A SIMPLE MODEL FOR STUDYING THE GRAVITATIONALLY INDUCED ELECTRIC FIELD INSIDE A METAL

by

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ABSTRACT

If a metal object is placed in a gravitational field, the nuclei and electrons in the metal will sink. This will produce a new charge distribution inside the metal. A modified charge distribution implies a modified electric field in the metal interior.

This thesis investigates some possible physical processes which give rise to the gravitationally induced electric field inside a metal. To this end, a simple model of a metal is constructed.

Comprising the model are ions, arranged on a differentially compressed lattice, and a gas of conduction electrons. An ion is represented by a nucleus and an electron which are confined together inside a hard, massless, spherical shell. The nucleus is treated as a point particle while the electron is represented by a wave function. The conduction electron constituent is modelled as a gas of noninteracting fermions which is subject to an external linear potential.

The design of the model facilitates the investigation of two possible sources of the electric field: gravitationally induced ionic dipole moments, and the charge imbalance in the metal. To first order in $g$ only the first source matters, contributing approximately $-Mg^*/q_e$ to the electric field, where $M$ is the ionic mass, $g^*$ is the acceleration due to gravity, and $q_e$ is the electronic charge. The net gravitationally induced electric field is also found to be approximately $-Mg^*/q_e$. 
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NOTE ON NUMBERING OF EQUATIONS, FOOTNOTES, AND REFERENCES TO THE LITERATURE

Equations are numbered individually in each section of each chapter: equation (7.4), for example, means the fourth equation of section 7. In a given chapter, if an equation is referred to from another chapter, the chapter number is included. Otherwise it is not. Equation (2-2.3) means the third equation in the second section of chapter 2, whereas equation (2.3) means the third equation of the second section of the present chapter.

Footnotes are numbered consecutively throughout a chapter. They are denoted by curved parentheses: (3) means the third footnote in the present chapter. The footnotes are listed at the end of the chapter.

References to the literature are symbolized by square brackets: [9] refers to the ninth item listed in the Bibliography.
CHAPTER 1

INTRODUCTION

(1.1) STATEMENT AND ORIGIN OF THE PROBLEM

If a metal object is placed in a gravitational field, a macroscopic electric field will be created in the interior of the metal. The electric field results because gravity causes the nuclei and electrons to reside at positions which are different than their corresponding positions in zero gravitational field. A different positioning of the nuclei and electrons implies a different charge density inside the metal. A modified internal charge density produces a modified electric field in the metal interior. For similar reasons, gravity also induces an electric field exterior to the metal.

The following problem will be considered in this thesis: what is the gravitationally induced electric field in a metal, and what are the main physical processes which give rise to this electric field?

The interest in such gravitationally induced electric fields first arose because of a series of experiments by Witteborn and Fairbank\(^{[8]}\) designed to measure the acceleration of ions, electrons, and positrons in the earth's gravitational field. To shield against external electrostatic fields, the particles were constrained to fall in a cavity formed by a
conductor. The results of the experiments seemed to indicate that an electric field $mg/q_e$ pervaded the cavity of the conductor, where $m$ was the electron mass, $g$ the acceleration due to gravity, and $q_e$ the electronic charge. Witteborn suggested that gravity had affected the conductor in such a way as to induce the electric field $mg/q_e$ inside the cavity.

Schiff and Barnhill then did the first theoretical calculation of the gravity-induced electric field $E_{\text{ext}}$ in a cavity surrounded by a metal. The result of their calculation was $E_{\text{ext}} = mg/q_e$. However, another theoretical calculation was done by Dessler, Michel, Rorschach and Trammell. They obtained for $E_{\text{ext}}$ a field directed oppositely to $g$ and with a magnitude of approximately $Mg/q_e$, where $M$ is the ionic mass. Besides being in opposite directions, these two electric fields differ in strength by approximately five orders of magnitude!

To confuse the issue, this discrepancy has been observed experimentally as well. Fairbank, Lockhart and Witteborn reported a temperature dependence of $E_{\text{ext}}$: they found the magnitude of $E_{\text{ext}}$ to vary from about $mg/q_e$ at low temperatures to about $Mg/q_e$ at higher temperatures, with a transition at about 4 K.

Schiff and Barnhill also examined the question of the gravitationally induced electric field $E_{\text{int}}$ inside a metal. They claimed that $E_{\text{int}}$ would be approximately $mg/q_e$. Dessler et. al. calculated $E_{\text{int}}$ and concluded that it would be opposite to $g$ and have a magnitude of approximately $Mg/q_e$.

This discrepancy is rather interesting. This introduction
now presents a brief description of the techniques employed in the literature to calculate \( \mathbf{E}_{\text{ext}} \) and \( \mathbf{E}_{\text{int}} \).

(1.2) REVIEW OF THE LITERATURE

The approach Schiff and Barnhill used to calculate \( \mathbf{E}_{\text{ext}} \) was to introduce a classical test particle of infinitesimal charge into the cavity formed by the conductor. They showed that \( \mathbf{E}_{\text{ext}} \) could be expressed in terms of the shift induced by the test charge in the location of the vertical component of the center of the mass of the conductor. In their analysis, Schiff and Barnhill ignored the shift contributed by the nuclei. They calculated only the contribution of the electronic constituent of the metal, and obtained \( mg/\epsilon_0 \) for \( \mathbf{E}_{\text{ext}} \).

In their paper, Schiff and Barnhill also briefly discussed the internal electric field, and made the following claim:

It is apparent that each electron and nuclei in the metal must be acted upon by an average electric field of such magnitude that it exactly balances its weight.\(^{(1)}\)

For an electron, this field is \( mg/\epsilon_0 \). They further argued that, because the electrons occupy most of the volume of the metal and the nuclei only a small fraction, \( \mathbf{E}_{\text{int}} \) is very close to \( mg/\epsilon_0 \). This same field, they stated, would be expected inside the cavity of the conductor.
Dessler et. al. pointed out that Schiff and Barnhill had not taken into account the compression of the metal in the direction of the gravitational field. They presented the following heuristic discussion about $\vec{E}^{\text{int}}$.

The net charge density inside the metal must be very small, for otherwise there would result a huge internal electric field. Using elasticity theory, it is easy to calculate the number density of ions as a function of height inside the metal. Charge neutrality then gives the number density of electrons as a function of height. Treating the electrons, locally, as a free Fermi gas allows one to in turn compute the pressure gradient experienced by the electrons. Balancing this force against the electric and gravitational forces felt by the electrons gives $\vec{E}^{\text{int}}$. The final expression obtained by this approach is

$$\vec{E}^{\text{int}} = (m - \frac{2}{3} \varepsilon_F q_i \frac{1 - 2\sigma}{Y} M) \vec{g}/q_e$$  \hspace{1cm} (1)$$

where $\varepsilon_F$ is the Fermi energy of the electron gas, $q_i$ is the average number density of ions in the metal, $\sigma$ is the Poisson ratio of the metal and $Y$ its Young's modulus.

Dessler et. al. pointed out that typical values for metals for the parameters in equation (1) give $\vec{E}^{\text{int}}$ oppositely directed to $\vec{g}$ and with a magnitude of the order of $Mg/q_e$.

In their paper, Dessler et. al. also calculated $\vec{E}^{\text{ext}}$, again obtaining a field opposite to $\vec{g}$ and of the order of $Mg/q_e$. 
Subsequent to the work of Dessler et. al., Herring reexamined the Schiff and Barnhill approach to the problem. He found that the shift induced by the test charge in the mass moment of the nuclear constituent of the metal was much greater than that of the electronic constituent. Herring estimated that the cavity field would be of the order of $Mg/q_e$ and opposite to $\vec{g}$.

The basic physical ideas and assumptions of the Dessler et. al. heuristic discussion have been restated by Harrison and Leung but in different terms. Leung, for example, used the Boltzmann transport equation to obtain equation (1) for $E_{\text{int}}^\text{'n't}$.

Dessler et. al. went beyond their heuristic discussion in attempting to determine $E_{\text{int}}^\text{'n't}$. They introduced a model of a metal which they used to derive the following equation for $E_{\text{int}}^\text{'n't}$:

$\vec{E}_{\text{int}} = \left(m g \vec{q} - \nabla \mu\right)/q_e$ ,

(2)

where $\mu$ is the local chemical potential of electrons in the metal. They then assumed that $\mu$ depends only on the local number density of electrons $n$ at the height $z$, and replaced $\nabla \mu$ by $(\partial \mu/\partial n)(\partial n/\partial z)$. Assuming charge neutrality, they calculated $\partial n/\partial z$ from elasticity theory. Estimating $\partial \mu/\partial n$ gave them an estimate for $E_{\text{int}}^\text{'n't}$. Again they found $E_{\text{int}}^\text{'n't}$ to be opposite to $\vec{g}$ and to have a magnitude of order $Mg/q_e$.

Peshkin presented an expression for $E_{\text{int}}^\text{'n't}$ similar to equation (2):

$E_{\text{int}}^\text{'n't} = \left(m g \vec{q} - \nabla \mu^{(0)}\right)/q_e - \vec{F}$

(3)
where \( \mu^{(0)} \) is the local chemical potential for free electrons. \( \Phi \) is a correction to account for the effects not included in the free electron representation. \( \mathbf{E}^{\text{in}} \) may be estimated from equation (3) if an estimate for \( \Phi \) is available. As such, equations (2) and (3) may be regarded to be the same.

One other approach has been presented in the literature for the purpose of finding \( \mathbf{E}^{\text{int}} \). Rieger calculated \( \mathbf{E}^{\text{int}} \) via a consideration of the electron-phonon interaction. He first determined a transformation between the usual phonon operators when there is no gravity and the ones which apply when there is. Then, he replaced the former by the latter in the energy expression associated with the electron-phonon interaction. The result he obtained included a scalar part (i.e. it involved no phonon operators), which he interpreted as being the electrostatic potential energy experienced by the electrons due to the differential compression of the lattice.

Leung, Papini and Rystephanick criticized Rieger's analysis, partly because of his choice of normal modes for the lattice. They avoided choosing normal modes. Instead, they calculated the electrostatic potential felt by the electrons in terms of the deviation from periodicity of the lattice sites.

Both Rieger and Leung et. al. obtained \( \mathbf{E}^{\text{int}} \) oppositely directed to \( \mathbf{g} \) and of magnitude roughly \( Mg/q_e \).
PURPOSE OF THIS THESIS

The literature provides one with a partial understanding of what physical processes are important in this problem. The Dessler et. al. heuristic discussion, for example, points out the differential compression of the lattice due to gravity, and the pressure gradient experienced by the electrons as a result. In the literature, one also finds expressions for $\vec{E}^\text{int}$. However, one does not obtain from the literature an understanding of what the principal sources of $\vec{E}^\text{int}$ are. Nor does one learn how the metal responds to the gravitational field so as to support itself, or how this response generates the sources of $\vec{E}^\text{int}$.

Moreover, one does not feel quite convinced that $\vec{E}^\text{int}$ has in fact been found. The heuristic discussion of Dessler et. al. should be taken as an indication of some of the basic physical responses of a metal to a gravitational field and not as an unequivocal determination of $\vec{E}^\text{int}$. This is why Dessler et. al. constructed a model with which to calculate $\vec{E}^\text{int}$. But in equation (2) -- the result of their model -- it is not obvious that $\nabla \mu$ is any better known than $\vec{E}^\text{int}$, or that the assumptions Dessler et. al. made about $\mu$ are valid. Finally, Rieger and Leung et. al. both assumed that $\vec{E}^\text{int}$ was primarily due to the compression of the lattice. Again, it is not obvious that this is necessarily so.

In order to contribute to the understanding of this problem of the gravitationally induced electric field in a metal, this
thesis presents a simple model which includes some possible sources of $E^{int}$. The related challenge of finding $\vec{E}^{ext}$ shall not be considered here. (Attempts have been made by Hutson and Hanni to provide a theoretical explanation of the temperature dependance of $\vec{E}^{ext}$ reported by Fairbank, Lockhart and Witteborn.)

The basic features of the model are described in the next section of this introduction. The model has been designed with two basic purposes in mind. One is to calculate the average electric field inside a metal. The other to provide some physical insight into the problem of gravitationally induced electric fields in metals.

(1.4) OUTLINE OF THE MODEL

In this model, a metal shall be regarded as comprised of an ionic constituent and an electronic constituent.

The ions are represented by the following composite entity: a classical point particle of mass $M$ and charge $Z_n q_e$, and a single quantum mechanical electron, are enclosed together inside of a massless, undeformable, impenetrable shell (see figure 1). The point particle, treated classically, represents the nucleus of the ion. The electron, represented by a wave function, models the tightly bound electron cloud surrounding the nucleus. The net charge of the ion is $(Z_n-1)q_e$ and its mass is $M+m$.

The electronic constituent of the metal is modelled by a
noninteracting electron gas which will be spread throughout the inside of the metal.

The shells are arranged, locally, in a lattice pattern. However, they will be more tightly packed near the bottom of the metal than near the top. This differential packing is done in order to simulate a fact revealed by elastic theory: the density of an object placed in a gravitational field decreases with height. The differential packing may be achieved in one of two ways.

One way is to have the radii of these shells increase with height and to situate the shells in actual contact with one another, as in figure 2(a). The other way is to arrange the shells such that they do not touch one another. In this way, the number of shells per unit volume may diminish with height without requiring the radius of the shells to change (see figure 2(b)).

In either case, the change is very gradual: in a typical
metal bar 1 meter high, the density near the bottom of the bar is about one part in $10^6$ times greater than near the top\(^{(2)}\). As such the arrangement of the shells, locally, may be regarded to constitute a lattice pattern.

The reader may protest that, because of gravity, the shells
may not be arranged as in figure 2(b). Because of this possible objection, the following comment is made.

The model has been constructed to take into consideration some of the key physical phenomena which give rise to the gravitationally induced electric field inside a metal, hereupon denoted by $\mathbf{E}_{\text{ave}}$. However, the model does not purport to be realistic in all respects. In particular, for the purposes of calculating $\mathbf{E}_{\text{ave}}$ and providing physical insight into the problem of gravity induced electric fields, it is not important to distinguish between figures 2(a) and 2(b).

What is important is how the nucleus and electron within each shell respond to gravity: the function of the model is to give an idea of how a metal will be affected by a gravitational field.

Consider what will happen inside of each shell because of gravity. When there is no gravity, the nucleus will be at the center of the shell and the ground state wave function of the electron will be spherically symmetric. Gravity will displace both the nucleus and the electron downwards; in the case of the electron, this means that more of the electron will be in the lower half of the shell than in the upper half. The nucleus, being much heavier than the electron, will sink more than the electron. In consequence, the electron will hold the nucleus up against gravity.

This redistribution of charge inside the shell will endow the ion with a gravitationally induced dipole moment. It shall be shown in the next chapter that these ionic dipole moments are
a key source of $E_{\text{ave}}$.

The effect of gravity on the electronic constituent will be taken into account by regarding the noninteracting electron gas to be subject to an external linear potential. A calculation shall be made to determine the number density of those electrons as a function of height. The charge density as a function of height may be found by comparing the number densities of shells and electrons. This internal charge density represents another source of $E_{\text{ave}}$.

Gravity induces an electric field in the metal interior. The microscopic version of this field -- not $E_{\text{ave}}$! -- plays a key role in polarizing the ions. As such, this microscopic field must be taken into account in deriving the induced dipole moment. The microscopic field pervading a shell will be assumed from the outset to be uniform through the shell and have a nonzero component only in the vertical direction.

The macroscopic version of the gravity induced electric field, $E_{\text{ave}}$, will be regarded to influence the electronic constituent of the metal. Thus, the linear potential to which the electron gas is subject shall be taken as due to both gravity and $E_{\text{ave}}$. This assumes that $E_{\text{ave}}$ does not depend on height.

Several simplifying features have been incorporated into the model. The impenetrable shells were introduced so as to render tractable the solving of Schrödinger's equation for the electron. For the same reason, the electric field pervading the shell is assumed to be uniform. This assumption will be quite
good if the shells are arranged as in figure 2(b), and spaced far apart. The interactions between the individual conduction electrons as well as those between the electrons and the lattice, have been taken into account in an approximate manner, via the linear potential the electron gas experiences. In other words, it has been assumed that the detailed arrangement of the shells may be ignored. Conceptually, this is much the same as the free electron approximation, which is made for metals in zero gravitational field and with zero internal net charge density. Finally, $E_{\text{ave}}$ has been assumed to be independent of height. Actually, $E_{\text{ave}}$ varies with height, but only slightly. This claim will be verified.

The sources of $E_{\text{ave}}$ are the ionic dipoles, which contribute an average electric field $E_{\text{dipoles}}$, and the internal charge density, giving rise to a field $E_{\text{ch}}$. The field due to all other sources -- such as charge external to the metal, the surface charge density, and the surface dipole density -- shall be included together by a term $E_{\text{ext}}$. The equation for $E_{\text{ave}}$ is

$$\vec{E}_{\text{ave}} = \vec{E}_{\text{dipoles}} + \vec{E}_{\text{ch}} + \vec{E}_{\text{ext}}.$$  \hfill (4)

In Chapter 2, $E_{\text{dipoles}}$ will be calculated. The result will be that $E_{\text{dipoles}}$ is opposite to $\mathbf{g}$ and of the order of $Mg/e$. $E_{\text{ch}}$ will be calculated in Chapter 3. $E_{\text{ch}}$ will turn out to be second order in $g$. 

The ultimate objective of this chapter is to calculate $\mathbf{E}_{\text{dipoles}}$, the average electric field due to the dipole moments of the ions. In order to calculate $\mathbf{E}_{\text{dipoles}}$, it is necessary to know the gravitationally induced dipole moment $\mathbf{\hat{p}}$ of each ion. $\mathbf{\hat{p}}$ may be calculated if the distribution of charge inside the shell is known. As such, the position of the nucleus inside the shell and the electron wave function must be found. The location of the nucleus will be determined by requiring that there be zero net force on the nucleus. The electron wave function will be obtained by solving Schrödinger's equation.

The problem of determining the wave function for the electron has three important characteristics: (1) the wave function must vanish on the shell and is identically zero outside of the shell, (2) the singularity of the Coulomb potential experienced by the electron is at the site of the nucleus, which is not the center of the shell, and (3) in addition to the Coulomb potential, the electron also experiences a potential which is linear in the vertical direction.

This linear potential is a combination of the gravitational potential and the potential due to the electric field which
pervades the shell. Thus, the electric field in the shell will be taken to be the sum of three terms: $E_{ch}$, $E_{ext}$, and the electric field in the shell due to the dipole moments of all of the other ions.

As noted in chapter 1, the electric field pervading the shell will not, in fact, be uniform. However, the field will be approximated to be uniform. This simplification is made so that the Schrödinger equation for the electron can be readily solved. The farther apart the shells are spaced, the better this approximation will be.

Let $\tilde{E}_p(\vec{r})$ denote the electric field at the point $\vec{r}$ inside a shell that is due to the dipole moments of all of the other ions. In the Schrödinger equation, $\tilde{E}_p(\vec{r})$ will be replaced by a uniform field. A reasonable choice for this representative uniform field is is the average value of $\tilde{E}_p(\vec{r})$ inside the shell. Electrostatic theory tells us that this average is the value of $\tilde{E}_p(\vec{r})$ at the center $\vec{r}_c$ of the shell, $\tilde{E}_p(\vec{r}_c)$. As will be shown in this chapter, the equilibrium position of the nucleus, $\vec{r}_n$, is a very small distance from the center of the shell. As such, $\tilde{E}_p(\vec{r}_c)$ will differ from $\tilde{E}_p(\vec{r}_n)$ by a tiny amount.

$\tilde{E}_p(\vec{r}_n)$ has a simple interpretation. Imagine replacing each ion by a point dipole $\vec{p}$ and situating the dipoles at the sites of the nuclei. One then has a lattice of dipoles. $\tilde{E}_p(\vec{r}_n)$ is the electric field at the site of one of those dipoles due to all of the other dipoles in the lattice. As such, $\tilde{E}_p(\vec{r}_n)$ will hereupon be denoted by $\tilde{E}_p$.

Thus, the electric field in a shell created by the dipole
moments of all of the other ions will be taken to be uniform and equal to \( \vec{E}_p \). It is \( \vec{E}_p \) which will enter into the Schrödinger equation for the electron. For an appropriate choice of lattice, \( \vec{E}_p \) will be in the vertical direction.

The reader will notice that the electron wave function is going to depend on \( \vec{E}_p \) and \( \alpha \), where \( \alpha \) is the distance between the center of the shell and the nucleus. This means that \( \vec{p} \) will depend on \( \vec{E}_p \) and \( \alpha \). It is easy to see that \( \alpha \) will depend on \( \vec{E}_p \).

Three forces act on the nucleus: gravity, the electrostatic force due to the electron, and the electrostatic force due to all charge exterior to the shell. The second of these forces depends on the electron wave function, or \( \alpha \) and \( \vec{E}_p \). The latter depends on \( \vec{E}_p \). Requiring these forces to cancel gives an equation for \( \alpha \) in terms of \( \vec{E}_p \). That \( \alpha \) may be expressed in terms of \( \vec{E}_p \) implies that \( \vec{p} \) can be written in terms of \( \vec{E}_p \). Since \( \vec{E}_p \) can be calculated in terms of \( \vec{p} \) -- for a given choice of lattice -- \( \vec{p} \) can be determined. Having found \( \vec{p} \), \( \vec{E}_{dipoles} \) may be calculated.

Summarizing, the plan of this chapter is as follows:

1. Set up the Schrödinger equation for the electron inside the shell, with the nucleus displaced a distance \( \alpha \) from the center and a uniform electric field \( \vec{E}_{ch} + \vec{E}_{ext} + \vec{E}_p \) pervading the shell.

2. Solve for the wavefunction and energy of the electron as a function of \( \alpha \) and \( \vec{E}_p \).

3. Solve for the position of the nucleus by requiring that there be zero net force acting on the nucleus.
4. Find the dipole moment $\mathbf{p}$ in terms of $\mathbf{E}_p$.
5. Choose a lattice and find $\mathbf{E}_p$ in terms of $\mathbf{p}$.
6. Solve the two equations combining $\mathbf{E}_p$ and $\mathbf{p}$ to determine $\mathbf{p}$ in terms of $\mathbf{g}$, $\mathbf{E}_{ch}$, $\mathbf{E}_{ext}$ and $Z_n$.
7. Calculate $\mathbf{E}_{dipoles}$.

These steps are now carried out in detail.

(2.1) SETTING UP THE SCHRODINGER EQUATION FOR THE ELECTRON INSIDE THE IMPENETRABLE SHELL

Let $\hat{x}$, $\hat{y}$, and $\hat{z}$, be unit, mutually perpendicular, dimensionless vectors in the x-, y-, and z-directions, respectively. A cartesian coordinate system is employed; the space is Euclidean. Choose the z-direction such that the gravitational field $\mathbf{g} = -g\hat{z}$ with $g > 0$. Down shall mean in the direction of $\mathbf{g}$ and up in the opposite direction. Place the nucleus at a distance $\alpha$ below the center of the shell, i.e.: at $(0,0,-\alpha)$, so $\alpha > 0$ means the nucleus is indeed below the center of the shell (see figure 3). Let $\alpha$ be the value of $\alpha$ for which there is zero net force on the nucleus. If $\alpha \neq a$, an external, imaginary force is required to hold the nucleus in place. Choose the origin of the coordinate system to coincide with the nucleus.

The electric field inside the shell, due to all charges exterior to the shell, is
Figure 3. Placement of the Nucleus Inside the Impenetrable Shell

\[ \vec{E}_s = E_s \hat{z} = (E_p + E_x) \hat{z}, \]  

(1.1)

where

\[ E_x = E_{ch} + E_{ext}, \]

(1.2)

and \( E_p, E_{ch}, E_{ext} \) have all been defined previously.

The Hamiltonian for the electron is,

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + U \]

(1.3A)

\[ U = \begin{cases} 
-k \frac{Z_n q_e}{r} + \varepsilon Z_c, \text{ inside shell} \\
+\infty, \text{ outside shell} \end{cases} \]

(1.3B)
where $\hbar=h/2\pi$, $h$ is Planck's constant, $k=\sqrt{\hbar/4\pi\varepsilon_0}$, $\varepsilon_0$ is the electric permittivity of free space, $r$ is the distance of the point $(x,y,z)$ from the nucleus, $r=\sqrt{x^2+y^2+z^2}$, $z_c$ is the elevation from the center of the shell, and

$$\varepsilon = mg + q_e E_s .$$

Schrödinger's (time-independent) equation for the electron is

$$\frac{-\hbar^2}{2m} \psi = E \psi ,$$

or

$$\left\{ \begin{array}{c} \left(-\frac{\hbar^2}{2m} - k \frac{Znq_e^2}{r} + \varepsilon z_c \right) \psi = E \psi , \text{ inside shell} \\
\psi = 0 , \text{ on shell} \\
\psi = 0 , \text{ outside shell} \end{array} \right\}$$

Equation (1.6) will be solved by using perturbation theory. $\alpha$ and $\varepsilon$ are treated as very small parameters; that is, $\alpha$ is small compared to $R$, and $\varepsilon$ is small compared to $kZnq_e^2/R^2$. As such, $\psi$ and $E$ are expanded in Taylor series about $\alpha=0$, $\varepsilon=0$:

$$\psi = \psi_0 + \alpha \psi_1 + \alpha^2 \psi_2 + \alpha^3 \psi_3 + \cdots + \varepsilon \psi_1 + \alpha \varepsilon \psi_2 + \alpha^2 \varepsilon \psi_3 + \cdots$$

(1.7)
Note that only the ground state eigenfunction and ground state energy eigenvalue are sought. The reason for this is that, in most metals at or below room temperature, the energy gap between the ground state of the ion and the first excited state is large compared to $k_B T$, where $k_B$ is the Boltzmann constant. Consequently, the proportion of ions not in the ground state is a very small number.

The $\psi_i$, $\phi_i$, and $X_i$ are all functions of $\vec{r}$, where $\vec{r}$ is position inside the shell, as measured from the nucleus. The $^\alpha E_i$, $^\varepsilon E_i$ and $\xi_i$ are all constants.

Since $\alpha$ and $\varepsilon$ are very small, it is sufficient for the purposes of this model to determine $\psi$ and $E$ to lowest order in $\alpha$ and $\varepsilon$. Accordingly, the approximate solution for $\psi$ will be taken to be

$$\psi = \psi_0 + \alpha \psi_1 + \varepsilon \phi_1 .$$ (1.9)

As will be proven, $^\alpha E_i$ and $^\varepsilon E_i$ are both zero, and so the approximate solution for $E$ will be taken as

$$E = E_0 + \alpha^2 E_2 + \varepsilon^2 E_2 + \alpha \varepsilon \xi_1 .$$ (1.10)

The problem reduces to finding $\psi_0$, $\psi_1$, $\phi_1$ in equation (1.9), $E_0$, $^\alpha E_2$, $^\varepsilon E_2$, $\xi_1$ in equation (1.10), and to showing that
both $\alpha E_1$ and $\xi E_1$ are zero. All of these quantities, except for $\xi_1$, may be found by breaking the problem down into three separate problems.

One of these is "the unperturbed problem". As the name suggests, $\alpha=0$ and $\xi=0$ in this case; the nucleus is at the center of the shell, and there is no external potential. $\psi_0$ and $E_0$ are the solutions for $\psi$ and $E$, respectively, when $\alpha=0$ and $\xi=0$, and are referred to as the unperturbed eigenfunction and the unperturbed eigenvalue.

The other two reduced problems are "the perturbed potential problem", in which $\alpha=0$ but $\xi \neq 0$, and "the perturbed boundary problem", wherein $\xi=0$ but $\alpha \neq 0$. It is clear that the $\psi_i$ and the $\xi_i$ may be found by solving the perturbed potential problem. Similarly, the $\psi_i$ and the $E_i$ are determined by solving the perturbed boundary problem.

Before proceeding to determine the quantities in equations (1.9) and (1.10), two points should be made regarding equations (1.7) and (1.8). First, it is not necessary that these be Taylor series; equations (1.9) and (1.10) will still be excellent approximations to $\psi$ and $E$ provided that equations (1.7) and (1.8) are at least asymptotic expansions. Second, $\alpha$ and $\xi$ are not dimensionless. It is possible to define dimensionless parameters $\tilde{\alpha} = \alpha/R$ and $\tilde{\xi} = (kq_\xi^2/R^2)$, but it is certainly not mandatory. These parameters, $\tilde{\alpha}$ and $\tilde{\xi}$, emerge naturally in solving for $\psi_1$, $\psi_2$, $\xi_2$, and $\xi_1$, as shall be seen shortly.

The next step is to set up the perturbed potential problem.
and obtain expressions for the $\phi_i$ and the $\varepsilon E_i$. Then, the perturbed boundary problem shall be posed, and expressions for the $\psi_i$ and the $\varepsilon E_i$ found.

(A) Setting up the Equations for the Perturbed Potential Problem

The perturbed potential problem is so named because it differs from the unperturbed problem only in that the electron experiences the small linear potential $\varepsilon z_c$. With the nucleus at the centre of the shell, $\alpha=0$, $z=z_c$ and Schrödinger's equation becomes

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - k \frac{Znq_e^2}{r} + \varepsilon z\right)\psi = E\psi \quad , \quad r<R$$

with the boundary condition

$$\psi \bigg|_{r=R} = 0 .$$

This problem will be solved to the lowest nontrivial order in the small parameter $\varepsilon$. To this end, write
\[ H = H_0 + \epsilon Z , \]

where

\[ H_0 = -\frac{\hbar^2}{2m} \nabla^2 + U_0 \]  

\[ U_0 = \begin{cases} -k \frac{Z_n e^2}{r}, & 0 < r < R \\ +\infty, & r > R \end{cases} \]

Express \( \psi \) and \( E \) as perturbative expansions about \( \epsilon = 0 \):

\[ \psi = \psi_0 + \epsilon \phi_1 + \epsilon^2 \phi_2 + \ldots \]  

\[ E = E_0 + \epsilon E_1 + \epsilon^2 E_2 + \ldots \]

Substituting these expansions into the equation \( H \psi = E \psi \) leads to the following equations:

\[ H_0 \psi_0 = E_0 \psi_0 \]
\begin{align*}
Z \psi_0 + H_0 \phi_1 &= \epsilon E_1 \psi_0 + E_0 \phi_1 \\
Z \phi_1 + H_0 \phi_2 &= \epsilon E_2 \psi_0 + \epsilon E_1 \phi_1 + E_0 \phi_2 \\
&\vdots \quad \vdots \\
Z \phi_{n-1} + H_0 \phi_n &= \epsilon E_n \psi_0 + \epsilon E_{n-1} \phi_1 + \cdots + E_0 \phi_n
\end{align*}

The boundary condition (1.12) implies that

\[
\phi_i \bigg|_{r=R} = 0
\] (1.18.0)

\[
\phi_i \bigg|_{r=R} = 0
\] (1.18.1)

\[
\phi_i \bigg|_{r=R} = 0
\] (1.18.n)
Equations (1.17.0) and (1.18.0) verify that $\psi_0$ and $E_0$ are the unperturbed eigenfunction and eigenvalue. It is in terms of these two quantities that the $E_i$ and the $\phi_i$ are expressed.

Using the standard techniques of perturbation theory, it is found that

$$
E_i = \frac{\int_R d^3r \psi_0^* \phi_{i-1} - \sum_{n=1}^{i-1} \epsilon E_{i-n} \int_R d^3r \psi_0^* \phi_n}{\int_R d^3r \psi_0^* \psi_0}
$$

(1.19)

where the integrations are over the region $r<R$.

The normalization condition,

$$
\int_R d^3r \psi_0^* \psi_0 = 1
$$

(1.20)

gives rise to the equations

$$
\left\{ \begin{align*}
\int_R d^3r & \psi_0^* \psi_0 = 1 \\
\int_R d^3r & \sum_{n=0}^{i} \phi_{i-n}^* \phi_n = 0, \quad i = 1, 2, 3, ...
\end{align*} \right.
$$
Equation (1.20) reduces equation (1.19) to

\[ \epsilon E_i = \int_R d^3r \psi_o^* \sum_{n=1}^{i-1} \epsilon E_{i-n} \int_R d^3r \psi_n \phi_n \quad (1.21) \]

According to the results of standard perturbation theory, equations (1.17) and (1.18) and (1.20) allow for the determination of all of the \( \phi_i \) and all of the \( \epsilon E_i \), in terms of \( \psi_o \) and \( E_o \).

It is worthwhile to write out the equations which specify \( \phi_1 \), \( \epsilon E_1 \) and \( \epsilon E_2 \). Before doing so, note that a simple physical argument demonstrates that \( \epsilon E_i = 0 \) for all odd \( i \). The idea is simply that the physical energy \( E \) is invariant under a change in sign of \( \epsilon \). This implies that \( E(\epsilon) - E(-\epsilon) = 2\epsilon \epsilon E_1 + 2\epsilon^3 \epsilon E_3 + \ldots = 0 \), which can be true for all \( \epsilon \) only if \( \epsilon E_1 = 0, \epsilon E_3 = 0, \ldots \). In particular, \( \epsilon E_1 = 0 \). Consequently, the equations specifying and \( \epsilon E_2 \) are:

\[
(H_0 - E_o) \phi_1 = -Z \psi_o \quad (1.22.\text{a})
\]

\[
\phi_1 \bigg|_{r=R} = 0 \quad (1.22.\text{b})
\]

\[
\int_R d^3r (\phi_1^* \psi_o + \psi_o^* \phi_1) = 0 \quad (1.22.\text{c})
\]
For the sake of completeness, the equation for $\varepsilon E_1$ is also given:

$$\varepsilon E_1 = \int_R d^3r \psi_o^* Z \psi_0 .$$  \hspace{1cm} (1.24)

Once $\psi_o$ has been determined, it shall be shown that equation (1.24) gives $\varepsilon E_1=0$, as required.

(B) Setting up the Equations for the Perturbed Boundary Problem

In this problem, the nucleus is placed a distance $\alpha$ below the centre of the shell, as in figure 3, and there is no external linear potential. The electron wave function is given by the solution to

$$\left\{ \begin{array}{l}
L_0 \psi = E \psi \\
L_0 \equiv -\frac{\hbar^2}{2m} \nabla^2 - \frac{k}{r} \frac{Z_n q_e}{r} 
\end{array} \right\} \hspace{1cm} (1.25)$$

inside the shell, and is zero outside the shell. Note that the function $\psi$, given by equation (1.25), will not itself be zero.
exterior to the shell. This difference between the electron wave function and the function $\psi$ should be carefully noted by the reader.

The Hamiltonian for this problem differs from that for the unperturbed problem only in that the position of the shell relative to the nucleus is different. If $\alpha$ is small, then this difference in position of the boundary is a small one, and the problem may be regarded as a problem in which the boundary has been slightly perturbed.

Figure 4. Position of the Boundary Relative to the Nucleus

An equation for the position of the boundary can be derived by examining figure 4. The boundary in the unperturbed problem is a shell of radius $R$ entered on the nucleus. Here it is a shell of radius $R$ centered on a point a distance $\alpha$ above the nucleus. Let $r_b(\theta)$ be the distance from the nucleus to the boundary in the perturbed boundary problem, where $\theta$ is the polar
angle. From figure 5, note that
\[(r_b(\theta) - \alpha \cos \theta)^2 + (\alpha \sin \theta)^2 = R^2\]
or, solving for \(r_b(\theta)\),
\[r_b(\theta) = \sqrt{R^2 - \alpha^2 \sin^2 \theta} + \alpha \cos \theta \tag{1.26}\]

Expanding \(r_b(\theta)\) in a Taylor series about \(\alpha = 0\) gives
\[r_b(\theta) = R \left( 1 + \frac{\alpha}{R} \cos \theta - \frac{1}{2} \left( \frac{\alpha}{R} \right)^2 \sin^2 \theta - \frac{1}{2 \cdot 4} \left( \frac{\alpha}{R} \right)^4 \sin^4 \theta - \ldots \right) \tag{1.27}\]

**Figure 5.** Relationship between \(\theta\), \(r_b(\theta)\), \(\alpha\) and \(R\)

Expanding \(\psi\) and \(E\) in Taylor series about \(\alpha = 0\):
\[\psi = \psi_0 + \alpha \psi_1 + \alpha^2 \psi_2 + \ldots \tag{1.28}\]
Again, all of the $E_i$, with $i$ odd, are zero. The reason is the same as in the perturbed potential problem; the physical energy $E$ can not depend on the sign of $\alpha$.

In consequence, equation (1.29) simplifies to

$$E = E_0 + \alpha^2 E_2 + \alpha^4 E_4 + \cdots$$

(1.30)

Inserting equations (1.28) and (1.30) into $L_0 \psi = E \psi$ leads to the set of equations:

$$L_0 \psi_0 = E_0 \psi_0 \quad (1.31.0)$$

$$L_0 \psi_1 = E_0 \psi_1 \quad (1.31.1)$$

$$L_0 \psi_2 = \alpha E_2 \psi_0 + E_0 \psi_2 \quad (1.31.2)$$

$$\vdots$$

The boundary conditions which must be obeyed by the $\psi_i$ are obtained by writing $\psi$ in the form of a Taylor series about $r=R$:

$$\psi(r, \theta, \varphi) = \sum_{n=0}^{\infty} (r-R)^n \frac{1}{n!} \psi^{(n)}(R, \theta, \varphi) \quad (1.32)$$
where

\[ \psi^{(n)}(r, \theta, \varphi) = \frac{\partial^n \psi(r, \theta, \varphi)}{\partial r^n} \Bigg|_{r=R} \]

and \( \varphi \) is the azimuthal angle. \( \psi \) vanishes on the shell, at \( r=r_b(\theta) \). Accordingly, inserting the form (1.28) for \( \psi \) into the right hand side of equation (1.32), and evaluating at \( r=r_b(\theta) \), leads to

\[
\begin{align*}
\psi_0(R, \theta, \varphi) + \alpha \left\{ \psi_1(R, \theta, \varphi) + \cos \theta \psi_0(R, \theta, \varphi) \right\} \\
+ \alpha^2 \left\{ -\frac{1}{2} \frac{1}{R} \sin^2 \theta \psi_0'(R, \theta, \varphi) + \frac{1}{2} \cos^2 \theta \psi_0''(R, \theta, \varphi) \right\} \\
+ \cdots = 0
\end{align*}
\]

where the result has been expressed as a power series in \( \alpha \). Equation (1.33) can be true for arbitrary \( \alpha \) only if the coefficient of each power of \( \alpha \) is zero. This means that

\[ \psi_0(R, \theta, \varphi) = 0 \tag{1.34.0} \]

\[ \psi_1(R, \theta, \varphi) + \cos \theta \psi_0'(R, \theta, \varphi) = 0 \tag{1.34.1} \]
The only other condition to satisfy is the normalization of the eigenfunction:

\[
\int_{S, \alpha} d^3r \psi^* \psi = 1
\]

where the integration is over the interior of the shell.

The left hand side of equation (1.35) may be expanded in powers of \( \alpha \). To see how to do so, consider figure 6. \( V_n \) is the region interior to a spherical surface of radius \( R \) centered on the nucleus, \( V_U \) is the region exterior to \( V_n \) and interior to the shell, and \( V_L \) is the region interior to \( V_n \) and exterior to the shell. Note that

\[
\int_{S, \alpha} d^3r = \int_R d^3r + \int_{V_U} d^3r - \int_{V_L} d^3r
\]

\( \int_R d^3r \) means to integrate over the region \( V_n \), where \( r < R \). Equation (1.36) may be applied to the left hand side of the equation (1.35).
Using the expansion (1.28) for $\psi$, and equation (1.36), the left hand side of equation (1.35) may be converted into a power series in $\alpha$. Equation (1.35) is true only if the order unity term in this power series is equal to one and if the coefficient of every other power of $\alpha$ is zero. The only term of order unity in the power series is $\int_V d^3r \psi_0^* \psi_0$, since the integrals $\int_{V_\nu} d^3r \psi_0^* \psi_0^*$ and $\int_{V_\ell} d^3r \psi_0^* \psi_0$ are of order $\alpha^j$. Thus,

$$\int_R d^3r \psi_0^* \psi_0 = 1$$

(1.37)

The condition in which $\psi$ enters is

$$\int_R d^3r (\psi_1^* \psi_0 + \psi_0^* \psi_1) = 0$$

(1.38)

obtained by recognizing that the coefficient of $\alpha$ is zero. The
higher order terms give equations involving \( \psi_2, \psi_3, \ldots \), but since only \( \psi_0 \) and \( \psi_1 \) will be required, ultimately, there is no need to write these equations down.

Summarizing, equations (1.31.0), (1.34.0) and (1.37) define the unperturbed eigenfunction and eigenvalue, while equations (1.31.1), (1.34.1) and (1.38) specify \( \psi_1 \). Grouping these latter three equations together,

\[
L_0 \psi_1 = E_0 \psi_1
\]

(1.39.a)

\[
\left[ \psi_1 \right]_{r=R} = \cos \Theta \left[ \psi_0 \right]_{r=R}
\]

(1.39.b)

\[
\int_{R} d^3r (\psi_1^* \psi_0 + \psi_0^* \psi_1) = 0
\]

(1.39.c)

Equations for the \( \alpha E_1 \) may also be derived. Only those for \( \alpha E_1 \) and \( \alpha E_2 \) shall be presented.

Proceeding from the expansions (1.28) and (1.29) for \( \psi \) and \( E \), \( L_0 \psi = E \psi \) implies that

\[
L_0 \psi_1 = \alpha E_1 \psi_0 + E_0 \psi_1
\]

(1.40)

shall be used to generate an equation for \( \alpha E_1 \). Multiplying both sides by \( \psi_0^* \), integrating over \( V_\alpha \), and using equation (1.37)
Combining equation (1.25) for \( L_0 \), the relationships (1.31.0) and (1.34.0), and Green's theorem, equation (1.41) simplifies to

\[
\alpha E_1 = \int_R d^3r \psi_0^* \psi_1 - E_0 \int_R d^3r \psi_0^* \psi_1 .
\]  

where \( dS \) is the element of area on the surface of \( V_n \) and the integration is over the surface of \( V_n \), where \( r=R \). The boundary condition (1.39.b) allows \( \psi_1 \) to be eliminated from equation (1.42), giving

\[
\alpha E_1 = \frac{\kappa^2}{2m} \int_R \psi_0 \psi_0^* \cos \Theta \, dS .
\]  

Equation (1.43) shall be used to verify that \( \alpha E_1 = 0 \).

Using the same techniques, equation (1.31.2) may be converted into the following expression for \( \alpha E_2 \):

\[
\alpha E_2 = \frac{\kappa^2}{2m} \int_R \psi_2 \psi_0^* \, dS .
\]  

The form of \( \psi_2 \) on the surface of \( V_n \) is described by equation (1.34.2). As such, once \( \psi_1 \) has been determined, \( \alpha E_2 \) may be calculated.
An equation for $\varepsilon_i$ may be obtained by dealing with the full perturbation problem. The method to use to get this expression for $\varepsilon_i$ begins by equating the $\alpha \varepsilon$ terms on each side of the equation $(L_0 + \varepsilon z_c) \psi = E \psi$. Recall that $z_c$ is height as measured from the center of the shell, while $z$ is height as measured from the nucleus. $z_c$ and $z$ are therefore related by

$$z_c = z - \alpha. \quad (1.45)$$

Using the expansions (1.7) and (1.8) for $\psi$ and $E$ along with equation (1.45), equating the coefficients of $\alpha \varepsilon$ on each side of $(L_0 + \varepsilon z_c) \psi = E \psi$ gives

$$L_0 \chi_1 + z \psi_1 - \psi = E_0 \chi_1 + \varepsilon_i \psi_1, \quad (1.46)$$

where $\varepsilon_i$ and $\alpha E_i$ have been acknowledged as being zero.

Performing the same operations on equation (1.46) as were used to derive expressions for $\alpha E_1$ and $\alpha E_2$,

$$\varepsilon_i = \int_R d^3r \psi_0^* \chi_1 + \frac{\alpha^2}{\lambda^2} \int_R \chi_1 \psi_0^* dS - 1. \quad (1.47)$$

The form of $\chi$, on the surface of $V_n$ is obtained by requiring $\psi$, as given by equation (1.7), to vanish on the surface of the shell. Using the same approach as that which led
to the boundary conditions (1.34), it is found that

$$\chi_{ij}^l|_{r=R} = -\cos \Theta \frac{\partial \phi}{\partial r}^l|_{r=R}.$$  

(1.48)

This result transforms equation (1.47) into

$$\varepsilon_1 = \int_R d^3r \psi_0^* Z \psi_1 - \frac{\kappa^2}{2m} \int_R \phi \psi_0^* \psi_1^* dS - 1$$

(1.49)

At this stage, equations have been derived for all of the quantities appearing in the approximate solutions for \( \psi \) and \( E \) given by equation (1.9) and (1.10). Summarizing:

(1.50.a)

\[ (L_0 - E_0) \psi_0 = 0 \]

(1.50.b)

\[ \psi_0|_{r=R} = 0 \]

(1.50.c)

\[ \int_R d^3r \psi_0^* \psi_0 = 1 \]
\[ (L_0 - E_0) \phi_1 = -Z \psi_0 \]  

(1.51.a)

\[ \int_{r=R} \phi_1 = 0 \]  

(1.51.b)

\[ \int_{r=R} d^3r \left( \phi_1^* \psi_0 + \psi_0^* \phi_1 \right) = 0 \]  

(1.51.c)

\[ (L_0 - E_0) \psi_1 = 0 \]  

(1.52.a)

\[ \psi_1 \bigg|_{r=R} = -\cos \theta \psi_0 \bigg|_{r=R} \]  

(1.52.b)
\[ \int_{\mathbb{R}} d^3r \left( \psi_1^* \psi_0 + \psi_0^* \psi_1 \right) = 0 \]  

(1.52.c)

\[ \varepsilon E_1 = \int_{\mathbb{R}} d^3r \psi_0^* Z \psi_0 \]  

(1.53.a)

\[ \varepsilon E_2 = \int_{\mathbb{R}} d^3r \psi_0^* Z \phi_1 \]  

(1.53.b)

\[ \alpha E_1 = -\frac{\hbar^2}{2m} \int_{\mathbb{R}} \psi_0 \psi_0^* \cos \Theta dS \]  

(1.53.c)

\[ \alpha E_2 = \frac{\hbar^2}{2m} \int_{\mathbb{R}} \psi_2 \psi_0^* dS \]  

(1.53.d)
Note that the approximate solution \( \psi \) is not identically zero on the shell, but differs from zero by terms of order \( \alpha^2 \) and \( \alpha \epsilon \). This is acceptable, because the wavefunctions are required to only first order.
(A) The Unperturbed Problem; Determination of $\psi_0$ and of $E_0$

The essential features of the model will be independent of the choice made for $R$. $R$ is chosen for convenience to be

$$R = \frac{2a_z}{Z_n}$$

where

$$Q_0 \equiv \frac{\hbar^2}{mk_e^2}$$

is the Bohr radius.

For this choice of $R$, when $r < R$ it is easy to see that $\psi_0$ is essentially the hydrogenic wavefunction $\psi_{100}$, but with a different normalization; $\psi_{100}$ is the spherically symmetric wave function belonging to the first excitation energy of the hydrogenic problem. Thus,

$$\psi_0 = N \left( \frac{Z_n}{a_z} \right)^{3/2} (2 - \rho) e^{-\rho/2} \quad 0 \leq \rho \leq 2$$  \hspace{1cm} (2.3)

$$\psi_0 \equiv 0 \quad \rho > 2$$

where

$$\rho \equiv \frac{Z_n r}{a_z}$$  \hspace{1cm} (2.4)

$N$ is determined from the normalization condition (1.51.a) and is
The first thing to observe is that having found \( \psi_0 \), it is trivial to verify that equation (1.53a) gives \( E_0 = 0 \).

Using equation (2.6) in equation (1.51.a) and performing some simple manipulations, the following equation for \( \phi \), results:

\[
\frac{q_e^2}{Z_n^2} \nabla^2 \phi + \left( \frac{2}{\rho} - \frac{1}{4} \right) \phi = \frac{2N}{Z_n^{3/2}} \frac{a_o^{1/2}}{kq_e^2} \cos \Theta \rho (2-\rho) e^{-\rho^2/2}.
\]  

(2.7)

It is easy to verify from equation (2.7) that \( \phi \) is of the form

\[
\phi = \frac{2N}{Z_n^{3/2}} \frac{a_o^{1/2}}{kq_e^2} \cos \Theta t(\rho) e^{-\rho^2/2}.
\]  

(2.8)
Using equation (2.8), it is easy to show that condition (1.51.c) is satisfied. Where \( t(\rho) \) must satisfy

\[
\rho^2 t''(\rho) + \rho(2-\rho)t'(\rho) + (\rho-2)t(\rho) = \rho^3(2-\rho). \tag{2.9}
\]

The boundary condition (1.51.b) for \( \phi \), translates into

\[
t(2) = 0. \tag{2.10}
\]

Putting

\[
t(\rho) = \rho \zeta(\rho) \tag{2.11}
\]

simplifies the problem to

\[
\zeta''(\rho) + \left( \frac{4}{\rho} - 1 \right) \zeta'(\rho) = 2 - \rho. \tag{2.12}
\]

Solving equation (2.12) for \( \zeta' \) by using the well known "integrating factor method", and then integrating to get \( \zeta \), it is found that

\[
\zeta(\rho) = \frac{1}{2} \rho^3 + \frac{3}{2} \rho^2 + 12 \rho \ln \rho - 36 - 36 \rho^{-1} - 24 \rho^{-2} + C_1 \rho - C_2 \left( \frac{1}{3} \rho^{-2} + \frac{1}{6} \rho^{-1} + \frac{1}{6} \right) e^\rho + \frac{1}{6} C_2 \rho \int_0^\rho e^x dx. \tag{2.13}
\]
The constants $c_1$ and $c_2$ must be determined. One condition to be satisfied is $t(2) = 0$. Another is needed in order to determine both constants. The second condition is that $\phi$, must not have a $C^2$ singularity. This requirement is a consequence of the need for $|\psi|^2$ to be integrable. Recalling the expansion (1.7) for $\psi$, in expressing $\int d^3x \phi^* \phi$ as a power series in $\alpha$ and $\epsilon$, it is seen that the coefficient of the $\epsilon^2$ term will be
\[
\int d^3r \left( \psi_0^* \phi_2 + \phi_1^* \phi_1 + \phi_2^* \psi_0 \right) .
\]

In order that the $\int d^3r \phi_i^* \phi_i$ part of this be finite, it is necessary that $\phi$, have no worse a singularity at $\rho = 0$ than $\rho^{-1}$. There are only two terms in (2.13) which blow up like $\rho^{-1}$. One involves $c_2$. The two will cancel if the choice
\[
c_2 = -72
\]
is made. With this determination of $c_2$, equation (2.13) may be written as
\[
t(\rho) = c_1 \rho + 3 \rho^2 + \frac{1}{2} \rho^3 + 12 \left[ \left( 1 + \rho^{-1} + 2 \rho^{-2} \right) \epsilon^0 - \left( 3 + 3 \rho^{-1} + 2 \rho^{-2} \right) \int \frac{\rho^* \psi}{x} dx \right]
\]

The form (2.15) for $t(\rho)$ is very obscure. However, using power series expansions for $\epsilon^0$ and $\int \frac{\rho^* \psi}{x} dx$ reveals that not only the $\epsilon^{-1}$ terms in equation (2.15) cancel, but so do the $\epsilon^{-2}$ terms. As such, $t(\rho)$ may be expressed as a power series:
Inserting equation (2.16) into equation (2.9) allows the $c_j$ to be determined. The result is:

$$t(q) = C_1q + \frac{1}{5}q^3 + \sum_{j \geq 5}^{\infty} C_j q^j$$  \hspace{1cm} (2.17)$$

where

$$C_j = \left( \frac{j-2}{j(j+2)} \right) C_{j-1}, \quad j \geq 5$$  \hspace{1cm} (2.18)$$

The boundary condition (2.10) fixes $c_1$ to four decimal places:

$$C_1 = -0.4622$$  \hspace{1cm} (2.19)$$

Before using the solution for $\phi$, to calculate $\varepsilon E_2$, note that $t(q) < 0$ in the range $0 < \varepsilon < 2$, which implies $\phi < 0$ in the upper half of the shell and $\phi > 0$ in the lower half. Physically, this means that the electron sinks down (assuming $\varepsilon > 0$) under the influence of the external perturbing potential.
\( \varepsilon \mathcal{E}_2 \) is determined by evaluating equation (1.53.b). Using equations (2.3) and (2.8),

\[
\varepsilon \mathcal{E}_2' = \frac{8\pi N^2}{3Z_n^4} \frac{a_e^3}{k_e^2} \varepsilon \mathcal{E}_2'
\]

(2.20)

where

\[
\varepsilon \mathcal{E}_2' = \int_0^2 \rho^3 (2-\rho) t(\rho) e^\rho d\rho
\]

(2.21)

The simplest way to solve for \( \varepsilon \mathcal{E}_2' \) is to put

\[
\int_0^2 \rho^3 (2-\rho) t(\rho) e^\rho d\rho = w(\rho) e^{-\rho}
\]

(2.22)

\( w(\rho) \) must satisfy

\[
w' - w = (2-\rho) \rho^3 t(\rho).
\]

(2.23)

Using the power series form of \( t(\rho) \), the following solution for \( w(\rho) \) results:

\[
w(\rho) = \sum_{j=5}^{\infty} w_j \rho^j
\]

(2.24)
where

\[ W_5 = \frac{2}{5} c_1 \]
\[ W_6 = -\frac{1}{10} c_1 \]
\[ W_7 = \frac{1}{35} (2 - \frac{1}{2} c_1) \]
\[ W_8 = \frac{1}{8} (W_7 - \frac{8}{35}) \]
\[ W_9 = \frac{1}{9} (W_8 + \frac{11}{420}) \]
\[ W_j = \frac{1}{j} (W_{j-1} + 2c_j - 4c_{j-2}) , \quad j \geq 10 \]  

(2.25)

Since \( w(0) = 0 \), equations (2.21) and (2.22) combine to give

\[ \frac{\epsilon}{E_2} = w(2)e^{-2} . \]  

(2.26)

Evaluating equation (2.26) to four decimal places,

\[ \frac{\epsilon}{E_2} = -0.1082 . \]  

(2.27)

From equations (2.20) and (2.5) it is found that, to four decimal places,
It is easy to show that equation (1.53.c) says that $\alpha E_i = 0$. All that is required is to observe, using equation (2.3), that the radial integral in equation (1.53.c) is finite. Since the integral of $\cos \theta$ over the surface of a sphere is zero, $\alpha E_i = 0$ follows immediately.

$\psi_i$ is found almost as easily. First note by comparing equations (1.50.a) and (1.52.a) as well as equations (1.50.b) and (1.52.b) that $\psi_i$ satisfies the same equation as $\psi_o$, but a different boundary condition.

In consequence, $\psi_i$ is essentially the hydrogenic wave function

$$\psi_i = \frac{N_1}{a_0^{3/2}} r e^{-r/2} \cos \theta$$

(2.29)

Insisting that $\psi_i$ satisfy equation (1.52.b) fixes $N_1$:

$$N_1 = \frac{1}{Z} Z_n^{5/2} N$$

whence,
\[ \psi_1 = \frac{1}{2} \left( \frac{Z_n}{\alpha_o} \right)^{5/2} N \rho e^{-\rho/2} \cos \theta \] (2.30)

Equation (2.30) also satisfies the requirement (1.52.c). Notice that \( \psi_1 \) is positive in the part of the shell above the nucleus, and negative below it. This means that, when the shell is moved slightly upwards, the electron gets pushed up above the nucleus a little bit, so more of the electron will be above the nucleus than below it. The physical reason for this is basically just that there is slightly more room available inside the shell above the nucleus than below it: the extra room lies in the vicinity of the shell.

Equation (1.53.d) is readily evaluated by making use of equation (1.53.d) and equations (2.3) and (2.30) for \( \psi_0 \) and \( \psi_1 \), respectively. The final result is

\[ \alpha F_2 = \frac{8 \pi}{3 \varepsilon^2} N^2 \sum_{n < q}^4 \frac{\varepsilon}{q e^2} \] (2.31)

There are at least two other ways to derive equation (2.31). They serve as a check and are therefore presented. One of these methods involves some key physical ideas, and is described below. The other is more mathematical and is given in Appendix A.

The physical method begins with the realization that
\[
\Gamma_{el}(\alpha) = \frac{\partial E}{\partial \alpha},
\]  

(2.32)

where \( \Gamma_{el}(\alpha) = F_{el}(\alpha, \alpha) \) is the electrostatic force exerted on the nucleus by the electron as a function of \( \alpha \), and \( E \) is the energy eigenvalue in the perturbed boundary problem:

\[
E = E_0 + \alpha \Delta E_0 + \alpha^2 \Delta E_1 + \alpha^3 \Delta E_2 + \cdots
\]  

(2.33)

Equation (2.33) is constructed as follows:

In the perturbed potential problem it is clear that an external force is required to act on the nucleus, when \( \alpha \neq 0 \), in order to keep it in place. This force must be equal in magnitude to \( \Gamma_{el}(\alpha) \), but oppositely directed. If \( \alpha \) is increased by an infinitesimal amount, \( \delta \alpha \), while maintaining the magnitude of the external force the same as that of \( \Gamma_{el}(\alpha) \), then the external agent, acting in the same direction as the displacement of the nucleus, does an amount of work \( F_{el}(\alpha) \delta \alpha \). This work goes into increasing the energy of the nucleus-electron system by \( \delta E \): \( F_{el}(\alpha) \delta \alpha = \delta E \), which is equation (2.32).

Notice that equation (2.32) indicates that \( \alpha = 0 \), for the force exerted on the nucleus by the electron when \( \alpha = 0 \) is zero; using \( E = E_0 + \alpha \Delta E_1 + \alpha^2 \Delta E_2 + \cdots \) in equation (2.32) and evaluating at \( \alpha = 0 \):

\[
\Gamma_{el}(\alpha)|_{\alpha=0} = \alpha \Delta E_1 = 0.
\]

Inserting equation (2.33) into equation (2.32):
\[ F_{el}(\alpha) = 2 \alpha \alpha E_2 + 4 \alpha^3 \alpha E_4 + \cdots \]  

(2.34)

\( \alpha E_2 \) may be found by obtaining an expression for \( \tilde{F}_{el}(\alpha) \), expanding it, and finding the order \( \alpha \) term.

Regarding the electron in the shell as a cloud of charge with charge density \( q_e |\psi(r)|^2 \),

\[ \tilde{F}_{el}(\alpha) = k Z_n q_e \int_{S_{\alpha}} d^3r \frac{\mathbf{r}}{r^3} |\psi(r)|^2. \]  

(2.35)

By symmetry, the \( x - \) and \( y - \) components of \( \tilde{F}_{el}(\alpha) \) are zero; hence, only \( \tilde{F}_{el}(\alpha) \) is interesting. It is

\[ \tilde{F}_{el}(\alpha) = k Z_n q_e \int_{S_{\alpha}} d^3r \frac{\mathbf{r}}{r^3} |\psi(\mathbf{r})|^2 \cos^2 \frac{\theta}{r^2} \psi(\mathbf{r}). \]  

Using the expansion

\[ \psi = \psi_0 + \alpha \psi_1 + \alpha^2 \psi_2 + \cdots \]  

(2.37)

in equation (2.36),

\[ F_{el}(\alpha) = k Z_n q_e \left\{ \int_{S_{\alpha}} d^3r \frac{\psi_0}{r^2} \psi_0 \cos^2 \frac{\theta}{r^2} + 2 \alpha \int_{S_{\alpha}} d^3r \frac{\psi_0}{r^2} \psi_1 \cos^2 \frac{\theta}{r^2} \right\}. \]  

(2.38)

Only the order \( \alpha \) term on the right hand side is desired, so the
terms not explicitly written down may be ignored. Further, note that the first integral is of order $\alpha^3$.

The order $\alpha$ portion of $F_{\alpha}$ is obtained by finding the order one portion of the second integral in equation (2.38). Writing

$$
\int_{\alpha} \int d^3r \, \psi_0 \frac{\cos \theta}{r^2} \psi_1 = \int \int d^3r \, \psi_0 \frac{\cos \theta}{r^2} \psi_1
$$

it is clear that the order one term here is the first integral on the right hand side. The other two integrals are of order $\alpha^2$.

Taking this order one term from equation (2.39), comparison of equations (2.39) and (2.38) shows that

$$
E_2 = k^2 Z \nu_e \int d^3r \, \psi_0 \frac{\cos \theta}{r^2} \psi_1.
$$

Evaluating the integral in equation (2.40) reproduces the expression for $E_2$ found earlier:
To four decimal places:

$$a E_2 = 0.2142 \frac{Z \hbar^4 k^4 e^2}{Q_0^3}$$  \hspace{1cm} (2.41)

(D) Calculation of $\xi_i$; Summary

Using the expressions obtained for $\varphi_0$, $\varphi_i$, and $\rho$, equation (1.53,e) for $\xi$, is easy to evaluate. The result obtained is

$$\xi_i = \frac{16 \pi N^2}{3e^2} \left[ \xi' + (67 - 9e^2) \right] - 1  \hspace{1cm} (2.42)$$

The numerical value of $\xi'(2)$ is best found by working from equation (2.15). Denoting

$$h(\rho) = \int\frac{e^x}{x} dx  \hspace{1cm} (2.43)$$

differentiation and evaluation at $\rho=2$ gives

$$\xi'(2) = C_1 + 18 + \left[ \frac{5}{4} e^2 \left( -\frac{5}{4} + h(2) + 2h'(2) \right) \right]$$  \hspace{1cm} (2.44)

An equation for $c_i$, which is instrumental in simplifying equation
(2.44) may be arrived at by evaluating equation (2.15) at \( p = 2 \).

Recalling that \( t(2) = 0 \), the required expression for \( c_1 \) is

\[
C_1 = -8 - 12 \left[ e^2 - \left( \frac{\pi}{2} + \zeta(2) \right) \right].
\]

(2.45)

Combining equation (2.43) and (2.44), it follows that

\[
t'(2) = 67 - 9 e^2.
\]

(2.46)

Equation (2.46) reduces equation (2.42) to

\[
\xi = \frac{32 \pi}{3} \left( 67 - 9 e^2 \right) - 1.
\]

(2.47)

To four decimal places,

\[
\xi = -0.5729.
\]

(2.48)

\( \xi \) is dimensionless because \( \alpha \epsilon \) has units of energy.

A second method of calculating \( \xi \) is now presented. This method is in essence the same as the second method used to determine \( \alpha E_2 \) and it brings forth some key physical ideas.

In the full perturbation problem, when \( \alpha \neq 0 \) an external force is required to act on the nucleus to keep it in place; see figure 7. Since this external force will be in the \( z \)-direction,
Similarly, as in the treatment used earlier to get $\alpha E_z$, write

$$\vec{F}_{el}(\alpha) = \vec{F}_{el}(\alpha) \frac{Z}{Z} \quad (2.50)$$

where, again, $\vec{F}_{el}(\alpha)$ is the electrostatic force exerted on the nucleus by the electron. There are two other forces experienced by the nucleus: its weight, $-Mgz$, and the force applied to it by the electric field $\vec{E}_s = E_s \hat{z}$, which is $q_e Z_n E_s \hat{z}$. Demanding that these four forces cancel gives

$$\vec{F}_{ext}(\alpha) = \vec{F}_{ext}(\alpha) \frac{Z}{Z}$$

$$\text{Figure 7. Forces Acting on the Nucleus in the Full Perturbation Problem}$$
Imagine the nucleus to be lowered by an amount $\delta \alpha$ -- so $\alpha$ increases by $\delta \alpha$ -- with the four forces just cancelling, as in equation (2.51). Then the external agent does an amount of work $\delta W = -F_{\text{ext}} \delta \alpha$ on the system of nucleus, electron and the fields $E_5 \hat{z}$ and $-g \hat{z}$. The system gains potential energy $q_e Z_n E_5 \delta \alpha$, loses potential energy $M g \delta \alpha$, and has the energy eigenvalue $E$ change by $\delta E$:

$$
\delta W = -F_{\text{ext}} \delta \alpha = q_e Z_n E_5 \delta \alpha - M g \delta \alpha + \delta E .
$$  \hspace{1cm} (2.52)

Note that the $\delta E$ term includes the change in the kinetic energy of the electron, the change in the electrostatic potential energy of the nucleus-electron configuration, as well as the change in the potential energy of the electron in the fields $E_5 \hat{z}$ and $-g \hat{z}$. Recall that this latter potential energy was included in the Hamiltonian via the term $\epsilon z_e = \epsilon (z - \alpha)$. Compiling equations (2.51) and (2.52):

$$
F_{\text{el}}(\alpha) = \frac{\partial E}{\partial \alpha} .
$$  \hspace{1cm} (2.53)

$F_{\text{el}}(\alpha)$ is given by equation (2.36). The expansion for $E$ gives

$$
\frac{\partial E}{\partial \alpha} = 2 \alpha \alpha E_2 + \epsilon \xi_1 + \ldots
$$  \hspace{1cm} (2.54)
\( \varepsilon \), may be obtained by finding the part of \( F_{01}(\alpha) \) which is proportional to \( \xi \).

Working from equation (2.36), substituting in the expansion for \( \psi \), expanding in powers of \( \alpha \) and \( \varepsilon \), and extracting the \( \varepsilon \)-proportional part,

\[
\xi_1 = 2kZ_n q_0^2 \sum \frac{c_{35}\Theta}{r^2} \varphi_1.
\]

Performing the integration indicated,

\[
\xi_1 = \frac{16\pi}{3} N^2 \int_0^2 (2-\rho) \phi_0 \rho d\rho. \tag{2.56}
\]

Write

\[
\int_0^\rho (2-x)x^n dx = v(\rho) e^{-\rho} \tag{2.57}
\]

\( v(\rho) \) must satisfy

\[
v'(\rho) - v(\rho) = (2-\rho) t(\rho),
\]

or, using equation (2.17) for \( t(\rho) \),

\[
v'(\rho) - v(\rho) = 2c_1 \rho - c_1 \rho^2 + \frac{2}{3} \rho^3 - \frac{3}{15} \rho^4 + \frac{11}{120} \rho^5 + \sum_{j=6}^{\infty} (2c_{j-2} - c_j) \rho^j. \tag{2.58}
\]

A power series solution, beginning with a term in \( \rho^2 \), will
satisfy equation (2.58):

\[ V(\rho) = \sum_{j=2}^{\infty} v_j \rho^j \]  

(2.59)

Substitution of equation (2.59) into equation (2.58) leads to the solving of the \( v_j \). The result is

\[ \begin{align*}
V_2 &= C_1 \\
V_3 &= 0 \\
V_4 &= \frac{1}{10} \\
V_5 &= -\frac{1}{30} \\
V_6 &= -\frac{1}{840}
\end{align*} \]  

(2.60)

whence equation (2.59) becomes

\[ v_j = \frac{2C_{j-1} + V_{j-1} - C_{j-2}}{j}, \quad j \geq 2 \]  

(2.61)

Evaluating equation (2.61) at \( \rho=2 \):

\[ V(2) = 4C_1 + \frac{12}{35} + \sum_{j=7}^{\infty} V_j 2^j \]  

(2.62)

to four decimal places:

\[ V(2) = -1.3373 \]  

(2.63)
Inserting equation (2.63) and
\[ \int_0^2 (2\rho) \xi^2 \rho \, d\rho = V(\xi) \xi^{-2}, \]
-- true because \( v(0) = 0 \) -- into (2.61), to four decimal places,

\[ \xi_1 = -0.5729, \]  

(2.64)

which is the same as equation (2.48).

Note that \( \xi_1 \) is negative. The physical reason for this is captured in equations (2.55) and (2.56). Imagine the nucleus to be at the center of the shell, as in the perturbed potential problem. Then, according to equations (2.53) and (2.54),

\[ \int_{\xi = 0}^{\xi_1}(\alpha) \, d\alpha = C \xi_1 + \cdots \]  

(2.65)

Assuming \( \epsilon > 0 \), the electron will have sunk down a little inside the shell, and will be pulling the nucleus down. This means that \( F_{\text{el}}(\alpha) \bigg|_{\alpha = 0} \) will be negative -- see equation (2.49). Equation (2.65) says that, in consequence, \( \xi_1 \) must be negative. (If \( \epsilon < 0 \), the electron has been pulled up, \( F_{\text{el}}(\alpha) \bigg|_{\alpha = 0} > 0 \) and \( \xi_1 < 0 \).)

With \( \xi_1 \) having been found, the problem has been completely solved to first order correction in \( \alpha \) and \( \epsilon \). The eigenfunction is

\[ \psi = \psi_0 + \epsilon \psi_1 + \cdots \]  

(2.66)
to lowest nontrivial order, where

\[ \psi_0 = N \left( \frac{Z_n}{q_s} \right)^{3/2} (2 - \rho) e^{-\rho^2/2} \]

(2.67)

\[ \psi_1 = \frac{N}{2} \left( \frac{Z_n}{q_s} \right)^{5/2} \rho e^{-\rho^2/2} \cos \theta \]

(2.68)

\[ \phi_1 = \frac{2N}{Z_n^{3/2}} \frac{\alpha}{k_B^2} \left[ (\rho) e^{-\rho^2/2} \cos \theta \right] \]

(2.69)

\[ N = \frac{1}{4\sqrt{2}\pi (1 - 7e^{-2})} \]

(2.70)

\[ \alpha_0 = \frac{\hbar^2}{mk_B^2} \]

(2.71)
\[ \rho = \frac{Z_n r}{\alpha} \quad ; \]  

and \( t(\rho) \) is given by either

\[ t(\rho) = C_1 \rho + \frac{1}{5} \rho^3 - \frac{1}{30} \rho^4 + \sum_{j=5}^{\infty} C_j \rho^j, \]  

\[ C_j = \frac{j-2}{(j-1)(j+2)} C_{j-1}, \quad j \geqslant 5 \]

\[ C_4 = -\frac{1}{30} \]  

or

\[ t(\rho) = C_1 \rho + 3 \rho^2 + \frac{1}{2} \rho^3 + 12 \left[ (1 + 2 \rho^2) e^\rho - (3 + 3 \rho^2 + 2 \rho^2 + \int \rho e^x dx) \right] \]  

with

\[ C_1 = -0.4622 \]  

The energy eigenvalue is

\[ E = E_0 + \alpha^2 \alpha E_2 + \epsilon^2 \epsilon E_2 + \alpha \epsilon \epsilon E_1 \]  

to lowest nontrivial order, where
\[
E_0 = -\frac{mk^2 Z_n^2 q_{le}^4}{8r_n^2}, \\
\]

(2.78)

\[
\epsilon E_2 = \int_{\mathcal{R}} d^3r \psi_0 Z \phi_1 = \frac{8\pi N^2}{3Z_n^4} \frac{\alpha_0^3}{k_{ge}^2} \epsilon E_2' ,
\]

(2.79)

\[
\epsilon E_2' = \int_0^2 \rho^3 (2-\rho) t(\rho)e^{-\rho}d\rho = -0.1082 ,
\]

(2.80)

\[
\epsilon E_2 = -0.1713 \frac{\alpha_0^3}{Z_n^4 k_{ge}^2} ,
\]

(2.81)

\[
\alpha E_2 = \left\{ \frac{k^2}{2m} \int_{\mathcal{R}} \psi_2 \psi_0' dS \right\} = \frac{8\pi N^2 Z_n^4}{3e^2} \frac{k_{ge}^2}{\alpha_0^3}
\]

(2.82)
Having found these quantities, the task remaining is to use them to calculate the gravitationally induced electric field inside a metal.

\[ (2.3) \text{THE POSITION OF THE NUCLEUS} \]

The gravitational field, will displace the nucleus from the center of the shell. The electron inside the impenetrable shell responds to resist this displacement, exerting an upwards pull on the nucleus. The nucleus also experiences a force due to the electric field \( \vec{E}_s \). The position of the nucleus, a distance \( a \) down from the center of the shell, is determined by the cancelling of these forces. Mathematically,

\[
F_{el}(\alpha)\big|_{\alpha=a} = M g - Z_n q_e E_s .
\]

Using equations (2.53) and (2.54)

\[
F_{el}(\alpha)\big|_{\alpha=a} = 2 a \vec{E}_z + \varepsilon \vec{E}_1 + \ldots .
\]
Combining these two equations, the solution for $a$, to lowest order, is

$$a = \frac{Mg - Z_n q_e E_s - \epsilon E_f}{2 \alpha E_2} \quad (3.2)$$

The value of $a$ is dependent on the field $E_p$, as discussed earlier. To show this dependence more clearly, substitute $mg + q_e E_s$ for $\epsilon$, and $E_p + E_f$ for $E_s$ -- equations (1.4) and (1.1), respectively -- into equation (3.2), to obtain

$$a = \frac{(M - m \epsilon_E)(g - (Z_n + \epsilon_E)q_e E_I) - (Z_n + \epsilon_E)q_e E_f}{2 \alpha E_2} \quad (3.3)$$

Equation (3.3) shows how $a$ depends on $E_p$.

Having found $a$, the next few steps are to determine the dipole moment $p$ of each of the model ions, arrange the ions in a chosen lattice pattern, and calculate $E_p$ in terms of $p$. Since $p$ will depend on $a$, and $a$ in turn on $E_p$, it will be possible to determine both $p$ and $E_p$.

Notice that $a/a_0$ is indeed very small, as was claimed early in this thesis. This is easy to see by using equation (2.82) in equation (3.3) and taking $E_p$ to be of the order $Mg/q_e$. The result is $a/a_0 \approx 10^{-18}$.
(2.4) CALCULATION OF THE DIPOLE MOMENT OF EACH ION IN TERMS OF $E_{\vec{p}}$

An important question at this stage of development of the model for the ions is: what is the electric field in a shell which is due to the nuclei and electrons in all of the other shells? To find the answer, it is necessary to first answer a closely related question: what is the electric field due to an ion far away from that ion? By an ion is meant here a nucleus and an electron bounded by an impenetrable shell.

Recalling the discussion at the beginning of this chapter, the electric field at the site of an ion, due to all of the others, will be given to a very good approximation simply in terms of the dipole moment $\vec{p}$ of each ion. The monopole moments are taken into account by $E_{\text{eh}}$.

Relative to a chosen origin, the dipole moment $\vec{p}$ of a charge distribution $\rho(\vec{r})$ is

$$\vec{p} = \int \vec{r} \rho(\vec{r}) \, d^3r$$

(4.1)

where the integration goes over all of the charge distribution. Relative to that same origin, the contribution to the electric field at $\vec{r}_0$, due to the dipole moment of the charge distribution, is

$$\vec{E}(\vec{r}_0) = \frac{3 \vec{r}_0 (\vec{p} \cdot \vec{r}_0) - \vec{r}_0 \vec{r}_0 \cdot \vec{p}}{r_0^5}$$

(4.2)
assuming that $\mathbf{r}_n$ lies outside the charge distribution. Equation (4.1) shall be used to calculate the dipole moment of each ion. The origin shall be chosen to coincide with the site of the nucleus. The charge density $\rho(\mathbf{r})$ is given by

$$
\rho(\mathbf{r}) = Z_n e \delta(\mathbf{r}) - q_e |\psi(\mathbf{r})|^2
$$

whence

$$
\mathbf{p} = -q_e \int_{S,\alpha} \mathbf{r} |\psi(\mathbf{r})|^2 \, d^3 r .
$$

It is clear that the physical features of the problem are invariant under rotations around the $\hat{z}$-axis. That is, the problem has axial symmetry, and as such, $\mathbf{p}$ must be in the $\hat{z}$-direction. With this realization, equation (4.4) simplifies to

$$
\mathbf{p} = p \hat{z}
$$

where

$$
p = -q_e \int_{S,\alpha} d^3 r \ z |\psi(\mathbf{r})|^2
$$

Using the familiar expansion for $\psi$, $\psi = \psi_0 + a \psi_1 + \ldots$ (note that $\alpha = a$ now, because the nucleus is held up without the imagined force $\mathbf{F}_{\text{ext}}$), equation (4.6) may be expanded out:
To the lowest order,

\[ p = -\varrho e \left\{ 2a \int_R d^3r \psi \psi' z \psi' + 2\epsilon \int_R d^3r \psi \psi z \phi \right\} \quad \text{(4.7)} \]

The integrals here are familiar. From earlier work,

\[ \int_R d^3r \psi \psi' z \psi' = \frac{1}{2} \left( 1 + \varepsilon \right) \quad \text{(4.8)} \]

and

\[ \int_R d^3r \psi \psi z \phi = eE_2 \quad \text{(4.9)} \]

Equation (4.9) is an old result. Equation (4.8) follows from equation (1.47) and

\[ \frac{\hbar^2}{2m} \int_R \chi \psi \psi' ds = \int_R d^3r \psi \psi z \psi' \]
which itself follows from equations (1.48) and (2.46).

Making the replacements (4.7) and (4.9) in (4.7),

\[ p = -q_e \left\{ (1 + \varepsilon_1) \alpha + 2e E_f \right\}. \quad \text{(4.10)} \]

The insertion of equation (3.4) into equation (4.10) gives \( p \) explicitly in terms of \( E_p \):

\[ p = p_0 + p'E_p \quad \text{(4.11)} \]

where

\[ p_0 = \left[ \frac{q_e^2}{2e} \left( \frac{(1 + \varepsilon_1)(Z_n + \varepsilon_1)}{2 \alpha E_2} - 2E_f \right) \right] E_f - q_e \left[ \frac{(1 + \varepsilon_1)(M - m \varepsilon_1)}{2 \alpha E_2} + 2mE_2 \right] q \quad \text{(4.12)} \]

and

\[ p' = \left( \frac{(1 + \varepsilon_1)(Z_n + \varepsilon_1)}{2 \alpha E_2} - 2E_f \right) q_e^2. \quad \text{(4.13)} \]

As desired, \( p \) has now been expressed in terms of \( E_p \).
The task of this section is to calculate the electric field inside a shell due to the nuclei and electrons in all of the other shells. As noted at the very beginning of this chapter, this electric field may be taken to be uniform inside the shell. The basic reason behind this approximation shall now be repeated.

Denote by \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) the electric field at the position \( \mathbf{r} \) inside of a shell, which is due to all of the other model ions, that is, all of the nuclei and electrons in the other shells. \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) will vary a little as \( \mathbf{r} \) varies inside the shell. To include this spatial variation of \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) in the Schrödinger equation for the electron inside a shell would have rendered the problem a very difficult one. For example, \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) is not initially known, and so the form of the potential to enter in the Schrödinger equation would not have been known. This dilemma was circumvented from the outset by replacing \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) by a uniform field in the \( \hat{z} \)-direction. Since the average of \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) over the interior of the shell is just the value of \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) at the center of the shell, \( \mathbf{E}_{\text{ions}}(\mathbf{r}_c) \), it was decided to replace \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) in the Schrödinger equation by \( \mathbf{E}_{\text{ions}}(\mathbf{r}_c) \), with the idea that the model would be constructed so that \( \mathbf{E}_{\text{ions}}(\mathbf{r}_c) \) would be in the \( \hat{z} \)-direction. But notice that \( \mathbf{E}_{\text{ions}}(\mathbf{r}_c) \) will differ only slightly from \( \mathbf{E}_{\text{ions}}(\mathbf{r}_n) \), the value of \( \mathbf{E}_{\text{ions}}(\mathbf{r}) \) at the site of the nucleus, because the nucleus sits a
very small distance a below the center of the shell. As such, it
is just as good to replace $\vec{E}^\text{ions} (r)$ by $\vec{E}^\text{ions} (r_n)$.

In the introductory passage to this chapter, it was noted
that $\vec{E}^\text{ions} (r_n)$ is equal to $E_p$. Recall what $E_p$ is: in a lattice
of electric dipoles, $\vec{E}_p$ is the electric field at the site of one
dipole due to all of the others. As such $\vec{E}^\text{ions}$ shall be
replaced by $\vec{E}_p$.

To summarize, the electric field inside of a shell due to
the nuclei and electrons inside all of the other shells is
approximated, in this work, to be uniform and equal to $\vec{E}_p$.

The shells will be arranged so that $\vec{E}_p$ is in the $\hat{z}$-direction. An expression for $\vec{E}_p$ in terms of $\vec{p}$ will now be
found.

Consider the shells to be arranged in a lattice. Then the
nuclei are arranged in the same lattice. To calculate $\vec{E}_p$,
imagine replacing each shell by a dipole with moment $\vec{p}$. These
dipoles are arranged, therefore, in the original lattice of the
shells.

The electric field at the site of one of these dipoles due
to all of the others will be a sum of terms like the right hand
side of equation (4.2). Choose a coordinate system with its
origin at the site of the dipole in question. Denote the
primitive translation vectors of the lattice $\vec{a}_1, \vec{a}_2, \vec{a}_3$. Then
the dipoles are located at positions $\vec{r}_n= n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, where $n$
is abbreviated notation for the three integers $n_1, n_2, n_3$. From
equation (4.2), the electric field at the origin due to the
dipole at $\vec{r}_n$ is
where it has been assumed that not all of $n, n', n''$ are zero. The net electric field at the origin, $\vec{E}_p$, is obtained by summing the right hand side of equation (5.1) over all lattice sites, excluding the one at the origin

$$\vec{E}_p = \sum_{n''}^{'} \frac{3 \vec{r}_{n''} \cdot (\vec{p} \cdot \vec{r}_{n''}) - \vec{r}_{n''}^2 \vec{p}}{r_{n''}^5} k$$

(5.2)

$\vec{E}_p$ must be in the $\hat{z}$-direction. This can be achieved by a suitable choice of lattice. Recall that $\vec{p}$ is in the $\hat{z}$-direction. Therefore, according to equation (5.2), if for every dipole located at $(x, y, z)$, there is one at $(x, y, -z)$, the $x$- and $y$-components of $\vec{E}_p$ will vanish.

$$\vec{E}_p = E_p \hat{z}$$

(5.3)

where

$$E_p = p \sum_{n''}^{'} \frac{3 Z_{n''}^2 - r_{n''}}{r_{n''}^5} k$$

(5.4)

and $Z_{n''}$ is the $z$-component of $\vec{r}_{n''}$.

Denoting by $d$ the lattice constant, equation (5.4) may be written as

$$E_p = \frac{S_p k}{d^3}$$

(5.5)
where the dimensionless sum $S$ is

$$S = d^3 \sum \frac{3z_{\alpha}^2 - \bar{r}_{\alpha}^2}{\bar{r}_{\alpha}^5}$$

(5.6)

Equation (5.5) is the relation which gives $E_p$ in terms of $p$.

**2.6 SOLUTIONS FOR $p$ AND $E_p$**

Equations (4.11) and (5.5) may be combined to solve for both $p$ and $E_p$. The results are:

$$p = \frac{b_0}{1 - \frac{S p' k}{d^3}}$$

(6.1)

$$E_p = \frac{S k}{d^3} \frac{p_0}{1 - \frac{S k' k}{d^3}}$$

(6.2)

Using equations (4.12) and (4.13), equation (6.1) may be written out in full as
Equation (6.3) is a very important result, for, as will be seen in the next chapter, it enters directly into the expression for the average electric field resulting from the lattice of ions.

\[
\rho = \frac{\left(\frac{(1+\varepsilon_1)(Z_n+\varepsilon_1)}{2\varepsilon_E_2} - 2eE_2\right) q_e^2}{E_1} - \left[\frac{(1+\varepsilon_1)(M-m\varepsilon_1)}{2\varepsilon_E_2} + 2mE_2\right] q_e^2 \tag{6.3}
\]

\[1 + \left(\frac{2eE_2 - (1+\varepsilon_1)(Z_n+\varepsilon_1)}{2\varepsilon_E_2}\right)\int \frac{kq_e^2}{d^3}
\]

Far away from a model ion, the electric field due to the ion may be taken as that produced by an electric dipole placed at the site of the nucleus (again, the monopole moment is being ignored). In order to calculate the average electric field due to the lattice of ions, however, it is necessary to consider the electric field due to an ion for positions very close to that ion, and even for positions inside of the ion! Consequently, it is not at all obvious that the average field created by the ion will be given in terms of just its dipole moment. As such, a proof is now presented that this is indeed so.

To begin with, it is necessary to decide how to go about calculating the average field due to the lattice of dipoles. Keeping in mind that one of the key purposes of the model is to express ideas, the following method is adopted:

Let \( V_c \) denote the volume of a primitive cell of the lattice. Consider a spherical region with volume \( V_c \), centered
on the middle of one of the shells, as in figure 8. Call this region "$\Sigma$"

The average electric field due to the lattice of ions shall be taken to be the average electric field inside of $\Sigma$ that is due to the ions.

The electric field at the point $\mathbf{r}'$ in the region, due to the nucleus and electron inside the shell which lies in $\Sigma$, is

$$
\overrightarrow{E}(\mathbf{r}') = k \frac{Z_n q_e}{r'^3} \mathbf{r}' + \int_{\Sigma} d^3r \ k \frac{q_e |\psi(r)|^2}{|r-r'|^3} (\mathbf{r}-\mathbf{r}')
$$

(7.1)

where the contribution due to the monopole moment is included explicitly. A few simple steps show that the average of this in the region $\Sigma$ is

![Figure 8. The Spherical Region $\Sigma$](image)
The integral over $\mathbf{r}'$ in equation (7.2) may be recognized as
the electric field at a point $\mathbf{r}$ inside of a sphere of radius $R = (3\hbar/4\pi)^{1/3}$ with a uniform charge density $q_0e/\nu_c$. By spherical
symmetry, this electric field must point radially outward and depend only on $r$:

$$\int_{S} d^3 r' / k \frac{q_0}{\nu_c} \frac{(r^2 - r'^2)}{(r^2 - r'^2)^{3/2}} = E(r) \hat{r}$$

Using Gauss' law,

$$E(r) = k \frac{q_0}{\nu_c} \frac{4\pi}{3} r$$

and so

$$\mathbf{E}_{\text{ave, } \hat{r}} = k \frac{q_0}{\nu_c} \frac{4\pi}{3} \int_{S, \alpha} d^3 r' |\psi(\mathbf{r'})|^2 \hat{r}.$$ 

Recalling equation (4.4), the expression for $\mathbf{p}$, and realizing that $\nu_c = 1/n_5$, where $n_5$ is the number of shells per unit volume, equation (7.3) becomes

$$\mathbf{E}_{\text{ave, } \hat{r}} = -\frac{4\pi}{3} n_5 k \mathbf{p}.$$ 

(7.4)
Equation (7.4) gives the average electric field, due to the nucleus and electron in a shell, in a sphere of volume $\frac{4\pi}{3} \frac{1}{n_5}$ that is concentric with the shell.

It is easy to see that equation (7.4) is in fact a general result for any charge distribution whose dipole moment is $\mathbf{P}^*$, where $\mathbf{P}^*$ is given by equation (4.1). All that is required is to retrace the steps from equation (7.1) to equation (7.4) for a charge distribution with density $\rho(r)$.

The electric field given by equation (7.4) is not quite the average field due to the lattice of dipoles; it includes only the contribution by the ion inside the region. Required still is the contribution by the ions, or dipoles, exterior to the region, as well as the so called boundary-dipole contribution. It is a well known result of electrostatics that the average value of the electric field over a spherical region, due to changes exterior to the region, is equal to the electric field due to those exterior charges at the center of the spherical region. Accordingly, the average field in the spherical region $\Sigma$ due to the dipoles exterior to it, is the value of the field they create at the center of the sphere, and this is just $E_p$.

The boundary-dipole contribution $E_{b.d.}$ is the contribution of an effective surface charge density $\delta_b$ to the ambient electric field. The cause of $\delta_b$ is the termination of the dipole density distribution $\mathbf{P}(\mathbf{r})$ on the surface of the metal. $\delta_b$ is given by

$$\delta_b(r_b^*) = \mathbf{P}(r_b^*) \cdot \hat{n}(r_b^*)$$
where \( \vec{r}_0 \) locates a point on the metal surface and \( \hat{n} \) is the unit outward normal. Ignoring contributions from the sides of the metal, \( E_{b.d.} \) is given by

\[
E_{b.d.} = -4\pi k n_s \vec{p}
\]

where \( n_s \) is the average number density of shells in the metal.

\( \vec{E}_{b.d.} \), \( \vec{E}_{ave,p} \), and \( E_p \) involve \( n_s \), and all contribute to \( \vec{E}_{dipoles} \).

In conclusion, the average field due to the lattice of dipoles is just \( \vec{E}_{ave,p} + \vec{E}_p + \vec{E}_{b.d.,} \) or:

\[
\vec{E}_{dipoles} = \left( \frac{S}{d^3} - \frac{16\pi}{3} n_s \right) k\vec{p}
\]  \( (7.5) \)

In order to evaluate equation (7.5), lattices must be chosen, and \( S \) must be determined.

(2.8) LATTICE TYPES

Recall the requirement that each lattice must meet: for every lattice site at \((x,y,z)\), there must be one at \((x,y,-z)\). Some lattices are now described which meet this requirement.
(A) Cubic Lattice

The primitive translation vectors in this case are $\mathbf{d}_x$, $\mathbf{d}_y$, $\mathbf{d}_z$. The cubic lattice is a very special case, for the field $\mathbf{E}_p$, given by equation (5.2), is zero, regardless of the orientation of $\mathbf{p}$. To see this, consider the $x$-component of $\mathbf{E}_p$:

$$\mathbf{E}_p = \frac{1}{d^3} \sum_{n_1, n_2, n_3} \frac{2 n_1^2 \mathbf{p}_x + 3(n_1 n_2 p_y + n_1 n_3 p_z) - (n_2^2 + n_3^2) \mathbf{p}_x}{(n_1^2 + n_2^2 + n_3^2)^{3/2}}$$

where $\mathbf{r}'_n = (n_1 \mathbf{e}_x + n_2 \mathbf{e}_y + n_3 \mathbf{e}_z) d$, and the sum excludes $n_1 = n_2 = n_3 = 0$. Summing over the cross terms $n_1 n_2$ and $n_1 n_3$ will give zero. Also, by symmetry,

$$\sum_{n_1, n_2, n_3} \frac{n_1^2}{(n_1^2 + n_2^2 + n_3^2)^{3/2}} = \sum_{n_1, n_2, n_3} \frac{n_2^2}{(n_1^2 + n_2^2 + n_3^2)^{3/2}} = \sum_{n_1, n_2, n_3} \frac{n_3^2}{(n_1^2 + n_2^2 + n_3^2)^{3/2}}$$

and in consequence, the entire sum vanishes identically.

For a cubic lattice, $\mathbf{E}_p = 0$ and $S$ is zero in equation (7.1).

---

(B) Face-centered Cubic Lattice

Consider a face-centered cubic structure, oriented as in figure 9, such that the primitive translation vectors are
The lattice satisfies the requirement that the lattice sites come in pairs with the same $x$- and $y$-coordinates, but $z$-coordinates differing in sign.

It turns out that $E_p$ for this lattice is zero. To see this, break up the sum over lattice sites into two parts. Consider first the sum over the lattice sites located at

\[
\vec{a}_1 = \frac{1}{\sqrt{2}} d (\hat{x} + \hat{y}) \\
\vec{a}_2 = \frac{1}{\sqrt{2}} d (\hat{y} + \hat{z}) \\
\vec{a}_3 = \frac{1}{\sqrt{2}} d (\hat{z} + \hat{x})
\] (8.1)
where \( n_1, n_2, n_3 \) assume all integer values except \( n_1=n_2=n_3=0 \). This gives \( E_P \) for a cubic lattice with lattice constant \( \sqrt{2} d \), and is therefore zero. Now consider the sum over the rest of the lattice sites. Each of these sites falls into one of the following three sets:

\[
\vec{R}_1 = \sqrt{2} d \left( n_1 \hat{x} + (n_2 + \frac{1}{2}) \hat{y} + (n_3 + \frac{1}{2}) \hat{z} \right)
\]

\[
\vec{R}_2 = \sqrt{2} d \left( (n_1 + \frac{1}{2}) \hat{x} + n_2 \hat{y} + (n_3 + \frac{1}{2}) \hat{z} \right)
\]

\[
\vec{R}_3 = \sqrt{2} d \left( n_1 \hat{x} + n_2 \hat{y} + (n_3 + \frac{1}{2}) \hat{z} \right)
\]

In each case, \( n_1, n_2, n_3 \) assume all integer values, including \( n_1=n_2=n_3=0 \). It is easy to show that the net contribution to \( E_P \) by the dipoles at these lattice sites is also zero: one need only be aware that the \( n_1, n_2, n_3 \) in the sums are simply dummy variables.
(C) Closest Packing; Type 1

In this lattice, the shells are arranged such that a layer of closest packed shells, in the x-y plane repeats in the z-direction. This is expressed precisely by the primitive translation vectors

\[
\vec{a}_1 = d \hat{x} \\
\vec{a}_2 = \frac{1}{2} d \hat{x} + \frac{1}{2} \sqrt{3} d \hat{y} \\
\vec{a}_3 = d \hat{z}
\]

(8.2)

(D) Closest Packing; Type 2

This case differs from the previous one only in that \( \vec{a}_3 \) is different:

\[
\vec{a}_1 = d \hat{x} \\
\vec{a}_2 = \frac{1}{2} d \hat{x} + \frac{1}{2} \sqrt{3} d \hat{y} \\
\vec{a}_3 = 2 \sqrt{\frac{2}{3}} d \hat{z}
\]

(8.3)

This lattice may be thought of as hexagonal closest packing with
every second layer missing.

(E) Hexagonal Closest Packed

This is not a lattice, but is a lattice with a two-point basis. Even so, it meets the requirement of having a shell at \((x,y,-z)\) for one at \((x,y,z)\). The basis vectors are \(\vec{b}_1 = 0\) and

\[
\vec{b}_2 = \frac{1}{\sqrt{3}} \vec{a}_1 \wedge \vec{a}_3.
\]

Having outlined the types of shell arrangements to be considered, evaluation of \(S\) for each type shall now be discussed.

Before leaving this section, the values of \(n_s\) for each arrangement are presented. \(n_s\) is given by \(1/\mathcal{V}_c\) and \(\mathcal{V}_s\) is given by \(\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)\). The values of \(n_s\) are:

- **(A) Cubic Lattice:** \(n_s d^3 = 1\)
- **(B) Face-centered Cubic Lattice:** \(n_s d^3 = \sqrt{2}\)
- **(C) Closest Packing; Type 1:** \(n_s d^3 = 2/\sqrt{3}\) \hspace{1cm} (8.4)
- **(D) Closest Packing; Type 2** \(n_s d^3 = 1/\sqrt{2}\)
- **(E) Hexagonal Closest Packed:** \(n_s d^3 = \sqrt{2}\)
The obvious way to evaluate $S$ for a given arrangement of shells is to insert

$$\vec{r}_{2r} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

into equation (5.6). This is not a very successful procedure, however, because the resultant sum is very slowly converging, and many terms need to be added up together to obtain reasonably good accuracy in the final result. It is not practical to proceed in this manner. A more rapidly converging expression for $S$ is required. It is the objective of this section to provide such an expression.

The electrostatic potential $\Phi(\vec{r})$ at $\vec{r}$ due to a dipole $\vec{p}$ at $\vec{r}'$ is

$$\Phi(\vec{r}) = \frac{\vec{p} \cdot (\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} \kappa$$

(9.1)

where it has been assumed in writing equation (9.1) that $\vec{r} \neq \vec{r}'$. The electric field $\vec{E}(\vec{r})$ at $\vec{r}$ due to the dipole at $\vec{r}'$ is obtained from $\Phi(\vec{r})$ by

$$\vec{E}(\vec{r}) = -\nabla \Phi(\vec{r})$$

(9.2)

It is easy to verify that
Since \( \mathbf{p} = p \mathbf{\hat{z}} \), \( \mathbf{p} \cdot \nabla = p \partial / \partial z \). Only the \( \mathbf{\hat{z}} \) component of \( \mathbf{E}(\mathbf{r}) \) is of interest, so consider only

\[
\left[ E_z(\mathbf{r}) \right] = \mathbf{p} \frac{\partial^2}{\partial z^2} \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right) k. \tag{9.4}
\]

\( E_p \) is obtained by summing equation (9.4) over all dipoles except for the one at the origin. \( E_p \) is:

\[
E_p = \mathbf{p} \left[ \sum_{\mathbf{r}', \mathbf{b}_i} \frac{\partial^2}{\partial z^2} \left( \frac{1}{|\mathbf{r} - \mathbf{r}' - \mathbf{b}_i|} \right) \right] \bigg|_{\mathbf{r}' = \mathbf{0}}. \tag{9.5}
\]

The \( \mathbf{r}' \)'s in equation (9.5) are the lattice sites, the \( \mathbf{b}_i \) are the basis sites associated with each lattice point, and the prime means to omit the term at \( \mathbf{r}' = \mathbf{0} \), \( \mathbf{b}_i = \mathbf{0} \).

Define

\[
S_z'(\mathbf{r}) = \sum_{\mathbf{r}', \mathbf{b}_i} \frac{\partial^2}{\partial z^2} \left( \frac{1}{|\mathbf{r} - \mathbf{r}' - \mathbf{b}_i|} \right). \tag{9.6}
\]

Note that \( S_z'(\mathbf{0}) = S/\mathbf{d}^3 \).

The problem of determining \( E_p \) is tantamount to the problem of evaluating \( S_z'(\mathbf{r}) \) at \( \mathbf{r} = 0 \). No delta functions are hidden in
equation (9.6), since the domain of \( \vec{r} \) under study excludes all of the sites \( \vec{r}', \vec{b}_i \). Specifically, equation (9.6) is of interest only for \( \vec{r} \) near the origin.

Use (2)

\[
\frac{1}{|a|} = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-a^2 \rho^2} \, d\rho
\]  

(9.7)

to write \( S'(\vec{r}) \) as

\[
S'(\vec{r}^\circ) = \sum' \frac{2}{\vec{r}', \vec{b}_i} \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{\partial}{\partial \rho} e^{-r^2 \rho^2} d\rho 
\]  

(9.8)

(It is easy to verify that the operator \( \partial^2 / \partial z^2 \) may be taken inside the integral sign.)

The next step is to break the integration up into two parts: from zero to \( G \), and from \( G \) to infinity, where \( G \) is any finite positive number. The expression for \( S'(\vec{r}) \) then becomes

\[
S'(\vec{r}^\circ) = \sum' \frac{2}{\vec{r}', \vec{b}_i} \frac{1}{\sqrt{\pi}} \int_0^G \frac{\partial}{\partial \rho} e^{-r^2 \rho^2} \, d\rho + \sum' \frac{2}{\vec{r}', \vec{b}_i} \frac{1}{\sqrt{\pi}} \int_G^\infty \frac{\partial}{\partial \rho} e^{-r^2 \rho^2} \, d\rho
\]  

(9.9)

At this point, the term

\[
\frac{2}{\sqrt{\pi}} \int_0^G \frac{\partial}{\partial \rho} e^{-r^2 \rho^2} \, d\rho
\]  

is added and subtracted from equation (9.9). The advantage of doing this is that the first sum will then be periodic, with the
periodicity of the lattice, a property which will be exploited shortly.

It is easy to show that

$$\left. \left( \frac{-z}{\sqrt{\pi}} \int_0^z \frac{d^2}{dz^2} e^{-r^2 \rho^2} d\rho \right) \right|_{r=0} = \frac{4G^3}{3\sqrt{\pi}} \tag{9.10}$$

Now define

$$F(r') = \sum_{r', b=1}^n \frac{2}{r', b} \int_0^{\infty} \frac{d^2}{dz^2} e^{-r^2 \rho^2} d\rho, \tag{9.11}$$

where the term for \( r'=0, \ b=0 \) is included. \( F(\cdot) \) has the periodicity of the lattice. Using equations (9.10) and (9.11), equation (9.9) may be written as:

$$\left[ S(r') \right]_{r'=0} = \left[ F(r') \right]_{r'=0} + \left[ \sum_{r', b=1}^n \frac{2}{r', b} \int_0^{\infty} \frac{d^2}{dz^2} e^{-r^2 \rho^2} d\rho - \int_0^{\infty} \rho^2 e^{-r^2 \rho^2} d\rho \right]_{r'=0} + \frac{4G^3}{3\sqrt{\pi}} \tag{9.12}$$

Now evaluate the middle term on the right-hand side of equation (9.12):

$$\left[ \int_0^{\infty} \frac{d^2}{dz^2} e^{-r^2 \rho^2} d\rho \right]_{r'=0} = 4 \left( \sum_{r', b=1}^n \frac{2}{r', b} \right) \int_0^{\infty} \rho^4 e^{-r^2 \rho^2} d\rho - 2 \int_0^{\infty} \rho^2 e^{-r^2 \rho^2} d\rho \tag{9.12}$$

Doing the first integral here by parts simplifies the right-hand
Doing the remaining integral by parts now gives

$$2 \frac{(Z' + (b_i, z))^2}{|r'' + b_i|^2} G^3 e^{-|r'' + b_i|^2} \frac{r'' + b_i}{2} + (3 \frac{(Z' + (b_i, z))^2}{|r'' + b_i|^2} - 1) \int_0^\infty \rho^2 e^{-|r'' + b_i|^2} d\rho$$

Using

$$\int_0^\infty e^{-|r'' + b_i|^2} r'' d\rho = \frac{\sqrt{\pi}}{2} \frac{1}{|r'' + b_i|^3} \text{erfc}(\frac{|r'' + b_i|^2}{2})$$

allows that this be expressed as

$$\frac{2 (Z' + (b_i, z))^2}{|r'' + b_i|^2} G^3 e^{-|r'' + b_i|^2} \frac{r'' + b_i}{2} + (3 \frac{(Z' + (b_i, z))^2}{|r'' + b_i|^2} - 1) \int_0^\infty \rho^2 e^{-|r'' + b_i|^2} d\rho$$

where

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt \quad (9.13)$$

The result of this simplification is

$$\left[ \sum_{i=0}^\infty \frac{2^2}{|r'' + b_i|^2} \int_0^\infty e^{-|r'' + b_i|^2} \rho^2 d\rho \right]_{r'' = 0} = \frac{2}{\sqrt{\pi}} \sum_{i=0}^\infty \left[ \frac{(Z' + (b_i, z))^2}{|r'' + b_i|^2} G^3 e^{-|r'' + b_i|^2} \frac{r'' + b_i}{2} \right.$$

$$+ \left(3 \frac{(Z' + (b_i, z))^2}{|r'' + b_i|^2} - 1 \right) \frac{1}{|r'' + b_i|^2} \left\{ G e^{-|r'' + b_i|^2} \frac{r'' + b_i}{2} \right\}$$

$$\text{erfc}(|r'' + b_i|^2) \left\{ \frac{1}{2} \int_0^\infty \rho^2 e^{-|r'' + b_i|^2} d\rho \right\} \quad (9.14)$$
Only $F(\mathbf{r})$ still needs to be found. As noted previously, $F(\mathbf{r})$ has the periodicity of the lattice. As such, $F(\mathbf{r})$ has an expansion of the form

$$F(\mathbf{r}) = \sum_{\mathbf{g}} F_{\mathbf{g}} e^{i \mathbf{g} \cdot \mathbf{r}}$$

(9.15)

where the $\mathbf{g}$ are the reciprocal lattice vectors. The $F_{\mathbf{g}}$ are given by

$$F_{\mathbf{g}} = \frac{1}{V_c} \int_{c} d^3 r F(\mathbf{r}) e^{-i \mathbf{g} \cdot \mathbf{r}}$$

(9.16)

where $V_c$ is the volume of a primitive cell and the integration is carried out over a primitive cell. Note that $e^{i \mathbf{g} \cdot \mathbf{r}}$ has the periodicity of the lattice, by definition of reciprocal lattice vectors, and so equation (9.16) may be written as

$$F_{\mathbf{g}} = \frac{1}{V_N} \int_{Nc} d^3 r F(\mathbf{r}) e^{-i \mathbf{g} \cdot \mathbf{r}}$$

(9.17)

where $V_N = N V_c$ and the integration goes over $N$ primitive cells. Equation (9.17) shall be used in the limit $N \to \infty$, as is now
demonstrated. Inserting equation (9.11) into equation (9.17), and simplifying:

\[ F_{\mathbf{g}} = \frac{1}{\mathcal{V}_N \sqrt{\pi}} \sum_{\mathbf{b}_i} \int_0^G d\rho \sum_{\mathbf{r}} \int_{N_c} d^3r \frac{\partial^2}{\partial z^2} \left( e^{-|\mathbf{r}'-\mathbf{b}_i|^2/\rho^2} \right) e^{-i \mathbf{j} \cdot (\mathbf{r}'-\mathbf{r})} \]

Now, let \( N \rightarrow \infty \) in such a manner as to cover all of \( \mathbf{r}' \)-space. Then the \( \mathbf{r}' \) integral is the same for every \( \mathbf{r}' \), reducing the expression above to

\[ F_{\mathbf{g}} = \frac{1}{\mathcal{V}_N \sqrt{\pi}} \sum_{\mathbf{b}_i} \int_0^G d\rho \int d^3r \frac{\partial^2}{\partial z^2} \left( e^{-|\mathbf{r}'-\mathbf{b}_i|^2/\rho^2} \right) e^{-i \mathbf{j} \cdot \mathbf{r}'}, \]  

(9.18)

where the \( \mathbf{r}' \) integral is over all of \( \mathbf{r}' \)-space now.

It is not difficult to show that, for \( \mathbf{g} \not= 0 \),

\[ \int d^3r \frac{\partial^2}{\partial z^2} \left( e^{-|\mathbf{r}'-\mathbf{b}_i|^2/\rho^2} \right) e^{-i \mathbf{j} \cdot \mathbf{r}'} = -g_2 e^{-i \mathbf{j} \cdot \mathbf{b}_i} \int d^3r' e^{-r'^2/4\rho^2} \]

and in turn that

\[ \int d^3r e^{-r^2/4\rho^2} = \frac{1}{\rho^3} e^{-\frac{3}{2} / 4\rho^2} \]

thereby reducing equation (9.18) to

\[ F_{\mathbf{g}} = \frac{2\pi}{\mathcal{V}_N} g_2 \sum_{\mathbf{b}_i} e^{-i \mathbf{j} \cdot \mathbf{b}_i} \int_0^G \frac{d\rho}{\rho^3} e^{-g^2/4\rho^2} \]  

(9.19)
The integral over $\rho$ is easily evaluated, with the result
\[
\int_0^\infty \frac{1}{\rho^3} e^{-\frac{q^2}{4\rho^2}} d\rho = \frac{2}{q^2} e^{-\frac{q^2}{4\rho^2}}
\]

This simplifies equation (9.19) to:
\[
F_{ij} = -\frac{4\pi}{\nu_c} \frac{q_x^2}{q^2} e^{-\frac{q^2}{4\rho^2}} \sum_{\vec{b}_i} e^{i\vec{b}_i \cdot \vec{r}} \tag{9.20}
\]

Equation (9.20) applies for $\vec{g} \neq 0$. To finish it is necessary to find $F_0$. Equation (9.18) will not be used to evaluate $F_0$. Instead, use will be made of the following information: if the dipoles at the sites $\vec{r}'$ in a lattice vary in direction according to $\vec{p}(\vec{r}') = p e^{i\vec{q} \cdot \vec{r}'}$, where $p$ and $q$ are constants, then the $g^0$ term of the reciprocal lattice sum makes the following contribution to $\vec{E}(\vec{r})$:
\[
-\frac{4\pi}{\nu_c} \frac{\vec{p}(\vec{r}) \cdot \vec{q}^2}{q^2} \hat{q} \cdot \hat{r} + \frac{4\pi}{\nu_c} \left(1 - e^{-\frac{q^2}{4\rho^2}}\right) \frac{\vec{b}(\vec{r}) \cdot \vec{q}^2}{q^2} \hat{q} \cdot \hat{r}
\]

The first term here is the macroscopic electric field $\vec{E}(\vec{r})$ due to a macroscopic polarization wave $\vec{P}(\vec{r}) = \frac{\vec{p}}{\nu_c} e^{i\vec{q} \cdot \vec{r}'}$, so the contribution is simply
\[
\vec{E}(\vec{r}) + \frac{4\pi}{\nu_c} \left(1 - e^{-\frac{q^2}{4\rho^2}}\right) \frac{\vec{b}(\vec{r}) \cdot \vec{q}^2}{q^2} \hat{q} \cdot \hat{r}
\]
As \( \vec{q} \) goes to \( \vec{0} \), the second term vanishes. The first term becomes the average electric field due to a uniform polarization distribution \( P = \frac{\vec{E}}{V_c} \), and is \( -\frac{4\pi}{3V_c} \vec{p} \).

Thus, \( F_{0}^* = -\frac{4\pi}{3V_c} \vec{p} \) for a lattice. Taking into account the basis sites,

\[
F_{0}^* = -\frac{4\pi}{3V_c} \sum_{b_i} \langle 1 \rangle = -\frac{4\pi}{3V_c} N_{b_i}
\]

(9.21)

where \( N_{b_i} \) is the number of basis sites. Combining equations (9.20), (9.21), (9.5) and (9.4), equation (9.12) becomes

\[
\left[ S'(\vec{r}) \right]_{\vec{r} \to \vec{0}} = -\frac{4\pi}{V_c} \sum_{j} \frac{g_z^2}{g^2} e^{-g^2/4\alpha^2} \sum_{b_i} e^{i\vec{r} \cdot \vec{b}_i}
\]

\[
+ \frac{4\alpha^3}{3\sqrt{\pi}} N_{b_i}^2 - \frac{3\pi}{3V_c} N_{b_i}
\]

(9.22)

where only the real part of equation (9.20) matters physically.

Recall that \( E_p \) is given in terms of \( S'(\vec{0}) \) by

\[
E_p = \int S'(\vec{0}) \, d^3 k = \frac{S}{d^3}
\]

As a check of equation (9.22), it has already been seen that \( E_p \) is zero for a cubic lattice: does equation (9.22) give
the value 0 for a cubic lattice?

The primitive lattice vectors are $d \hat{x}$, $d \hat{y}$, $d \hat{z}$: the reciprocal lattice is also cubic, with lattice constant $2\pi/d$. Notice that, in consequence of this, the sum over the $g$ and the first term in the sum over the $r'$ are very similar. $S'(0)$ is independent of $G$, and the convenient thing to do is to choose $G$, so the power of $e$ is the same in both sums. To achieve this, take $G = \frac{\pi}{d}$. With this choice of $G$, the sum over the $g$ and the first term of the sum over the $r'$ cancel one another, since $V_c = d^3$. Moreover, the terms $4G^3/3\sqrt{\pi}$ and $-4\pi/3V_c$ add to zero, leaving only the other terms in the $r'$ sum. This also vanishes, due to the $3z'^2 - r'^2$, for the same reason that equation (5.4) vanishes when evaluated for a cubic lattice.

The expression (9.22) therefore passes the test.

The presence of the exponentials and the complimentary error function in equation (9.22) render it a much more quickly converging expression than the expression (5.6) for $S$. Equation (5.6) would require the summation of many more terms than equation (9.22) to obtain the same accuracy in the resultant partial sum.
Equation (9.22) has been evaluated for the three latter shell arrangements, (C) to (E), described in chapter 8. In each case, the formula is particularized to the arrangement being studied. A generalized computer program was written, and the formula evaluated for each pattern of shells. The evaluation in cases (C), (D) and (E) was very similar. In each case, the expression was analyzed for several values of G, to ensure that the final answer would be independent of G. This in fact turned out to be so. As a further check, equation (9.22) was also evaluated for lattice (B). As required, the result was effectively zero, independent of G. The values of S obtained in cases (C) to (E) were as follows:

(C) Closest Packing; Type 1: \( S = -0.9095420544 \)

(D) Closest Packing; Type 2: \( S = -5.105810840 \)  

(E) Hexagonal Closest Packed: \( S = 2.968683281 \)

The number of significant figures shown indicates the extent to which the result did not vary with G.

\( E_{dipole} \), given by equation (7.5), will now be calculated for each lattice and for several values of \( Z^* \) in each case.

To begin with, using equation (6.3) for \( p \) and the expressions for \( \Delta E_L \) and \( \epsilon E_L \), it is found that
\[
\frac{k}{d^3}p = \frac{[0.99700(Z_n^4 + E_1) + 0.34256]E_1 - 0.99686 \text{Mg}/q_e}{(d/a_0)^3Z_n^4 - [0.99700(Z_n^4 + E_1) + 0.34256]}S
\]

(10.2)

Write

\[
E_{\text{dipoles}} = \frac{\alpha_1 \text{Mg}/q_e - \alpha_2 E_1}{Z_n^4(d/a_0)^3 + \alpha_3}
\]

(10.3)

Then, using equations (8.4) for \(n_d d^3\) and (10.1) for \(S\), the following values are found for \(\alpha_1\), \(\alpha_2\), and \(\alpha_3\):

<table>
<thead>
<tr>
<th>Lattice:</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value of (\alpha_1):</td>
<td>16.70</td>
<td>23.62</td>
<td>20.13</td>
<td>16.90</td>
<td>20.66</td>
</tr>
</tbody>
</table>

Table I: Value of \(\alpha_1\) for lattice types (A) through (E).

\(\alpha_1\) does not depend on \(Z_n\).

<table>
<thead>
<tr>
<th>Value of (Z_n):</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.88</td>
<td>18.21</td>
<td>15.56</td>
<td>13.03</td>
<td>15.93</td>
</tr>
<tr>
<td>2</td>
<td>262.4</td>
<td>372.6</td>
<td>318.5</td>
<td>266.7</td>
<td>325.9</td>
</tr>
<tr>
<td>3</td>
<td>1349</td>
<td>1908</td>
<td>1631</td>
<td>1365</td>
<td>1669</td>
</tr>
<tr>
<td>4</td>
<td>4272</td>
<td>6044</td>
<td>5164</td>
<td>4323</td>
<td>5286</td>
</tr>
</tbody>
</table>

Table II: Values of \(\alpha_2\) for lattices (A) through (E) for some values of \(Z_n\).
\( \alpha_3 \) is zero for all \( Z_n \) for both lattices (A) and (B). For lattices (C) through (E):

<table>
<thead>
<tr>
<th>Value of ( Z_n )</th>
<th>Lattice:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C)</td>
</tr>
<tr>
<td>1</td>
<td>0.6989</td>
</tr>
<tr>
<td>2</td>
<td>14.30</td>
</tr>
<tr>
<td>3</td>
<td>73.24</td>
</tr>
<tr>
<td>4</td>
<td>231.9</td>
</tr>
</tbody>
</table>

Table III: Values of \( \alpha_3 \) for lattices (C) through (E) for some values of \( Z_n \).

The objective of Chapter 2 has been fulfilled.

\[ \text{It is indeed easy to see that } \frac{\varepsilon}{(k_0 e^2 / R^2)} \text{ is small.} \]

Take \( R \) to be one of the order of \( a_0 \), the Bohr radius, and \( E_0 \) to be of order \( Mg/q_e \). Then \( \varepsilon/(k_0 e^2 / R^2) \) is of the order \( 10^{-16} \).

In the last chapter, a model of the ions, in a metal was presented. This model was used to calculate the contribution to $\vec{E}_{ave}$ of the gravitationally induced ionic dipole moments. In this chapter, a model of the conduction electrons is constructed. The objective of this chapter is to use the model to calculate the number density of the electrons as a function of height. The reason this calculation is interesting is because it leads to an investigation of the charge distribution in the interior of the metal. Charge neutrality in the metal interior is not assumed in this thesis. Instead, the charge density inside a metal is calculated. The charge density is determined by comparing the number densities of ions and electrons as functions of height. The density of ions may be found using elasticity theory; finding the electron density is the goal of this chapter. Once the charge density is known, its contribution $\vec{E}_{ch}$ to $\vec{E}_{ave}$ may be calculated.

The basic physical idea underlying the model is that the electron constituent must be distributed in the metal in such a manner that the electron gas is held up against gravity. Basically, two physical processes are involved in countering the
force of gravity on the electrons. One is the electrostatic force experienced by the electrons. The other is the fermion nature of the electrons, for if there is a nonuniformity in the electron number density, there will be a gradient in the local pressure in the gas.

The manner in which these physical concepts are incorporated into the model is now described. The electronic constituent of a metal is treated as a system of noninteracting fermions that is subject to an external linear potential. It is assumed that this linear potential is in the vertical direction. The linear potential takes into account the electron-electron interactions, the interactions between the electrons and the lattice of ions, the weight of the electrons, and the externally imposed electric field $\vec{E}_{\text{ext}}$. Electron-electron interactions and electron-lattice interactions are taken into account by averaging them out. Specifically, each electron is regarded to be subject to an average potential created by the rest of the electrons, the lattice of ions, gravity, and the field $\vec{E}_{\text{ext}}$. The slope of this potential is $mg+q_e(E_{\text{ave}}+E_{\text{ext}})$, where $E_{\text{ave}}$ is positive of points in the direction opposite to $\vec{g}$, and similarly for $E_{\text{ext}}$. It is the $E_{\text{ave}}$ term in this slope that takes into account the electron-electron and electron-lattice interactions.

Notice the assumption that $E_{\text{ave}}$ is a uniform field. Once again, this is a simplification which is made for convenience. As will be seen later in this thesis, $E_{\text{ave}}$ in fact depends on height. However, this dependence is extremely small. Taking
\( \vec{E}_{\text{ave}} \) as uniform, therefore, is an assumption that leads to results with which the assumption is consistent: the assumption and the results are consistent to the order to which \( \vec{E}_{\text{ave}} \) is calculated. The physical reason for this agreement is that the charge imbalance in this model, although not identically zero, is very small. This point shall be further clarified at the appropriate stage in this thesis.

There is a very simple way to obtain an expression for the number density of electrons as a function of height. In this approach, it is assumed that the electron gas behaves, locally, as if it were a free gas. The calculation is done in Appendix B.

A more mathematically rigorous treatment, however, leads to a better understanding and appreciation of the problem. In addition, some interesting results are obtained along the path to the solution.

In the next section of this chapter, the problem is specified in more detail. Subsequent sections deal with the solving of the problem and the ensuing implications in terms of gravitationally induced electric fields in metals.
(3.1) DESCRIPTION OF THE PROBLEM OF A FREE FERMI GAS SUBJECT TO AN EXTERNAL LINEAR POTENTIAL

The system to be studied consists of \( N \) identical, noninteracting fermions, confined to a cube of edge length \( L \), and subject to an external linear potential. Because the particles do not interact, the Hamiltonian of the \( N \) particle composite is simply the sum of \( N \) single particle Hamiltonians:

\[
\hat{H}_{N,L}^{\oplus} (\hat{p}_i, \hat{r}_i) = \sum_{i=1}^{N} \hat{H}_L^{\ominus} (\hat{p}_i, \hat{r}_i). \tag{1.1}
\]

The caret denotes an operator, while the tilde is short for a collection of \( N \) operators. The subscripts \( N \) and \( L \) serve as reminders that there are \( N \) fermions and they are confined to a cube of edge length \( L \). \( \hat{p}_i \) and \( \hat{r}_i \) are, respectively, the momentum and position operators of the \( i^{th} \) fermion. The single particle Hamiltonian is:

\[
\hat{H}_L^{\ominus} (\hat{p}_i, \hat{r}_i) = \frac{\hat{p}_i^2}{2m} + \phi_L (\hat{r}_i), \tag{1.2}
\]

where \( m \) is the mass of each fermion and \( \phi_L (\hat{r}_i) \) is the external potential experienced by each.

Because of equation (1.1) the eigenfunctions and energy eigenvalues of \( \hat{H}_{N,L}^{\oplus} \) can be expressed in terms of the single particle eigenfunctions and energy eigenvalues. The latter are
given by

\[ H^0_L(\vec{r}_i, \vec{r}_f) \psi_k^{(\ell)}(\vec{r}_f) = E_k^{(\ell)} \psi_k^{(\ell)}(\vec{r}_i) \]  

(1.3)

where \( k \) labels the eigenfunction and the corresponding eigenvalue.

It is crucial to mark well the meaning of \( k \). \( k \) is a multilabel which includes the spin label. Later in this section, a label \( \vec{k} \) shall be used. The label \( k \) is short for the composite of labels \( \vec{k} \) and the spin label.

The \( H^0 \) in equation (1.3) may be thought of as the position representation of equation (1.2). For the case of a linear potential and absolutely confining walls,

\[ H^0_L = -\frac{\hbar^2}{2m} \nabla^2 + \phi_L(\vec{r}) \]

(1.4)

The eigenfunctions and eigenvalues of \( \hat{H}_{\nu, \ell} \) are expressed in terms of the \( \psi_k^{(\ell)}(\vec{r}) \) and \( E_k^{(\ell)} \) through the use of occupation numbers \( n_k \). Thus, the eigenstate \( \tilde{\psi}_{E}^{(\nu, \ell)}(\vec{r}) \) belonging to the eigenvalues \( E_{\nu, \ell} \) of \( \hat{H}_{\nu, \ell} \) may be labelled by the \( n_k \): \( \tilde{\psi}_{E}^{(\nu, \ell)}(\vec{r}) \) is denoted \( \tilde{\psi}_{n_k}^{(\nu, \ell)}(\vec{r}) \). Similarly, \( E_{\nu, \ell}^{(\nu, \ell)} \) is denoted \( E_{\nu, \ell}^{(\nu, \ell)} \), and is given
by

\[ E^{(\{n_k\})} = \sum_k n_k \varepsilon_k \]  

(1.5)

The expression for \( \Upsilon_{n_k}(r) \) is more complicated.

The important thing to be aware of here is that \( \Psi_{n_k}(r) \) may be thought of as a state of the N particles in which the number of particles in the single particle state \( \Psi_k(r) \) is \( n_k \); equation (1.5) supports this point of view. So does the requirement

\[ N = \sum_k n_k \]  

(1.6)

The bulk properties of the Fermi gas at a temperature T may be determined by employing the rules of statistical mechanics. One piece of information obtained in this way is the average occupancy of the state \( \Psi_k(r) \), denoted \( <n_k>_L \). More will be said about \( <n_k>_L \) in the next section. For the moment, \( <n_k>_L \) may be thought of as the number of particles existing in the state \( \Psi_k(r) \) at temperature T, although it should be noted that this is only a coarse, intuitive way to think of \( <n_k>_L \).

These average occupation numbers \( <n_k>_L \) play a key role in determining the value of the local number density of fermions, denoted by \( n_L(r) \). It is possible to proceed from the complicated expression for \( \Upsilon_{n_k}(r) \) to derive the following equation:
\[ \eta^{(L)}(\vec{r}) = \sum_{k} \langle n_{k} \rangle \left| \psi^{(L)}_{k}(\vec{r}) \right|^2 . \]  

Equation (1.7), however, is clear on intuitive grounds, by thinking of \( \langle n_{k} \rangle \) as being the number of fermions in the state \( \psi^{(L)}_{k}(\vec{r}) \).

It is reasonable to expect that, deep inside the metal, the local number density of free electrons will be independent of \( L, x \) and \( y \). This fact emerges from equation (1.7) in a mathematically precise manner by taking the thermodynamic limit: letting \( L \to \infty \) in such a way that the average particle density remains constant. Intuitively, therefore, it is to be expected that, in the thermodynamic limit, equation (1.7) will go over to

\[ n(u) = \sum_{k} \langle n_{k} \rangle \left| \psi^{(L)}_{k}(\vec{r}') \right|^2 , \]

where \( u = z/L, \vec{r}' = \vec{r}/L \), \( n(u) \) is the limit of \( n^{(L)}(\vec{r}) \) and \( \psi^{(L)}_{k}(\vec{r}') \) is the limit of \( \psi^{(L)}_{k}(\vec{r}) \).

\( n(u) \) is a temperature dependent function, the temperature dependence entering through the \( \langle n_{k} \rangle \). According to equation (1.8), \( n(u) \) may be determined by finding the \( \langle n_{k} \rangle \) and the \( \psi^{(L)}_{k}(\vec{r}') \), and performing the indicated summation. The result for \( n(u) \) may then be determined for the model by taking \( T=0 \); recall that the model is for the metal in its ground state. This method of determining \( n(u) \) is the one presented in the next section.
An alternate method is presented thereafter. In this method, the specification \( T=0 \) is made at the beginning, which further simplifies the expression for \( n(u) \). The external potential is treated as a perturbation, and the \( \psi_k(r) \) are found by using perturbative techniques. \( n(u) \) is evaluated to lowest order in the perturbative parameter.

A comparison between the two methods is made, and it is shown that both lead to the same result.

\( (3.2) \) STATISTICAL MECHANICS APPROACH

Recently, a paper appeared in the literature\(^{(1)} \) which considers the problem of a noninteracting Bose gas subject to a weak external potential of power form. Study of this paper reveals that it is very easy to extend the results of the paper to the case of a Fermi gas, provided that the fugacity does not exceed unity. The fugacity is \( e^{\beta \mu} \), where

\[
\beta = \frac{1}{\kappa B T},
\]

\( k_B \) is Boltzmann's constant, \( T \) is the absolute temperature, and \( \mu \) is the chemical potential. It is for \( 0 \leq e^{\beta \mu} \leq 1 \) that the aforementioned extension may be made. For this range of the fugacity, the results obtained are as follows:

The grand canonical pressure \( p \) is given by
where \( c \) is the slope of the external linear potential, and \( \xi \) is given in terms of the average particle density \( \rho \) by

\[
\rho = \frac{2^{s+1}}{\lambda^3} \int_0^1 du f_{3/2} (\xi e^{-\beta z u}),
\]

where

\[
\lambda = \sqrt{\frac{2\pi \kappa^2 \beta}{m}},
\]

\[
f_{3/2} (y) = \frac{4}{\sqrt{\pi}} \int_0^\infty dx \ x^2 \log (1 + ye^{-x^2}),
\]

\[
\tilde{c} = c L
\]
The local pressure and local number density of fermions are given by

\[ p(u) = \frac{2s+1}{\lambda^3} \int_{S^3} (\xi e^{-\beta \tilde{\xi} u}) \]  

(2.8)

and

\[ n(u) = \frac{2s+1}{\lambda^3} \int_{S^3} (\xi e^{-\beta \tilde{\xi} u}) \]  

(2.9)

where

\[ \xi = \frac{Z}{L} \]  

(2.10)

The $\xi$ in the above equations is in fact the fugacity:

\[ \xi = e^{\beta \mu} \]  

(2.11)

Equation (2.6) establishes a one-to-one correspondence between $p$ and $\xi$, whence equations (2.2) and (2.6) determine a unique plot of $p$ in terms of $\rho$, for a given temperature.

$\lambda$ is called the thermal wavelength. $\tilde{\xi}$ is the difference in potential energy between the "bottom" of the cube, at $u=0$, and the "top", at $u=1$. 


Notice that equations (2.8) and (2.9) are the pressure and number density for a free Fermi gas with chemical potential \( \mu - \xi \).

The appeal of the above results in terms of the investigation at hand is this: if these results could be shown to be true for all \( \xi \), \( n(\mu) \) could be obtained for the free electrons in a metal simply by evaluating (2.9) in the limit \( (T \to 0) \).

In the remainder of this section, an outline is presented describing how the above results are obtained for \( p, \rho, p(\mu) \) and \( n(\mu) \), a discussion is presented to indicate that these results are indeed valid for all \( \xi \), and the expressions are evaluated in the limit \( \beta \to \infty \).

\( \text{(A) Review of Some Basic Statistical Mechanical Ideas} \)

The work to be done here shall be done using the grand canonical ensemble. The grand canonical partition function is

\[
Z(\beta, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} Q(\beta, N, V)
\]  \hspace{1cm} (2.12)

where \( \beta = 1/k_B T \), \( T \) is the temperature of the heat bath, \( V \) is the volume of the system, \( \mu \) is the chemical potential of the heat bath and \( Q(\beta, N, V) \) is the partition function for the canonical
ensemble:

$$Q(\beta, N, \nu; \nu) = \sum_{\{n_k\}}^{N} e^{-\beta E_{\nu}^{(\nu)}(n_k)} \quad (2.13)$$

The sum in equation (2.13) is over all occupation number sets satisfying equation (1.6) and $$E_{\nu}^{(\nu)}(n_k)$$ is as defined previously.

Combining equations (2.12) and (2.13), and using equation (1.5),

$$Z(\beta, N, \nu; \nu) = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^{N} e^{-\beta \sum_k \xi_k n_k} \quad (2.14)$$

Because the fermions are noninteracting, equation (2.13) may be simplified. Using equation (1.6),

$$Z(\beta, N, \nu; \nu) = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^{N} e^{\beta \sum_k (\mu - \xi_k) n_k} = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^{N} \prod_k \left[ e^{\beta (\mu - \xi_k)} \right]^{n_k} \quad (2.15)$$

It is easy to verify that the two summations in equation (2.15) may be replaced, equivalently, by summing each $$n_k$$ independently. This gives:

$$= \sum_{n_0}^{\infty} \sum_{n_1}^{\infty} \cdots \prod_k \left[ e^{\beta (\mu - \xi_k)} \right]^{n_k}$$
may assume only the values 0 and 1 because of the Pauli exclusion principle. Equation (2.15) has become

\[ Z(\beta, \mu, V) = \prod_{k=0}^{1} \left( 1 + e^{\beta(\mu - \epsilon_k)} \right). \quad (2.16) \]

Equation (2.16) is the grand canonical partition function for noninteracting fermions confined to a volume \( L^3 \); the \( \epsilon_k \) refer to a cube of edge length \( L \).

The grand canonical pressure is obtained from \( Z \) via

\[ p^{(v)}(\beta, \mu) = \frac{1}{\beta V} \log Z(\beta, \mu, V). \quad (2.17) \]

Using equation (2.16), equation (2.17) becomes

\[ p^{(v)}(\beta, \mu) = \frac{1}{3L^3} \sum_{k} \log \left( 1 + e^{\beta(\mu - \epsilon_k)} \right). \quad (2.18) \]

The mean particle number \( \langle N \rangle_L \) is given by
\[ \langle N \rangle_L = \frac{1}{Z} \sum_{N=0}^{\infty} N e^{\beta \mu N} \sum_{\{\eta_k\}} e^{-\beta \sum_k \varepsilon_k^\omega \eta_k} = \frac{1}{\beta Z} \frac{\partial Z}{\partial \mu}, \]

or

\[ \langle N \rangle_L = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z(\beta, \mu, V). \tag{2.19} \]

Inserting equation (2.16) into equation (2.19) gives

\[ \langle N \rangle_L = \sum_k \frac{1}{e^{\beta (\varepsilon_k^\omega - \mu)} + 1}, \tag{2.20} \]

in terms of which the average particle number density is

\[ \rho = \frac{\langle N \rangle_L}{L^3}. \tag{2.21} \]

\(\rho\) is not a function of \(L\). In the thermodynamic limit, as \(L\) goes to infinity, so does \(\langle N \rangle_L\), in such a way that \(\rho\) stays constant.

The ensemble average occupation numbers are given by

\[ \langle \eta_k \rangle_L = \frac{1}{Z} \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{\{\eta_k\}} \langle \eta_k \rangle e^{-\beta \sum_k \varepsilon_k^\omega \eta_k} = \frac{1}{\beta Z} \frac{\partial Z}{\partial \varepsilon_k^\omega}, \]

or
Use of equation (2.16) once again gives

$$
\langle n_k \rangle_L = \frac{1}{\varepsilon_k^{(w)} - \mu} - \frac{1}{\varepsilon_k^{(w)} + 1} + \frac{1}{\varepsilon_k^{(w)} - \mu + 1}.
$$

(2.22)

A comparison of equations (2.20) and (2.23) shows that

$$
\langle N \rangle_L = \sum_k \langle n_k \rangle_L.
$$

(2.24)

The thermodynamic limit consists of letting \( L \to \infty \) but such that \( \lim_{L \to \infty} L \varepsilon_k^{(w)} - \mu \) remains constant. By equations (2.20) and (2.21), this gives an implicit equation for \( \mu \), or \( \xi = e^{\beta \mu} \), in terms of \( \rho \):

$$
\rho = \lim_{L \to \infty} \frac{1}{\beta L^3} \sum_k \frac{1}{\varepsilon_k^{(w)} - \mu + 1}.
$$

(2.25)

\( \rho \) denotes the limit of \( p^{(w)}(\beta, \mu) \):

$$
\rho = \lim_{L \to \infty} \frac{1}{\beta L^3} \sum_k \log \left( 1 + e^{\beta (\mu - \varepsilon_k^{(w)})} \right).
$$

(2.26)
Equations (2.25) and (2.26) together give $p$ in terms of $\rho$, at a given temperature $T$.

The limit of equation (2.23), with $\mu$ given by equation (2.25), gives the $\langle n_k \rangle$ which enter into equation (1.8).

(B) Specialization to Case of no External Potential; Review of the Ideal Fermi Gas

When there is no external potential, the single particle eigenvalues are $p^2/2m$, where $\vec{p} = 2\pi n\vec{\mathbf{r}}/L$ and $\vec{\mathbf{r}}$ is a vector whose components are integers. As such, in the limit $L \to \infty$, the sums over $k$ may be replaced by integrals over $p$, as in

$$\sum_k \to (2s+1) \frac{L^3}{\hbar^3} \int d^3 p,$$

where $s$ is the spin of the fermion ($s = \frac{1}{2}$ for electrons).

In this case, the expression for $p$, equation (2.26), becomes

$$p = \frac{(2s+1)4\pi}{\beta \hbar^3} \int_0^\infty dp \, p^2 \log(1 + \frac{e^{-\beta p^2/2m}}{s-1}),$$

and the equation for $\rho$, equation (2.25), gives

$$\rho = \frac{(2s+1)4\pi}{\hbar^3} \int_0^\infty dp \, p^2 \frac{1}{s-1 + e^{\beta p^2/2m}}.$$
where $\xi$ is the fugacity, given by equation (2.12).

Equations (2.27) and (2.28) may be written as

$$\rho = \frac{2^{s+1}}{\lambda^3} \int_{S_2} (\xi) ,$$

and

$$\rho = \frac{2^{s+1}}{\lambda^3} \int_{S_2} (\xi) ,$$

with $\lambda$ given by equation (2.3), $\int_{S_2} (\xi)$ by equation (2.4) and $\int_{S_2} (\xi)$ by equation (2.7).

If $0 \leq \xi \leq 1$, these integral expressions may be written as power series expansions. It is easy to do this. The results are:

$$\int_{S_2} (\xi) = \sum_{j=1}^{\infty} (-1)^{j+1} \frac{\xi^j}{j^{3/2}} , \quad 0 \leq \xi \leq 1$$

and

$$\int_{S_2} (\xi) = \sum_{j=1}^{\infty} (-1)^{j+1} \frac{\xi^j}{j^{3/2}} , \quad 0 \leq \xi \leq 1$$

Notice that

$$\int_{S_2} (\xi) = \int_{S_2} (\xi) .$$
This is in fact true for all \( \zeta \), as equations (2.4) and (2.7) show. Also notice the source of the symbol to denote the integral expressions (2.4) and (2.7): the subscript is the power of 1/j in the sum when 0<\( \zeta \)<1.

Equations (2.31) and (2.32) are useful for expanding equations (2.29) and (2.30) in the limit \( \rho \lambda^3 << 1 \). For, from equations (2.30) and (2.32), \( \xi \) may be expressed in powers of \( \rho \lambda^3 \), with the result

\[
\xi = \frac{\rho \lambda^3}{2^s+1} + \frac{1}{2^{3/2}} \left( \frac{\rho \lambda^3}{2^s+1} \right)^2 + \cdots \quad (2.34)
\]

Use of equations (2.31) and (2.34) in equation (2.29) then gives

\[
\beta = \frac{\rho \lambda^3}{2^s+1} \left( 1 + \frac{1}{2^{3/2}} \frac{\rho \lambda^3}{2^s+1} + \cdots \right) \quad (2.35)
\]

Observe that \( \rho \lambda^3 << 1 \) corresponds physically to the high temperature and/or low density limit of the Fermi gas. As required, therefore, equation (2.35) reproduces, to leading order, the classical ideal gas law. This result is due to the fact that \( \rho \lambda^3 << 1 \) means that the average particle separation is much larger than the thermal wavelength, so quantum effects are small. The corrections in equation (2.35) to the classical ideal gas law are due to precisely those quantum effects.
Equation (2.34) may also be inserted into equation (2.23), with the result that

\[ \langle \eta_p^3 \rangle = \frac{\rho \lambda^3}{2^{j+1}} e^{-\beta \rho^2/2m} \]  

(2.36)

to leading order. Equation (2.36) is just the Maxwell-Boltzmann distribution function.

The other extreme for which equations (2.29) and (2.30) may be approximated is the low temperature and/or high density limit, \( \rho \lambda^3 \gg 1 \). In this case, it is necessary to find an expansion for \( f_{3/2}(\xi) \) as \( \xi \to \infty \).

Such an expansion may be obtained by starting with equation (2.7). One obtains, as \( \xi \to \infty \),

\[ \int_{3/2} (\xi) \sim \frac{4}{3 \sqrt{\pi}} \left[ (l_0 \xi)^{3/2} + \frac{\pi^2}{8} (l_0 \xi)^{1/2} + \cdots \right] + O(\xi^{-1}) \]  

(2.37)

Similarly,

\[ \int_{5/2} (\xi) \sim \frac{8}{75 \sqrt{\pi}} \left[ (l_0 \xi)^{5/2} + \frac{\pi^2}{4} (l_0 \xi)^{1/2} + \cdots \right] + O(\xi^{-1}) \]  

(2.38)

Equations (2.30) and (2.37) give, to lowest order,

\[ \frac{4}{3 \sqrt{\pi}} (l_0 \xi)^{3/2} \to \frac{\rho \lambda^3}{2^{j+1}} \text{ as } \rho \lambda^3 \to \infty \]
or, using equation (2.3) for $\lambda$, and equation (2.11) for $\xi$,

$$\mu \to \frac{k^2}{2m} \left( \frac{6 \pi^2 \rho}{25} \right)^{2/3} \xi \to \xi_F \quad \text{as} \quad \rho \lambda^3 \to \infty. \quad (2.39)$$

Expanding in powers of $k_B T / \xi_F$, equations (2.37) and (2.30) give

$$\mu = \xi_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\xi_F} \right)^2 + \ldots \right]. \quad (2.40)$$

$<\eta_p>$ is given by

$$<\eta_p^2> = \frac{1}{e^{\beta (p^2 / 2m - \mu)} + 1} \quad , \quad (2.41)$$

with $\mu$ given by equation (2.40). Thus,

$$<\eta_p^2> \to \begin{cases} 1 & \text{if} \quad p^2 / 2m < \xi_F \\ 0 & \text{if} \quad p^2 / 2m > \xi_F \end{cases} \quad \text{as} \quad T \to 0. \quad (2.42)$$

The expansion for $p$ is obtained using equations (2.29), (2.39), (2.39), and (2.40):

$$p = \frac{2}{\xi_F} \rho \xi_F \left[ 1 + \frac{5 \pi^2}{12} \left( \frac{k_B T}{\xi_F} \right)^2 + \ldots \right]. \quad (2.43)$$

These results are very different from the classical result.
This is because the limit $\rho \lambda^3 \gg 1$ corresponds to a thermal wavelength which is large compared to average particle separation, and so quantum effects are very important.

It is clear from equations (2.4) and (2.7) that $f_{\beta,4} (\xi)$ and $f_{\beta,4} (\xi)$ are monotonic increasing functions. As such, $p$ is a monotonic increasing function of $\rho$, for a given temperature. Moreover, the relationships are smooth, and as a result the ideal Fermi gas exhibits no phase transitions.

(C) Case of an External Linear Potential

Consider in more detail now the Schrodinger equation (1.3), with $H$ given by equation (1.4), and with the eigenfunctions normalized as usual according to

$$\int_{\text{Cube}} |\psi_k^{(L)} (\mathbf{r})|^2 d^3r = 1$$

That $\phi_L (\mathbf{r})$ is infinite outside the cube means $\psi_k^{(L)} (\mathbf{r}) = 0$ outside the cube, and further that $\psi_k^{(L)} (\mathbf{r})$ vanish on the walls of the cube.

It is straightforward to see that the eigenfunctions are given by

$$\psi_k^{(L)} (\mathbf{r}) = \sqrt{\frac{2}{L}} \sin(k_x x) \sqrt{\frac{2}{L}} \sin(k_y y) \psi_k^{(L)} (z)$$

(2.45)
where

\[ \left( -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + \kappa z \right) f_{k_z}(z) = E_{k_z} f_{k_z}(z) \tag{2.46} \]

and the eigenvalues \( E_{k_z}^{(z)} \) are given by

\[ E_{k_z}^{(z)} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2) + E_{k_z} \tag{2.47} \]

The label \( \vec{k} \) denotes the triple \((k_x, k_y, k_z)\), with

\[ k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L}, \tag{2.48} \]

where \( n_x = 1, 2, 3, \ldots, n_y = 1, 2, 3, \ldots \). \( f_{k_z}(z) \) must satisfy the normalization condition

\[ \int_0^L dz \left| f_{k_z}(z) \right|^2 = 1 \tag{2.49} \]

as well as the boundary conditions.
The problem specified by equations (2.46), (2.49) and (2.50) may be solved exactly for \( f_{k_z}(z) \) and \( E_{k_z} \). Putting

\[
\int_{-L}^{L} f_{k_z}(Z) = 0
\]  \hspace{1cm} (2.50)

and

\[
U \equiv \frac{Z}{L}
\]  \hspace{1cm} (2.52)

converts the problem to

\[
\left( \frac{d^2}{du^2} - \frac{2mc}{L} \right) q_{k_z}(u) = 0
\]  \hspace{1cm} (2.53)

\[
\int_{0}^{1} du \left| q_{k_z}(u) \right|^2 = 1
\]  \hspace{1cm} (2.54)
Equation (2.53) reveals that the important dimensionless parameter in the problem is

$$\alpha \equiv \frac{2mcL^3}{\hbar^2}.$$  \hspace{1cm} (2.56)

If $\alpha$ is small, a useful approach is perturbation theory, even though an exact solution is possible. This approach is undertaken in the next section. The extreme where $\alpha$ is very large shall be examined below.

Denoting

$$\gamma_{kz} = \frac{E_{kz}}{cL},$$  \hspace{1cm} (2.57)

and putting

$$\eta_{kz}(v) = \gamma_{kz}(u).$$  \hspace{1cm} (2.58)
expresses the problem as

\[
\left( \frac{d^2}{dv^2} - \nu \right) h_{kz}(v) = 0 ,
\]

(2.60)

\[
\alpha^{1/3}(1 - \gamma_{kz}) \int_{-\alpha^{1/3} \gamma_{kz}}^{x} d\nu \left| h_{kz}(v) \right|^2 = \alpha^{1/3} ,
\]

(2.61)

\[
h_{kz}(-\alpha^{1/3} \gamma_{kz}) = h_{kz}(\alpha^{1/3} [1 - \gamma_{kz}]) = 0 .
\]

(2.62)

The exact solutions to equation (2.60) are the two Airy functions \( A_i(v) \) and \( B_i(v) \) depicted graphically in figures 10(a) and 10(b). Hence,

\[
h_{kz}(v) = a_{kz} A_i(v) + b_{kz} B_i(v) .
\]

(2.63)
Figure 10. The Airy Functions $A_i(v)$ and $B_i(v)$

$a_{kz}$, $b_{kz}$ and $\gamma_{kz}$ must be chosen to satisfy equations (2.61) and (2.62); thus:

$$a_{kz} A_i(-\alpha'^3 \gamma_{kz}) + b_{kz} (-\alpha''^3 \gamma_{kz}) = 0,$$

(2.64)
Equations (2.64) and (2.65) combine to read

\[
\frac{Q_{kz}}{b_{kz}} = -\frac{B_i(-\alpha^{1/3} \gamma_{kz})}{A_i(-\alpha^{1/3} \gamma_{kz})} = -\frac{B_i(\alpha^{1/3} [-\gamma_{kz}])}{A_i(\alpha^{1/3} [-\gamma_{kz}])},
\]

or

\[
\frac{B_i(-\alpha^{1/3} \gamma_{kz})}{A_i(-\alpha^{1/3} \gamma_{kz})} = \frac{B_i(-\alpha^{1/3} \gamma_{kz} + \alpha^{1/3})}{A_i(-\alpha^{1/3} \gamma_{kz} + \alpha^{1/3})}.
\]

By figure 10(a), it is clear that equation (2.68) fixes a discrete set of values \( \gamma_{kz} \), where \( k_z \) labels those values. Equation (2.67) then gives the ratio \( q_{kz}/b_{kz} \) for that value of \( \gamma_{kz} \). From there, equation (2.66) may be solved for one of the two constants, whence the other is also known. In this way the problem is exactly soluble.

Unfortunately, the solution is highly implicit. In fact,
to the author's knowledge, expressions are not available in the literature which give the $\mathcal{K}_2$'s satisfying equation (2.68).

What shall be done, therefore, is to study the problem specified by equations (2.60) - (2.62) for the cases $\alpha \ll 1$ and $\alpha \gg 1$. The extreme $\alpha \ll 1$ will be dealt with by using perturbation theory on equations (2.53) - (2.55).

The problem posed by equations (2.60) - (2.62) for $\alpha \gg 1$ has been studied by the author. Some interesting results emerged which relate to the case of a low density Fermi gas at absolute zero in a gravitational field. These results are presented in Appendix C.

For the purposes of the present chapter, the key thing to notice is the emergence of the dimensionless parameter $\alpha$.

In analyzing the expressions for $\varphi$ and $p$, equations (2.25) and (2.26), $L$ is to be taken to increase without bound. What does this imply for $\alpha$? Is $\alpha$ to increase without bound as well? What about $c$? Should $c$ remain constant as $L$ increases? Or is it better to hold something else fixed?

Van den Berg and Lewis chose to hold $cL$ fixed as $L \to \infty$. In that case $\alpha$ blows up with $L$ like $L^2$. Their reason for holding $cL$ fixed was to ensure that the effect of the external potential would not be so extreme as to destroy the thermodynamic behavior of the system. They desired this because they were investigating the modification of Bose-Einstein condensation due to the external potential.

This approach to the Fermi gas problem -- holding $cL$ fixed as $L \to \infty$ -- shall be considered next. The steps to be outlined
follow those employed by Van den Berg and Lewis.

(i) Approach due to Van den Berg and Lewis

The physical system considered by Van den Berg and Lewis in their paper is a noninteracting Bose gas subject to an external potential of power form, \( \tilde{c} (r)^{\xi} \), where \( \xi > 0 \). (In this thesis, the potential is linear, so \( \xi = 1 \).) They derive expressions for \( p, \xi, \rho(u) \) and \( n(u) \) in terms of \( \xi \) in the limit \( L \to \infty \) with \( \tilde{c} \) held constant.

As mentioned previously, the mathematical techniques employed in this paper may be easily extended to the Fermi gas when the temperature and density are such that \( \xi < 1 \). For a complete understanding of these techniques, the reader should consult the paper itself. A brief sketch of the key ideas, however, is presented here, along with the particular form they take for the case of a noninteracting Fermi gas in an external linear potential.

First, define

\[
\xi^{(L)}(L) \equiv \oint \frac{e^{\beta \xi^{(L)}}}{e^{\beta \xi^{(L)}}} 
\]

(2.69)

and

\[
\eta^{(L)}_{\xi} \equiv \beta \left( \xi^{(L)} - \xi^{(0)} \right) 
\]

(2.70)
where the $\xi^{(\omega)}_k$ are given by equation (2.47) and $\varepsilon^{(\omega)}$ is the smallest eigenvalue.

In terms of $\xi^{(\omega)}$ and $\eta^{(\omega)}$, the occupation numbers (2.23) may be written as

$$\langle \eta^{(\omega)}_k \rangle_L = \frac{\xi^{(\omega)}_L}{\delta^{(\omega)}_L + \xi^{(\omega)}_L}$$

$\xi^{(\omega)}$ is to be determined via the conditions (2.24) and (2.71); i.e.:

$$\rho = \frac{\langle N \rangle_L}{L^3} = \frac{2s+1}{L^3} \sum_k \langle \eta^{(\omega)}_k \rangle_L$$

The first step is to prove that equation (2.72) leads to equation (2.6) in the limit $L \to \infty$. The second step is to show that equation (2.18), which can be written as

$$p^{(\omega)} = \frac{2s+1}{2L^3} \sum_k \log \left(1 + \frac{\xi^{(\omega)}_L}{\Delta^{(\omega)}_k} \right)$$

gives equation (2.2) for $L^{\to \infty}$. Then, expressions (2.8) and (2.9) for $p(\omega)$ and $n(\omega)$ have to be derived.

The starting point of the above proofs is to rewrite $\rho$ and $p^{(\omega)}$. $\rho$ may be expressed as
\[ \rho = \frac{2s+1}{L^3} \sum_{k} \frac{S(L)e^{-\eta_{k}^{m}}}{1 + S(L)e^{-\eta_{k}^{m}}} = \frac{2s+1}{L^3} \sum_{k}^\infty \sum_{n=1}^\infty (-1)^{n+1} \left( S(L) \right)^n e^{-n\eta_{k}^{m}} \]

or

\[ \rho = (2s+1) \sum_{n=1}^\infty (-1)^{n+1} \left( S(L) \right)^n S_L(n) \tag{2.74} \]

where

\[ S_L(n) = \frac{1}{L^3} \sum_{k} e^{-n\eta_{k}^{m}} \tag{2.75} \]

It has been assumed that \( S(L) < 1 \) (which implies \( \xi < 1 \)) in order to employ

\[ \frac{X}{|1-X|} = \sum_{n=1}^\infty (-1)^{n+1} X^n \]

with \( x \) identified as \( S(L)e^{-\eta_{k}^{m}} \).

Similarly, using

\[ \log(1+x) = \sum_{n=1}^\infty (-1)^{n+1} \frac{x^n}{n} \]

with the identification of \( x \) as \( S(L)e^{-\eta_{k}^{m}} \), \( \rho^{(n)} \) may be written as

\[ \rho^{(n)} = \frac{2s+1}{\beta^3} \sum_{n=1}^\infty (-1)^{n+1} \left( S(L) \right)^n S_L(n) \tag{2.76} \]
Define $G(n)$ via

$$G(n) = \frac{1}{\lambda^3} \frac{3}{n \beta \gamma} \int_0^1 du \, e^{-\eta \beta \gamma u}$$  \hspace{1cm} (2.77)

Combining equations (2.6), (2.32) and (2.77), one result to be proven is that, in the limit $L \to \infty$,

$$\rho = \frac{2^{s+1}}{\beta} \sum_{n=1}^{\infty} (-)^{n+1} \frac{n^s}{n^3} G(n) \quad (2.78)$$

From equations (2.2), (2.31) and (2.77), another result to prove is

$$\lim_{L \to \infty} \mathbb{P}(\omega) = \frac{1}{\beta} \sum_{n=1}^{\infty} (-)^{n+1} \frac{n^s}{n^3} \frac{G(n)}{n} \quad (2.79)$$

Proving equations (2.78) and (2.79) is by no means a trivial task. However, the equations

$$\lim_{L \to \infty} \xi(L) = \xi \quad (2.80)$$

and
certainly suggest that equations (2.78) and (2.79) will result in the thermodynamic limit. Equations (2.80) and (2.81) are not sufficient in themselves to show that equations (2.78) and (2.79) result from equations (2.74) and (2.76), respectively. The asymptotic forms of $L$ and $S(n)$ as $L \to \infty$ are required. The mathematical manipulations required to prove equations (2.78) and (2.79) are somewhat lengthy, but the basic idea involved is captured in equations (2.80) and (2.81).

Combining equations (1.7) and (2.71),

$$
\chi^{(2)}(u) = \frac{2s+1}{2} \sum_{k} \frac{\xi(L)}{\xi(L)} \left| \frac{\psi^{(u)}(L, u)}{\xi(L)} \right|^2
$$

(2.82)

where the $x$- and $y$-dependences are omitted: they will disappear as $L \to \infty$. Similarly, the equation for $p^{(2)}(u)$ is

$$
p^{(2)}(u) = \frac{2s+1}{\beta} \sum_{k} \frac{2}{3} \log \left( 1 + \frac{\xi(L)}{\xi(L)} \right) \left| \psi^{(u)}(L, u) \right|^2.
$$

(2.83)

Equation (2.82) may be cast into the form

$$
\chi^{(2)}(u) = \frac{2s+1}{2} \sum_{n=1}^{\infty} \left( \frac{\xi(u)}{\xi(L)} \right)^n Q_L(n, u)
$$

(2.84)
where

$$Q_L(n, u) = \sum_k e^{-n\gamma k^2} |\psi_k(nL)|^2.$$  \hspace{1cm} (2.85)

From equations (2.84) and (2.85), by using a simple extension of one of the lemmas stated in the Van den Berg and Lewis paper, it is easy to see that equation (2.9) results, where

$$\eta(u) = \lim_{L \to \infty} \eta_L(u).$$  \hspace{1cm} (2.86)

In a similar fashion, equation (2.8) can be shown to result by taking the limit $L \to \infty$ in equation (2.76).

This completes the sketch of the proofs for equations (2.2), (2.6), (2.8) and (2.9). As noted previously, the proofs are valid only for $0 \leq \xi \leq 1$. The reason for this is simply that all of the proofs in the Van den Berg and Lewis paper use power series expansions for the functions in question: in order to extend those proofs to the case of a Fermi gas, the power series forms for $f_{\frac{1}{2}}(\xi)$ and $f_{\frac{3}{2}}(\xi)$ must be valid, and this is so only if $0 \leq \xi \leq 1$.

To summarize, if $\xi$ is in the range $[0, 1]$, the following equations may be easily proven by extending the results of the Van den Berg and Lewis paper:

$$\rho = \frac{2s+1}{\lambda^2} \int_0^1 du f_{\frac{3}{2}}(5e^{-\beta \xi u}).$$  \hspace{1cm} (2.87)
Since equations (2.87) to (2.90) result in the limit $L \to -\infty$ if $c_L$ is held fixed, the physical interpretation of these equations is as follows: the external potential is so weak that, locally, the gas behaves as if it were a free Fermi gas with chemical potential $\mu - \tilde{c} u$; $\zeta$ and $p$ are simply the average particle density and average pressure, respectively. For a more direct route to this result, see Appendix B.

The obvious requirement at this stage is to show that equation (2.89) is valid for all $\zeta$. Reasons why this should be expected are given next. Then, equations (2.87) to (2.90) are particularized to temperature $T=0$ K.
A physical reason shall now be presented which indicates that \( n(\nu) \), as given by equations (2.86) and (2.82), is equal to the function

\[
n(\nu; \xi) = (2s+1)\lambda^{-3} \int_{3/2}^{\infty} (\xi e^{-\lambda \xi \nu})
\]

(2.91)

for all \( \xi \geq 0 \).

Equation (2.89) is valid for \( 0 < \xi < 1 \). \( n(\nu; \xi) \) is an analytic function of \( \xi \). If \( n(\nu) \) is also analytic in \( \xi \), it will follow, from the theory of analytic functions, that \( n(\nu) \) is equal to \( n(\nu, \xi) \) for all \( \xi \).

There is a convincing physical argument which indicates this must be so. Assume that \( n(\nu) \) is not analytic in \( \xi \). Then there must be a phase transition in the gas for some value of \( \xi \). But the gas is comprised of noninteracting fermions. As such, the Fermi statistics which the particles obey give rise to a repulsion between the individual fermions, whereas a phase transition can only result if there is an attractive force between the individual particles. Thus, there can be no phase transition, and \( n(\nu) \) must be analytic in \( \xi \). This means that equation (2.89) is valid for all \( \xi \).

Similar reasoning can be applied to equations (2.87), (2.88) and (2.90) to indicate that all four expressions are valid for all \( \xi \).
A mathematical proof of the analyticity of \( n(u) \) is not presented in this thesis.

(iii) Specialization to Case \( T=0 \)

Using the asymptotic forms for \( f_{3+}^R (f) \) and \( f_{3-}^R (f) \) -- equations (2.37) and (2.38), respectively -- it is easy to show that, in the limit \( \beta \to \infty \), when \( E_F > \tilde{c}^{(5)} \), equations (2.87) to (2.90) become, for \( s=\frac{1}{2}, \)

\[
\eta(u) = \frac{1}{3\pi^2} \left( \frac{2mE_F(u)}{k^2} \right)^{3/2},
\]

(2.92)

\[
\rho(u) = \frac{2}{3} n(u) E_F(u),
\]

(2.93)

\[
\rho = \frac{1}{3\pi^2} \left( \frac{2mE_F}{k^2} \right)^{3/2} \frac{2}{5} \frac{E_F}{c} \left( 1 - \left[ 1 - \frac{\tilde{c}^{(5)}}{E_F} \right]^{5/2} \right),
\]

(2.94)

\[
\rho = \frac{2}{3} \frac{E_F}{c} \frac{1}{3\pi^2} \left( \frac{2mE_F}{k^2} \right)^{3/2} \frac{2}{7} \frac{E_F}{c} \left( 1 - \left[ 1 - \frac{\tilde{c}^{(5)}}{E_F} \right]^{7/2} \right),
\]

(2.95)

where
In this section, \( \alpha \) shall be taken to be a small number, and perturbation theory will be used to derive an expression for \( n(u) \) correct to the first order in \( \alpha \). The gas shall be taken to be at absolute zero (and it is to be assumed from the outset that the number of particles in the system is very large, i.e., that the system is large enough to be regarded as macroscopic).

The perturbation problem is specified by the following equations:

\[
\begin{align*}
\mathcal{H} \psi^{(2)} &= \mathcal{E}^{(2)} \psi^{(2)} \\
\mathcal{H} &= \mathcal{H}_0 + \frac{\alpha}{L} Z \\
\mathcal{H}_0 &= -\frac{\hbar^2}{2m} \nabla^2 \\
\psi^{(2)} &= \psi^{(0)} + \alpha \psi^{(1)} + \alpha^2 \psi^{(2)} + \ldots
\end{align*}
\]
Since the system is large, $\psi^{(r)}(\vec{r})$ shall be taken to be periodic in the x and y directions, with periodicity L. $\psi^{(r)}(\vec{r})$ is to vanish on the planes $z=0$ and $z=L$. This choice of boundary conditions is made for convenience.

Using standard perturbation theory techniques, one finds that

$$
\psi^{(r)}(\vec{r}) = \sqrt{\frac{2}{L^3}} e^{i(k_x x + k_y y)} \sin(k_z z), \quad (3.6)
$$

$$
E^{(r)}_{0} = \hbar^2 k^2, \quad (3.7)
$$

where

$$
k_x = \frac{2n_x \pi}{L}, \quad k_y = \frac{2n_y \pi}{L}, \quad k_z = \frac{n_z \pi}{L}, \quad (3.8)
$$

$$
n_x, n_y = 0, \pm 1, \pm 2, \ldots \quad (3.9)
$$
and also

\[ E_1 = \frac{1}{2} \]

(3.11)

where

\[ \psi_{k_z}(z) = A_{k_z} \sin(k_z z) + \frac{1}{4Lk_z} \left[ \frac{1}{Lk_z} 2 \sin(k_z z) + \left( \frac{z}{L} - \left( \frac{z}{L} \right)^2 \right) \cos(k_z z) \right] \]

(3.13)

Normalizing the eigenfunction determines \( A_{k_z} \):

\[ A_{k_z} = -\frac{1}{8} \frac{1}{(Lk_z)^2} \]

(3.14)

By virtue of equation (3.11), each energy level is elevated
by the same amount, \( \frac{1}{2} \tilde{c} \), independent of \( \vec{k} \). In consequence, to this order in the perturbation calculation, the Fermi surface for the gas is spherical, just as for a free gas. The Fermi wave number \( k_F \) may therefore be immediately expressed in terms of the average particle density \( \bar{\rho} \):

\[
k_F = (3\pi^2 \bar{\rho})^{1/3}.
\] (3.15)

(the spin \( s \) of the fermions has been taken to be \( \frac{1}{2} \)).

To first order in \( \bar{c} \), the local number density of fermions \( n(\mathbf{r}) \) is

\[
\mathbf{n}(\mathbf{r}) = \sum_{\mathbf{k} : |\mathbf{k}| < k_F} \left\{ \left| \psi_{p}^{(\mathbf{r})}(\mathbf{r}) \right|^2 + 2 \tilde{c} \left| \phi_{s}^{(\mathbf{r})}(\mathbf{r}) \right| \left| \psi_{s}^{(\mathbf{r})}(\mathbf{r}) \right| \right\}.
\] (3.16)

The summation in equation (3.16) is over all \( \mathbf{k} \) with magnitude \( k \) less than \( k_F \). The factor 2 preceding the summation sign arises because the fermions are spin \( \frac{1}{2} \) particles.

Equation (3.16) is easily simplified to

\[
\mathbf{n}(\mathbf{r}) = \frac{\pi}{L^3} \sum_{n_z = 1}^{n_F} \left( \eta_F^2 - \eta_z^2 \right) \sin^2(n_z \pi \mathbf{u}) + 2 \alpha \frac{\pi}{L^2} \sum_{n_z = 1}^{n_F} \left( \eta_F^2 - \eta_z^2 \right) \sin(n_z \pi \mathbf{u}) \phi_{n_z}(\mathbf{r}).
\] (3.17)
Using the well known formulae

\[
\sum_{k=1}^{n} \sin^2 kx = \frac{n}{2} - \frac{\cos((n+1)x) \sin nx}{2 \sin x}, \tag{3.19}
\]

\[
\sum_{k=1}^{n} k^2 = \frac{n^3}{3} + \frac{n^2}{2} + \frac{n}{6}, \tag{3.20}
\]

\[
\sin^2 x = \frac{1}{2} (1 - \cos 2x) \tag{3.21}
\]

it is straightforward to check that, to dominant order in the large number \( n_F \), the first term on the right hand side of equation (3.17) is simply \( \rho \). Combining this result and equations (3.13) and (3.14), equation (3.17) reduces to

\[
\eta(w) = \rho + 2\alpha \frac{\pi}{L^3} \left\{ \frac{1}{4\pi^2} (u - \frac{1}{2}) \sum_{n_z=1}^{n_F} \left( \frac{\eta_{n_z}}{n_z} - 1 \right) \sin^2 (n_z \pi w) \right. \\
+ \left. \frac{1}{4\pi} (u' - u') \sum_{n_z=1}^{n_F} \left( \frac{\eta_{n_z}^2}{n_z^2} - \eta_z \right) \sin (n_z \pi w) \cos (n_z \pi w) \right\}. \tag{3.22}
\]
Combining equations (3.19), (3.21) and the relations

\[ \sin x \cos x = \frac{1}{2} \sin 2x, \]

\[ (3.23) \]

\[ \sum_{k=1}^{n-1} \frac{k \sin kx}{4 \sin^2 \frac{x}{2}} = 2 \cos \frac{2n-1}{2} \frac{x}{2}, \quad (7) \]

\[ (3.24) \]

\[ \sum_{k=1}^{\infty} \frac{1}{k} \sin kx = \frac{\pi - x}{2}, \quad 0 < x < 2\pi, \]

\[ (3.25) \]

\[ \sum_{k=1}^{\infty} \frac{1}{k^2} \cos kx = \frac{\pi^2}{6} - \frac{\pi x}{2} + \frac{x^2}{4}, \quad 0 < x < 2\pi, \]

\[ (3.26) \]

it follows that the terms of order \( n_F^2 \) in the curly parentheses in equation (3.22) cancel out. As such, it is necessary to go to order \( n_F \). The following expressions supplement those already cited:

\[ \sum_{k=1}^{\infty} \frac{1}{k^2} \sim \frac{1}{n_F} \quad \text{as} \quad n_F \to \infty, \]

\[ (3.27) \]
Using these three equations, equation (3.22) becomes, to leading order,

$$\eta(u) = \rho + \alpha \left( \frac{1}{L^2} \frac{\eta_F}{2\pi} \right) \left( \frac{1}{2} - u \right).$$  

(3.30)

Equation (3.27) is proven by showing that $\sum_{k=0}^{\infty} k^2$ is bound from below by $\int_{\eta_F}^{\infty} dx/x^2$ and from above by $\int_{\eta_F}^{\infty} dx/(x-1)^2$. Equations (3.28) and (3.29) are proven in Appendix D.

Equation (3.30) gives the first order expression for the local number density. The mathematical criterion for which the preceding derivation is valid is $\alpha << 1$, or $L << (h^2/2mc) = \ell_0$. If $c$ is of the order of $mg$, $\ell_0$ is of the order of $10^{-3}$ meters! This would seem to suggest that, unless $c$ turns out to be extremely small, equation (3.30) will be of no use in the present work.
This, in fact, turns out to be not so, and as shall be seen, equation (3.30) will play a key role in the model metal.

(3.4) LINEARITY OF THE LOCAL NUMBER DENSITY IN THE PARAMETER $\alpha$

Equations (2.92) to (2.95) are valid for $\alpha \gg 1$ and $\tilde{c} \ll \varepsilon_F$. Consider the extreme $\tilde{c} \ll \varepsilon_F$. Expanding equations (2.92) and (2.94) in terms of the small parameter $\tilde{c}/\varepsilon_F$, and retaining terms only up to first power in $\tilde{c}/\varepsilon_F$, the following expressions result:

\begin{equation}
\eta(u) = \frac{1}{3\pi^2} \left( \frac{2m\varepsilon_F}{\hbar^2} \right)^{3/2} \left( 1 - \frac{3}{2} \frac{\tilde{c}}{\varepsilon_F} u \right),
\end{equation}

\begin{equation}
\rho = \frac{1}{3\pi^2} \left( \frac{2m\varepsilon_F}{\hbar^2} \right)^{3/2} \left( 1 - \frac{3}{4} \frac{\tilde{c}}{\varepsilon_F} \right).
\end{equation}

Using equation (4.2) to eliminate $\varepsilon_F$ from equation (4.1),

\begin{equation}
\eta(u) = \rho + \frac{3}{2} \left( \frac{3}{4\pi^2} \right)^{1/3} \frac{2m\tilde{c}}{\hbar^2} \left( \frac{1}{2} - u \right)^{1/3}
\end{equation}

or, equivalently:

\begin{equation}
\eta(u) = \rho + \frac{1}{2} \left( \frac{3}{4\pi^2} \right)^{1/3} \alpha \left( \frac{1}{2} - u \right) \rho^{1/3}.
\end{equation}
Compare equations (3.30) and (4.3). From equations (3.15) and (3.18) it is seen that the two expressions for \( n(\mu) \) are identical. Yet equation (3.30) was derived assuming \( \alpha \ll 1 \), whereas equation (4.3) was derived assuming \( \alpha \gg 1 \) and \( \tilde{\varepsilon} \ll \varepsilon_F \). The condition \( \tilde{\varepsilon} \ll \varepsilon_F \) translates, using equation (4.2), into \( \alpha \ll (3\pi^2 N)^{2/3} \). This means that equation (4.3) is the asymptotic form for \( n(\mu) \) both when \( \alpha \) is small, and when \( \alpha \) is large, provided \( \alpha \) is not too large.

The obvious inference from this result is that equation (4.3) is also valid for all \( \alpha \) in between these extremes, or, simply, as long as \( \alpha \ll (3\pi^2 N)^{2/3} \). The reasoning behind this assertion is as follows.

One can imagine increasing \( \alpha \) by holding \( L \) fixed and increasing \( c \). As long as \( c \) is not too large -- i.e.: as long as \( \alpha \ll (3\pi^2 N)^{2/3} \) --, the external potential may be thought of as a perturbation. As \( c \) increases, \( n(\mu) \) will change smoothly. Physically, one does not expect \( n(\mu) \) to fluctuate with \( c \). That is, if \( n(\mu) \) is linear in \( \alpha \) when \( \alpha \) is small, and also when \( \alpha \) is large, with the same slope in both regimes, it is reasonable to assume that \( n(\mu) \) is also linear, with the same slope, in between the two extremes. See figure 11 to help clarify this concept.

In conclusion, equation (4.3) is assumed to be valid for all \( \alpha \) small compared to \( N^{2/3} \).
A nonzero internal charge density will contribute to the average internal electric field. This contribution shall now be calculated.

The charge density at height $u$, denoted $q(u)$, is given in terms of the number density of electrons, $n_e(u)$, and the number density of ions, $n_I(u)$, by the following equation:

$$q(u) = (Z_n - 1)q_e n_I(u) - q_e n_e(u).$$

(5.1)

$n_e(u)$ is given in turn by equation (4.3), while $n_I(u)$ may be found via macroscopic elasticity theory, which produces the following equation for an isotropic body subject to a uniform gravitational field:
\[ \frac{\partial(n_\mathcal{I})}{\partial Z} = -\frac{1-2\nu}{Y} \rho_\mathcal{I}^2 M_a g \] (5.2)

\( \phi \) is Poisson's ratio, \( Y \) is Young's modulus and \( M_a \) is the atomic mass for the material in question. \( \rho_\mathcal{I} \) is the number density of ions when there is no external field, while \( n_\mathcal{I}(u) \) is \( n_\mathcal{I}(u) - \rho_\mathcal{I} \).

If \( n_\mathcal{I}(u) \) is chosen to be \( \rho_\mathcal{I} \) at \( u = \frac{1}{2} \), then it follows that

\[ n_\mathcal{I}(u) = \rho_\mathcal{I} + \frac{1-2\nu}{Y} \rho_\mathcal{I}^2 M_a g L (\frac{1}{2} - u) \] (5.3)

where \( M_a \) has been replaced by \( M \), the ionic mass.

Denote by \( \phi(u) \) the charge per unit area at height \( u \) in the large \( L \) limit. Since \( \phi(u) = Lq(u) du \),

\[ \phi(u) = A q_e (\frac{1}{2} - u) \, du \] (5.4)

where

\[ A = \left( Z_n - 1 \right) \frac{1-2\nu}{Y} \rho_\mathcal{I}^2 M_a g - \left( \frac{3}{\pi^2} \right)^{\frac{1}{3}} \left( \frac{Z_n^2}{k_b^2} \rho_\mathcal{I} \right) \frac{1}{m_c} \] (5.5)

Equation (5.4) follows from equations (4.3), (5.1), (5.3) and the assumption of overall charge neutrality:

\[ (Z_n - 1) q_e \rho_\mathcal{I} = q_e \rho_e \] (5.6)
where $\rho_e$ is the average number density of free electrons.

Using equation (5.4), the contribution by the internal charge density to the average internal electric field is easily found to be

$$E_{ch}(u) = 2\pi A \rho_e u(1-u)$$  \hspace{1cm} (5.7)

Note that $E_{ch}$ depends on height. It was assumed at the outset that $E_{ave}$ is independent of height. The question arises as to how to reconcile this apparent conflict.

Recall that the objective of the model is to develop ideas, not to produce a precise calculation of $E_{ave}$. Specifically, it is of interest in this chapter to see if the internal charge imbalance in a metal contributes a first order term to $E_{ave}$. Since the calculations in this model have been made to only first order in $g$, $E_{ave}$ will be independent of height to first order in $g$ if $E_{ch}$ is an order $g^2$ quantity. It will be shown in the next chapter that $E_{ch}$ does, in fact, vanish to first order in $g$.

There are two possible ways to proceed. One is to use equation (5.7) as it is, and to show that $A$ turns out to be of order $g^2$. The other is to use the maximum value of $E_{ch}(u)$, which occurs at $u = 1$, and to show that $A$ is zero to first order in $g$. Both approaches lead to the same result.

To be more specific, replace $E_{ch}(u)$ by $E_{ch}(1/2)$. Thus,
Using equation (5.8), a self-consistent solution for $E_{\text{ave}}$ shall be found in the next chapter. The term "self-consistent" is used because $E_{\text{ave}}$ depends on $E_{ch}$, but $E_{ch}$ depends on $E_{\text{ave}}$. The latter point follows because $A$ in equation (5.8) depends on $c$, the slope of the external linear potential experienced by the conduction electrons, which in turn is given by

$$C = m g + q_e E_{\text{ave}}$$

(5.9)

It is certainly possible to calculate what $n(u)$ would have to be in order to give rise to the $E_{\text{ave}}(u)$ which in turn gives rise to $n(u)$. This problem, however, is not relevant to this thesis. The reason is because one does not expect the electric field in a metal to vary much in the metal interior. As such, $E_{\text{ave}}$ has been assumed to be approximately uniform inside the model metal. Once $A$ has been shown to be of order $g^2$, this assumption will have been verified.

---


Equation (2.45) actually only gives the part of the eigenstate which can be expressed in the position representation. This may be labelled by "k". The label "k" denotes both "k" and the spin label of the eigenstate.


At T=0 K, μ is equal to the Fermi Energy, $\xi_F$.


Ibid., p.31.
CHAPTER 4

DETERMINATION OF $E_{\text{ave}}$

The basic result of chapter 2 was the construction of a model of the ions and the calculation of $E_{\text{dipole s}}$. In chapter 3, a modelling of the free electrons produced a result for $E_{\text{ch}}$. Using these findings, and the equation

$$E_{\text{ave}} = E_{\text{dipole s}} + E_{\text{ch}} + E_{\text{ext}}$$

(1)

$E_{\text{ave}}$ will now be determined.

Write

$$E_{\text{dipole s}} = \beta_1 \frac{Mg}{q_e} + \beta_2' E_{\text{ch}} + \beta_2 E_{\text{ext}}$$

(2)

where $\beta_1$ and $\beta_2'$ are found by comparing equation (2) to equation (2-10.3):

$$\beta_1 = \frac{\alpha_1}{(d/a_0)^3 Z_n^4 + \alpha_3}$$

(3)

$$\beta_2' = -\frac{\alpha_2}{(d/a_0)^3 Z_n^4 + \alpha_3}$$

(4)

Substituting equation (2) into equation (1):

$$E_{\text{ave}} = \beta_1 \frac{Mg}{q_e} + \beta_2 E_{\text{ch}} + \beta_2 E_{\text{ext}}$$

(5)
where

$$\beta_2 = 1 + \beta_2'.$$  \hspace{1cm} (6)

Now write

$$E_{ch} = \beta_3 \left( \beta_4 - \beta_5 \left[ \frac{q_e E_{ave}}{g} + m \right] \right),$$  \hspace{1cm} (7)

where, from equations (3-5.5) and (3-5.8):

$$\beta_3 = \frac{\pi}{2} kL^2 \rho e,$$ \hspace{1cm} (8)

$$\beta_4 = (Z-1)^{\frac{3}{2}} \frac{1 - 2\rho}{y} \rho^2 M g,$$ \hspace{1cm} (9)

$$\beta_5 = \left( \frac{3}{\pi^4} \right)^{\frac{1}{3}} M g \left( \frac{3}{h^2} \right)^{\frac{1}{3}} \rho^3,$$ \hspace{1cm} (10)

Inserting equation (7) into equation (5), and solving for $E_{ave}$:

$$E_{ave} = \frac{\beta_1 M g / q_e + \beta_2 E_{ext} + \beta_3 \beta_4 - \beta_2 \beta_5 m}{1 + \beta_2 \beta_3 \beta_5 q_e / g},$$ \hspace{1cm} (11)

is a number. For $L$ of the order of $10^{-2}$ meters and $\rho$ of the order of $10^{29}$/meters$^3$, a typical value for metals, $\beta_3 \beta_5 q_e / g$ is of the order of $10^{16}$. By equations (4) and (6), and
tables II and III, it is clear that $\beta_2 \beta_3 \beta_5 q_e / g \gg 1$, and so equation (11) may be replaced by

$$E_{\text{ave}} = \frac{\beta_1 M q_e / \beta_2 E_{\text{ext}} + \beta_2 \beta_3 \beta_4 - \beta_2 \beta_3 \beta_5 m}{\beta_2 \beta_3 \beta_5 q_e / g} \left( 1 - \frac{1}{\beta_2 \beta_3 \beta_5 q_e / g} \right), \quad (12)$$

It will turn out that the term in the numerator involving $\beta_4$ is large compared to the other terms. In consequence, the expression for $E_{\text{ave}}$ which is consistent to first order in the small parameter $(\beta_2 \beta_3 \beta_5 q_e / g)$ is

$$E_{\text{ave}} = \frac{\beta_1 M q_e / \beta_2 E_{\text{ext}} + \beta_2 \beta_3 \beta_4 - \beta_2 \beta_3 \beta_5 m}{\beta_2 \beta_3 \beta_5 q_e / g} - \frac{1}{\beta_2 \beta_3 \beta_5 q_e / g} \frac{\beta_4}{\beta_5 q_e / g} \quad (13)$$

Into equation (13) put

$$E_{\text{ave}} = E_{\text{ave}}^{(0)} + \Delta E_{\text{ave}}, \quad (14)$$

where

$$E_{\text{ave}}^{(0)} = \frac{\beta_4}{\beta_5 q_e / g} \quad (15)$$

The resultant equation for $\Delta E_{\text{ave}}$ is

$$\Delta E_{\text{ave}} = \frac{\beta_1 / \beta_2}{\beta_3 \beta_5 q_e / g} M q_e / q_e + \frac{1}{\beta_3 \beta_5 q_e / g} E_{\text{ext}} - \frac{1}{\beta_2 \beta_3 \beta_5 q_e / g} E_{\text{ave}}^{(0)}, \quad (16)$$

or, using $\beta_3 \beta_5 q_e / g \approx 10^6$,

$$\Delta E_{\text{ave}} \approx \frac{\beta_1}{\beta_2} 10^{-16} M q_e / q_e + 10^{-16} E_{\text{ext}} - 10^{-16} E_{\text{ave}}^{(0)}. \quad (17)$$
Rewrite equation (15) as

$$E_{\text{ave}}^{(o)} = \frac{\beta_4}{M_2} \frac{M_3}{q_e}$$  \hspace{1cm} (18)

Equations (17) and (18) show that $\Delta E_{\text{ave}}^{(o)}$ is small compared to $E_{\text{ave}}^{(o)}$. From tables I, II and III, it is clear that $\beta_1/\beta_2$ will not be very large, and will certainly not be of order $10^6$.

From equations (9) and (10), using typical values for $\delta$ and $\gamma^{(o)}$ (specifically, those for copper), it follows that $\beta_4/M_2$ is an order one number.

Unless $E_{\text{ext}}$ is very large, $\Delta E_{\text{ave}}^{(o)} << E_{\text{ave}}^{(o)}$, and

$$E_{\text{ave}} \approx E_{\text{ave}}^{(o)}.$$  \hspace{1cm}

To verify the consistency of this result, put equation (13) into equation (7) to obtain

$$E_{\text{ch}} = -\frac{\beta_1}{\beta_2} \frac{M_3}{q_e} E_{\text{ext}} + \frac{1}{\beta_2} E_{\text{ave}}^{(o)}$$  \hspace{1cm} (19)

and put equations (6) and (19) into equation (2) to get

$$E_{\text{dipoles}} = \frac{\beta_1}{\beta_2} \frac{M_3}{q_e} - \frac{1}{\beta_2} E_{\text{ave}}^{(o)} + E_{\text{ave}}^{(o)}.$$  \hspace{1cm} (20)

Equations (19) and (20) combine with equation (1) to say that

$$E_{\text{ave}} = E_{\text{ave}}^{(o)} = \int \frac{M_3}{q_e}$$  \hspace{1cm} (21)

where

$$f = \left( \frac{\mu^4}{3} \right)^{1/3} \left( Z_n - 1 \right)^{2/3} \frac{5/3}{\gamma^{(o)}} \frac{r^2}{m} \frac{1-2\theta}{\gamma}.$$  \hspace{1cm} (22)

It has been assumed in this model that the dependence of $E_{\text{ave}}$ on $u$ is very weak. The consistency of this assumption with
the above results will now be demonstrated.

First, using equations (14), (15) and (16), note that $E_{\text{ave}}^{(o)}$ differs from $E_{\text{ave}}^{(o)} - mg/q_e$ by terms that are of the order of $10^{-16}$ of $E_{\text{ave}}^{(o)}$. Replacing $E_{\text{ave}}$ by $E_{\text{ave}}^{(o)} - mg/q_e$ in equation (7), and using equation (15) for $E_{\text{ave}}^{(o)}$, gives $E_{ch}=0$. In other words, equations (14), (15), (16) and (7) imply that $E_{ch} \approx 10^{-16} E_{ave}$. Equivalently, replacing $E_{ave}$ by $E_{ave}^{(o)} - mg/q_e$ in equation (5.5) gives $A=0$ (recall that $c=mg+q_e E_{ave}$), which means that $A$ is of order $10^{-16}$; equation (5.7) then says that $E_{ch}(z) \approx 10^{-16} E_{ave}$. Since $E_{ch}$ is very small, equation (19) indicates that

$$E_{ext} \approx -\frac{\beta_1}{\beta_2} \frac{M_g}{q_e} + \frac{1}{\beta_2} E_{ave}^{(o)}.$$  

Combining equations (1), (20) and (23) along with the fact that $E_{ch}$ is negligible reveals that $E_{ave} \approx E_{ave}^{(o)}$, as stated earlier in this chapter.

Because $E_{ch} << E_{ave}^{(o)}$, the assumption that $E_{ave}$ is uniform in the metal interior is consistent with the results of this chapter.

Equation (21) for $E_{ave}$ is the same result as produced by the heuristic argument due to Dessler et. al. This result, however, has been arrived at here in a different manner than it was by Dessler et. al. Moreover, the present approach also determines how much of $E_{ave}$ is made up by the charge imbalance inside the metal, and how much by the ionic dipoles. It is not surprising though, that the answer obtained here for $E_{ave}$ is the same as in the heuristic treatment of Dessler et.al., for the basic physics is very much the same in each case: the lattice
compression is calculated using elasticity theory, and the electrons are treated, basically, as if they were free locally.

Moreover, although the local number density of electrons differs from the local number density of ions in the model presented here, the difference between the two is very small. In consequence, to dominant order, $E_{\text{ave}}$ as calculated in the model is the same as $E_{\text{ave}}$ as calculated by the heuristic Dessler et. al. approach.

Obtaining a final answer for $E_{\text{ave}}$ was only one of the objectives of the model, as was stressed in the introduction to this work. In the next part of this thesis, the model is compared to the literature so as to demonstrate what the model has contributed towards understanding the problem of the gravitationally induced electric field.

\[ (1-2\delta)/\gamma = 1/3K \] where $K$ is the "modulus of compressibility". $K$ is of order $10^{16}$ Joules/metre$^3$ for most metals.
In this thesis, a simple model of a metal has been constructed. The model has been used to calculate the gravitationally induced electric field in terms of the sources of the field. The sources which have been considered explicitly are the ionic dipole moments and the charge imbalance inside the metal; all other sources have been grouped together into $E_{\text{ext}}$. A brief summary of this model is now presented.

The ions are arranged, locally, in a lattice pattern. The number density of ions decrease linearly with height. Because of gravity, these ions have a dipole moment $p$. These dipole moments create an average electric field $E_{\text{dipoles}}$ inside the metal.

In the model, $p$ and $E_{\text{dipoles}}$ are calculated to only first order in $g$. Because the density of ions changes with height, the ions do not all have the exact same dipole moment. However, the change in dipole moment with height is very small. Similarly, $E_{\text{dipoles}}$ also depends very weakly on height.

Nevertheless, the expressions calculated for $p$ and $E_{\text{dipoles}}$ are correct to first order in $g$, for all positions inside the metal. Taking into account the height dependence on the number density of shells would produce corrections of second order in $g$. 
The conduction electron number density, like the ionic number density, decreases linearly with height. The slopes of the number densities differ by a tiny amount, giving rise to a net charge density inside the metal. This charge density produces an electric field $E_{ch}(u)$. A self-consistent solution for $E_{ave}$ shows that $E_{ch}(u) \ll E_{ave}$, thereby verifying the initial assumption that $E_{ave}$ depends only weakly on height. The solution obtained for $E_{ave}$ is the same as the Dessler et. al. heuristic expression for $E_{ave}$. In the final analysis, $E_{dipole}$, $E_{ext}$, and $E_{ch}$ are all of order $Mg/q_e$ and directed opposite to $\vec{g}$, while $E_{ch}$ is negligible to the order of calculation in the model.

The value of the model is not the value of $E_{ave}$ that it produces. The model represents a metal far too simply to give a value of $E_{ave}$ that can be trusted. The real worth of the model is the physical insight it provides.

Through the model, one can understand how the gravitationally induced electric field comes about. One can envisage how a metal responds to gravity, and how this response generates sources of $E_{ave}$. In particular, the model provides insight into how the requirement that the nuclei be held up against gravity can give rise to ionic dipole moments. Moreover, the model shows very clearly how the electric field at the site of the nucleus can be exactly $-Mg/q_e$, yet be something considerably different on the average. Finally, the model reveals that charge neutrality in the metal interior need not be assumed; the charge imbalance in a metal may be shown to be so
minute that $E_{ch}$ makes a negligible contribution to $E_{ave}$.

The model has demonstrated that, in addition to the compressibility of the lattice, charge imbalance and gravitationally induced ionic dipoles are important concepts in the problem of gravity induced electric fields in metals.

Besides metals, the model also generates some insight into the question of gravity induced electric fields in dielectrics. For a dielectric, there are no conduction electrons. The model then reduces to simply a lattice of ions, with $Z_n=1$. Note that the model still predicts $E_{ave}$ of order $Mg/q_e$, and opposite to $g$, whether the lattice is compressible or not! According to the model, the key source of $E_{ave}$ for a dielectric is the field due to the ionic dipole moments; the effect of lattice compressibility is not important. But in a metal, both lattice compressibility and the ionic dipole moments are significant. The model therefore suggests the following question: What relative importance do these two effects have in a semiconductor?

The model presented here is a very simple model. What is needed is to supplant this model with one which takes into account the ionic polarization and the charge imbalance in a more refined manner. The lattice compression will also need to be considered carefully. One would also like to see this proposed model possess some flexibility, so that it could give some conclusions about dielectrics, semiconductors and metals.

As a final point, the model of this thesis does not deal with the physics involved in the support against gravity of the
ion as a unit. It would be interesting to include this feature into a more elegant model, and to see what sources of the gravity induced electric field this feature would lead to.


Define coordinates from the center of the shell, \( x, y, z \).

See figure A.1. Let \( \psi(r^*) \) be the ground state eigenfunction for the perturbed boundary problem, where \( r^* \) denotes position from the center of the shell. The (ground state) energy eigenvalue is still given by equation (1.30). It is also given by

\[
E = \int d^3r_0 \int_{r_0}^* (r^*) H(x^*) \psi(r^*),
\]

where the integral is over the region interior to the shell, that is, over all \( \Theta^* \) and all \( \phi^* \) (the polar and azimuthal angles,

![Figure A.1. Coordinates from the Center of the Shell Versus Coordinates from the Nucleus.](image)
as measured from the center of the shell) and over $0 \leq r_o < R$, and where $H(r_o)$ is the Hamiltonian expressed in coordinates from the center of the shell:

\[
\begin{align*}
H(r_o^o) &= \frac{-\hbar^2}{2m} \nabla^2 + U(r_o^o) \\
U(r_o^o) &= \begin{cases} \\
-\frac{Ze^2}{r_o^{2} + \alpha^2} & , 0 < r_o < R \\
+\infty & , r_o > R
\end{cases}
\end{align*}
\] (A.2)

$E_z$ is determined by differentiating equation (A.1) twice with respect to $\alpha$ and determining the order one term:

\[
\frac{\partial^2 E}{\partial \alpha^2} = 2 \bar{E}_2 + 12 \bar{E}_4 + \cdots = \frac{\partial^2}{\partial \alpha^2} \int d r_o [\bar{H} \bar{\Phi}^* + \bar{\Phi} \frac{\partial}{\partial \alpha} (\bar{H} \bar{\Phi})].
\] (A.3)

Notice that the limits of integration in equation (A.3) do not depend on $\alpha$. This is precisely why $H(r_o)$, and $\bar{\Phi}(r_o)$ were introduced. Differentiating the integral once

\[
\frac{\partial}{\partial \alpha} \int d r_o [\bar{H} \bar{\Phi}^* + \bar{\Phi} \frac{\partial}{\partial \alpha} (\bar{H} \bar{\Phi})] = \int d r_o [\bar{\Phi} \frac{\partial}{\partial \alpha} [\bar{H} \bar{\Phi}^* + \bar{\Phi} \frac{\partial}{\partial \alpha} (\bar{H} \bar{\Phi})]].
\] (A.4)

Write

\[
H = -\frac{\hbar^2}{2m} \nabla^2 + U
\]

Inside the shell,
It follows that

\[ \frac{d}{d\alpha} (\mathcal{H}^R) = \mathcal{H} \frac{\partial \Phi}{\partial \alpha} + \Phi \frac{\partial \mathcal{U}}{\partial \alpha} \cdot \]

As a result, the right hand side of equation (A.4) becomes

\[ \int_R d^3 \mathbf{r}_o \left[ \frac{\partial \Phi^*}{\partial \alpha} \mathcal{H} \Phi + \Phi^* \mathcal{H} \frac{\partial \Phi}{\partial \alpha} + \Phi^* \frac{\partial \mathcal{U}}{\partial \alpha} \Phi \right] = \int_R d^3 \mathbf{r}_o \Phi^* \frac{\partial \Phi}{\partial \alpha} \phi \cdot \]

Equation (A.6) follows because

\[ \int_R d^3 \mathbf{r}_o \frac{\partial \Phi^*}{\partial \alpha} \mathcal{H} \Phi = \mathcal{E} \int_R d^3 \mathbf{r}_o \frac{\partial \Phi^*}{\partial \alpha} \Phi \cdot \]

which implies that

\[ \int_R d^3 \mathbf{r}_o \left[ \frac{\partial \Phi^*}{\partial \alpha} \mathcal{H} \Phi + \Phi^* \mathcal{H} \frac{\partial \Phi}{\partial \alpha} \right] = \mathcal{E} \int_R d^3 \mathbf{r}_o \left[ \frac{\partial \Phi^*}{\partial \alpha} \Phi + \Phi^* \frac{\partial \Phi}{\partial \alpha} \right] \]
Differentiating a second time:

$$\frac{\partial^2}{\partial \alpha^2} \int d^3r_0 \Phi^* \Phi = \frac{\partial}{\partial \alpha} \int d^3r_0 \Phi^* \Phi$$

$$= \int d^3r_0 \left( \Phi^* \frac{\partial \Phi}{\partial \alpha} + \Phi \frac{\partial \Phi^*}{\partial \alpha} \right) \frac{\partial U}{\partial \alpha}$$

$$+ \int d^3r_0 \frac{\partial^2 \Phi^* \Phi}{\partial \alpha^2} \rho \frac{\partial^2 U}{\partial \alpha^2}$$

(A.7)

Expressions for $\frac{\partial U}{\partial \alpha}$ and $\frac{\partial^2 U}{\partial \alpha^2}$ are required. From equation (A.5),

$$U = -kZnq_e^2 \left[ x_0^2 + y_0^2 + (z_0 + \alpha)^2 \right]^{-1/2}$$

$$\frac{\partial U}{\partial \alpha} = kZnq_e^2 \frac{Z_0 + \alpha}{\left[ x_0^2 + y_0^2 + (z_0 + \alpha)^2 \right]^{3/2}} = kZnq_e^2 \frac{r \cos \theta}{r^3}$$

or

$$\frac{\partial U}{\partial \alpha} = kZnq_e^2 \frac{\cos \theta}{r^2}$$

(A.8)

where $r$ and $\theta$ are measured from the nucleus.

Notice at this point that, since $\Phi^* \Phi d^3r_0 = \Phi^* \Phi d^3r$ -- where $d^3r_0$ and $d^3r$ refer to the same physical volume element --
equation (A.8) may be plugged into equation (A.6) to give

$$kZ_n g^2 \int_{S_0} d^2 r \psi^* \frac{\partial \psi}{\partial \alpha} \cos \theta \frac{1}{r^2} = \frac{\partial}{\partial \alpha} = 2 \alpha E_2 + \ldots$$

The order $\alpha$ term on the left here is

$$2 \alpha kZ_n g^2 \int_{S_0} d^2 r \psi \cos \theta \frac{1}{r^2} \psi$$

thereby recovering equation (2.40):

$$\alpha E_2 = kZ_n g^2 \int_{S_0} \psi \cos \theta \frac{1}{r^2} \psi d^2 r$$

Calculating $\frac{\partial^2 U}{\partial \alpha^2}$:

$$\frac{\partial^2 U}{\partial \alpha^2} = \frac{\partial^2 U}{\partial z^2} = \frac{1}{3} \nabla^2 U - \frac{1}{3} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} - 2 \frac{\partial^2}{\partial z^2} \right) U,$$

$$\frac{\partial^2}{\partial x^2} \left( \frac{1}{|r_0 + \alpha z|^2} \right) = 3 \frac{x_0^2}{|r_0 + \alpha z|^4} - \frac{1}{|r_0 + \alpha z|^3},$$

$$\frac{\partial^2}{\partial y^2} \left( \frac{1}{|r_0 + \alpha z|^2} \right) = 3 \frac{y_0^2}{|r_0 + \alpha z|^4} - \frac{1}{|r_0 + \alpha z|^3},$$

$$\frac{\partial^2}{\partial z^2} \left( \frac{1}{|r_0 + \alpha z|^2} \right) = 3 \frac{(z_0 + \alpha)^2}{|r_0 + \alpha z|^4} - \frac{1}{|r_0 + \alpha z|^3},$$

$$\nabla^2 \left( \frac{1}{|r_0 + \alpha z|^2} \right) = - 4 \pi \delta \left( r_0 + \alpha z \right),$$

and so, using equation (A.6),
where, again, $\theta$ and $r$ are measured from the nucleus.

Insert equations (A.8) and (A.9) into (A.7), and equate this to $\frac{d^2 E}{d\alpha^2}$:

$$2^{\alpha}E_2 + \cdots = kZnq_e^2 \int_R d^3r_o \left( \hat{\phi}^* \frac{\partial \phi}{\partial \alpha} + \phi \frac{\partial \phi^*}{\partial \alpha} \cos \theta \right)$$

$$+ \frac{4\pi}{3} kZnq_e^2 \int_R d^3r_o \hat{\phi}^* \hat{\phi} \delta (r_o + \alpha \frac{\lambda}{2})$$

$$+ kZnq_e^2 \int_R d^3r_o \hat{\phi}^* \hat{\phi} \frac{1 - 3\cos^2 \theta}{r^3} \ .$$

It is required to find the order one term on the right hand side of equation (A.10).

Notice that $\hat{\phi}^* \hat{\phi} d^3r_o$ in the latter two integrals may be replaced by $\psi^* \psi d^3r$ if the integral is also changed from $\int_R d^3r_o$ to $\int d^3r$. The integral with the delta function then becomes

$$\int_{S_\alpha} d^3r \psi^* \psi \delta (\vec{r})$$

for which the order one term is

$$\int_R d^3r \psi^2 \psi \delta (\vec{r}) = \left[ \psi(\vec{r}) \right]^2 = \left( \frac{Zn}{\alpha_o} \right)^3 4N^2 ,$$
As such, the second term in equation (A.10) makes an order one contribution of

$$\frac{16\pi}{3} \sum_n N^2 \frac{k_0^2}{\alpha_0^3}$$

(A.11)

Replacing $\Phi^* \varphi d^3r_0$ by $\varphi^* \varphi d^3r$ makes the final integral in equation (A.10)

$$\int_{S, \alpha} d^3r \varphi^* \frac{1 - 3 \cos^2 \Theta}{r^3} \varphi$$

for which the order one portion is

$$\int_{R} d^3r \varphi^* \frac{1 - 3 \cos^2 \Theta}{r^3} \varphi$$

This vanishes on account of the $\Theta$ integration.

The first integral in equation (A.10) also makes an order one contribution. To see this, break up the integration into two parts. One part consists of a sphere with a radius of order $\alpha$, but greater than $\alpha$. The integration within this sphere will give a contribution of order higher than $\alpha^0$, and may be discarded. For the rest of the integration, expand $\Phi$ as
Only $\bar{\Phi}_0$ and $\bar{\Phi}_1$ need to be known in order to obtain the order one term being sought. To obtain $\bar{\Phi}_0$ and $\bar{\Phi}_1$, expand $\psi_0$ and $\psi_1$ out in powers of $\alpha$ and, of course, in terms of $r_0, \theta_0, \phi_0$. Doing this gives

$$\bar{\Phi}_0 = N \left( \frac{Z_0}{\alpha_0} \right)^{3/2} (2\pi \alpha_0) e^{i \rho_0/2}$$ \hspace{1cm} (A.13)

and

$$\bar{\Phi}_1 = N \left( \frac{Z_0}{\alpha_0} \right)^{5/2} \left( \frac{\rho_0 \cos \theta_0}{\rho_0 - 2} \right) e^{i \rho_0/2} \cos \Theta_0$$ \hspace{1cm} (A.14)

To lowest order in $\alpha$:

$$\frac{\cos \Theta}{r^2} = \frac{\cos \Theta_0}{r_0^2}$$ \hspace{1cm} (A.15)

Plugging equations (A.13), (A.14) and (A.15) into the first integral in equation (A.10) gives the order one term sought:
Combining equation (A.11) and (A.16) gives the order one term which is required to determine \( \varepsilon_2 \). Using equation (A.10),

\[
Z^\alpha E_2 = \frac{16\pi}{3} eN^2 \frac{kq_e^2}{a_o^3} Z_n \quad \text{and} \quad \frac{\alpha E_2}{\text{max}} = \frac{16\pi}{3} eN^2 \frac{kq_e^2}{a_o^3},
\]

just as before.
This appendix deals with a central problem of Chapter 3 of this thesis, namely that of determining the local number density $n(u)$ of fermions which are subject to an external potential. The approach here assumes, from the outset, that the local properties of the Fermi gas are the same as those of a free Fermi gas. As such, $n(u)$ is given by

$$n(u) = \frac{2s+1}{\lambda^3} \int \frac{d^3}{2} \left( e^{\beta \mu(u)} \right)^{1/3},$$

where all these symbols are the same as in Chapter 3. The local chemical potential $\mu(u)$ is determined by the requirement that there is no gradient in the local potential energy, i.e., that

$$\mu(u) + \tilde{U}u = \mu,$$

where $\mu$ is the chemical potential of the gas. Thus:

$$n(u) = \frac{2s+1}{\lambda^3} \int \frac{d^3}{2} \left( e^{\beta (\mu - \tilde{U}u)} \right).$$

This is the same as equation (3-2.89).
This appendix deals with some properties of a low density Fermi gas which is subject to an external linear potential. Expressions shall be derived for the Fermi energy, the pressure, and the internal energy density of the gas in terms of its average particle density. The treatment shall be restricted to absolute zero.

The starting point is part c of section 3.2. Consider equation (2.65) in the case $\gamma_{k_2} < 1$ and in the limit $\alpha \to \infty$. Using the asymptotic forms for the Airy functions $A_1(v)$ and $B_1(v)$ as $v \to \infty$,

\begin{align}
A_1(v) &\sim \frac{1}{2\pi^{1/4} v^{1/4}} \exp\left\{-\frac{2}{3} \frac{1}{v^{3/2}}\right\} \quad \text{as } v \to \infty \tag{C.1} \\
B_1(v) &\sim \frac{1}{2\pi^{1/4} v^{1/4}} \exp\left\{\frac{2}{3} \frac{1}{v^{3/2}}\right\} \quad \text{as } v \to \infty \tag{C.2}
\end{align}

equation (2.65) implies that

$$\frac{b_{k_2}}{a_{k_2}} \sim -\frac{1}{2} \exp\left(-\frac{4}{3} \alpha^{1/2} \sqrt{1-\gamma_{k_2}}\right) \quad \text{as } \alpha \to \infty, \text{ for } \gamma_{k_2} < 1.$$  

(C.3)
From equations (2.64) and (C.3) it follows that

$$A_i\left(\alpha^{1/3}k_z\right) \sim \frac{1}{2} \exp\left(-\frac{4}{3} \alpha^{1/2} [1 - \gamma_k]^{3/2}\right) B_i\left(-\alpha^{1/3}k_z\right)$$  \hspace{1cm} (C.4)

as $\alpha \to \infty$, for $\gamma_k < 1$.

The asymptotic forms of $A_i(v)$ and $B_i(v)$ as $v \to -\infty$ are\(^{(2)}\)

$$A_i(v) \sim \frac{1}{\pi^{1/2} (-v)^{1/4}} \sin\left(\frac{\pi}{4} (v)^{3/4} + \frac{\pi}{4}\right) \text{ as } v \to -\infty.$$  \hspace{1cm} (C.5)

$$B_i(v) \sim \frac{1}{\pi^{1/2} (-v)^{1/4}} \cos\left(\frac{\pi}{4} (v)^{3/4} + \frac{\pi}{4}\right) \text{ as } v \to -\infty.$$  \hspace{1cm} (C.6)

Equations (C.4), (C.5) and (C.6) demand that, to lowest order,

$$E_{n_z} \to \frac{\gamma_k}{\alpha^{1/3}} (-v_{n_z}) \text{ as } \alpha^{1/3} \to \infty.$$  \hspace{1cm} (C.7)

where $v_{n_z}$ denotes the $n_z^{th}$ zero of $A_i(v)$, and $\gamma_k$ has been replaced by $E_{k_z}/\gamma$.

As figure 10(a) shows, all of the zeros of $A_i(v)$ are negative. From equation (C.5), the asymptotic form of the zeros is
The integer labels of the zeros have been chosen to increase with ascending absolute magnitude of the zero. Equation (C.8) is an excellent approximation to the precise value of the zeros of $A_i(v)$, even for those close to the origin. For the purposes of this appendix, no significant error is incurred by using equation (C.8) in equation (C.7). This gives

$$(-\gamma_{n_z}) \sim \left(\frac{3 [4n_z-1] \pi}{8} \right)^{2/3} \text{ as } n_z \to \infty;$$

Equation (C.8) is an excellent approximation to the precise value of the zeros of $A_i(v)$, even for those close to the origin. For the purposes of this appendix, no significant error is incurred by using equation (C.8) in equation (C.7). This gives

$$E_{n_z} = \frac{k^2}{2m} \left( \frac{2m \tilde{c}}{k^2} \right) \frac{3 [4n_z-1] \pi}{8}^{2/3}$$

where the definition of $\tilde{c}$ has been used. The limit may be regarded as holding $\tilde{c}$ fixed and letting $L \to \infty$. As such, equation (C.9) gives those eigenvalues $E_{n_z}$ which are less than $\tilde{c}$ in the limit $L \to \infty$.

A mathematical point should now be clarified. Equation (C.9) is valid only for

$$\alpha^{1/3} (1 - \gamma_{n_z}) \gg 1.$$ (C.10)

This is because the asymptotic forms (C.1) and (C.2) may be employed in equation (2c.22) only if the arguments of the Airy functions are large. In consequence, if $E_{n_z}$ is too close to $\tilde{c}$, $\alpha^{1/3} (1 - \gamma_{n_z})$ may not be large, and equation (C.9) will not be valid. Let $\bar{n}_z$ denote the value of $n_z$ for which the right hand side of equation (C.9) is equal to $\tilde{c}$.
\[ \bar{n}_z = \frac{1}{4} + \frac{2}{3\pi} \left( \frac{2m\tilde{c}}{\hbar^2} \right)^{1/2} L. \]  

Equation (C.9) will be a good approximation for \( E_{nz} \) provided that \( n_z \) is sufficiently less than \( \bar{n}_z \) so as to render equation (C.10) true. To determine how much less, write

\[ n_z = \bar{n}_z - \Delta n_z \]  

From equations (C.9) and (C.11), in the large \( L \) limit, \( \Delta n \) must satisfy

\[ \Delta n \gg \frac{U}{\sqrt{2\pi}} \alpha^{1/6} \]  

in order that equation (C.10) hold. Equation (C.13) indicates by how much \( n_z \) must be less than \( \bar{n}_z \) in order that equation (C.9) be valid.

In terms of

\[ k_z = \frac{n_z \pi}{L}, \quad n_z = 1, 2, 3, \ldots, \]

equation (C.9) may be written as

\[ E_{k_z} = \frac{\hbar^2}{2m} \left( \frac{3m\tilde{c}}{\hbar^2} \left( k_z - \frac{\pi}{4L} \right) \right)^{2/3}. \]  

Using equation (C.15) in equation (2.47):

\[ E_{k_z} = \frac{\hbar^2}{2m} \left( k_x^2 + k_y^2 + \left[ \frac{3m\tilde{c}}{\hbar^2} \left( k_z - \frac{\pi}{4L} \right) \right]^{2/3} \right). \]
Equation (C.16) may be used to determine the constant energy surfaces in $\mathbf{k}$-space. Let

$$\chi^2 = k_x^2 + k_y^2. \quad (C.17)$$

For the constant energy surface $E_k$, $k_z$ is given in terms of $X$ by

$$k_z = \frac{(a_1^2 - \chi^2)^{3/2}}{a_2} + a_3 \quad (C.18)$$

where

$$a_1^2 = \frac{2mE_c}{\hbar^2},$$

$$a_2 = \frac{3mc}{\hbar^2},$$

$$a_3 = \frac{11}{4L} \quad (C.19)$$

The limiting form as $L \to \infty$ of the function $k_z(X)$ specified by equation (C.18) is given graphically in figure C.1. Figure C.2 shows the constant energy surface $E_0$.

This information about the constant energy surfaces may be used to determine the average number density $\rho$, the internal energy density $\rho$, and the pressure $p$ in terms of the Fermi energy $\varepsilon_F$. The preceding results apply provided that $\varepsilon_F$ is less than $c$ by enough to make equation (C.13) true.

$\varepsilon_F$ is determined in terms of $N$ and $L$, in the limit $L \to \infty$, by the equation

$$N = 2\left(\frac{\hbar}{\pi}\right)^3 \int_{\varepsilon_F < \varepsilon_k} d^3k. \quad (C.20)$$
A glance at figure C.2 indicates that equation (C.20) is equivalent to

$$N = \frac{L^3}{2\pi^2} \int_0^{\frac{2}{3} \frac{\varepsilon_0}{C} \varepsilon_s} d\kappa_z \chi_f^2$$

(C.21)
where

\[ \chi_F^2 = a_F^2 - (a_z k_Z)^{2/3} \]  \hspace{1cm} (C.22)

\[ Q_F^2 = \frac{2m \epsilon_F}{\hbar^2} \] \hspace{1cm} (C.23)

Evaluating equation (C.21) gives

\[ \rho = \frac{2}{15\pi^2} \frac{\epsilon_F}{c} \left( \frac{2m \epsilon_F}{\hbar^2} \right)^{3/2} \] \hspace{1cm} (C.24)

where \( \rho = N/L \). Equation (C.24) may be solved for \( \epsilon_F \):

\[ \epsilon_F = \left( \frac{\hbar^2}{2m} \right)^{3/5} \left( \frac{15\pi^2 \rho}{2} \right)^{2/5} \] \hspace{1cm} (C.25)

In a similar fashion, the equation for the total internal energy \( U \),

\[ U = 2 \left( \frac{L}{\pi} \right)^3 \int_{\epsilon_F}^{\infty} d^3k \epsilon_k \] \hspace{1cm} (C.26)

may be simplified to get \( u \):
\[ U = \frac{U}{N} = \frac{2}{2\pi^2} \frac{\varepsilon_F}{\varepsilon} \left( \frac{2m\varepsilon_F}{k^2} \right)^{3/2} \varepsilon_F \]  
\hspace{10cm} (C.27)

or

\[ U = \frac{5}{7} \varepsilon_F \rho . \]  
\hspace{10cm} (C.28)

\( p \) is calculated from \( U(N,V), V=L^3 \), via

\[ p = -\frac{\partial U(N,V)}{\partial V} . \]  
\hspace{10cm} (C.29)

The result is

\[ p = \frac{2}{3} \varepsilon_F \rho . \]  
\hspace{10cm} (C.30)

For comparison, the corresponding results for \( u \) and \( p \) for the ideal Fermi gas (no external potential) are

\[ U = \frac{3}{5} \varepsilon_F \rho , \]  
\hspace{10cm} (C.31)

\[ p = \frac{2}{5} \varepsilon_F \rho . \]  
\hspace{10cm} (C.32)

It was claimed that the results of this appendix are valid only for a low density Fermi gas. This claim emerges from equation (C.25). In order that \( \varepsilon_F < \tilde{c} \), it follows from equation (C.25) that
where

\[ \rho_o = \frac{2}{15n^2} \left( \frac{\lambda m c}{\hbar^2} \right)^{3/2} \]

To get an idea of the magnitude of \( \rho_o \), consider the case \( c=mg \) and \( L=10^{-3} \) meters. This gives \( \rho_o = 756 \text{ cm}^{-3} \). Compare this to the typical number densities in metals, of the order of \( 10^{12} \text{ cm}^{-3} \)!

The densities for which the results of this appendix apply are very small indeed.


2. Ibid., pp.448-449.
Consider the function
\[ S(x, \eta_F) = \sum_{k=\eta_F}^{\infty} \frac{\cos kx}{k^2}, \quad 0 < x < 2\pi. \]  

Putting \( u = kx \), it is easy to see that
\[ S(x, \eta_F) \sim x \int_{\eta_F}^{\infty} \frac{\cos u}{u^2} \, du \quad \text{as} \quad x \to 0 \]  

\[ \frac{\partial S}{\partial \eta_F} \sim -\frac{\cos(x\eta_F)}{\eta_F} \quad \text{as} \quad x \to 0 \]  

From equation (D.3), it follows that the asymptotic form of \( S \) as \( \eta_F \to \infty \) is
\[ S(x, \eta_F) \sim -\frac{1}{x} \frac{\sin(x\eta_F)}{\eta_F^2} \quad \text{as} \begin{cases} x \to 0 \\ \eta_F \to \infty \end{cases} \]  

This claim may be verified by writing
\[ S(x, \eta_F) \sim -\frac{1}{x} \frac{\sin(x\eta_F)}{\eta_F^2} \left( 1 + f(x; \eta_F) \right) \quad \text{as} \begin{cases} x \to 0 \\ \eta_F \to \infty \end{cases} \]  

and showing that
\[ f(x, \eta_F) = O\left( \frac{1}{\eta_F^2} \right) \quad \text{as} \quad \eta_F \to \infty \]  

Equation (D.4) verifies equation (3-3.28) for small \( x \).
Consider $S(x; n_F)$ for $x = \pi$. In this case,

$$S(\pi; n_F) = (\text{(-1)}^0 \sum_{s=0}^\infty \frac{1}{(n_F + 2s)^2} - \sum_{s=0}^\infty \frac{1}{(n_F + 2s + 1)^2})$$

Since,

$$\int_0^\infty \frac{ds}{(n_F + 2s)^2} \leq \sum_{s=0}^\infty \frac{1}{(n_F + 2s)^2} \leq \int_{-1}^\infty \frac{ds}{(n_F + 2s)^2}$$

it follows that

$$\frac{1}{2n_F} \leq \sum_{s=0}^\infty \frac{1}{(n_F + 2s)^2} \leq \frac{1}{2(n_F - 1)}$$

Similarly,

$$\frac{1}{2(n_F + 1)} \leq \sum_{s=0}^\infty \frac{1}{(n_F + 2s + 1)^2} \leq \frac{1}{2(n_F - 1)}$$

From equations (D.9) and (D.10),

$$S(\pi; n_F) = O\left(\frac{1}{n_F^2}\right) \quad \text{as} \quad n_F \to \infty$$

This treatment for $x = \pi$ can be repeated for $x = \frac{\pi}{2}, \ x = \frac{\pi}{4}, \ x = \frac{3\pi}{4}, \ etcetera$. In each case, it will be found the $S$ is of order $n_F^{-2}$ as $n_F \to \infty$. Since $S$ is this order for all these distinct points, and also for a continuous range of $x$ when $x$ is small, one is led by intuition to expect it to be true for all $x$ in the range $0 < x < 2\pi$.

As such, equation (3-3.28) has been "proven".

If equation (3-3.28) is true, then a similar procedure shows that the function

$$F(x; n_F) = \sum_{k=n_F}^\infty \frac{\sin(kx)}{k}, \quad 0 < x < 2\pi$$

is of order $n_F^{-1}$ as $n_F \to \infty$. Accordingly, write
Using equation (3.3.24), it follows that

\[ 2 \sin \frac{x}{2} \frac{d^2 W}{dx^2} \sim -\eta F^2 \cos \left( \frac{2\eta F - 1}{2} x \right) \quad \text{as} \quad \eta F \to \infty \]  

(D.14)

It is straightforward to verify that equation (D.14) is satisfied by

\[ W(x; \eta F) \sim \frac{\cos \left( \frac{2\eta F - 1}{2} x \right)}{2 \sin \frac{x}{2}} \quad \text{as} \quad \eta F \to \infty \]  

(D.15)

Thus,

\[ F(x; \eta F) \sim \frac{1}{2 \eta F} \cos \left( \frac{2\eta F - 1}{2} x \right), \quad 0 < x < 2\pi, \]  

(D.16)

\[ \text{as} \quad \eta F \to \infty, \]  

which is equation (3.3.29).