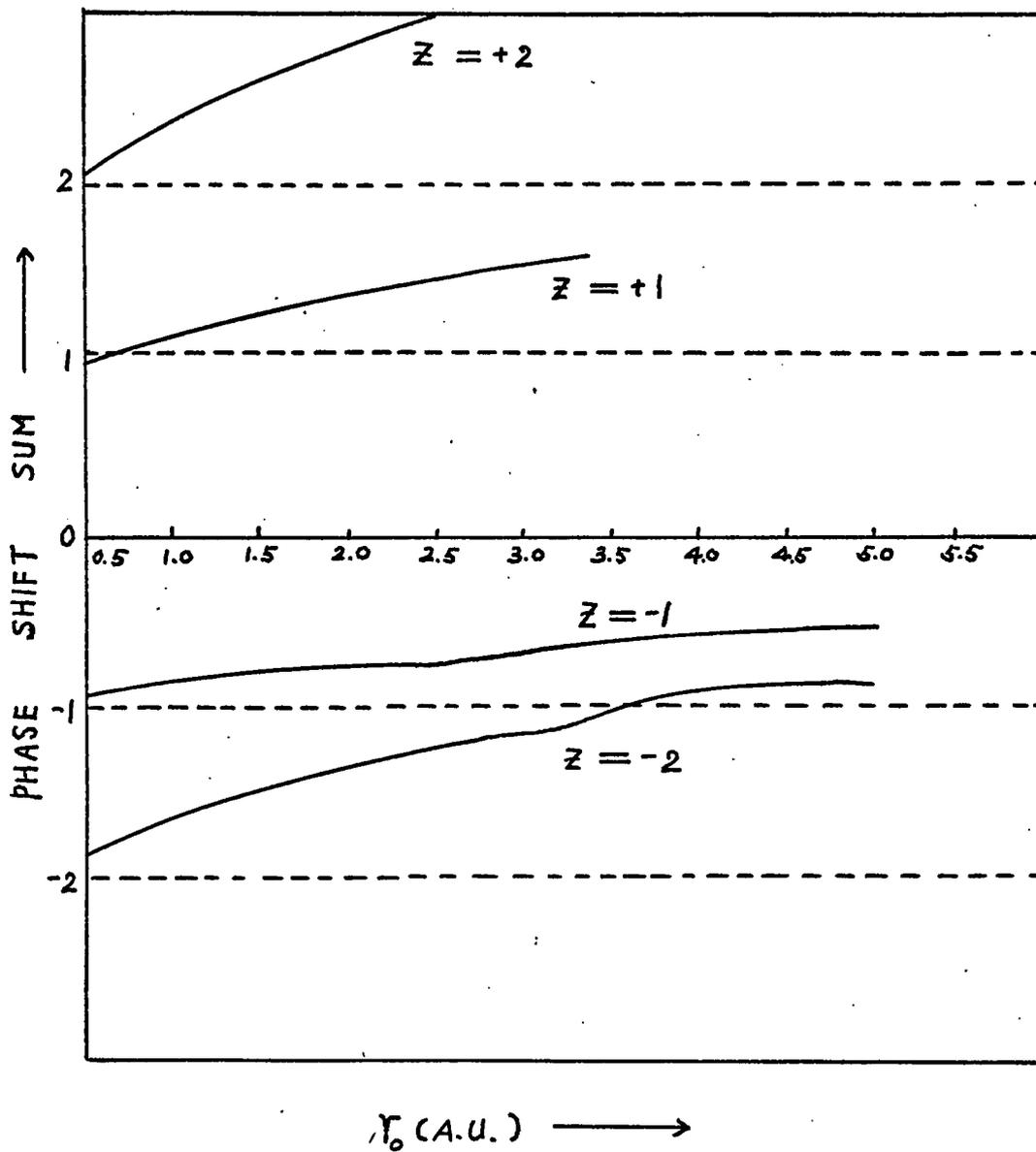


FIGURE IV

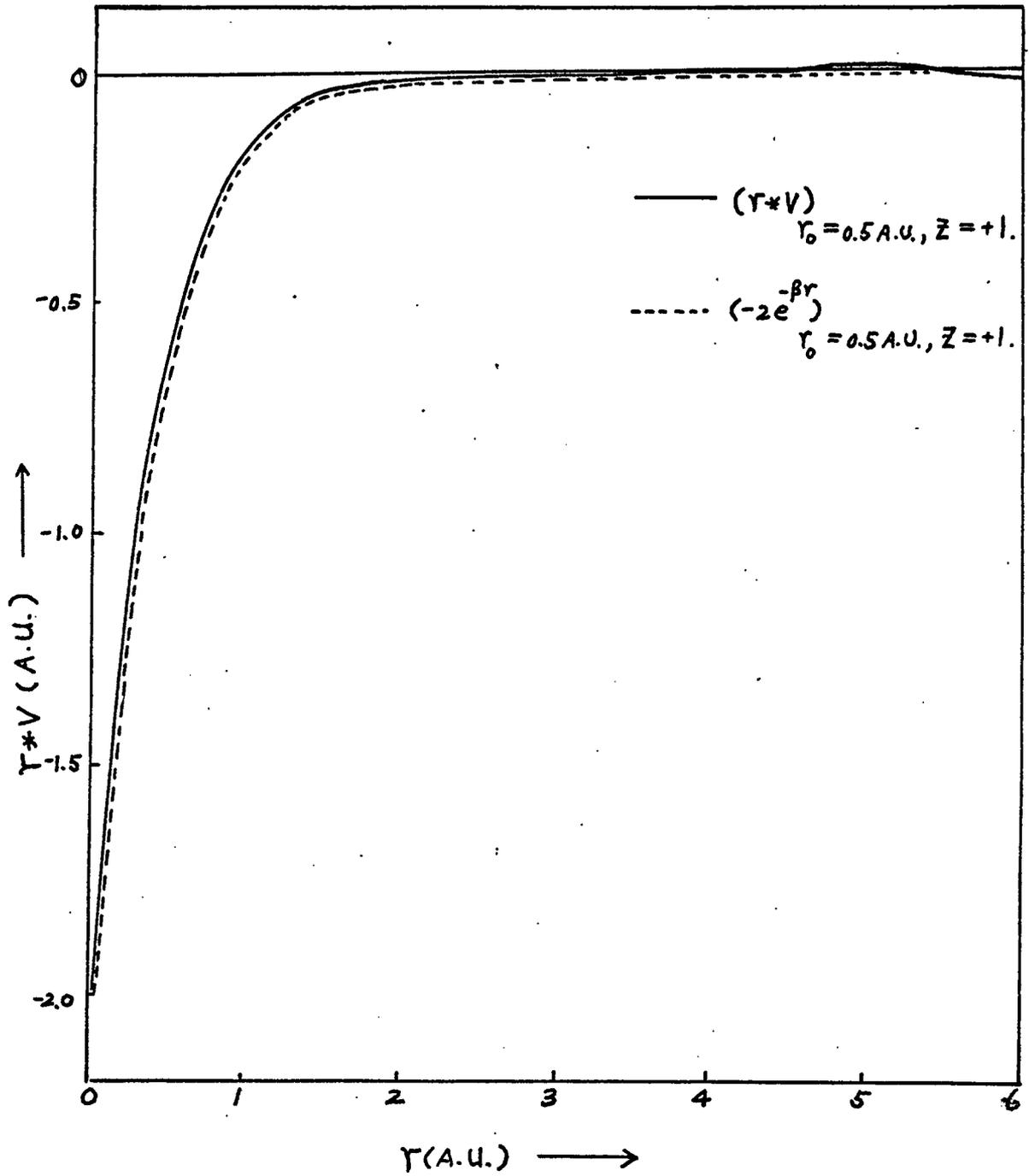


TABLE I

THEORETICAL DATA OF  $r^*V$  FOR  $Z = +1$  AND  $r_0 = A.U.$ 

| $r$<br>(A.U.) | $r^*V$<br>(A.U.) |
|---------------|------------------|
| 0.05000       | -1.99660         |
| 0.05500       | -1.80410         |
| 0.10500       | -1.63103         |
| 0.15500       | -1.46643         |
| 0.20499       | -1.31290         |
| 0.30499       | -1.04382         |
| 0.40499       | -0.82700         |
| 0.50499       | -0.65728         |
| 0.60499       | -0.52561         |
| 0.70499       | -0.42246         |
| 0.80499       | -0.33997         |
| 0.90499       | -0.27273         |
| 1.00499       | -0.21756         |
| 1.20499       | -0.13691         |
| 1.40499       | -0.08735         |
| 1.60499       | -0.05697         |
| 1.80499       | -0.03642         |
| 2.00499       | -0.02249         |
| 2.20499       | -0.01433         |
| 2.60499       | -0.00622         |
| 3.00499       | -0.00224         |
| 3.40499       | -0.00115         |
| 3.80499       | -0.00027         |
| 4.40499       | -0.00003         |
| 4.48499       | +0.00003         |
| 4.64499       | 0.00001          |
| 4.80499       | -0.00010         |
| 5.04499       | -0.00009         |
| 5.20499       | 0.00003          |
| 5.36499       | 0.00007          |
| 5.44499       | 0.00005          |
| 5.60499       | -0.00004         |
| 5.76499       | -0.00008         |
| 6.08499       | 0.00005          |
| 6.16499       | 0.00006          |
| 6.24499       | 0.00005          |
| 6.32499       | 0.00001          |
| 6.40499       | -0.00002         |
| 6.56499       | -0.00006         |

TABLE I (Continued)

| $r$<br>(A.U.) | $r \cdot V$<br>(A.U.) |
|---------------|-----------------------|
| 6.72499       | -0.00002              |
| 6.88499       | 0.00004               |
| 6.96499       | 0.00005               |
| 7.04499       | 0.00004               |
| 7.12499       | 0.00002               |
| 7.20499       | -0.00001              |
| 7.36499       | -0.00005              |
| 7.60499       | 0.00001               |
| 7.76499       | 0.00004               |
| 7.84499       | 0.00003               |
| 7.92499       | 0.00002               |

## CHAPTER IV

### CONCLUSIONS

A first order perturbation theory for an electron gas based upon Hartree's approximation has been developed which yields a self-consistent potential around given impurities. Mathematical complexities make it necessary to use the plane wave approximation to describe their unperturbed motion. Numerical calculations have been carried out based upon the theoretical formulations. The results of perturbation theory was compared with that resulting from the statistical approximation and the differences between these results were found to be very small. Perturbation theory, contrary to the statistical theory, predicts long range oscillations in the potential. Friedel's sum rule was applied as a test of self-consistency of the calculated potentials. The result of this work indicates that neither the statistical treatment nor the perturbation treatment are valid for real metals, at least for point impurities. It appears the only way to formulate the problem within the framework of Quantum Mechanics is to extend the calculation to second or higher order perturbation theory for which the mathematical difficulties seem intractable.

## REFERENCES

1. G. F. Koster and J. C. Slater, Phys. Rev. 1167 (1954).
2. A. De Pre, Thesis, M.I.T. (1957).
3. L. Roth, Thesis, Harvard University (1956).
4. S. Raines, The Wave Mechanics of Electrons in Metals. (Amsterdam: North-Holland Publishing Company, 1961).
5. J. Bardeen, Phys. Rev. 52, 688 (1937).
6. D. R. Hartree, Proc. Cambridge Phil. Soc. 24, 89 (1928).
7. D. Bohm and D. Pines, Phys. Rev. 80, 903 (1950).
8. D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951).
9. D. Bohm and D. Pines, Phys. Rev. 85, 338 (1952).
10. D. Bohm and D. Pines, Phys. Rev. 92, 609 (1953).
11. J. Friedel, Suppl. Nuovo Cimento 2, 287 (1958).
12. R. H. Walker, Thesis, M.I.T. (1962).
13. P. M. Morse and H. Feshbach, Method of Theoretical Physics. (New York: McGraw-Hill, 1953).
14. N. F. Mott, Proc. Phys. Soc. 46, 680 (1934).
15. L. I. Schiff, Quantum Mechanics (New York: McGraw-Hill, 1955).
16. E. P. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).
17. J. C. Slater, Phys. Rev. 81, 385 (1951).
18. N. Levinson, Kel. Danske Vid. Sels., Mat-fys. Medd. 25, No. 9 (1948).
19. J. M. Rawls and M. Schulz, Am. J. Phys. 33, No. 6, 444 (1965).
20. L. N. G. Filon, Proc. Roy. Soc. Edinburg, 49, 38 (1928).
21. B. Mayes III, Thesis, University of Houston (1965).