THE EFFECT OF LATTICE PERIODICITY ON THE ELECTRONIC CONFIGURATION NEAR A METAL SURFACE

by

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ABSTRACT

A method is developed for calculating single electron wave functions in a semi-infinite metal. The effect of the lattice periodicity is explicitly taken into account so that the solution in the far interior is consistent with the band structure of the infinite crystal. The solution is sufficiently general to include surface states. The single electron potentials are reconsidered and some new features are discussed. These include the elimination of the singular zero-order Fourier terms of the ion-electron and Hartree potentials which leads to the surface dipole barrier. Also a simple formula is derived for the exchange potential in the zero-order approximation which allows to calculate the exchange potential for wave vectors which have components of velocity parallel to the surface. The method is finally applied to a semi-infinite sodium crystal with a (001) orientation.

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PART ONE

SUMMARY

CHAPTER 1

OUTLINE OF THE THESIS

The effect of the lattice structure on the electronic properties of metallic surfaces is a problem of great theoretical and technological importance. This problem, besides having theoretical complexities, also has many experimental difficulties; the latter have been partially overcome in the last few years and at the same time the "surface problem" has attracted the activities of many theoretical studies. It is the theoretical part of this problem we aim to investigate in this thesis.

Our investigation uses the single electron approximation, while many body theory techniques are employed in formulating the single electron potentials of "the interacting electron system".

The difficulties of the surface problem are mainly related to the solution of the Schrödinger's equation for an electron in the "surface region" of the metal. The lack of the three dimensional periodicity in the surface region introduces a complexity that is not present in the case of the "infinite metal". In general a boundary plane may be defined between that part of the semi-infinite crystal where three-dimensional periodicity exists, and the surface region where only two-dimensional periodicity is present. The problem of setting up an exact single electron wave function is just the problem of matching the possible solutions on the

/n two sides of the boundary surface (Hei~~y~~e, V., 1962). This requires that all the evanescent waves, which are produced by the physical surface of the system, must be included in the matching procedure. The "matching problem" appears to be the most difficult problem in obtaining a complete solution of the Schrödinger's equation; such a solution has not appeared in the literature so far. For example, the evanescent surface waves are completely ignored in the most successful treatment of the surface problem presented so far, namely the treatment of Appelbaum and Hamann (Appelbaum, J.A., Hamann, D.R., 1972). This is in fact the reason that no "surface states" can be calculated from their theory.

It is one of the aims of this work to present a solution of the Schrödinger's equation for an electron in a semi-infinite metal, which is consistent with the existence of surface states and with the band structure of the corresponding infinite metal. The solution to be presented belongs to the class of the self-consistent solutions.

In solving Schrödinger's equation the two-dimensional periodicity of the system along the planes parallel to the surface is used. This allows us to expand the single electron wave functions and potentials in Fourier series with respect to the two-dimensional reciprocal lattice associated with the surface plane. In these expansions the Fourier coefficients depend on one coordinate; it is the coordinate along the axis perpendicular to the surface. At the same time the Schrödinger equation takes the form of a matrix differential equation. Furthermore the single electron potentials become matrices with respect to the two-dimensional reciprocal space.

In the process of forming the single electron Hamiltonian we discuss the analytical behaviour of the Fourier coefficients of the single electron potentials considered as functions of the reciprocal lattice vectors. Firstly the ion-electron interaction is discussed and the singularity of the zero-order Fourier coefficient is pointed out. Then the electron-electron interactions are introduced in the Hartree approximation.

It is shown (Chapter 4) that the inclusion of the Hartree potential in the Hamiltonian of the "non-interacting" system is necessary in order to eliminate the singularities which appear in the zero-order Fourier coefficients of the ion-electron and Hartree potentials. On the one hand, these singular coefficients have been tacitly ignored so far. On the other hand, Poisson's equation has been used in order to determine a zero order Fourier coefficient for the combined ion-electron and Hartree potentials. Here, a direct elimination of the singularities is presented which yields the zero-order Fourier term of the single electron Hamiltonian. The result is identical to that obtained from Poisson's equation. Therefore, the "surface dipole barrier" may be obtained from the Hartree Hamiltonian, while the consistency of the Hartree Hamiltonian with Poisson's equation is proved. An application to a system for which the "electron density profile" at the surface region is given by a step function, shows that the surface dipole barrier is strongly dependent on the lattice structure and orientation of the crystal.

In the next stage (Chapter 5) the exchange potential is taken into account self-consistently in a way analogous to that given by Bardeen (Bardeen, J., 1936). For the non-locality of the exchange potential is explicitly taken into account in contrast to the local approximations used by other workers. In the limit of the jellium approximation, we derive an expression for the exchange potential which allows us to calculate the exchange potential for electrons with components of velocity parallel to the surface. Bardeen's treatment was confined to electrons moving perpendicular to the surface and the result obtained was assumed valid for electrons with arbitrary direction of velocity.

Finally we include correlation effects by introducing the correlation potential. This is defined through a diagrammatic representation (Fetter, A.L., Walecka, J.D., 1971) and an approximation is made at the level of the Random Phase Approximation (RPA).

Having completed the discussion about the single electron Hamiltonian, we proceed (Chapter 6) by developing a solution of Schrödinger's equation which is consistent with the band structure of the bulk crystal and the existence of surface states. The solution is of the self-consistent type. It is necessary to obtain the general solution of Schrödinger's equation in three physically different regions of the system. Then the boundary conditions are employed to determine the constants of integration. These are 6N if N is the number of terms kept in the Fourier series expansion. In each of the three regions the solution is obtained numerically by solving a matrix differential equation. The result is the fundamental matrix of the system of equations. The solution in the bulk crystal is associated with the diagonalization of the fundamental matrix and can be expressed within N constants of integration and a phase factor. The remaining boundary conditions lead to a system of homogeneous linear equations. This can be solved by determining the phase factor in such a way as to make the determinant of the associated matrix equal to zero.

Finally the above formalism is applied to a sodium crystal with a (001) surface plane (Chapter 7). Nine terms were used in the Fourier series expansions. The results obtained for the electron density profile, the exchange and Hartree potentials and the work function are in agreement with those of Bardeen (Bardeen, J., 1936), Lang and Kohn (Lang, N.D., Kohn, W., 1970 and 1971) and Appelbaum and Hamann (Appelbaum, J.A., Hamann, D.R., 1972). An interesting short-cut was discovered. The numerical results do not change appreciably if only zero-order terms are retained in Fourier series expansions. However the terms of non-zero order are probably important in some other crystals.

PART TWO

INFINITE BLOCH ELECTRON SYSTEM

CHAPTER 2

NON-INTERACTING INFINITE SYSTEM

2.1 INTRODUCTION

The system of our investigation may be referred to as "the semi-infinite Bloch electron system". The term "semi-infinite" is used to designate the presence of an infinite surface, whereas the term "infinite" is used to indicate systems without surfaces. The term "Bloch electron system" is associated with the basic assumption that the system possesses a Bravais lattice. As a result, the single electron wave functions are Bloch functions which satisfy the periodicity of the lattice.

The semi-infinite system becomes identical with the infinite system at a region, to be called "bulk region", far from the surface region. This observation justifies the idea that an analysis of the surface problem may be carried out along the lines of the theories of the infinite metal. In fact, our formulation is based on the techniques used for the infinite systems. But as will soon be observed, the mathematical formalism becomes much more complicated. This means that the semi-infinite system requires computer techniques which give an altogether different character to the surface problem.

In order to indicate the inter-relation between the infinite and the semi-infinite systems, and for the sake of comparison, we thought it necessary to include a brief discussion on the infinite system here. In this way, the basic physical arguments become clear and the complexities which are introduced by the surface of the system become clearer.

The jellium approximation to the metallic system will be frequently referred to during our discussion. In this approximation, the positive ions are assumed smeared throughout the whole crystal resulting in a positive uniform charge distribution, which ensures the charge neutrality of the system. Although the nature of this approximation does not allow any consideration of the lattice effects, nevertheless this is still a very widely used approximation in studying metallic surfaces. For example, in an attempt to investigate the lattice effects on the electronic properties of the metallic surfaces, Lang and Kohn (Lang, N.D. - Kohn, W., 1970 and 1971) start with the jellium approximation to a semi-infinite metal and calculate the zero order contribution of the lattice "pseudopotential" in evaluating the work function and the surface energy of a wide class of metals.

Since the zero-order approximation of our formalism for the semi-infinite Bloch electron system is equivalent to the jellium model approximation to the semi-infinite electron system, the latter will not be discussed here. However, whenever it is required, results obtained in the jellium approximation will be referred to for comparison.

2.2 THE SYMMETRY OF THE SYSTEM

The infinite Bloch electron system is a metallic system which is extended over the whole space and possesses a

Bravais lattice. The ions are located at lattice points defined by the lattice vectors $\vec{r}_{\ell mn}$,

$$\vec{r}_{lmn} = l\vec{r}_1 + m\vec{r}_2 + n\vec{r}_3 \tag{2.2.1}$$

where ℓ,m,n are integers and $\vec{r}_i$,i=1,2,3 are the unit lattice vectors. For this space, a reciprocal space is defined, spanned by the reciprocal lattice vectors $\vec{G}_{\ell mn}$, which belong to the set $\{\vec{G}\}$,

$$\{\vec{G}\} : \vec{G}_{lmn} = l\vec{G}_1 + m\vec{G}_2 + n\vec{G}_3 \tag{2.2.2}$$

where

$$\vec{G}_i = 2\pi \frac{\vec{r}_j \times \vec{r}_k}{\vec{r}_i \cdot (\vec{r}_j \times \vec{r}_k)} , \tag{2.2.3}$$

(i,j,k) being a cyclic permutation of (1,2,3).
In contrast to the term "reciprocal lattice", the space described by eqn. (2.2.1) is called "direct lattice".

A conduction electron which moves in the field of the direct lattice is affected by the periodic condition implied by eqn. (2.2.1). The periodic potential of the lattice imposes a fundamental boundary condition on the single electron wave function which may be defined as follows:

If $\hat{T}(\vec{r}_m)$ is an operator which translates a single electron wave function $\psi_{\vec{k}}(\vec{r})$ from the position $\vec{r}$ to $\vec{r} + \vec{r}_m$, where $\vec{r}_m$ is a lattice vector and $\vec{k}$ the momentum vector, the symmetry of the crystal implies

$$\hat{T}(\vec{r}_m)\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}_m}\psi_{\vec{k}}(\vec{r}) . \tag{2.2.4}$$

Eqn. (2.2.4) has an important consequence. It implies that a single electron wave function, $\psi_{\vec{k}'}(\vec{r})$, with momentum $\vec{k}' = \vec{k} + \vec{G}$ such as $\vec{G}\epsilon\{\vec{G}\}$, (the three indices are suppressed), has the same eigenvalues as $\psi_{\vec{k}}(\vec{r})$ under the operation $\hat{T}(\vec{r}_m)$. This follows since $\vec{G}\cdot\vec{r}_m$ is a multiple of 2π (eqns. (2.2.1) and (2.2.3)). Eqn. (2.2.4) also proves that a single electron wave function cannot be uniquely determined by only the wave vector.

A unique set of single electron wave functions may be defined (Zak, J., 1968) by choosing the wave vector $\vec{k}$ to be in the first Brillouin zone and specifying the energy of the electron. Equivalently an index, n, called the "band index", may be used instead of the energy. In this way it is possible to define an orthonormal set of eigenstates which are simultaneously the eigenstates of the Hamiltonian of the system, $\hat{H}$, and the "translational" operator $\hat{T}(\vec{r}_m)$. Therefore, a single electron wave function $\psi_{\vec{k}n}(\vec{r})$ is defined as

$$\{\psi_{\vec{k}n}(\vec{r})\} : \left\{ \begin{array}{l} \hat{H}(\vec{r})\psi_{\vec{k}n}(\vec{r}) = \varepsilon_n(\vec{k})\psi_{\vec{k}n}(\vec{r}) \\ \hat{T}(\vec{r}_m)\psi_{\vec{k}n}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}_m}\psi_{\vec{k}n}(\vec{r}) \end{array} \right\} . \tag{2.2.5}$$

It can be directly verified that the Bloch functions

$$\psi_{\vec{k}n}(\vec{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} y_{\vec{k}n\vec{G}} \, e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \qquad (2.2.6)$$

$$\vec{G} \in \{\vec{G}\}$$

where Ω is the volume of the system, satisfy eqn. (2.2.5), and therefore may be used as the single electron wave functions of the infinite Bloch electron system.

2.3 SOLUTION OF SCHRÖDINGER'S EQUATION

The Hamiltonian, $\hat{H}_o(\vec{r})$, of the non-interacting infinite Bloch electron system is defined as

$$\hat{H}_o(\vec{r}) = -\frac{1}{2}\nabla^2 + V^{i-e}(\vec{r}) \quad , \qquad (2.3.1)$$

where atomic units are used, i.e. $m = |e| = h = 1$, and $V^{i-e}(\vec{r})$, to be called "ion-electron interaction", is the potential energy of an electron in the field of the ions.

$V^{i-e}(\vec{r})$ is taken as a superposition of single ion-electron Coulomb potentials, $v^{i-e}(\vec{r})$, located at each ion site, $\vec{r}_i$, i.e.

$$V^{i-e}(\vec{r}) = \sum_i v^{i-e}(|\vec{r}-\vec{r}_i|) \quad , \qquad (2.3.2)$$

where

$$v^{i-e}(r) = \frac{-1}{r} \quad . \tag{2.3.3}$$

The valency of the ions is taken equal to one.

For single electron wave functions of the form (2.2.6) with corresponding energies $\varepsilon_n(\vec{k})$, the Schrödinger's equation

$$\hat{H}_0(\vec{r})\,\psi_{\vec{k}n}(\vec{r}) = \varepsilon_n(\vec{k})\,\psi_{\vec{k}n}(\vec{r}) \quad , \tag{2.3.4}$$

takes the following form after multiplication on the left by $e^{-i\vec{k}\cdot\vec{r}}e^{-i\vec{G}'\cdot\vec{r}}$ and integration over $\vec{r}$.

$$\frac{1}{2}(\vec{k}+\vec{G})^2\,y_{\vec{k}n\vec{G}} + \sum_{\vec{G}'\neq\vec{G}} V^{i-e}_{\vec{G}-\vec{G}'}\,y_{\vec{k}n\vec{G}} = \\ = \varepsilon_n(\vec{k})\,y_{\vec{k}n\vec{G}} \tag{2.3.5}$$

where

$$V^{i-e}_{\vec{G}} = \frac{1}{\Omega}\int d\vec{r}\; e^{-i\vec{G}\cdot\vec{r}}\,V^{i-e}(\vec{r})$$

$$= -\frac{4\pi}{\omega_0}\,\frac{1}{G^2} \quad , \qquad \vec{G} \in \{\vec{G}\} \quad . \tag{2.3.6}$$

is the Fourier transform of $V^{i-e}(\vec{r})$ with respect to the reciprocal lattice space, and where ω_0 is the volume of the unit cell of the direct lattice.

Eqn. (2.3.5) may be written in matrix form as

$$\underline{\underline{V}}^{i-e}\vec{Y}_{\vec{k}n} = \mathcal{E}_n(\vec{k})\vec{Y}_{\vec{k}n} \quad , \qquad (2.3.7a)$$

where (1)

$$\left(\underline{\underline{V}}^{i-e}\right)_{ij} = \frac{1}{2}(\vec{k}+\vec{G}_i)^2\,\delta_{ij} + V^{i-e}_{\vec{G}_i-\vec{G}_j}\left(1-\delta_{ij}\right) \qquad (2.3.7b)$$

$$\left(\vec{Y}_{\vec{k}n}\right)_j = y_{\vec{k}n\vec{G}_j} \qquad (2.3.7c)$$

Therefore the solution of Schrödinger's equation in this case reduces to the diagonalization of the matrix (2.3.7b), from which the band structure and the single electron wave functions are obtained.

The difficulties in solving eqn. (2.3.7a) come from the fact that any numerical calculation makes it necessary to truncate the infinite series expansion (2.2.6) consistently with the convergence requirements. This problem has led to the invention of the "pseudopotential" concept (Harrison, W.A., 1966), (Heine, V., 1970).

The pseudopotential, $V^{i-e}_{ps}(\vec{r})$, replaces the true potential $V^{i-e}(\vec{r})$, in eqn. (2.3.1) which becomes a "pseudo-wave" equation, i.e.

$$\left\{-\frac{1}{2}\nabla^2 + V^{i-e}_{ps}(\vec{r})\right\}\psi_{\vec{k}n,ps}(\vec{r}) = \mathcal{E}_n(\vec{k})\,\psi_{\vec{k}n,ps}(\vec{r}) \qquad (2.3.8)$$

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(1) Double underlined letters denote matrices.

An essential property of $V_{ps}^{i-e}(\vec{r})$ is that its energy eigenvalues in eqn. (2.3.8) are identical with those of the true potential in eqn. (2.3.1) for the bands of interest. Eqn. (2.3.8) is just a mathematical transformation of the Schrödinger's equation, eqn. (2.3.1), which retains the energy eigenvalues but alters the wave functions. Simultaneously, the use of the pseudopotential ensures fast convergence of the series (2.2.6) which now can be trancated within the range of computer abilities.

In our case, the pseudopotential $V_{ps}^{i-e}(\vec{r})$ is assumed to be a superposition of ion-electron pseudopotentials of Ashcroft's type (Ashcroft, N.W., 1966). The Coulombic ion-electron interaction, eqn. (2.3.3), is replaced by the ion-electron Ashcroft's pseudopotential, namely

$$v_{ps}^{i-e}(r) = \begin{cases} 0 & r \leq r_c \\ -\dfrac{1}{r} & r > r_c \end{cases} , \qquad (2.3.9)$$

which differs from the Coulomb potential only in the core region of the ion defined through the core radius r_c. The above model pseudopotential has proved quite successful for the simple metals and is widely used. In our application for the Na-crystal, we have taken $r_c = 1.67$ a.u.

The speudo-wave equation, eqn. (2.3.8), leads to the same matrix equation, eqn. (2.3.7a), but the Fourier terms (2.3.6) take the form

$$V^{i-e}_{\vec{G},ps} = -\frac{4\pi}{\omega_o}\frac{\cos(G r_c)}{G^2} \qquad (2.3.10)$$

Using the Fourier terms $V^{i-e}_{\vec{G},ps}$ we have solved eqn. (2.3.7a) for the infinite Na-crystal and the band structure obtained is shown in Fig. 2.1. In Fig. 2.2 the band structure of the Na-crystal is presented as given by Gupta (Haque, M.S. et al., 1973). It should be mentioned that in our calculations we kept 19 Fourier terms in the expansion (2.2.6).

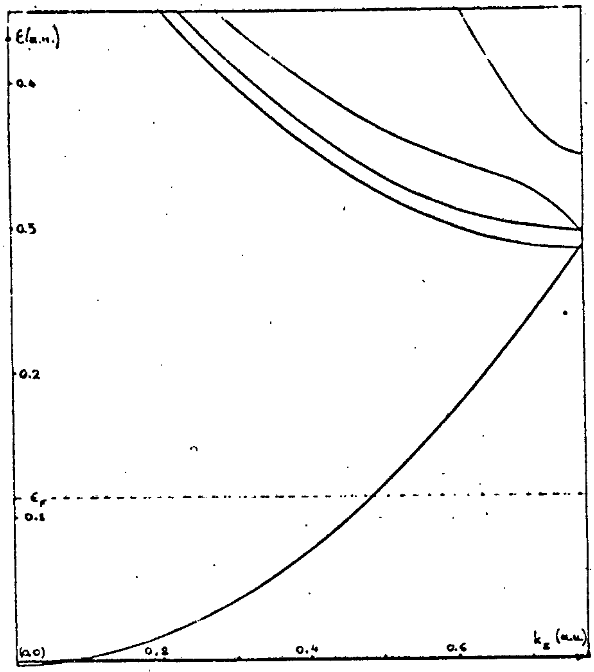


Fig. 2.1:

Band structure of the Na-crystal along the (001) direction obtained from eqn. (2.3.7a) using the Ashcroft's ion-electron pseudopotential.

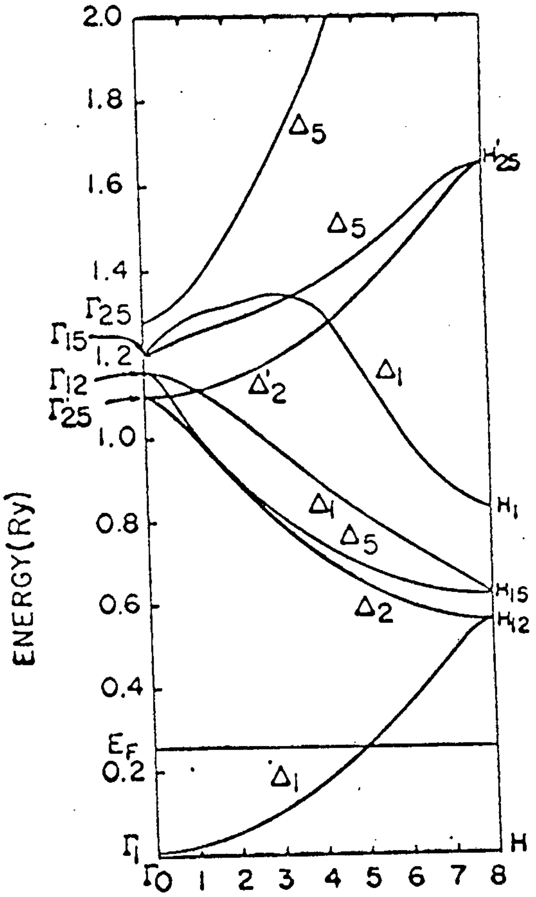


Fig. 2.2:

Band structure of the Na-crystal along the (001) direction as calculated by R.P. Gupta (Haque, M.S. et al., 1973). The lattice constant was taken 7.984 a.u.

Finally, we close this section by considering one tacit assumption in the previous discussion about the zero-order Fourier term of the ion-electron (pseudo) potential. The singularity which is present in this term for $\vec{G}=0$ is removed by assuming that the ion-ion interaction may be added to the divergent terms of the ion-electron interaction and to the electron-electron interaction in the Hartree approximation, to obtain a combined zero-order Fourier term which may be put equal to zero (Taylor, P.L., 1970). This in fact can be done because the zero-order Fourier term of the Hartree-Hamiltonian affects only the zero-level energy of the crystal. Although this type of cancellation of the divergent terms has no particular significance in the case of an infinite system, it will be shown that it is of considerable importance in the case of the semi-infinite system. This term describes the "surface dipole barrier", which is such an important factor in the electronic properties of the metallic surfaces.

PART THREE

SEMI-INFINITE BLOCH ELECTRON SYSTEM

CHAPTER 3

INTRODUCTION

A formalism for the semi-infinite Bloch electron system will be presented here along the lines of the previous section.

The presence of the surface reduces the symmetry of the system, and as a result we cannot any longer use the three dimensional Fourier expansion with respect to the reciprocal lattice space. However a two-dimensional periodicity is retained along the planes parallel to the surface, and correspondingly a two-dimensional reciprocal lattice space, associated with the lattice of the "surface plane", is introduced. As a result, a Fourier series representation is possible, but, now, this is dependent on the coordinate variable along the direction perpendicular to the surface. Consequently the matrix eqn. (2.3.7a) becomes a differential matrix equation which is solved numerically. It is evident that the use of an ion-electron pseudopotential is unavoidable, as it is related to the truncation of the Fourier series. For this purpose the Ashcroft's type pseudopotential is used.

3.1 THE SYMMETRY OF THE SYSTEM

It is assumed that the semi-infinite Bloch electron system occupies the half space, $Z \leqq 0$. This system possesses a surface which is defined as the boundary between the crystal and the region where there are not any ions present. If this boundary is a plane, it is called "surface plane", and it is defined by the centres of ions of the surface. In the case of a Bloch electron system, the surface plane is assumed to be a lattice plane and its specification determines the "orientation of the crystal". In our case it is assumed that the semi-infinite system has a surface plane with (001) orientation (Fig. 3.1). In addition, it should be mentioned that the surface plane is a mirror plane for the infinite crystal, and the two dimensional (direct) lattice of the surface plane possesses a centre of symmetry.

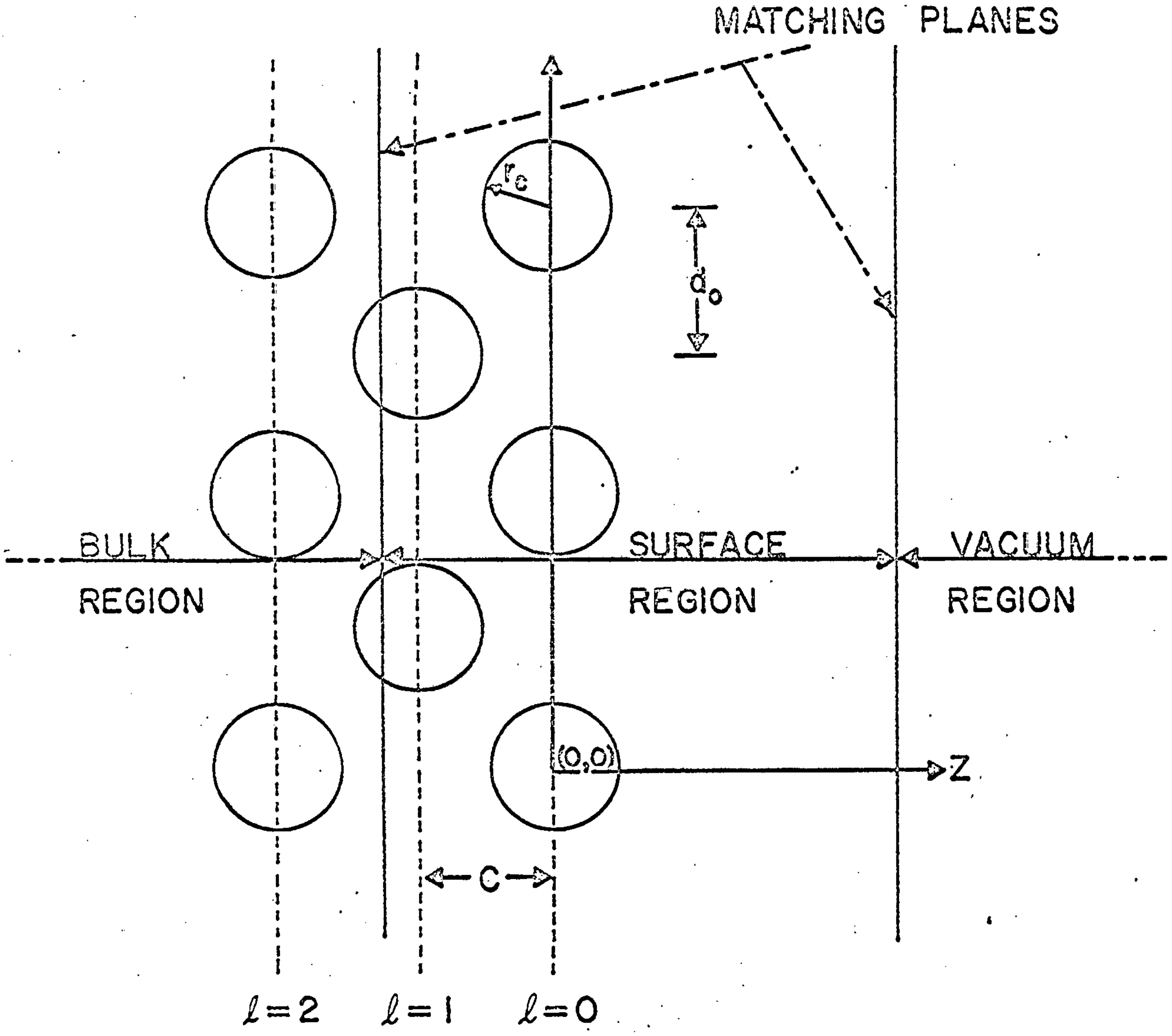


Fig. 3.1: Semi-infinite Na-crystal with an (001) orientation.

The above mentioned symmetries are basic assumptions in the formalism which we shall describe.

As is shown in Fig. 3.1, the semi-infinite system may be divided in three physically different regions:

i) The "bulk region" which is identical with the infinite Bloch electron system;

ii) The "vacuum region" which has not any ions present and where the effect of the periodic lattice is negligible, and

iii) The "surface region" which is a transition region from the bulk to the vacuum region.

In order to determine the boundary planes which specify these regions we study the variation of the single electron potentials along the z-axis. The boundary plane between the bulk and the surface region is taken inside the crystal at a region where the single electron potentials have reached their asymptotic form, that of the bulk region. Similarly the boundary plane between the surface and the vacuum region is chosen far outside the crystal at a region where the off-diagonal terms of the single electron potentials (to be defined later) become negligible. Although this specification does not define the boundary planes uniquely it is nevertheless sufficient as it leads to a unique solution of the Schrödinger's equation.

For the type of crystals we are interested in, in other words for crystals with one ion per unit cell, the lattice planes which are parallel to the surface plane are topologically equivalent. These planes may be obtained from the surface plane by a translational operation. By this, each ion of the surface plane is translated through the same constant vector $\vec{d}_o$ parallel to the surface plane. Consequently, each ion may be assigned with a two-dimensional position vector $\vec{\rho}_{s\ell}$ which relates the sth ion of the ℓ^{th} plane (parallel to the surface) to the sth ion of the surface plane. If ℓ = o defines the surface plane, for the (001) orientation of a bcc crystal we may write

$$\vec{\rho}_{s\ell} = \vec{\rho}_{so} + \frac{\vec{d}_o}{2} - (-1)^{\ell}\frac{\vec{d}_o}{2} \qquad \ell = 0, 1, 2, \ldots \tag{3.1.1}$$

with

$$\vec{d}_o = \frac{1}{2}\left(\vec{\rho}_1 + \vec{\rho}_2\right) \tag{3.1.2}$$

where $\vec{\rho}_1$ and $\vec{\rho}_2$ are the unit vectors of the direct lattice of the surface plane (Fig. 3.2a). As Boudreaux (Boudreaux, D.S., 1970) observes, the descriptions of the form (3.1.1) apply for most of the common crystals with low-rational-index orientations, and have the advantage of simplifying the mathematics of the surface problem drastically. This will become evident in this work, where the use of eqn. (3.1.1) helps in finding closed analytical forms for the Fourier components of the ion-electron interaction.

The two-dimensional periodicity of the surface plane is the most significant symmetry of the semi-infinite system, since this is conserved throughout the whole space. It therefore allows one to use a Fourier series representation for the single electron potentials and wave functions with respect to a corresponding two-dimensional reciprocal space. This space is defined as follows (Allen, R.E. et al., 1971). Having defined $\vec{\rho}_1$ and $\vec{\rho}_2$, the unit vectors of the direct lattice of the surface plane, a third vector $\vec{\rho}_3$ is chosen perpendicular to the surface plane in such a way that the volume ω_0, eqn. (3.1.3),

$$\omega_0 = \vec{\rho}_3 \cdot (\vec{\rho}_1 \times \vec{\rho}_2) \tag{3.1.3}$$

is equal to the volume of the unit cell of the infinite lattice. The two-dimensional reciprocal lattice space of the surface lattice is the space which is spanned by the reciprocal lattice vectors $\vec{h}_{\ell m} \in \{\vec{h}\}$, where the set $\{\vec{h}\}$ is defined as

$$\{\vec{h}\} : \left\{ \begin{array}{l} \vec{h}_1 = \dfrac{2\pi}{\omega_0} (\vec{\rho}_2 \times \vec{\rho}_3) \\ \vec{h}_2 = \dfrac{2\pi}{\omega_0} (\vec{\rho}_3 \times \vec{\rho}_1) \\ \vec{h}_{\ell m} = \ell \vec{h}_1 + m \vec{h}_2 \end{array} \right\} \tag{3.1.4}$$

where ℓ, m are integers.

By analogy with the three-dimensional reciprocal lattice space, the two-dimensional one may be supplied with two-dimensional Brillouin zones as shown in Fig. 3.2b.

For later purposes we define a sub-set of $\{\vec{h}\}$, which we denote as $\{\vec{h};N\}$. This sub-set contains N specified reciprocal lattice vectors of $\{\vec{h}\}$ near to the origin. (In other words, N determines the last term kept in a Fourier series expansion with respect to the two-dimensional reciprocal lattice space.)

/to Although we have restricted ourselves ~~in~~ bcc crystals with (001) orientation during the above description, only equations (3.1.1) and (3.1.2) have to be redefined for any other crystal and orientation which satisfies the assumptions of this formalism.

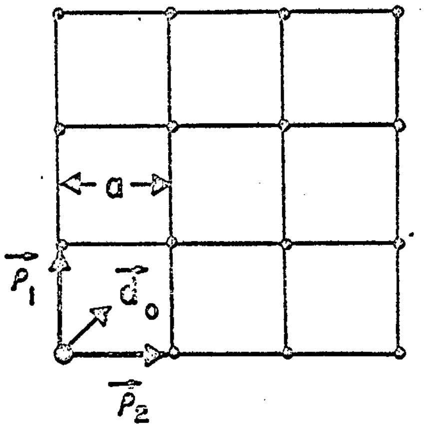


Fig. 3.2a: Direct lattice of an (001) lattice plane of a Na-crystal.

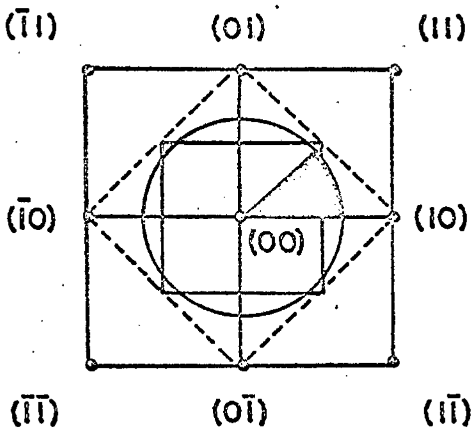


Fig. 3.2b: Reciprocal lattice space of an (001) lattice plane of a Na-crystal. The circle represents the projection of the Fermi-sphere onto the (001) reciprocal lattice plane. The first and second Brillouin zones are defined by the internal solid and dotted squares respectively.

CHAPTER 4

NON-INTERACTING SEMI-INFINITE SYSTEM

The non-interacting electron system is strictly speaking the system in which the electrons are assumed non-interacting with each other. However in the so-called non-interacting electron system an average effect of the electron-electron interaction is tacitly taken into account. This is necessary for the stability of the system. For example, in the non-interacting infinite system, the elimination of the singular zero order Fourier term of the ion-electron interaction becomes possible only if it is added to the singular zero-order Fourier term of the Hartree potential and the ion-ion interaction term. There were not any other complications in this elimination, since this elimination could affect the zero-level energy of the system. Unfortunately in the case of the semi-infinite system, the elimination of the singular zero-order term of the ion-electron and Hartree potentials leads to a zero-order Fourier term of the Hamiltonian of the system which is not a constant, as in the case of the infinite system. It therefore becomes necessary to reconsider the elimination of the singular terms of the Hartree-Hamiltonian which, as it is going to be shown, includes significant information about the semi-infinite system.

4.1 THE ION-ELECTRON INTERACTION

As in the case of the infinite system, section 2.3, the single electron potential, $V^{i-e}(\vec{r})$, due to the field of the ions is taken as a superposition of ion-electron pseudopotentials of Ashcroft's type, eqn. (2.3.9), i.e.

$$V^{i-e}(\vec{r}) = \sum_i v_{ps}^{i-e}(|\vec{r}-\vec{r}_i|) \tag{4.1.1}$$

where $\vec{r}_i$ is the lattice vector defining the ith ion.

The coordinate Fourier transform, $f_{\vec{q}}(z)$, of a function $f(\vec{r})$ with respect to the two-dimensional reciprocal lattice space (3.1.4) is defined as

$$f_{\vec{q}}(z) = \frac{1}{a}\int e^{-i\vec{q}\cdot\vec{\rho}} f(\vec{r})\, d\vec{\rho} \tag{4.1.2a}$$

or

$$f(\vec{r}) = \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{\rho}} f_{\vec{q}}(z) \tag{4.1.2b}$$

where

$$\vec{r} = (\vec{\rho}, z) \quad , \quad \vec{q} \in \{\vec{h};N\}. \tag{4.1.2c}$$

a is the area of the surface plane and $\vec{\rho}$ is the projection of the vector $\vec{r}$ onto the surface plane. (Throughout this work the coordinate Fourier transform $f_{\vec{q}}(z)$ will be referred to as "Fourier term" or "Fourier coefficient".)

In the description given by eqns. (3.1.1) and (3.1.2) the lattice vectors $\vec{r}_i$ take the form

$$\vec{r}_i \equiv \vec{r}_{s\ell} = \left(\vec{\rho}_{s\ell} \,, z_\ell \right) \quad . \tag{4.1.3}$$

They may be substituted into eqn. (4.1.1) and, using the definition (4.1.2a), we obtain the following expression for the coordinate Fourier transform, $V_{\vec{q}}^{i-e}(z)$, of the ion-electron interaction.

$$V_{\vec{q}}^{i-e}(z) = \frac{1}{a} \sum_{s\ell} \int d\vec{\rho} \; e^{-i\vec{q}\cdot\vec{\rho}} \; v_{ps}^{i-e}\left(|\vec{r} - \vec{r}_{s\ell}| \right) \tag{4.1.4a}$$

$$= \frac{1}{a} \sum_{s\ell} e^{-i\vec{q}\cdot\vec{\rho}_{s\ell}} \int d\vec{\rho} \; e^{-i\vec{q}\cdot(\vec{\rho}-\vec{\rho}_{s\ell})} \; v_{ps}^{i-e}\left(|\vec{r} - \vec{r}_{s\ell}| \right)$$

$$= -\frac{2\pi}{N_A \alpha} \sum_{s\ell} e^{-i\vec{q}\cdot\vec{\rho}_{s\ell}} \int_{\sqrt{r_c^2 - |z-z_\ell|^2}}^{\infty} \frac{\rho \, d\rho \, J_0(q\rho)}{\sqrt{\rho^2 + (z-z_\ell)^2}} \tag{4.1.4b}$$

where $J_0(x)$ is the Bessel function of the first kind, α is the area of the unit cell of the lattice of the surface plane, and N_A the number of the ions on the surface plane. Direct substitution for $\vec{\rho}_{s\ell}$ as given by eqn. (3.1.1) yields

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha} \left\{ \sum_{\ell=0,2,4\ldots}^{\infty} 1 + \sum_{\ell=1,3,5\ldots}^{\infty} e^{-i\vec{q}\cdot\vec{d}_0} \right\} \times$$

$$\times \int_{\sqrt{r_c^2 + (z-z_\ell)^2}}^{\infty} \frac{\rho \, d\rho \, J_0(q\rho)}{\sqrt{\rho^2 + (z-z_\ell)^2}} \quad . \tag{4.1.5}$$

It should be mentioned that the identity

$$\sum_s e^{i\vec{q}\cdot\vec{\rho}_{so}} = N_A \tag{4.1.6}$$

was used in deriving eqn. (4.1.5).

The integral in eqn. (4.1.5) may be written as

$$\int_{\sqrt{r_c^2+(z-z_\ell)^2}}^{\infty} \frac{\rho\, d\rho\, J_0(q\rho)}{\sqrt{\rho^2+(z-z_\ell)^2}} = \frac{e^{-q|z-z_\ell|}}{q} - \mathcal{D}_q(z,z_\ell) \tag{4.1.7}$$

where

$$\mathcal{D}_q(z,z_\ell) = \int_0^{\sqrt{r_c^2+(z-z_\ell)^2}} \frac{\rho\, d\rho\, J_0(q\rho)}{\sqrt{\rho^2+(z-z_\ell)^2}} \tag{4.1.8}$$

and finally

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha}\left\{\sum_{\ell=0,2,4\ldots}^{\infty} 1 + \sum_{\ell=1,3,5\ldots}^{\infty} e^{-i\vec{q}\cdot\vec{d}_0}\right\} \times \left\{\frac{e^{-q|z-z_\ell|}}{q} - \mathcal{D}_q(z,z_\ell)\right\} . \tag{4.1.9}$$

If c denotes the distance between two adjacent planes which are parallel to the surface, and $\ell = 0$ defines the surface plane,

$$z_\ell = -\ell c \tag{4.1.10}$$

For the Na-crystal we have

$$2r_c < c \qquad (4.1.11)$$

which implies that the term $\mathcal{D}_q(z,z_\ell)$ contributes to $V_{\vec{q}}^{i-e}(z)$ only for z inside the core region of an ℓ^{th} ion. Therefore we obtain the following expressions for $V_{\vec{q}}^{i-e}(z)$ in the different regions of the crystal:

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha}\left\{\frac{1+e^{-qc}\cos(\vec{q}\cdot\vec{d}_0)}{1-e^{-2qc}}\right\} + \frac{2\pi}{\alpha}\,\vartheta(r_c - z)\,\mathcal{D}_q(z,0) \quad , \; z \geqslant 0 \, , \qquad (4.1.12a)$$

where the ϑ-function has its usual meaning, i.e.

$$\vartheta(x) = \begin{cases} 0 & x < 0 \\ 1 & x \geqslant 0 \end{cases} .$$

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha}\left\{\frac{e^{-q|z|}}{q} + \frac{e^{+q|z|}}{q}\left(\frac{e^{-2qc}+e^{-qc}\cos(\vec{q}\cdot\vec{d}_0)}{1-e^{-2qc}}\right)\right\} +$$

$$+\frac{2\pi}{\alpha}\Big\{\mathcal{D}_q(z,0)\,\vartheta(r_c-|z|) + \mathcal{D}_q(c-|z|,0)\left(\cos\vec{q}\cdot\vec{d}_0\right)\vartheta\left(r_c-c+|z|\right) , \qquad (4.1.12b)$$

$$z \leqq 0 \, , \; |z| \in [0,c] .$$

Letting $z \to -\infty$, $V_{\vec{q}}^{i-e}(z)$ becomes a periodic function in z with period 2c, and as is shown in Appendix A.1, $V_{\vec{q}}^{i-e}(z)$ takes the following form:

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha}\left\{\frac{\cosh(q|z|) + (\cos(\vec{q}\cdot\vec{d}_0))\cosh(q|z|-qc)}{q\sinh(qc)}\right\} +$$

$$+\frac{2\pi}{\alpha}\left\{\mathcal{D}_q(z,0)\,\vartheta(r_c-|z|)\cos\vec{q}\cdot d_0 + \mathcal{D}_q(c-|z|,0)\,\vartheta(r_c-c+|z|)\right\},$$

$$z<0 \quad , \ |z| \in [0,c] \qquad (4.1.12c)$$

where the interval $[0,c]$ is defined as the interval $[-Nc,-(N-1)c]$.

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha}\left\{\frac{\cosh(q|z|-qc) + (\cos(\vec{q}\cdot\vec{d}_0))\cosh(q|z|)}{q\sinh(qc)}\right\} +$$

$$+\frac{2\pi}{\alpha}\left\{\mathcal{D}_q(z,0)\,\vartheta(r_c-|z|) + \mathcal{D}_q(c-|z|,0)(\cos\vec{q}\cdot\vec{d}_0)\,\vartheta(r_c-c+|z|)\right\},$$

$$z<0 \quad , \ z \in [0,c] \quad , \qquad (4.1.12d)$$

and the interval $[0,c]$ is defined as the interval $[-(N+1)c,-Nc]$.

In all the above expressions only the real part of the Fourier terms has been retained.

It is quite interesting to notice that far from the surface the q^{-2} singularity of the zero-order Fourier term of the ion-electron interaction of the infinite system is rediscovered. Near the surface the zero-order Fourier term behaves as q^{-1}. It may be thought that the denominator $(1-e^{-2qc})$ contributes another singularity, but this is not the case. This apparent complexity is due to the fact that we are taking the limit $\vec{q} \to o$ after having taken the limit $z_\ell \to \infty$ in the summation over ℓ, (eqn. 4.1.9). If the limit $\vec{q} \to o$ is taken first, we see that the denominator $(1-e^{-2qc})$ is associated with the structure factor of the crystal and has no singularities. We shall return to this point in section 4.3.

4.2 THE HARTREE-POTENTIAL

The Hartree-potential, $B(\vec{r})$, is defined as

$$B(\vec{r}) = \int \frac{\rho(\vec{r}', \vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r}' \tag{4.2.1}$$

where $\rho(\vec{r}, \vec{r}')$ is the electron density, which in terms of the single electron wave functions $\psi_s(\vec{r})$ is given by

$$\rho(\vec{r}, \vec{r}') = \sum_s \psi_s(\vec{r}) \psi_s^*(\vec{r}') \vartheta(\epsilon_F - \varepsilon_s) \ . \tag{4.2.2}$$

where ϵ_F denotes the Fermi-energy.

The symmetry of the system makes us assume two-dimensional Bloch-functions as single electron wave functions, i.e.

$$\begin{aligned} \psi_s(\vec{r}) &= \sum_{\vec{h}} \zeta_{s\vec{h}}(z) \, e^{i(\vec{k}_s + \vec{h}) \cdot \vec{\rho}} \\ \vec{h} &\in \{\vec{h}; N\}, \quad s \equiv (\varepsilon_s, \vec{k}_s) \ . \end{aligned} \tag{4.2.3}$$

where $\vec{k}_s$ is the projection of the electron wave vector $\vec{K}_s$ onto the surface plane and ε_s is the energy of the electron. In terms of these wave functions, it is easily shown that the coordinate Fourier transform, $B_{\vec{q}}(z)$, of $B(\vec{r})$ takes the form

$$B_{\vec{q}}(z) = 2\pi \int_{-\infty}^{+\infty} dz' \, \rho_{\vec{q}}(z',z') \, \frac{e^{-q|z-z'|}}{q} \, , \qquad \vec{q} \in \{\vec{h};N\} \tag{4.2.4}$$

which exhibits a q^{-1} singularity in the zero-order term. $\rho_{\vec{q}}(z',z')$ is the Fourier transform of $\rho(\vec{r}',\vec{r}')$ in the sense of the definition (4.1.2a). Therefore, neither the $V_{\vec{q}}^{i-e}(z)$ nor the $B_{\vec{q}}(z)$ can be defined for $\vec{q} = o$. But as will be shown in the next paragraph, it is possible to obtain a finite zero-order term, $V_o(z)$, defined as

$$V_o(z) \equiv \lim_{\vec{q}\to o} \left\{ V_{\vec{q}}^{i-e}(z) + B_{\vec{q}}(z) \right\} . \tag{4.2.5}$$

4.3 THE SURFACE DIPOLE BARRIER

In the jellium model approximation the positive charge is assumed uniformly distributed all over the crystal. Let us assume that n_+ is the positive charge density and $n_-(z)$ is the negative charge (electron) density. Then, Poisson's equation may be used to determine the electrostatic potential, $V(z)$, i.e.

$$\frac{d^2 V(z)}{dz^2} = -4\pi n(z) \tag{4.3.1a}$$

where

$$n(z) = \begin{cases} n_+ - n_-(z) & z \leqq 0 \\ -n_-(z) & z > 0 \end{cases} . \tag{4.3.1b}$$

The potential V(z) is the single electron potential due to the average positive and negative charge distributions. It is therefore equivalent to the $V_0(z)$ defined in eqn. (4.2.5).

The integration of eqn. (4.3.1a) yields

$$V(z) = -4\pi \int_{z}^{+\infty} dz' \; z' n(z') \quad . \tag{4.3.2}$$

By definition (Lang, N.D., Kohn, W., 1970) the electrostatic "surface dipole barrier", D_0, is defined as

$$D_0 = V(+\infty) - V(-\infty) \tag{4.3.3a}$$

$$= -4\pi \int_{-\infty}^{+\infty} dz' \; z' n(z') \quad . \tag{4.3.3b}$$

Taking eqn. (4.3.1b) into account explicitly, we rewrite eqn. (4.3.3b) as

$$D_0 = 4\pi \int_{-\infty}^{+\infty} dz' \; z' n_-(z') - 4\pi \int_{-\infty}^{0} dz' \; z' n_+ \quad . \tag{4.3.4}$$

For a Bloch-electron system, the positive charge density, $n_+(\vec{r})$, is given by

$$n_+(\vec{r}) = \sum_{\ell s} \delta(\vec{\rho} - \vec{\rho}_{s\ell}) \, \delta(z - z_\ell) \tag{4.3.5}$$

and

$$n_+(z) = \frac{1}{\alpha} \sum_{\ell=0}^{M} \delta(z - z_\ell) \tag{4.3.6}$$

where M is the number of planes which are parallel to the surface and may be taken to the limit $M \to \infty$ in the case of a semi-infinite system. Using eqn. (4.3.6), eqn. (4.3.4) yields the following expression for the electrostatic surface dipole barrier, $D_0^{(B)}$, for a semi-infinite Bloch electron system

$$D_0^{(B)} = \lim_{M\to\infty} \left\{ 4\pi \int_{-\infty}^{+\infty} dz'\, z' n_-(z') + \frac{2\pi c}{\alpha} M(M+1) \right\} . \qquad (4.3.7)$$

We may start from the definition (4.3.3a) and use $V_0(z)$ as defined by eqn. (4.2.5) to write

$$D_0^{(B)} = V_0(+\infty) - V_0(-\infty)$$

$$= \lim_{\substack{\vec{q}\to 0 \\ z\to+\infty}} \left\{ V_{\vec{q}}^{i-e}(z) + B_{\vec{q}}(z) \right\} - \lim_{\substack{\vec{q}\to 0 \\ z\to-\infty}} \left\{ V_{\vec{q}}^{i-e}(z) + B_{\vec{q}}(z) \right\} . \qquad (4.3.8)$$

It is easily verified, that in the limit $\vec{q} \to 0$, the distinction between "odd" and "even" terms in eqn. (4.1.9) is no longer present, and ignoring for the moment the $\mathcal{D}_0$ term, we obtain

$$V_0^{i-e}(z) = \lim_{\substack{\vec{q}\to 0 \\ M\to\infty}} \left\{ - \frac{2\pi}{\alpha} \, \frac{e^{-q|z|}}{q} \, \frac{1 - e^{-(M+1)qc}}{1 - e^{-qc}} \right\} \qquad (4.3.9a)$$

$$z \geqslant 0$$

$$V_{o}^{i-e}(z) = \lim_{\substack{\vec{q}\to 0 \\ M\to\infty}} \left\{ -\frac{2\pi}{\alpha}\, \frac{e^{-q|z|}}{q}\, \frac{1-e^{+(M+1)qc}}{1-e^{+qc}} \right\}_{z\to-\infty} \tag{4.3.9b}$$

where in the last expression z → -∞ means that z is taken on the left side of the M^{th} lattice plane. Then, using eqns. (4.3.9a,b) and (4.2.4), eqn. (4.3.8) takes the form

$$D_{o}^{(B)} = \lim_{\substack{\vec{q}\to 0 \\ M\to\infty \\ z\to+\infty}} \left\{ \frac{ -\frac{2\pi}{\alpha}\, e^{-q|z|_{+\infty}}\, \frac{1-e^{-(M+1)qc}}{1-e^{-qc}} + 2\pi \int_{-\infty}^{+\infty} \rho_{\vec{q}}(z',z')\, e^{-q|z-z'|_{+\infty}}\, dz' }{q} \right\} +$$

$$+ (-1) \lim_{\substack{\vec{q}\to 0 \\ M\to\infty \\ z\to-\infty}} \left\{ \frac{ -\frac{2\pi}{\alpha}\, e^{-q|z|_{-\infty}}\, \frac{1-e^{+(M+1)qc}}{1-e^{+qc}} + 2\pi \int_{-\infty}^{+\infty} \rho_{\vec{q}}(z',z')\, e^{-q|z-z'|_{-\infty}}\, dz' }{q} \right\} \tag{4.3.10}$$

where the indices ± ∞ in the absolute values indicate that the variable z has to be taken in the limit z → ± ∞ respectively. Each of the above numerators takes the following form in the limit $\vec{q} \to 0$,

$$-\left\{ \lim_{M\to\infty} \frac{2\pi}{\alpha}(M+1) \right\} + 2\pi \int_{-\infty}^{+\infty} \rho_{o}(z',z')\, dz' .$$

which, by charge neutrality, is identically equal to zero. Therefore, using L'Hospital's rules, we obtain

$$D_0^{(B)} = \lim_{M\to\infty}\left\{\frac{2\pi c}{\alpha}M(M+1) + 2\pi\int_{-\infty}^{+\infty}\rho_0(z',z')\left\{|z-z'|_{-\infty} - |z-z'|_{+\infty}\right\}dz'\right.$$

$$= \lim_{M\to\infty}\left\{\frac{2\pi c}{\alpha}M(M+1) + 4\pi\int_{-\infty}^{+\infty}\rho_0(z',z')z'dz'\right\} . \qquad (4.3.11)$$

In the derivation of eqn. (4.3.11) the following result is useful:

$$\lim_{q\to 0}\left\{\frac{\partial}{\partial q}\left(\frac{1-e^{\pm Nqc}}{1-e^{\pm qc}}\right)\right\} = \pm\frac{c}{2}N(N-1) . \qquad (4.3.12)$$

It is therefore shown, eqn. (4.3.11), that by eliminating the singular zero-order Fourier terms of the ion-electron and Hartree potentials we reobtained the result arrived at in eqn. (4.3.7) which was obtained starting from Poisson's equation.

Furthermore, in order to obtain an expression for $V_0(z)$ which is independent of the explicit appearance of the number M, $V_0(z)$ is redefined with respect to its value at $z = +\infty$, i.e.

$$\tilde{V}_0(z) = V_0(z) - V_0(+\infty)$$

$$= \left\{V_0(z) - V_0(-\infty)\right\} - \left\{V_0(+\infty) - V_0(-\infty)\right\} . \qquad (4.3.13)$$

Following the same procedure as was used in the derivation of $D_0^{(B)}$ leads to

$$\tilde{V}_0(z) = \frac{4\pi|z|}{\alpha}\mu - \frac{2\pi c}{\alpha}\mu(\mu-1) +$$

$$+ (-1)\, 4\pi \int_z^{+\infty} \rho_0(z',z')\, z'\, dz' - 4\pi|z| \int_z^{+\infty} \rho_0(z',z')\, dz'$$

$$z \leqslant 0 \;, \quad z \in \left[-(\mu-1)c, -\mu c\right] \;, \qquad (4.3.14a)$$

$$\tilde{V}_0(z) = -4\pi \int_z^{+\infty} z'\, \rho_0(z',z')\, dz' + 4\pi|z| \int_z^{+\infty} \rho_0(z',z')\, dz'$$

$$z \geqslant 0 \;. \qquad (4.3.14b)$$

This is the zero-order Fourier term due to the Coulombic part of the ion-electron and Hartree potentials.

It may be argued that one could have included the ion-ion interaction potential in the elimination of the singularity of the zero-order Fourier term of the ion-electron and Hartree potentials (Taylor, P.L., 1970). We avoided to include this term in the preceding derivations because it is not consistent with our single-electron approximation. Also, the contribution of the ion-ion interaction to the zero-order field, eqn.

(4.2.5), will not affect the results for the surface dipole moment, eqn. (4.3.8), and the zero-order field $\tilde{V}_o(z)$, eqn. (4.3.13).

In order to complete the discussion about the zero-order Fourier terms of the ion-electron and Hartree potentials we notice that one must add the term $\mathfrak{D}_o(z)$ to the expression for $\tilde{V}_o(z)$ arrived at in eqns. (4.3.14a,b). There is not any difficulty in this calculation since $\mathfrak{D}_o(z)$, obtained from eqn. (4.1.8), is an analytic function of the reciprocal lattice vectors and very easily calculated.

Finally, we generalize the definition for the surface dipole moment $D_o^{(B)}$ given in eqn. (4.3.8) as follows:

$$D_o^{(B)} = \left\langle \tilde{V}_o(+\infty) \right\rangle - \left\langle \tilde{V}_o(-\infty) \right\rangle \tag{4.3.15a}$$

$$= -\frac{1}{c} \int_0^c \left\{ \lim_{z \to -\infty} \tilde{V}_o(z) \right\} dz \tag{4.3.15b}$$

where the symbol $< >$ denotes average value and $\tilde{V}_o(z)$ is taken from eqns. (4.3.14a,b).

4.4 APPLICATION ON A SIMPLIFIED SYSTEM

The following model may be regarded as a reasonable first approximation for any crystal.

It is assumed, Fig. 4.1, that for a semi-infinite crystal

$$\rho_o(z,z) \equiv \rho_o(z) = \begin{cases} \dfrac{1}{w_o}, & z \leq \dfrac{c}{2} \\ 0, & z > \dfrac{c}{2} \end{cases} \tag{4.4.1}$$

where c and ω_o have their previous meanings.

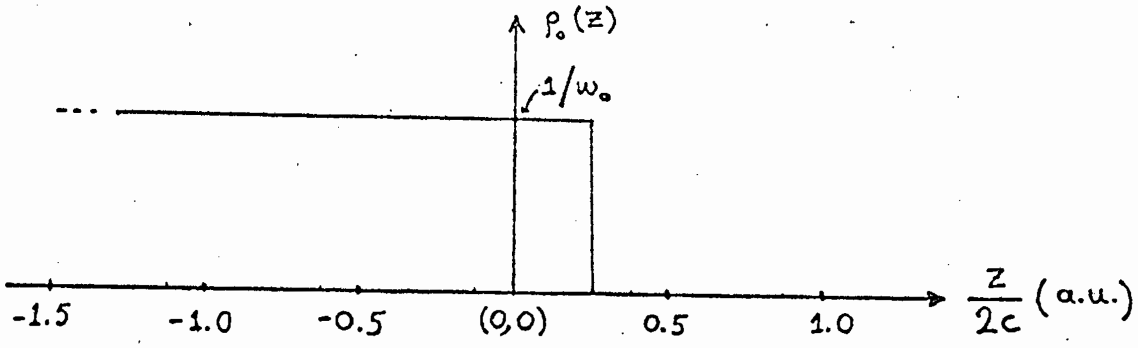


Fig. 4.1: Electron density profile of a simplified system.

For this system, the $\tilde{V}_o(z)$ term, as given by eqns. (4.3.14a,b), is calculated and shown in Fig. 4.2.

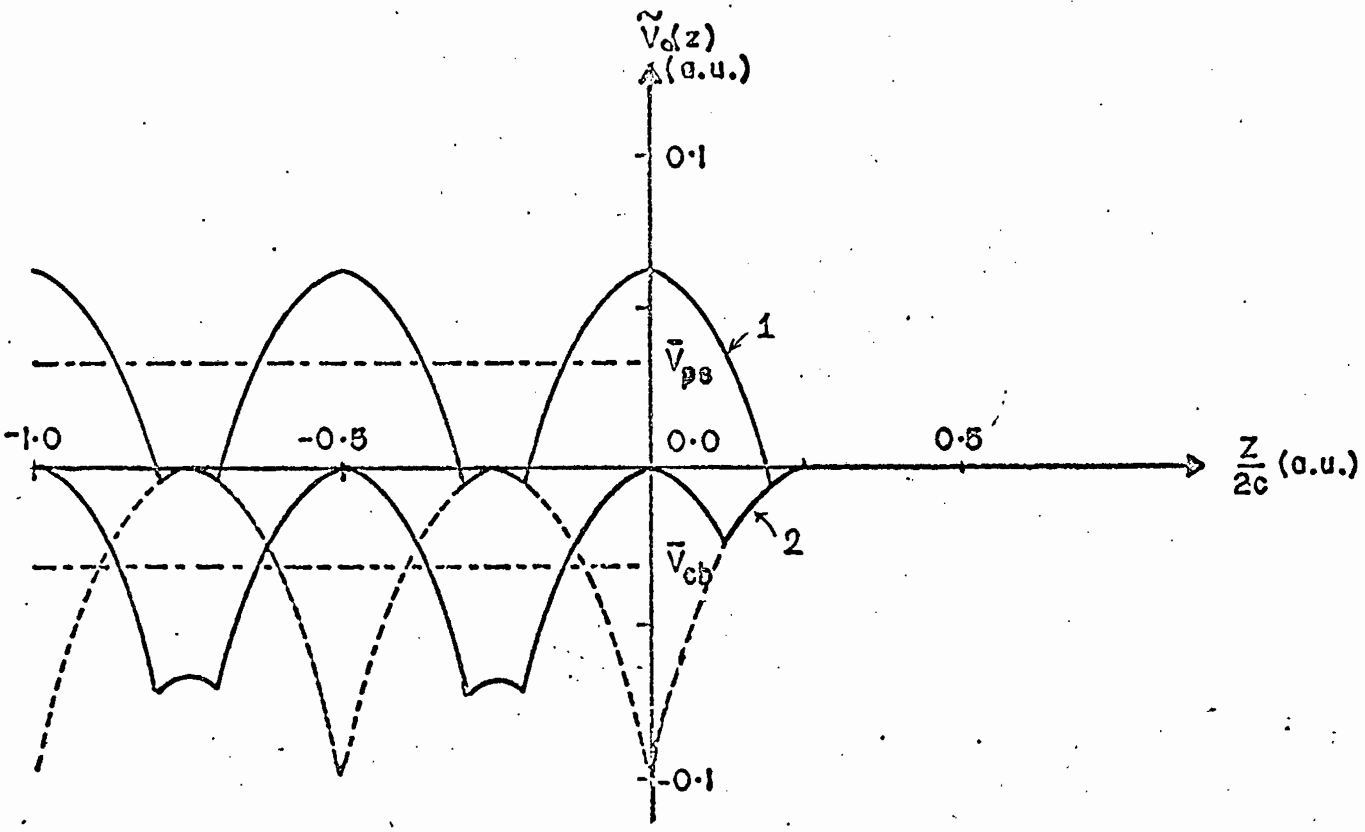


Fig. 4.2: Zero-order Fourier term of the combined ion-electron and Hartree potentials. The dotted curve is the result of eqns. (4.3.14a,b); it takes the form of the curve labelled 1 when $\mathfrak{D}_o$ is added. Curve 2 corresponds to a $\tilde{V}_o(z)$ term which conserves the surface dipole moment.

The corresponding surface dipole barrier, defined as the average value of $\tilde{V}_o(z \rightarrow -\infty)$, takes the simple form

$$D_o^{(B)} = -\frac{\pi c}{6\alpha} \quad . \tag{4.4.2}$$

This simple expression shows a strong dependence of $D_o^{(B)}$ on the lattice structure and orientation. Calculated values of $D_o^{(B)}$ for some metals in three different orientations are shown in Table I. It can be verified that the predictions of eqn. (4.4.2) are in reasonable agreement with the results of the jellium approximation (Lang, N.D., Kohn, W., 1970) as calculated by Lang and Kohn. The large value obtained for gold (Au) may be justified because of the high value (5.22eV)

TABLE I

Element	Lattice Constant (au)	$-\overline{V}_{CB}$ (eV)			$-V_{LK}$
		(001)	(011)	(111)	(eV)
Li	6.662	1.069	2.138	1.425	1.76
Na	8.091	.880	1.760	1.174	.91
K	10.073	.707	1.414	.942	.36
RB	10.622	.670	1.341	.894	.28
Cs	11.434	.623	1.246	.830	.13
Au	7.702	1.849	.925	9.862	2.32

$\overline{V}_{CB} = -\pi C/6\alpha$, as from eqn. (4.4.2); V_{LK} is the calculated values in the jellium approximation as reported by Lang and Kohn (Phys. Rev. 3B, 1215 (1971)).

of the work function. The fact that the Friedel oscillations which are present in the electron density profile become significant only at low electron densities supports the result of eqn. (4.4.2).

Another interesting feature may be pointed out in this simplified model. As is shown in Fig. 4.2, the inclusion of the term $\mathfrak{D}_o$ in the $\tilde{V}_o(z)$ shifts the average value of the potential $\tilde{V}_o(z)$. Apparently, a change in the reference level of the single electron energies takes place inside the bulk region, while no such change takes place inside the vacuum region. It is therefore necessary to shift the pseudopotential average value to the average value of the Coulomb field inside the bulk crystal, eqn.(4.3.15b), so as to keep a unique reference level. At the same time, the pseudopotential must join smoothly onto the Coulombic field near the surface ions, as obtained from eqn. (4.3.14b). This may be thought as a consequence of the fact that the pseudopotential formalism does not change the electrostatic surface dipole moment.

4.5 THE SCHRÖDINGER'S EQN. IN THE HARTREE APPROXIMATION

The single electron Hamiltonian, $\hat{H}_o(\vec{r})$, for an electron in a semi-infinite metal takes the following form in the Hartree approximation:

$$\hat{H}_o(\vec{r}) = -\frac{1}{2}\nabla^2 + V^{i-e}(\vec{r}) + B(\vec{r}) \quad . \tag{4.5.1}$$

We are looking for single electron wave functions, $\psi_s(\vec{r})$, with corresponding eigenvalues ε_s which satisfy the

Schrödinger's equation

$$\hat{H}_o(\vec{r})\,\psi_s(\vec{r}) = \varepsilon_s\,\psi_s(\vec{r}) \;. \qquad (4.5.2)$$

Using the symmetry of the system, the quantum state s may be labelled by specifying the energy ε_s and the projection, $\vec{k}_s$, of the single electron wave vector $\vec{K}_s$ onto the surface plane. This determination, although not what one could have expected by generalizing the corresponding case of the infinite metal (section 2.2), nevertheless is a widely used representation. The possible values of $\vec{k}_s$ are taken inside the projection of the Fermi-surface onto the reciprocal surface plane. For completeness we recall that the Fermi-surface is the geometrical locus of values of $\vec{K}$ for which the single electron energies are equal to the Fermi-energy, ϵ_F, which in turn is defined as the chemical potential of the system at zero temperature.

Recalling once again the symmetry of the system, we may assume that the single electron wave functions are two-dimensional Bloch functions which satisfy the periodic lattice of the surface plane. In other words

$$\psi_s(\vec{r}) = \sum_{\vec{h}} \xi_{s\vec{h}}(z)\, e^{i(\vec{k}_s+\vec{h})\cdot\vec{\rho}}$$

$$\vec{r} \equiv (\vec{\rho}, z) \quad , \vec{h} \in \{\vec{h}\, ; N\} \;. \qquad (4.5.3)$$

Substituting in eqn. (4.5.2) for $\psi_s(\vec{r})$ as given above a set of simultaneous differential equations is obtained

$$-\frac{d^2\xi_{s\vec{h}_i}}{dz^2} + \left\{ (\vec{k}_s+\vec{h}_i)^2 - 2\mathcal{E}_s + 2\tilde{V}_o(z) \right\} \xi_{s\vec{h}_i} +$$

$$+ 2\sum_{\vec{h}_j \neq \vec{h}_i} \left\{ V^{i-e}_{\vec{h}_i-\vec{h}_j}(z) + B_{\vec{h}_i-\vec{h}_j}(z) \right\} \xi_{s\vec{h}_j} = 0 ,$$

$$\forall\, (\vec{h}_i, \vec{h}_j) \in \{\vec{h}; N\} \times \{\vec{h}; N\} , \qquad (4.5.4)$$

where all the symbols have their previously defined meaning.

The resultant system of differential equations (4.5.4) is the form of the Schrödinger's equation in the Hartree approximation. This form is retained in every local approximation for the exchange and correlation potentials. In this particular case the solution follows exactly the same lines as in the case where the non-locality of the exchange and correlation potential is explicitly taken into account, as described in the next chapter. Therefore we postpone the discussion on the solution of eqns. (4.5.4) until after the discussion on the exchange and correlation potentials.

CHAPTER 5

INTERACTING ELECTRON SYSTEM

When the electrons are "allowed" to interact with each other, besides the Hartree term, some other "local" or "non-local" terms are introduced in the single electron Hamiltonian. Generally these terms are referred to as "exchange" and "correlation" potentials. The first is a standard contribution to the single-electron Hamiltonian due to the antisymmetrization of the single electron wave functions. The second includes everything other than the Hartree and exchange contributions. In our case the correlation effects will be treated only at the level of the Random Phase Approximation.

The mathematical formulation will be presented in the Green's function formalism, following the systematic analysis of Fetter and Walecka (Fetter, A.L., Walecka, J.D., 1971).

5.1 GENERAL FORMULATION

By solving the Schrödinger's equation in the Hartree approximation, i.e. eqn. (4.5.2), a set of orthornormal wave functions, $\{\psi_s(\vec{r})\}$, is obtained. In terms of this set of basis states the Green's function, $\hat{G}^{(0)}(\vec{r},\vec{r}\,',\omega)$, associated with eqn. (4.5.2) can be written

$$\hat{G}^{(0)}(\vec{r},\vec{r}\,',\omega) = \sum_{s} \psi_s(\vec{r})\,\psi_s^*(\vec{r}\,') \left\{ \frac{\theta(\varepsilon_s-\epsilon_F)}{\omega-\varepsilon_s+i\eta} + \frac{\theta(\epsilon_F-\varepsilon_s)}{\omega-\varepsilon_s-i\eta} \right\} \qquad (5.1.1)$$

with $0 < \eta \ll 1$.

When the electron-electron interactions are included, the system may be described by a Green's function, $\hat{G}(\vec{r},\vec{r}',\omega)$, which can be obtained from the solution of the following Dyson's equation:

$$\hat{G}(\vec{r},\vec{r}',\omega) = \hat{G}^{(0)}(\vec{r},\vec{r}',\omega) + \int d\vec{r}_1\, d\vec{r}_2\, \hat{G}^{(0)}(\vec{r},\vec{r}_1,\omega)\, \mathcal{L}(\vec{r}_1,\vec{r}_2,\omega)\, \hat{G}(\vec{r}_2,\vec{r}',\omega) \,. \tag{5.1.2}$$

The term $\mathcal{L}(\vec{r}_1,\vec{r}_2,\omega)$ is called the proper self-energy part. In the diagrammatic representation the proper self-energy is defined as any part of a diagram that is connected to the rest of the diagram by two "particle-lines" and cannot be separated into two pieces by cutting a single particle line.

If it happens that $\mathcal{L}(\vec{r}_1,\vec{r}_2,\omega)$ is ω-independent, a solution of $\hat{G}(\vec{r},\vec{r}',\omega)$ may be sought in the form of $\hat{G}^{(0)}(\vec{r},\vec{r}',\omega)$, i.e.

$$\hat{G}(\vec{r},\vec{r}',\omega) = \sum_s \tilde{\psi}_s(\vec{r})\, \tilde{\psi}^*_s(\vec{r}') \left\{ \frac{\vartheta(\tilde{\varepsilon}_s - \epsilon_F)}{\omega - \tilde{\varepsilon}_s + i\eta} + \frac{\vartheta(\epsilon_F - \tilde{\varepsilon}_s)}{\omega - \tilde{\varepsilon}_s - i\eta} \right\} \tag{5.1.3}$$

where $\tilde{\psi}_s(\vec{r}) \in \{\tilde{\psi}(\vec{r})\}$, with $\{\tilde{\psi}_s(\vec{r})\}$ a complete set of single electron wave functions with energies $\tilde{\varepsilon}_s$.

Most commonly, $\mathcal{L}(\vec{r}_1,\vec{r}_2,\omega)$ depends on $\tilde{\psi}_s(\vec{r})$. If their functional relationship is known, then in combination with the Dyson's eqn. (5.1.2) an integral equation for $\tilde{\psi}_s(\vec{r})$ in terms of $\psi_s(\vec{r})$ may be derived. This equation is obtained as follows:

Define the operator $\hat{L}_1$,

$$\hat{L}_1(\vec{r}) = \omega - \hat{H}_0(\vec{r}) \tag{5.1.4a}$$

$$= \omega + \frac{1}{2}\nabla^2 - V^{i\text{-}e}(\vec{r}) - B(\vec{r}) \tag{5.1.4b}$$

and apply it on $\hat{G}^{(0)}(\vec{r},\vec{r}\,',\omega)$. It yields:

$$\hat{L}_1(\vec{r})\,\hat{G}^{(0)}(\vec{r},\vec{r}\,'\omega) = \delta(\vec{r}-\vec{r}\,') \tag{5.1.5}$$

which implies that $\hat{L}_1$ is the inverse operator $(\hat{G}^{(0)})^{-1}$. Application of $\hat{L}_1$ on both sides of Dyson's eqn. (5.1.2) yields (after an extra integration over $\vec{r}\,'$):

$$\left\{-\frac{1}{2}\nabla^2 + V^{i\text{-}e}(\vec{r}) + B(\vec{r})\right\}\tilde{\psi}_s(\vec{r}) + \\ + \int d\vec{r}_2\,\mathcal{L}(\vec{r},\vec{r}_2)\,\tilde{\psi}_s(\vec{r}_2) = \tilde{\varepsilon}_s\,\tilde{\psi}_s(\vec{r}) \;. \tag{5.1.6}$$

The last equation, which is a Schrödinger's like equation, indicates that the proper self-energy $\mathcal{L}(\vec{r},\vec{r}\,')$ acts as a static non-local potential. It is noticed that besides the assumption that the proper self-energy part is independent of the frequency ω, the operator $\mathcal{L}(\vec{r},\vec{r}\,')$ must be assumed to be Hermitian in order to ensure the orthogonality of $\tilde{\psi}_s(\vec{r})$'s.

In general the solution of eqn. (5.1.6) is a very difficult job. When the functional relationship of $\mathcal{L}(\vec{r},\vec{r}\,')$ and $\tilde{\psi}_s(\vec{r})$ is known, then eqn. (5.1.6) may be solved self-consistently. In other words, an initial set of orthonormal eigenstates, $\tilde{\psi}_s^{(0)}(\vec{r})$ is assumed known, and the corresponding self-energy is calculated. Then eqn. (5.1.6) reduces to an eigenvalue problem; when solved a new set of eigenfunctions $\tilde{\psi}_s^{(1)}(\vec{r})$ is obtained and the corresponding proper self-energy is recalculated. The whole procedure is repeated until a self-consistency is obtained for both the eigenfunctions and eigenvalues.

An equivalent way of solving the integrodifferential eqn. (5.1.6) self-consistently is the following:

A non-local single electron potential, $\Lambda^{(s)}(\vec{r})$, is defined by:

$$\Lambda^{(s)}(\vec{r})\,\psi_s(\vec{r}) = \int \mathcal{L}(\vec{r},\vec{r}\,')\,\psi_s(\vec{r}\,')\,d\vec{r}\,' , \qquad (5.1.7a)$$

or

$$\Lambda^{(s)}(\vec{r}) = \frac{1}{\psi_s(\vec{r})} \int \mathcal{L}(\vec{r},\vec{r}\,')\,\psi_s(\vec{r}\,')\,d\vec{r}\,' . \qquad (5.1.7b)$$

Then eqn. (5.1.6) takes the simple form:

$$\left\{-\frac{1}{2}\nabla^2 + V^{i-e}(\vec{r}) + B(\vec{r})\right\}\psi_s(\vec{r}) + \\ + \Lambda^{(s)}(\vec{r})\,\psi_s(\vec{r}) = \varepsilon_s\,\psi_s(\vec{r}) . \qquad (5.1.8)$$

In the sense of the self-consistent solution of the eqn. (5.1.8), the single electron potential $\Lambda^{(s)}(\vec{r})$ is calculated according to eqn. (5.1.7b) using the eigenfunctions $\psi_s(\vec{r})$ obtained in the previous iteration.

As it is going to be discussed in the next paragraphs, eqn. (5.1.7a) is a generalization of Bardeen's definition for a single electron exchange potential (Bardeen, J., 1936). Furthermore eqn. (5.1.7a) may be used to study the various contributions to the single electron potential $\Lambda^{(s)}(\vec{r})$, as for example those due to the correlation effects.

In the next paragraphs two contributions to the proper self-energy are discussed. The first describes the exchange interaction while the second includes the correlation effects in the Random Phase Approximation (RPA).

5.2 EXCHANGE POTENTIAL

The proper self-energy which describes the effect of the anti-symmetrization of the single electron wave functions, or in other words the exchange interaction, is defined as:

$$\mathcal{L}^{(E)}(\vec{r},\vec{r}\,') = \lim_{\eta\to 0} \frac{i}{2\pi} V^{e-e}(\vec{r},\vec{r}\,') \int d\omega\, e^{i\omega\eta} G(\vec{r},\vec{r}\,';\omega) \qquad (5.2.1)$$

which equivalently may be written as:

$$\mathcal{L}^{(E)}(\vec{r},\vec{r}\,') = -\frac{1}{2} V^{e-e}(\vec{r},\vec{r}\,')\, \rho(\vec{r},\vec{r}\,') \qquad (5.2.2)$$

where

$$V^{e-e}(\vec{r},\vec{r}\,') = \frac{1}{|\vec{r}-\vec{r}\,'|} \qquad (5.2.3)$$

is the repulsive electron-electron Coulomb potential, and

$$\rho(\vec{r},\vec{r}\,') = \sum_{s} \psi_s(\vec{r})\, \psi_s^{*}(\vec{r}\,')\, \vartheta(\epsilon_F - \varepsilon_s) \qquad (5.2.4)$$

is the electron density function where the set of quantum numbers, s, includes also the electron spin.

The proper self-energy part $\mathcal{L}^{(E)}(\vec{r},\vec{r}\,')$ may be used in eqns. (5.1.7a.b) to define the exchange potential, $A^{(s)}(\vec{r})$, as follows:

$$A^{(s)}(\vec{r}_1)\,\psi_s(\vec{r}_1) = \int \mathcal{L}^{(E)}(\vec{r}_1,\vec{r}_2)\,\psi_s(\vec{r}_2)\,d\vec{r}_2 \quad . \tag{5.2.5}$$

Direct substitution from eqn. (5.2.2) yields:

$$A^{(s)}(\vec{r}_1)\,\psi_s(\vec{r}_1) = -\frac{1}{2}\int V^{e\text{-}e}(\vec{r}_1,\vec{r}_2)\,\rho(\vec{r}_1,\vec{r}_2)\,\psi_s(\vec{r}_2)\,d\vec{r}_2$$

$$= -\frac{1}{2}\sum_{s'}\int \frac{\psi_{s'}(\vec{r}_1)\,\psi^*_{s'}(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}\,\psi_s(\vec{r}_2)\,\vartheta(\epsilon_F-\varepsilon_{s'})\,d\vec{r}_2 . \tag{5.2.6}$$

Furthermore, we substitute for the wave functions $\psi_s(\vec{r})$, as given by eqn. (4.5.3). The result is:

$$A^{(s)}(\vec{r}_1)\sum_{\vec{h}}\zeta_{s\vec{h}}(z_1)\,e^{i(\vec{k}_s+\vec{h})\cdot\vec{\rho}_1} =$$

$$= -\frac{1}{2}\sum_{s'\vec{h}_1\vec{h}_2\vec{h}_3}\vartheta(\epsilon_F-\varepsilon_{s'})\,\zeta_{s'\vec{h}_1}(z_1)\,e^{i(\vec{k}_{s'}+\vec{h}_1)\cdot\vec{\rho}_1}\times$$

$$\times\int\frac{d\vec{\rho}_2\,dz_2}{|\vec{r}_1-\vec{r}_2|}\,\zeta^*_{s'\vec{h}_2}(z_2)\,\zeta_{s\vec{h}_3}(z_2)\,e^{-i(\vec{k}_{s'}+\vec{h}_2)\cdot\vec{\rho}_2}\,e^{i(\vec{k}_s+\vec{h}_3)\cdot\vec{\rho}_2} \tag{5.2.7a}$$

$$= -\frac{1}{2}\sum_{s'\vec{h}_1\vec{h}_2\vec{h}_3}\vartheta(\epsilon_F-\varepsilon_{s'})\,\zeta_{s'\vec{h}_1}(z_1)\,e^{i(\vec{k}_s-\vec{h}_2+\vec{h}_3+\vec{h}_1)\cdot\vec{\rho}_1}\times$$

$$\times\, 2\pi \int_{-\infty}^{+\infty} dz_2\, \xi^*_{s'\vec{h}_2}(z_2)\, \xi_{s\vec{h}_3}(z_2)\, \frac{e^{-|\vec{k}_{s'}-\vec{k}_s+\vec{h}_2-\vec{h}_3|\,|z_1-z_2|}}{|\vec{k}_{s'}-\vec{k}_s+\vec{h}_2-\vec{h}_3|}$$

$$\vec{h}_i \in \{\vec{h};N\},\ i=1,2,3. \qquad (5.2.7b)$$

Multiplication of both sides of the last equation by $e^{-i(\vec{k}_s+\vec{h}')\cdot\vec{\rho}_1}$ and integration over $\vec{\rho}_1$ yields:

$$\sum_{\vec{h}} \Big\{ A^{(s)}_{\vec{h}'-\vec{h}}(z_1)\, \xi_{s\vec{h}}(z_1) + \pi \sum_{s'\vec{h}_2\vec{h}_3} \delta_{\vec{h}+\vec{h}_3,\,\vec{h}'+\vec{h}_2}\, \xi_{s'\vec{h}}(z_1) \times$$

$$\times\, \vartheta(\epsilon_F-\varepsilon_{s'}) \int_{-\infty}^{+\infty} dz_2\, \xi^*_{s'\vec{h}_2}(z_2)\, \xi_{s\vec{h}_3}(z_2) \times$$

$$\times\, \frac{e^{-|\vec{k}_{s'}-\vec{k}_s+\vec{h}_2-\vec{h}_3|\,|z_1-z_2|}}{|\vec{k}_{s'}-\vec{k}_s+\vec{h}_2-\vec{h}_3|} \Big\} = 0\,, \qquad (5.2.8)$$

where

$$A^{(s)}_{\vec{h}}(z) = \frac{1}{a} \int d\vec{\rho}\; e^{-i\vec{h}\cdot\vec{\rho}}\, A^{(s)}(\vec{r})\,,\quad \vec{h}\in\{\vec{h};N\} \qquad (5.2.9)$$

is the Fourier transform of the exchange potential. From eqn. (5.2.8) one obtains in the sense of Bardeen

$$A^{(s)}_{\vec{h}'-\vec{h}}(z_1) = -\frac{\pi}{\zeta_{s\vec{h}}(z_1)} \sum_{s'\vec{h}_2\vec{h}_3} \vartheta\,(\epsilon_F - \varepsilon_{s'})\,\delta_{\vec{h}-\vec{h}',\,\vec{h}_2-\vec{h}_3}\,\zeta_{s'\vec{h}}(z_1) \times$$

$$\times \int_{-\infty}^{+\infty} dz_2\,\zeta^{*}_{s'\vec{h}_2}(z_2)\,\zeta_{s\vec{h}_3}(z_2)\,\frac{e^{-|\vec{k}_{s'}-\vec{k}_s+\vec{h}_2-\vec{h}_3|\,|z_1-z_2|}}{|\vec{k}_{s'}-\vec{k}_s+\vec{h}_2-\vec{h}_3|}\,. \qquad (5.2.10)$$

Finally, in the case when only the zero-order Fourier term of the wave function is non-vanishing, Bardeen's result is reobtained, i.e.

$$A^{(s)}_{0}(z_1) = -\frac{\pi}{\zeta_{s,0}(z_1)} \sum_{s'} \vartheta(\epsilon_F - \varepsilon_{s'})\,\zeta_{s',0}(z_1) \times$$

$$\times \int_{-\infty}^{+\infty} dz_2\,\zeta^{*}_{s',0}(z_2)\,\zeta_{s,0}(z_2)\,\frac{e^{-|\vec{k}_{s'}-\vec{k}_s|\,|z_1-z_2|}}{|\vec{k}_{s'}-\vec{k}_s|}\,. \qquad (5.2.11)$$

Eqn. (5.2.10) is the generalization of eqn. (5.2.11) in the case of the semi-infinite Bloch electron system. The lattice periodicity results in a matrix representation of the exchange potential with respect to the reciprocal lattice vectors. It is noticed that in eqn. (5.2.10) the delta function ensures that the projection of the wave vector onto the surface plane is conserved within a reciprocal lattice vector. From the scattering point of view, this type of momentum conservation is known as umklapp scattering process. Another characteristic of eqn. (5.2.10) is the presence of singularities at the boundaries of the two-dimensional Brillouin zones. Although this could have been expected from the theory of the infinite Bloch electron system, it becomes more important in the case of the semi-infinite Bloch electron system. This is because the Fermi surface lies within the first Brillouin zone of the three-dimensional reciprocal space, while projected onto the reciprocal surface plane occupies part of the first and the second Brillouin zones of the two-dimensional reciprocal space. The apparent singularity in the zero-order Fourier term $A_0^{(s)}(z)$, has to be excluded since $\vec{k}_{s'}$ should be different from $\vec{k}_s$ by Pauli's principle. In general, $A_0^{(s)}(z)$ is evaluated by taking the principal value integral in eqn. (5.2.11) over the variable $\vec{k}_{s'}$.

The zero-order Fourier term, $A_0^{(s)}(z)$, is a very important factor in investigating the surface properties of a metal. Like the $\tilde{V}_0(z)$ term, eqns. (4.3.14a,b), $A_0^{(s)}(z)$ determines the average potential energy, due to the exchange interaction, for an electron inside and outside the metal. The difference

$$D_{0s}^{(EXC)} = A_0^{(s)}(+\infty) - A_0^{(s)}(-\infty) \qquad (5.2.12)$$

is analogous to the electrostatic surface dipole barrier, eqn. (4.3.8), and may be called the "exchange surface barrier". Its effect is the same as that of $D_0^{(B)}$ but it appears that for the Na-crystal $D_{0s}^{(EXC)}$ is much larger than $D_0^{(B)}$ and therefore $D_0^{(EXC)}$ is more responsible for the electronic behaviour of Na. This is also related with the fact that a corresponding contribution, $D_{os}^{(CORR)}$,

$$D_{os}^{(CORR)} = C_o^{(s)}(+\infty) - C_o^{(s)}(-\infty) \qquad (5.2.13)$$

due to the correlation potential, $C_o^{(s)}(z)$, is also much smaller than $D_{os}^{(EXC)}$.

We define as "surface barrier", $\tilde{D}_s$, the sum

$$\tilde{D}_s = D_o^{(B)} + D_{os}^{(EXC)} + D_{os}^{(CORR)} . \qquad (5.2.14)$$

An important point can be noticed here. The surface barrier is not the same for every electron; it depends on its energy and this behaviour has to be taken into account in studying the electronic properties of metal surfaces.

In this section we shall examine the exchange surface barrier while the correlation contribution $D_{os}^{(CORR)}$ will be the subject of the next paragraph.

An exact analytic expression for $A_o^{(s)}(z)$ is very difficult to obtain. This is because the wave functions $\xi_{s\vec{h}}(z)$ are determined numerically. As a result, the calculation of $A_o^{(s)}(z)$ is a numerical problem. It is only when the solution of the Schrödinger's equation has only the zero-order Fourier term $\xi_{s,o}(z) \neq 0$, that analytical results may be obtained. In this particular case the single electron wave functions take the following asymptotic form in the bulk region

$$\xi_{s,o}(z) \sim \cos(q_s z + \phi_{q_s}) , \; z \to -\infty , \qquad (5.2.15)$$

where q_s is the z-component of the wave vector $\vec{K}_s$ and ϕ_{q_s} a phase factor.

Using this asymptotic form, it can be shown (Appendix A.2) that in the bulk region,

$$A_o^{(s)}(z_j) \equiv A_o^{(\vec{k}_s, q_s)}(z_j)$$

$$= -\frac{1}{2\pi}\,\frac{1}{\cos(q_s z_j + \phi_{q_s})} \int_{-k_F}^{+k_F} dq_2 \left\{ C_1 \left[\sinh^{-1} \frac{k_F^2 - q_s^2 - \vec{k}_s^2 + Q_1^2}{2|Q_1||\vec{k}_s|} \right.\right.$$

$$\left. - \sinh^{-1} \frac{Q_1^2 - \vec{k}_s^2}{2|\vec{k}_s||Q_1|} \right] + C_2 \left[\sinh^{-1} \frac{k_F^2 - q_s^2 - \vec{k}_s^2 + Q_2^2}{2|Q_2||\vec{k}_s|} \right.$$

$$\left.\left. - \sinh^{-1} \frac{Q_2^2 - \vec{k}_s^2}{2|\vec{k}_s||Q_2|} \right] \right\} \cos(q_2 z_j + \phi_{q_2}) \qquad (5.2.16)$$

where $k_F^2 = 2\epsilon_F$ and

$$Q_1 = q_s - q_2 \qquad (5.2.17a)$$

$$Q_2 = q_s + q_2 \qquad (5.2.17b)$$

$$C_1 = \cos(\phi_{q_s} - \phi_{q_2} + q_s z_j - q_2 z_j) \qquad (5.2.17c)$$

$$C_2 = \cos(\phi_{q_s} + \phi_{q_2} + q_s z_j + q_2 z_j) \quad . \qquad (5.2.17d)$$

It is quite interesting to notice that for $\vec{k}_s = 0$ and $\phi_{q_s} = 0$, eqn. (5.2.16) yields:

$$A_o^{(q)}(z_j = o) = -\frac{2k_F}{\pi}\left\{\frac{1}{2} + \frac{1-\beta^2}{4\beta}\ln\left|\frac{1+\beta}{1-\beta}\right|\right\}, \quad (5.2.18)$$

$$\beta = \frac{q}{k_F}$$

which is the result of the jellium model approximation of the infinite metal. Also it can be easily verified that for

$$\left.\begin{aligned} \phi_{q_s} &= -\frac{\pi}{2} \\ \vec{k}_s &= o \end{aligned}\right\} \forall(\vec{k}_s, q_s), \quad (5.2.19)$$

eqn. (5.2.16) gives the following result at z = o,

$$A_o^{(q)}(z=o) = -\frac{k_F}{\pi}\left\{\frac{3}{4} - \frac{1}{4\beta^2} + \frac{1}{8\beta^3}(1+2\beta^2-3\beta^4)\ln\left|\frac{1+\beta}{1-\beta}\right|\right\} \quad (5.2.20)$$

where

$$\beta = \frac{q}{k_F}.$$

This is the result obtained by Bardeen (Bardeen, J., 1936) for the semi-infinite metal which is described by an infinite potential well at the surface. The significance of the eqn. (5.2.16) is that it allows to consider electrons with components of velocity parallel to the surface in contrast with Bardeen's model in which the results obtained for electrons with velocities perpendicular to the surface were assumed valid for arbitrary velocities by replacing β in eqn. (5.2.20) with

$$\beta = \frac{\sqrt{q^2 + k^2}}{k_F}, \quad \vec{K} = (\vec{k}, q). \quad (5.2.21)$$

It should be mentioned that one should not have underestimated the contribution to the surface dipole moment due to the non-zero Fourier terms of the exchange and correlation potentials. It is only the limited class of the nearly free electron metals in which the non-zero order Fourier terms of the exchange and correlation potentials have no importance (Chapter 7).

5.3 CORRELATION POTENTIAL

It is assumed here that the correlation potential can be approximated at the level of the Random Phase Approximation (RPA). According to the general eqns. (5.1.7a,b), the correlation potential, $C^{(s)}(\vec{r})$, is defined as

$$C^{(s)}(\vec{r})\psi_s(\vec{r}) = \int \mathcal{L}^{(CORR)}(\vec{r},\vec{r}\,')\,\psi_s(\vec{r}\,')\,d\vec{r}\,' \qquad (5.3.1)$$

where

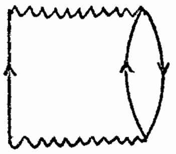
$$\mathcal{L}^{(CORR)}(\vec{r},\vec{r}\,') = \lim_{\omega\to 0}\int \frac{d\varepsilon}{2\pi}\,d\vec{r}_1\,d\vec{r}_2\,G(\vec{r},\vec{r}\,',\omega-\varepsilon)\times$$

$$\times V^{e-e}(\vec{r},\vec{r}_1)\,V^{e-e}(\vec{r}\,',\vec{r}_2)\,\Pi(\vec{r}_1,\vec{r}_2,\varepsilon) \qquad (5.3.2)$$

and $\Pi(\vec{r}_1,\vec{r}_2,\varepsilon)$ is the polarization function.

Diagrammatically, eqn. (5.3.2) is expressed by the following diagram:

$$\hat{\mathcal{L}}^{(CORR)} =$$



(5.3.3)

where the straight line corresponds to the Green's function $\hat{G}$, the wiggled line to the electron-electron interaction $\hat{V}^{e-e}$, (cf. eqn. (5.2.3)), and the symbol $\bigcirc$ denotes the polarization function $\hat{\Pi}$ which has the following analytical expression:

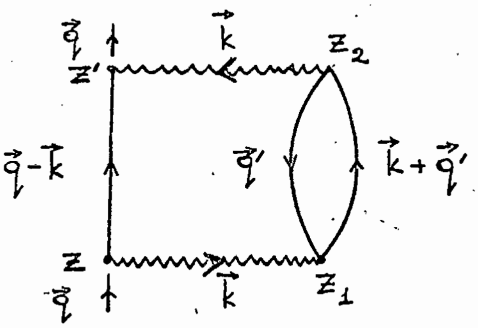
$$\Pi(\vec{r}_1,\vec{r}_2,\omega) = -2i\int \frac{d\varepsilon}{2\pi}\, G(\vec{r}_1,\vec{r}_2,\omega+\varepsilon)\, G(\vec{r}_2,\vec{r}_1,\varepsilon) \,. \tag{5.3.4}$$

When the electron system exhibits a translational invariance for spatial translations parallel to the surface, one can take the Fourier transform of eqn. (5.3.2) and write

$$\Sigma^{(CORR)}_{\vec{q}}(z,z') = \lim_{\omega\to 0}\int \frac{d\varepsilon}{2\pi} \sum_{\vec{k}} dz_1\, dz_2\, G_{\vec{q}-\vec{k}}(z_1,z',\omega-\varepsilon)\,\cdot$$

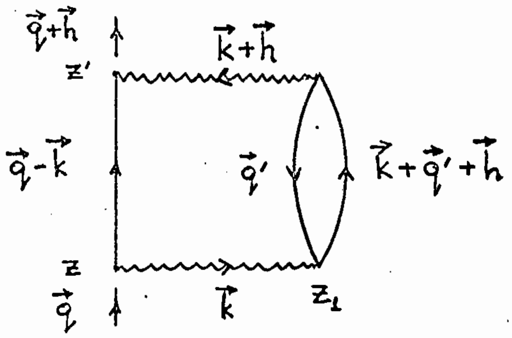
$$\cdot\, 4\pi^2\, \frac{e^{-k|z-z_1|}}{k}\, \frac{e^{-k|z'-z_2|}}{k}\, P_{\vec{k}}(z_1,z_2,\varepsilon) \tag{5.3.5}$$

where $P_{\vec{k}}(z_1,z_2,\varepsilon)$ is the Fourier transform of the polarization function $\Pi(\vec{r}_1,\vec{r}_2,\varepsilon)$. It represents the propagation of an electron-hole pair of wave vector $\vec{k}$ parallel to the surface. Physically, the correlation potential in the RPA is the contribution to the single electron potential which arises from the creation and reabsorption of an electron-hole pair. As is shown below in more detail,



an electron with wave vector $\vec{q}$ creates an electron-hole pair due to the electron-electron interaction and reabsorbs it later on. It is remarkable that such processes conserve the momentum of the electron.

In the presence of the lattice, the existence of the Umklapp scattering processes allow contributions to the correlation potential of the form (Inkson, J.C., 1974):

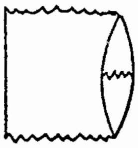
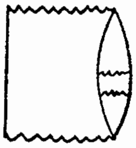


$, \quad \vec{h} \in \{\vec{h}\}$.

As Adler observes (Adler, S.L., 1962), such processes give rise to local field corrections which in turn arise because the electric field changes rapidly inside the unit cell of the crystal.

We can include these local field corrections in the correlation potential $C^{(s)}(\vec{r})$ if we proceed in evaluating the Fourier coefficients, $C^{(s)}_{\vec{h}_i-\vec{h}_j}(z)$, of the correlation potential along the lines of the previous section 5.2. But the obtained expressions are too complicated to be used for computational purposes. For this reason we have restricted ourselves in the zero-order approximation.

Before we proceed discussing the zero-order Fourier coefficient of the correlation potential, it is quite interesting to notice that one can go beyond the Random Phase Approximation by including diagrams of the form

 ,  etc.,

The zero-order Fourier coefficient, $\Sigma_0^{(\mathrm{CORR})}(z,z')$, of the self-energy part which gives rise to the correlation potential can be obtained from eqn. (5.3.5). We have

$$\Sigma_0^{(\mathrm{CORR})}(z,z',\omega) = \int \frac{d\varepsilon}{2\pi} \sum_{\vec{Q}} G_{-\vec{Q}}(z,z',\omega-\varepsilon) \int dz_1\, dz_2 \; 4\pi^2 \cdot$$

$$\times \frac{e^{-Q|z-z_1|}}{Q} \, \frac{e^{-Q|z'-z_2|}}{Q} \, P_{\vec{Q}}(z_1,z_2,\varepsilon) \qquad (5.3.6a)$$

$$= 2\pi \sum_{\vec{Q}} \int d\varepsilon\, dz_1\, dz_2 \, \frac{e^{-Q|z-z_1|}}{Q} \, \frac{e^{-Q|z'-z_2|}}{Q} \cdot$$

$$\times \left\{ \mathrm{Re}\, G_{-\vec{Q}}(z,z',\omega-\varepsilon)\, \mathrm{Re}\, P_{\vec{Q}}(z_1,z_2,\varepsilon) - \mathrm{Im}\, G_{-\vec{Q}}(z,z',\omega-\varepsilon)\, \mathrm{Im}\, P_{\vec{Q}}(z_1,z_2,\varepsilon) \right\}. \qquad (5.3.6b)$$

Eqns. (5.3.6a,b) become relatively easier to calculate if the free electron dispersion relation is assumed valid. Although in this case the effects of the lattice are completely ignored, nevertheless we can obtain a reasonable approximation for the correlation potential. It appears necessary to obtain a relatively easier computer-wise expression for the correlation potential in order to be able to include explicitly this single electron potential in the calculation of the single-electron wave functions. One could solve the Schrödinger equation in the Hartree-Fock approximation and proceed by finding the Random Phase Approximation to the Hartree-Fock solution (Feibelman, P.J., 1968)(Feibelman, P.J., 1971). But in this case the effect of the correlation potential to the surface dipole moment will not be explicitly taken into account unless a self-consistent iteration is performed.

Let $\psi_{\vec{K}_i}(\vec{r})$ be a single electron wave function of (three-dimensional) wave vector $\vec{K}_i$ which has a component $\vec{k}_i$ parallel to the surface and a component q_i perpendicular to the surface. We assume like in the jellium approximation that

$$\psi_{\vec{K}_i}(\vec{r}) = e^{i\vec{k}_i\cdot\vec{\rho}}\,\xi_{q_i}(z)\ . \qquad (5.3.7)$$

The Fourier coefficients of the Green and polarization function have the following real and imaginary parts

$$\mathrm{Re}\,G_{\vec{Q}}(z,z',\omega-\varepsilon) = \sum_{q_3} \xi_{q_3}(z)\,\xi^*_{q_3}(z')\,\frac{\theta(\varepsilon_3-\epsilon_F)+\theta(\epsilon_F-\varepsilon_3)}{\omega-\varepsilon-\varepsilon_3} \qquad (5.3.8)$$

$$\mathrm{Im}\,G_{\vec{Q}}(z,z',\omega-\varepsilon) = \sum_{q_3} (-\pi)\,\delta(\omega-\varepsilon-\varepsilon_3)\,\xi_{q_3}(z)\,\xi^*_{q_3}(z')\ \times$$
$$\times\left\{\theta(\varepsilon_3-\epsilon_F)-\theta(\epsilon_F-\varepsilon_3)\right\} \qquad (5.3.9)$$

$$\mathrm{Re}\,P_{\vec{Q}}(z_1,z_2,\varepsilon) = 2\sum_{\vec{k}_1 q_1 q_2} \delta_{\vec{k}_1-\vec{k}_2,\,\vec{Q}}\ \xi_{q_1}(z_1)\,\xi^*_{q_1}(z_2)\,\xi_{q_2}(z_2)\,\xi^*_{q_2}(z_1)\ \times$$

$$\times\ \vartheta(\varepsilon_1-\epsilon_F)\,\vartheta(\epsilon_F-\varepsilon_2)\cdot\frac{2\,(\varepsilon_1-\varepsilon_2)}{\varepsilon^2-(\varepsilon_2-\varepsilon_1)^2} \qquad (5.3.10)$$

$$\operatorname{Im} P_{\vec{Q}}(z_1,z_2,\varepsilon) = 2\sum_{\vec{k}_1 q_1 q_2} \delta_{\vec{k}_1-\vec{k}_2,\vec{Q}}\ \xi_{q_1}(z_1)\,\xi^*_{q_1}(z_2)\,\xi_{q_2}(z_2)\,\xi^*_{q_2}(z_1)$$

$$\times(-\pi)\,\vartheta(\varepsilon_1-\epsilon_F)\,\vartheta(\epsilon_F-\varepsilon_2)\Big\{\delta(\varepsilon+\varepsilon_1-\varepsilon_2)+\delta(\varepsilon+\varepsilon_2-\varepsilon_1)\Big\} \qquad (5.3.11)$$

where

$$\varepsilon_i = \frac{1}{2}\left(\vec{k}_i^2+q_i^2\right)\ ,\ i=1,2,3. \qquad (5.3.12)$$

The real part of the Fourier coefficients of the polarization function is a very useful quantity in studying surface plasmons (Inglesfield, J.E., Wikborg, E., 1973). In Appendix A.3 it is shown that

$$\operatorname{Re} P_{\vec{Q}}(z_1,z_2,\omega) = \frac{a}{\pi}\,\frac{1}{Q^2}\sum_{q_1 q_2}\Big\{-Q^2+\sqrt{A^2-Q^2r_1^2}\ \cdot$$

$$\times\left(1+\vartheta(A)-\vartheta(-A)\right)\vartheta\left(\frac{A^2}{Q^2}-r_1^2\right)\ \cdot$$

$$\times\ \xi_{q_1}(z_1)\,\xi_{q_2}(z_2)\,\xi^*_{q_1}(z_2)\,\xi^*_{q_2}(z_1)\ . \qquad (5.3.13)$$

where

$$r_i^2 = k_F^2 - q_i^2 \quad , \quad i = 1, 2, 3, \tag{5.3.14}$$

$$A = \omega + \frac{1}{2} \left(Q^2 + q_2^2 - q_1^2 \right) . \tag{5.3.15}$$

Eqn. (5.3.13) may easily be used in the calculation of the dispersion relation of surface plasmons. It also determines the linear response of a semi-infinite crystal to external fields (Newns, D.M., 1970), (Beck, D.E., Celli, V., 1970).

Using eqns. (5.3.8) and (5.3.10), it can easily be verified that the first term of eqn. (5.3.6b) gives no contribution to the self-energy $\mathcal{L}_0^{(CORR)}(z,z')$. Then the presence of the delta functions in eqns. (5.3.9) and (5.3.11) allows us to do the integration over the energy variable, ε, in eqn. (5.3.6b). Subsequently, using eqn. (5.3.12) and for the case of $\omega = 0$, we obtain

$$\mathcal{L}_0^{(CORR)}(z,z') = -4\pi^3 \sum_{\substack{\vec{Q}, \vec{k}_1 \\ q_1 q_2 q_3}} \int dz_1 \, dz_2 \, \xi_{q_3}(z) \, \xi^*_{q_3}(z') \, \xi_{q_1}(z_1) \, \xi^*_{q_1}(z_2) \times$$

$$\times \, \xi_{q_2}(z_2) \, \xi^*_{q_2}(z_1) \, \delta_{\vec{k}_1 - \vec{k}_2, \vec{Q}} \, \vartheta(\varepsilon_1 - \varepsilon_F) \, \vartheta(\epsilon_F - \varepsilon_2) \, \delta\left(A - \vec{k}_1 \cdot \vec{Q}\right) \times$$

$$\times \left\{ \vartheta(\varepsilon_3 - \epsilon_F) - \vartheta(\epsilon_F - \varepsilon_3) \right\} \tag{5.3.16}$$

where

$$A = \frac{1}{2} \left(q_2^2 - q_1^2 - q_3^2 \right) . \tag{5.3.17}$$

Without loss of generality it can be assumed that $\vec{Q} = (Q, 0)$

and using the property

$$\delta(ax) = |a|^{-1}\,\delta(x) \tag{5.3.17}$$

we can easily do the integration over the variable $\vec{k}_1$. We can therefore write the following expression for the correlation potential $C_o^{(s)}(z)$,

$$C_o^{(s)}(z) \equiv C_o^{(q_i)}(z) = \frac{1}{\xi_{q_i}(z)} \int dz'\, \xi_{q_i}(z')\,(-4\pi^3)\, \times$$

$$\times \sum_{\substack{\vec{Q},\vec{k}_1 \\ q_1 q_2 q_3}} \int dz_1\, dz_2\, \xi_{q_3}(z)\,\xi^*_{q_3}(z')\,\xi_{q_1}(z_1)\,\xi^*_{q_1}(z_2)\,\xi_{q_2}(z_2)\,\xi^*_{q_2}(z_1)\, \times$$

$$\times\, \theta(\varepsilon_1-\epsilon_F)\,\theta(\epsilon_F-\varepsilon_2)\left\{\theta(\varepsilon_3-\epsilon_F)-\theta(\epsilon_F-\varepsilon_3)\right\}\delta_{\vec{k}_1-\vec{k}_2,\vec{Q}}\;\delta\!\left(\frac{A}{Q}-k_{1x}\right)\frac{1}{Q} \tag{5.3.18}$$

where $\vec{k}_1 = (k_{1x}, k_{2x})$ and A is defined by eqn. (5.3.17). The usefulness of eqn. (5.3.18) is that it provides a means of calculating the z-dependence of the correlation potential. It becomes even simpler if one assumes that

$$\xi_{q_i}(z) \sim \sin q_i z$$

in which case the q_1-dependence of the bulk values of the correlation potential may be found. It is our aim to use eqn. (5.3.18) in an attempt to include correlation effects in our calculations.

CHAPTER 6

SOLUTION OF SCHRÖDINGER'S EQUATION

In each iteration during the process of the self-consistent solution, Schrödinger's equation is solved in each of the three regions of the semi-infinite system. This implies that, for the general case where the Schrödinger's equation reduces to N second order simultaneous differential equations, the general solution is given within 6N constants of integration. A unique determination of these constants is achieved here by applying the boundary conditions of the system. These boundary conditions ensure the continuity of the wave functions and their derivatives over the whole space. They also ensure the stability of the wave functions at $z = \pm\infty$, and the Bloch character of the solutions inside the bulk region.

6.1 MATRIX REPRESENTATION OF SCHRÖDINGER'S EQUATION

The differential equation given in eqn. (5.1.8) is rewritten here for completeness as eqn. (6.1.1):

$$\left\{-\frac{1}{2}\nabla^2 + V^{i-e}(\vec{r}) + B(\vec{r})\right\}\psi_s(\vec{r}) + \Lambda^{(s)}(\vec{r})\,\psi_s(\vec{r}) = \varepsilon_s\,\psi_s(\vec{r}) \; . \qquad (6.1.1)$$

It is assumed that the Fourier coefficients of the exchange and correlation potential $\Lambda^{(s)}(\vec{r})$ have the following properties:

$$\Lambda^{(s)}_{\vec{q}}(z) = \Lambda^{*(s)}_{-\vec{q}}(z) \qquad (6.1.2a)$$

$$\Lambda^{(s)}_{\vec{q}}(z+c) = e^{i\vec{q}\cdot\vec{d}_o}\Lambda^{(s)}_{\vec{q}}(z) \qquad (6.1.2b)$$

$$\vec{q} \in \{\vec{h};N\} .$$

The single electron wave functions $\psi_s(r)$ are assumed to be defined by eqn. (4.5.3). A direct substitution into eqn. (6.1.1) and some straight-forward algebra yields a set of simultaneous differential equations:

$$-\frac{d^2\xi_{s\vec{h}_i}}{dz^2} + \left\{(\vec{k}_s+\vec{h}_i)^2 - 2\mathcal{E}_s + 2\tilde{V}_o(z)\right\}\xi_{s\vec{h}_i} +$$

$$+ 2\sum_{\vec{h}_i\neq\vec{h}_j}\left\{V^{i-e}_{\vec{h}_i-\vec{h}_j} + B_{\vec{h}_i-h_j}\right\}\xi_{s\vec{h}_j} + 2\sum_{h_j}\Lambda^{(s)}_{\vec{h}_i-\vec{h}_j}\xi_{sh_j} = 0$$

$$\forall\,(\vec{h}_i,\vec{h}_j) \in \{\vec{h};N\}\times\{\vec{h};N\} . \qquad (6.1.3)$$

Eqn. (6.1.3) is the form of the Schrödinger's equation for the interacting semi-infinite Bloch electron system. The only difference of eqn. (6.1.3) from eqn. (4.5.4) is that the former contains the extra Fourier terms of the exchange and correlation potential $\Lambda^{(s)}(\vec{r})$. The solution of these two systems of differential equations goes along the same lines if the Fourier terms of the exchange and correlation potential $\Lambda^{(s)}_{\vec{q}}(z)$ satisfy eqn. (6.1.2a). As is shown in Appendix A.4, eqn. (6.1.2a) is satisfied by both the $V^{i-e}_{\vec{q}}(z)$

and $B_{\vec{q}}(z)$ terms. The second assumption stated in eqn. (6.1.2b) (which is satisfied by the Fourier terms of the ion-electron and Hartree potentials) is not necessary in obtaining the solution of either the set of eqns. (6.1.3) or (4.5.4). It only helps to reduce the computer time in obtaining the solution of the Schrödinger's equation in the bulk region (Appendix A.4).

The set of the N differential equations, (6.1.3), may be written as a matrix differential equation

$$\frac{d\vec{\mathcal{Z}}_s(z)}{dz} = \underline{\underline{\mathcal{D}}}_s(z)\,\vec{\mathcal{Z}}_s(z)\,, \tag{6.1.4}$$

where

$$\vec{\mathcal{Z}}_s(z) = \left\{ \begin{matrix} \xi'_{s\vec{h}_1}(z) \\ \xi'_{s\vec{h}_2}(z) \\ \vdots \\ \xi'_{s\vec{h}_N}(z) \\ \xi_{s\vec{h}_1}(z) \\ \vdots \\ \xi_{s\vec{h}_N}(z) \end{matrix} \right\} \tag{6.1.5a}$$

$$\xi'_{s\vec{h}_i}(z) = \frac{d\xi_{s\vec{h}_i}}{dz}\,, \quad i = 1, 2, \ldots, N \tag{6.1.5b}$$

$$\underline{\underline{\mathcal{D}}}_s(z) = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{M}}_s(z) - \underline{\underline{\Delta}}_s(z) \\ \underline{\underline{I}} & \underline{\underline{0}} \end{pmatrix} \tag{6.1.5c}$$

$$\left(\underline{\underline{M}}_s(z)\right)_{ij} = 2\left\{ V^{i\text{-}e}_{\vec{h}_i-\vec{h}_j}(z) + B_{\vec{h}_i-\vec{h}_j}(z) + \Lambda^{(s)}_{\vec{h}_i-\vec{h}_j}(z) \right\} \,, i \neq j \tag{6.1.5d}$$

$$\left(\underline{\underline{\Delta}}_s(z)\right)_{ij} = \left\{ 2\varepsilon_s - 2\tilde{V}_0(z) - 2\Lambda^{(s)}_{\vec{h}_i - \vec{h}_i}(z) - (\vec{k}_s + \vec{h}_i)^2 \right\} \delta_{ij} \qquad (6.1.5e)$$

$$i = 1, \ldots, N \ , \quad j = 1, 2, \ldots, N, \qquad \vec{h}_i \in \{\vec{h}; N\}, \ i = 1, \ldots, N \ ,$$

and $\underline{\underline{O}}$, $\underline{\underline{I}}$ are the (N×N) null and unit matrix respectively.

The solution of eqn. (6.1.4) is related with the solution of the matrix differential equation, (6.1.6), (Kappos, D., 1960),

$$\frac{d\,\underline{\underline{P}}_s(z)}{dz} = \underline{\underline{\mathcal{D}}}_s(z)\,\underline{\underline{P}}_s(z)$$

$$\underline{\underline{P}}_s(o) = \underline{\underline{I}} \qquad (6.1.6)$$

where the matrix $\underline{\underline{P}}_s(z)$ is a (2N×2N) matrix called propagation matrix (Jepsen, D.W., Marcus, P.M., 1971). The relation of eqn. (6.1.4) with eqn. (6.1.6) may be stated as follows:

If $\vec{P}_s^{\,(i)}$, i=1,...,2N are 2N solutions of eqn. (6.1.4), these solutions form a set of basis states if and only if the determinant of the matrix whose columns are the vectors $\vec{P}_s^{\,(i)}$ is different from zero for every value of z in the region of definition of $\underline{\underline{\mathcal{D}}}_s(z)$.

Therefore the solution of eqn. (6.1.6) satisfying the boundary condition $\underline{\underline{P}}_s(o) = \underline{\underline{I}}$ will yield all the linear independent solutions of eqn. (6.1.4). As a consequence, the general solution of eqn. (6.1.4) may be written as:

$$\vec{\mathcal{Z}}_s(z) = \underline{\underline{P}}_s(z)\,\vec{\alpha} \quad , \qquad (6.1.7)$$

where $\vec{\alpha}$ is a constant vector of 2N-components which is determined by the boundary conditions of the problem. These boundary conditions determine uniquely the solution, and in the case of a semi-infinite system may be summarized as follows:

For any solution, $\vec{\mathfrak{Z}}_s(z)$,

i) $\vec{\mathfrak{Z}}_s(z)$, $\dfrac{d\vec{\mathfrak{Z}}_s(z)}{dz}$ are continuous functions of z,

$\forall\ z \in (-\infty, +\infty)$.

ii) $$\lim_{z \to +\infty} \vec{\mathfrak{Z}}_s(z) = \vec{0}$$

iii) $$\lim_{z \to -\infty} \vec{\mathfrak{Z}}_s(z) \text{ is finite}$$

iv) $$\vec{\mathfrak{Z}}_s(z+2c) = \lambda_s \vec{\mathfrak{Z}}_s(z)$$

$z \to -\infty$

λ_s = constant (independent of z).

The boundary conditions i), ii), iii) ensure that the solutions are continuous and finite while the last condition ensures that the solution satisfies the periodicity of the crystal along the z-axis within the bulk region.

In the following paragraphs, the solution to the Schrödinger's equation is obtained independently in each of the three different regions of the crystal. Finally, the matching of these solutions along the boundaries of the regions is carried out resulting in the solution of the Schrödinger's equation for an electron in the semi-infinite metal.

6.2 SOLUTION IN THE BULK AND SURFACE REGIONS

A significant property of the bulk region is that it exhibits three-dimensional periodicity. This is reflected into the single electron wave functions $\vec{\mathcal{Z}}_s(z)$, which become Bloch functions. More precisely, $\vec{\mathcal{Z}}_s(z)$ has to obey the following property:

$$\vec{\mathcal{Z}}_s(z+2c) = \lambda_s \vec{\mathcal{Z}}_s(z) \tag{6.2.1}$$

where λ_s is a constant, and 2c is the period along the z-axis.

If $\underline{\underline{P}}_s^{(B)}(z)$ is the propagation matrix in the bulk region, eqn. (6.1.7) is rewritten as:

$$\vec{\mathcal{Z}}_s(z) = \underline{\underline{P}}_s^{(B)}(z)\,\vec{\alpha}_s \quad . \tag{6.2.2}$$

A direct substitution of eqn. (6.2.1) into eqn. (6.2.2) results in:

$$\underline{\underline{P}}_s^{(B)}(z+2c)\,\vec{\alpha}_s = \lambda_s \underline{\underline{P}}_s^{(B)}(z)\,\vec{\alpha}_s \quad . \tag{6.2.3}$$

But the periodicity along the z-axis implies that

$$\underline{\underline{\mathcal{D}}}_s\,(z+2c) = \underline{\underline{\mathcal{D}}}_s\,(z)\,, \tag{6.2.4}$$

a relation which, according to Floquet's theorem, ensures that

$$\underline{\underline{P}}_s^{(B)}(z+2c) = \underline{\underline{P}}_s^{(B)}(z)\,\underline{\underline{P}}_s^{(B)}(2c)\,. \tag{6.2.5}$$

As a result, eqn. (6.2.3) yields

$$\underline{\underline{P}}_s^{(B)}(2c)\,\vec{\alpha}_s = \lambda_s\,\vec{\alpha}_s\,. \tag{6.2.6}$$

It is therefore proved that the possible values of λ_s in eqn. (6.2.1) are the eigenvalues of the propagation matrix $\underline{\underline{P}}_s^{(B)}(z)$, at $z = 2c$, and $\vec{\alpha}_s$ is the corresponding eigenvector of $P_s^{(B)}(2c)$. There exist 2N such solutions $\mathcal{Z}_s(z)$, and a linear combination of them may be written as:

$$\vec{\mathcal{Z}}_s\,(z) = \underline{\underline{P}}_s^{(B)}(z)\,\underline{\underline{Q}}_s\,\vec{a}\,, \tag{6.2.7}$$

where $\underline{\underline{Q}}_s$ is the matrix of eigenvectors of $\underline{\underline{P}}_s^{(B)}(2c)$, i.e.

$$\underline{\underline{P}}_s^{(B)}(2c)\,\underline{\underline{Q}}_s = \underline{\underline{Q}}_s\,\underline{\underline{L}}_s \tag{6.2.8}$$

where $\underline{\underline{L}}_s$ is a diagonal matrix whose diagonal elements are the eigenvalues of $\underline{\underline{P}}_s^{(B)}(2c)$. The 2N components of the vector $\vec{a}$ are determined by the boundary conditions of the problem.

The stability of the wave function at $z = -\infty$ implies that the solutions which correspond to eigenvalues λ_s with $|\lambda_s| > 1$ may be excluded from eqn. (6.2.7). This is equivalent to setting the corresponding components of the vector $\vec{a}$ equal to zero.

If M solutions exist which correspond to eigenvalues with absolute value greater than one, the symmetry of the system may be used to prove that there exist M solutions with absolute value less than one, and hence also 2(N-M) solutions which correspond to eigenvalues with absolute value equal to one. The validity of the above sentence follows from the following theorem.

THEOREM:

For a semi-infinite crystal whose surface plane is a lattice plane which has a centre of symmetry and is a mirror plane for the crystal, the propagation matrix $\underline{\underline{P}}_s^{(B)}(z)$ defined by eqn. (6.1.6) has the following properties:

i) No eigenvalue of $\underline{\underline{P}}_s^{(B)}(2c)$ is equal to zero.

ii) To every eigenvalue λ_{s_i} of $\underline{\underline{P}}_s^{(B)}(2c)$ corresponding to the eigenvector $\vec{Q}_{s_i}$, there exists an eigenvalue λ_{s_j} with corresponding eigenvector $\vec{Q}_{s_j}$ such that:

$$\lambda_{s_j} = \frac{1}{\lambda_{s_i}} \quad , \quad i,j = 1,2,\ldots 2N \qquad (6.2.9)$$

and if:

$$\vec{Q}_{s_i} \equiv \begin{pmatrix} \vec{Q}^{(1)}_{s_i} \\ \vec{Q}^{(2)}_{s_i} \end{pmatrix} \quad , \quad i = 1,2,\ldots,2N$$

it follows:

$$\vec{Q}_{s_j} = \begin{pmatrix} -\vec{Q}_{s_i}^{(1)} \\ +\vec{Q}_{s_i}^{(2)} \end{pmatrix} \quad , i, j = 1, 2, \ldots, 2N \tag{6.2.10}$$

PROOF:

Since the determinant of $P_s^{(B)}(2c) \neq 0$, it follows that no eigenvalue is zero. This proves the first property. The second property is a result of the symmetry of the crystal. The presence of the centre of symmetry in the surface plane ensures that the matrix $\underline{\underline{M}}_s$ in eqn. (6.1.5c) has the property

$$\underline{\underline{M}}_s(z) = \underline{\underline{M}}_s^T(z) \tag{6.2.11}$$

where T denotes the transpose of a matrix. Eqn. (6.2.11) implies that

$$\underline{\underline{\tilde{P}}}_s^{(B)}(z) = \underline{\underline{\Gamma}}^T \left\{ \left[\underline{\underline{P}}_s^{(B)}(z) \right]^{-1} \right\}^T \underline{\underline{\Gamma}} \tag{6.2.12}$$

where

$$\underline{\underline{\Gamma}} = \begin{pmatrix} \underline{\underline{0}} & -\underline{\underline{I}} \\ \underline{\underline{I}} & \underline{\underline{0}} \end{pmatrix} \tag{6.2.13}$$

is also a solution of eqn. (6.1.6), as can be verified by direct substitution. The uniqueness of the solution of eqn. (6.1.6) yields

$$\underline{\underline{P}}_s^{(B)}(z) = \underline{\underline{\tilde{P}}}_s^{(B)}(z) \tag{6.2.14}$$

This proves that $\underline{\underline{P}}_s^{(B)}(z)$ and $\{\underline{\underline{P}}_s^{(B)}(z)\}^{-1}$ have the same eigenvalues, which proves the statement (6.2.9).

Furthermore, the assumption that the surface plane is a mirror plane, implies that if $\underline{\underline{P}}_s^{(B)}(z)$ is partitioned according to

$$\underline{\underline{P}}_s^{(B)}(z) = \begin{pmatrix} \underline{\underline{P}}_1(z) & \underline{\underline{P}}_2(z) \\ \underline{\underline{P}}_3(z) & \underline{\underline{P}}_4(z) \end{pmatrix} \tag{6.2.15}$$

then

$$\underline{\underline{P}}_s^{(B)}(-z) = \begin{pmatrix} \underline{\underline{P}}_1(z) & -\underline{\underline{P}}_2(z) \\ -\underline{\underline{P}}_3(z) & \underline{\underline{P}}_4(z) \end{pmatrix} . \tag{6.2.16}$$

It is not difficult to prove that $\underline{\underline{P}}_s^{(B)}(z)$ and $\underline{\underline{P}}_s^{(B)}(-z)$ are related through a similarity transformation, i.e.

$$\underline{\underline{P}}_s^{(B)}(-z) = \underline{\underline{S}}^{-1}\, \underline{\underline{P}}_s^{(B)}(z)\, \underline{\underline{S}} \tag{6.2.17}$$

where

$$\underline{\underline{S}} = \underline{\underline{S}}^{-1} = \begin{pmatrix} -\underline{\underline{I}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{I}} \end{pmatrix} . \tag{6.2.18}$$

Therefore $\underline{\underline{P}}_s^{(B)}(2c)$ and $\underline{\underline{P}}_s^{(B)}(-2c)$ have the same eigenvalues and if $\vec{Q}_{s_i}$ is an eigenvector of $\underline{\underline{P}}_s^{(B)}(2c)$ the vector

$$\vec{Q}_{s_j} \equiv \vec{R}_{s_i} = S^{-1}\vec{Q}_{s_i} = S^{-1}\begin{pmatrix} \vec{Q}_{s_i}^{(1)} \\ \vec{Q}_{s_i}^{(2)} \end{pmatrix} = \begin{pmatrix} -\vec{Q}_{s_i}^{(1)} \\ +\vec{Q}_{s_i}^{(2)} \end{pmatrix} \tag{6.2.19}$$

is an eigenvector of $\underline{\underline{P}}_s^{(B)}(-2c)$. It remains now to prove that if

$$\underline{\underline{P}}_s^{(B)}(2c)\,\vec{Q}_{s_i} = \lambda_{s_i}\vec{Q}_{s_i} \qquad (6.2.20a)$$

it follows

$$\underline{\underline{P}}_s^{(B)}(2c)\,\vec{Q}_{s_j} = \frac{1}{\lambda_{s_i}}\vec{Q}_{s_j}\,, \qquad (6.2.20b)$$

$$\vec{Q}_{s_j} = \vec{R}_{s_i}\,. \qquad (6.2.20c)$$

From eqn. (6.2.5) we obtain

$$\underline{\underline{P}}_s^{(B)}(-2c)\,\underline{\underline{P}}_s^{(B)}(2c) = \underline{\underline{P}}_s^{(B)}(0) = \underline{\underline{I}} \qquad (6.2.21)$$

or

$$\underline{\underline{P}}_s^{(B)}(-2c)\,\underline{\underline{P}}_s^{(B)}(2c)\,\vec{Q}_{s_i} = \underline{\underline{I}}\,\vec{Q}_{s_i}$$

which yields

$$\underline{\underline{P}}_s^{(B)}(-2c)\,\vec{Q}_{s_i} = \frac{1}{\lambda_{s_i}}\vec{Q}_{s_i}$$

Finally, using eqn. (6.2.17), we obtain

$$\underline{\underline{S}}^{-1}\,\underline{\underline{P}}_s^{(B)}(2c)\,\underline{\underline{S}}\,\vec{Q}_{s_i} = \frac{1}{\lambda_{s_i}}\vec{Q}_{s_i}$$

or

$$\underline{\underline{P}}_s^{(B)}(2c)\,\vec{R}_{s_i} = \frac{1}{\lambda_{s_i}}\vec{R}_{s_i}\,.$$

which proves the last part of the theorem.

An obvious result of the above theorem is that the eigenvalues with absolute value equal to one occur in pairs of complex conjugate numbers. Every pair of such eigenvalues corresponds to two-propagating solutions; one propagates to the left and the other to the right. If λ_{s_i} is such as

$$\left| \lambda_{s_i} \right| = 1$$

we can write (Jepsen, D.W., Marcus, P.M., 1971)

$$\lambda_{s_i} \equiv e^{i k_z^{(s_i)} 2c} \tag{6.2.22}$$

or

$$k_z^{(s_i)} = \frac{1}{2c} \operatorname{arctg} \frac{\operatorname{Im} \lambda_{s_i}}{\operatorname{Re} \lambda_{s_i}} , \tag{6.2.23}$$

from which the wave vectors, $k_z^{(s_i)}$, of the propagating solutions are obtained.

Assuming that there are (N-M) pairs of eigenvalues with absolute value equal to one, it follows that there exist 2(N-M) propagating solutions. The solutions which have positive wave vectors, $k_z^{(s_i)}$, may be grouped together to form an "incident" wave while the others which have negative wave vectors, $k_z^{(s_i)}$, are grouped together to form the "reflected" wave.

The incident wave, $\vec{\mathcal{Z}}_s^{\,inc}(z)$, may be written as

$$\vec{\mathcal{Z}}_s^{inc}(z) = \underline{\underline{P}}_s^{(B)}(z)\begin{pmatrix}\vec{Q}_{s1} \cdots \vec{Q}_{s,N-M}\end{pmatrix}\begin{pmatrix}a_{s,1}\\ \vdots \\ a_{s,N-M}\end{pmatrix}, \qquad (6.2.24)$$

where $a_{s,i}$, i=1,...2(N-M) are components of the vector $\vec{a}_s$ and $\vec{Q}_{s,i}$, i=1,...,(N-M) are the eigenvectors of $\underline{\underline{P}}_s^{(B)}$ (2c) which correspond to eigenvalues, $\lambda_{s,i}$, which have absolute value equal to one and result in positive $k_z^{(s_i)}$. Similarly the reflected wave $\vec{\mathcal{Z}}_s^{ref}(z)$ is written as

$$\vec{\mathcal{Z}}_s^{ref}(z) = \underline{\underline{P}}_s^{(B)}(z)\begin{pmatrix}\vec{R}_{s1} \cdots \vec{R}_{s,N-M}\end{pmatrix}\begin{pmatrix}a_{s,N-M+1}\\ \vdots \\ a_{s,2N-2M}\end{pmatrix} \qquad (6.2.25)$$

where

$$\vec{R}_{s,i} \equiv \underline{\underline{S}}\,\vec{Q}_{s,i} \qquad , i = 1,\ldots, N-M. \qquad (6.2.26)$$

Eqn. (6.2.25) is equivalent to

$$\vec{\mathcal{Z}}_s^{ref}(z) = \underline{\underline{S}}\,\underline{\underline{P}}_s^{(B)}(-z)\begin{pmatrix}\vec{Q}_{s1} \cdots \vec{Q}_{s,N-M}\end{pmatrix}\begin{pmatrix}a_{s,N-M+1}\\ \vdots \\ a_{s,2N-2M}\end{pmatrix} \qquad (6.2.27)$$

as may be seen with the help of eqns. (6.2.26) and (6.2.17).

It is assumed that both the incident and reflected waves are normalized so as to carry the unit of current per unit area, i.e.

$$(\vec{A}_R^*)^T\vec{A}_R = (\vec{A}_I^*)^T\vec{A}_I = 1 \qquad (6.2.28)$$

where

$$\vec{A}_R = \begin{pmatrix} a_{s,N-M+1} \\ \vdots \\ a_{s,2N-2M} \end{pmatrix} \qquad (6.2.29)$$

$$\vec{A}_I = \begin{pmatrix} a_{s,1} \\ \vdots \\ a_{s,N-M} \end{pmatrix} \qquad (6.2.30)$$

Then it is easy to show that

$$\vec{\mathcal{Z}}_s^{\,ref}(z) = \underline{\underline{P}}_s^{(B)}(z)\,\underline{\underline{S}}\,\left\{\underline{\underline{P}}_s^{(B)}(z)\right\}^{-1}\vec{\mathcal{Z}}_s^{\,inc}(z)\;\frac{1}{\vec{A}_R^{*T}\vec{A}_I} \quad . \qquad (6.2.31)$$

In the transformation defined by eqn. (6.2.31) the matrix $\underline{\underline{P}}_s^{(B)}(z)\;\underline{\underline{S}}\{\underline{\underline{P}}_s^{(B)}(z)\}^{-1}$ is equal to its own inverse. Using this property and the symmetry of the system we obtain

$$\left|\vec{A}_R^{*T}\,\vec{A}_I\right| = 1 \quad . \qquad (6.2.32)$$

Eqns. (6.2.28) and (6.2.32) may be satisfied if we choose

$$a_{s,i} = A_i\,e^{-i\phi_s/2}$$

$$a_{s,i+N-M} = A_i\,e^{+i\phi_s/2} \qquad (6.2.33)$$

$$\forall \; i = 1,2,\ldots\; N-M \;,$$

where the phase factor ϕ_s is a real number and where A_i is a complex number. Then the general solution of Schrödinger's eqn. in the bulk region takes the form

$$\vec{\mathfrak{Z}}_s^{(B)} = \underline{\underline{P}}_s^{(B)}(z) \left\{ \begin{bmatrix} \vec{Q}^{(1)}_{s,1} m_1 & \cdots & \vec{Q}^{(1)}_{s,N-M} m_1 & \vec{Q}^{(1)}_{s,N-M+1} & \cdots & \vec{Q}^{(1)}_{s,N} \\ \vec{Q}^{(2)}_{s,1} & \cdots & \vec{Q}^{(2)}_{s,N-M} & \vec{Q}^{(2)}_{s,N-M+1} & \cdots & \vec{Q}^{(2)}_{s,N} \end{bmatrix} \left\{ \begin{matrix} a_1 \\ \vdots \\ a_N \end{matrix} \right\} \right\} \qquad (6.2.34)$$

where

$$m_1 = -2i \, tg \, \phi_s \qquad (6.2.35)$$

The solution in the surface region, $\vec{\mathfrak{Z}}_s^{(S)}(z)$, is obtained through the propagation matrix, $\underline{\underline{P}}_s^{(S)}(z)$, defined in the surface region

$$\vec{\mathfrak{Z}}_s^{(S)}(z) = \underline{\underline{P}}^{(S)}(z)\, \vec{\beta} \qquad (6.2.36)$$

where $\vec{\beta}$ is a (2N×1) column matrix determined by the boundary conditions of the problem.

In conclusion, it is important to note that the solution in the bulk region is given within N constants and a phase factor, while the solution in the surface region is given within 2N constants.

Both solutions are determined numerically. Most of the work is associated with the calculation of the propagation matrices, $\underline{\underline{P}}_s^{(B)}(z)$ and $\underline{\underline{P}}_s^{(S)}(z)$. These calculations require large amounts of computer time and this is mainly the reason that such calculations are limited. Fortunately, the calculation of the propagation matrix in the bulk region can be obtained with less expense if the symmetry of the system is used. For the case of bcc crystals with the (001) lattice plane as the surface plane it can be proved (Torrini, M., Zanazzi, E., 1972) that a complete determination of the propagation matrix $P_s^{(B)}(z)$ requires a knowledge of the propagation matrix in the first quarter of the period 2c. Because we have used this theory in our calculations, it is included in the Appendix A.4.

6.3 SOLUTION IN THE VACUUM REGION

In the vacuum region, the effect of the periodic lattice potential is negligible. This means that the off-diagonal elements of the single-electron potentials may be assumed to be zero, a fact which results in the decoupling of the simultaneous differential eqns. (6.1.3). Hence, each Fourier component of the single electron wave function, $\xi_{s\vec{h}}(z)$, satisfies the differential equation

$$-\frac{1}{2}\frac{d^2\xi_{s\vec{h}}}{dz^2} + \frac{1}{2}(\vec{k}_s+\vec{h})^2\xi_{s\vec{h}} + \left\{\tilde{V}_0(z) + A_0^{(s)}(z) + C_0^{(s)}(z)\right\}\xi_{s\vec{h}} = \varepsilon_s\xi_{s\vec{h}}, \quad \vec{h}\in\{\vec{h};N\}. \tag{6.3.1}$$

Furthermore, in this region the combination of the exchange and correlation potentials is assumed to have reached its asymptotic form which is the image potential, i.e.

$$A_0^{(s)}(z) + C_0^{(s)}(z) = -\frac{1}{4z} \tag{6.3.2}$$

while $\widetilde{V}_0(z)$ has also reached its asymptotic value which is zero. Therefore eqn. (6.3.1) takes the form

$$\frac{d^2 \xi_{s\vec{h}}}{dz^2} - \frac{1}{2z}\xi_{s\vec{h}} = \omega^2_{s\vec{h}}\xi_{s\vec{h}} \quad , \vec{h} \in \{\vec{h}; N\} \qquad (6.3.3)$$

where

$$\omega^2_{s\vec{h}} = (\vec{k}_s + \vec{h})^2 - 2\,\varepsilon_s \quad . \qquad (6.3.4)$$

Eqn. (6.3.3) is solved analytically, and yields two linearly independent solutions for each $\xi_{s\vec{h}}$. Finally, the boundary condition at $z=+\infty$ is applied which reduces the two constants of integration to one. Therefore, the solution of the Schrödinger's equation in the vacuum region is obtained within N constants of integration.

In more detail, the solution of eqn. (6.3.3) is determined as follows. Firstly, the transformation (6.3.5) is applied:

$$\xi_{s\vec{h}}(z) = f_{s\vec{h}}(z)\, e^{-\omega_{s\vec{h}} z} \qquad (6.3.5)$$

which transforms eqn. (6.3.3) into

$$\frac{d^2 f_{s\vec{h}}}{dz^2} - 2\omega_{s\vec{h}} f_{s\vec{h}} + \frac{f_{s\vec{h}}}{2z} = 0 \quad . \qquad (6.3.6)$$

Then a change of variable:

$$z' = 2\,\omega_{s\vec{h}}\, z \qquad (6.3.7)$$

transforms eqn. (6.3.6) into

$$\frac{d^2 f_{s\vec{h}}}{dz'^2} - \frac{d f_{s\vec{h}}}{dz'} + \frac{f_{s\vec{h}}}{4\omega_{s\vec{h}} z'} = 0 \qquad (6.3.8)$$

which is the confluent hypergeometric differential equation. A solution of eqn. (6.3.8) consistent with the boundary condition

$$\zeta_{s\vec{h}}(z=+\infty) = 0 \quad , \forall \vec{h} \in \{\vec{h}; N\} \qquad (6.3.9)$$

is obtained in series form

$$f_{s\vec{h}}(z') = \gamma_{s\vec{h}} \{z'\}^{-\alpha} \left\{ 1 - \frac{\alpha(\alpha+1)}{1!\, z'} + \frac{\alpha(\alpha+1)(\alpha+1)(\alpha+2)}{2!\, (z')^2} - \cdots \right\} \qquad (6.3.10)$$

where $\gamma_{s\vec{h}}$ is a constant and

$$\alpha = -\frac{1}{4\omega_{s\vec{h}}} \, . \qquad (6.3.11)$$

A direct substitution of eqn. (6.3.10) into eqn. (6.3.5) yields

$$\zeta_{s\vec{h}}(z) = \gamma_{s\vec{h}} e^{-\omega_{s\vec{h}} z} (z')^{-\alpha} \left\{ 1 - \frac{\alpha(\alpha+1)}{1!\, z'} + \frac{\alpha(\alpha+1)(\alpha+1)(\alpha+2)}{2!\, (z')^2} - \cdots \right\} \qquad (6.3.12)$$

where

$$z' = 2\omega_{s\vec{h}} z$$

Depending on the value of $\omega_{s\vec{h}}$, eqn. (6.3.12) exhibits problems of convergence. The number of terms required for a satisfactory convergence are determined by a trial and error method. Firstly, we assume a number of terms and then calculate the solution $\xi_{s\vec{h}}(z)$ as given by eqn. (6.3.12). Then, substituting into the differential eqn. (6.3.3), we check whether it is satisfied or not.

6.4 THE MATCHING

So far, the solutions of the Schrödinger equation in the three regions of the crystal have been obtained. Because of the continuity of the wave functions and their derivatives all over the space, it is required that both the wave functions and their derivatives should be matched along the boundaries of the regions. From this matching procedure the remaining (4N+1) constants of integrations are to be determined.

The solutions in the bulk, surface and vacuum regions are rewritten as follows. In the bulk region

$$\vec{\xi}_s^{\,(B)}(z) = \underline{\underline{P}}_s^{(B)}(z)\,\underline{\underline{Q}}_s(\phi_s)\,\vec{\alpha} \qquad (6.4.1)$$

where $\vec{\alpha}$ is a (N×1) column vector, and $\underline{\underline{Q}}_s(\phi_s)$ is a (2N×N) matrix depending on the phase factor ϕ_s, as it is given by eqns. (6.2.34) and (6.2.35). Eqn. (6.2.36), which gives the solution in the surface region, is rewritten as in the eqn. (6.4.2), i.e.

$$\vec{\xi}_s^{\,(S)}(z) = \underline{\underline{P}}_s^{(S)}(z)\,\vec{\beta} \qquad (6.4.2)$$

It may be recalled that $\vec{\beta}$ is a $(2N\times 1)$ column vector.

Finally, the solution in the vacuum region may be written as

$$\vec{\mathfrak{Z}}_s^{(V)}(z) = \underline{\underline{P}}_s^{(V)}(z)\,\vec{\gamma} \tag{6.4.3}$$

where $\underline{\underline{P}}_s^{(V)}(z)$ is a $(2N\times N)$ matrix, and $\vec{\gamma}$ is a $(N\times 1)$ column vector. The elements of $\underline{\underline{P}}_s^{(V)}(z)$ are given as

$$\left(\underline{\underline{P}}_s^{(V)}(z)\right)_{ij} = \xi'_{s\vec{h}_i}(z)\,\frac{1}{\gamma_{s\vec{h}_i}}\,\delta_{ij} \tag{6.4.4a}$$

$$\left(\underline{\underline{P}}_s^{(V)}(z)\right)_{i+N,j} = \xi_{s\vec{h}_i}(z)\,\frac{1}{\gamma_{s\vec{h}_i}}\,\delta_{ij} \tag{6.4.4b}$$

$$i,j = 1,2,\ldots N\ .$$

If $z=z_1$ defines the boundary plane between the bulk and surface regions, and $z=z_2$ defines the boundary plane between the surface and vacuum regions, the continuity condition yields

$$\vec{\mathfrak{Z}}_s^{(B)}(z_1) = \vec{\mathfrak{Z}}_s^{(S)}(z_1) \tag{6.4.5a}$$

$$\vec{\mathfrak{Z}}_s^{(S)}(z_2) = \vec{\mathfrak{Z}}_s^{(V)}(z_2) \tag{6.4.5b}$$

This pair of equations can be written in the equivalent form

$$\underline{\underline{P}}_s^{(B)}(z_1)\,\underline{\underline{Q}}_s(\phi_s)\,\vec{\alpha} = \underline{\underline{P}}_s^{(S)}(z_1)\,\vec{\beta} \tag{6.4.6a}$$

$$\underline{\underline{P}}_s^{(V)}(z_2)\,\vec{\gamma} = \underline{\underline{P}}_s^{(S)}(z_2)\,\vec{\beta} \quad . \tag{6.4.6b}$$

From eqns. (6.4.6a) and (6.4.6b) we obtain

$$\underline{\underline{P}}_s^{(S)}(z_2)\left\{\underline{\underline{P}}_s^{(S)}(z_1)\right\}^{-1}\underline{\underline{P}}_s^{(B)}(z_1)\,\underline{\underline{Q}}_s(\phi_s)\,\vec{\alpha} = \underline{\underline{P}}_s^{(V)}(z_2)\,\vec{\gamma} \tag{6.4.7}$$

which is just a system of 2N-homogeneous linear equations with respect to the components of the vectors $\vec{\alpha}$ and $\vec{\gamma}$. Therefore there exists a non-zero solution if the corresponding matrix has zero determinant. In other words, if

$$\vec{A} \equiv \begin{pmatrix} \vec{\alpha} \\ \vec{\gamma} \end{pmatrix} \tag{6.4.8}$$

and

$$\underline{\underline{M}}(\phi_s) \equiv \left\{ \underline{\underline{P}}_s^{(S)}(z_2)\left[\underline{\underline{P}}_s^{(S)}(z_1)\right]^{-1}\underline{\underline{P}}_s^{(B)}(z_1)\,\underline{\underline{Q}}_s(\phi_s) \qquad \underline{\underline{P}}_s^{(V)}(z_2) \right\} \tag{6.4.9}$$

then the system

$$\underline{\underline{M}}\,\vec{A} = \vec{0} \tag{6.4.10}$$

has a non-zero solution if $|M|=0$. This requirement may be satisfied if the phase factor ϕ_s is determined such that

$$\left|\underline{\underline{M}}(\phi_s)\right| = 0 \tag{6.4.11}$$

In this way all but one of the components of the vector $\vec{A}$ are determined. Then, the vector $\vec{\beta}$ is determined through eqn. (6.4.6a) and finally the normalization condition is used to determine the one remaining unknown component. In this way, a unique solution of Schrödinger's equation is obtained.

It is remarkable that in the case where only one pair of propagating solutions exists, the solution obtained is similar to that of the jellium case. In this case the phase factor determined by eqn. (6.4.11) is significant in the calculation of the surface energy (Huntington, H.B., 1951), (Stratton, R., 1953).

A final point to be noted is that the number of pairs of propagating solutions depends on how many Brillouin zones of the surface lattice are within the projection of the Fermi-sphere onto the reciprocal surface plane. In the case of the Na-crystal with the (001) lattice plane as the surface plane, two Brillouin zones are within the Fermi-sphere projection, Fig. 3.2b, and therefore a maximum of two pairs of propagating solutions is present. In fact only a small portion of the second Brillouin zone is occupied, and this is the reason that most of the solutions exhibit only one pair of propagating solutions.

6.5 EXISTENCE OF SURFACE STATES

The solution presented in the previous paragraphs is consistent with the existence of surface states. Such states are predicted by the band structure of the infinite metal and appear when energy gaps are present in it.

A surface state is a state localized at the surface of the metal. In other words, the wave function describing a surface state tends to zero in regions far from the surface. This does not necessarily imply that the propagation matrix $\underline{\underline{P}}_s(2c)$ has no eigenvalues with absolute value equal to one. But nevertheless the surface state is a self-sustained state which can exist even in the absence of the incident Bloch wave. Therefore the surface state will be described by the reflected Bloch and evenescent waves inside the crystal, i.e.

$$\vec{\mathcal{Z}}_s^{(SS)}(z) = \underline{\underline{P}}_s^{(B)}(z)\left\{\vec{R}_{s1}\cdots\vec{R}_{s,N-M}\,\vec{Q}_{s,N-M+1}\cdots\vec{Q}_{s,N}\right\}\vec{c}$$

$$= \underline{\underline{P}}_s^{(B)}(z)\,\tilde{\underline{\underline{Q}}}_s\,\vec{c} \qquad (6.5.1)$$

where the index (ss) refers to "surface state" and

$$\tilde{\underline{\underline{Q}}}_s = \left\{\vec{R}_{s1}\cdots\vec{R}_{s,N-M}\,\vec{Q}_{s,N-M+1}\cdots\vec{Q}_{s,N}\right\} .$$

The matching conditions (6.4.5a) and (6.4.5b) imply that a surface state will exist if and only if

$$\underline{\underline{P}}_s^{(V)}(z_2)\,\vec{\gamma} = \underline{\underline{P}}_s^{(S)}(z_2)\left\{\underline{\underline{P}}_s^{(S)}(z_1)\right\}^{-1}\tilde{\underline{\underline{Q}}}_s\,\vec{c} \qquad (6.5.2)$$

or

$$\det\left(\underline{\underline{P}}_s^{(V)}(z_2) \qquad \underline{\underline{P}}_s^{(S)}(z_2)\left\{\underline{\underline{P}}_s^{(S)}(z_1)\right\}^{-1}\tilde{\underline{\underline{Q}}}_s\right) = 0 \; . \qquad (6.5.3)$$

Quite recently, Pendry and Gurman (Pendry, J.B., Gurman, S.J., 1975) derived a new condition for the existence of surface states. They consider the surface state as a bound state which can be identified from a pole in the scattering amplitude. According to our formalism, this condition for the existence of surface states may be derived from eqn. (6.2.31). Since the propagation matrix is non-singular, a surface state will exist, according to the Pendry and Gurman criterion, if

$$(\vec{A}_R^*)^T \vec{A}_I = 0 \quad , \qquad (6.5.4)$$

when analytically continued.

CHAPTER 7

APPLICATION TO THE SODIUM CRYSTAL

The theory that was presented for semi-infinite metals in the earlier chapters has been applied to a semi-infinite sodium (Na) crystal with the (001) orientation (Fig. 3.1).

Sodium is a body-centre-cubic metal with lattice constant 8.091 a.u. The core radius r_c of the Na-ions, which appears as a parameter in the model Ashcroft's pseudopotential, is taken as 1.67 a.u.

Nine terms were kept in the Fourier series expansions. The corresponding set $\{\vec{h};N\}$ of the two-dimensional reciprocal lattice vectors was chosen to be the following

$$\left\{\vec{h};\,9\right\} \equiv \left\{(00),(01)(10),(0\bar{1}),(\bar{1}0),(11),(1\bar{1}),(\bar{1},1),(\bar{1}\bar{1})\right\}.$$

The projection of the Fermi-sphere onto the (001) reciprocal lattice plane occupies parts of the first and second Brillouin zones of the two-dimensional reciprocal lattice space of the surface plane (Fig. 3.2b). Therefore it is expected that the solution of the Schrödinger's equation in the bulk region will exhibit at most two pairs of propagating solutions. For completeness it is mentioned that the Fermi wave vector $\vec{K}_F$ was calculated assuming the free electron dispersion relation.

To start our calculations an electron density function $\rho_0(z)$ was assumed as in the simplified model described in section 4.4. This enabled us to calculate the zero order Fourier term of the combined ion-electron and Hartree potential. The non-diagonal matrix elements of the Hartree, exchange and correlation potentials are assumed zero in this initial stage. The off-diagonal elements of the ion-electron potential are calculated from the expressions derived in section 4.1. For the zero order Fourier term of the exchange potential it was assumed that its value in the bulk region is given as in the jellium approximation. In other words:

$$A_0^{(s)}(z\to-\infty) \equiv A_0^{(\vec{k}_s,q_s)}(-\infty) =$$

$$= -\frac{2k_F}{\pi}\left\{\frac{1}{2} + \frac{1-\alpha_s^2}{4\alpha_s}\ln\left|\frac{1+\alpha_s}{1-\alpha_s}\right|\right\}$$

where

$$\alpha_s = \sqrt{k_s^2+q_s^2}\Big/k_F \quad .$$

The correlation potential was obtained from the local expression

$$C_0^{(s)}(z) = \frac{-0.44}{7.8 + r_s(\rho_0(z,z))} \;(a.u.)\,,\; z\to-\infty$$

(where $\frac{4\pi}{3}r_s^3$ defines the volume per electron)

for every value of the set of the quantum numbers s.

Following Bardeen (Bardeen, J., 1936) the algebraic sum of the exchange and correlation potential in the bulk region was smoothly joined with its asymptotic value in the vacuum region, which is just the image potential, eqn. (6.3.2).

For these types of potential the boundary planes between the bulk and surface regions and between the surface and vacuum regions were chosen at $z = -1.98$ a.u. and $z = 11.5$ a.u. respectively.

At this stage we have all that is needed to start the numerical integration of Schrödinger's equation. The particular methods used and the results obtained are discussed in the following paragraphs.

All the numerical calculations were carried out with an 1100 Univac computer at the Computer Centre of the University of Cape Town.

7.1 CALCULATION OF THE SINGLE ELECTRON WAVE FUNCTIONS

The general solution of the system of the differential equations (6.1.3) in the bulk region was obtained by using Torrini's and Zanazzi's theory described in Appendix A.4. According to their theory it is sufficient to integrate eqns. (6.1.3) over one quarter of the period along the ⟨001⟩ direction. As a result, the computer time necessary for this calculation is reduced and also better accuracy is obtained. An average time of 2.5 minutes was required to obtain the propagation matrix in the bulk region. For this integration a version of the Runge-Kutta method was used which allowed a maximum error of $\pm 10^{-3}$.

In the surface region the Adam's-Bashforth's predictor-corrector method was used in the derivation of the propagation matrix. This method is slightly quicker than the Runge-Kutta and keeps the numerical errors in the same range. It was required an average time of 5.5 min for the derivation of the propagation matrix in the surface region.

The general solution in the vacuum region was calculated as given by eqn. (6.3.12). In the range of the values of $\omega_{s\vec{h}}$, eqn. (6.3.4), the convergence of the series (6.3.12) is fast and the number of terms to be kept may be taken arbitrarily between ten and thirty.

In the next step of the calculation the general solution in the bulk region is expressed as in eqn. (6.2.7). This requires us to derive the propagation matrix $\underline{\underline{P}}_s^{(B)}(2c)$ from the matrix $\underline{\underline{P}}_s^{(B)}(c/2)$ according to Torrini's and Zanazzi's theory. Then the diagonalization of $\underline{\underline{P}}_s^{(B)}(2c)$ is carried out from which the matrix of the eigenvectors, $\underline{\underline{Q}}_s$, and the eigenvalues of $\underline{\underline{P}}_s(2c)$ are derived. A sorting of the eigenvalues with respect to their absolute value is then carried out and the solution in the bulk region is expressed as in eqns. (6.2.34) and (6.2.35).

Finally, the matching process is performed which will determine the phase factor ϕ_s and the rest of the constants of integration.

The diagonalization of the propagation matrix $\underline{\underline{P}}_s^{(B)}(2c)$ is the most critical part of the calculation of the single electron wave functions. High accuracies are required specially in the determination of the eigenvalues which correspond to the propagating solutions. It became necessary to perform all the calculations in complex double precision format in order to achieve satisfactory accuracy. This made it necessary to build up our own library functions in using the 1100 Univac computer because this system did not accept a complex double precision calculation. An average of 20 sec was the time required for the matrix diagonalization while the matching process required an average of 4 minutes. Thus the overall average time in calculating a wave function was 12.5 min. As regards the accuracy obtained, it was found that eigenvalues that should have an absolute value equal to one had calculated values lying within the range of values (1 ± 10^{-5}).

A total of 26 wave functions were calculated. Their numerical values were stored onto magnetic tapes. These wave functions have energies between 0.00 and 0.12 a.u. and their wave vectors $\vec{k}_s$ were taken from a mesh of points produced as follows. Along the (01) and ⟨10⟩ directions of the two-dimensional reciprocal lattice, Fig. 3.2b, we divided a length of $2\pi/a$, where a is the lattice constant, into six equal parts. Assuming for instance the free-electron dispersion relation, a total of 26 points may be found in the first octant of the projection of the Fermi-sphere onto the (001) reciprocal lattice plane with energies 0.00, 0.03, 0.06, 0.09 and 0.12 a.u. For these points we performed a complete calculation of the wave function. If one uses the point group symmetry, these 26 points give a total number of 113 points in the total projection of the Fermi-sphere onto the (001) reciprocal lattice plane. Subsequently we are going to use the numerical values of the wave functions at these points in interpolation techniques, which will produce the wave functions at intermediate points. This will become necessary in evaluating the single electron potentials. But before we come to this point two intermediate results will be discussed: The calculation of the band structure along the ⟨001⟩ direction and the functional relation of the phase factor to the wave vector.

7.2 A BAND STRUCTURE CALCULATION

The periodicity along the z-axis in the bulk region allowed us to express the eigenvalues of absolute value equal to one, eqn. (6.2.22), as

$$\lambda_s = e^{i2ck_z^{(s)}} \tag{7.2.1}$$

where $k_z^{(s)}$ is the z-component of the wave·vector $\vec{K}_s$ (Jepsen, D.W., Marcus, P.N., 1971). From eqn. (7.2.1) is easily obtained

$$k_z^{(s)} = \frac{1}{2c} \operatorname{arctg} \frac{\operatorname{Im} \lambda_s}{\operatorname{Re} \lambda_s} \quad . \tag{7.2.2.}$$

It is therefore obvious that for any pair of energy, ε_s, and projection, $\vec{k}_s$, of the wave vector $\vec{K}_s$, a z-component of $\vec{K}_s$ may be found via the eigenvalues of $\underline{\underline{P}}_s(2c)$ whose absolute value is equal to one. If we keep $\vec{k}_s$ equal to zero then we can trace the band structure along the ⟨001⟩ direction by finding the relation between the energy ε_s and the resulting $k_z^{(s)}$.

Such a calculation was carried out for sodium and the resulting band structure along the <001> direction is shown in Fig. 7.1. The result is identical with that obtained from eqn. (2.3.7a), keeping 19 Fourier terms in the Fourier series expansions with respect to the three-dimensional reciprocal lattice, Fig. 2.1.

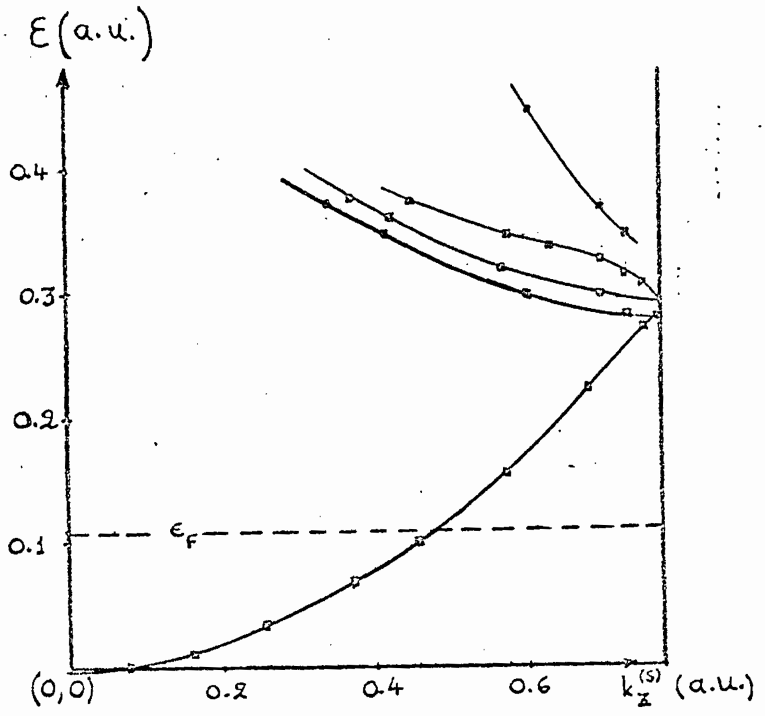


Fig. 7.1: A band structure calculation along the <001> direction for a sodium crystal as obtained using eqn. (7.2.2).

7.3 THE PHASE FACTOR

In the particular case where only one pair of propagating solutions exists, the asymptotic form of the wave function in the bulk region takes the form

$$\zeta_{s,0}(z \to -\infty) \sim \sin\left(k_z^{(s)} z + \tilde{\phi}_{k_z}^{(s)}\right) \qquad (7.3.1)$$

where $\tilde{\phi}_{k_z}^{(s)}$ is a phase factor. This phase factor, $\tilde{\phi}_{k_z}^{(s)}$, is related to $\phi_{k_z}^{(s)}$ obtained from eqn. (6.4.11) during the process of the "matching problem" by the relation

$$\tilde{\phi}_q^{(s)} = \frac{\pi}{2} + \phi_q^{(s)} \quad . \tag{7.3.2}$$

Therefore the wave functions take the form of the wave functions calculated in the jellium approximation. The phase factor $\phi_q^{(s)}$ is expected to depend more on the z-component of the wave vector than on the energy, and to have the following property.

The Fermi-surface average of $\tilde{\phi}_q^{(s)}$ is equal to $(-\pi/4)$, i.e.

$$\langle \tilde{\phi}_q^{(s)} \rangle \equiv \frac{\int_{FS} |\cos\vartheta| \, \phi_q^{(s)} \, dA}{\int_{FS} |\cos\vartheta| \, dA} = -\frac{\pi}{4} \tag{7.3.3}$$

where FS indicates that the integral is taken over the Fermi-surface. Eqn. (7.3.3) is a sum rule firstly stated by Sugiyama (Sugiyama, A., 1960) and later proved by Langreth (Langreth, D.C., 1970).

This sum rule was recently generalized for the case where explicit account is taken of the energy bands and crystalline structure of the solid (Appelbaum, A.J., Blount, E.I., 1973). In this generalization it is proved that for the case where one pair of propagating solutions exists the sum rule retains the form given in eqn. (7.3.3). Therefore this sum rule provides a test for the calculated values of the phase factors when our formalism is applied to systems which exhibit one pair of propagating solutions.

The functional relation

$$\phi^{(s)}_{q} = f(q_s)$$

for our calculated phase factors is shown in Fig. 7.2. The results of Fig. 7.2 refer to the zero-order approximation, i.e. in the case where only one pair of propagating solutions is taken into account.

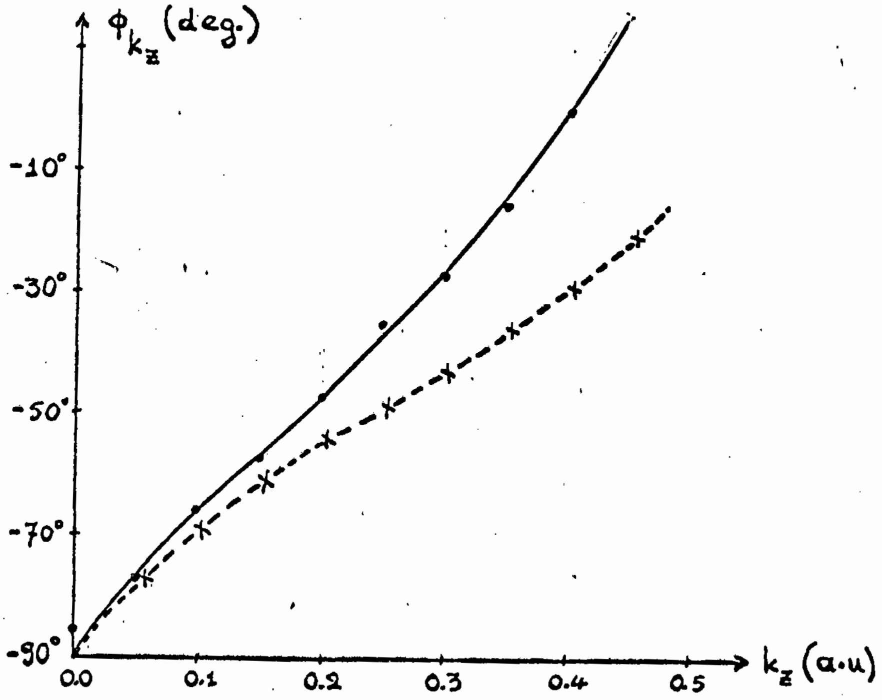


FIG. 7.2: Phase factor calculation. The results we obtained (solid line) are compared with the results obtained by Huntington (dotted line) (Huntington, H.B., 1951).

7.4 CALCULATION OF THE ELECTRON DENSITY PROFILE. ZERO-ORDER FOURIER TERM OF THE HARTREE-HAMILTONIAN

Having calculated the single electron wave functions we proceed to calculate the electron density $\rho(\vec{r},\vec{r}')$, as given by eqn. (5.2.4). Particularly, we are interested in the Fourier coefficients $\rho_{\vec{q}}(z,z)$ of the function $\rho(\vec{r},\vec{r})$. These Fourier terms are calculated according to the definition (4.1.2a) considering the function $\rho(\vec{r},\vec{r})$ as a function of one variable.

The zero-order Fourier term

$$\rho_0(z,z) \equiv \rho_0(z) = \sum_{s\vec{h}} \left| \xi_{s\vec{h}}(z) \right|^2 \theta\left(\epsilon_F - \varepsilon_s\right) \qquad (7.4.1)$$

is of considerable importance; it describes the average density of the electrons along the z-axis of the system. The plot of the function $\rho_0(z)$ against the z-variable is called "electron density profile".

The calculation of $\rho_0(z)$ according to eqn. (7.4.1) requires us to perform the summation over the occupied states s. In fact this is an integration with respect to the energy, ε_s, and the two-dimensional wave vector $\vec{k}_s$. Therefore, we require to know the wave functions at many points $(\varepsilon_s,\vec{k}_s)$. Unfortunately our knowledge is limited to a set of 26 wave functions with wave vectors $\vec{k}_s$ in the first octant of the projection of the Fermi-sphere onto the (001) reciprocal lattice plane. In order to find the wave function at other points it is necessary to resort to methods of interpolation.

One hopes to find the wave functions at other points by using point group symmetry operations. The symmetry operations allow us to calculate the single electron wave functions which correspond to the same energy, ε_s, and the same magnitude of the wave vector $\vec{k}_s$. The directions of the (equal in magnitude) wave vectors $\vec{k}_s$ are determined by the point group symmetry. Such operations interchange the components of the vectors $\vec{\xi}_s(z)$. Therefore the calculation of $\rho_0(z)$ is not affected by increasing the number of points in this way.

One has to proceed with interpolation techniques in order to achieve it. From the early stages of our calculations it was evident that interpolation with respect to the wave vectors $\vec{k}_s$ which have the same energy ε_s required a finer mesh of points than that of the 26 points. But the calculation becomes dramatically expensive and it is not of practical use. The same was true if the energy was used as the interpolated variable and the wave vector $\vec{k}_s$ was kept constant. Fortunately an interpolation with respect to the z-component, $k_z^{(s)}$, of the wave function proved successful. It was found that if one interpolates with respect to the $k_z^{(s)}$ variable defined by eqn. (7.2.2), very accurate results are obtained compared with those of a direct calculation.

This type of interpolation requires an interpolation method based on un-equally spaced arguments. For this purpose we used Lagrange's method.

In order to proceed with this interpolation technique it was required to calculate the wave functions for some extra points $(\varepsilon_s,\vec{k}_s)$ in order to obtain values of $k_z^{(s)}$ well distributed over the range of values $[o,k_F]$. In our case we had to calculate the wave functions for five more points $(\varepsilon_s,\vec{k}_s)$. It was also assumed that such an interpolation method could also work for pair of points $(\varepsilon_s,\vec{k}_s)$ for which the wave vector $\vec{k}_s$ is in the second Brillouin zone. Direct verification indicates the validity of this assumption although the accuracy of the method is reduced for such points.

In this way we performed the integration over $\vec{k}_s$ and ε_s in eqn. (7.4.1). The same calculation was performed once more, but this time with the summation over the reciprocal lattice vectors, $\vec{h}$, reduced to the single zero-order Fourier term of the wave function. In both calculations we obtained the same electron density profile. Therefore we found that the effect of the non-zero Fourier terms of the wave functions do not affect the electron density profile for the semi-infinite sodium crystal.

At first sight this result may seem surprising, but it is easily explained. Sodium is a nearly free electron metal and one could have expected that the effect of the lattice periodicity on its electronic configuration to be of no importance. This situation has also been proved true in our calculations for the exchange potential and the phase factors of the single electron wave functions. For example, in Fig. 7.3 we show the results for the phase factor as obtained from two separate calculations: one keeping nine terms in the Fourier series expansion of the wave function and the other in which only the zero-order Fourier term of the series expansion was kept (Tables II, III). In the next paragraph, where the calculation of the exchange potential is discussed, similar results are obtained in comparing the effect of the non-zero Fourier terms of the wave functions. But nevertheless we had to perform the calculation in the general case in order

TABLE II

ε_s a.u.	k_{sx} a.u.	k_{sy} a.u.	$k_z^{(s)}$ a.u.	$\phi_{k_z}(s)$ degrees
.09	.3236	.2589	.1231	-70.49
.03	.1294	.1294	.1807	-61.79
.03	.0000	.0000	.2574	-49.32
.12	.2589	.2589	.3371	-36.62
.09	.0000	.0000	.4325	-11.43

Calculated phase factors using the complete theory with nine Fourier terms in the series expansions. Here $\vec{k}_s \equiv (k_{sx}, k_{sy})$ and $k_z^{(s)}$ has been obtained using eqn. (7.2.2).

TABLE III

k_z a.u.	ϕ_{k_z} degrees
.00	-83.69
.05	-80.01
.10	-73.18
.15	-65.67
.20	-58.04
.25	-49.84
.30	-41.88
.35	-33.23
.40	-23.69
.45	- 3.27

Calculated phase factors in the zero-order approximation. k_z is obtained using the free electron dispersion relation.

to prove the validity of our method in the calculation of the wave functions in a semi-infinite Bloch electron system. Besides that we became able to enumerate the particular programming difficulties in a complete calculation.

After having proved the validity of the given solution of the Schrödinger equation for an electron in the semi-infinite metal we used the zero-order approximation in obtaining a self-consistent solution for the sodium crystal. This calculation will allow us to investigate the calculation of the $\tilde{V}_o(z)$ presented in Chapter 4 and the exchange potential as presented in Chapter 5. In what follows the calculation of the $\tilde{V}_o(z)$ term is presented as being related to the electron density profile while in the next paragraph we discuss the results obtained for the exchange potential.

In Fig. 7.4 the electron density profile is shown as obtained in the zero-order approximation. Finally, in Fig. 7.5 the corresponding calculation yielding the term $\tilde{V}_o(z)$ is presented.

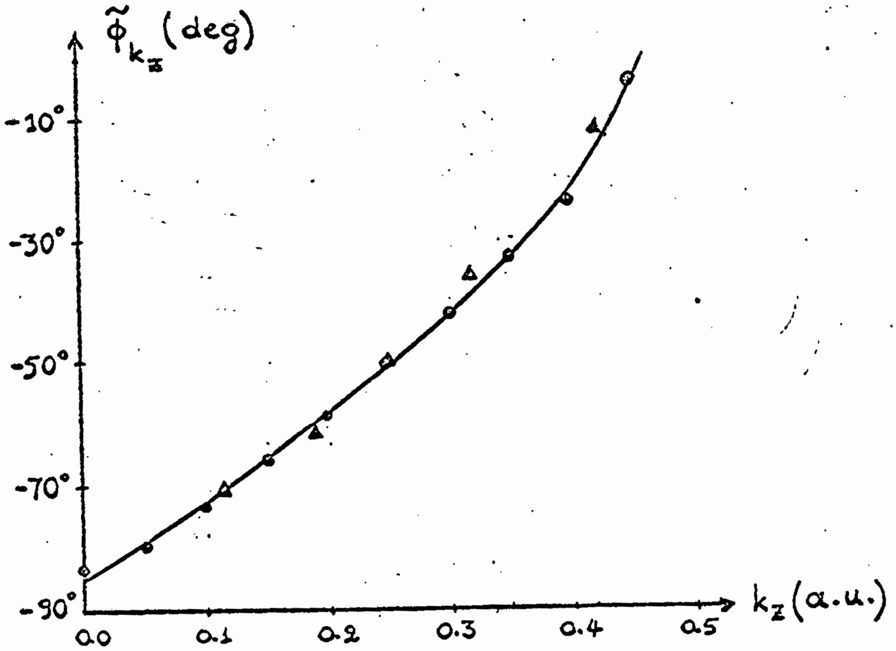


Fig. 7.3: Phase factor calculation in two approximations during the first iteration. The circles correspond to the results obtained in the zero-order approximation. The triangles correspond to those of the complete calculation keeping nine terms in the Fourier series expansions.

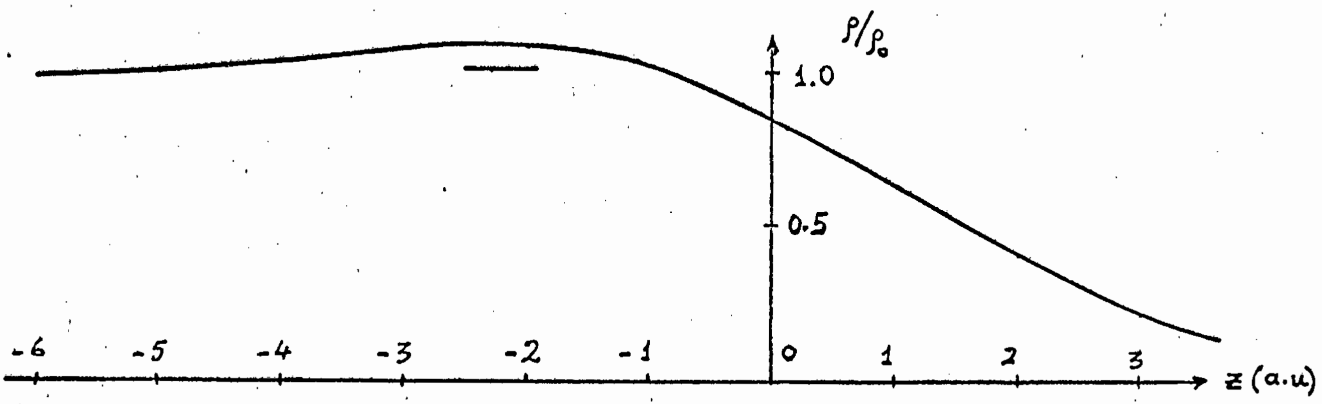


FIG. 7.4: Calculated Electron density profile using the exchange and correlation potential shown in Fig. 7.7. $\rho_0 = 0.003825\ (a.u.)^{-3}$.

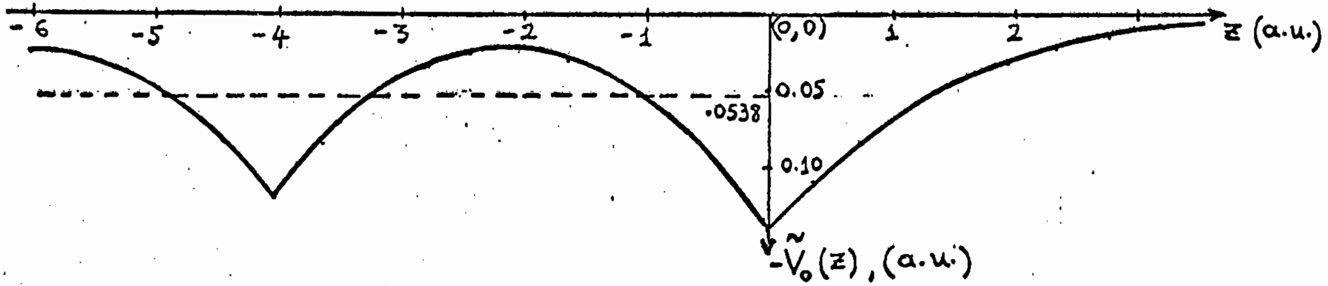


FIG. 7.5: Calculation of the term $\tilde{V}_0(z)$ according to eqns. (4.3.14a,b) and corresponding to the electron density profile of Fig. 7.4.

7.5 CALCULATION OF THE EXCHANGE POTENTIAL

In evaluating the matrix elements $A^{(s)}_{\vec{h}_i-\vec{h}_j}(z)$ of the exchange potential, eqn. (5.2.10), we used the wave functions obtained after one stage of iteration. Due to the fact that all our previous calculations proved that there was not any significant contribution from the non-zero Fourier terms of the wave functions, we firstly investigated the effect of these terms.

The point group symmetry of the system was used and allowed us to increase the number of points at which the wave functions are known. The numerical data of the initial twenty-six wave functions were read from a magnetic tape in groups of eight or nine. This was necessary because of computer core capacity and required three individual runs for this calculation. Consequently, we had to store temporarily the result of the summations over the reciprocal lattice vectors in eqn. (5.2.10) for every calculated wave function. Finally we added the temporary results and obtained the integrand of the right hand side of eqn. (5.2.10) for a specified quantum number s and specified points z_1, z_2. It required an average time of 80 sec for such a calculation. This implies that a complete calculation requires a huge amount of computer time and it is not of practical use. Fortunately when this calculation was repeated using only the zero-order Fourier term of the wave functions, we found out that a maximum discrepancy of 3.5% was present in the two values of the integrand at points $z_1 = z_2$. One could therefore concentrate on the most significant diagonal element

$$A^{(s)}_{\vec{h}_i-\vec{h}_i}(z) = A^{(s)}_{o}(z) \qquad , \vec{h}_i = \vec{o}$$

in the calculations of our interest

Another calculation we are interested in is the application of eqn. (5.2.16) which allows us to calculate the exchange potential for electrons with components of velocity parallel to the surface. Using eqn. (5.2.16) we calculated the exchange potential $A_0^{(\vec{K}_s, q_s)}(z)$ in the bulk region for wave vectors, $\vec{K}_s$, along four different directions. In this calculation we used wave functions of the form

$$\zeta_{s,o}(z) \sim \sin(q_s z) \tag{7.5.1}$$

and the results obtained are given in Table IV. As is shown there, the results obtained for $A^{(s)}$ do not differ appreciably from the corresponding values $A^{(s)}_{jell}$, which were obtained using eqn. (5.2.18) with

$$\beta = \sqrt{k_s^2 + q_s^2} \Big/ k_F \quad . \tag{7.5.2}$$

This check allowed us to use eqn. (5.2.16) with $\vec{k}_s = o$ during the self-consistent solution in the zero-order approximation. The results obtained for the self-consistent exchange potential are shown in Fig. 7.6.

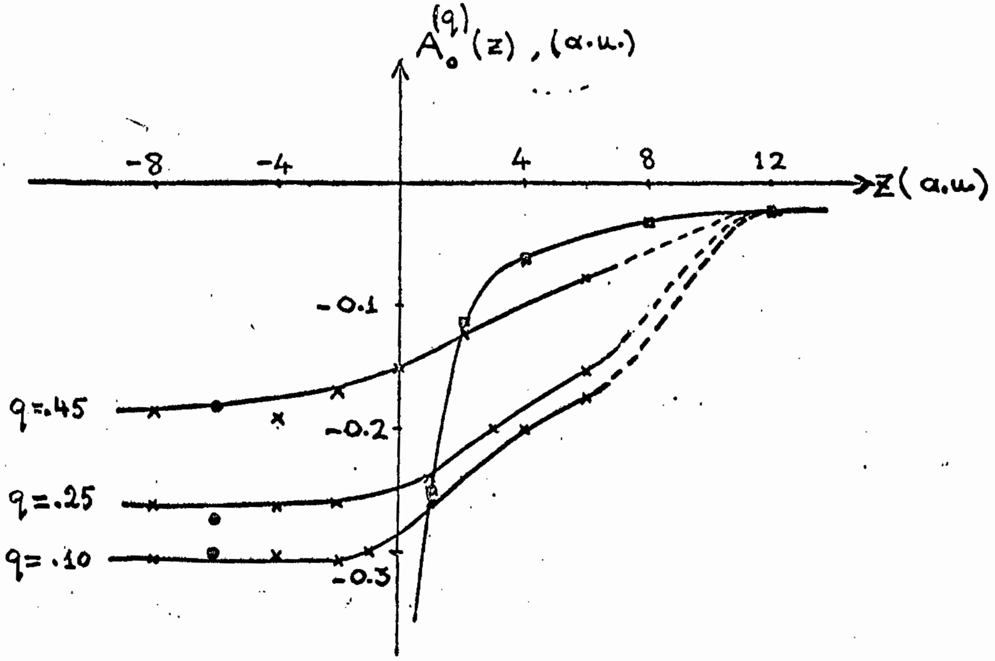


Fig. 7.6: Exchange potential calculation as obtained using eqn. (5.2.11). The self-consistency obtained is 5-10%. For comparison the image potential (square points) and the value of the exchange potential in the jellium approximation (circles) are indicated.

TABLE IV

$\vec{k}_s$ // <001>			$\vec{k}_s$ // <011>			$\vec{k}_s$ // <111>			$\vec{k}_s$ // <hko>		
β_s	$A^{(s)}$	$A^{(s)}_{jell}$	β_s	$A^{(s)}$	$A^{(s)}_{jell}$	β_s	$A^{(s)}$	$A^{(s)}_{jell}$	β_s	$A^{(s)}$	$A^{(s)}_{jell}$
.1047	.304	.303	.0000	.299	.304	.0000	.299	.304	.0000	.299	.304
.2094	.301	.300	.1481	.301	.302	.1814	.300	.300	.1047	.298	.303
.3141	.295	.294	.2962	.295	.295	.4911	.278	.278	.2094	.295	.300
.4189	.287	.285	.4443	.283	.283	.9424	.184	.184	.3141	.289	.294
.5236	.276	.274	.5929	.266	.265				.4189	.281	.285
.6283	.262	.260	.7404	.241	.240				.5236	.270	.274
.7330	.243	.242							.6283	.256	.260
.8377	.219	.218							.7330	.237	.242
.9424	.185	.184							.8377	.214	.218
									.9424	.180	.184

Exchange potential calculations (in a.u.).

$\beta_s = \sqrt{k_s^2+q_s^2}/k_F$, $A^{(s)}$ as calculated from eqn. (5.2.16) and $A^{(s)}_{jell}$ as calculated from eqn. (5.2.18).

The evaluation of the exchange potential was carried out in every iteration. It required an average time of 25 min to obtain the complete information for values of $z \in [-2,+6]$ a.u. in steps of 1.0 a.u. and for values of $q_s \in [0.05, 0.45]$ a.u. The average errors in the numerical values of the exchange potential are $\pm 10^{-2}$ a.u. and are mostly due to the integration over the z-variable in eqn. (5.2.16). It should be noted that for values of $z > 6.0$ a.u. the small values of the wave functions introduced large errors in the numerical integration. For $z > 6.0$ a.u. we had to interpolate the combined exchange and correlation potential to its value in the vacuum region, $z > 11.5$ a.u., at which it was assumed it had reached its asymptotic value, i.e.

$$A_0^{(s)}(z) + C_0^{(s)}(z) = -\frac{1}{4z} \quad , \forall s \; .$$

Unfortunately our self-consistent calculation does not include the correlation potential as was originally planned. Because of a call to fulfil my military service I had to omit this part of the calculation although the theory was worked out (section 5.3). To save time the correlation effect was estimated numerically in this way. From the local approximation

he following

$$C_0^{(s)}(z) = \frac{-0.44}{7.8 + r_s\left(\rho_0(z)\right)} \,(\text{a.u.}) \quad , z \rightarrow -\infty \quad , \forall s$$

we obtained the average correlation potential in the bulk region and we used it as a uniform correction to the exchange potential. The combined self-consistent exchange and correlation potential obtained on this basis is shown in Fig. 7.7. Fig. 7.8 shows the corresponding self-consistent single electron potential. This is the total potential which is the sum of the ion-electron, Hartree, Exchange and correlation potential. As shown in Fig. 7.6, the self-consistency is about 10%. With more computation the figure could be improved. However the computation has been taken far enough to give a work function of 3.1 eV, which is in good agreement with the result of Appelbaum (Appelbaum, J.A., Hamann, D.R., 1972).

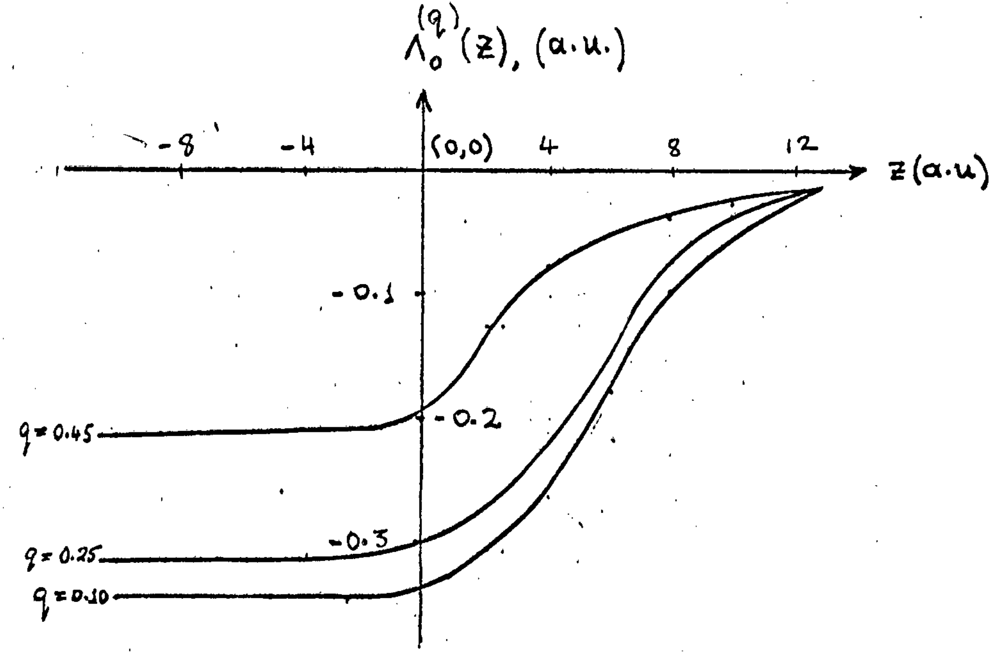


FIG. 7.7: Exchange and correlation potential.

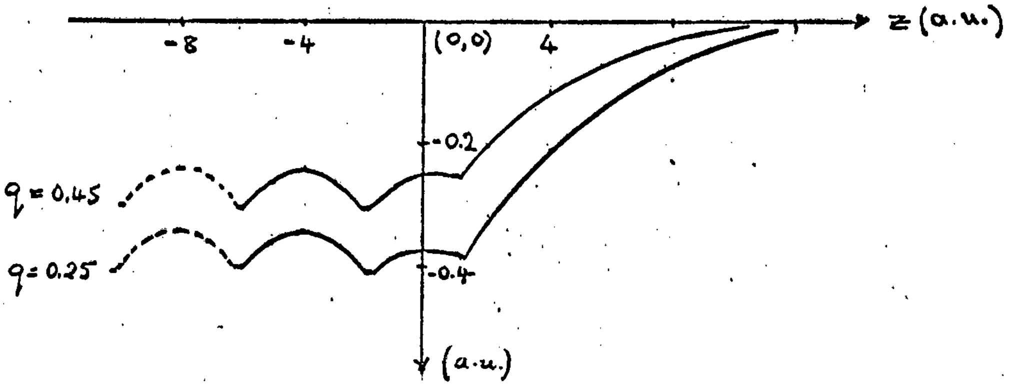


FIG. 7.8: Total single electron pseudopotential.

7.6 GENERAL CONCLUSIONS

In this thesis we studied the effects of the lattice periodicity on the electronic configuration near a metal surface. It was shown that when the lattice effects are taken into account, Schrödinger's equation takes the form of a matrix differential equation. Furthermore it was shown that the single electron potentials take the form of matrices in which the elements are the Fourier coefficients of the potential relative to the two-dimensional reciprocal lattice of the surface plane. In particular, we have succeeded in

i) presenting a solution of Schrödinger's equation for an electron in a semi-infinite Bloch electron system which is consistent with the band structure of the bulk crystal and the existence of surface states;

ii) incorporating the effects of the lattice periodicity in the single electron potentials, especially the ion-electron, Hartree and Exchange potentials;

iii) proving the equivalence of Poisson's equation with the single electron Hamiltonian;

iv) predicting the relation of the surface dipole moment to the structure and orientation of the crystal;

v) and presenting a complete analysis of the exchange potential.

APPENDICES

APPENDIX A.1

CALCULATION OF THE FOURIER COEFFICIENTS OF THE ION-ELECTRON INTERACTION IN THE BULK REGION

It is assumed that the variable z in eqn. (4.1.9) is defined in the range

$$z \in \left[-Nc\ ,\ -(N-1)c\right] \tag{A.1.1}$$

where N is assumed a very large integer, N → ∞, and (without loss of generality) N to be even. Then

$$|z - z_\ell| = \begin{cases} -\ell c + |z| & ,\ \ell < N-1 \\ -|z| + \ell c & ,\ \ell \geqslant N-1 \end{cases} \tag{A.1.2}$$

Therefore

$$\left\{ \sum_{\ell=0,2,4,\ldots}^{\infty} 1 + \sum_{\ell=1,3,\ldots}^{\infty} \mathrm{Re}\, e^{-i\vec{q}\cdot\vec{d}_0} \right\} e^{-q|z-z_\ell|} =$$

$$= \sum_{\ell=0,2,\ldots}^{N-2} e^{-q|z|+q\ell c} + \sum_{\ell=N,N+2,\ldots}^{\infty} e^{q|z|-q\ell c} +$$

$$+ \sum_{\ell=1,3,\ldots}^{N-1} e^{-q|z|+q\ell c} \cos(\vec{q}\cdot\vec{d}_0) + \sum_{\ell=N+1,N+3,\ldots}^{\infty} \cos(\vec{q}\cdot\vec{d}_0)\, e^{+q|z|-q\ell c} . \tag{A.1.3}$$

Define $|z| = (N-1)\,c+\delta$, $\delta\in\left[0,c\right]$. Then

$$\sum_{\ell=0,2,\ldots}^{N-2} e^{-q(N-1)c}\, e^{-q\delta}\, e^{q\ell c} = e^{-q\delta-q(N-1)c}\, \frac{e^{Nqc}-1}{e^{2qc}-1} \tag{A.1.4}$$

which in the limit N → ∞ takes the form

$$\sum_{\ell=0,2,\ldots}^{N-2} e^{-q(N-1)c-q\delta+q\ell c} = \frac{e^{-q\delta}}{2\sinh(qc)} . \qquad \text{(A.1.5a)}$$

Similarly

$$\sum_{\ell=N,N-2,\ldots}^{\infty} e^{-\ell qc+q(N-1)c+q\delta} = \frac{e^{+q\delta}}{2\sinh(qc)} \qquad \text{(A.1.5b)}$$

$$\sum_{\ell=1,3,\ldots}^{N-1} \cos(\vec{q}\cdot\vec{d}_o)\, e^{-q(N-1)c-q\delta+\ell qc} = \frac{e^{-q\delta+qc}\cos(\vec{q}\cdot\vec{d}_o)}{2\sinh(qc)} \qquad \text{(A.1.5c)}$$

$$\sum_{\ell=N+1,N+3,\ldots}^{\infty} \cos(\vec{q}\cdot\vec{d}_o)\, e^{-\ell qc+q(N-1)c+q\delta} = \frac{e^{q\delta-qc}\cos(\vec{q}\cdot\vec{d}_o)}{2\sinh(qc)} . \qquad \text{(A.1.5d)}$$

Direct substitution of eqns. (A.1.5a-d) into eqn. (A.1.3) yields

$$\left\{\sum_{\ell=0,2,\ldots}^{\infty} + \sum_{\ell=1,3,\ldots}^{\infty} \cos(\vec{q}\cdot\vec{d}_o)\right\} e^{-q|z-z_\ell|} = \frac{\cosh(q\delta)+\cos(\vec{q}\cdot\vec{d}_o)\cosh(q\delta-qc)}{\sinh(qc)} \qquad \text{(A.1.6)}$$

and eqn. (4.1.9) takes the form (keeping the real part only)

$$V_{\vec{q}}^{i-e}(z) = -\frac{2\pi}{\alpha}\,\frac{\cosh(q\delta)+\cos(\vec{q}\cdot\vec{d}_o)\cosh(q\delta-qc)}{q\sinh(qc)} +$$

$$+\frac{2\pi}{\alpha}\left\{\mathcal{D}_q(\delta,0)\,\partial(r_c-|\delta|)\cos\vec{q}\cdot\vec{d}_o + \mathcal{D}_q(c-|\delta|,0)\,\vartheta(r_c-c+|\delta|)\right\} \qquad \text{(A.1.7)}$$

with $|z| \in [(N-1)c,\ Nc]$ and $\delta \in [0,c]$.

Eqn. (A.1.7) is identical to eqn. (4.1.12c). Similarly we obtain eqn. (4.1.12d) if we let $z \in [-(N+1)c,\ -Nc]$.

APPENDIX A.2

ZERO-ORDER FOURIER TERM OF THE EXCHANGE POTENTIAL IN THE BULK REGION

Eqn. (5.2.11) takes the following form if the sumation over s' is replaced by an integral over $\vec{k}_{s'}$, and if $\xi_{s,o}(z)$ is assumed to be of the form

$$\xi_{s,o}(z) \sim \cos(q_s z + \phi_{q_s}) \quad . \tag{A.2.1}$$

$$A_o^{(s)}(z_1) \equiv A_o^{(\vec{k}_s, q_s)}(z_1) = -\frac{\pi}{\cos(q_s z_1 + \phi_{q_s})} \frac{2}{\pi} \int \frac{d\vec{k}_{s'}}{4\pi^2} \cos(q_{s'} z_1 + \phi_{q_{s'}}) \times$$

$$\times \int_{-\infty}^{+\infty} dz_2 \cos(q_{s'} z_2 + \phi_{q_{s'}}) \cos(q_s z_2 + \phi_{q_s}) \frac{e^{-|\vec{k}_{s'} - \vec{k}_s| |z_1 - z_2|}}{|\vec{k}_{s'} - \vec{k}_s|} \tag{A.2.2a}$$

$$= \frac{-\pi}{\cos(q_s z_1 + \phi_{q_s})} \frac{2}{4\pi^3} \int_{-\infty}^{+\infty} dz_2 \int_{-k_F}^{+k_F} dq_{s'} \int_0^{2\pi} d\vartheta \int_0^{\sqrt{k_F^2 - q_{s'}^2}} k_{s'} dk_{s'} \frac{e^{-|z_1 - z_2| [k_s^2 + k_{s'}^2 - 2 k_s k_{s'} \cos\vartheta]^{1/2}}}{[k_s^2 + k_{s'}^2 - 2 k_s k_{s'} \cos\vartheta]^{1/2}} \times$$

$$\times \frac{1}{2} \left\{ C_1 \cos Q_1 z_2 + C_2 \cos Q_2 z_2 + S_1 \sin Q_1 z_2 + S_2 \sin Q_2 z_2 \right\} \cos(q_{s'} z_1 + \phi_{q_{s'}}) \quad . \tag{A.2.2b}$$

where

$$\left. \begin{aligned} Q_1 &= q_s - q_{s'} \\ Q_2 &= q_s + q_{s'} \\ C_1 &= \cos(\phi_{q_s} - \phi_{q_{s'}}) \\ C_2 &= \cos(\phi_{q_s} + \phi_{q_{s'}}) \\ S_1 &= \sin(\phi_{q_s} - \phi_{q_{s'}}) \\ S_2 &= \sin(\phi_{q_s} + \phi_{q_{s'}}) \end{aligned} \right\} \tag{A.2.3}$$

A change in variable z_2 by the transformation

$$z = z_2 - z_1 \tag{A.2.4}$$

results in

$$A_o^{(\vec{k}_s,q_s)}(z_1) = \frac{-\pi}{\cos\tilde{\phi}_{q_s}} \frac{2}{4\pi^3} \int_{-\infty}^{+\infty} dz \int_{-k_F}^{+k_F} dq_{s'} \int_0^{2\pi} d\vartheta \int_0^{\sqrt{k_F^2-q_{s'}^2}} k_{s'}\, dk_{s'}$$

$$\times \frac{e^{-[k_s^2+k_{s'}^2-2k_sk_{s'}\cos\vartheta]^{1/2}|z|}}{[k_s^2+k_{s'}^2-2k_sk_{s'}\cos\vartheta]^{1/2}} \cos(\tilde{\phi}_{q_{s'}}) \times$$

$$\times \frac{1}{2}\left\{\tilde{C}_1 \cos Q_1 z + \tilde{C}_2 \cos Q_2 z + \tilde{S}_1 \sin Q_1 z + \tilde{S}_2 \sin Q_2 z\right\} \tag{A.2.5}$$

where

$$\left.\begin{aligned} \tilde{C}_1 &= \cos(\tilde{\phi}_{q_s} - \tilde{\phi}_{q_{s'}}) \\ \tilde{C}_2 &= \cos(\tilde{\phi}_{q_s} + \tilde{\phi}_{q_{s'}}) \\ \tilde{S}_1 &= \sin(\tilde{\phi}_{q_s} - \tilde{\phi}_{q_{s'}}) \\ \tilde{S}_2 &= \sin(\tilde{\phi}_{q_s} + \tilde{\phi}_{q_{s'}}) \end{aligned}\right\} \tag{A.2.6}$$

$$\tilde{\phi}_{q_s} = \phi_{q_s} + q_s z_1 \quad . \tag{A.2.7}$$

The terms which contain the factors $\sin Q_i z$, $i=1,2$ give no contribution to $A_o^{(\vec{k}_s,q_s)}(z_1)$. Also the exponential factor in eqn. (A.2.5) integrated over the angle may be written as

$$\int_0^{2\pi} d\vartheta \, \frac{e^{-|\vec{k}_s-\vec{k}_{s'}||z|}}{|\vec{k}_s-\vec{k}_{s'}|} = \int_0^{2\pi} d\vartheta \int_0^{\infty} \frac{\rho \, d\rho \, J_0(\rho|\vec{k}_s-\vec{k}_{s'}|)}{\sqrt{\rho^2+z^2}}$$

$$= 2\pi \int_0^{\infty} \frac{\rho \, d\rho \, J_0(\rho k_s) J_0(\rho k_{s'})}{\sqrt{\rho^2+z^2}} \qquad \text{(A.2.8)}$$

where $J_0(x)$ is the Bessel's function of the first kind. Then, eqn. (A.2.5) takes the form

$$A_0^{(\vec{k}_s,q_s)}(z_1) = -\frac{\pi}{\cos(\tilde{\phi}_{q_s})} \frac{4\pi}{4\pi^3} \int_{-k_F}^{+k_F} dq_{s'} \int_0^{\sqrt{k_F^2-q_{s'}^2}} k_{s'} \, dk_{s'} \int_{-\infty}^{+\infty} dz \int_0^{\infty} \frac{\rho \, d\rho \, J_0(\rho k_s) J_0(\rho k_{s'})}{\sqrt{\rho^2+z^2}} \times$$

$$\times \frac{1}{2}\left\{ \tilde{C}_1 \cos Q_1 z + \tilde{C}_2 \cos Q_2 z \right\} \cos \tilde{\phi}_{q_{s'}} \qquad \text{(A.2.9a)}$$

$$= \frac{-1}{\pi \cos \tilde{\phi}_{q_s}} \int_{-k_F}^{k_F} dq_{s'} \int_0^{\sqrt{k_F^2-q_{s'}^2}} k_{s'} \, dk_{s'} \int_0^{\infty} \rho \, d\rho \, J_0(\rho k_s) \, J_0(\rho k_{s'}) \times$$

$$\times \left\{ \tilde{C}_1 K_0(|Q_1|\rho) + \tilde{C}_2 K_0(|Q_2|\rho) \right\} \cos \tilde{\phi}_{q_{s'}} \qquad \text{(A.2.9b)}$$

where $K_0(x)$ is the Bessel function of second kind and the formula (Gradshteyn, I.S. et al., 1965)

$$\int_0^{\infty} \frac{\cos(\alpha x) \, dx}{\sqrt{\beta^2+x^2}} = K_0(\alpha\beta) \qquad \text{(A.2.10)}$$

$$\alpha > 0$$

$$\mathrm{Re}\,\beta > 0$$

was used. With the help of another formula,

$$\int_0^\infty x\, J_0(\alpha x)\, K_0(bx)\, J_0(cx)\, dx \quad =$$

$$= \frac{1}{\sqrt{\alpha^4+b^4+c^4-2\alpha^2c^2+2\alpha^2b^2+2b^2c^2}}\,, \qquad \text{(A.2.11)}$$

$$c>0, \quad \mathrm{Re}\, b > |\mathrm{Im}\,\alpha|,$$

eqn. (A.2.9b) takes the form

$$A_0^{(\vec{k}_s,q_s)}(z_1) = \frac{-1}{\cos\tilde{\phi}_{q_s}}\,\frac{1}{\pi}\int_{-k_F}^{k_F} dq_{s'} \int_0^{\sqrt{k_F^2-q_{s'}^2}} k_{s'}\,dk_{s'}\,\cos(\tilde{\phi}_{q_{s'}}) \;\times$$

$$\times \left\{ \frac{\tilde{C}_1}{\sqrt{k_s^4+Q_1^4+k_{s'}^4-2k_{s'}^2k_s^2+2k_s^2Q_1^2+2k_{s'}^2Q_1^2}} \;+ \right.$$

$$\left. + \frac{\tilde{C}_2}{\sqrt{k_s^4+Q_2^4+k_{s'}^4-2k_{s'}^2k_s^2+2k_s^2Q_2^2+2k_{s'}^2Q_2^2}} \right\} \qquad \text{(A.2.12)}$$

from which eqn. (5.2.16) follows.

APPENDIX A.3

POLARIZATION FUNCTION AND ITS FOURIER TRANSFORM

The polarization function $\Pi(\vec{r}_1, \vec{r}_2, \omega)$ is defined as

$$\Pi(\vec{r}_1,\vec{r}_2,\omega) = -2i \int G(\vec{r}_1,\vec{r}_2,\omega+\varepsilon)\, G(\vec{r}_2,\vec{r}_1,\varepsilon)\, \frac{d\varepsilon}{2\pi} \qquad \text{(A.3.1)}$$

Using eqn. (5.1.3), eqn. (A.3.1) takes the form

$$\begin{aligned} \Pi(\vec{r}_1,\vec{r}_2,\omega) = -2i \int \frac{d\varepsilon}{2\pi} \sum_{s_1 s_2} \psi_{s_1}(\vec{r}_1)\, \psi^*_{s_1}(\vec{r}_2)\, \psi_{s_2}(\vec{r}_2)\, \psi^*_{s_2}(\vec{r}_1) \times \\ \times \left\{ \frac{\vartheta(\varepsilon_{s_1}-\epsilon_F)}{\omega+\varepsilon-\varepsilon_{s_1}+i\delta} + \frac{\vartheta(\epsilon_F-\varepsilon_{s_1})}{\omega+\varepsilon-\varepsilon_{s_1}-i\delta} \right\} \times \\ \times \left\{ \frac{\vartheta(\varepsilon_{s_2}-\epsilon_F)}{\varepsilon-\varepsilon_{s_2}+i\delta} + \frac{\vartheta(\epsilon_F-\varepsilon_{s_2})}{\varepsilon-\varepsilon_{s_2}-i\delta} \right\} . \end{aligned} \qquad \text{(A.3.2)}$$

Performing the integration over , we obtain

$$\begin{aligned} \Pi(\vec{r}_1,\vec{r}_2,\omega) = 2 \sum_{s_1 s_2} \psi_{s_1}(\vec{r}_1)\, \psi^*_{s_1}(\vec{r}_2)\, \psi_{s_2}(\vec{r}_2)\, \psi^*_{s_2}(\vec{r}_1) \times \\ \times \left\{ \frac{\vartheta(\varepsilon_{s_1}-\epsilon_F)\,\vartheta(\epsilon_F-\varepsilon_{s_2})}{\omega+\varepsilon_{s_2}-\varepsilon_{s_1}+i\delta} - \frac{\vartheta(\epsilon_F-\varepsilon_{s_1})\,\vartheta(\varepsilon_{s_2}-\epsilon_F)}{\omega+\varepsilon_{s_2}-\varepsilon_{s_1}-i\delta} \right\} . \end{aligned} \qquad \text{(A.3.3)}$$

If $\psi_s(\vec{r})$ is taken as the zero order Fourier term in eqn. (4.5.3), i.e.

$$\psi_s(\vec{r}) \equiv \psi_{\vec{k}_s q_s}(\vec{r}) = e^{i\vec{k}_s\cdot\vec{\rho}}\, \xi_{q_s}(z) \qquad \text{(A.3.4)}$$

then

$$\Pi(\vec{r}_1,\vec{r}_2,\omega)=\Pi(\vec{\rho}_1-\vec{\rho}_2,z_1,z_2,\omega) \tag{A.3.5}$$

and taking the Fourier transform with respect to the $(\vec{\rho}_1-\vec{\rho}_2)$ variable, we obtain

$$P_{\vec{Q}}(z_1,z_2,\omega)=2\sum_{\vec{k}_{s_1}\vec{k}_{s_2}q_{s_1}q_{s_2}}\xi_{q_{s_1}}(z_1)\,\xi^*_{q_{s_1}}(z_2)\,\xi_{q_{s_2}}(z_2)\,\xi^*_{q_{s_2}}(z_1)\;\cdot$$

$$\cdot\,\delta_{\vec{k}_{s_1}-\vec{k}_{s_2},\vec{Q}}\left\{\frac{\theta(\varepsilon_{s_1}-\epsilon_F)\,\theta(\epsilon_F-\varepsilon_{s_2})}{\omega+\varepsilon_{s_2}-\varepsilon_{s_1}+i\delta}-\frac{\theta(\epsilon_F-\varepsilon_{s_1})\,\theta(\varepsilon_{s_2}-\epsilon_F)}{\omega+\varepsilon_{s_2}-\varepsilon_{s_1}-i\delta}\right\} \tag{A.3.6}$$

We also assume that

$$\varepsilon_s=\frac{1}{2}\left\{\vec{k}_s^{\,2}+q_s^2\right\} \quad . \tag{A.3.7}$$

Then the theta functions may be interpreted according to the Fig. A.1.

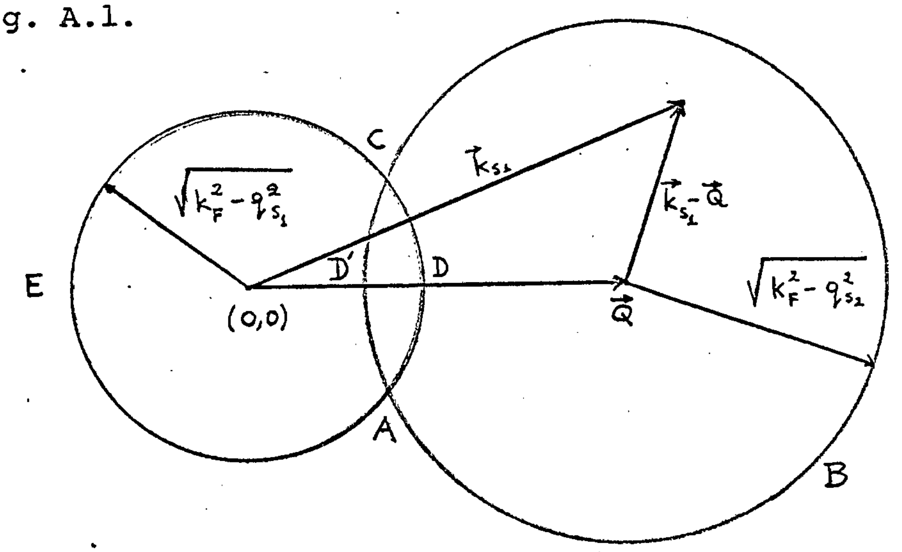


Fig. A.1: Geometric interpretation of the theta functions of eqn. (A.3.6).

The term $\theta(\mathcal{E}_{s_1}-\epsilon_F)\theta(\epsilon_F-\mathcal{E}_{s_2})\delta_{\vec{K}_{s_1}-\vec{k}_{s_2},\vec{Q}}$ gives contribution to $P_{\vec{Q}}(z_1,z_2,\omega)$, only for $\vec{K}_{s_1} \in \{A\,B\,C\,D\,A\} \equiv \{A_1\}$. Similarly the term $\theta(\mathcal{E}_{s_2}-\epsilon_F)\theta(\epsilon_F-\mathcal{E}_{s_1})\delta_{\vec{K}_{s_1}-\vec{k}_{s_2},\vec{Q}}$ gives contribution to $P_{\vec{Q}}(z_1,z_2,\omega)$ for $\vec{K}_{s_1} \in \{A\,D'\,C\,E\,A\} \equiv \{A_2\}$. Therefore we can rewrite eqn (A.3.6) as follows:

$$P_{\vec{Q}}(z_1,z_2,\omega) = \frac{2\alpha}{4\pi^2} \sum_{q_{s_1}q_{s_2}} \xi_{q_{s_1}}(z_1)\,\xi^*_{q_{s_1}}(z_2)\,\xi_{q_{s_2}}(z_2)\,\xi^*_{q_{s_2}}(z_1)\, \times$$

$$\times \left\{ \int_{\{A_1\}} d\vec{k}_{s_1} - \int_{\{A_2\}} d\vec{k}_{s_1} \right\} \times \frac{1}{\omega + \frac{1}{2}\left(Q^2 + q_{s_2}^2 - q_{s_1}^2 - 2\vec{k}_{s_1}\cdot\vec{Q}\right)} \tag{A.3.8}$$

Notice that

$$\int_{\{A_2\}} d\vec{k}_{s_1} = \int_{\{A_2\}} d\vec{k}_{s_1} + \int_{\{ADCD'A\}} d\vec{k}_{s_1} - \int_{\{ADCD'A\}} d\vec{k}_{s_1} = \int_{\{ADCEA\}} d\vec{k}_{s_1} - \int_{\{ADCD'A\}} d\vec{k}_{s_1}$$

and

$$\int_{\{A_1\}} d\vec{k}_{s_1} - \int_{\{A_2\}} d\vec{k}_{s_1} = \int_{\{ABCD'A\}} d\vec{k}_{s_1} - \int_{\{ADCEA\}} d\vec{k}_{s_1} \quad . \tag{A.3.9}$$

It remains to calculate the integral $I_{\vec{Q}}(q_{s_1}q_{s_2})$

$$I_{\vec{Q}}(q_{s_1} q_{s_2}) = \left\{ \int_{\{ABCD'A\}} d\vec{k}_{s_1} - \int_{\{ADCEA\}} d\vec{k}_{s_1} \right\} \cdot \frac{1}{\omega + \frac{1}{2}\left(Q^2 + q_{s_2}^2 - q_{s_1}^2 - 2\vec{k}_{s_1}\cdot\vec{Q}\right)} \qquad \text{(A.3.10)}$$

which is quite easily evaluated. We obtain

$$I_{\vec{Q}}(q_{s_1} q_{s_2}) = \frac{2\pi}{Q^2}\left\{ -Q^2 + \sqrt{A^2 - Q^2 r_1^2}\left\{1 + \partial(A) - \partial(-A)\right\} \partial\left(\frac{A^2}{Q^2} - r_1^2\right)\right\} \qquad \text{(A.3.11)}$$

where

$$A = \omega + \frac{1}{2}\left(Q^2 + q_{s_2}^2 - q_{s_1}^2\right) \qquad \text{(A.3.12)}$$

$$r_1^2 = k_F^2 - q_1^2 \qquad \text{(A.3.13)}$$

APPENDIX A.4

USE OF SYMMETRY IN EVALUATING THE PROPAGATION MATRIX

As a result of the fact that the surface plane is a mirror plane of the crystal, we have

$$\underline{\underline{\mathcal{D}}}_s(z) = \underline{\underline{\mathcal{D}}}_s(-z) \qquad \text{(A.4.1)}$$

where $\underline{\underline{\mathcal{D}}}_s(z)$ is the matrix defined in eqn. (6.1.5c).

The second assumption in our formalism was that the surface plane is a lattice plane which possesses a centre of symmetry. The consequence of this assumption is that the Fourier coefficients, $V_{\vec{q}}^{i-e}(z)$, of the ion-electron interaction have the following property

$$V_{\vec{q}}^{i-e}(z) = V_{-\vec{q}}^{*\,i-e}(z) \quad . \qquad \text{(A.4.2a)}$$

The property stated in eqn. (A.4.2a) is also satisfied by the Fourier terms of the Hartree and exchange potentials. For the Fourier coefficients of the exchange potential this is easily verified from eqn. (5.2.10). Similarly for the coefficients of the Hartree potential this may be verified by noticing that the Fourier coefficients of the electron density function $\rho(\vec{r},\vec{r})$, eqn. (5.2.4), satisfy eqn. (A.4.2a), i.e.

$$\rho_{\vec{q}}(z,z) \equiv \rho_{\vec{q}}(z) = \rho_{-\vec{q}}^{*}(z) \quad . \qquad \text{(A.4.2b)}$$

Finally it is assumed that property (A.4.2a) is satisfied by the correlation potential, eqn. (6.1.2a).

The last of our assumptions was that the system possesses a Bravais lattice. Then the ion-electron interaction $V^{i-e}(\vec{r})$ satisfies

$$V^{i-e}(\vec{\rho}, z-c) = V^{i-e}(\vec{\rho}-\vec{d}_0, z) \qquad (A.4.3)$$

where c is the distance between successive lattice planes parallel to the (001) lattice plane. From the above equation one easily obtains

$$V^{i-e}_{\vec{q}}(z-c) = e^{-i\vec{q}\cdot\vec{d}_0}\, V^{i-e}_{\vec{q}}(z) \quad . \qquad (A.4.4)$$

It can easily be verified that the property of the Fourier coefficients of the ion-electron interaction stated in eqn. (A.4.3) is also satisfied by the coefficients of the Hartree and exchange potentials. This follows from the fact that the single electron wave functions and consequently the electron density function satisfy

$$\psi_s(\vec{r}) = \psi_s(\vec{r}+\vec{r}_m) \quad , \qquad (A.4.5)$$

$$\rho(\vec{r}) = \rho(\vec{r}+\vec{r}_m) \quad . \qquad (A.4.6)$$

Eqn. (6.1.2a) assures also that the correlation potential satisfies the property stated by eqn. (A.4.4).

Without loss of generality we take only the real part of the single electron potentials. Then the assumptions of Torrini's and Zanazzi's theory are satisfied (Torrini, M., Zanazzi, E., 1972) and their theory may be used to calculate the propagation matrix $\underline{\underline{P}}_s^{(B)}(z)$.

The following matrices are defined.

$$(\underline{\underline{T}})_{ij} = \delta_{ij}\, exp(i\vec{q}_i\cdot\vec{d}_o) \tag{A.4.7}$$

$$(\underline{\underline{V}}^{i-e})_{ij} = V^{i-e}_{\vec{q}_i-\vec{q}_j}(z) \tag{A.4.8}$$

$$(\underline{\underline{B}})_{ij} = B_{\vec{q}_i-\vec{q}_j}(z) \quad ,(\vec{q}_i,\vec{q}_j)\in\{\vec{h};N\}\times\{\vec{h};N\} \tag{A.4.9}$$

$$\underline{\underline{\Theta}} = \begin{pmatrix} \underline{\underline{T}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{T}} \end{pmatrix} \tag{A.4.10}$$

Then it can easily be verified that

$$\underline{\underline{\mathcal{P}}}_s(z+c) = \underline{\underline{\Theta}}^* \underline{\underline{\mathcal{P}}}_s(z)\, \underline{\underline{\Theta}} \tag{A.4.11}$$

and that the matrix $\underline{\underline{\Theta}}\ \underline{\underline{P}}(z+c)$ satisfies the same equation, eqn. (6.1.6), as $\underline{\underline{P}}(z)$. From the uniqueness of the solution of eqn. (6.1.6) it follows that

$$\underline{\underline{\Theta}}\ \underline{\underline{P}}(z+c) = \underline{\underline{P}}(z)\,\underline{\underline{\Delta}} \tag{A.4.12}$$

where $\underline{\underline{\Delta}}$ is a constant matrix. Using the condition $\underline{\underline{P}}(o) = \underline{\underline{I}}$, the matrix $\underline{\Delta}$ is determined and we obtain

$$\underline{\underline{P}}(z+c) = \underline{\underline{\theta}}^{*}\,\underline{\underline{P}}(z)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c)\,. \tag{A.4.13}$$

For $z = -{}^{c}/_{2}$ the last equation becomes

$$\underline{\underline{P}}(c/2) = \underline{\underline{\theta}}^{*}\,\underline{\underline{P}}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c) \tag{A.4.14}$$

from which follows

$$\underline{\underline{P}}(c) = \underline{\underline{\theta}}^{*}\,\underline{\underline{P}}^{-1}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c/2)\,. \tag{A.4.15}$$

Finally from eqn. (A.4.13) the $\underline{P}(2c)$ is determined if we let $z = c$. Therefore

$$\begin{aligned}
\underline{\underline{P}}(2c) &= \underline{\underline{\theta}}^{*}\,\underline{\underline{P}}(c)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c)\\
&= \underline{\underline{\theta}}^{*}\left[\underline{\underline{\theta}}^{*}\,\underline{\underline{P}}^{-1}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c/2)\right]\underline{\underline{\theta}}\left[\underline{\underline{\theta}}^{*}\,\underline{\underline{P}}^{-1}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c/2)\right]\\
&= \underline{\underline{P}}^{-1}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c/2)\,\underline{\underline{P}}^{-1}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c/2)\\
&= \left[\underline{\underline{P}}^{-1}(-c/2)\,\underline{\underline{\theta}}\,\underline{\underline{P}}(c/2)\right]^{2}
\end{aligned}$$

which shows that we require to know the propagation matrix across a quarter of a period in the <001> direction in order to determine completely the solution in the bulk region.

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