A MODEL PSEUDOPOTENTIAL TECHNIQUE FOR CALCULATING SOME PHYSICAL PROPERTIES OF METALS

UKPONG, ANIEKAN MAGNUS
PHY/98/1844

A THESIS DISSERTATION SUBMITTED IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF
THE DEGREE OF MASTER OF TECHNOLOGY (M.TECH)
IN
PHYSICS

DEPARTMENT OF PHYSICS,
SCHOOL OF SCIENCES,
FEDERAL UNIVERSITY OF TECHNOLOGY, AKURE,
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CERTIFICATION

This is to certify that this research work was carried out by Ukpong, Aniekan Magnus, (PHY/98/1844), and has been approved as meeting the requirements of the Department of Physics, School of Sciences, Federal University of Technology, Akure, Nigeria for the award of the degree of Master of Technology (M.Tech) in Physics, and that to the best of my knowledge has not been submitted elsewhere for the award of a degree.

Dr. (Mrs.) I. A. Fuwape, Ph.D.	Dr. I. A. Ashaolu, Ph.D.
(Major Supervisor)	(Minor Supervisor)

DEDICATION

This work is dedicated to all scientists who are interested in the study of physical systems through the field of Theoretical Condensed Matter Physics.

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ABSTRACT

A Wigner-Seitz cell dependent 'relaxed core' model pseudopotential is developed from first principles consideration of the stationary state perturbation theory and the free electron gas approximation. The Fourier transform of the local potential is evaluated and applied within existing theoretical frameworks in calculating the form factors, binding energy, monovacancy resistivity and paramagnetic spin susceptibility of metals under a scheme that requires no fittings to experimental data. In all these calculations, the screening due to the electron gas is accounted for through the modified Hartree dielectric function. The results obtained in these calculations are in good agreement with experimental values and show a general improvement on the results of previous researches.

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CHAPTER ONE

1.0 INTRODUCTION

A good knowledge of the atomic-like potentials experienced by electrons within the self-consistent field approximation is essential for a complete understanding of the nature of the crystal potential, the nature of the bonds and the physical properties of metals. Accurate calculations of such potentials have become more feasible in contemporary times as a result of fast computers and refined methods of carrying out electronic structure calculations. Such improved methods include the use of pseudopotentials.

Phillips and Kleinman (1959) suggested that the pseudopotential method involves replacing the actual potential of the valence electrons in the Schroedinger equation with an effective potential experienced by the valence electrons as a result of the effects of the core electrons. As a result, Austin et al. (1962) and Animalu and Heine (1965), and Harrison (1970) demonstrated that the resulting eigenvalue equation gives the pseudopotential equation, with the all-electron wave function equivalently replaced with the pseudowave function. Furthermore, Harrison (1966, 1970), and Animalu (1977) showed that the eigenvalues of the resulting pseudopotential equation are similar to free atom eigenvalues.

In otherwords, the pseudopotential that is employed in solving the one-body Schroedinger equation can only be accurately known if the eigenfunctions corresponding to the free atom eigenvalues are adequately known. Therefore, constructing a self-consistent pseudopotential would be a considerable task because the net potential would arise as a result of the contributions of a wide range of interactions. This suggests that any such calculation would seek to evaluate the sum of the electron-electron correlation interaction, electron-electron exchange interaction and electron-lattice interaction, which would be difficult to justify in metals.

However, Harrison (1970) suggested that the pseudopotential approach suffered some major drawbacks. Such drawbacks include the need to evaluate the determinants of an infinite-dimensional matrix. This is difficult and prone to errors. Also, the need for an accurate knowledge of the core state functions and the core state eigenvalues is essential in the pseudopotential method. The core state eigenvalues are not adequately known because the core state eigenvalues shift in metals in contrast to free atoms. As a result, model potentials have been introduced. For instance, Heine and Abarenkov (1964) introduced the 'model potential' approach in order to overcome the complexity of calculating pseudopotentials from first principles. This was achieved by calculating the model potential parameters directly from atomic term values obtained from atomic spectroscopy.

Shaw and Harrison (1967) stated that the choice of calculating the Heine-Abarenkov (HA) model potential parameters from atomic term values was made possible with the hope that it would be possible to account more accurately for the interaction of the valence electrons with the ion cores, suggesting that pseudopotentials arise as a result of the effects of the interaction of the core electrons with the valence electrons. However, in spite of the popularity of the HA model potential, it is not self-consistent and could not provide a functional basis for calculating the physical properties of metals.

It is therefore the aim of this research to develop a model pseudopotential technique with appropriate choice of screening parameters that require no fittings to experimental data. This work also aims at calculating the bare-ion pseudopotential and the screened form factors using the technique. In addition, the model is used in calculating some physical properties of metals such as binding energy, monovacancy resistivity and paramagnetic spin susceptibility at an enhanced accuracy.

1.1 THE FREE ELECTRON GAS APPROXIMATION

A simple model that allows for an adequate understanding of the physical properties of metals is the view that the valence electrons of constituent atoms become conduction electrons and therefore free to move about in the metal. Kittel (1976) statedthat this approximation considers the valence electrons as being free to move in the crystal lattice and as such, the electron states are completely described by wave functions that obey the Bloch function.

It has always been surprising that this simplified model works because all metals have a large charge distribution of conduction electrons due to the strong electrostatic potential of the ion cores. The basis for the success of the free electron model according to Kittel (1976) is the fact that valence electrons can move over a mean free path of the order 10^8 Å. The reason for this long mean free path is of two fold; firstly, a valence electron cannot be scattered on the ion cores of the periodic lattice because matter waves propagate freely in a periodic structure according to the Bloch theorem. Secondly, the electron - electron scattering is a rare event as a direct consequence of the Pauli exclusion principle.

Therefore, the free electron gas is understood as a gas of free electrons subject to Pauli principle. The one-body Schroedinger equation for free electrons confined to a length, L is expressed in three dimensions as,

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(r) = \mathrm{E}_k\psi_k(r) \tag{1.1}$$

where m is the mass of the electron, ∇^2 is the Laplacian in 3D Cartesian coordinates, ħ is the normalized Planck constant. If the electron is confined to a cube of length L, the wave function is a standing wave of the form,

$$\psi_k(r) = A\sin(\frac{\pi n_x x}{L})\sin(\frac{\pi n_y y}{L})\sin(\frac{\pi n_z z}{L}) \qquad (1.2)$$

where n_x, n_y, n_z, are positive integers. However, the only useful wave vectors are the ones that satisfy the periodic conditions of the form,

$$\psi(x+L,y,z) = \psi(x,y,z) \qquad (1.3)$$

The wave functions that satisfy the Schroedinger equation and the periodicity condition are plane waves of the form,

$$\psi(r) = \exp(ik.r) \qquad (1.4)$$

provided that the wave vectors $k_x, k_y, k_z = 0, \pm(2\pi)/L, \pm(4\pi)/L, \pm(2n\pi)/L$. A direct substitution of equation (1.4) into equation (1.1) gives the energy eigenvalues of the form

$$E(k) = \frac{\hbar^2 k^2}{2m} \qquad (1.5)$$

Within this approximation, a system of N free electrons in the ground state can be represented as points inside a sphere in k - space. The energy at the surface of the sphere is called the Fermi energy and consequently the wave vector at the surface of the sphere is called the Fermi wave vector. The volume of the Fermi sphere of radius k_f is of magnitude,

$$V = \frac{4\pi k_f^3}{3} \qquad (1.6)$$

such that the total number of occupied orbitals in k-space is expressed as,

$$n = \frac{Vk_f^3}{3\pi^2} \qquad (1.7)$$

It can be concluded that the free electron gas model is useful in providing a good insight into some of the physical properties of metals such as heat capacity, thermal conductivity, magnetic susceptibility and the electrodynamics of metals. However it fails to provide a suitable framework for distinguishing between metals, semimetals, insulators and semiconductors.

1.2 THE KRONIG – PENNEY MODEL

This is a square well potential in which the electron motion reveals the existence of the allowed and forbidden energy bands as observed in crystals. The electrons are assumed in this model to move through a periodic potential barrier that assumes the periodicity of the crystal. The solutions of the Schroedinger equation in the potential wells and the potential barriers show that the energy bands are not a continuum but separated into allowed and forbidden bands, separated by forbidden regions of energy called band gaps or energy gaps.

It is also a conclusion of this model that the allowed energy bands become broader as the wave vector increases and narrower as the wave vector decreases. This model offers an elegant scheme for explaining the existence of energy bands but it could not present a functional scheme for calculating the physical properties of metals.

1.3 BAND THEORY OF SOLIDS

In free atoms, electrons are arranged in energy levels or orbitals such that the Pauli exclusion principle is obeyed. However, in condensed matter, a large number of such electrons are made to come in close proximity to form a solid. Intuitive arguments from Kittel (1976), Animalu (1977), and Alonso and Finn (1971) suggest that energy bands arise in solids as a result of the changes in the atomic energy levels of the isolated atom when a large number of such atoms are brought together to form a solid. Therefore, electrons in solids are arranged in energy bands that are separated by band gaps. Energy bands associated with inner complete shells in the parent atoms have their full quota of electrons as allowed by the Pauli exclusion principle.

Alonso and Finn (1971) had stated that in metals, the valence band electrons are the ones that give rise to transport properties of the metal. This implies that the conduction band is not filled and therefore the effect of the unpaired electron spins give rise to a wide array of magnetic and electrical properties. Generally, the last filled band below the conduction band is the valence band and it is possible to excite an electron from the valence band to the conduction band through the application of energy.

In conductors, the conduction band is not filled but in insulators the conduction band is completely filled thereby rendering the spin of the electrons of such systems completely paired. The band theory therefore provides a qualitative approach for interpreting the basis for classifying solids into conductors, semiconductors and insulators.

1.4 BAND STRUCTURE CALCULATIONS

There are various methods of carrying out band structure calculations. These methods involve calculating the energy and wave number characteristics of electrons in atoms of the crystal structure under study. The concept seeks to unravel the arrangement of electronic states and their corresponding energies under a standard scheme. Animalu (1977) shows that if the electron potential energy is set to zero and the Schroedinger equation is solved for the wave functions and the eigenvalues, the results obtained give the empty lattice band structure. The results of the empty lattice band structure calculations show that the electron wave functions are only plane waves that satisfy the Bloch theorem in line with the conclusions of the free electron approximation.

Within the free electron gas approximation, the highest occupied energy level in the ground state of an atom is the Fermi energy of the atom. The corresponding Fermi wave vector is of considerable importance in band structure calculations such that standard schemes are developed to estimate these parameter. These include the cellular method, the plane waves method, the augmented plane waves method the orthogonalized plane waves method and the pseudopotential method.

Wigner and Seitz (1933) carried out the first known energy band calculation using the cellular method. In doing this, they only considered the low lying states in the band such that only the states with wave number $\boldsymbol{k} = 0$ were considered and this allowed the wave functions used, to be Bloch functions that have the full symmetry of the lattice. This method consists basically of dividing the crystal into atomic cells, such that the cell associated with each atom contains points closer to that atom than to any other atom.

From symmetry considerations, the normal component of the gradient of the wave function vanishes at all the atomic cell boundaries in simple structures. Therefore, Harrison (1970) concluded that for a given potential, the eigenvalue problem reduces to a calculation of the atomic states for a single cell with well-defined boundary conditions on the wave functions at the cell surfaces. The free ion potential was used in the calculation of the states and this potential was spherically symmetrical.

In order to solve the problem more readily, the atomic cells were replaced by a primitive cell sphere of equal volume called the Wigner-Seitz sphere. This reduces the calculation to a spherically symmetric problem in close analogy to free atom calculations.

However, the only difference is the vanishing boundary condition applied on the gradient of the wave function at the Wigner-Seitz sphere rather than on the cell boundary. This allowed the calculation of the energy difference between the bottom of the first band and the free atom state. It facilitated the estimation of the cohesive energy of simple metals.

This approach has been generalized to treat other states in the band but it is widely believed that the difficulty in matching the wave functions at the boundaries makes the result inaccurate, even though Altmann et al. (1968) showed that this problem is surmountable by imposing appropriate boundary conditions. In spite of this, the approach is not fashionable because of the rigorous nature of computing energy band parameters by considering the discrete energy bands.

1.5 THE PLANE WAVES METHOD

The solutions of the Schroedinger equation in the free electron approximation gives plane waves in periodic structures that are subject to the Bloch theorem. For the energy bands, the eigenvalue problem is of the form,

$$H|\psi_k\rangle = (T+V)|\psi_k\rangle = E|\psi_k\rangle \tag{1.8}$$

where T is the kinetic energy operator and V is the electron potential obtained as a superposition of free atom potentials. In coordinate representation the wave function is written as,

$$\psi_k(r) \equiv \langle r|\psi_k\rangle \equiv u_k(r)\exp(ik.r) \tag{1.9}$$

and,

$$\langle\psi_k|r\rangle = u_k^*(r)\exp(-ik.r) \tag{1.10}$$

are the Bloch functions. The plane waves method of solving the equation (1.8) uses the fact that in principles, any of the Bloch functions can be represented exactly in terms plane waves as a Fourier series of the form,

$$|\psi_k\rangle = \sum_g a_g|k-g\rangle \tag{1.11}$$

where,

$$\langle r|k-g\rangle = \Omega^{-\frac{1}{2}}\exp[i(k-g).r] \tag{1.12}$$

is a plane wave of wave vector **k-g**, normalized over the volume of the whole crystal, and {**g**} is a set of reciprocal lattice vectors. The constants 'a_g' are the Fourier coefficients which are obtained by substituting (1.11) into (1.8) to have the form,

$$\sum_g a_g(T+V-E)|k-g\rangle = 0 \tag{1.13}$$

Animalu (1977) showed that allowing the wave function <k-g| to act on equation (1.13) from the left hand side, where **k-g'** is a fixed reciprocal lattice vector and using the orthorgonality of the plane waves of the form,

$$\langle k-g'|k-g\rangle = \delta_{gg'} \tag{1.14}$$

results in the expression,

$$\sum_g \left\{ \left[\frac{\hbar^2(k-g)^2}{2m} - E \right] \delta_{gg'} + \langle k-g'|V|k-g\rangle \right\} a_g \ = \ 0 \tag{1.15}$$

where,

$$\langle k-g'|V|k-g\rangle \equiv \frac{1}{\Omega}\int \exp[-i(k-g').r]V(r)\exp[+i(k-g).r]dr \tag{1.16}$$

It is observed in equation (1.16) that $V(r)$ is a local potential, (that is the potential is coordinate dependent), implying that the potential $V(r)$ is diagonal in **r** representation as

$$\langle r'|V|r\rangle = V(r)\delta(r-r') \tag{1.17}$$

Animalu (1977) showed that a secular equation is obtainable from equation (1.15) for the energy bands under this approach in the form of a determinantal equation as:

$$\det\left\| \left[\frac{\hbar^2}{2m}(k-g)^2 - E \right] \delta_{gg'} + \langle k-g'|V|k-g\rangle \right\| = 0 \tag{1.18}$$

From the solution of this equation, it is possible to re-substitute the energy eigenvalue back into equation (1.15) to obtain the Fourier coefficients a_g, although this is not necessary in band structure calculations. Since the dimension of the secular determinant is $\infty \times \infty$, it is difficult to evaluate the determinant, therefore only a truncated form is evaluated and the truncation point is arbitrarily chosen. This arbitrariness introduces truncation errors in the computed band structure parameters and therefore renders the plane waves method inaccurate in calculating the experimental band structures of crystals.

Also, the plane wave of equation (1.11) accommodates two distinctively different features of the Bloch function due to the form of the lattice potential in the unit cells. This is because the potential is spherically symmetrical in the ion core regions and the wave functions have rapid oscillations. However, in the region between cores, the potential is nearly flat and reflects the translational periodicity of the crystal lattice. As a result, ψ_k varies slowly in the manner of plane waves joining smoothly from cell to cell according to Bloch theorem.

Furthermore, Animalu (1977) stated that in simple metals, the plane wave part of the Bloch function is very large compared to the total atomic volume. This is because the atomic radii are far greater than the ion-core radii. Consequently, a large number of plane waves are needed to represent the atomic-like oscillations of ψ_k. As a result of this, the plane waves method requires a large number of terms for convergence to be achieved. This makes the plane wave method unsuitable for heavy metals.

1.6 THE ORTHOGONALIZED PLANE WAVES (OPW) METHOD

Herring (1940) proposed the orthogonalized plane waves (OPW) method as a way of dealing with the poor convergence of the plane wave method, which arises from the atomic-like oscillations. The first step in the orthogonalized plane waves method is the classification of atomic levels into ion core and valence levels. For instance, the core levels in aluminium are those associated with the $1s^2 2s^2 2p^6$ atomic shells, while the valence levels are those associated with $3s^2 3p$ shells.

Orthogonalized plane waves are wave functions that have been made orthogonal to the occupied ion-core orbitals. An orthogonalized plane wave is defined mathematically as,

$$\left|OPW_{k-g}\right\rangle = \left|k-g\right\rangle - \sum_{c,l} \left|\psi_{cl}\right\rangle\left\langle\psi_{cl}\right|k-g\rangle \qquad (1.19)$$

where ψ_{cl} is the core electron wave function that has been made orthogonal to an orbital at lattice site l and **g** is the reciprocal lattice vector.

Animalu (1977) had shown that in the coordinate representation **r**, the orthogonalized plane wave is explicitly written as

$$OPW_{k-g}(r) = \left\langle r\middle|OPW_{k-g}\right\rangle = -\frac{1}{\sqrt{\Omega}}\exp\left[i(k-g).r\right]+\ldots$$

$$\ldots-\frac{1}{\sqrt{N}}\sum_{c,l}\psi_c(r-l)\left\{\frac{1}{\sqrt{\Omega}}\int dr'\exp\left[i(k-g).r'\right]\psi_c^*(r'-l)\right\} \qquad (1.20)$$

where $\psi_c(r-l)$ is a core electron wave function centred at the lattice site l and k-g is the reciprocal lattice vector. For instance, in aluminium the sum over the core states c, extends to the $1s$, 2s, $2p_x$, $2p_y$ and $2p_z$ atomic core wave functions. The 3s and 3p valence state functions are made orthogonal to the core state functions. It is however noted that two orthogonalized plane waves are not orthogonal, that is,

$$\langle OPW_{k-g'}|OPW_{k-g}\rangle = \delta\delta_{gg'} - \sum_{cl}\langle k-g'|\psi_{cl}\rangle\langle\psi_{cl}|k-g\rangle \tag{1.21}$$

where $\delta\delta_{gg'}$ is a dimensionless constant that depends on the reciprocal lattice. Additionally, even when it is assumed that atomic orbitals centred on different lattice sites are orthogonal, Animalu (1977) demonstrates that two orthogonalized plane waves are not orthogonal implying that,

$$\langle\psi_{c'l'}|\psi_{cl}\rangle = \delta_{cc'}\delta_{ll'} \tag{1.22}$$

Finally, the Bloch functions can then be expanded in terms of the orthogonalized plane waves as a Fourier series of the form,

$$|\psi_{k-g}\rangle = \sum_{g} a_g|OPW_{k-g}\rangle \tag{1.23}$$

When this is substituted in equation (1.8) the result becomes,

$$\begin{aligned} 0 = (T+V-E)|\psi_k\rangle &= \sum a_g(T+V-E)|k-g\rangle \\ &\quad -(T+V-E)\sum|\psi_{cl}\rangle\langle\psi_{cl}|k-g\rangle \end{aligned} \tag{1.24}$$

Equation (1.24) can be further simplified by noting that the one-body Schroedinger equation can be written as,

$$H|\psi_{cl}\rangle = (T+V)|\psi_{cl}\rangle = E_c|\psi_{cl}\rangle \tag{1.25}$$

where the atomic energy eigenvalue of an appropriate core level is denoted as E_c and H is the unperturbed ground state Hamiltonian operator of the electron system.

Allowing an orthogonalized plane wave function to operate on equation (1.25) from the left and using the fact that equation (1.25) holds for all quantum states to obtain,

$$\sum_{g} a_g\left\{\left[\frac{\hbar^2(k-g)^2}{2m} - E\right]\langle OPW_{k-g'}|OPW_{k-g}\rangle + \langle k-g'|U|k-g\rangle\right\} = 0 \tag{1.26}$$

where m is the mass of the electron. Animalu (1977) showed that the first terms of equation (1.26) are kinetic energy dependent while the second terms define an effective potential energy $U(r)$, known as the orthogonalized plane waves pseudopotential. As a result, the OPW pseudopotential can be expressed in the braket notation as,

$$\langle k-g'|U|k-g\rangle \equiv \langle k-g'|U|k-g\rangle + \\ +\sum_{cl}(E-E_c)\langle k-g'|\psi_{cl}\rangle\langle\psi_{cl}|k-g\rangle \qquad (1.27)$$

In conclusion therefore, it is stated that the orthogonalized plane waves are coupled only for states with wave numbers differing by a lattice wave number. As a result, the appropriate matrix elements can be evaluated for known potentials and core wave functions. Harrison (1970) showed that this reduces to a problem of solving a set of simultaneous equations. However, the matrix elements coupling $a_{k'}$ with a_k vanishes more rapidly in this case than that of the plane waves method, and as a result, a much smaller set of simultaneous equations are required in this approach.

For some applications only two or three orthogonalized plane waves are required, however for full band calculations, a large number of orthogonalized plane waves are required and for accurate full band calculations, a very large number of orthogonalized plane waves are required. The use of orthogonalized plane waves has greatly reduced the computational efforts required in calculating the energy band of solids.

However, as a result of the dependence of the accuracy of the calculated band structure of metals in this approach on the number of orthogonalized plane waves employed in the calculation, it becomes cumbersome to deal with a very large number of orthogonalized plane waves. Also, evaluating the determinant of a matrix of very large dimension is not easy. As a result of these difficulties, the orthogonalized plane waves method was extended to the pseudopotential method.

1.7 THE AUGMENTED PLANE WAVES (APW) METHOD

Slater (1937) proposed that the augmented plane waves could also be used for expanding the Bloch functions. In constructing the augmented plane waves, the effective potential of the electron is approximated and used in solving the Schroedinger equation for the electron states. It is noted that near each nucleus, the potential is spherically symmetrical and relatively flat in the region between two successive nuclei. This implies that a hypothetical sphere is constructed around each nucleus such that the radii of the spheres are sufficiently small such that they do not overlap each other and the potential within the spheres are spherically symmetrical, therefore the potential is constant within the crystal.

However, the usual procedure is to construct the true potential expected in the crystal and then to approximate it by the 'muffin tin' form. Prescribing this form for the potential prevents an accurate calculation of a self-consistent eigenvalue problem. It also becomes a serious difficulty if this approach is to be generalized to crystals with defects. The augmented plane waves are then constructed as plane waves in the region between the spheres. For reference energies of interest, the augmented plane waves are constructed for the spherically symmetrical potential.

The Fourier coefficients are then adjusted to eliminate the discontinuities in the wave function at the surface of the sphere, although it is not possible to remove discontinuities in the gradient of the wave functions. The electron eigenstates for any given system can then be simulated in terms of these augmented plane waves. These replace the plane waves or the orthogonalized plane waves in the band structure calculation. The augmented plane waves approach requires a limited number of terms and this has been accepted as an efficient method of band structure calculation. However, it requires high-speed computers for accurate calculations.

1.8 THE PSEUDOPOTENTIAL METHOD

Phillips and Kleinman (1959) observed that the pseudopotential method is a direct extension of the OPW method of band structure calculation. They concluded that the rapid convergence of the OPW comes as a result of the fact that the effective potential U, defined in equation (1.27) is weaker than the true potential V. This weak potential is called the pseudopotential. They further observed that since the first term of equation (1.27) is positive and the second is negative, then there is a cancellation between the first and second terms of equation (1.27), leading to a net weak potential.

Physically, the cancellation between the true attractive potential and the repulsive orthogonalization term is a direct consequence of the Pauli exclusion principle, which requires in this context, that the valence electron wave functions (Bloch functions) should be orthogonal to the atomic core (occupied) orbitals. This requirement of orthogonality expresses itself through the rapid oscillation of the true wave function in the ion core region where the true potential is deep and attractive. These rapid oscillations account for the high kinetic energy of the valence electrons, which acts as a repulsive potential in the ion core region. Animalu (1977) states that as a result, the valence electrons only see the net weak potential called the pseudopotential.

Cohen and Heine (1961) and Austin et al. (1962) and Chelikowsky (2000) have demonstrated that pseudopotentials are non-unique. This is because if an arbitrary function is added to the pseudo wave function, then the results of the eigenvalue problem remain unchanged. However, this is possible only when the arbitrary function has been made orthogonal to the core state. This non-uniqueness is an inherent property of the pseudopotential method and has been demonstrated by Chelikowsky (2000). The significance of this is that the only absolute requirement on any pseudopotential is that it should lead to the same energy eigenvalue as the all-electron potential.

However, as a result of the fact that an accurate knowledge of the core state functions and the core state eigenvalues are necessary requirements of the pseudopotential method, as reflected in equation (1.24), which are not adequately known because the core state energies shift in condensed matter in contrast with that of the free atoms, Heine and Abarenkov (1964) have introduced model potentials. The model potential consists basically of replacing the true potential by an equivalent square well potential such that the energy eigenvalues of the electrons are still the same as those of the true potential.

This approach overcomes the problem of arbitrarily choosing pseudo wave functions in the general pseudopotential method and has a remarkable advantage of being calculated from atomic term values. This implies that phenomenological potentials can be successfully measured for all elements of the periodic table using wide range atomic spectroscopy techniques. However, such potentials would not be self-consistent because they are calculated from atomic term values of metals of interest and are therefore not transferable potentials.

1.9 MOTIVATION AND SPECIFIC OBJECTIVES OF RESEARCH

It is noted that metallic properties computed using a wide range of model potentials only show a limited agreement with experimental values. For instance, Ashcroft (1966) developed the 'empty core' model pseudopotential and used it in calculating the binding energy of some metals. This model is successful in calculating the binding energy of some alkali metals and fails completely for other group of metals. This failure could be attributed to the fact that the effect of the electron-electron repulsive interactions within the core region was neglected.

In addition, Behari (1973) developed a model potential for lead that depends explicitly on two adjustable parameters of the electron gas. These parameters were selected strictly for computational convenience and were fitted to two experimentally determined points q, equal to (111) and (200) reciprocal lattice vectors that were derived from Fermi surface data. This model potential was used within two standard approximations for the computation of the metallic properties of lead.

This model also failed to predict the physical properties of lead accurately but had some measure of success in the computed binding energy using the random phase approximation (RPA). However, the computed binding energy for lead using the self-consistent field approximation (SC) failed completely because the predicted value was far larger than the experimental value. This large discrepancy is attributed to the explicit dependence of the model on arbitrary parameters of the electron gas, which could not be linked to any experimentally observable property of lead. Also, the model has been adjudged unsuitable because it not self-consistent and therefore cannot be applicable to other metals except lead and therefore cannot be generalised.

Furthermore, the results of the physical properties of metals computed with the model potential of Hussain and Akinlade (1987) shows a limited success. The model was particularly successful in predicting the binding energy of alkali metals but failed completely for metals of higher valences. Equally, the results for monovacancy resistivity and paramagnetic spin susceptibility showed an irregular pattern and only had a relative agreement with results of other models for the metals treated.

Vackář, et al. (1998) showed that it is possible to construct an all-electron pseudopotential that could be applied to all condensed matter. Although they did not present a functional expression for this, they concluded that for this to be achieved, the effects of the core electrons must be included to account for the shifts in energy levels of condensed systems in contrast with that of free atoms. Equally, Shore and Rose (1999) had shown that the jellium model can be extended to the pseudopotential by replacing the jellium by the pseudo jellium such that the pseudopotential becomes the 'ideal metal pseudopotential' which could be applicable in the accurate computation of the physical properties of all metals.

This research was therefore motivated by the need to develop a self-consistent model pseudopotential, which can be applied successfully to all metals within the available theoretical frameworks for calculating the various metallic properties such as binding energy, monovacancy resistivity and paramagnetic spin susceptibility of metals to a high accuracy.

As a result, this research seeks primarily to develop and propose a self-consistent model pseudopotential with an appropriate choice of screening parameters that require no fittings to experimental data. Consequently, this work seeks to compute the bare-ion pseudopotential and the screened form factor of metals using the proposed model. Not only these but also, this research work is aimed at calculating atomic-like potentials of metals from first principles consideration of the stationary state perturbation theory and the free electron gas approximation without solving the cumbersome Kohn-Sham equation.

Finally, this work aims at providing a standard scheme for calculating the various metallic properties within the pseudopotential framework in addition to developing computer programs to calculate the binding energy, monovacancy resistivity and paramagnetic spin susceptibility of metals.

CHAPTER TWO

2.0 THEORETICAL BACKGROUND

In this chapter, a succinct review of the established approaches to the concept of pseudopotentials and the relevant theoretical foundations of such approaches has been given. The chapter also examines the general basis for adopting the pseudopotential approach in solving electronic structure problems. It also highlights the strengths and limitations of the various types of pseudopotential formalisms available. A brief account of the different types of pseudopotentials has also been given. These range from the empirical pseudopotentials through the *ab initio* pseudopotentials to first principles model pseudopotentials.

2.1 THE EMPIRICAL PSEUDOPOTENTIAL (EPM) METHOD

In the empirical pseudopotential approach, a physical quantity like the dielectric function of an insulator is first calculated. This is calculated using the results of the eigenvalue problem solved with an approximate potential. Secondly, the calculated value is compared with experimental value to obtain a good fit. The approximate potential is chosen such that the calculated physical quantity reproduces the experimental values of such quantity. On the other hand, if the physical quantity gives a poor fit with experiment, the parameters of the potential are adjusted until a good fit is obtained.

For instance, a veritable example is the complex dielectric function for insulators and semiconductors expressed as,

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \qquad (2.1)$$

where ε_1, ε_2 are the real and the imaginary parts of the dielectric function respectively. This is also related to the refractive index of the material as,

$$\varepsilon = (n + iK)^2 \tag{2.2}$$

where n and K represent the complex refractive index and the absorption coefficient of the material respectively. The dielectric function and the refractive index are taken to be complex. As such, Pulci et al. (1997) and Chelikowsky (2000) express the imaginary part of this function as,

$$\varepsilon_2 = \frac{4\pi^2}{3m^2\omega^2} e^2\hbar^2 \sum_{v,c} \frac{2}{8\pi^3} \int_{BZ} \partial^3 k \delta(\omega_{vc}(k) - \omega) |M_{vc}(k)|^2 \tag{2.3}$$

where the integral is taken over the first Brillouin Zone and

$$|M_{v,c}(k)|^2 = |\langle u_v(\bar{k},\bar{r}) \nabla u_c(\bar{k},\vec{r}) \rangle|^2 \tag{2.4}$$

is a dipole matrix element.

Chelikowsky (2000) had demonstrated amply that the summation in equation (2.3) is over all possible transitions from the valence band states to conduction band states and where u_v and u_c represent the wave function of the valence and conduction band electrons respectively. These are obtained from the solution of an eigenvalue problem solved using an approximate potential. The real part of the dielectric function is obtained by the Kramers-Kronig transformation expressed as,

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \mathrm{P} \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega \tag{2.5}$$

ω is the angular frequency at which transitions occur from the valence bands to the conduction bands. P is a parameter of the Kramers-Kronig transformation that is called the 'principal part of the integral'.

The complex dielectric constant, absorption coefficient and refractive index of a material are then calculated using the equations above. The calculated results of these physical quantities are then compared with those obtained from experiments. If the results are in good agreement with the experiment, then the approximate potential used in solving the eigenvalue problem is considered to be a 'valid pseudopotential'.

Similarly, Hill (1981) expressed the normal reflectivity of a metal as,

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{2.6}$$

where k is the wave vector of the incident radiation and n is the refractive index of the material. The energy-wave vector characteristic of a metal is evaluated using an approximate potential as pointed earlier.

The reflectivity is then calculated using equation (2.6) and the results can then be compared with the experimentally observed reflectivity. If a good fit is obtained, then the approximate potential is then considered as a valid pseudopotential. However, if a poor fit is obtained, then parameters of the approximate potential are adjusted and the entire process is repeated until a good fit is obtained.

Equally, Alonso and Finn (1971) expressed the density of states as,

$$\mathrm{N}(E) = \sum_{n} \frac{2}{8\pi^3} \int_{BZ} d^3k \partial(\mathrm{E}_n(k) - E) \tag{2.7}$$

where $E_n(k)$ is the energy of an electron in the nth quantum state and E is the ground state energy of the electron. The summation is over all the occupied states and the integral is over the first Brillouin Zone.

The density of states is then calculated using the results of the eigenvalue problem with an approximate potential and equation (2.7), and then comparisons are made with experimentally observed data on density of states of such metal. Chelikowsky (2000) has also shown that the density of states can be measured experimentally by using the data on photoemission and therefore comparisons are made between the calculated values and experimental values to obtain a good fit.

2.2 BASIC STEPS IN GENERATING AN EMPIRICAL PSEUDOPOTENTIAL

Chelikowsky (2000) had enumerated the basic procedures for generating empirical pseudopotentials. First of all, an arbitrary local pseudopotential $V(r)$, is selected in real space such that it is related to the equivalent pseudopotential in reciprocal space according to the transformation,

$$V(r) = \sum_{G} V(G)S(G)\exp(iG.r) \tag{2.9}$$

where V(G), S(G) and G represent the equivalent local pseudopotential in reciprocal space, the structure factor and the reciprocal lattice vector respectively. The discrete Fourier transform of the local pseudopotential in reciprocal space is obtained using Bracewell (1986) as,

$$F(q) = \frac{1}{\Omega}\sum_{N} f(r)\exp(-iq.r) \tag{2.10}$$

It has also been shown by Chelikowsky (2000) that given a choice of an approximate potential $V(r)$ in real space, the true Hamiltonian in the one–body Schroedinger equation, $H=P+V$ is replaced by the pseudo Hamiltonian, $H^I = H+V(r)$, where H^I is the perturbed Hamiltonian of the system and P is the kinetic energy operator and V is the potential energy of the electron in ground state. Therefore, the eigenvalue problem $H^I\Psi = E\Psi$ is then solved analytically to obtain the eigenvalues and eigenfunctions $E(k)$ and $\Psi(r)$ of the pseudo Hamiltonian H^I.

From the calculated values of $E(k)$ and $\Psi(r)$, the reflectivity is calculated using equation (2.6) and the density of states is also calculated using equation (2.7). The results obtained are compared with experimental data. If the results are in good agreement with experimental data, then $V(r)$ is considered to be a valid pseudopotential, but if not, then the parameters of the potential are altered and the whole process is repeated until an arbitrary pseudopotential that agrees with experimental data is selected.

Abe (1963) had used an empirical pseudopotential to obtain an insight into the spin paramagnetism of an electron gas in a lattice of positive ions. The approach only shows a limited success for some alkali metals. In particular, a large discrepancy was observed in the paramagnetic spin susceptibility of caesium. The discrepancy was attributed to the fact that the Wigner-Seitz primitive sphere of caesium has the largest radius compared to other alkali metals. Therefore, it was concluded that the theory is valid only at the high-density limit and as such cannot be applied to caesium.

Furthermore, Ashcroft and Langreth (1967) had used a simple analytic form for the electron-ion potential fitted to metallic data near the Bragg reflection planes to calculate the compressibility and binding energy of simple metals. Although reasonable results were obtained for the calculated properties, it is observed that the potential adopted in these calculations require a fitting procedure. In addition, the potential adopted is not a self-consistent potential because the fitting must be carried out for a given metal before its metallic properties can be calculated.

Similarly, Horsfield and Ashcroft (1993) used the accurately determined energy levels at fixed points on the Brillouin zone obtained from low-temperature galvanometric measurements of the Fermi surface of aluminium to determine an empirical pseudopotential and to test the precision of the standard scheme for calculating band structures. They asserted that empirical pseudopotentials that accurately reproduce one-particle structures near the Fermi energy could be constructed.

As an illustration, they applied such a concept in evaluating the ionic pair potential of molten aluminium and the results were found to be in good agreement with results of other theories. However, electrical conductivity determined using the constructed pseudopotential was found to give a poor agreement with experiment.

Chelikowsky (2000) had also shown that the empirical pseudopotential method is advantageous because it is easy to implement and run on a personal computer. In addition, the method has successfully established the validity of the 'one-body' potential thereby showing that it is possible to construct an accurate potential. Finally, the empirical pseudopotential band structures for semiconductors still stand as the most accurate after several years. For instance, those of silicon are still accepted as the best after about thirty years.

However, in spite of the above strengths, the fact that this approach requires experimental inputs especially for solid-state properties constitutes a major limitation. For example, in complex systems accurate experimental inputs may not be available because the structural parameters of such systems such as clusters, powders, binary structures, surfaces and defects may not be adequately known. This makes the computation of forces and structural energies remarkably difficult using this approach. In addition, the wave functions employed in the computation of the physical observables in this approach may be suspect and therefore, since accuracy is a priority in such calculations, employing uncertain inputs can render the entire scheme inaccurate.

Finally, the potentials generated using this method are not self-consistent potentials and are generally not transferable. This implies that if such a potential V(G) is generated for a particular element, it cannot be transferred to another element or used for the calculation of the properties of other elements even if such elements share a common physical or chemical property. This constitutes a serious weakness because it would lead to a multiplicity of potentials, which completely excludes a possibility of the development of a self-consistent potential as a standard scheme for the calculation of the physical properties of all elements.

2.3 *AB INITIO* PSEUDOPOTENTIALS

Kohn and Hohenberg (1964) and Kohn and Sham (1965) had shown that theoretical calculations based on the density functional theory (DFT) is capable of providing exact solutions of the full many-body Schroedinger equation describing a condensed matter system in its ground state, which is otherwise impossible to evaluate. The *ab initio* calculations suggest that the valence electron states are completely described by the Kohn-Sham formalism. Jarvis et al. (1997) showed that the total energy functional in this case is written as a sum of the kinetic energy, electron-ion interaction energy, electron-electron correlation energy and the electron-electron exchange energy functionals, where the electron-ionic interaction energy is directly influenced by the pseudopotential.

However, Onwuagba (1995) and Jarvis et al. (1997) asserted that since the exact form of the electron-electron exchange-correlation energy functional is not known explicitly, approximations to this functional are usually adopted in carrying out total energy calculations. Slater (1951), Gunnarsson and Lundquist (1976), Ceperley and Alder (1980), and Perdew and Zunger (1981) had provided different approximate forms for the exchange-correlation interaction. In most calculations, the DFT is used within the local density approximation (LDA) or the local spin density approximation (LSDA) to calculate the total energy based on the assumption that the energy functional are completely describable in terms of the number density of electrons or spin densities respectively.

In recent *ab initio* pseudopotential calculations of a wide range of properties of the electron gas, Cho and Terakura (1997), Pulci et al. (1997), Briley et al. (1998), Satta et al. (1999), Antonelli et al. (1999), and Meyer et al. (2001) used plane wave basis sets to expand the valence electron wave function, using arbitrary cut-off kinetic energies of several rydbergs that are usually chosen to ensure total energy convergence to reasonable accuracies.

Chelikowsky (2000) provides the general basis for such theoretical calculations, noting that the valence electron motion is represented by the one-body wave function ψ_i, which satisfies the Schroedinger equation of the form,

$$[-\hbar^2 \frac{\nabla^2}{2m} + V_{ion}(r) + V_H(r) + V_{XC}(r)]\psi_n(r) = \mathrm{E}_n \psi_n(r) \qquad (2.11)$$

where ∇^2 is the Laplacian defined in the 3D Cartesian coordinate system as, $\nabla^2 = d^2/dx^2 + d^2/dy^2 + d^2/dz^2$, V_{ion} is the ionic potential and, V_H is the Hartree potential given in terms of the Poisson equation as,

$$\nabla^2 V_H(r) = 4\pi e \rho(r) \qquad (2.12)$$

and V_{xc} is the exchange-correlation potential of Slater (1951), expressed as a function of the electronic charge density as,

$$V_{xc}(r) = V_{xc}\left[\rho(r)\right] \qquad (2.13)$$

where the charge density is expressed as,

$$\rho(r) = \sum_{occupied} N(r)\left|\psi_n(r)\right|^2 \qquad (2.14)$$

It has also been shown that the sum of the Hartree potential and the ionic potential is the same as the classical electron-electron repulsive potential.

2.4 INVERTING THE SCHROEDINGER EQUATION

The *ab initio* pseudopotential method assumes explicitly that the pseudowave functions ϕ_n are known accurately and as a result the electronic pseudocharge density is written in terms of the number of valence electrons n as follows,

$$\rho^{ps}(r) = \sum_{Z} n|\phi_n|^2 \tag{2.15}$$

It is then possible to invert the Schroedinger equation to obtain the Khon–Sham equation for the ion potential expressed as,

$$V_{ion}(r) = \frac{\hbar^2 \nabla^2 \phi_n(r)}{2m\phi_n(r)} - V_H(r) - V_{XC}(r) + \mathrm{E}_n \tag{2.16}$$

When this potential is screened, it is known to have solutions for the pseudowave functions, ϕ_n and energy, $E_n(k)$ obtainable by construction. For instance, if a 'smooth' wave function is considered, then the pseudowave function will match the all electron wave functions outside the core region. Therefore, these smooth wave functions are nodeless and simple to replicate and as a result the chemical properties are preserved.

2.5 BASIC STEPS IN DESIGNING AN AB INITIO PSEUDOPOTENTIAL

The fundamental steps in designing an *ab initio* pseudopotential have been given by Troullier and Martins (1991). In this procedure, the pseudo wave function is assumed to be defined as follows,

$$\phi_l(r) = r^l \exp[P(r)] \qquad r < r_c \tag{2.17}$$

within the core region, where l is the orbital angular momentum and r_c is the radius of the ion core and $P(r)$ is a polynomial defined as,

$$P(r) = c_0 + c_2 r^2 + c_4 r^4 + c_6 r^6 + ... + c_n r^n \tag{2.18}$$

However, since the pseudowave function must match the all electron wave function outside the core region, the pseudowave function is explicitly defined in this region as,

$$\phi_l(r) = \psi_l(r) \qquad r > r_c \tag{2.19}$$

where ψ_l is the all electron solution of the Schroedinger equation of equation (2.11).

Vackar et al. (1998) have shown that the pseudowave function outside the core region matches the all electron wave function and that it is nodeless and smooth and consequently, the ion core radius is chosen to reside outside the outermost node, but within the radial maximum of the all electron wave function. All these conditions are prescribed on the pseudo wave function to ensure that the pseudo eigenvalues are also identical with the all electron eigenvalues. These conditions require that there must be some criteria for selecting the polynomial coefficients, c_n in equation (2.18).

2.6 CRITERIA FOR SELECTION OF TROULLIER-MARTINS POLYNOMIAL COEFFICIENTS

Chelikowsky (2000) had shown that the coefficients of the Troullier-Martins polynomial must not be arbitrarily chosen. This is because the pseudowave function must match with the all electron wave function outside the ion core region as such must have the same first four derivatives at the core radius, r_c. Also, the pseudopotential must be made to have zero curvatures at the origin as a precondition for the construction of a valid pseudopotential under this formalism.

Finally, the pseudo wave function must be norm conserving within the ion core. This implies that the inner product of the pseudo wave function must be identical with that of the all electron wave function such that within the ion core region such that,

$$\int_0^{r_c} \left|\phi_l(r)\right|^2 r^2 dr = \int_0^{r_c} \left|\Psi_k(r)\right|^2 r^2 dr \tag{2.20}$$

This ensures that the pseudo wave function and the all electron wave function do not differ by a scaling constant outside the core region.

2.7 PLANE WAVES SOLUTION OF THE KOHN-SHAM EQUATION

It is noted that an effective approximation is required for the exchange-correlation energy functional of the Kohn-Sham formulation. Such approximations suggest that the exchange-correlation energy will have a quasilocal form expressed as,

$$E_{xc}\left[n(r)\right] = \int \left(e_{xc}(r;[n(\bar{r})])n(r)\right)dr \tag{2.21}$$

where e_{xc} (r;[n(r)]) represents an exchange-correlation energy per particle at point r, which is a function of the density distribution n(r). Kohn (1999) asserts that all the components of the Kohn-Sham energy, except the long-ranged Coulomb interaction can generally be expressed in terms of the one– and two– particle density matrices of the interacting and non interacting system as $G_1(r_1;r'_1)$, $G_2(r_1,r_2;r'_1,r'_2)$ and $G^0_1(r_1;r'_1)$, $G^0_2(r_1,r_2;r'_1,r'_2)$, all corresponding to and uniquely defined by the same density distribution n(r).

The calculation of the energy components involve the use of these Green's functions with arguments such as $(r_1;r'_1)$ and $(r_1,r_2;r'_1,r'_2)$. On the other hand, Jarvis et al. (1997) had earlier showed that the ionic interaction term of the Kohn-Sham total energy is directly dependent on the atomic-like potentials as,

$$V_{ion}(r) = \sum_{l}\sum_{\alpha}\phi_{\alpha}(r+l) \qquad (2.22)$$

where the double summation denotes a linear combination of the atomic-like potentials for atom α, evaluated over all lattice vectors l.

However, pseudopotentials generated within the density functional theory are inherently non-local or angular momentum dependent. Jarvis et al. (1997), Vackar et al. (1998), Chelikowsky (2000), and Meyer et al. (2001) have independently shown that the semi-local ionic potential can be written as a sum of the local potential and a non-local potential as,

$$V^{P}_{ion}(r) = V^{P}_{ion,local}(r) + \sum_{l} P^{+}_{l}\left[V^{core}_{ion,l}(\rho) - V^{valence}_{ion,l}(\rho)\right]P_{l} \qquad (2.23)$$

P_l represents the projection operator, which projects the valence states onto the core states. $V^{val}_{ion,l}(\rho)$ and $V^{core}_{ion,l}(\rho)$ represent the charge density dependent non-local ionic pseudopotential of the valence and core electrons respectively. Therefore, in line with Kleinman and Bylander (1959), solving the self-consistent Kohn-Sham equations require evaluating a secular determinant for the Hamiltonian matrix elements. This is done in terms of atomic reference functions and spherical harmonics, which is cumbersome and computationally demanding. This arises as a result of the unsuitability of the plane waves as a basis set for expanding these atomic reference functions.

However, Pollack et al. (1997) have used a density based local pseudopotential obtained in the *ab initio* formalism to obtain a clue to the band structure, phonon frequencies and bulk moduli of some metals. Also, Vogel et al. (1998) have evaluated the electronic structure of silver halides using pseudopotentials obtained in the *ab initio* approach. The results obtained in each of these cases were in agreement with experimental results. However, these calculations required fitting the pseudopotential to specific crystallographic axes and lattice planes, which is prone to errors and ambiguity.

2.8 JUSTIFICATION FOR PSEUDOPOTENTIALS

It is assumed in the electronic structure problems that the one-body Schroedinger equation can be written such that the wave function obeys the Bloch theorem. It is further assumed that the crystal potential can be written as a linear combination of atomic-like potentials as follows,

$$V(r) = \sum_{\tau,R} V_a(r) \tag{2.24}$$

where $V_a(r)$ is an atomic-like potential. However, if all the electrons are included in the calculations, plane waves are no longer suitable as a basis set for the expansion of the all electron wave function. This is primarily because the potential near the nuclei will diverge and as a result the wave function will have cusps. These cusps cannot be expanded in plane waves.

For instance, the orbitals of conduction electrons in simple metals are simple and smooth in the region between the ion cores, but these orbitals are complicated by a nodal structure in the region of the cores. In the outer region, the potential energy of a conduction electron is relatively weak. It is the Coulomb potential energy of the positive charge of ions, but reduced by the electrostatic screening of the other conduction electrons. In the outer region the wave functions are like plane waves. It is neither complicated by the strong and rapidly varying potential near the nuclei nor by the requirements of orthogonality to the wave function of the core electrons. Apart from this, the lowest eigenvalues of the valence electrons will converge to core states, which can be highly localized in contrast to valence states.

Also, orthogonality conditions require that the valence electron wave functions have numerous nodes, which again will require numerous plane waves for expansion. Also, if the conduction orbitals in the outer region are approximately plane waves, the energy must depend on the wave vector as obtained in the free electron approximation. However, Kittel (1976) stated that in the core region, the wave function is not plane wave and the potential is strong. Also, the effect of the core electron interaction does not influence the dependence of the energy on wave vector.

Furthermore, Chelikowsky (2000) suggested that the tightly bound core states contain little chemical information because of the inert gas configuration it assumes, whereas the 'all-electron' potential approach requires a solution for all eigenvalues. Besides, it has been observed experimentally by Harrison (1970), that the ground state energy bands of most metals resemble free electron bands, which can misleadingly suggest that the electrons are nearly free and that the potential arising from the ions is quite small.

This is however not the case because the electron wave functions do not resemble plane waves near the ion cores and therefore the effect of the potential on the wave function is appreciably large. It has also been observed experimentally that the effect of the potential on the energy bands is quite small. This apparent absurdity is very nicely resolved by the idea of pseudopotentials, which represents the effect of the potential on the energy bands.

2.9 THE PSEUDOPOTENTIAL PERTURBATION THEORY

It is assumed that the valence state functions for a metal (or any condensed matter system) are composed of two parts:

$$\Psi = \phi + \sum_{t} b_t \phi_t \tag{2.25}$$

where the sum is over all occupied states and the coefficients, b are constants. Herring (1940) proposed that if the wave function, $\phi(r)$ is a plane wave, that is,

$$\phi = \exp(ik.r) \tag{2.26}$$

then the coefficients b are given by,

$$b_t = -\int d^3 r \phi^* \exp(ik.r) = -\langle \phi_t | k \rangle \tag{2.27}$$

Harrison (1966, 1970) and Animalu (1977) independently showed that this choice corresponds to the orthogonalized plane waves method. The OPW method reflects the following properties; firstly, it shows that near the nucleus, the wave function looks like atomic-like functions. Secondly, in the bonding region between atoms, the wave function looks like plane waves. Thirdly, the valence electron wave functions are orthogonal to the core states and therefore the lowest eigenvalue for this wave function will not converge to a core state. A substitution of the OPW–like wave function of (2.26) in the Schroedinger equation yields,

$$\mathrm{H}\left(\phi - \sum_{t}\langle\phi_t|k\rangle\phi_t\right) = \mathrm{E}\left(\phi - \sum_{t}\langle\phi_t|k\rangle\phi_t\right) \tag{2.28}$$

Rearranging the terms to have,

$$H\phi - \sum_{t}\langle\phi_t|k\rangle E_t\phi_t = E\phi - E\sum_{t}\langle\phi_t|k\rangle\phi_t \tag{2.29}$$

or, $$H\phi + \sum_{t}(E - E_t)\langle\phi_t|k\rangle\phi_t = E\phi \tag{2.30}$$

Therefore, (2.30) can be re-written as,

$$(\mathrm{H} + \upsilon_R)\phi = \mathrm{E}\phi \tag{2.31}$$

where the repulsive operator v_R is defined as,

$$\upsilon_R\phi = \sum_{t}(\mathrm{E} - \mathrm{E}_t)\langle\phi_t|k\rangle\phi_t \tag{2.32}$$

This operator acts like a short-ranged, non-Hermitian, non-local, repulsive potential.

Therefore, the combination of this repulsive potential and the all-electron potential gives the pseudopotential. Phillips and Kleinman (1959) postulated the cancellation theorem showing that the effect of the operator v_R is to cancel most of the effects of the all-electron potential arising from the high kinetic energy of the valence electrons. This results in a net weak potential which when substituted into the one–body Schroedinger equation yields the same solution as that of free atoms.

Harrison (1966, 1970) showed that the resulting weak, non-repulsive potential is considerably small and as such is treated as a perturbation. However, the results of such calculations show that there are considerable shifts in the valence states energy for atoms in ground state contrary to the results obtained for free atoms, therefore, carrying out the perturbation calculation to higher orders does not necessarily increase the accuracy, but instead reveals that the contribution of the core electrons to the physical properties is appreciable.

2.10 BASIC FEATURES OF A PSEUDOPOTENTIAL IN REAL AND RECIPROCAL SPACE

Kittel (1976) stated that the pseudopotential generally represents the interaction of a valence electron with the nucleus and the tightly bound core electrons, that is, the valence electron with the ion-core. Also, Cohen and Heine (1961) and Chelikowsky (2000) suggest that this potential needs to be screened by the other valence electrons present in the metal. In real space, the pseudopotential and the all-electron potential merges in the regions away from the core. Within the core region, the pseudopotential behaves like an effectively weak potential whose effect on the valence electrons is similar to that of the free electron potential.

Chelikowsky (2000) demonstrates that since the pseudopotential can be expanded in terms of plane waves, it can be written in terms of the atomic form factors. Generally, in the momentum space, the reciprocal lattice vector is denoted by q, where q defines the measure of transfer of momentum along the reciprocal lattice. Consequently, the atomic-like potential in momentum space are obtained from the inverse Fourier transform of the crystal potential as follows

$$V_a(q) = \frac{1}{\Omega} \int d^3r V_a(r) \exp(-iq.r) \qquad (2.33)$$

Hussain and Akinlade (1987), stated that in the low wavelength limit, that is as $q \rightarrow 0$, the screened potential tends to a limiting value of $-2/3E_f$ and that in the limit as $q \rightarrow \infty$, the screened potential tends to the Fourier component of the bare-ion Coulomb potential in reciprocal space. It is however observed that only the discreet values of the form factors in momentum space are required in band structure calculations as a consequence of the periodicity of the lattices.

2.11 NON-LOCALITY IN PSEUDOPOTENTIALS

Pseudopotentials are often treated using non-local atomic potentials. Behari (1973) had suggested that this non-locality arises as a result of the variation of the atomic potential with angular momentum. Ziman (1961) had shown that the nonlocal pseudopotential could be written as a sum of the atomic potentials. It can therefore be written as,

$$V_{Pseudo} = V_S + V_p + V_d + V_f + V_g + \ldots \tag{2.34}$$

In this case, s, p, d, f and g represent the spectroscopic energy level corresponding to states where the orbital angular momentum quantum numbers are 0, 1, 2, 3 and 4 respectively.

This suggests therefore, that the total potential can be written as a summation of the atomic-like potential and the bare ion Coulomb potential experienced by electrons in the unfilled orbitals. In this way full non-local pseudopotential have been developed with considerable computational convenience.

2.12 PREVIEW OF PREVIOUS WORKS

The point ion potential or the delta function potential is the first model potential that has ever been proposed. Rossiter (1987) expressed the local form of this potential as a sum of the Coulomb potential and a delta function potential expressed as,

$$w(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \delta(r) \tag{2.35}$$

The screened form factor of this potential has the form,

$$w_s(q) = \langle k+q\,|w(r)|\,k+q'\rangle = \frac{1}{\Omega_0}\left(-\frac{Ze^2}{\varepsilon_0 q^2} + \delta\right) \tag{2.36}$$

The repulsive interaction of the core electrons is reflected by the delta (δ) function and this is modified by a damping factor $e^{-r/R}$ such that the local potential tends to zero at large r like true pseudopotentials. In effect, the point ion potential could not be successfully applied in computations because the effective core interactions cannot fluctuate as prescribed by the delta (δ) function.

Ashcroft (1966) proposed the empty core pseudopotential in which the core electron interactions were neglected. The local form of the empty core model potential is expressed as,

$$\begin{aligned} w(r) &= 0 && r < R_c \\ &= -\frac{Ze^2}{4\pi\varepsilon_0 r} && r > R_c \end{aligned} \tag{2.37}$$

and the corresponding screened form factor is expressed as,

$$\langle k+g|w(r)|k+g'\rangle = -\frac{Ze^2}{\Omega_0\varepsilon_0 q^2}\cos(qR_c) \tag{2.38}$$

The main feature of this model potential is that the core electron interaction is neglected. This model had only a limited success in the prediction of the experimental values of binding energy of some metals. The discrepancies in the calculated values could be ascribed to the fact that the core electron interaction was not included in the model.

However, Shaw and Harrison (1967) stated that the most popular model potential has been the Heine-Abarenkov pseudopotential in which the pseudopotential is set to an arbitrary term, A_H within the core region and a Coulombic potential outside this region. A_H is an energy and angular momentum dependent term obtained from spectroscopic term values for the atom of interest. This model assumes a core radius that is radically different from the core radius of all other models, denoted by R_{HL} which is a property of the electron gas. The screened form factor of this potential is expressed as,

$$\langle k+g|w(r)|k+g'\rangle = -\frac{Ze^2}{\Omega_0\varepsilon_0 q^2}\cos(qR_H) - \frac{A_H}{\Omega_0\varepsilon_0 q^2}\left(\sin(qR_H) - qR_H\cos(qR_H)\right) \qquad (2.39)$$

The screening adopted in the calculation of the screened form factors in this model is the static Hartree dielectric function.

The optimised form of this potential has been described by Shaw (1968), in which a cut off radius R_S is chosen and the core electron interaction is set to A_S. These were chosen to avoid discontinuities in the potential at the edge of the core region. Furthermore, Shaw and Harrison (1967) carried out a systematic reformulation of the screened Heine-Abarenkov model potential. In this case, they calculated the electron density in a metal in terms of the parameters of the model potential and concluded that a major contribution to the total electron charge density is the depletion hole which is analogous to orthogonalization hole in the pseudopotential theory.

However, Rossiter (1987) concludes that in the full non-local forms, the parameters characterising the screened HA model potential depend on the orbital angular momentum quantum number and the energy of the particular quantum states. Therefore, the computed form factors are explicitly dependent on orbital angular momentum of the electrons. This further confirmed the relevance of the orbital angular momentum to the band structure of the metals considered. It however failed in providing a functional scheme for calculating metallic properties because the potentials were not self-consistent and non-transferable.

Furthermore, Hussain and Akinlade (1987) expressed the Fourier transform of a model potential in the form,

$$w(q) = -\frac{4\pi Ze^2}{\Omega_0 q^2}\left[\cos x - (\sin x - x\cos x)e^{-x}\right], \quad x = \frac{qr_s}{2} \tag{2.40}$$

A wide range of metallic properties was computed using this model potential and the results obtained showed a limited agreement with experiment. There are noticeable discrepancies in the results of the computed binding energy for metals with Z >1. For other properties however, the results show a good agreement with results of other theories.

CHAPTER THREE

3.0 RESEARCH METHODOLOGY

A self-consistent model pseudopotential has been developed from first principles considerations of the stationary state perturbation theory and the free electron gas approximation. This is based on the fact that the eigenvalues of the valence electron states shift in condensed matter systems in contrast with free atoms and therefore the core-valence response to the all-electron eigenvalues is incorporated in terms of the number density of electrons. The local pseudopotential is derived so that it depends only on parameters of the electron gas that require no fitting procedures.

This local pseudopotential was Fourier-transformed to momentum space and the Fourier components were computed for some metals that were chosen based on the availability of experimental data and results of other models. The unscreened form factor is used within the existing theoretical framework in the computation of the binding energy of these metals.

Furthermore, an appropriate screening scheme is chosen for this potential. The corresponding screened form factor is evaluated and used in calculating the monovacancy resistivity of these metals. In addition, the screened form factor is used in calculating the paramagnetic spin susceptibility of these metals using two standard methods. The calculated values are compared with experimental values and with results of other theories.

Finally, graphs of the unscreened and screened form factors of the metals under consideration are plotted as functions of the momentum transfer vector and the results obtained are discussed.

3.1 THE PROPOSED MODEL PSEUDOPOTENTIAL

Harrison (1970) and Kittel (1976) express the Fermi wave vector in the free electron approximation as

$$k_F = (3\pi^2 N_v)^{1/3} \tag{3.1}$$

where the number density N_v is given in terms of the number of valence electrons per atom, Z divided by the volume per atom, Ω_0. Consequently, the Fermi energy is obtained in terms of equation (1.5) as

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 N_v)^{2/3} \tag{3.2}$$

The average kinetic energy of electrons in the free electron approximation is expressed as

$$\langle KE \rangle = \frac{\int_0^{k_F} \left(\frac{\hbar^2 k^2}{2m}\right) 4\pi k^2 dk}{\int_0^{k_F} 4\pi k^2 dk} = \frac{3}{5}\left(\frac{\hbar^2 k_F^2}{2m}\right) = \frac{3}{5} E_F \tag{3.3}$$

The fact that ions are not isolated points, instead core electrons lie outside the nucleus means that an additional potential well is localised at the core. It is noted that outside the core region, the electron-ion interaction is represented by the Coulomb potential, $-Ze/r$.

It is assumed that the difference between the true potential of the core electrons and the Coulomb potential outside each core is denoted by a local potential $V(r)$. Since this potential is relatively weak at each core, it is treated as a perturbation of the ground state energy. Messiah (1965) and Squires (1995) showed that the first order correction to the ground state energy in stationary state perturbation theory is expressed as

$$E = \langle \psi | V(r) | \psi \rangle \tag{3.4}$$

This implies that each core shifts the energy of the valence electrons by an energy term

$$E = \int \psi^* V(r) \psi d^3 r \tag{3.5}$$

This yields a total shift in energy of the crystal per ion of

$$E_{Total} = \int N_v V(r) dV \tag{3.6}$$

In an atom at ground state, the electrons can be divided into the core states electrons and the valence state electrons. This implies for instance that a sodium atom will have ten core electrons, with configuration $1s^2\ 2s^2\ 2p^6$ and one valence electron with configuration $3s^1$ at ground state. In the metal, these atoms are arranged in a tightly packed manner such that the deep core states are localized in the crystal leaving only the valence electrons to move freely.

Since all the energy levels are completely filled and all the electron spins are completely paired within the core according to Pauli exclusion principles, the core assumes an inert gas configuration. It is assumed in this derivation that since these inert cores are localized within the atom, it is impossible for any two successive ion cores to overlap, in line with the frozen core approximation.

The above background allows for a formulation that the total number density of electrons $N(r)$ can be expressed as the sum of the core electron density $N_c(r)$ and the valence electron density $N_v(r)$ so that

$$N(r) = N_v(r) + N_c(r) \tag{3.7}$$

As a result, the average kinetic energy is expressed in terms of the total number density of electrons $N(r)$, using equation (3.7). However, it is noted that the average kinetic energy in the free electron gas approximation is expressed only in terms of the number density of valence electrons only.

Substituting equation (3.7) into equation (3.1) to obtain,

$$k_F = 3\pi^2 \left(N_v(r) + N_c(r) \right)^{1/3} \tag{3.8}$$

so that the Fermi energy is written in terms of equation (3.7) as,

$$E_F = \frac{\hbar^2}{2m}\left\{\left(3\pi^2\right)^{2/3}\left(N_v(r)+N_c(r)\right)^{2/3}\right\} \tag{3.9}$$

The average kinetic energy of an electron is therefore expressed as,

$$\langle KE\rangle = \frac{3}{5}E_F = \frac{3}{5}\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(N_c(r)+N_v(r)\right)^{2/3}\right) \tag{3.10}$$

Multiplying equation (3.10) by equation (3.7), and integrating over the crystal volume yields the total electronic kinetic energy as,

$$KE_{Total} = \int \frac{3}{5}E_F N(r)dV \tag{3.11}$$

$$KE_{Total} = \int \frac{3}{5}\left\{\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(N_v(r)+N_c(r)\right)^{5/3}\right\}dV \tag{3.12}$$

It is noteworthy to state at this point that the total electronic kinetic energy is calculated in terms of both the core electrons and the valence electrons contrary to the free electron approximation. This implies that, as a departure from usual practice, the otherwise 'bound' core electrons contribute to the total kinetic energy. This apparent absurdity is physically justifiable if it is noted that within the core region, the $N_c(r) >> N_v(r)$, hence a power series expansion of equation (3.12) in terms of $Nc(r)$ yields,

$$\begin{aligned} KE_{Total} = {} & \frac{3}{5}\left(\int_0^V \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{5/3}(r)dV\right) + \frac{3}{5}\left(\frac{5}{3}\int_0^V \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{2/3}(r)N_v(r)dV\right) + \\ & \frac{3}{5}\left(\frac{5}{9}\int_0^V \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{-1/3}(r)N_v^2(r)dV\right) + \frac{3}{5}\left(-\frac{10}{162}\int_0^V \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{-4/3}(r)N_v^3(r)dV\right) + \dots \end{aligned} \tag{3.13}$$

This reduces to,

$$KE_{Total} = \frac{3}{5}\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\int_0^V N_c^{5/3}(r)dV\right) + \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\int_0^V N_c^{2/3}(r)N_v(r)dV + \frac{1}{3}\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\int_0^V N_c^{-1/3}(r)N_v^2(r)dV\right) +$$
$$-\frac{1}{27}\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\int_0^V N_c^{-4/3}(r)N_v^3(r)dV\right) + \ldots \qquad (3.14)$$

A comparison of equations (3.6) and (3.14) indicates that the first term of equation (3.14) is the free ion kinetic energy, which is similar to the kinetic energy of a free atom. The second term and higher order terms give a shift in the total kinetic energy exactly as if a potential well of the form,

$$W(r) = V_1(r) + V_2(r) + V_3(r) + \ldots \qquad (3.15)$$

has been introduced. In this case, the atomic-like potentials are expressed as,

$$V_1(r) = \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{2/3}(r) \qquad (3.16)$$

$$V_2(r) = \frac{1}{3}\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{-1/3}(r)N_v(r)\right) \qquad (3.17)$$

$$V_3(r) = -\frac{1}{27}\left(\frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3} N_c^{-4/3}(r)N_v^2(r)\right) \qquad (3.18)$$

It is noted that if the truncation point of the power series increases, the contributions from the valence electrons increase exponentially and vice versa. Furthermore, it is observed that a linear combination of the atomic-like potentials lead to a cancellation of the repulsive potential associated with the high kinetic energy of the electrons close to the positive ions in agreement with the Phillips-Kleinman theorem.

A combination of equations (3.16), (3.17), (3.18) and higher order terms show that the shift in total energy is caused by a pseudopotential, relaxed across the core as,

$$W(r) = K \sum_{\substack{\text{occupied}\\ \text{states}}} N_c^{\frac{2-3t}{3}} N_v^{t} \qquad (3.19)$$

where K is a constant that varies with the truncation point. On the other hand, if instead of the kinetic energy being obtained explicitly in terms of the total number density *N(r)* as shown above, it is computed as a sum of the contributions due to the 'free' valence electrons, and the 'bound' core electrons respectively; then the Fermi energy becomes,

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(N_c(r)\right)^{2/3} + \frac{\hbar^2}{2m}\left(3\pi^2\right)^{2/3}\left(N_v(r)\right)^{2/3} \qquad (3.20)$$

which under estimates the Fermi energy and consequently over estimates the potential. Therefore, carrying out the entire process of derivation again using equation (3.20) yields results that are inconsistent with the observed shifts in energy.

This inconsistency arises from the fact that $[N_v(r)+N_c(r)]^{2/3} \neq N_v^{2/3} + N_c^{2/3}$ as observed from comparing equations (3.9) and (3.20). Therefore, a local pseudopotential of the form,

$$\begin{aligned} V(r) &= W(r) && r \langle r_s \\ V(r) &= \frac{-Ze^2}{4\pi\varepsilon_0 r} && r \rangle r_s \end{aligned} \qquad (3.21)$$

is hereby proposed. The discrete Fourier transform of this potential is evaluated using Bracewell (1986) as,

$$\phi_b(q) = \frac{1}{\Omega}\int d^3r W(r)\exp(-iq.r) \qquad (3.22)$$

where q is the momentum transfer vector, Ω is the atomic volume and *W(r)* is the local pseudopotential. However, for computational applications the potential varies with the momentum transfer vector q, in reciprocal space. Equation (3.22) transforms to,

$$\phi_b(q) = -\frac{1}{\Omega}\sum_{0}^{r_s}\frac{4\pi Ze^2}{q^2}\exp(-iq.r) \tag{3.23}$$

where the integral sign is replaced by the summation over the atomic volume and the effective ionic radius is the radius of the Wigner–Seitz sphere, r_s.

It is observed that within the core region, the effective interaction *W(r)* is short ranged and as such, the Coulombic potential outside this region is constantly dampened by this interaction. Expanding equation (3.23) using Euler relation and noting that Harrison (1970) and Hussain and Akinlade (1987) express the Fourier transform of the Coulomb potential as $(-4\pi Ze^2/q^2)$ to obtain,

$$\phi_b(q) = \quad -\frac{4\pi Ze^2}{\Omega q^2}\cos(\frac{qr_s}{2}) \quad + \quad i\frac{4\pi Ze^2}{\Omega q^2}\sin(\frac{qr_s}{2}) \tag{3.24}$$

However, since the potential is real valued, the imaginary component of the potential is neglected. Also, to ensure that the potential approaches the Coulomb potential in the short wavelength limit (low momentum transfer vector) and zero in the long wavelength limit (large momentum transfer vector), Hussain and Akinlade (1987) showed that an exponential term must be added. Therefore, the Fourier component of the relaxed core model pseudopotential has the form,

$$\phi_b(q) = -\frac{4\pi Ze^2}{\Omega q^2}\cos(\frac{qr_s}{2})\exp(\frac{-qr_s}{2}) \tag{3.25}$$

A FORTRAN 77 program was developed to calculate the Fourier components of this model pseudopotential at momentum transfer vectors ranging from 0.1 to 5.0 for sixteen metals that were chosen based on the availability of experimental data.

3.2 SCREENING CONSIDERATIONS

The ions contain electrons that are closely bound to the nucleus. The 'free' valence electrons flow through the ions under the control of two major influences. First, the electrostatic attractive interaction of the positive ions and second, a complicated response to those electrons 'bound' to the nuclei. This second influence has been treated mathematically as if it were an electrostatic influence like the first, except that it is an electrostatic repulsive interaction, which partially cancels the electrostatic attractive interaction. The net effect is quite small, and it is called the pseudopotential.

An electron passing through an ion is therefore considered as being deviated by the relaxed core pseudopotential. However, the ion does not suddenly exert an influence as the electron crosses the ionic boundary. The ions are positively charged and the electron gas is mobile, therefore, the ions exert a long-ranged force on the gas by attracting the electrons to themselves. Meanwhile, the electrons are repelling each other in line with Pauli exclusion principles suggesting that a complex balance of forces has set in.

The ultimate effect of this balance of forces is to envelope each ion in an electron cloud. Since this cloud is negatively charged, it neutralizes the electrostatic effect of the positive charges of the ions completely at large distances and less completely at small distances. The cloud of electrons piled up near an ion is called the ion screening cloud. Its total effect on an approaching electron of a given pseudopotential is called the screened pseudopotential.

Harrison (1966), Animalu (1977), Hussain and Akinlade (1987), Horsfield and Ashcroft (1993), and Chelikowsky (2000) suggest that the screened pseudopotential is equivalent to the screened form factor. This is obtained in the self-consistent field approximation as the ratio of the bare ion pseudopotential and the dielectric function. In metals, the system of ion-core and valence electrons is electrically neutral. Moreover, the fact that the electrons are highly mobile shows that if an excess of positive or negative charge appears in some locality in any of these systems, the electrons will quickly rearrange themselves so as to maintain electrical neutrality. These rapid motions of the electrons will therefore screen out any Coulomb force due to the localised charge.

Harrison (1970) showed that if an electron system is subjected to a weak applied potential due to the introduction of an electron, then there will be a fluctuation in the electron density. As a result, if the potential is sufficiently weak, the response of the electron density to the applied potential is linear. The fluctuation in electron density gives rise to an additional potential seen by the electrons. This is called the screening potential. There is no distinction between the direct and the conjugate potentials because the electron states are distorted by the net pseudopotential causing a modification of the charge density, hence there is a strong need for a choice of appropriate screening parameters for the relaxed core model pseudopotential.

It is however observed in this work that the self-consistent solution of the screening problem using the static Hartree dielectric function fails completely in reproducing the screened form factors of the various metals considered. Also, the Hubbarb screening scheme (Horsfield and Ashcroft, 1993) fails to reproduce the observed screened form factors in reciprocal space. It instead introduces cusps and localised discontinuities in the form factor, which is difficult to justify under the pseudopotential perturbation theory.

On the other hand, the screening scheme that works effectively for this model pseudopotential is the modified Hartree dielectric function,

$$\varepsilon(q) = \left(1 + \frac{0.9273}{k_f}\right)(\varepsilon_{Al} - 1) \qquad (3.26)$$

where k_f is the Fermi wavevector of the metal whose dielectric constant at momentum transfer vector q, is being calculated and 0.9273 is a constant representing the Fermi wave vector of aluminium, ε_{Al} is the dielectric constant of aluminium at momentum transfer vector, q.

This screening scheme successfully reproduces the features of the screened form factor in reciprocal space without localised oscillations in the core region. This further shows that there are no discontinuities in the occupation of states within the core region despite the relaxation condition on the ion core and therefore suggesting that there are no localised charges within the region. Harrison (1966) showed that the dielectric function of equation (3.26) uses the tabulated dielectric constants of aluminium at discrete momentum transfer vectors for computing the dielectric constants of other elements.

Hence, using Harrison (1970), Behari (1973), Hussain and Akinlade (1987) and Ashcroft and Horsefield (1993), the response of the electrons to the relaxed core model pseudopotential or the screened form factor is computed using the relation,

$$u_b(q) = \frac{\phi_b(q)}{\varepsilon(q)} \qquad (3.27)$$

A FORTRAN 77 program was developed to calculate the unscreened form factor, the screened form factor and the dielectric constants for sixteen metals at momentum transfer vectors ranging from 0.1 to 5.0 using equations (3.25), (3.26) and (3.27). The results obtained are used in calculating some physical properties of metals.

3.3 PHYSICAL PROPERTIES OF METALS

3.3.1 BINDING ENERGY

Saxena and Bhattacharya (1968) had carried out the quantum mechanical treatment of binding energy within the pseudopotential framework and showed that the functional form of the expression adopted in the calculation of binding energy is given by,

$$BE = \frac{0.737}{r_s^2}\left(\frac{2}{3}\right)\frac{0.916 + 1.752Z^{\frac{2}{3}}}{r_s} - 0.105 + 0.031\ln(r_s) +$$

$$16\pi^{\frac{2}{3}}(12\pi^2)^{\frac{1}{3}}\frac{1}{r_s^4}\sum_{q\neq 0}^{5.0}\frac{|\phi_b(q)|^2}{2x}\ln\left|\frac{1+x}{1-x}\right| \qquad where \quad x = \frac{q}{2k_f} \tag{3.28}$$

where r_s is the radius of the Wigner-Seitz sphere, Z is the valence, $\phi(q)$ is the unscreened form factor, k_f is the Fermi wave vector and x is a measure of the change in momentum across the reciprocal lattice. A FORTRAN 77 program was developed to calculate the binding energy using equation (3.25) and the results are presented in Table 1.

3.3.2 MONOVACANCY RESISTIVITY

The expression adopted in calculating the monovacancy resistivity of metals is that of Ziman (1961). This is expressed as,

$$\rho_v = \frac{3\pi\Omega}{4\hbar e^2 v_f^2 k_f^4}\int_0^{2k_f}|u_b(q)|^2 q^3 dq \tag{3.29}$$

where $\hbar$ is the normalised Planck constant, $u_b(q)$ is the screened form factor, e is the electronic charge, q is the momentum transfer vector, Ω is the atomic volume, and v_f and

k_f are the Fermi velocity and wavevector respectively. A separate FORTRAN 77 program was developed to calculate the monovacancy resistivity using equation (3.29) and the results obtained were tabulated in Table 2.

3.3.3 PARAMAGNETIC SPIN SUSCEPTIBILITY

In calculating the paramagnetic spin susceptibility using this model pseudopotential, the expression of Abe (1963), is adopted within two standard approaches. This is given by,

$$\chi = \left(\frac{\Delta E_{kinetic\,energy}}{\Delta E_o} \right) \chi_o \qquad (3.30)$$

where χ_o is the paramagnetic spin susceptibility of the electron gas at absolute zero, $\Delta E_{kinetic\,energy}$ is the change in kinetic energy of the electron gas and ΔE_o is the total change in the energy of the electron gas with polarization. The change in total energy ΔE_o, is evaluated as the sum of the changes in the kinetic energy, the exchange energy, the correlation energy and the electron-lattice energy.

Hence, the total change in the energy of the electron gas is given as,

$$\Delta E_o = \Delta E_{kinetic\,energy} + \Delta E_{exchange} + \Delta E_{correlation} + \Delta E_{electron-lattice} \qquad (3.31)$$

where $\Delta E_{kinetic\,energy}$, $\Delta E_{exchange}$, $\Delta E_{correlation}$, $\Delta\ E_{electeron-lattice}$ are the changes in the kinetic energy, the exchange energy, the correlation energy and the electron-lattice energy respectively.

However, two approaches are adopted in calculating the change in correlation energy of the electron gas in this work. Firstly, the expression of Brueckner and Sawada (1958) is used and secondly, the expression of Bohm and Pines, Pines (1954). The results of the change in correlation energy obtained from these approaches are used in calculating the paramagnetic spin susceptibility for the metals under consideration. Hussain and Akinlade (1987) gave the expressions for the changes in kinetic energy, exchange energy, correlation energy and electron-lattice energy respectively as,

$$\Delta E_{\text{kinetic energy}} = \frac{4.91}{r_s^2} \tag{3.32}$$

$$\Delta E_{\text{exchange energy}} = -\frac{0.814}{r_s} \tag{3.33}$$

$$\Delta E^{BS}_{\text{correlation energy}} = 0.162 - 0.0432 r_s - 0.0032 r_s^{-\frac{1}{2}} \tag{3.34}$$

$$\Delta E^{BP}_{\text{correlation energy}} = -0.0676 \ln r_s + 0.225 \tag{3.35}$$

$$\Delta E_{\text{electron-lattice energy}} = -\frac{2r_s^2}{9(12\pi^2)^{\frac{1}{3}}} \sum_{q=0.1}^{5.0} \frac{|\phi(q)|^2}{x^2-1} \left\{ 1 + \frac{1-x^2}{2x} \ln\left|\frac{1+x}{1-x}\right| \right\} \quad \textit{where} \quad x = \frac{q}{2k_f} \tag{3.36}$$

where $\Delta E^{BS}{}_{correlation}$ is the Brueckner-Sawada expression of the change in correlation energy of an electron gas with polarization and $\Delta E^{BP}{}_{correlation}$ is the Bohm -Pines expression of the change in the correlation energy of an electron gas with polarization.

A FORTRAN 77 program was developed to calculate the paramagnetic spin susceptibility using the Brueckner-Sawada and Bohm-Pines expressions for the change in correlation energy and the results obtained are presented in Table 3. The change in electron-lattice energy is calculated using equation (3.36), where $\phi_b(q)$ is the unscreened form factor.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

In this chapter, the results obtained for the proposed unscreened and screened form factors, the binding energy, the monovacancy resistivity and the paramagnetic spin susceptibility are presented and discussed.

4.1 THE UNSCREENED MODEL PSEUDOPOTENTIAL AND SCREENED MODEL PSEUDOPOTENTIAL

The results of the calculated unscreened form factors, the modified Hartree dielectric constants and the screened form factors at momentum transfer vectors ranging from 0.1 to 5.0 for sixteen metals that were chosen based on the availability of experimental results and results of other theories are used in calculating some physical properties of metals.

Graphs of the unscreened and the screened form factors are plotted as functions of the momentum transfer vector for these metals. The results obtained are as shown in figures (1-5) and figures (6-10) respectively. Figures (1–5) and (6-10) show the variations of the unscreened and the screened form factors with momentum transfer vector for alkali, alkaline-earth, trivalent, base and heavy metals respectively.

It is observed from figures (1-5) that the unscreened form factor approaches the zero limits in the region $0.5k_f < q < 5.0k_f$. In addition, it is also observed that there is a deep attractive potential within the region $0 < q < 0.5k_f$ that represents the core electron interaction effect for these metals. This replicates the general property of the pseudopotentials in momentum space, because the form factor assumes the periodic structure of the lattice in good agreement with the Bloch theorem.

It is also observed in figures (6–7) that the screened form factor has inflexions at points on the reciprocal lattice where $q=k_f$ and at $q=2.5k_f$ for alkali and $q = 2.0k_f$ and at $q = 5.0k_f$ alkaline-earth metals. However, at large momentum transfer vectors, the screened form factor drops to zero as expected. Figure (8) shows inflexions at points where $q = 2.5k_f$ and $q = 3.0k_f$ for trivalent metals. Similarly, it is observed from figure (9) that the form factor follows almost the same pattern for base metals. The inflexion occurs at $q = 2.6k_f$ and $q = 3.5k_f$ for the elements chosen and the form factor also drops rapidly to zero at the large momentum transfer vector limits.

Finally, figure (10) shows that there is a slight shift in the points at which inflexion occurs for heavy metals. This occurs at $q = 3.0k_f$ and $6.0k_f$. It is therefore observed from the above results that points of occurrence of inflexions in the screened form factor increases with increasing valence. This is because the core electron interaction effect is stronger in metals of higher valences, which suggests that the potential becomes stronger for metals with large ion cores and otherwise for smaller ion cores.

Generally, the calculation of the true pseudopotential for virtually all metals would be a considerable task and of doubtful significance except the effects of spin-orbit interaction are explicitly included. It is therefore anticipated that the coupling of the angular momentum and spin for all electron states in the metals considered would enter the theory indirectly through the parameters of the perturbation potential as suggested by Behari (1973).

In the formulations above, the whole solid-state calculations are done in terms of the plane waves basis set and therefore no partial waves derived from isolated atoms are necessary. As a result, there is no need for an arbitrary cut-off kinetic energy for expanding the plane wave basis, which suggests a perfect convergence of total kinetic energy. This is because the model pseudopotential is simulated in terms of the shift in the kinetic energy of ground state atoms of metals.

In addition, the deep core states have been relaxed and accommodated to the crystal environment in line with the frozen core approximation. It is noted that the transformation from the all-electron quantities to the corresponding pseudopotential quantities are directly dependent on the charge density in terms of the number density which is a necessary input in the *ab initio* scheme of pseudopotential generation.

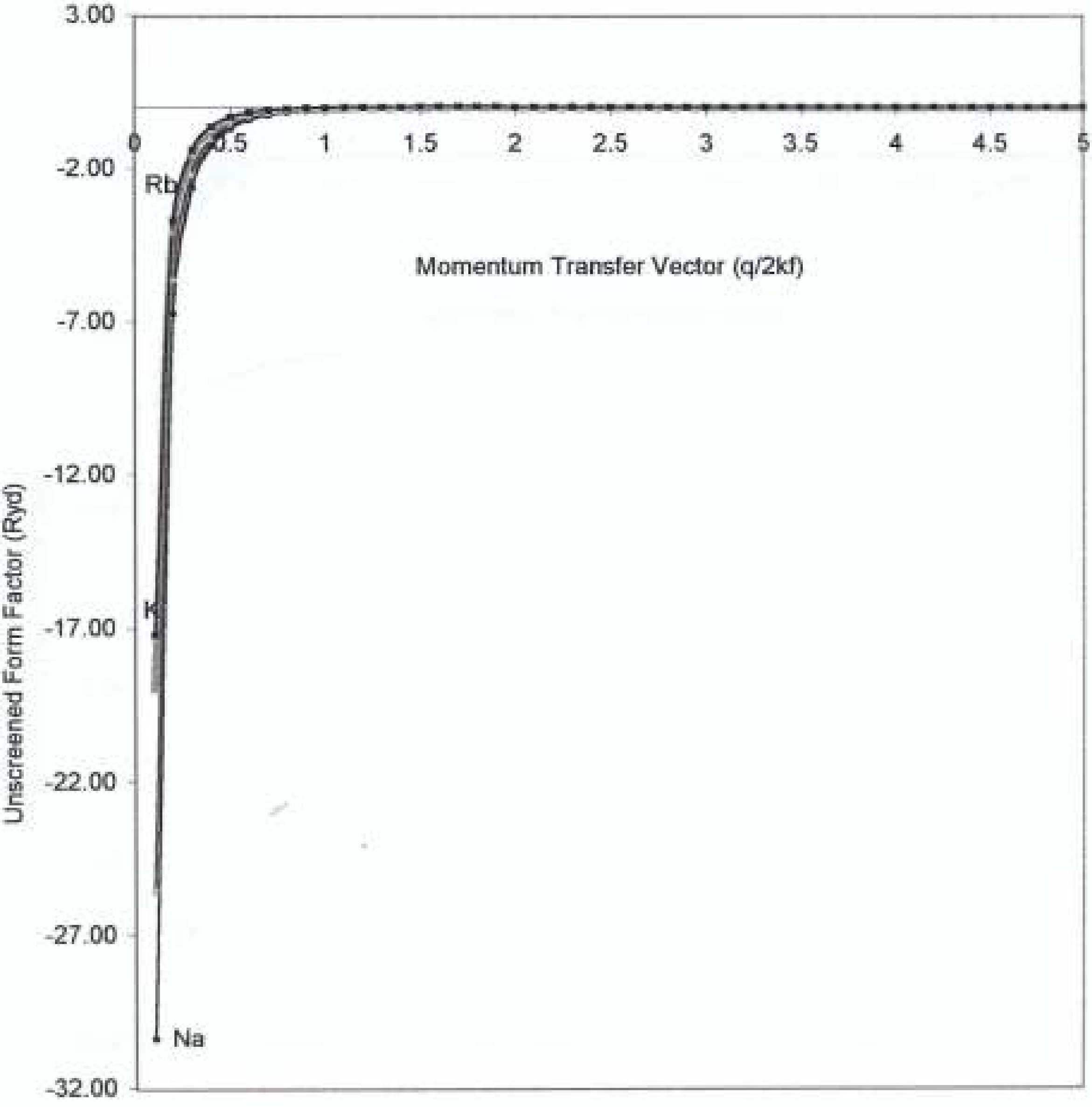


Figure 4.1: A graph of the unscreened form factor against momentum transfer vector for alkali metals.

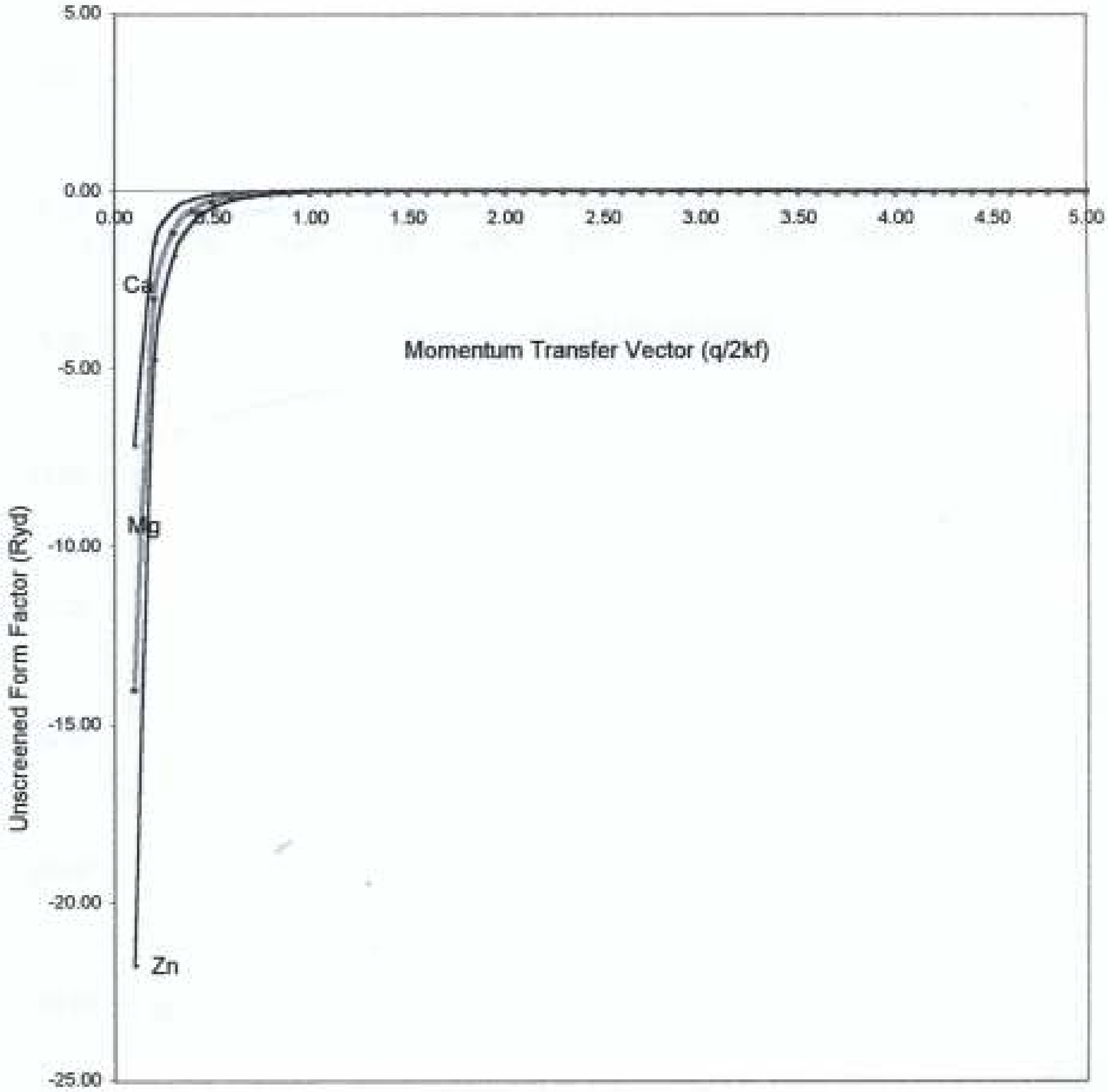


Figure 4.2: A graph of unscreened form factor against momentum transfer vector for alkaline earth metals.

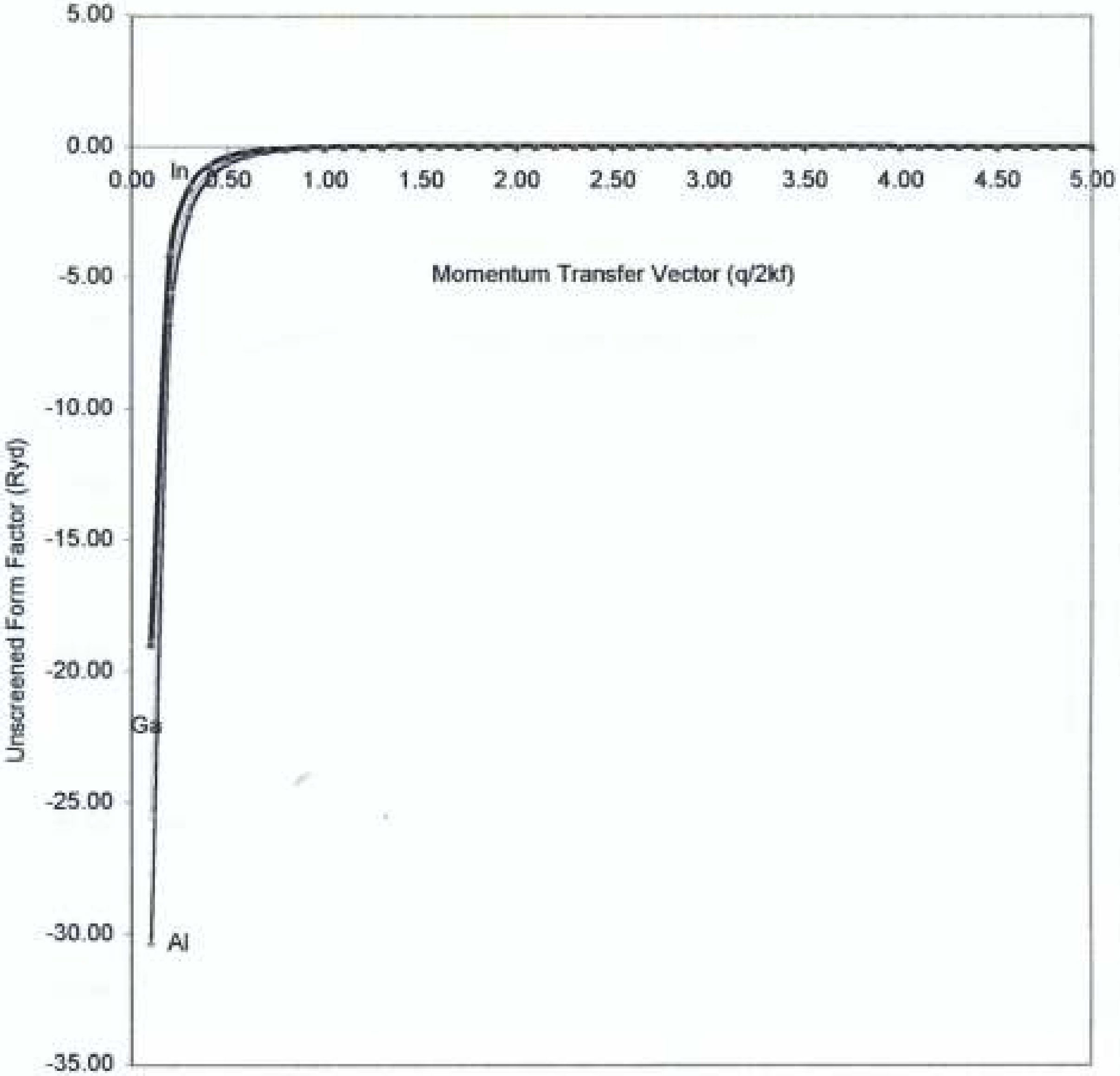


Figure 4.3: A graph of the unscreened form factor against momentum transfer vector for some trivalent metals.

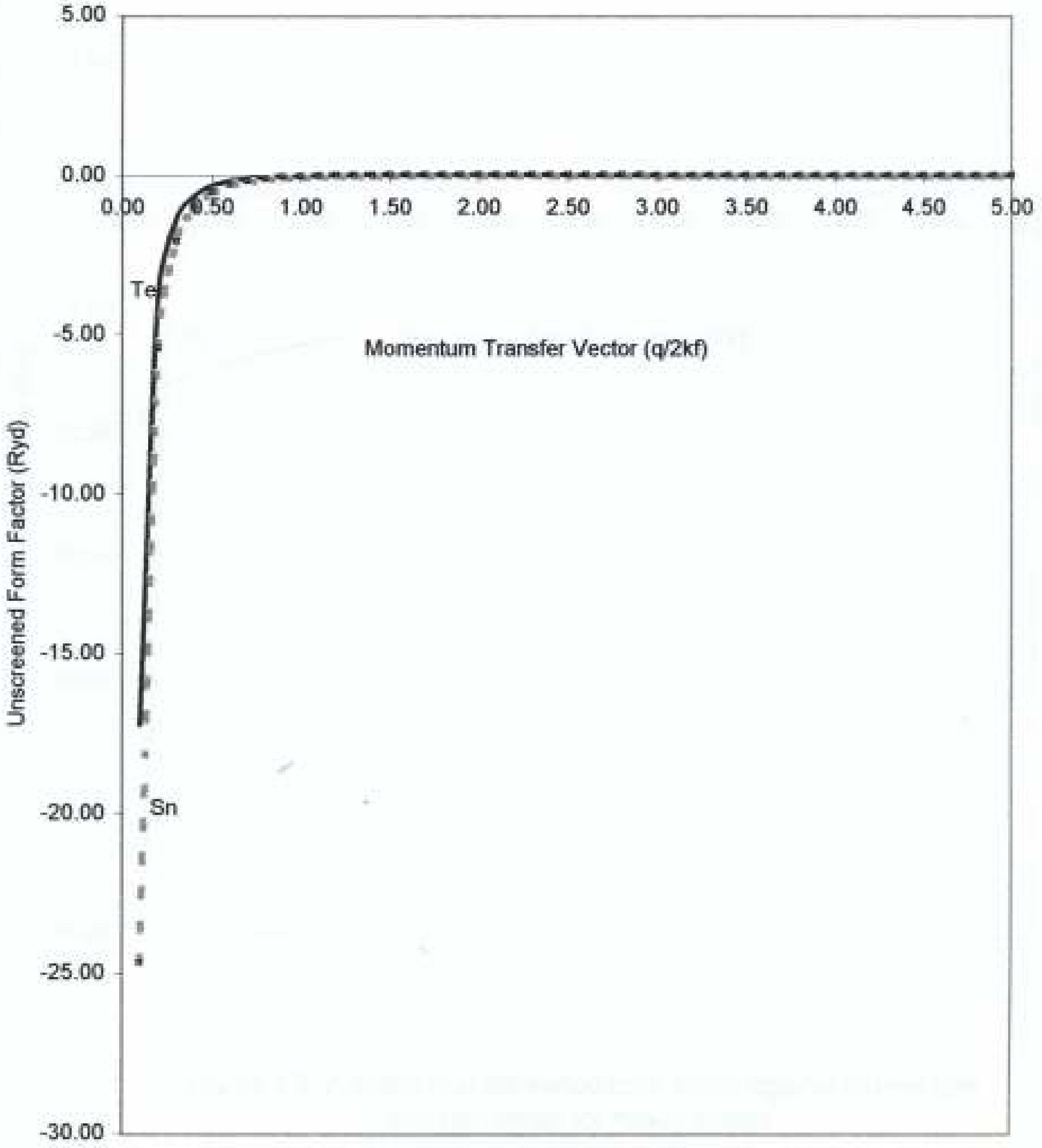


Figure 4.4: A graph of unscreened form factor against momentum transfer vector for base metals.

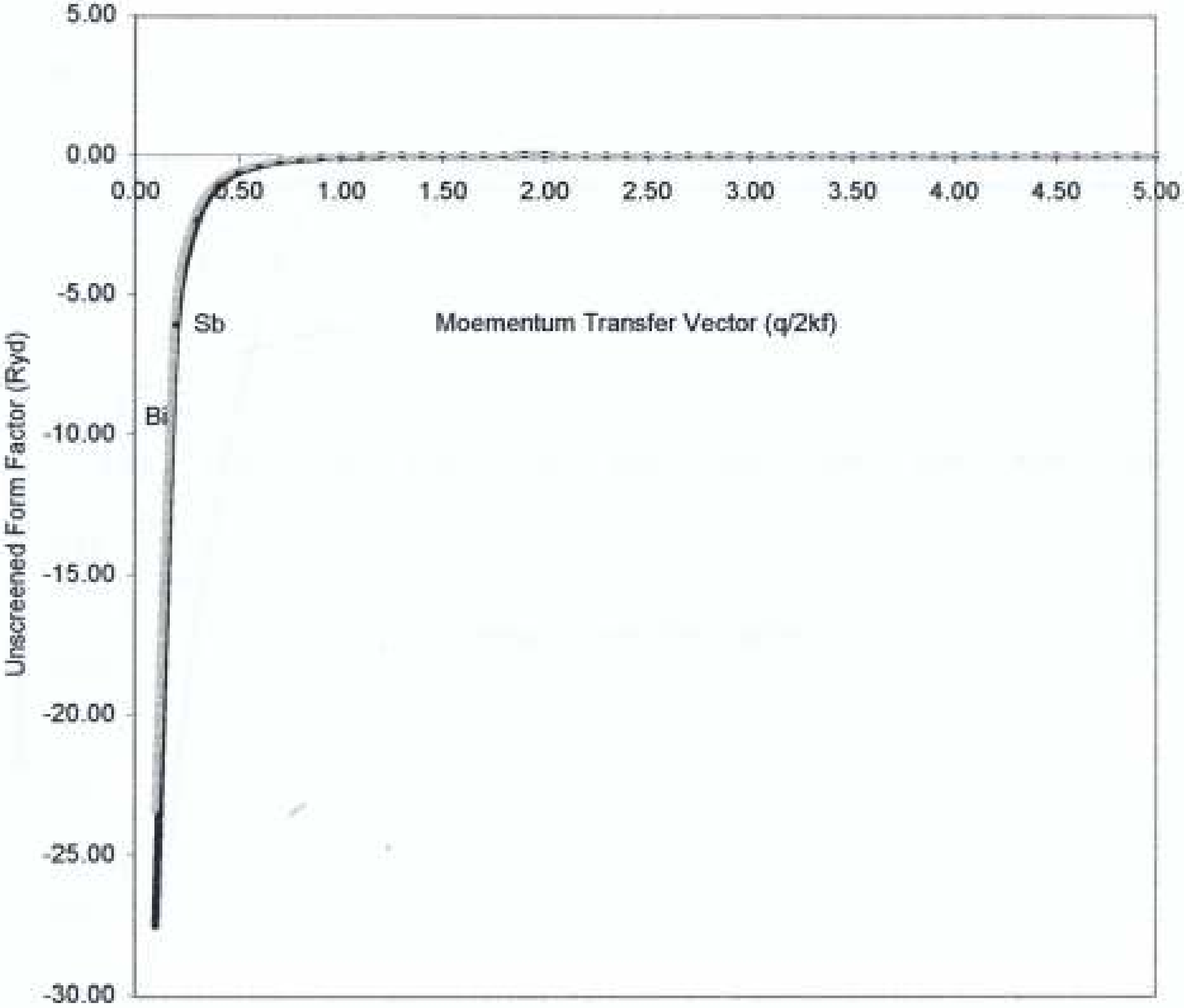
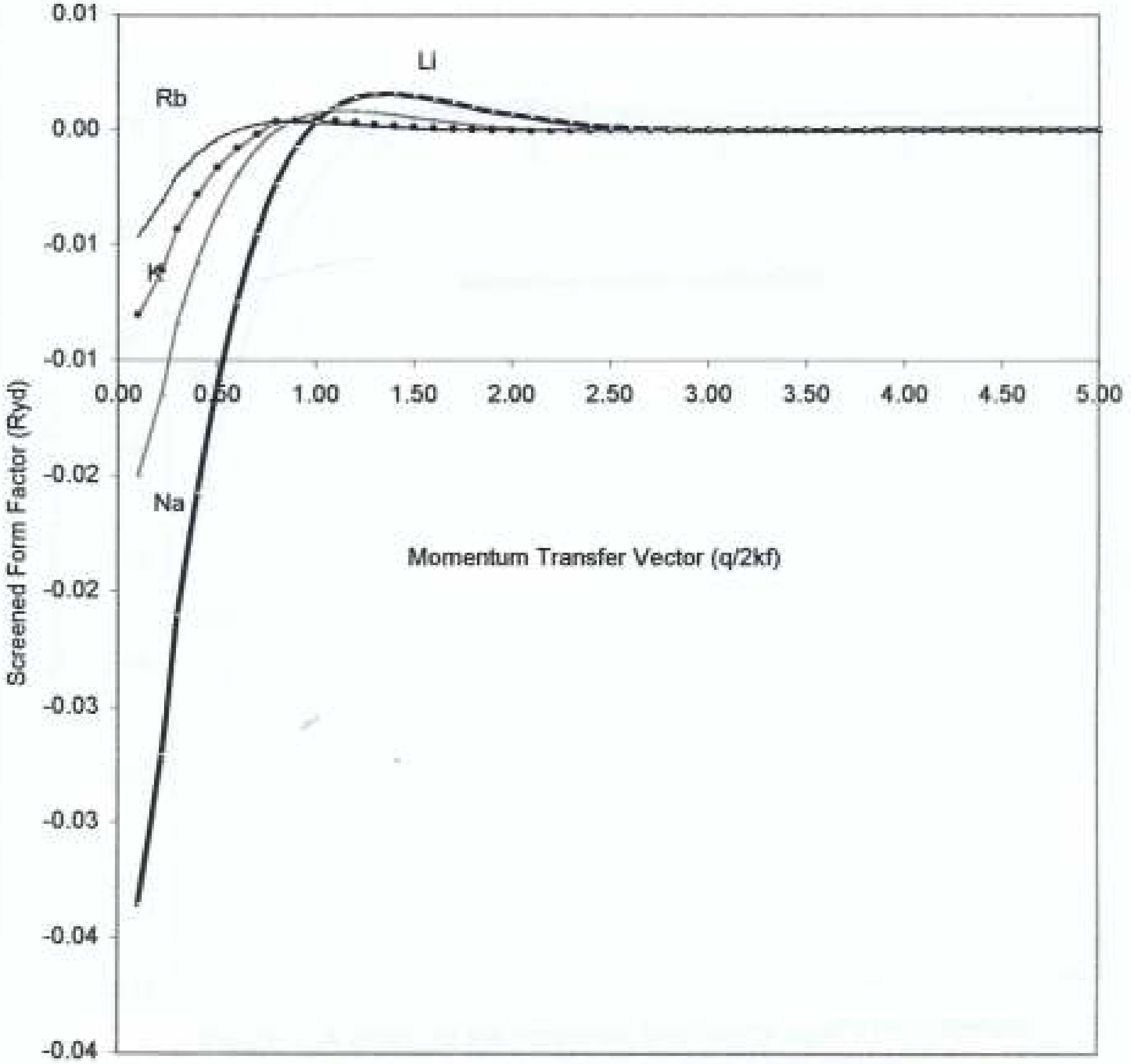


Figure 4.5: A graph of unscreened form factor against momentum transfer vector for heavy metals.



Fiigure 6: A graph of screened form factor against momentum transfer vector for alkali metals.

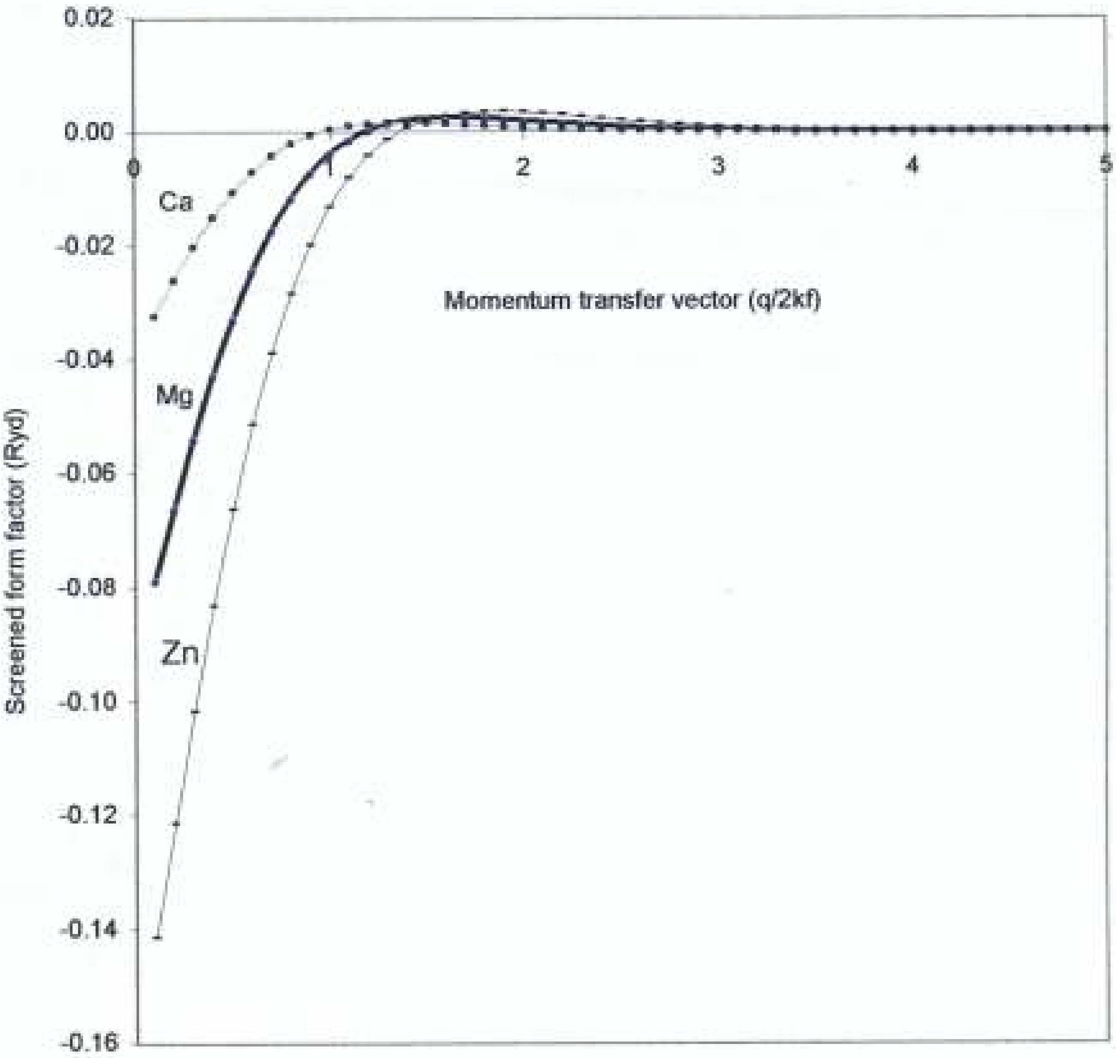


Figure 7. A graph of the screened form factor against momentum transfer vector for some alkaline earth metals.

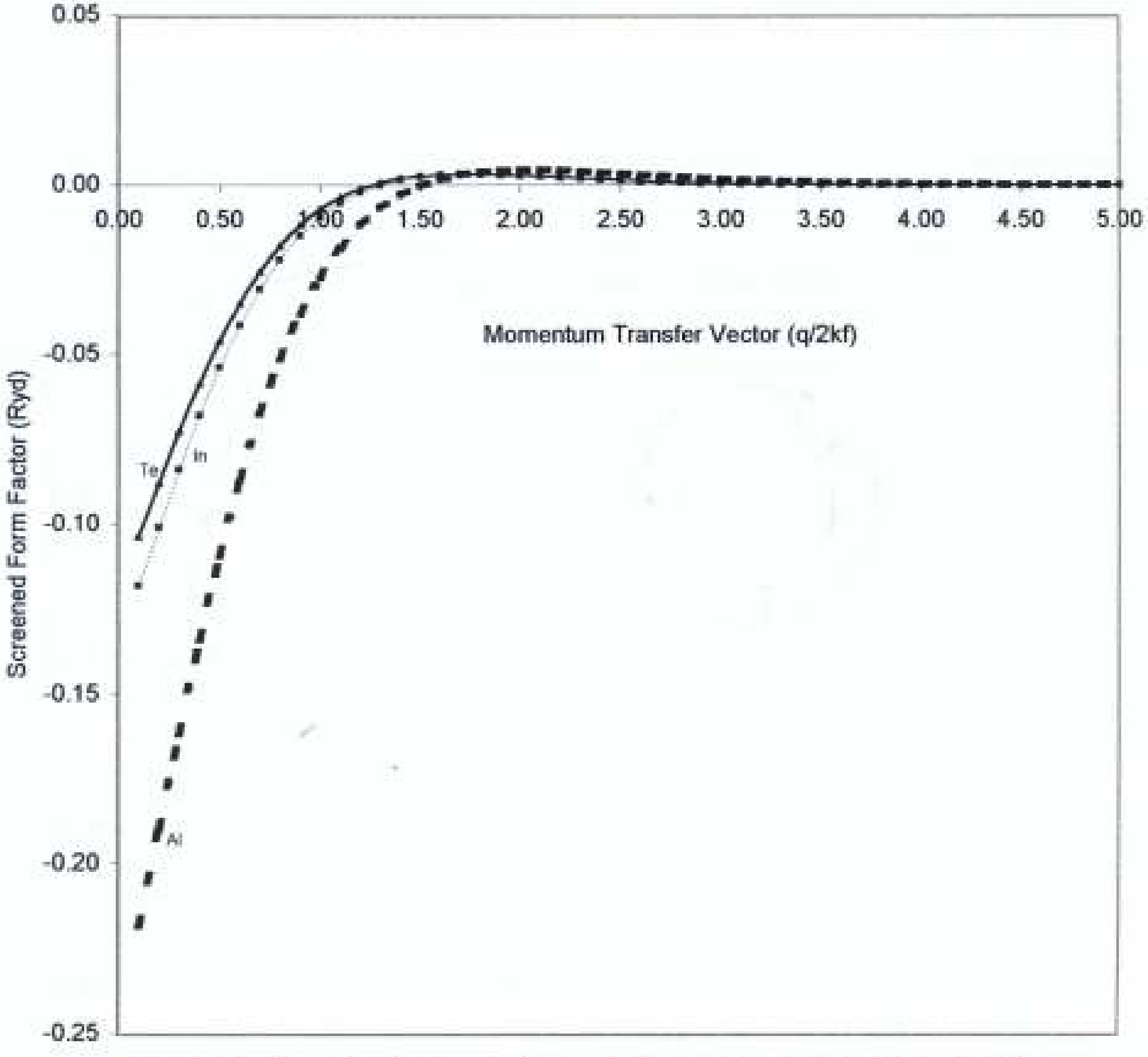


Figure 8: A graph of screened form factor against momentum transfer vector for some trivalent Metals.

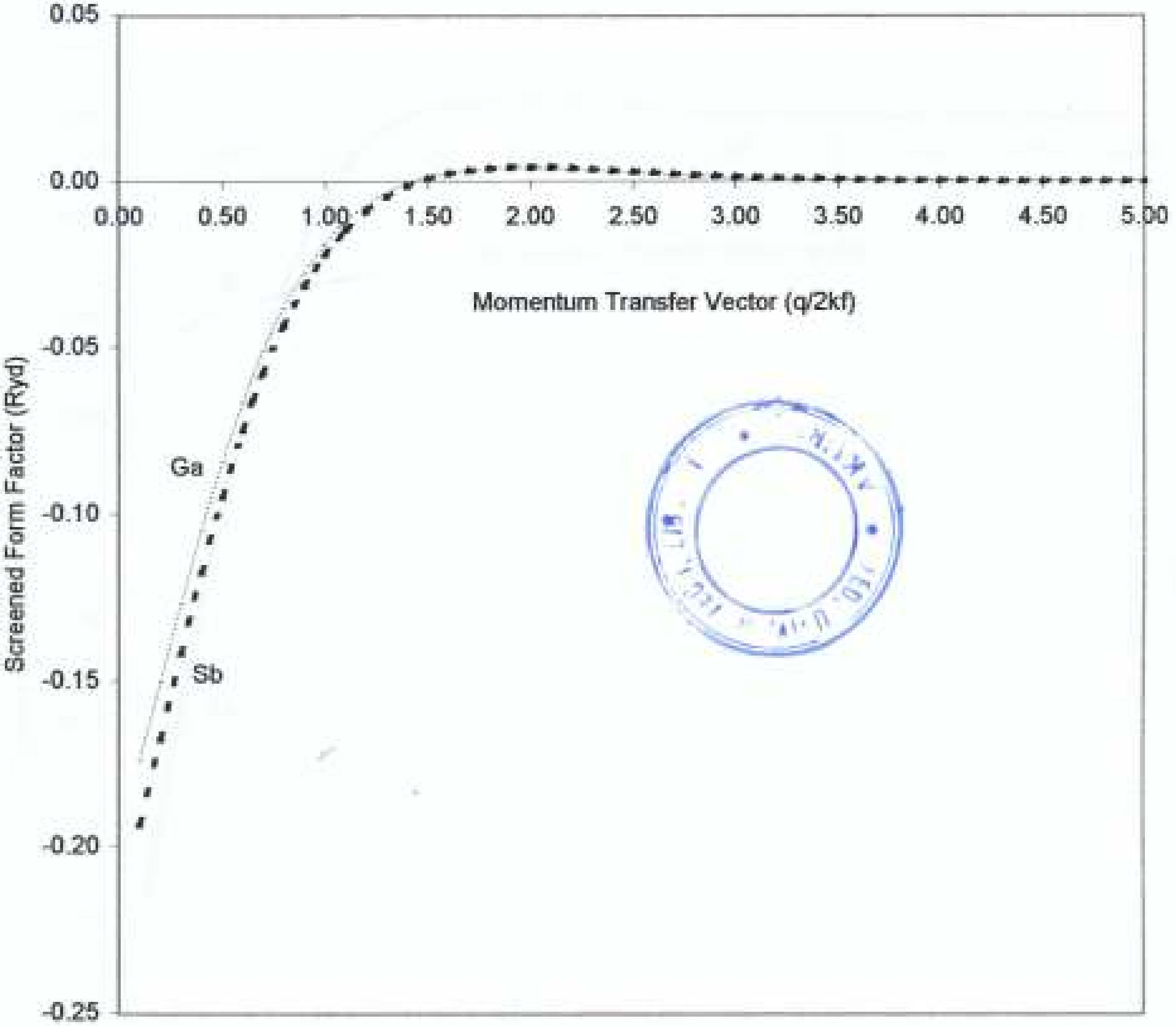


Figure 9: A graph of screened form factors against momentum transfer vector for base metals.

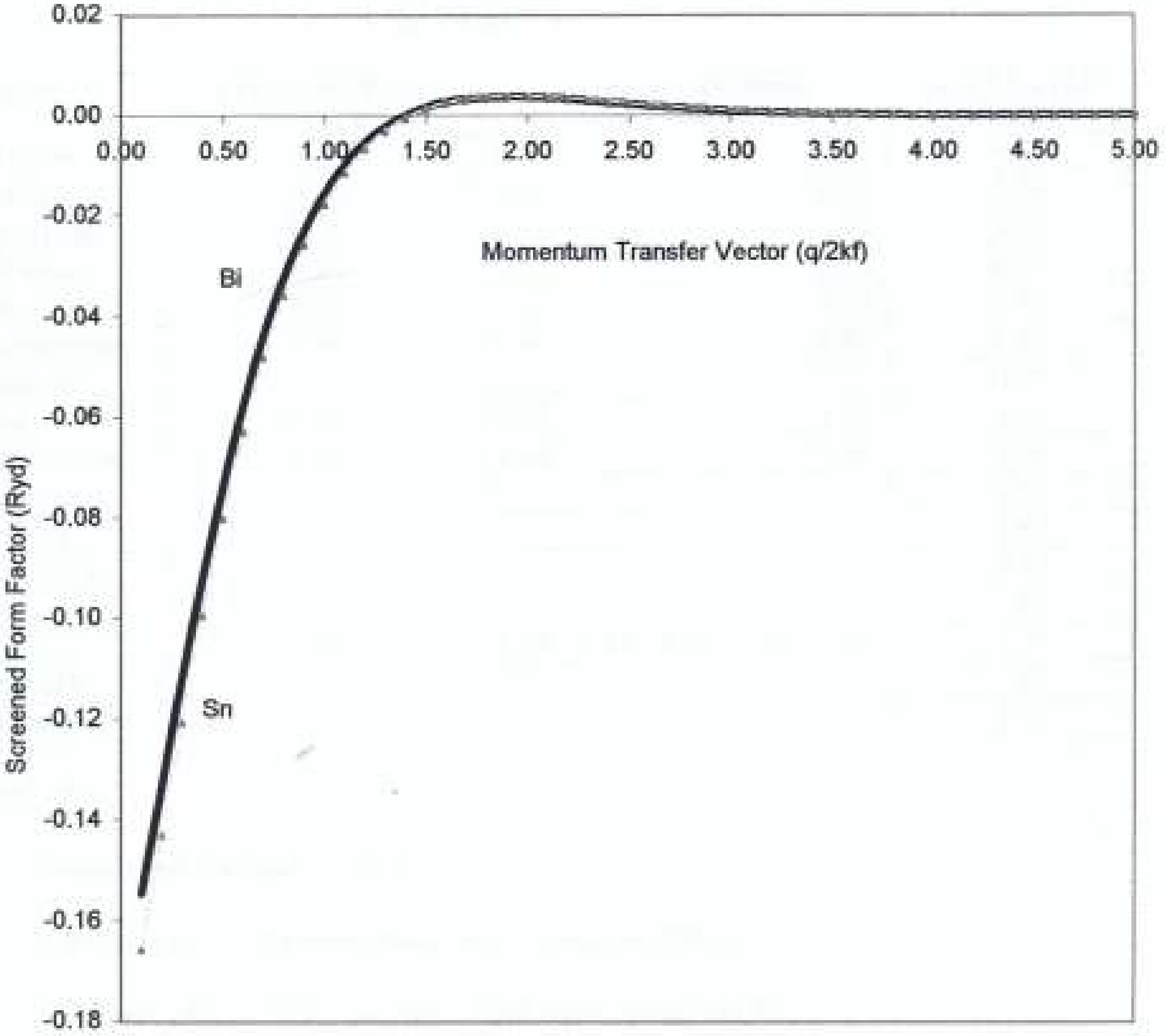


Figure 10: A graph of the screened form factor against momentum transfer vector for heavy metals.

4.2 BINDING ENERGY

The binding energy was calculated using the proposed model and the results obtained were tabulated as shown in Table 1 below.

TABLE 1. THEORETICAL AND EXPERIMENTAL VALUES OF BINDING ENERGY OF SOME METALS
(-Rydbergs/Electron)

ELEMENT	EXPERIMENTAL VALUE	OTHER THEORIES					CALCULATED VALUE
		/A/	/B/	/C/	/D/	/E/	
Lithium	0.51	0.53				0.56	0.51
Sodium	0.46	0.47				0.45	0.46
Potassium	0.39	0.39				0.38	0.39
Rubidium	0.37	0.37				0.34	0.37
Caesium	0.35	0.35				0.32	0.35
Magnesium	0.89	0.84				0.86	0.89
Calcium							0.97
Zinc	1.05	0.85				1.10	1.05
Aluminium	1.38	1.06				1.41	1.38
Gallium							1.32
Indium							0.83
Tellurium							0.70
Tin							1.59
Lead	1.79	1.33	1.88	2.03	1.24	1.55	1.79
Bismuth							1.81
Antimony							2.22

KEY: (I)

/A/ - Hussain and Akinlade (1987).

/B/ - J. Behari (1973): Random Phase Approximation (RPA).

/C/ - J. Behari (1973): Self-Consistent Field Approximation (SC).

/D/ - J. Behari (1973).

/E/ - Ashcroft and Langreth (1967).

KEY: (II) Experimental values: Animalu (1977), Hussain and Akinlade (1987).

The values of binding energy obtained using this model agree perfectly with the experimental values for elements of all valences as a remarkable improvement on the previous works. The discrepancies in the calculated values of the binding energy of metals with $Z > 1$ observed in other theories has been nicely resolved by using the 'relaxed core' model pseudopotential. There is also a remarkable improvement on the accuracy of the calculated values of the binding energy of metals with $Z = 1$ over the previous works.

4.3 MONOVACANCY RESISTIVITY

The monovacancy resistivity was calculated using the proposed model and the results obtained were tabulated as shown in Table 2 below.

TABLE 2. THEORETICAL AND CALCULATED VALUES OF THE MONOVACANCY RESISTIVITY OF SOME METALS (μΩcm)

ELEMENT	OTHER THEORIES						CALCULATED VALUE
	/1 /	/2 /	/3/	/4 /	/5/	/6/	
Lithium		0.40					0.40
Sodium	0.67	0.57	0.77				0.56
Potassium	0.98	0.85	1.00				0.87
Rubidium	1.06	0.95					1.02
Caesium	1.21	0.63					0.61
Beryllium		0.34					
Magnesium		0.54					0.55
Calcium							0.70
Zinc							0.73
Aluminium	0.44	0.50	0.55				0.52
Gallium							0.78
Indium							1.10
Tellurium							2.48
Tin							1.78
Lead	0.84	0.81	1.64	0.56	1.88	1.64	0.82
Bismuth							1.28
Antimony							1.66

KEY:
/1/ and /3/ - Khanna, K. (1978)

/2/ - Hussain and Akinlade (1987)

/4/ - Ashcroft, N. and Lekner J. (1966)

/5/ - Behari, J. (1973): Self-Consistent Field Approximation (SC).

/6/ - Behari, J. (1973): Random Phase Approximation (RPA).

In this case, the calculated results are compared with those of other models, as there are no experimental values. The results obtained in this model calculation are in good agreement with the results of other theoretical calculations.

4.4 PARAMAGNETIC SPIN SUSCEPTIBILITY

The paramagnetic spin susceptibility was calculated using the proposed model within two standard approaches and the results obtained were tabulated as shown in Table 3 for comparison with experimental values and with the results of other theories.

TABLE 3. THEORETICAL AND EXPERIMENTAL VALUES OF THE PARAMAGNETIC SPIN SUSCEPTIBILITY OF SOME METALS (in 10^{-6} cgs volume units).

	/1/	/2/	/3/	/4/	/5/	/6/	/7/	/8/	/9/	/10/	/11/	/12/
Li	1.79	2.92	1.17	1.87	1.90	0.802	1.061	1.118		2.08	1.84	0.82
Na	0.86	1.21	0.64		0.85	0.652	0.901	0.917	0.901	1.09	0.94	0.66
K	0.73		0.61		0.60	0.529	0.740	0.697	0.713		0.71	0.53
Rb	0.85		0.44		0.52	0.498	0.662	0.634	0.663		0.65	0.50
Cs	1.78		0.38		0.43	0.463					0.59	0.47
Mg											1.61	1.03
Ca											1.52	1.02
Zn											1.68	1.04
Al											1.72	1.05
Ga											1.70	1.04
In											1.66	1.04
Tl											1.64	1.03
Sn											1.69	1.04
Pb											1.68	1.04
Bi											1.69	1.04
Sb											1.71	1.04

KEY:

/1/ - Abe, R. (1963)

/2/ - Hussain and Akinlade (1987), Abe, R. (1963)

/3/ - Pauli spin paramagnetism. (Hussain and Akinlade 1987, Abe, R. 1963)

/4/ - Pines, D. (1954)

/5/ - Bohm -Pines Results. (Hussain and Akinlade 1987, Abe, R. 1963)

/6/ - The spin susceptibility at absolute zero. (Hussain and Akinlade 1987, Abe, R. 1963)

/7/ - The spin susceptibility obtained with Brueckner-Sawada expression for the change in correlation energy using Hussain and Akinlade model (1987).

/8/ - The spin susceptibility obatained with Bohm-Pines expression for the change in correlation energy using Hussain and Akinlade model potential (1987).

/9/ - Khanna and Sharma (1978).

/10/ - Experimental Values: Abe, R (1963), Hussain and Akinlade (1987).

/11/ - Results obtained using the proposed model pseudopotential using the Brueckner-Sawada expression for the change in correlation energy.

/12/ - Results obtained using the proposed model pseudopotential using the Bohm-Pines expression for the change in correlation energy.

The paramagnetic spin susceptibility obtained using the proposed model pseudopotential show that for the alkali metals using the Brueckner-Sawada expression for the change in the correlation energy of the electron gas with polarization, the results agree with the earlier results of Abe (1963). However, the results obtained using the Bohm-Pines expression for the change in the correlation energy of the electron gas with polarization in the model calculations show a very good agreement with the values of the paramagnetic spin susceptibility of the alkali metals measured at absolute zero.

However, since there are no experimental values for the paramagnetic spin susceptibility of polyvalent metals for comparative analysis, it is concluded that the model is successful in predicting of the paramagnetic spin susceptibility of alkali metals, and provides a scheme for predicting the paramagnetic spin susceptibility of polyvalent metals.

CHAPTER FIVE

5.0 GENERAL CONCLUSION

It is therefore concluded that in order to carry out a successful calculation of the physical properties of metals within the pseudopotential framework, it is necessary to account for the core electron interactions. It can also be concluded that the 'relaxed core' model pseudopotential is able to offer a satisfactory interpretation of the electronic properties of metals. It is therefore successful in the accurate prediction of the binding energy, monovacancy resistivity and paramagnetic spin susceptibility of metals.

5.1 SUMMARY

A Wigner- Seitz dependent 'relaxed-core' model pseudopotential has been developed from first principles consideration of the stationary state perturbation theory to he first order correction in ground state energy and the free electron gas approximation. The Fourier transform of the bare-ion pseudopotential is evaluated and appropriate screening parameters have been chosen for the potential. This require no fitting procedures.

The computed screened and unscreened form factors have been applied within available theoretical frameworks in calculating some physical properties of metals. These properties include binding energy, monovacancy resistivity and paramagnetic spin susceptibility. The metals were chosen from all the groups of the periodic table based on he availability of experimental values and the results of other model calculations.

Generally, the results obtained show reasonable agreements with experimental values and also show a remarkable improvement over the works of previous researchers.

5.2 APPLICATION OF RESULTS

The results obtained in this analysis can be successfully extended to all the metals in the periodic table. It can therefore form a standard scheme for calculating and predicting the various physical properties of metals. This is possible if the electron gas parameters of such elements such as the atomic volume Ω, and the radius of the Wigner-Seitz sphere r_s are accurately known.

Also, the atomic-like potentials proposed in this work can be used to evaluate the phonon dispersion characteristics of crystals. Consequently, the proposed form factors can be used to obtain a qualitative insight into the role of crystal potentials in optical transitions and lattice vibrations, where the pseudopotential is treated as a scattering potential.

In addition, the proposed form factors can be applied in further studies on metallic charge density of condensed matter systems. This could further provide the theoretical basis of investigating Friedel oscillations in charge density of metals. Finally, the atomic-like potentials proposed in this work could be successfully used in calculating the monovacancy formation energy using the supercell approach as a variation to the computationally demanding plane waves pseudopotential approach.

5.3 SUGGESTIONS FOR FURTHER STUDIES

It is suggested that subsequent research efforts should focus on the possibilities of extending this derivation to binary structures, molecules, clusters, powders and other types of condensed matter systems. This is because the above analysis has been restricted to metals, where there are no overlap interactions between the occupied ion cores in contrast with other condensed matter systems.

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```
IS PROGRAM  CALCULATES THE VALUES OF A MODEL PSEUDOPOTENTIAL AT
ARIOUS MOMENTUM TRANSFER VECTORS,THE DIELECTRIC CONSTANTS USING
HE MODIFIED HATREE DIELECTRIC FUNCTION,THE SCREENED FORM FACTOR
 AND THE CRYSTAL BINDING ENERGY OF SIXTEEN METALS.
        11 SEPTEMBER,2000.


CONSTANT VALUE ENTRY  E
NTEGER Z,L
CHARACTER ELEMENT*2
REAL RATIO,NUM1,KONST
REAL NUM2,POT,GSPR
DIMENSION RATIO(50)
REAL R,N,Kf,ATOMVOL,M
ARAMETER(PI=3.142)
ARAMETER(E=1.0)
ARAMETER(M=1.0)
  OPEN FILES
  OPEN(3,FILE='UKP1.DAT',STATUS='OLD')
  OPEN(5,FILE='UKP33.DAT',STATUS='NEW')
  OPEN(7,FILE='UKP44.DAT',STATUS='NEW')
  OPEN(9,FILE='UKP55.DAT',STATUS='NEW')
    READ FILES
VRITE(*,*) 'ENTER K'
READ(*,*) K
VRITE(5,*)'--------------------------------------------------------'
VRITE(5,5)
ORMAT('q/2Kf',8X,'|',8x,'Qb',14X,'|','DIELF',16X,'|','FOMFAC')
 WRITE(5,*)'--------------------------------------------------------'
VRITE(7,*)'------------------------------'
VRITE(7,7)
FORMAT('ELEMENT',8X,'EB(Ryd/elect)')
VRITE(7,*)'------------------------------'
VRITE(9,*)'------------------------------'
VRITE(9,9)
FORMAT('q/2Kf',16x,'DATA')
VRITE(9,*)'------------------------------'
  DO 100 J=1,K
EADING THE VALUES OF SAMPLED ELEMENT Z,Kf,ATMVOL,R,FEMEN
  READ(3,*)ELEMENT,Z,Kf,ATMVOL,R,GSPR,FEMEN,DEN,PAL,CHI
  SUM=0.0
 DO 60 I=1,50
 X=I*0.1
  RATIO(I)=X
 KONST = -4.0*PI*Z*E*E
  VALU= EXP(-RATIO(I)*R*0.5)
  NUM1= KONST/(RATIO(I)*RATIO(I))
  NUM2=COS(RATIO(I)*R*0.5)
  POT =NUM1*VALU*NUM2
  Q1=POT*POT
  Q2=(RATIO(I)/Kf)*0.5
```

```
   PSIL= -(0.5*Kf*M)/(PI*PI)
   SQ2=Q2*Q2
   PQ2=2.0*Q2
   DIFQ2=1.0-SQ2
   QUOT2=DIFQ2/PQ2
   Q3=Q1/Q2
   Q4=1.0 + Q2
   Q5=1.0 - Q2
         IF(Q5.NE.0.0)THEN
   Q6= ABS(Q4/Q5)
      RLINQ=LOG(Q6)
          END IF
   RKERNEL=Q3*RLINQ
   ADDQ2=RLINQ+1.0
   CHIQ=PSIL*QUOT2*ADDQ2
   PALTUD= 1.76/R
   SIQ= NUM1+PALTUD
   ALTUD=SIQ*CHIQ
   DIELF=1.0 - ALTUD
   FOMFAC=POT/DIELF
   PRODCT=FOMFAC*FOMFAC
   CUBDATA=RATIO(I)**3.0
   DATA=PRODCT*CUBDATA
   WRITE(5,70)RATIO(I),POT,DIELF,FOMFAC
   WRITE(9,90)RATIO(I),DATA
0    CONTINUE
    SUM=SUM+RKERNEL
  Q7=SUM/(R**4.0)
  Q8=(PI**0.667)*16.0
  Q9=(12.0*(PI**2.0))**0.333
  Q10=Q7*Q8*Q9
  Q11=(0.737/(R**2.0))*0.667
  Q12=1.752*(Z**0.667)
  Q13=0.916+Q12
  Q14=Q13/R
  Q15=Q11*Q14
  Q16=0.031*LOG(R)
  Q17=-0.105+Q16
  Q18=(Q10+Q15+Q17)
   EB=GSPR*Q18
    FORMAT(F6.4,8X,F14.8,8X,F14.8,8X,F14.8)
    FORMAT(F6.4,8X,F16.8)
  WRITE(7,10)ELEMENT,EB
   FORMAT(A2,8X,F10.5)
0   CONTINUE
  STOP
  END
```

```
C   THIS PROGRAM  CALCULATES THE MONOVACANCY
C     RESISTIVITY OF SELECTED METALS USING
C       THE EXPRESSION OF J. ZIMAN
C       11 SEPTEMBER,2000.

C
C      CONSTANT VALUE ENTRY  E
      INTEGER Z,L
      CHARACTER ELEMENT*2
      REAL RATIO,MONOVAC
      REAL ERNEL
      REAL NEL,MEL
      DIMENSION RATIO(800)
      REAL R,N,Kf,ATMVOL,M
      PARAMETER(M=1.0)
     PARAMETER(HEIGHT=0.1)
     PARAMETER(FO=0.0)
     PARAMETER(PI=3.142)
     PARAMETER(CONST=3.13E-22)
C        OPEN FILES
        OPEN(3,FILE='UKP1.DAT',STATUS='OLD')
        OPEN(5,FILE='UKP55.DAT',STATUS='OLD')
        OPEN(7,FILE='UKP77.DAT',STATUS='NEW')
        OPEN(9,FILE='UKP99.DAT',STATUS='NEW')
C          READ FILES
      WRITE(*,*) 'ENTER K'
      READ(*,*) K
      WRITE(7,*)'-----------------------------------'
      WRITE(7,7)
  7    FORMAT('ELEMENT',8X,'MONOVACANCY RESISTIVITY')
      WRITE(7,*)'-----------------------------------'
C     INITIALISING THE SUM OF VARIABLES
      SUM1=0.0
      SUM2=0.0
      DO 100 J=1,K
C     READING THE VALUES OF SAMPLED ELEMENT Z,Kf,ATMVOL,R,FEMEN
        READ(3,*)ELEMENT,Z,Kf,ATMVOL,R,GSPR,FEMEN,DEN,PAL,CHI
        READ(5,*)RATIO(I),DATA
           DO 60 I=1,50,2
       NEL=2.0*DATA
       SUM1=FO+NEL
          DO 80 L=2,50,2
       MEL=4.0*DATA
       SUM2=SUM2+MEL
       RLIMIT=2.0*Kf
        IF(RATIO(I).LT.RLIMIT)THEN
        SUM3=SUM1+SUM2
         END IF
 80      CONTINUE
 60      CONTINUE
       WIGS=HEIGHT/3.0
```

```
      RESY=WIGS*SUM3
      RNOVAC=((CONST*RESY*ATMVOL)/(Kf**6.0))*DEN
      MONOVAC=RNOVAC*PAL
      WRITE(7,70)ELEMENT,MONOVAC
      WRITE(9,90)ELEMENT,SUM3
70       FORMAT(A2,8X,E20.12)
90       FORMAT(A2,8X,E20.6)
100    CONTINUE
     STOP
     END
```

```
C   THIS PROGRAM  CALCULATES THE PARAMAGNETIC          SPIN
C   SUSCEPTIBILITY OF SELECTED METALS USING
C         THE EXPRESSION ADOPTED BY
C          AKINLADE AND HUSSAIN
C           11 SEPTEMBER,2000.
C
C        CONSTANT VALUE ENTRY  E
       INTEGER Z,L
       CHARACTER ELEMENT*2
       DIMENSION RATIO(50)
       REAL R,N,Kf,ATOMVOL,Qb,KONST
       REAL LINP,MRESULT,IRESULT,JRESULT,KRESULT
       REAL MODULP,QSQUARE,KEAF
       REAL NRESULT,LRESULT
       PARAMETER(PI=3.142)
       PARAMETER(E=1.0)
C         OPEN FILES
          OPEN(3,FILE='UKP1.DAT',STATUS='OLD')
          OPEN(8,FILE='UKP33.DAT',STATUS='OLD')
          OPEN(10,FILE='PROJECT1.DAT',STATUS='NEW')
          OPEN(12,FILE='PROJ2.DAT',STATUS='NEW')
C           READ FILES
         WRITE(10,*)'------------------------------------------'
         WRITE(10,10)
  10  FORMAT('ELEMENT',8X,'PARAMAGNETIC SPIN SUSCEPTIBILITY')
         WRITE(10,*)'------------------------------------------'
         WRITE(12,*)'------------------------------------------'
         WRITE(12,12)
  12   FORMAT('ELEMENT',8X,'PARAMAGNETIC SPIN SUSCEPTIBILITY')
         WRITE(12,*)'------------------------------------------'
          WRITE(*,*) 'ENTER K'
          READ(*,*) K
        DO 100 J=1,K
C      READING THE VALUES OF SAMPLED ELEMENT,Z,R,Kf
        READ(3,*)ELEMENT,Z,Kf,ATMVOL,R,GSPR,FEMEN,DEN,PAL,CHI,Q2
        READ(8,*)RATIO(I),Qb,DIELF,FOMFAC
C     INITIALIZATIOMN OF SUMS OF VARIABLES
        SUM=0.0
           DO 60 I=1,50
          X = I*0.1
        KEAF = 4.91/R*R
        EAEX = -0.814/R
        CORR = 0.162-(0.0032*R)
        EXPO = -0.5
        ROR = R**EXPO
        ACORR = CORR - ROR
        BPACORR = -0.0676*LOG(R) + 0.225
        MODULQb = ABS(Qb)
        QbSQ = ABS(Qb)*ABS(Qb)
        TOP = 2.0*R*R
```

```
      PRODR=RATIO(I)*Kf*0.5
      OTOM = (12.0*PI*PI)
      TOM = OTOM**0.333
      BOTOM = TOM * 12.0
      COEFISE = TOP/BOTOM
      U22=1.0 + PRODR
      V33=1.0 - PRODR
         IF (V33.NE.0.0)THEN
            MODULP=ABS(U22/V33)
            RLINP = LOG(MODULP)
          END IF
      IRESULT = (PRODR*PRODR) - 1.0
      JRESULT = QbSQ/IRESULT
      KRESULT = 1.0 - (PRODR*PRODR)
      LRESULT = 2.0*PRODR
      ORESULT = KRESULT/LRESULT
      PRESULT = 1.0 + ORESULT
      MRESULT = RLINP * PRESULT
      NRESULT = JRESULT * MRESULT
60    CONTINUE
        SUM = SUM + NRESULT
      ALL = -COEFISE * SUM
      AAA = KEAF + EAEX + ACORR + ALL
      SUCEP1 = KEAF/AAA
      BBB = KEAF + EAEX + BPACORR + ALL
      PSUCEP2 = KEAF/BBB
      WRITE(10,80)ELEMENT,PSUCEP2
      WRITE(12,30)ELEMENT,SUCEP1
80     FORMAT(A2,4X,F12.4)
30     FORMAT(A2,4X,F12.4)
100      CONTINUE
       STOP
       END
```