ELECTRON DENSITY DISTRIBUTION IN METALLIC LITHIUM

NON-LINEAR SELF-CONSISTENT CALCULATION OF THE ELECTRON DENSITY DISTRIBUTION IN METALLIC LITHIUM

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SCOPE AND CONTENTS:

An approximate non-linear self-consistent calculation of the charge density distribution about a point charge of Z=3, appropriate to lithium, imbedded in an electron gas of mean density equal to the free electron gas density of metallic lithium has been carried out. The major difference between this and previous work on lithium now in the literature is the manner in which the two core electrons have been treated. The previous work simply considered the screened potential of an Li^+ ion and solved for the "valence" charge density in the presence of that potential. The present procedure has included these bound electrons in obtaining self-consistency; these states therefore have the wave functions appropriate to the metal instead of the free atom.

We have also gone beyond the previous work in that approximate corrections for correlation as well as exchange effects among the electrons have been included.

Because the neighbouring ions present in the solid affect the electron charge distribution, these results repre-

sent an approximation to the true density distribution of the metal. However, to a large extent, the ions are well separated, so this is expected to be a reasonable approximation, in particular in regions very near the ion. Because of this, the results are used to calculate the Knight shift, and good agreement with experiment is obtained.

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This thesis is dedicated to my parents, Harold and Doris Whitmore.

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CHAPTER I

INTRODUCTION

1.1 SCOPE OF THESIS

The development of the density functional formalism by Hohenberg and Kohn (1964) and Kohn and Sham (1965) has provided a new approach to studying the ground state properties, such as electronic charge distributions, and total energies, of metals as well as free atoms and even nuclei. From a variational approach equations have been developed which would ideally produce the exact ground state density distribution and total energy of the system in the presence of any external potential. In fact, the solution is not exact only because the exchange-correlation contribution to the energy is not treated exactly. In this formalism, as the name suggests, the local density $n(\underset{\sim}{r})$ plays a central role, and the terms contributing to the energy are shown to be functionals of n.

Using a method based on this work, we have calculated the charge displaced by a lithium nucleus when imbedded in an electron gas of mean density which is the same as that of lithium metal. The resulting charge distribution should be a good approximation to the actual distribution in the metal, especially useful for considering non-structural properties of lithium. In order to obtain a reasonable total electron density distribution in the metal, one could simply imagine the calculated distribution to be located around each nucleus in the solid, and sum over these nuclei, in the spirit of the neutral atom model (Ziman 1964,1967)

$$n_T(\underset{\sim}{r}) \simeq \sum_a n(\underset{\sim}{r}-\underset{\sim}{R}_a)$$

where $n(\underset{\sim}{r})$ is the electron distribution presented here and the sum is over all the ionic positions $\underset{\sim}{R}_a$. Although this of course will not give the exact $n_T(\underset{\sim}{r})$ because of the perturbing effects neighbouring ions have on each other, one would expect it to be quite good, especially in regions close to the nuclei, as the relative effect of the neighbouring potentials becomes very small in those regions. In particular, the density right at any nucleus should be very well represented.

In the first section of Chapter II, an outline of the density functional formalism, along with the main results of it, are presented in a form useful to this thesis. The significance of the Hartree-Fock type parameters entering this theory, and the relation of this to the present work, are also briefly discussed. In section 2.2, the form taken for the exchange and correlation potentials used here is described.

Following this chapter the procedure used in the approximate non-linear self-consistent calculation is described. Following this, some further problems which should be approachable in this general way are suggested.

The results of the work on lithium are presented and discussed in Chapter IV. First, the self-consistent potential and the electron density $n(\underset{\sim}{r})$ are exhibited; the latter is compared both with the free atom electron density, and also with the work of L. Dagens (1972) who performed a similar type of calculation on lithium. The results obtained by us for the valence density are qualitatively similar to those obtained by Dagens, but quantitatively different. The $1s^2$ bound state electron density for the metal does not differ much from that for the free atom, justifying the usual assumption that for a metal, the core orbitals can be taken to be just those of the free atom.

In section 4.2, the atomic structure factors for this work, and for both the free atom and for Dagens' results are exhibited. At the present time, we are not aware of any experimental measure of this quantity, but such a measurement would provide a useful test of the distributions $n(\underset{\sim}{r})$ as calculated by Dagens, and by the present method.

In the last part of this chapter, the Knight shift is discussed, and through it results are compared with experimental values. Although it is not clear that the usual expression in the Knight shift formula is exactly applicable when wave functions which are produced by the density functional formalism are used, still, good agreement with experiment is obtained. This result seems to shed some light on the suggestion (Harrison 1970 and Hedin and Lundqvist 1971) that the one electron parameters for states near the Fermi surface are significant. In any case, the agreement with experiment indicates the self consistent potential, and hence the electron distribution obtained here are accurate.

As mentioned earlier, similar work on lithium has been performed by Dagens (1972). He imbedded a fully screened ionic potential in an electron gas, and then solved self-consistently for the "valence" electron distribution displaced by that potential. The screening density was then taken into account by first order perturbation theory. This procedure does not allow for changes in the bound state electron density distribution, and hence restricts to some degree the allowed form of the potential. Because the actual $1s^2$ density turns out to be not very different in the metal, this is in practice probably not a serious restriction; on the other hand, it is probably better to show this is the case than to assume it. Also, as he points out, the valence density which he calculates is dependent on the way in which the potential is screened in the first step of his calculation.

There is another potential difficulty with his procedure which is avoided here, and that refers to the fact that the density functional formalism involves the complete electron density at any point. It is then difficult to assess the significance of attempts to separate out what part of the density is due to the bound electrons and what part is due to the "valence" electrons. By inclusion of all the electrons in the density, this difficulty has been avoided in the present work; we expect therefore this work to be of a somewhat more fundamental nature than that done previously.

An improved form of the exchange and correlation potentials has also been used in this work.

Throughout this thesis the atomic system of units with $\hbar = e = m = 1$ is employed.

CHAPTER II

THE ELECTRON GAS IN THE PRESENCE OF AN EXTERNAL POTENTIAL

2.1 THE DENSITY FUNCTIONAL FORMALISM

A new approach to dealing with the ground state of an interacting electron gas has been provided by Hohenberg and Kohn (1964) and Kohn and Sham (1965), with their development of the density functional formalism. The local electron density $n(\underset{\sim}{r})$ plays a central role in this theory, and equations are developed which lead in principle to the exact total energy and density distribution $n(\underset{\sim}{r})$ for the ground state of the system.

In the first paper, it is proven that there is a universal functional of the density $F[n(\underset{\sim}{r})]$ which, except through the displaced density $n(\underset{\sim}{r})$, is independent of any external applied field $v(\underset{\sim}{r})$, and also has the property that the following expression for the total energy

$$E_v[n] = \int v(\underset{\sim}{r})n(\underset{\sim}{r})d\underset{\sim}{r} + F[n(\underset{\sim}{r})] \qquad (2.1)$$

has as its minimum value the correct ground state energy associated with $v(\underset{\sim}{r})$, and this minimum occurs when $n(\underset{\sim}{r})$ is the correct ground state density distribution.

There are basically two steps in the proof of this, the first showing that the external potential $v(\underset{\sim}{r})$ is, within a constant, a unique functional of $n(\underset{\sim}{r})$. Since $v(\underset{\sim}{r})$ determines the Hamiltonian H, which in turn determines the full many particle ground state, this establishes that all ground state properties are a unique fuctional of $n(\underset{\sim}{r})$.

In the second step it is shown that $E_v[n]$ assumes its minimum value relative to all density functions $n'(\underset{\sim}{r})$ associated with some other external potential $v'(\underset{\sim}{r})$, under the restriction that the total number of particles remains constant, so that $E_v[n(\underset{\sim}{r})]$ attains its minimum value for the correct ground state density distribution $n(\underset{\sim}{r})$.

Having established the minimal property of (2.1), the next step is rewriting F[n] as a sum of terms. Because of the long range of the Coulomb interaction, the classical Coulomb energy of the electrons can be separated out:

$$F[n] = G[n] + \frac{1}{2}\iint \frac{n(\underset{\sim}{r})n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, d\underset{\sim}{r}\, d\underset{\sim}{r}' \; . \qquad (2.2)$$

Similarly, the kinetic energy of a system of non-interacting electrons of density $n(\underset{\sim}{r})$ can be specified:

$$G[n] = \int T_s(n(\underset{\sim}{r}))\, d\underset{\sim}{r} + E_{xc}[n] \qquad (2.3)$$

$E_{xc}[n]$ is the exchange and correlation energies of a system of interacting electrons with density $n(\underset{\sim}{r})$. It will be discussed further in the next section, but for the present we use the result that for a slowly varying density $n(\underset{\sim}{r})$, it can be written as

$$E_{xc}[n] \approx \int n(\underset{\sim}{r})\varepsilon_{xc}(n(\underset{\sim}{r}))d\underset{\sim}{r} \qquad (2.4)$$

where $\varepsilon_{xc}(n(\underset{\sim}{r}))$ is the exchange and correlation energy per electron of a uniform electron gas of density n.

So far, as was anticipated in Chapter I, the only approximation used consists of assuming (2.4) represents $E_{xc}[n]$ adequately.

The total energy can now be (approximately) written

$$E[n] = \int v(\underset{\sim}{r})n(\underset{\sim}{r})d\underset{\sim}{r} + \frac{1}{2}\iint \frac{n(\underset{\sim}{r})n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}d\underset{\sim}{r}d\underset{\sim}{r}' \qquad (2.5)$$
$$+ \int T_s(n(\underset{\sim}{r}))d\underset{\sim}{r} + \int n(\underset{\sim}{r})\varepsilon_{xc}(n(\underset{\sim}{r}))d\underset{\sim}{r} \, .$$

From the stationary property of E[n], $\delta E = 0$. Applying this to (2.5) we obtain

$$\int v(\underset{\sim}{r})\delta n(\underset{\sim}{r})d\underset{\sim}{r} + \frac{1}{2}\iint \frac{n(\underset{\sim}{r})\delta n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}d\underset{\sim}{r}d\underset{\sim}{r}' + \frac{1}{2}\iint \frac{(\delta n(\underset{\sim}{r}))n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}d\underset{\sim}{r}d\underset{\sim}{r}'$$
$$+ \int \frac{\delta T_s(n)}{\delta n(\underset{\sim}{r})}\delta n(\underset{\sim}{r})d\underset{\sim}{r} + \int \mu_{xc}(n(\underset{\sim}{r}))\delta n(\underset{\sim}{r})d\underset{\sim}{r} = 0 \qquad (2.6)$$

Hence

$$\int \delta n(\underset{\sim}{r})\left(\phi(\underset{\sim}{r}) + \frac{\delta T_s(n(\underset{\sim}{r}))}{\delta n(\underset{\sim}{r})} + \mu_{xc}(n(\underset{\sim}{r}))\right)d\underset{\sim}{r} = 0 \qquad (2.7)$$

where

$$\phi(\underset{\sim}{r}) = v(\underset{\sim}{r}) + \int \frac{n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}d\underset{\sim}{r}' \qquad (2.8)$$

and

$$\mu_{xc}(n(\underset{\sim}{r})) = \frac{\delta(n(\underset{\sim}{r})\varepsilon_{xc}(n(\underset{\sim}{r})))}{\delta n(\underset{\sim}{r})} \qquad (2.9)$$

$\mu_{xc}(n(\underset{\sim}{r}))$ is thus the exchange and correlation contribution to the chemical potential of a uniform electron gas of density n.

Because the total number of particles must be conserved in the variation $\delta n(\underset{\sim}{r})$, there is the following constraint on this variation

$$\int \delta n(\underset{\sim}{r})d\underset{\sim}{r} = 0 \ . \tag{2.10}$$

Equations (2.7) and (2.10) are just those one obtains for a sytem of non-interacting electrons moving in the potential $\phi(\underset{\sim}{r}) + \mu_{xc}(n(\underset{\sim}{r}))$. Therefore, for a given potential $\phi(\underset{\sim}{r})$, and chemical potential μ, one obtains the $n(\underset{\sim}{r})$ which satisfies these equations through

$$n(\underset{\sim}{r}) = \sum_{i=1}^{N} |\psi_i(\underset{\sim}{r})|^2 \tag{2.11}$$

where the $\psi_i(\underset{\sim}{r})$ are obtained from the local, one-particle Schrödinger equation

$$[-\frac{1}{2}\nabla^2 + \phi(\underset{\sim}{r}) + \mu_{xc}(n(\underset{\sim}{r}))]\psi_i(\underset{\sim}{r}) = \varepsilon_i\psi_i(\underset{\sim}{r}) \ . \tag{2.12}$$

From the expression for the energy, (2.5), one can then show

$$E = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2}\iint \frac{n(\underset{\sim}{r})n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}d\underset{\sim}{r}d\underset{\sim}{r}' + \int n(\underset{\sim}{r})(\varepsilon_{xc}(n(\underset{\sim}{r}))-\mu_{xc}(n(\underset{\sim}{r})))d\underset{\sim}{r} \tag{2.13}$$

It should be emphasized at this point that the constants ε_i which enter into (2.12) do not have any direct physical meaning even within the approximation made for $v_{xc}(\underset{\sim}{r})$.

This is perhaps best illustrated by comparison with the Hartree-Fock approach to this type of calculation. In fact, the derivation of these equations is similar to the procedure outlined above, with the results looking formally the same, and so we give a brief description of the Hartree-Fock theory to illustrate this similarity.

In that theory, one starts with the following many particle Hamiltonian

$$H = \sum_{i=1}^{N} \left(- \frac{1}{2} \nabla_i^{\,2} + v(\underset{\sim}{r}_i)\right) + \frac{1}{2} \sum_{ij} \frac{1}{r_{ij}} \qquad (2.14)$$

For example, for an atom $v(\underset{\sim}{r}_i) = - \frac{Z}{r_i}$.

One approximates the many electron wave functions by an antisymmetrized product of one particle wave functions

$$\Psi = A\psi_1(\underset{\sim}{r}_1)\ldots\psi_N(\underset{\sim}{r}_N) \ . \qquad (2.15)$$

To find the best one-particle wave functions $\psi_i(\underset{\sim}{r})$, the expectation value of $<\Psi|H|\Psi>$ is minimized, subject to the N^2 conditions

$$\int \psi_i^{*}(\underset{\sim}{r})\psi_j(\underset{\sim}{r})d\tau = \delta_{ij} \ . \qquad (2.16)$$

This introduces N^2 Lagrange multipliers λ_{ij}. Then minimizing $<\Psi|H|\Psi>$ subject to (2.16) becomes

$$\delta<\Psi|H|\Psi> + \sum_{ij} \lambda_{ij} \ \delta<\psi_i|\psi_j> = 0 . \qquad (2.17)$$

This leads to the Hartree-Fock equation

$$\left(-\frac{1}{2}\nabla^2 + v(\underset{\sim}{r}) + \sum_j \int \frac{|\psi_j(\underset{\sim}{r}')|^2}{|\underset{\sim}{r}-\underset{\sim}{r}'|} d\underset{\sim}{r}'\right)\psi_i(\underset{\sim}{r})$$

$$- \sum_j \psi_j(\underset{\sim}{r}) \int \frac{\psi_j^*(\underset{\sim}{r}')\psi_i(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|} d\underset{\sim}{r}' = \varepsilon_i\psi_i(\underset{\sim}{r}) \qquad (2.18)$$

and the total density is given by

$$n(\underset{\sim}{r}) = \sum_{i=1}^{N} |\psi_i(\underset{\sim}{r})|^2 . \qquad (2.19)$$

These last two equations look very similar to (2.12) and (2.11), with $\phi(\underset{\sim}{r})$ in (2.12) corresponding to the second and third terms in (2.18), and the exchange part of $\mu_{xc}(n(\underset{\sim}{r}))$ corresponding to the last term, so it is seen that the form of the two theories is the same.

In (2.18), the parameters ε_i are intrinsically related to the Lagrange multipliers λ_{ij}, and hence appear to have no direct physical meaning, as is the case for the density functional formalism. However, by considering the expectation value of the Hamiltonian in the N particle state, and then in a state with a particle removed from state j, Koopmans (1933) has shown that within the Hartree-Fock model, and assuming the removal of one electron does not change the wave functions of all the other electrons, as one would expect to be approximately the case for a crystal, then the parameter ε_j can be regarded as the negative of the ionization energy for the corresponding state in the crystal. Thus we are able to attach physical meaning to parameters which originally entered theory simply as Lagrange multipliers.

In the density functional formalism however, there is nothing corresponding to Koopmans' theorem, so the significance of the one-electron parameters ε_i, and hence the calculated wave functions $\psi_i(\underset{\sim}{r})$ arising from (2.12) is not clear. Of course, the total energy and total density $n(\underset{\sim}{r})$ are still well defined in the theory, in spite of the difficulty in interpreting these one-electron states.

2.2 THE EXCHANGE AND CORRELATION POTENTIALS

It is because the exchange and correlation energies of an electron gas are not yet known exactly that the density functional formalism produces only approximate results. In this section the approximation used in this work is described.

As mentioned in the previous section, we assume this contribution to the energy can be written

$$E_{xc}[n] = \int n(\underset{\sim}{r})\,\varepsilon_{xc}(n(\underset{\sim}{r}))\,d\underset{\sim}{r} \qquad (2.20)$$

where $\varepsilon_{xc}(n)$ is the exchange and correlation energy of a uniform electron gas of density n, but $\varepsilon_{xc}(n(\underset{\sim}{r}))$ is evaluated for the local density n at $\underset{\sim}{r}$. We expect that (2.20) should represent a good approximation to $E_{xc}[n]$, if $n(\underset{\sim}{r})$ is slowly varying. Certainly it is exact in the limit that $n(\underset{\sim}{r})$ is uniform.

The exchange and correlation potential is then given by

$$v_{xc}(\underset{\sim}{r}) = \mu_{xc}(\underset{\sim}{r}) \qquad (2.21)$$

$$= \varepsilon_{xc}(n(\underset{\sim}{r})) + n(\underset{\sim}{r})\,\frac{\delta}{\delta n(\underset{\sim}{r})}\,\varepsilon_{xc}(n(\underset{\sim}{r})) \qquad (2.22)$$

$v_{xc}(\underset{\sim}{r})$ is thus approximated by the exchange and correlation part μ_{xc} of the chemical potential (evaluated for the local density $n(\underset{\sim}{r})$). With this approximation, work done on the uniform electron gas can be directly applied here.

We first consider the exchange term. This can be calculated from considering only the first order effects from the electron-electron interactions, which is equivalent to a Hartree-Fock approximation (Pines and Nozières 1966). The expression for the total energy of an electron gas then contains the total kinetic energy of the system, a Hartree energy, which is cancelled by the background of positive charges of the host lattice, and a third term which is the exchange. This is the term which appears because the ground state wave function is taken to be an antisymmetric product of one electron wave function.

This gives an average exchange energy per particle of

$$\varepsilon_x(n) = - \sum_{\substack{p<p_F \\ p'<p_F}} \frac{2\pi}{|\underset{\sim}{p}-\underset{\sim}{p}'|} \tag{2.23}$$

$$= - \left(\frac{3}{4\pi}\right)\left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s} \tag{2.24}$$

Here we have introduced the electron gas radius parameter defined by

$$\frac{1}{r_s} = \left(\frac{4\pi}{3}\, n\right)^{1/3} . \tag{2.25}$$

Equation (2.24) is then equivalent to

$$\varepsilon_x = -\left(\frac{3}{4\pi}\right)(3\pi^2 n)^{1/3} \quad . \tag{2.26}$$

Then from (2.22) we have

$$\begin{aligned} v_x(\underset{\sim}{r}) &\simeq \mu_x(\underset{\sim}{r}) \\ &= -\frac{1}{\pi}\left(3\pi^2 n(\underset{\sim}{r})\right)^{1/3} \end{aligned} \tag{2.27}$$

which is the result often referred to as the Kohn-Sham exchange potential. It should be noted here that this exchange potential is not the average felt by all electrons, but rather the exchange potential felt by electrons right at the Fermi level. This is a reasonable result since it is expected that most density adjustments are accomplished by the redistribution of electrons near this level.

The correlation energy has normally been defined as the difference between the energy as calculated in a Hartree-Fock approximation and the actual energy of the system. It arises because in the Hartree-Fock theory, the electrons are assumed to move in the average field of all the other electrons; except for this average field, the electrons are thus pictured as moving independently of each other. In actual fact, as one would expect, this is not the case; the electrons tend to stay away from each other because of the Coulomb repulsion. This would suggest the true energy is lower than what the Hartree-Fock theory gives, so the correlation energy is negative.

To our knowledge, the best available calculation for this has been performed by Singwi et al. (1970). With his results for this energy, Hedin and Lundqvist (1971) have developed an expression for the exchange and correlation potential. They write

$$\mu_{xc}(r_s) = \beta(r_s)\mu_x(r_s) \qquad (2.28)$$

where μ_x is again the Kohn-Sham exchange potential, and β is known as the correlation enhancement factor. The form of this is

$$\beta(r_s) = 1 + Bx\ell n(1 + \frac{1}{x}) \qquad (2.28)$$

where $x = \frac{r_s}{A}$.

Then

$$\begin{aligned} \mu_{xc}(r_s) &= \mu_x(r_s) + Bx\ell n(1 + \frac{1}{x})\mu_x(r_s) \\ &= \mu_x(r_s) + \mu_c(r_s) \end{aligned} \qquad (2.30)$$

The constants A and B are then chosen to fit $\mu_c(r_s)$ to the results of Singwi et al, and an essentially perfect fit is obtained for A = 21, B = .3867 (a.u.). This gives an exchange-correlation potential of

$$\mu_{xc}(r_s) = -.02909[\frac{21}{r_s} + .7734 \ \ell n(1 + \frac{21}{r_s})]. \qquad (2.31)$$

In order to make the potential vanish as $r \to \infty$, $v_{xc}(r_s)$ is redefined as

$$v_{xc}(r_s) = \mu_{xc}(n_o + \Delta n(\underset{\sim}{r})) - \mu_{xc}(n_o) \qquad (2.32)$$

This is the form used in this calculation.

It should be mentioned that this approximation for $v_{xc}(r)$ is expected to be valid in regions where the density is slowly varying. In the present case, where we are dealing with two bound electrons plus an electron gas surrounding a lithium nucleus, there will clearly be regions, near the nucleus, where this is not valid. However, the total potential, given by

$$V_{eff}(r) = -\frac{3}{r} + \int \frac{\Delta n(\underset{\sim}{r}')}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, d\underset{\sim}{r}' + v_{xc}(r) \qquad (2.33)$$

is dominated by the Coulomb part in this region, so this should not lead to any serious error. Note that $n(\underset{\sim}{r}')$ has been replaced in (2.8) by $\Delta n(\underset{\sim}{r}')$ in (2.33), again in order to make the potential vanish as $r \to \infty$.

CHAPTER III

APPROXIMATE NON-LINEAR SELF-CONSISTENT PROCEDURE

3.1 GENERAL THEORY

In this chapter, the procedure used to calculate the electron density in a metal is discussed, making particular reference to lithium, and in the next chapter the results obtained for lithium are presented.

The calculation is performed in the philosophy that each ion in the metal is sufficiently isolated from all the others, such that the only large effect of the others is the contribution of v valence electrons to the electron gas, producing a mean density for the gas of $n_o = \frac{Nv}{V}$ where N is the number of atoms in the crystal of volume V. Thus we consider one nucleus in an infinite electron gas of mean density n_o, and calculate the electron density $n(\underset{\sim}{r})$, including any bound state electrons, in the presence of that nucleus. This approximation should be especially good very close to any nuclear position in the solid, and probably remains quite good a fair distance from the nucleus, as the ions in the metal are in fact well separated.

It should then be possible to construct a good approximation to the total electron density in the metal $n_T(\underset{\sim}{r})$ by simply summing

$$n_T(\underset{\sim}{r}) = \sum_a n(\underset{\sim}{r}-\underset{\sim}{R}_a) \qquad (3.1)$$

where the $\underset{\sim}{R}_a$ are the ionic positions in the metal.

In order to approach the problem in the most general way, and to calculate the electron density as accurately as possible we shall not make the assumption that the bound state wave functions for the solid are the same for the free atom. It is not unreasonable to take this care with the core electrons when we have made the approximation of treating the rest of the metal as a uniform electron gas, because, as has been stated, this approximation is expected to be particularly good close to the nuclei, which is of course where the electrons in the bound state are located.

In addition to enabling a test of the usual assumption that the core orbitals do not change from those of the free atom, this step avoids the risk of imposing an arbitrary constraint on the form of the potential felt by the electron gas; if the core orbitals are different, then the Coulomb repulsion between the core and "valence" electrons, and hence the potential felt by the latter, would not be properly represented by taking the free atom core state.

Also, from the point of view of the density functional formalism this is a more satisfying approach. As has been emphasized, it is only the total density $n(\underset{\sim}{r})$ which is significant in this formalism; the individual wave functions corresponding to any Hartree-Fock like parameter ε_i do not necessarily have any direct physical meaning. Hence it is difficult to assess the significance of attempts to separate out what part of the density at any point is due to the bound electrons, and what part is due to the electron gas. By treating all the electrons contributing to $n(\underset{\sim}{r})$ in the same way, this potential problem is avoided.

The alternative approach has been used in an earlier work on lithium by Dagens (1972). He imbedded a fully screened ionic potential in an electron gas of the same mean density, and then solved for the "valence" density about it. Thus the present work has gone somewhat beyond that, and is somewhat more fundamental. We have also gone beyond that work in that in addition to exchange, an approximate correlation potential has been included whereas the previous calculation included only the Kohn-Sham exchange potential. Also, the present scheme is an improvement because it avoids the necessity of having to correct for an arbitrary, initial screening density by perturbation theory.

In view of the above considerations, a comparison of the results of the two methods will be interesting; this comparison is made in the following chapter.

The results of Chapter II will now be put into the form appropriate to the problem of a nucleus of charge Z imbedded in an electron gas of mean density n_0. In this case the external potential felt by the electron gas is

$$v(r) = -\frac{Z}{r} \; . \tag{3.2}$$

Clearly, the problem is now spherically symmetric. The effective potential becomes

$$V_{eff}(r) = -\frac{Z}{r} + \frac{1}{r}\int_0^r 4\pi r'^2 \Delta n(r')dr' + \int_r^\infty 4\pi r' \Delta n(r')dr' + v_{xc}(r) \; . \tag{3.3}$$

The one-particle Schrödinger equation then reduces to

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + V_{eff}(r) + \frac{\ell(\ell+1)}{r^2} - \varepsilon_k\right) rR_{\ell k}(r) = 0 \tag{3.4}$$

where $R_{\ell k}(r)$ is the radial wave function with angular momentum ℓ and k labelling the electronic states. For the non-localized states $\varepsilon_k = \frac{1}{2}k^2$.

As discussed above, in constructing the electron density n(r) the bound states must be included. The displaced electron density is thus, from (2.11)

$$\Delta n(r) = \frac{1}{\pi^2}\int_0^{k_F} k^2 dk \sum_{\ell=0}^{\ell_{max}} (2\ell+1)\left[|R_{\ell k}(r)|^2 - |j_\ell(kr)|^2\right] + \sum_i |\psi_i^b(r)|^2 \; . \tag{3.5}$$

Here j_ℓ is a spherical Bessel function of the first kind, and $\psi_i^b(r)$ is a bound state wave function. Because of the spherical symmetry of the problem, the angular parts of the wave functions, which are spherical harmonics, summed over the magnetic quantum number m give a constant, so only the radial parts need be considered. In the case of lithium, the bound state wave function is of s character, so is equal to the radial function $R_b(r)$.

For large r, where $rV_{eff}(r) \rightarrow 0$ which is the condition of complete screening of the nucleus by the displaced charge density, the asymptotic form for the positive energy states must have the form well known from the partial wave solution of the scattering problem

$$R_{\ell k}(r) \sim \cos\eta_\ell j_\ell(kr) - \sin\eta_\ell n_\ell(kr) \qquad (3.6)$$

where n_ℓ is a spherical Bessel function of the second kind, and the phase shifts η_ℓ depend on k. For the bound state, the asymptotic solution must be of the form

$$rR_b(r) \sim e^{-kr} \qquad (3.7)$$

with

$$k = \sqrt{-2\varepsilon_b} \qquad (3.8)$$

where ε_b plays the role of the bound state energy.

The sum over ℓ in (3.5) should theoretically go to $\ell_{max} \rightarrow \infty$. However for large ℓ, the effective potential in (3.4) will be dominated by the centrifugal term $\frac{\ell(\ell+1)}{r^2}$, so the wave function $R_{\ell k}(r)$ will not differ substantially from $j_\ell(kr)$. For lithium the phase shift η_5 is very small (of the order 10^{-4}) so it seems reasonable to expect that taking only six terms in the sum, (setting $\ell_{max} = 5$) will result in no appreciable error.

For $V_{eff}(r)$ to be a physically realistic potential, it must displace a number of electrons equal to the charge Z of the nucleus. To ensure this condition, we can use the well known Friedel Sum Rule, which states that the following sum

$$F = \frac{2}{\pi} \sum_{\ell=0}^{\ell_{max}} (2\ell+1)\eta_{\ell}(k_F) \qquad (3.9)$$

which is equal to the displaced charge, must equal the charge of the nucleus Z. In (3.9), $\eta_{\ell}(k_F)$ are the phase shifts evaluated for momentum equal to the Fermi momentum.

3.2 NUMERICAL PROCEDURE

To begin the calculation, some analytic form for a trial potential, such as $rV_{tr}(r) = -Ze^{-\alpha r^{\beta}}$ is assumed. A value for β is chosen and then α is determined in such a way that $V_{tr}(r)$ satisfies the Friedel sum rule. Then, through (3.4) and (3.5), using $V_{tr}(r)$ in (3.4) in place of $V_{eff}(r)$, the charge density distribution $\Delta n(r)$ displaced by $V_{tr}(r)$ is found. From this $\Delta n(r)$, a new potential $V_{eff}(r)$ is generated through (3.3). In general, this new potential is quite different from $V_{tr}(r)$, and will not have the correct Friedel sum. Therefore, the above procedure is repeated, but with a different value of β in $V_{tr}(r)$, which hopefully results in coming closer to achieving self consistency between $V_{tr}(r)$ and $V_{eff}(r)$, while at the same time producing a better Friedel sum for $V_{eff}(r)$. The procedure is repeated with different values of the parameters α and β, and also with various forms for $V_{tr}(r)$, until a $V_{tr}(r)$ is found which generates a $V_{eff}(r)$ which is self-consistent with $V_{tr}(r)$, and such that the Friedel sum rule is satisfied for both the potentials. When this has been achieved the procedure is terminated.

In the work done on lithium the Schrödinger equation is solved in steps of .05 out from the origin to a distance $r = 20$. Because of the singularity in the potential at $r = 0$, near the origin a power series solution is employed. A numerical solution is used out to $r = 15$, where for the positive energy states, this solution is matched to the partial wave asymptotic form (equation (3.6)), which is used out to $r = 20$. This form is valid in regions where $rV_{eff}(r) = 0$; this is initially assumed to be the case, and this assumption is justified by the result that for $r \geq 15$, $rV_{eff}(r)$ is of the order of 10^{-4}. In matching the solution $R_{\ell k}(r)$ to the form (3.6), the phase shifts $\eta_\ell(k_F)$ for use in calculating the Friedel sum are obtained.

To calculate the contribution to the density arising from all the positive energy states, radial wave functions for $0 \leq k \leq k_F$ are required. For the integration over k, a gauss integration formula of 48th order is used, and as previously mentioned, the sums over ℓ terminated after 6 terms.

Bound states of the potential show up automatically in the calculation of the phase shifts for small values of k. From Levinson's theorem we have

$$\lim_{k \to 0} \eta_\ell(k) = n_B(\ell)\pi \tag{3.10}$$

where $n_B(\ell)$ is the number of bound states of angular momentum number ℓ possessed by the potential. The bound state wave function is found by integration of the Schrödinger equation, and determining $\varepsilon_b<0$ in such a way that the solution for large r is of the form given by (3.7) and (3.8).

In actual fact, no satisfactory analytic trial solution which generated a second self-consistent potential $V_{eff}(r)$ was found, although one may indeed exist. Instead a trial potential which consisted of a table of numbers was used to generate a new $V_{eff}(r)$, which was then used to generate a third potential $V'_{eff}(r)$ in a second iteration. The original potential $V_{tr}(r)$ was varied until a pair of potentials $V_{eff}(r)$ and $V'_{eff}(r)$ was found that were self-consistent and had correct Friedel sums.

In the final solution, the potential $V_{tr}(r)$ had little in common with $V_{eff}(r)$ and $V'_{eff}(r)$. The first potential was not close to being self-consistent with the generated potentials, nor did it have a correct Friedel sum. Its sole virtue was that it generated a correct $V_{eff}(r)$.

It appears likely that the forms tried did not work on the first iteration because they did not contain any oscillations for large r, which are directly related to the Friedel oscillations in the density, and are a major feature of $V_{eff}(r)$ and $V'_{eff}(r)$. For the case of a proton imbedded in the electron gases appropriate to Mg and Al, Popovic and Stott (1975) were able to achieve approximate self-consistency for the screening cloud with a trial potential of the form

$-e^{-\alpha r^{\beta}}$, but it appears that for lithium, which is a stronger potential, the asymptotic oscillations must be included.

There is no obvious reason why the scheme outlined above could not be applied to other metals, or to considering various impurities in metals. As mentioned, Popovic and Stott (1975) have used this approach for the hydrogen impurity problem. They used the calculated screening cloud around the proton to calculate the activation energies for diffusion of hydrogen in Al and Mg, and found good agreement with experimental results, which were available only for Al. At the present time, we are preparing to apply the approach to helium impurities in metals, and do not expect results of less accuracy than those obtained for hydrogen.

There are two considerations that should be kept in mind in dealing with metals or impurities of higher charge Z. The first problem that might arise is basically one of difficulty. Achieving self-consistency was substantially more difficult in the case of lithium than in that of hydrogen, and in continuing to higher Z, one should probably expect further difficulties.

The other potential difficulty refers to the approximate form taken for the exchange and correlation potential. It has been argued that the form used here should be good for regions of slowly varying density, and that for regions where this is not the case, in particular near the origin, the inaccuracy of this assumption should not lead to serious error because the potential is dominated by the Coulomb part. However, it is possible that for higher Z there may be regions where rapidly varying density might lead to serious errors in $V_{eff}(r)$, and hence the density distribution.

In performing the calculation for different nuclei in different electron gas densities, one would also expect to have to change certain parameters in the numerical scheme, such as the size of the integration step in solving the Schrödinger equation, at what distance from the origin the asymptotic solution should be valid, or even how far out from the origin to continue the calculation. These modifications, though probably important, should pose no problem.

The scheme outlined above assumes that each orbital is occupied by two electrons, and treats them symmetrically. For this reason, the method would require some modification before it could be applied to a case where each orbital is not occupied symmetrically by spin up and spin down electrons. This change should be possible following the work of von Barth and Hedin (1972). In place of an exchange and correlation potential $v_{xc}(r)$, they have supplied two potentials, $v_{xc}^{\uparrow}(r)$ and $v_{xc}^{\downarrow}(r)$, which are the exchange-correlation potentials felt by spin up and spin down electrons, and these are given as functions of $n^{\uparrow}(r)$, $n^{\downarrow}(r)$, and $n(r)$, the spin up, spin down, and total electron density distributions. Such a potential should allow the study of problems such as the early peaking of the soft X-ray emission spectrum of metallic lithium. In this case, there is only one electron in the bound state orbital, the valence density distribution of $n^{\uparrow}(r)$ will not be the same as that of $n^{\downarrow}(r)$, and the potentials felt by spin up and spin down electrons will be different. This should be a very good problem to apply this scheme to.

CHAPTER IV

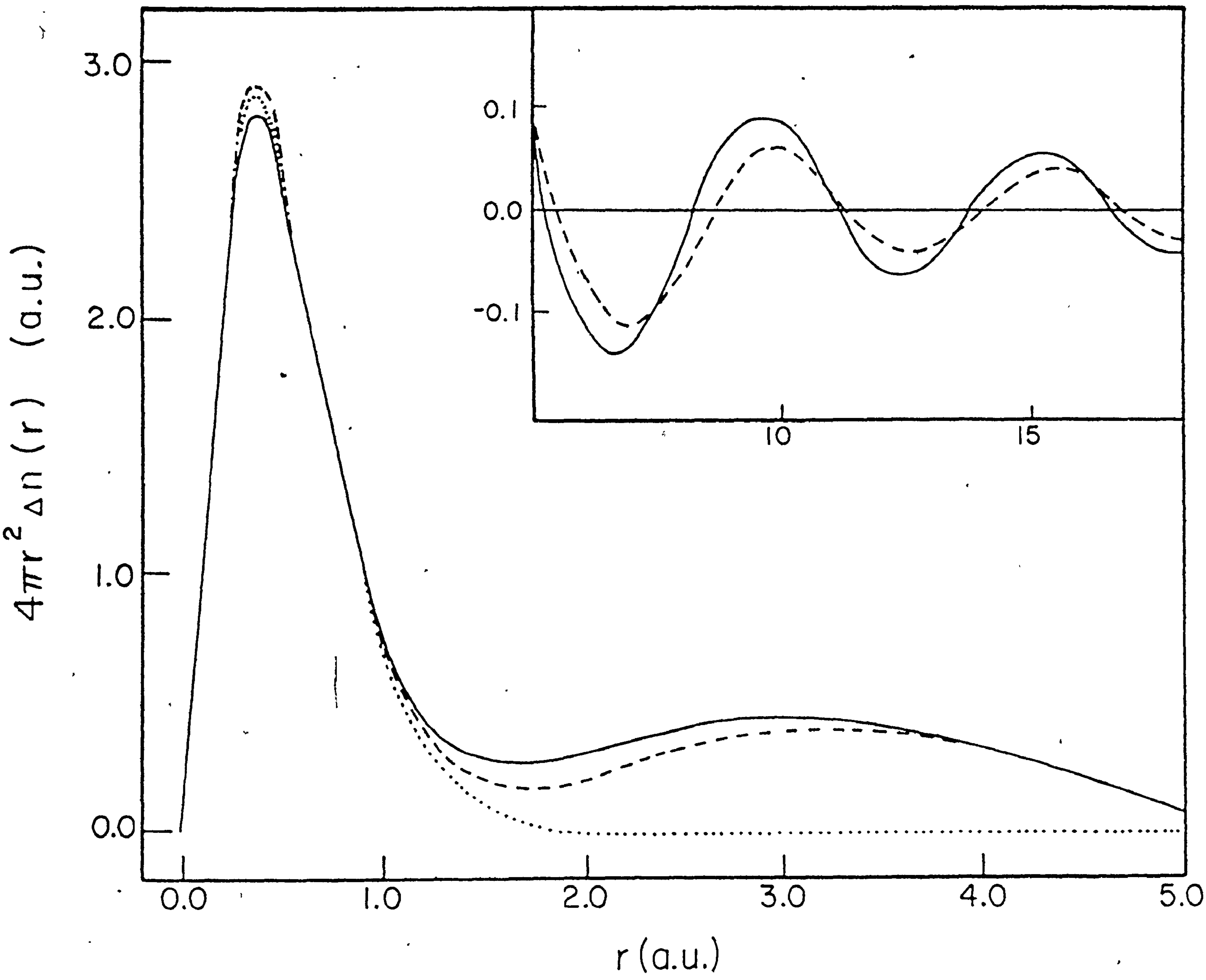
RESULTS OF CALCULATIONS ON LITHIUM

4.1 ELECTRON DENSITY DISTRIBUTION

In this section the displaced electron density distribution and self-consistent potential in lithium are presented. In the next section the atomic structure factors for the metal are exhibited with a brief discussion of their role in X-ray diffraction. Finally the derivation of the Knight shift formula is outlined, and the results obtained here for this shift presented.

The main result of the calculation, $4\pi r^2 \Delta n(r)$, is presented in figure 1, where we also present the work of Dagens for comparison. Because of the question of the significance of separating out the conduction electrons from the total electron density distribution, we choose to present first the total n(r). Therefore, to compare with the work of Dagens, his results have been combined with a Hartree-Fock calculation of the $1s^2$ electron density in the free atom (Herman and Skillman 1963), also illustrated in figure 1. Of course, where the bound state density is negligible, which is seen to be the case for $r \gtrsim 1.5$, a direct comparison of the valence density distributions is valid.

Fig. 1 Displaced electron density $4\pi r^2 \Delta n(r)$. The solid curve is the result of the present calculation. The dotted curve is the free atom $1s^2$ electron density, to which has been added the "valence" density of Dagens, to produce the dashed curve.


4πr²Δn (r) (a.u.)
3.0
2.0
1.0
0.0
0.0
1.0
2.0
3.0
4.0
5.0
r (a.u.)
0.1
0.0
-0.1
10
15

Before discussing this density, the self-consistent potential is given, illustrated in figure 2. The Fermi level phase shifts $\eta_\ell(k_F)$, along with a normalized Friedel sum, F/3, are presented in table 1. This normalized sum, which ideally should equal 1.0, is seen to be correct to within .07%. In figure 2, the oscillations in the potential for large r are readily apparent; they are of course related to the Friedel oscillations in the density by

$$4\pi n(\underset{\sim}{r}) = - \nabla^2 V_c(\underset{\sim}{r}) \qquad (4.1)$$

where $V_c(\underset{\sim}{r})$ is the Coulomb contribution to the total potential $V_{eff}(r)$. It can also be seen here that for $r > 15$, where the asymptotic form for the wave functions has been used, the potential is very small, so the use of this solution is justified.

The lithium lattice is bcc with lattice constant 6.60, so the nearest neighbour distance is 5.71. From the first two figures we see that most of the charge density about any nucleus is well separated from any other nuclei, so our approximation of replacing the rest of the metal by a free electron gas should be reasonable. The mean electron gas density is $n_o = .00070$.

The calculation has produced a bound state density very close to that in the free ion; however the Hartree-Fock like parameter ε_b is given by this calculation as $\varepsilon_b = -1.66$. For a free atom, the energy of the 1s state is -2.20 (Herman and Skillman 1963) and for an Li^+ ion it is -2.78 (Kuhn 1962).

Fig. 2 The effective potential, -rV(r), about a lithium nucleus in the electron gas.

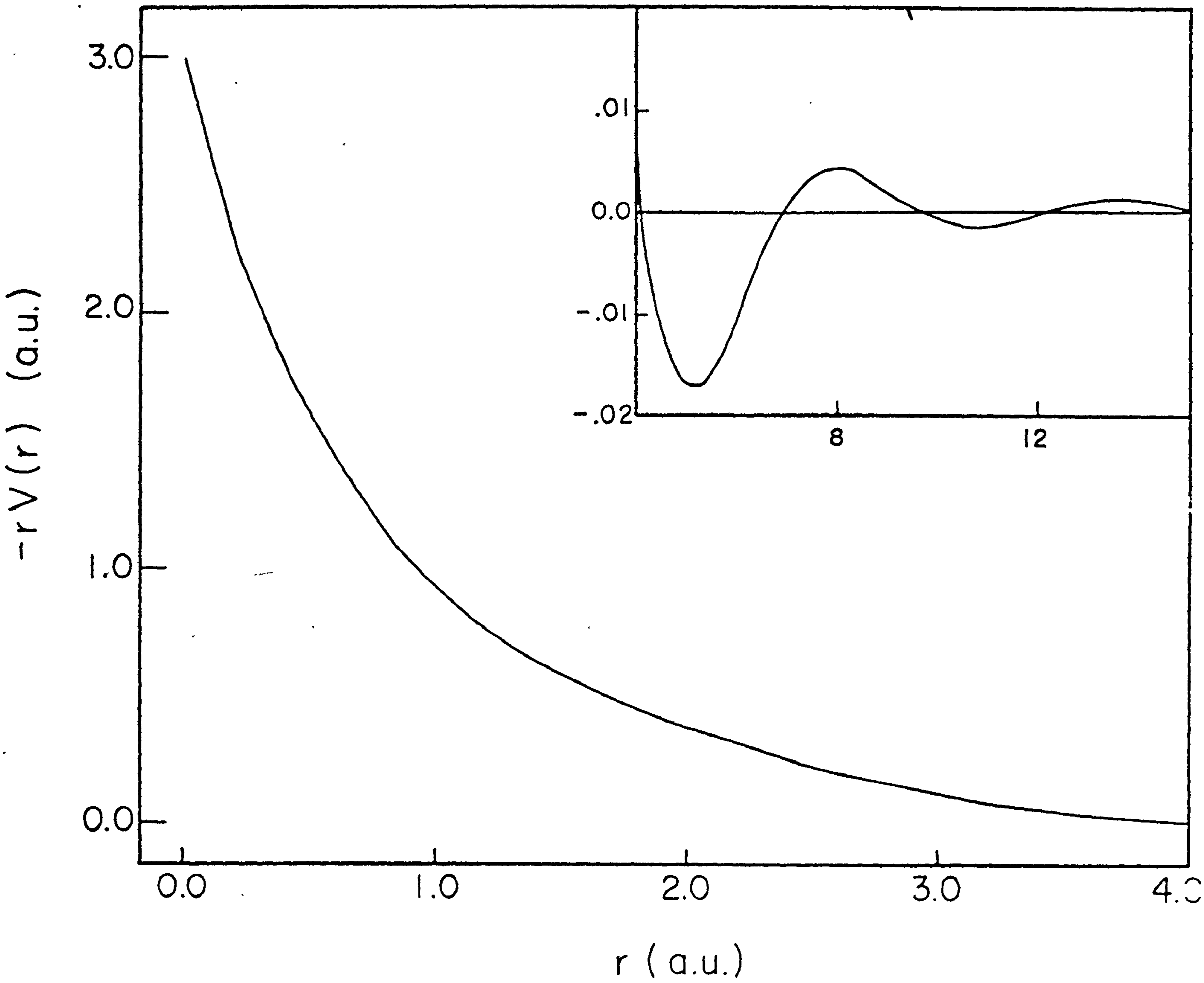

-rV(r) (a.u.)
3.0
2.0
1.0
0.0
0.0
1.0
2.0
3.0
4.0
r (a.u.)
.01
0.0
-.01
-.02
8
12

Table 1

The Fermi level phase shifts and normalized Friedel sum

η_0	η_1	η_2	η_3	η_4	η_5	F/3
3.237	.4753	.0096	-.00025	.00022	-.00018	0.9993

One would expect that for the metal, the energy of this state would be very close to these values, not substantially less. Therefore, as might be expected following the discussion of Section 2.1, the density functional formalism has given a value for the parameter ε_b, which does not appear to be a physically significant energy.

In discussing the density, the region of $r \leq 2.0$ is considered first. As can be seen from comparing the curve in figure 1 corresponding to the $1s^2$ electron density in the free atom, and the curve consisting of this density plus the valence density due to Dagens, the conduction electrons make very little contribution to the total density $\Delta n(r)$ in this region; except for the small region $0.3 \leq r \leq 0.6$, the density essentially consists entirely of the bound state density. Thus if we make a very small correction for the valence density in that region, we can compare our calculated curve directly with that of the bound state.

What is apparent from figure 1 is that the $1s^2$ density in the metal is almost exactly the same as in the free atom. It is often assumed that this is the case for the core orbitals in a metal, and here we have a calculation, which we expect to be particularly good in the regions of small r, justifying this assumption. It is probably also reasonable to suggest that this result is not just true for lithium, but also for other metals. Because lithium has only two core electrons, it is expected that the difference in these states between a metal and a free atom should be larger for lithium than is the case for other simple metals. Since the core electrons for lithium are little changed, we expect a similar result for other simple metals. Of course, this is just what is often assumed.

It should also be mentioned at this time that this means that the work of Dagens does not impose any unphysical constraint on the form of the potential felt by the valence electrons. His calculated density will still depend on how he screens the ionic potential, and the other approximations made, but the ionic potential used should be accurate.

Farther out from the origin, a direct comparison of our results with those of Dagens becomes more meaningful. The main feature of the solution here is the asymptotic form, shown by Friedel (1962) to be

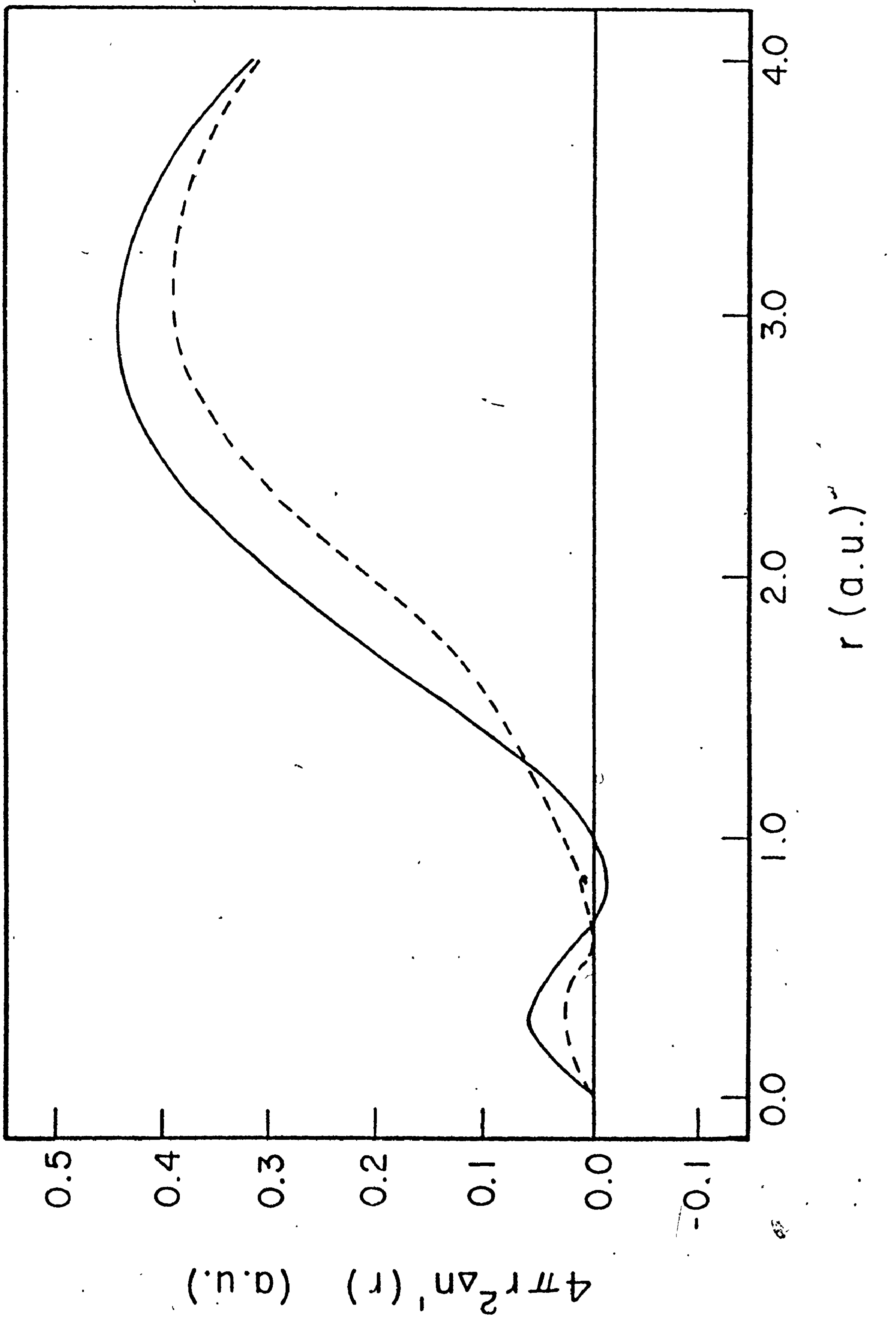
$$\Delta n(r) = \frac{A}{4\pi r^3} \cos(2k_F r+\phi) + O(\frac{1}{k_F r^4}). \qquad (4.2)$$

It is seen that both sets of results have this form, but are different quantitatively. We find a value for the amplitude A of about .92, whereas for Dagens' work it appears to be about .57. Also, the Friedel oscillations have been pulled in towards the origin in our work by a distance of about $\Delta r = .5$.

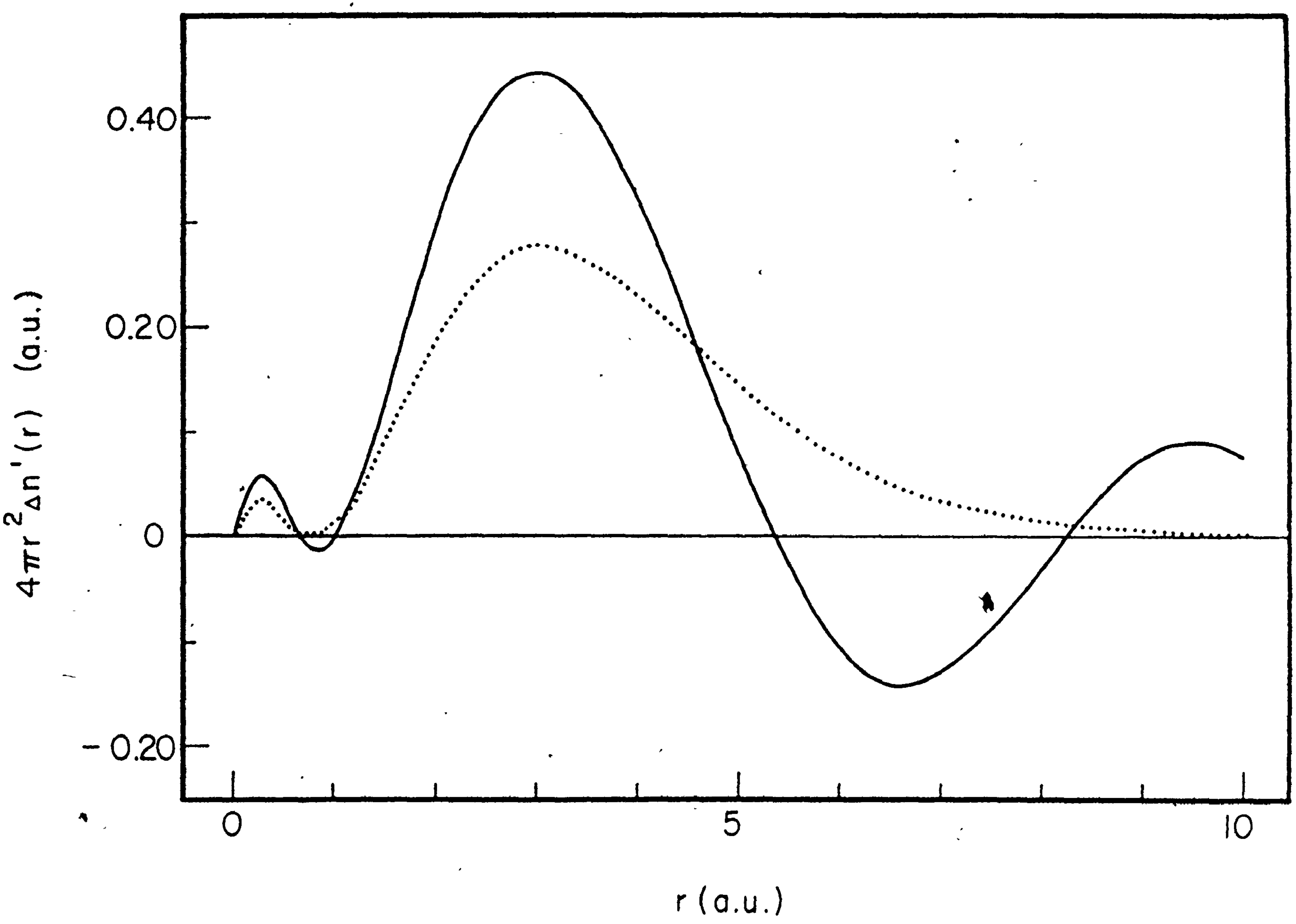
As yet it is hard to make a definite statement regarding the significance of these differences. Dagens, Rasolt and Taylor (1975) have used the results of Dagens (1972) to construct pseudo-potentials for lithium and sodium, and from these have calculated phonon dispersion curves. For sodium they found very good agreement with experiment, but for lithium they obtained results disagreeing by about 5%. They list a number of reasons why this discrepancy may exist, but are unable to make a definite statement regarding them. It is quite possible that a pseudopotential produced from our results would produce these curves more accurately; it would be interesting to see if this is the case.

Formally one can of course make another comparison between the two results. In our calculation a bound state with a density distribution $n_b(r)$ is obtained, which can formally be subtracted out from the total density $n(r)$, to obtain a "valence" density $\Delta n'(r)$, and this is presented in figures 3 and 4. In the first figure, this is compared directly with the results of Dagens, and again there are quantitative differences. The apparent node which he finds at $r = .7$ we find to be somewhat different. The electron density has a minimum at $r = .85$, but the density at this distance is actually less than that of the free electron gas. Also, the first local maximum which he finds at $r = .4$ with a value of .03 is found at $r = .30$ with a value of .056; similarly the main maxima are different in the two cases. Where Dagens found this to occur at $r = 3.2$ with a value of about .38, it

Fig. 3 Displaced "valence" electron density $4\pi r^2 \Delta n'(r)$. The dashed curve comes from Dagens. The solid curve has been obtained by subtracting from our total $4\pi r^2 \Delta n(r)$, what formally is the bound state electron density in this scheme. The figure is drawn out to only r = 4.0, since for larger r, this would merely reproduce figure 1.


0.5
0.4
0.3
0.2
0.1
0.0
-0.1
$4\pi r^2 \Delta n'(r)$ (a.u.)
0.0
1.0
2.0
3.0
4.0
r (a.u.)

<u>Fig. 4</u> Displaced "valence" electron density $4\pi r^2 \Delta n'(r)$. The solid curve comes from the present results as described in figure 3. The dotted curve is the valence electron density of the free lithium atom.


0.40
0.20
0
−0.20
$4\pi r^2 \Delta n'(r)$ (a.u.)
0
5
10
r (a.u.)

is found in this work to be located at about r = 2.8 with a value of .44. Farther out from the origin, the valence is represented in figure 1.

In figure 4 these results are compared with the 2s electron density of the free atom. It is interesting that for $\underset{\sim}{r} \leq 5$, the distribution has the same general features in the metal as in the free atom, although of course it differs quantitatively.

4.2 THE ATOMIC STRUCTURE FACTOR

In this section we discuss briefly the formula for the intensity of fast X-ray waves scattered from a perfect crystal, and show how the atomic structure factor appears. This factor is calculated and presented for the electron density calculated here, as well as for the free atom and the results of Dagens.

If we consider X-rays of unit intensity of wave vector $\underset{\sim}{k}$ incident in a perfect crystal, then the intensity of the scattered wave with wave vector $\underset{\sim}{k}'$ is given by

$$|A_{\underset{\sim}{q}}|^2 = \left|\int n_T(\underset{\sim}{r}) e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}\right|^2 \qquad (4.3)$$

$$= \left|\sum_{\ell k} \int dr\ n(r-(\underset{\sim}{R}_L+\underset{\sim}{R}_{LK}))\, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}\right|^2$$

$$= \left|\sum_{k=1}^{n} f_k(\underset{\sim}{q}) e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_{LK}}\right|^2 \left|\sum_{L=1}^{N} e^{i\underset{\sim}{q}\cdot\underset{\sim}{R}_L}\right|^2 \qquad (4.4)$$

$$= (2\pi)^3 \frac{N}{v} \delta(\underset{\sim}{q}-\underset{\sim}{G}) \left| \sum_{k=1}^{n} f_{\underset{\sim}{k}}(\underset{\sim}{q}) e^{-i\underset{\sim}{q}\cdot\underset{\sim}{R}_{LK}} \right|^2 \tag{4.5}$$

where $\underset{\sim}{q} = \underset{\sim}{k}'-\underset{\sim}{k}$.

$\underset{\sim}{R}_L$ refers to the position of the Lth unit cell, of which there are N in the crystal.

$\underset{\sim}{R}_{LK}$ is the position of the Kth atom in the Lth unit cell, with n atoms/unit cell.

v is the volume of the unit cell.

$\underset{\sim}{G}$ are the reciprocal lattice vectors of the crystal.

The quantity $f_k(\underset{\sim}{q})$ is known as the atomic structure factor, or form factor. For a monatomic crystal such as lithium, $f_{\underset{\sim}{q}}$ is the same for all the atoms. It is defined as

$$f_{\underset{\sim}{q}} = \int n(\underset{\sim}{r}) e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, d\underset{\sim}{r}. \tag{4.6}$$

If all the electrons were located right at the origin, then for an atom of Z electrons, we would have

$$\begin{aligned} f_{\underset{\sim}{q}} &= Z \int \delta(\underset{\sim}{r}) e^{-i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, d\underset{\sim}{r} \\ &= Z \end{aligned} \tag{4.7}$$

Therefore $f_{\underset{\sim}{q}}$ is the ratio of the radiation amplitude scattered by the actual electron distribution in an atom to that scattered by one electron localized at the origin.

For a spherically symmetric charge distribution n(r), (4.6) reduces to

$$f_q = \int_0^\infty 4\pi r^2 \frac{\sin qr}{qr} n(r)dr . \tag{4.8}$$

This factor has been calculated for our results for n(r) in lithium and is presented in figure 5. In addition, we present the structure factors for the free atom, and for the metallic density due to Dagens. The results have been plotted against half the scattering angle, θ, divided by the wavelength of the radiation λ. These are related to $\underset{\sim}{q}$ by

$$\begin{aligned} q &= 2k\sin\theta \\ &= \frac{4\pi}{\lambda}\sin\theta \end{aligned} \tag{4.9}$$

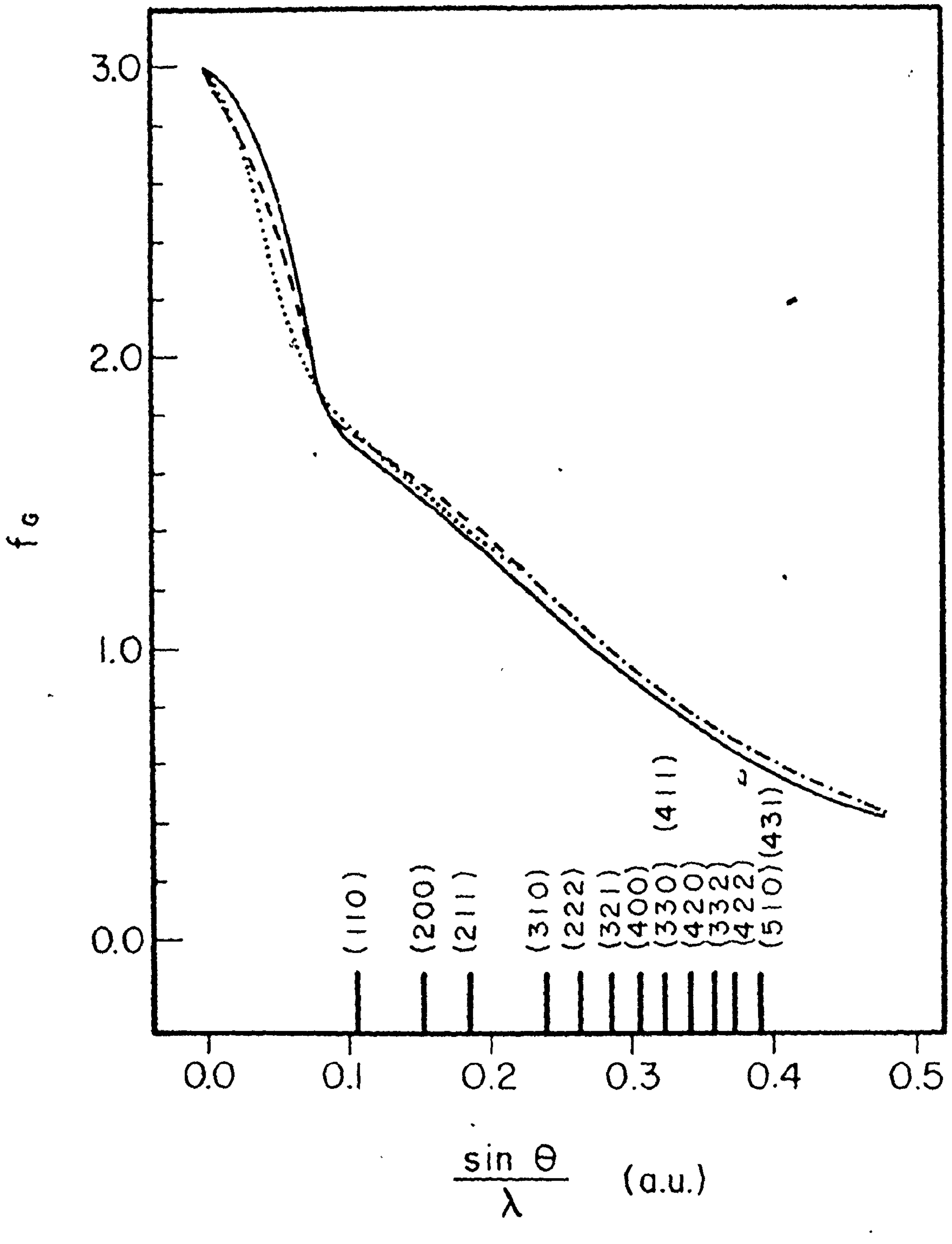
or

$$\frac{\sin\theta}{\lambda} = \frac{q}{4\pi} \tag{4.10}$$

Also labelled are the positions of the diffraction lines one might expect from a bcc lattice such as lithium. Note that, because of the geometrical structure factor of the basis, no reflections occur for which the sum of the indices is odd, and these have been left off the figure.

Unfortunately, to our knowledge there are no experimental values of the factor for lithium now in the literature. It has been suggested (Stott, private communication) that this would be a difficult measurement to make because of the lightness of the metal. On the other hand, the results of such a scattering experiment could be a valuable test of the density distribution we have presented.

Fig. 5 The atomic structure factors f_G. The solid curve is for the present results. The dotted curve is for the free atom, and the dashed curve comes from combining the results of Dagens with the free atom core electrons.


3.0
2.0
1.0
0.0
f_G
(110)
(200)
(211)
(310)
(222)
(321)
(400)
(330)
(411)
(420)
(332)
(422)
(510)
(431)
0.0
0.1
0.2
0.3
0.4
0.5
$\frac{\sin\theta}{\lambda}$ (a.u.)

4.3 THE KNIGHT SHIFT

Thus far we have not compared our results with any experimental information now available. This is now done through the Knight shift.

The Knight shift refers to the fact that at a given applied magnetic field H_o, the nuclear magnetic resonance frequency of a nucleus differs depending upon whether it is in a metal or a diamagnetic solid. For the metallic state, the frequency is almost always higher than for the corresponding diamagnetic solid. The correct explanation of this effect lies in considering the field the nucleus experiences as a result of its interaction with the conduction electrons through the s-state hyperfine coupling. In fact, the Knight shift can equivalently be described by the fact that at a given frequency, the NMR resonance occurs at a static magnetic field which is shifted by an amount ΔH.

We give here a brief derivation of the Knight shift formula, in order to illustrate the origin of the terms entering it.

We consider a system of nuclei and weakly interacting electrons, with a Hamiltonian given by

$$H = H_e + H_n + H_{en} \tag{4.11}$$

where H_e describes a system of weakly interacting electrons, H_n is the nuclear Hamiltonian and includes the Zeeman energy in the static field H_o as well as the magnetic dipole coupling among the nuclei, and H_{en} is the magnetic interaction between the nuclei and the electron spins.

The Hamiltonian H_{en} is given by

$$H_{en} = \frac{8\pi}{3} \gamma_e \gamma_n \sum_{j,\ell} \underset{\sim}{I}_j \cdot \underset{\sim}{S}_\ell \, \delta(\underset{\sim}{r}_\ell - \underset{\sim}{R}_j) \tag{4.12}$$

where $\underset{\sim}{r}_\ell$ is the position of the ℓth electron, and $\underset{\sim}{R}_j$ the position of the jth nucleus, $\underset{\sim}{S}_\ell$ and $\underset{\sim}{I}_j$ are their respective spins, and γ_e and γ_n their respective gyromagnetic ratios.

The nuclei and electrons are treated as weakly interacting and so the wave function is written in product form

$$\Psi = \psi_e \psi_n \tag{4.13}$$

where ψ_e is the wave function of the electrons, and ψ_n that of the nuclei. Because the electrons are assumed to be weakly interacting, ψ_e is taken to be an antisymmetrized product of single-particle wave functions.

We are interested in transitions in the nuclear system from ψ_n to ψ_n', so from a perturbation viewpoint we are interested in matrix elements of the form

$$E_{en} = \int \Psi^* H_{en} \Psi \, d\tau_e d\tau_n . \tag{4.14}$$

In fact what is happening can be understood by just considering the electronic integral

$$E_{en}' = \int \psi_e^* H_{en} \psi_e \, d\tau_e . \tag{4.15}$$

In order to evaluate this, the contribution to (4.15) due to only one, say the jth nuclear spin is required, which is given by

$$E'_{enj} = \frac{8\pi}{3} \gamma_e \gamma_n \underset{\sim}{I}_j \cdot \int \psi_e^* \sum_{\ell} \underset{\sim}{S}_\ell \, \delta(\underset{\sim}{r}_\ell) \psi_e d\tau_c \, . \qquad (4.16)$$

Now we assume the static applied field is $\underset{\sim}{H}_o = H_o \hat{\underset{\sim}{z}}$, so the electrons are quantized along the $\hat{z}$-direction. Then (4.16) becomes

$$E'_{enj} = \frac{8\pi}{3} \gamma_e \gamma_n \, I_{zj} \sum_{\underset{\sim}{k}s} |\psi_{\underset{\sim}{k}s}(o)|^2 \, m_s f(\underset{\sim}{k},s) \qquad (4.17)$$

where $\psi_{\underset{\sim}{k}s}(o)$ is the wave function of momentum $\underset{\sim}{k}$ and spin s right at the nucleus, and $f(\underset{\sim}{k},s)$ is the Fermi function. The sum over the spins can be removed by rewriting (4.17) as

$$E'_{enj} = -\frac{8\pi}{3} \gamma_e \gamma_n \, I_{zj} \sum_{\underset{\sim}{k}} \chi^s_{\underset{\sim}{k}} \, H_o |\psi_{\underset{\sim}{k}}(o)|^2 \qquad (4.18)$$

where

$$\bar{\mu}_{z\underset{\sim}{k}} = -\gamma_e \left(\tfrac{1}{2} f(\underset{\sim}{k},\tfrac{1}{2}) - \tfrac{1}{2} f(\underset{\sim}{k},-\tfrac{1}{2})\right) \qquad (4.19)$$

is the average contribution of the state $\underset{\sim}{k}$ to the z-component of electron magnetization of the sample in the static applied field H_o, and

$$\bar{\mu}_{z\underset{\sim}{k}} = \chi^s_{\underset{\sim}{k}} \, H_o \qquad (4.20)$$

The only remaining difficulty is the evaluation of the sum in (4.18). This is done by first transforming into an integral

$$\sum_{\underset{\sim}{k}} |\psi_{\underset{\sim}{k}}(o)|^2 \chi^s_{\underset{\sim}{k}} = \int \langle |\psi_{\underset{\sim}{k}}(o)|^2 \rangle \chi^s(E_{\underset{\sim}{k}}) \rho(E_{\underset{\sim}{k}}) dE_{\underset{\sim}{k}} \qquad (4.21)$$

where $\langle|\psi_{\underset{\sim}{k}}(o)|^2\rangle$ is the average value of $|\psi_{\underset{\sim}{k}}(0)|^2$ over the surface of constant energy $E_{\underset{\sim}{k}}$, and $\rho(E_{\underset{\sim}{k}})$ is the number of states between $E_{\underset{\sim}{k}}$ and $E_{\underset{\sim}{k}} + dE_{\underset{\sim}{k}}$. $\chi^s(E_{\underset{\sim}{k}})$ is zero for all values of $E_{\underset{\sim}{k}}$ not near the Fermi surface, since for small $E_{\underset{\sim}{k}}$ the two spin states are completely occupied. Thus $<|\psi_{\underset{\sim}{k}}(o)|^2>$ can be taken outside the integral, and (4.21) becomes

$$\sum_{\underset{\sim}{k}} |\psi_{\underset{\sim}{k}}(o)|^2 \chi_k^s = <|\psi_{k_F}(o)|^2>\chi_e^s \tag{4.22}$$

where

$$\chi_e^s = \int \chi^s(E_{\underset{\sim}{k}})\rho(E_{\underset{\sim}{k}})dE_{\underset{\sim}{k}} \tag{4.23}$$

is the total electronic spin susceptibility.

Thus we obtain

$$E'_{enj} = -\frac{8\pi}{3}\gamma_e\gamma_n I_{zj} <|\psi_{k_F}(o)|^2>\chi_e^s H_o . \tag{4.24}$$

This is seen to be equivalent to an extra applied field ΔH aiding H_o, of magnitude

$$\frac{\Delta H}{H_o} = -\frac{8\pi}{3} <|\psi_{k_F}(o)|^2>\chi_e^s . \tag{4.25}$$

Equation (4.25) is known as the Knight shift formula. What is involved is the value of the wave function averaged over the Fermi surface evaluated at $r = 0$, and the total spin susceptibility of the electrons. For lithium Schumacher and Slichter (1956) have measured χ_e^s which thus allows an experimentally determined value of $<|\psi_{k_F}(o)|^2>$ from a measurement of $\Delta H/H_o$.

The results are usually quoted in the form

$$\xi = <|\psi_{k_F}(o)|^2>/|\psi_A(o)|^2 \tag{4.26}$$

where $\psi_A(o)$ is the value of the 2s wave function of the free atom evaluated at the nucleus. Ryter (1960) has obtained an experimental value of $\xi_e = .442 \pm .015$.

In order to make a comparison with the value of $<|\psi_{k_F}(o)|^2>$ calculated here, a good value of $|\psi_A(o)|^2$ is needed. Based on measurements by Fox and Rabi (1935), Kohn (1954) has deduced a value of $|\psi_A(o)|^2 = .231$. From the present calculation a value of $|\psi_{k_F}(o)|^2 = .104 \pm .003$ is extracted, where the error is the probable numerical uncertainty. (For a spherical Fermi surface such as we have assumed, there is no need to average over this surface). This gives a theoretical value of $\xi_t = .455$, in good agreement with experiment. This compares with a previously obtained value (Kohn 1954) of $\xi_t = .49 \pm .05$.

It should again be pointed out that the value of $\psi_{k_F}(o)$ used in the Knight shift formula refers to the correct one-electron wave function right on the Fermi surface, and there is no guarantee that the value of $\psi_{k_F}(r)$ obtained from the density functional formalism is appropriate. Still, the good agreement with experiment obtained here indicates the trial potential, and hence the electron density n(r) obtained are accurate, and in addition lends support to the suggestion (Harrison 1970, Hedin and Lundqvist 1971) that the states near the Fermi surface produced in this way are physically significant.

CHAPTER V

GENERAL DISCUSSION AND CONCLUSIONS

This thesis has dealt with an improved scheme for calculating the electron density distribution in a metal, and reported results on metallic lithium. The method goes beyond other work on lithium in a number of ways. First, the bound state electrons have been free to vary as self-consistency is attained; second, there is no need to correct by perturbation theory for the presence of an assumed screening cloud; third, we have included a correction for the correlations of electrons, as well as for exchange effects.

The nature of the Hartree-Fock like parameters which enter into the density functional formalism has been discussed; it was pointed out that they have not been shown to have any direct physical significance. However,bearing in mind the possibility that states right near the Fermi surface may be significant, the Knight shift has been calculated, and good agreement with experiment obtained.

The total electron density distribution calculated here has been compared with two relevant sets of data. The first of these is the density in the free atom. It has been shown that the 1s wave function is similar to that in the free atom, which justifies the usual assumption that this is the case. On the other hand, the energy eigenstate for this state was not represented well by this method, as one might expect for the density functional formalism.

The valence electron density has also been compared with that of the free atom; for regions close to the nucleus the densities are of similar form, but farther out, of course, quite different.

The other set of data the present results have been compared with is the valence density calculated by Dagens. The two methods have produced results which are qualitatively similar, but are quantitatively different; perhaps the results of Dagens could be made to agree more closely with the present results if a different form of the screening potential were chosen.

The fast X-ray atomic structure factors have also been calculated and illustrated. The two different densities have lead to different structure factors, and it has been suggested that a measurement of this factor might provide a good test of these differences.

In addition to the above work, a small number of other applications of this scheme has been suggested. It should be possible to approach these other problems in this way with the only real difficulties anticipated being numerical. For example, for higher charge Z self-consistency might be more difficult to achieve. In addition to impurity problems, the feasibility of studying the soft X-ray emission spectrum of lithium, involving unequal numbers of spin up and spin down electrons, will be considered as a further extension of this scheme.

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