

THE WAVE FUNCTIONS OF CONDUCTION ELECTRONS
IN METALLIC LITHIUM

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ABSTRACT

The aim of this work has been to evaluate fairly reliable wavefunctions for electrons in the conduction band of lithium, mainly with the aim of bringing some light to the question of whether or not there is a marked variation of the wavefunction throughout k -space.

An approximately self-consistent potential was constructed, based on the Hartree-Fock-Slater equations and the atomic wavefunctions given by Holöien. The one-electron equation describing the electrons in the conduction band was solved by the method of orthogonalized plane waves, using up to 70-80 waves. The solutions were determined at the four points of highest symmetry in the Brillouin zone and at 14 other points on axes of symmetry. In effect, 126 points throughout the Brillouin zone were thus considered.

The eigenvalues are in fair agreement with those obtained by previous calculations, despite the use of a somewhat different potential. It should be stressed that the potential employed was an approximation to the true self-consistent potential in the metal, and not a "pseudopotential".

The main conclusions to be derived from the calculated wavefunctions are

1- Outside the region of the atomic cores the electrons behave essentially as free; near the nuclei the wavefunctions behave as a combination of s and p atomic functions.

2- The form of the wavefunctions does not change much throughout the occupied part of the Brillouin zone. This is particularly true for points with the same magnitude of k .

The Fermi surface is found to be distorted from a sphere, in the 110 direction. However, it does not touch the zone face, as previously predicted.

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I: THEORY

1- Main Assumptions

In deriving the equation to be satisfied by an electron in a solid we presuppose the validity of the following assumptions.

- I) The electronic motion could be treated separately from the nuclear motion.
- II) The electrons in the solid are classified into two categories, the core electrons and the valence electrons. The core electrons are considered as completely localised around their respective nuclei, and hence their effect on the valence electrons could be represented by a potential term similar to the term representing the effect of the nuclei on them: this approximation makes it possible to treat the valence electrons as though they were present in a field of ion-cores formed by the nuclei and the inner electrons surrounding each of them.
- III) The wave function of the system of valence electrons can be represented by a combination of one-electron functions.

2- Hartree Equations

Hartree assumed that one can write the wave function of a system of n valence electrons as the product of n

one-electron functions, viz.,

$$\Psi(\underline{x}_1, \underline{x}_2, \dots, \underline{x}_n) = \psi_1(\underline{x}_1)\psi_2(\underline{x}_2)\dots\psi_n(\underline{x}_n)$$

where the ψ 's are normalized, \underline{x}_i is the spacial coordinates of the i^{th} electron. The one-electron function $\psi_i(\underline{x}_i)$ would satisfy a one-electron Schrodinger equation; the potential in this equation contains two terms, one representing the Coulomb effect of the ion-cores and the second accounting for the Coulomb field of the other valence electrons. He considered the latter as the classical electrostatic potential of the $(n-1)$ normalized charge distributions $|\psi_j(\underline{x}_j)|^2$. Thus he assumed that the one-electron function $\psi_i(\underline{x}_i)$ satisfies **

$$-\nabla^2 \psi_i(\underline{x}_i) + \left\{ V_i(\underline{x}_i) + \sum_j' \int \frac{1}{r_{ij}} |\psi_j(\underline{x}_j)|^2 d\underline{x}_j \right\} \psi_i(\underline{x}_i) = \epsilon_i \psi_i(\underline{x}_i) \quad (1)$$

∇^2 being the kinetic energy operator. The prime on Σ shows that the term $i=j$ is excluded. There will be n such equations for $i=1,2,\dots,n$. These could be solved simultaneously by applying the self consistent technique. Although Hartree's derivation of his equations is not rigorous, yet as we shall see in the next section, the application of rigorously mathematical treatment would lead us to them.

**Throughout this work we use atomic units, i.e. we set

$$\hbar=1, m=\frac{1}{2}, \text{ and } e^2=2.$$

The Unit of length: 1 Bohr radius = 5.3×10^{-9} cm.

The Unit of energy: 1 Rydberg = 13.6 ev.

3- Hartree Equations by Variational Method

The Hamiltonian of n electrons in a crystal containing m ion-cores is

$$H = \sum_{i=1}^n -\nabla_i^2 + \sum_{i=1}^n V_i + \frac{1}{2} \sum_{i,j=1}^n \prime 2/r_{ij} \quad (2)$$

where V_i is the potential energy of the electron i due to the different ion-cores; $2/r_{ij}$ is the coulomb interaction between the i^{th} and j^{th} electrons, the prime on the last term means that we exclude the terms for which $i=j$.

Equation (2) could be written more compactly

$$H = \sum_i H_i + \sum_{i,j} 1/r_{ij} \quad (3)$$

where $H_i = -\nabla_i^2 + V_i$

It is clear that H_i depends only on the variables \underline{x}_i of the electron i , and that it is the same function of them as H_j of \underline{x}_j .

Let
$$\Psi(\underline{x}_1, \underline{x}_2, \dots, \underline{x}_n) = \prod_{i=1}^n \psi_i(\underline{x}_i) \quad (4)$$

$$= \psi_1(\underline{x}_1) \psi_2(\underline{x}_2) \dots \psi_n(\underline{x}_n)$$

where
$$\int \psi_i^* \psi_i d\underline{x}_i = 1 \quad \text{for all } i. \quad (5)$$

The variational method tells us that the "best" wave function is the one which minimizes the expectation value of the energy

i.e. they are those for which $\delta \int \Psi^* H \Psi d\underline{x} = 0$ (6)
 subject to the condition (5).
 equation (6) could be written

$$\int \delta \Psi^* H \Psi d\underline{x} + \int \Psi^* H \delta \Psi d\underline{x} = 0 \quad (7)$$

now substituting from (3) and (5) in (7) we get

$$\sum_i \int \Psi_i^* \left\{ \sum_{k \neq i} \int \psi_k^* H_k \psi_k d\underline{x}_k + \sum_{j, k \neq i} \int \frac{1}{r_{jk}} |\psi_j(\underline{x}_j)|^2 |\psi_k(\underline{x}_k)|^2 d\underline{x}_j d\underline{x}_k + H_i \right. \\ \left. + \sum_j \int \frac{2}{r_{ij}} |\psi_j|^2 d\underline{x}_j \right\} \delta \psi_i d\underline{x}_i + (\text{a symmetrical expression in } \delta \psi_i^*) = 0 \quad (8)$$

The variational equivalent to (5) is

$$\lambda_i \left[\int \psi_i^* \delta \psi_i d\underline{x}_i + \int \delta \psi_i^* \psi_i d\underline{x}_i \right] = 0 \quad (9)$$

where λ is a Lagrangian multiplier; the result of adding (8) to (9) is

$$\sum_i \int \psi_i^* \left\{ \sum_{k \neq i} \int \psi_k^* H_k \psi_k d\underline{x}_k + \sum_{j, k \neq i} \int \frac{1}{r_{jk}} |\psi_j(\underline{x}_j)|^2 |\psi_k(\underline{x}_k)|^2 d\underline{x}_j d\underline{x}_k + H_i + \sum_j \int \frac{2}{r_{ij}} |\psi_j|^2 d\underline{x}_j + \lambda_i \right\} \delta \psi_i d\underline{x}_i \\ + \text{similar expression in } \delta \psi_i^* = 0 \quad (10)$$

Since H is Hermitian we can reverse the position of $\delta \psi_k$ and ψ_k^* , also since $\delta \psi_i$ and $\delta \psi_i^*$ are independent variations and are independent of the variations of $\delta \psi_k$ and $\delta \psi_k^*$ ($k \neq i$), the necessary and sufficient condition that (10) is satisfied

is that the coefficients of both $\delta\psi_i$ and $\delta\psi_i^*$ are zero. We need only consider one of them since the other would be the complex conjugate of it. Thus we get

$$H_i \psi_i + \left\{ 2 \sum_j' \int \frac{1}{r_{ij}} |\psi_j|^2 d\underline{x}_j \right\} \psi_i + \left\{ \sum_{i \neq j} \int \psi_j^* H_j \psi_j d\underline{x}_j \right. \\ \left. + 2 \sum_{j, k \neq i} \int \frac{1}{r_{ij}} |\psi_j|^2 |\psi_k|^2 d\underline{x}_j d\underline{x}_k + \lambda_i \right\} \psi_i = 0$$

if we let

$$\sum_{i \neq j} \int \psi_j^* H_j \psi_j d\underline{x}_j + 2 \sum_{j, k \neq i} \int \frac{1}{r_{jk}} |\psi_j|^2 |\psi_k|^2 d\underline{x}_j d\underline{x}_k + \lambda_i = -\epsilon_i$$

we get

$$\left\{ H_i + 2 \sum_j' \int \frac{1}{r_{ij}} |\psi_j|^2 d\underline{x}_j \right\} \psi_i = \epsilon_i \psi_i$$

which is Hartree's equations.

4- Hartree-Fock Equations

In deriving the Hartree equations we have made two important simplifications. First we neglected the spin functions, and second we neglected the Pauli principle which requires that the total wave function of the whole system should be completely antisymmetric. These two simplifications are avoided in deriving the Hartree-Fock equations.

First we shall introduce the spin by writing the wave function of an electron as

$$\phi(\underline{r}) = \psi(\underline{x}) \eta(\zeta)$$

where ψ is the spacial part and η is the eigenfunction of the z-component of spin labeled as $\eta_{\frac{1}{2}}(\zeta)$ or $\eta_{-\frac{1}{2}}(\zeta)$; the spin coordinate ζ may have either of the values ± 1 .

It is customary to write $\eta_{+\frac{1}{2}} = \alpha$, $\eta_{-\frac{1}{2}} = \beta$, so that

$$\begin{aligned} \alpha(1) &= 1 & , & & \alpha(-1) &= 0 \\ \beta(1) &= 0 & , & & \beta(-1) &= 1 \end{aligned}$$

The only completely antisymmetric wavefunction that could be constructed from a complete set of n orthonormal functions ϕ each corresponding to one of the electrons in the system is

$$\Psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n) = [n!]^{-\frac{1}{2}} \sum_P (-1)^P [\phi_1(\underline{r}_1) \phi_2(\underline{r}_2) \dots \phi_n(\underline{r}_n)] \quad (11)$$

where P runs over the n! permutations of the variables, p is the parity of the permutation P, and $[n!]^{-\frac{1}{2}}$ is a normalisation factor. Equation (11) can be written in the determinantal form

$$\Psi = \left[\frac{1}{n!} \right]^{\frac{1}{2}} \begin{vmatrix} \phi_1(\underline{r}_1) & \phi_1(\underline{r}_2) \dots \phi_1(\underline{r}_n) \\ \phi_2(\underline{r}_1) & \phi_2(\underline{r}_2) \dots \phi_2(\underline{r}_n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(\underline{r}_1) & \phi_n(\underline{r}_2) \dots \phi_n(\underline{r}_n) \end{vmatrix}$$

Before proceeding to minimize the energy expectation value, we shall write down a useful mathematical theorem.

If Ψ is a normalized determinantal wave function with diagonal elements $\phi_1(\underline{r}_1), \phi_2(\underline{r}_2), \dots, \phi_n(\underline{r}_n)$, where the ϕ 's

are orthogonalized; And if F is a symmetric operator;

Then

$$\int \Psi^* F \Psi d\underline{r} = [n!]^{\frac{1}{2}} \int \Psi^* F \phi_1(\underline{r}_1) \phi_2(\underline{r}_2) \dots \phi_n(\underline{r}_n) d\underline{r}$$

Now the energy expectation value is

$$E = \int \Psi^* H \Psi d\underline{r}$$

where H is the Hamiltonian (11) and where $d\underline{r}$ means integration over all space coordinates plus summation over all spin coordinates. Since H is symmetric we can apply the above stated theory

$$\begin{aligned} E &= [n!]^{\frac{1}{2}} \int \Psi^* H \phi_1(\underline{r}_1) \phi_2(\underline{r}_2) \dots \phi_n(\underline{r}_n) d\underline{r}_1 d\underline{r}_2 \dots d\underline{r}_n \\ &= \int \left\{ \sum_P (-1)^P P[\phi_1^*(\underline{r}_1) \dots \phi_n^*(\underline{r}_n)] \right\} \left\{ \sum_l [\nabla_l^2 + V_l + \sum_j \frac{1}{r_{lj}}] \right\} \phi_1(\underline{r}_1) \dots \phi_n(\underline{r}_n) d\underline{r}_1 d\underline{r}_2 \dots d\underline{r}_n \end{aligned}$$

Due to the orthonormality of the ϕ 's the integral for the first and second terms in the Hamiltonian will vanish except when P is the identity operator. As for the last term in the Hamiltonian the integral will be non-zero only for the identity permutation operator and for the operator that permutes ϕ_i^* and ϕ_j^* . Hence we get

$$E = \sum_i \int \phi_i^*(\underline{r}_i) [-\nabla_i^2 + V_i] \phi_i(\underline{r}_i) d\underline{r}_i \\ + \sum_{i,j}' \int [\phi_i^*(\underline{r}_i) \phi_j^*(\underline{r}_j) - \phi_i^*(\underline{r}_j) \phi_j^*(\underline{r}_i)] \frac{1}{r_{ij}} \phi_i(\underline{r}_i) \phi_j(\underline{r}_j) d\underline{r}_i d\underline{r}_j$$

now we shall separate the space and spin variables

$$E = \sum_i \sum_{\zeta_i = \pm 1} \int \psi_i^*(\underline{x}_i) [-\nabla_i^2 + V_i] \psi_i(\underline{x}_i) |\eta_{\pm}(\zeta_i)|^2 d\underline{x}_i \\ + \sum_{i,j}' \sum_{\zeta_i, \zeta_j = \pm 1} \int \frac{1}{r_{ij}} |\psi_i(\underline{x}_i)|^2 |\psi_j(\underline{x}_j)|^2 |\eta_{\pm}(\zeta_i)|^2 |\eta_{\pm}(\zeta_j)|^2 d\underline{x}_i d\underline{x}_j \\ - \sum_{i,j}' \sum_{\zeta_i, \zeta_j = \pm} \int \frac{1}{r_{ij}} \psi_i^*(\underline{x}_j) \psi_j^*(\underline{x}_i) \psi_i(\underline{x}_i) \psi_j(\underline{x}_j) d\underline{x}_i d\underline{x}_j \\ \times \begin{cases} \alpha(\zeta_j) \alpha(\zeta_i) \alpha(\zeta_i) \alpha(\zeta_j) \\ \beta(\zeta_j) \beta(\zeta_i) \beta(\zeta_i) \beta(\zeta_j) \\ \alpha(\zeta_j) \beta(\zeta_i) \alpha(\zeta_i) \beta(\zeta_j) \end{cases}$$

It is clear that the first and second terms give results whatever the spin states are whereas the last term contributes only when the spin functions have similar states i.e. have parallel spin, Thus

$$E = \sum_i \int \psi_i^*(\underline{x}_i) [-\nabla_i^2 + V_i(\underline{x}_i)] \psi_i(\underline{x}_i) d\underline{x}_i \\ + \sum_{i,j}' \iint \frac{1}{r_{ij}} |\psi_i(\underline{x}_i)|^2 |\psi_j(\underline{x}_j)|^2 d\underline{x}_i d\underline{x}_j$$

$$- \sum_{\substack{i \\ \parallel \\ j}}' \iint \frac{1}{r_{ij}} \psi_i^*(\underline{x}_j) \psi_j^*(\underline{x}_i) \psi_i(\underline{x}_i) \psi_j(\underline{x}_j) d\underline{x}_i d\underline{x}_j \quad (12)$$

We can remove the primes on both the second and third terms since if we include the value $i=j$ in both these terms the additional terms cancel each other. The derivation of Hartree-Fock equations proceeds in a similar way to that of deriving Hartree's equations. Thus we minimize equation (12) subject to the condition that the ϕ 's should remain orthonormalized. Finally we get for the orbital $\psi_i(\underline{x}_i)$

$$\left\{ -\nabla_i^2 + V_i(\underline{x}_i) + 2 \sum_j \int \frac{1}{r_{ij}} |\psi_j(\underline{x}_j)|^2 d\underline{x}_j \right\} \psi_i(\underline{x}_i) - 2 \sum_{\substack{j \\ \parallel \\ i}} \left\{ \int \frac{1}{r_{ij}} \psi_j^*(\underline{x}_j) \psi_i(\underline{x}_j) d\underline{x}_j \right\} \psi_j(\underline{x}_i) = \sum_j \lambda_{ij} \psi_i(\underline{x}_i)$$

where the λ 's are undetermined multipliers. Since we can always find solutions such that Λ is a diagonal matrix, we need only consider the λ_{ii} which we call E_i .

The last term in the left hand side could be improved in appearance by multiplying and dividing by $\psi_i^*(\underline{x}_i) \psi_i(\underline{x}_i)$, thus Hartree-Fock equation take the form

$$\left\{ -\nabla_i^2 + V_i(\underline{x}_i) + 2 \sum_j \int \frac{1}{r_{ij}} |\psi_j(\underline{x}_j)|^2 d\underline{x}_j \right\} \psi_i(\underline{x}_i) -$$

$$2 \sum_j \left\{ \frac{1}{\psi_i(\underline{x}_i)\psi_i(\underline{x}_i)} \int \psi_j^*(\underline{x}_j)\psi_i^*(\underline{x}_i)\psi_j(\underline{x}_i)\psi_i(\underline{x}_j) \frac{1}{r_{ij}} d\underline{x}_j \right\} \psi_i(\underline{x}_i)$$

$$= E_i \psi_i(\underline{x}_i) \quad (13)$$

5- Physical Meaning of Hartree-Fock Equations

The first and second terms on the left hand side have a straightforward interpretation. The first is the Laplacian kinetic energy operator for the electron of coordinates \underline{x}_i , and the second is the Coulomb field of all the ion-cores acting on that electron.

The third term is the Coulomb potential energy acting on the electron at position \underline{x}_i of all the valence electrons including itself. The last term, called the exchange term, in some way corrects the inclusion of the i^{th} wave function in the third term since an electron does not act upon itself.

The exchange term may be interpreted as the exchange potential energy at position \underline{x}_i due to the presence of an exchange charge density

$$-\sqrt{2} \sum_j \frac{1}{\psi_i(\underline{x}_i)\psi_i(\underline{x}_i)} \psi_j^*(\underline{x}_j)\psi_i^*(\underline{x}_i)\psi_j(\underline{x}_i)\psi_i(\underline{x}_j)$$

at position \underline{x}_j . A detailed consideration of the interaction between the exchange charge and the electron at \underline{x}_i indicates

that the exchange interaction has the effect of removing from the vicinity of \underline{x}_i one electron of the same spin. It is as though the electron carries with it a hole. The occurrence of this effect is expected since by using a determinantal wave function we took into account the exclusion principle which prevents any two electrons having the same quantum number (including spin) from getting together. However, the correlation effect due to the electrostatic repulsion between electrons does not appear in the Hartree-Fock equations. The absence of this effect is not surprising since we are working in the framework of the one-electron approximation which assumes that the electrons move independently of each other.

The shape of the exchange hole depends upon the ψ_i under consideration; however, it is not very different for the various ψ_i 's specifying an electron system. Thus we can form a weighted mean of the exchange charges, weighted and averaged over the various electronic wave functions at each point of space and use this average in the exchange interaction term in each equation. This approximation would let all the electrons in the system move in the same potential field. Slater [23] suggested that one can even replace the average exchange charge by the corresponding value it would have in a free-electron gas whose local density is equal to the actual density at the position in

question, i.e. the exchange term takes the form

$$-6 \left\{ \frac{3}{8\pi} \sum_j \psi_j^*(\underline{x}_i) \psi_j(\underline{x}_i) \right\}^{1/3} \psi_i(\underline{x}_i)$$

Finally the quantity E_i which appears on the right hand side of equation (13) represents, according to Koopman's [13] theorem, the negative of the energy required to remove the i^{th} electron from the system.

6- Symmetry in Solids

A solid is not formed by a mere packing of its constituents (atoms or molecules) in any random fashion but -apart from a few exceptions - these constituents tend to come together in a particular order which is always the same for any particular solid. The regularity of the solid's structure makes it possible to classify a solid according to the way its constituents are arranged; moreover, because of this regularity solids exhibit symmetry properties which help immensely in describing the phenomena occurring in them.

Crystallographers have found that in a three dimensional space it is possible to arrange points (representing either atoms or molecules) only in one of 320 ways. In each of these possible ways one can move from one point in the structure to another - which is geometrically identical - by applying a symmetry operation. The symmetry operations in each of these arrangements form a group called the space

group. The operations in a space group may be translations, reflections, rotations, glide reflections, and screw displacements. The structure we are going to be concerned with does not include any operations of the last two types, thus we shall confine our discussion of space groups to those who do not contain screws and glides.

Such a space group contains two sub-groups, the first has as its members all the translation operations present and is called the Translation Group. The other, called the Point Group, includes the rest of the operations (rotations and reflections).

We shall write Hartree-Fock equations in the simple form

$$[-\nabla^2 + V(\underline{r})] \Psi(\underline{r}) = E \Psi(\underline{r})$$

where $V(\underline{r})$ is the crystal potential energy. Since this potential is due to the presence of the constituent elements of the solid, and since the arrangement of these has a definite symmetry, it is evident that the potential should possess the same symmetry as the crystal.

Thus the symmetry operations of this structure will commute with the Hamiltonian. And hence we should take into account while searching for solutions to our problem the general principle of Quantum Mechanics that states that the wave functions of a quantum system must form basis functions

for the irreducible representations of the group of operators which commute with the Hamiltonian of the system.

We shall discuss the consequences of the commutation of the Hamiltonian with both the translation group and the point group each on its own because the members of the former commute with each other whereas the members of the latter do not

7- The Unit Cell

We can divide the crystal into small identical cells. Each of these cells is called a unit cell. Obviously the division of a particular crystal structure into unit cells is not unique; however once a unit cell is chosen one can think of the crystal as being generated by the shifting of this unit cell along the directions of its three axes. Moreover, because of this characteristic the properties of the crystal at corresponding points in any two unit cells are identical. The smallest possible unit cell one can find is called the primitive cell. Let $\underline{a}_1, \underline{a}_2, \underline{a}_3$ be the three basic vectors of the primitive cell, then any translation of the form

$$\underline{R}_i = m_{i1}\underline{a}_1 + m_{i2}\underline{a}_2 + m_{i3}\underline{a}_3$$

where the m 's are positive or negative integers including zero, will take us from one point in the crystal into another point which is geometrically identical. For every translation \underline{R}_i we define an operator T_i which has the effect of adding to the coordinates of any function it operates on ~~the translation~~

the translation \underline{R}_i . The set of operators T_i form the translation group of the crystal. This group is Abelian since all its members commute with each other. This is because successive translations can be carried in any order. We shall be considering the consequences of this property in the next section. It should be noted that for a particular structure the choice of the primitive cell is not unique; nevertheless, all the primitive cells that one can choose for this structure have the same volume. It is usually more convenient to use the so-called the Wigner-Seitz cell which is the volume enclosed by the planes bisecting perpendicularly the lines joining an atom to the nearest and second, third, ... nearest neighbours. This primitive cell has the advantage of showing clearly the rotational symmetry of the crystal.

8- Bloch's Theorem

Bloch's theorem states that for any wave function that describes an electron in a crystal there exists a vector \underline{k} such that translation by a lattice vector \underline{R}_i is equivalent to multiplying by a phase factor $\exp.i\underline{k}.\underline{R}_i$.

Although Bloch theorem could be deduced formally from Group Theory as a corollary to the theorem that states that " In the field of complex numbers any representation of an Abelian group can be reduced to a sum of one dimensional representations. " we are not going to give its proof

from that standpoint but proceed instead as follows.

Our main problem is to solve the one-electron equation which could be written in the simple form

$$H\Psi(\underline{r}) = E\Psi(\underline{r})$$

where the Hamiltonian is

$$H = -\nabla^2 + V(\underline{r})$$

and $V(\underline{r})$ is the potential energy.

The periodicity of the crystal infers that the potential has the same periodicity of the crystal, i.e.

$$V(\underline{r} + \underline{R}_i) = V(\underline{r}) ,$$

\underline{R}_i being any translation vector.

Because of this property of V all the members of the translation group commute with the Hamiltonian. And since they also commute with each other it is always possible to find an eigenstate of H which would diagonalize all the operators simultaneously. Hence if $\Psi(\underline{r})$ was an eigenstate of H , then

$$\begin{aligned} T_i \Psi(\underline{r}) &= \sigma_i \Psi(\underline{r}) \quad , \text{where } \sigma_i \text{ is a constant} \\ &= \Psi(\underline{r} + \underline{R}_i) \quad , \text{by definition} \end{aligned}$$

or

$$|\Psi(\underline{r} + \underline{R}_i)|^2 = |\sigma_i|^2 |\Psi(\underline{r})|^2$$

but since the probability density should have the same periodicity as the crystal it follows that

$$|\sigma_i|^2 = 1$$

We shall write

$$\sigma_i = \exp.i\mathbf{k} \cdot \underline{R}_i$$

where \underline{k} is a real vector which is the same for all the operations. This is clearly a consistent way of writing α_i since the application of two transformations T_i, T_j , multiplies the wave function by

$$\exp. i\underline{k} \cdot (\underline{R}_i + \underline{R}_j)$$

Thus

$$T_i \Psi(\underline{r}) = \exp. (i\underline{k} \cdot \underline{R}_i) \Psi(\underline{r}) \quad (15)$$

which is Bloch's Theorem.

The particular vector \underline{k} which appears in the eigenvalue of each operator characterises the eigenstate of the Hamiltonian.

We define the function $U_k(\underline{r})$ by the relation

$$\Psi_k(\underline{r}) = \exp. (i\underline{k} \cdot \underline{r}) U_k(\underline{r}) \quad (16)$$

Now we shall show that $U_k(\underline{r})$ has the periodicity of the crystal

$$\Psi(\underline{r} + \underline{R}_i) = \exp. i\underline{k} \cdot \underline{R}_i \Psi(\underline{r})$$

substituting from (16)

$$= \exp. i\underline{k} \cdot \underline{R}_i \exp. i\underline{k} \cdot \underline{r} U_k(\underline{r})$$

also from the definition (16) directly

$$\Psi(\underline{r} + \underline{R}_i) = \exp. i\underline{k} \cdot (\underline{r} + \underline{R}_i) U_k(\underline{r} + \underline{R}_i)$$

Hence

$$U_k(\underline{r} + \underline{R}_i) = U_k(\underline{r})$$

9- Reciprocal Space

We define the vectors \underline{b}_1 , \underline{b}_2 , and \underline{b}_3 by the relation

$$\underline{a}_i \cdot \underline{b}_j = 2\pi \delta_{ij} \quad (17)$$

where the \underline{a} 's are the basic vectors of the primitive cell in real space. Relation (17) has the solution

$$\underline{b}_1 = 2\pi \frac{\underline{a}_2 \times \underline{a}_3}{\Omega} ; \quad \underline{b}_2 = 2\pi \frac{\underline{a}_3 \times \underline{a}_1}{\Omega} ; \quad \underline{b}_3 = 2\pi \frac{\underline{a}_1 \times \underline{a}_2}{\Omega} \quad (18)$$

where $\Omega = \underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)$

is the volume of the primitive cell in real space.

The vectors \underline{b} are said to be reciprocal to the vectors \underline{a} on account of their relation. The end points of the vectors of the form

$$\underline{K}_m = h_{m1}\underline{b}_1 + h_{m2}\underline{b}_2 + h_{m3}\underline{b}_3 \quad (19)$$

where the h 's are positive or negative integers, form a lattice of points, namely, the Reciprocal Lattice. **

The volume of the primitive cell in reciprocal space is inversely proportional to the volume of the primitive cell in real space. If Ω_p denotes the volume of the primitive cell in reciprocal space, then $\Omega_p = 8\pi^3 / \Omega$.

Let $F(\underline{r})$ be a periodic function in real space i.e.

$$F(\underline{r} + \underline{R}) = F(\underline{r}) \quad (20)$$

** Strictly speaking the lattice defined by the vectors (19) should be called K space, for the reciprocal space does not have a factor 2π .

where \underline{R} is a lattice translation of real space. We know that any such function can be expressed as a Fourier series, viz.

$$F(\underline{r}) = \sum_m A(m) \exp.i\underline{K}_m.\underline{r} \quad (21)$$

where the vectors \underline{K}_m are of the form (19).

The coefficients A are given by

$$A(m) = \int F(\underline{r}) \exp.-i\underline{K}_m.\underline{r} \, d\underline{r} \quad (22)$$

From the condition (17) one can easily verify that the expansion (21) implies (20).

10- Periodic Boundary Conditions

Let the crystal have dimensions $N_1 \underline{a}_1, N_2 \underline{a}_2, N_3 \underline{a}_3$ in the direction of the axes of the unit cell; hence the crystal contains $N = N_1 N_2 N_3$ unit cells.

We shall impose the boundary condition that the wave function should have the same value after undergoing the translation

$$\underline{R}_N = N_1 \underline{a}_1 + N_2 \underline{a}_2 + N_3 \underline{a}_3$$

i.e.

$$\Psi(\underline{r} + \underline{R}_N) = \Psi(\underline{r})$$

but from Bloch's Theorem

$$\Psi(\underline{r} + \underline{R}_N) = \exp.i \underline{k} \cdot \underline{R}_N \Psi(\underline{r})$$

hence

$$\exp.i \underline{k} \cdot \underline{R}_N = 1 \tag{23}$$

If we write

$$\underline{k} = g_1 \underline{b}_1 + g_2 \underline{b}_2 + g_3 \underline{b}_3 \tag{24}$$

where the b 's are the basic vectors of the reciprocal space, then equation (23) requires that

$$g_1 N_1 + g_2 N_2 + g_3 N_3 = \text{integer}$$

or

$$g_1 = \frac{\text{integer}}{N_1} \quad ; \quad g_2 = \frac{\text{integer}}{N_2} \quad ; \quad g_3 = \frac{\text{integer}}{N_3} \tag{25}$$

This shows that the \underline{k} vectors lie very closely on the reciprocal space, since there are N_1 allowed values along the vector \underline{b}_1 , N_2 along \underline{b}_2 , and N_3 along \underline{b}_3 .

We observe that the total number of allowed values of

\underline{k} in the primitive cell in reciprocal space is $N=N_1N_2N_3$, i.e. precisely the same number of primitive cells in direct space. In the same way as we constructed the Wigner-Seitz cell in real space we construct in reciprocal space the first Brillouin Zone (BZ). The BZ will have the same volume as the primitive cell in reciprocal space and therefore accommodate the same number of \underline{k} vectors.

It is sufficient to confine ourselves to values of \underline{k} in the BZ, since if we consider any vector \underline{k}' outside it we can write it in terms of a vector in the BZ, viz.

$$\underline{k}' = \underline{k} + \underline{K}_m$$

where \underline{K}_m is a reciprocal lattice vector; moreover the two states \underline{k} and \underline{k}' will be identical since

$$\exp.i\underline{k}.\underline{R}_n = \exp.i\underline{k}'.\underline{R}_n \quad \text{for all } \underline{R}_n$$

If we choose to limit ourselves to \underline{k} vectors in the BZ, then we shall be working in what is known as the reduced zone scheme. In this scheme the energy curves are quasi-continuous bands of energy levels separated by forbidden energy regions. However, in many cases it is more convenient not to restrict the values of \underline{k} to the BZ and work instead in the extended zone scheme. These two approaches are closely connected and one can actually start with either of them and reduce it to the other.

11- Representation of Point Groups

Let G be the space group of the direct lattice.

As we have mentioned before, this space group contains two sub-groups, the translation group T and the point group P . This can be written symbolically

$$G = T + P$$

We have found that the matrices representing the translation operators could be diagonalized simultaneously, where all the diagonal elements are one-dimensional matrices. Thus the matrix representing the operator T will have along its diagonal the numbers $\exp.i \underline{k} \cdot \underline{R}$, and \underline{k} takes values inside or on the surface of the Brillouin zone.

Now we shall focus our attention on the point group. Let p be the number of operations in P . It turns out that the reciprocal space is invariant under the operations of the point group P . If we apply the operations of P to a particular \underline{k} -vector, then they will either leave it unchanged or change it to a different \underline{k} -vector. The figure of these \underline{k} -vectors is called the star of \underline{k} . The operations of P that transform \underline{k} to a member \underline{k}' of the star,

having the property

$$\underline{k}' = \underline{k} + \underline{K}_m \quad (A)$$

where \underline{K}_m is a reciprocal lattice vector, (\underline{K}_m could be the zero reciprocal lattice vector) form a subgroup Q of the point group, which is called the point group of the \underline{k} -vector.

As an example, consider the point $\Lambda \equiv (\zeta\zeta\zeta)$ of the cubic structure. If we operate on Λ with each of the 48 operations of the cubic point group, we shall find that every 6 of them will transform the coordinates of Λ into one of the following 8 coordinates, $\zeta\zeta\zeta, \zeta\zeta\bar{\zeta}, \zeta\bar{\zeta}\zeta, \bar{\zeta}\zeta\zeta, \zeta\bar{\zeta}\bar{\zeta}, \bar{\zeta}\bar{\zeta}\zeta, \bar{\zeta}\zeta\bar{\zeta}, \bar{\zeta}\bar{\zeta}\bar{\zeta}$. These 8 points will form the star of Λ . Only the first of these points satisfy relation (A), with $K_m = 0$. Thus the 6 operations of Q that do not change the coordinates of Λ when they are applied to it, will form the point group of Λ . These are $Q_1=xyz; Q_2=zxy; Q_3=yzx; Q_4=yxz; Q_5=zyx; Q_6=xzy$.

As another example, consider the point $N \equiv (\frac{1}{2}\frac{1}{2}0)$ on the surface of the BZ for the B.C.C. structure. Again applying the 48 operations of the cubic point group to the coordinates of N , we shall find that every 4 of them will transform the coordinates of N

to one of the following 12 coordinates : $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}0$,
 $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$.

These 12 points will form the star of N. We observe that only the first and second of these points satisfy condition (A), with the reciprocal lattice vectors 000 , and $\bar{1}\bar{1}0$ respectively. Hence, the 8 operations which when applied to the coordinates of N produce the coordinates $\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}\frac{1}{2}0$, will form the point group of N.

To find the solutions of the one-electron equation at a particular \underline{k} -vector, one has to classify the wave functions at this point according to their symmetry with respect to the operations of the point group of \underline{k} . To do this one has to determine the irreducible representations of the point group of \underline{k} . We shall describe the procedure for the general case, and, at the same time, apply it to the point Λ , so as to give a concrete example.

Suppose that Q, the point group of the \underline{k} -vector, contains q elements which form s classes. We immediately deduce that Q will have s irreducible representations. In the case of Λ , q=6 and these 6 operations fall into 3 classes. Hence we have 3

irreducible representations which we denote by Λ_1 , Λ_2 , and Λ_3 .

If we denote the dimensionality of the irreducible representation i by d_i , then we can find the dimensionalities of all the irreducible representations from the relation

$$\sum_{i=1}^3 d_i^2 = q$$

which has a unique solution.

In our example this relation becomes

$$\sum_{i=1}^3 d_i^2 = 6$$

which gives $d_1 = 1$, $d_2 = 1$, and $d_3 = 2$.

For each irreducible representation we have to determine the matrices representing the different operations, and find a set of orthonormal functions that could serve as basis functions. The first thing to be done is to form the multiplication table of the group and then to construct the character table. The character table shows the essential properties of the representation, for it does not depend on the basis functions employed but only on the irre-

ducible representations and the classes of the group. In our example of the point Λ , the character table is given below.

class irr. rep.	$C_1 = Q_1$	$C_2 = Q_2 + Q_3$	$C_3 = Q_4 + Q_5 + Q_6$
Λ_1	1	1	1
Λ_2	1	1	-1
Λ_3	2	-1	0

The numbers in the character table indicate the trace of the matrices representing the operations. We notice that all the operations that are in the same class have the same trace. Obviously the numbers in the first column - i.e. the traces of the identity operator in the different irreducible representations - indicate the dimensionality of the representations.

For a one dimensional representation a glance at the character table will tell us that for the representation Λ_1 , all the six operators are represented by the number +1. Again for the representation Λ_2 , the operators Q_1, Q_2, Q_3 , and Q_4 are represented by +1 and Q_5 and Q_6 by -1.

The matrices for the two-dimensional representation can not be deduced immediately from the character table, and one has to make use of the multiplication table. Thus we get for the operators of the point group at Λ_3 , for the Λ_3 representation, the matrices

$$Q_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad Q_2 = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}, \quad Q_3 = \begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix},$$

$$Q_4 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad Q_5 = \begin{pmatrix} -1 & 0 \\ -1 & 1 \end{pmatrix}, \quad Q_6 = \begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}.$$

The existence of a two-dimensional representation implies that there are two independent functions such that each would transform either into itself or into the other, under every operation of the group. These two functions belong to the same energy value and are therefore degenerate.

Now we shall show how to find a solution that transforms according to one of the irreducible representations of the group of the wave vector. Let F be any arbitrary function. The function $\Phi_{i,j}^k$ defined by

$$\Phi_{i,j}^k = \sum_Q [Q]_{i,j,j} Q F \quad (B)$$

is a function which transforms according to the j^{th} row of the i^{th} irreducible representation of the point group of the vector \underline{k} .** In relation (B), Q represents an operation; the sum is taken over all the operations; and $[Q]_{i,j}$ is the jj^{th} matrix element in the i^{th} irreducible representation of the operator Q .

Applying this in our example for the first row of the third irreducible representation, while taking the arbitrary function as

$$e^{i(\underline{k} + \underline{K}_m) \cdot \underline{r}}$$

where \underline{K}_m is of the form 110, we get

$$\begin{aligned} \Lambda \\ \Phi_{31} &= Q_1 F - Q_3 F - Q_5 F + Q_6 F \\ &= e^{i(\zeta+1, \zeta+1, \zeta) \cdot \underline{r}} - e^{i(\zeta+1, \zeta, \zeta+1) \cdot \underline{r}} \\ &\quad - e^{i(\zeta, \zeta+1, \zeta+1) \cdot \underline{r}} + e^{i(\zeta+1, \zeta, \zeta+1) \cdot \underline{r}} \\ &= e^{i(\zeta+1, \zeta+1, \zeta) \cdot \underline{r}} - e^{i(\zeta, \zeta+1, \zeta+1) \cdot \underline{r}} \end{aligned}$$

** J. Callaway, Energy Band Theory ; Academic Press (1964)

The Orthogonalized Plane Wave Method

Consider a crystal. Let $\underline{a}_1, \underline{a}_2, \underline{a}_3$ be the vectors defining the unit cell in the crystal; the unit cell has a volume $\Omega = \underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3$. Let $N_1 \underline{a}_1, N_2 \underline{a}_2, N_3 \underline{a}_3$ be the dimensions of the crystal along the axes of the unit cell; the crystal contains $N = N_1 N_2 N_3$ unit cells. We assume periodic boundary conditions. Let each unit cell contain s atoms; the number of atoms in the crystal is sN .

We are interested in finding solutions of the Hartree-Fock one-electron equation

$$H\Psi_k(\underline{r}) = E_k\Psi_k(\underline{r}) \quad (26)$$

which correspond to the valence electrons; where

$$H = -\nabla^2 + V(\underline{r}) \quad (27)$$

The OPW method emphasises the fact that these solutions we are seeking for must be orthogonal to the solutions representing the lower states, i.e. the core states.

Since we assume that the core states in the isolated atom do not change appreciably when the atoms come together to form the crystal, the crystal core states could be described by atomic functions, which are modified to have the Bloch form so that they satisfy the periodic boundary conditions. Let

$$U_j(\underline{r}) \equiv U_{nlm}(\underline{r}) = \frac{1}{r} R_{nl}(r) Y_{lm}(\theta, \phi)$$

denote an atomic wave function for which the nucleus is at the origin of the coordinates; j stands for the ^{nos.} three/n, l, m which are respectively the principal, angular momentum, and magnetic quantum numbers. A similar localised atomic wave function situated at the lattice point \underline{R}_i is denoted by $U_j(\underline{r} - \underline{R}_i)$.

The crystal core wave function of wave vector \underline{k} is written

$$\Phi_{j,k} = [sN]^{-\frac{1}{2}} \sum_i \exp.(i\underline{k} \cdot \underline{R}_i) U_j(\underline{r} - \underline{R}_i) \quad (28)$$

Evidently the function (28) satisfies all our requirements.

Since the valence electrons in the crystal are almost free, it is reasonable to represent a valence electron by a plane wave

$$[N\Omega]^{-\frac{1}{2}} \exp.(i\underline{k} \cdot \underline{r}) \quad (29)$$

The OPW method requires that (29) should be orthogonalized to all the core functions (28), having the same \underline{k} vector, which are associated with lower eigenvalues. This could be achieved by subtracting from (29) appropriate multiples of these functions. Thus the OPW for the wave vector \underline{k} is

$$\chi(\underline{k}) = [N\Omega]^{-\frac{1}{2}} \exp.i\underline{k}.\underline{r} - \sum_J \mu(j, \underline{k}) \Phi_{j, \underline{k}} \quad (30)$$

where the orthogonality coefficients μ are to be determined by the Schmidt process.

To determine the solutions of equation (26) for a particular \underline{k} vector, we apply the variational principle. We use as a trial function a finite linear combination of OPW's having wave vectors which differ from the \underline{k} vector under consideration by a reciprocal lattice vector. The coefficients in the linear combination are treated as variable parameters so as to minimize the energy. Thus we take as a trial function

$$\Psi_{\underline{k}}(\underline{r}) = \sum_{\underline{m}=0}^p A(\underline{k}_m) \chi(\underline{k}_m) \quad (31)$$

where $\underline{k}_m = \underline{k} + \underline{K}_m$; \underline{K}_m is a reciprocal lattice vector, $\underline{K}_0 = 0$.

By analogy to equation (30)

$$\chi(\underline{k}_m) \equiv \chi(\underline{k} + \underline{K}_m) = [N\Omega]^{-\frac{1}{2}} \exp.i\underline{k}_m.\underline{r} - \sum_J \mu(j, \underline{k}_m) \Phi_{j, \underline{k}} \quad (32)$$

In this equation we wrote $\Phi_{j, \underline{k}}$ instead of the formal $\Phi_{j, \underline{k}_m}$. This is because by looking at equation (28) defining Φ we observe that its value depends only on

\underline{k} and does not change by adding a \underline{K}_m . We assume the Φ 's to be orthonormal solutions of H

$$\left. \begin{aligned} H\Phi_{j,k} &= E_j\Phi_{j,k} & a \\ \int \Phi_{j,k}^* \Phi_{j',k} d\underline{r} &= \delta_{jj'} & b \end{aligned} \right\} \quad (33)$$

Relation (33b) implies that the atomic functions U situated at different lattice sites do not overlap.

The μ 's are determined from the condition

$$\int \Phi_{j,k}^* \chi(\underline{k}_m) d\underline{r} = 0 \quad (34)$$

where the integration is taken over the volume of the crystal; in the limit we take this volume to occupy the whole of space. We shall get the μ 's explicitly, thus

$$\begin{aligned} \int \Phi_{j,k}^* \chi(\underline{k}_m) d\underline{r} &= [N\Omega]^{-\frac{1}{2}} \int \Phi_{j,k}^* \exp.i\underline{k}_m \cdot \underline{r} d\underline{r} \\ &\quad - \sum_{j'} \mu(j', \underline{k}_m) \int \Phi_{j,k}^* \Phi_{j',k} d\underline{r} \\ &= [N\Omega]^{-\frac{1}{2}} \int \Phi_{j,k}^* \exp.i\underline{k}_m \cdot \underline{r} d\underline{r} - \mu(j, \underline{k}_m) = 0 \end{aligned}$$

or

$$\mu(j, \underline{k}_m) = [N\Omega]^{-\frac{1}{2}} \int \Phi_{j,k}^* \exp.i\underline{k}_m \cdot \underline{r} d\underline{r} \quad (35a)$$

$$= [N\Omega]^{-\frac{1}{2}} [sN]^{-\frac{1}{2}} \sum_{\underline{t}} \int \exp.-i\underline{k} \cdot \underline{R}_t U_j^*(\underline{r} - \underline{R}_t) \times \exp.i\underline{k}_m \cdot \underline{r} d\underline{r}$$

$$= \frac{1}{N} [s\Omega]^{-\frac{1}{2}} \sum_{\underline{t}} \int \exp.i\underline{k}_m \cdot (\underline{r} - \underline{R}_t) U_j^*(\underline{r} - \underline{R}_t) d\underline{r}$$

$$= [s/\Omega]^{1/2} \int \exp.i\mathbf{k}_m \cdot \mathbf{r} \quad U_j^*(\mathbf{r}) \quad d\mathbf{r} \quad (35b)$$

Now we proceed to apply the variational method. The equations which determine the coefficients A of equation (31) that minimize the energy are

$$\sum_{m=0}^p \left\{ \int \chi^*(\mathbf{k}_n) H \chi(\mathbf{k}_m) \, d\mathbf{r} - E \int \chi^*(\mathbf{k}_n) \chi(\mathbf{k}_m) \, d\mathbf{r} \right\} A(\mathbf{k}_m) = 0$$

for $n = 0, 1, \dots, p$ (36)

The condition for this set of equations to have a non-trivial solution is that the determinant of the coefficients of the A's must vanish, i.e.

$$\det \left\{ \int \chi^*(\mathbf{k}_n) H \chi(\mathbf{k}_m) \, d\mathbf{r} - E \int \chi^*(\mathbf{k}_n) \chi(\mathbf{k}_m) \, d\mathbf{r} \right\} = 0 \quad (37)$$

From this determinant we get the eigenvalues E_0, E_1, \dots, E_p . Substituting for each of them in equation (36) we obtain the coefficients $A_0^i, A_1^i, \dots, A_p^i$ corresponding to E_i .

We shall consider more closely the matrix elements appearing in equations (36) and (37)

$$\int \chi^*(\mathbf{k}_n) H \chi(\mathbf{k}_m) \, d\mathbf{r} = I + II + III + IV$$

where

$$I = [N\Omega]^{-1/2} [N\Omega]^{-1/2} \int \exp.-i\mathbf{k}_n \cdot \mathbf{r} \, H \, \exp.i\mathbf{k}_m \cdot \mathbf{r} \, d\mathbf{r}$$

$$I = k_m^2 \delta_{k_m k_n} + V(\underline{k}_m - \underline{k}_n)$$

where

$$V(\underline{k}_m - \underline{k}_n) = \int \exp.i(\underline{k}_m - \underline{k}_n) \cdot \underline{r} V(\underline{r}) d\underline{r}$$

$$II = \int \sum_{j'} \mu^*(j', \underline{k}_n) \Phi_{j', \kappa} H \sum_j \mu(j, \underline{k}_m) \Phi_{j, \kappa} d\underline{r}$$

$$= \sum_j \sum_{j'} E_j \mu(j, \underline{k}_m) \mu^*(j', \underline{k}_n) \delta_{jj'}$$

$$= \sum_j E_j \mu(j, \underline{k}_m) \mu^*(j, \underline{k}_n)$$

$$III = [N\Omega]^{-\frac{1}{2}} \int \exp. -i\underline{k}_n \cdot \underline{r} H \sum_j \mu(j, \underline{k}_m) \Phi_{jk} d\underline{r}$$

$$= [N\Omega]^{-\frac{1}{2}} \sum_j \mu(j, \underline{k}_m) E_j \int \exp. -i\underline{k}_n \cdot \underline{r} \Phi_{j, \kappa} d\underline{r}$$

$$= \sum_j E_j \mu(j, \underline{k}_m) \mu^*(j, \underline{k}_n)$$

$$IV = [N\Omega]^{-\frac{1}{2}} \int \sum_j \mu^*(j, \underline{k}_n) \Phi_{j, \kappa}^* d\underline{r} H \exp.i\underline{k}_m \cdot \underline{r}$$

since H is Hermitian

$$\int f_1^* H f_2 d\underline{r} = \int (H f_1)^* f_2 d\underline{r} = \left\{ \int f_2^* H f_1 d\underline{r} \right\}^*$$

hence

$$IV = [N\Omega]^{-\frac{1}{2}} \left\{ \int \exp. -i\underline{k}_m \cdot \underline{r} H \sum_j \mu(j, \underline{k}_n) \Phi_{j, \kappa} d\underline{r} \right\}^*$$

$$\begin{aligned}
 \text{IV} &= \left\{ \sum_j E_j \mu(j, \underline{k}_n) \mu^*(j, \underline{k}_m) \right\}^* \\
 &= \sum_j E_j \mu(j, \underline{k}_m) \mu^*(j, \underline{k}_n)
 \end{aligned}$$

In simplifying the above written integrals we made use of equations (33) and (35a). Finally we get

$$\int \chi^*(\underline{k}_n) H \chi(\underline{k}_m) d\underline{r} = k_m^2 \delta_{mn} + V(\underline{k}_m - \underline{k}_n) - \sum_j E_j \mu(j, \underline{k}_m) \mu^*(j, \underline{k}_n)$$

by a similar procedure we get

$$\int \chi^*(\underline{k}_n) \chi(\underline{k}_m) d\underline{r} = \delta_{mn} - \sum_j \mu(j, \underline{k}_m) \mu^*(j, \underline{k}_n)$$

Although the procedure just outlined for obtaining the matrix elements of the Hamiltonian and Unity between OPW's as basis functions is the one formally applied when we are dealing with a general \underline{k} vector, yet in practice where we are usually concerned with \underline{k} vectors of high symmetry, this procedure has to be modified. This is because in such cases we would use symmetrized combinations of OPW's as our basis functions. We shall not develop this modification in the general case but postpone its discussion till later when we apply the OPW method in the case of Li.

II: CALCULATIONS

1- Real Space and Reciprocal Space of Li.

We have considered the body centred cubic structure of metallic Li, taking the cube side to be 6.6317 a.u. [27]. The structure is illustrated in fig.1. The unit cell indicated in this figure contains two atoms; one can also look upon the structure as being composed of two penetrating simple cubic sub-lattices defined by

$$L = a(l_1 \underline{i} + l_2 \underline{j} + l_3 \underline{k})$$

$$L' = a[(l_1 + \frac{1}{2}) \underline{i} + (l_2 + \frac{1}{2}) \underline{j} + (l_3 + \frac{1}{2}) \underline{k}]$$

where $\underline{i}, \underline{j}, \underline{k}$ are the three rectangular axes of the cube, and l_1, l_2, l_3 are positive or negative integers including zero. a is the side of the cube.

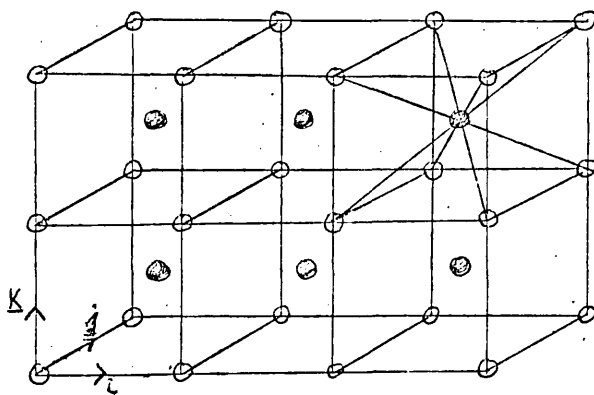


Fig.1. The B.C.C. structure.

A possible primitive cell, fig.2, could be obtained by writing

$$\underline{a}_1 = \frac{a}{2} (-\underline{i} + \underline{j} + \underline{k})$$

$$\underline{a}_2 = \frac{a}{2} (\underline{i} - \underline{j} + \underline{k})$$

$$\underline{a}_3 = \frac{a}{2} (\underline{i} + \underline{j} - \underline{k})$$

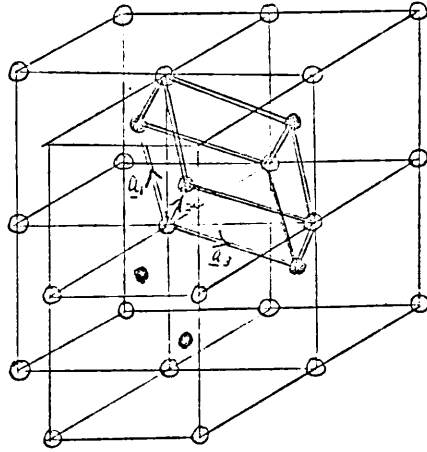


Fig.2. A primitive cell for the B.C.C. lattice.

Now any lattice point could be reached by a translation

$$R_i = m_{i1} \underline{a}_1 + m_{i2} \underline{a}_2 + m_{i3} \underline{a}_3$$

where the m 's are integers. According to whether $m_{i1} + m_{i2} + m_{i3}$ is odd or even, we shall find ourselves at a cube centre or corner respectively.

In fig.3 we show the Wigner-Seitz cell for the body centred cubic (B.C.C.) structure. This cell displays all the rotational symmetry of the crystal, for besides showing that $\underline{i}, \underline{j}, \underline{k}$ are axes of fourfold symmetry, it also shows clearly that $\underline{a}_1, \underline{a}_2, \underline{a}_3$ are axes of threefold rotational symmetry, since they pass through the hexagonal faces of the cell.

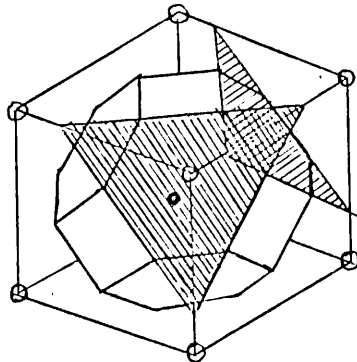


Fig.3. The W-S cell for the B.C.C. structure

The volume of the Wigner-Seitz cell is

$$\Omega = \underline{a}_1 \cdot \underline{a}_2 \times \underline{a}_3 = \frac{a^3}{2}$$

The reciprocal lattice is a face centred cube whose side is $\frac{4\pi}{a}$. The basic vectors of the primitive unit cell are

$$\underline{b}_1 = \frac{1}{a} 2\pi(\underline{j} + \underline{k}), \quad \underline{b}_2 = \frac{1}{a} 2\pi(\underline{i} + \underline{j}), \quad \underline{b}_3 = \frac{1}{a} 2\pi(\underline{i} + \underline{k})$$

Any point in the reciprocal lattice is reached by the translation

$$\underline{K}_m = h_{m1}\underline{b}_1 + h_{m2}\underline{b}_2 + h_{m3}\underline{b}_3$$

where the h's are positive or negative integers.

We write below some of the reciprocal lattice vectors listed in order of magnitude

1	vector of the form	$K_0 = \frac{1}{a} 2\pi(000)$
12	vectors of the form	$K_1 = \frac{1}{a} 2\pi(110)$
6	" " " "	$K_2 = \frac{1}{a} 2\pi(200)$
24	" " " "	$K_3 = \frac{1}{a} 2\pi(211)$
12	" " " "	$K_4 = \frac{1}{a} 2\pi(220)$
24	" " " "	$K_5 = \frac{1}{a} 2\pi(310)$
8	" " " "	$K_6 = \frac{1}{a} 2\pi(222)$
48	" " " "	$K_7 = \frac{1}{a} 2\pi(321)$
6	" " " "	$K_8 = \frac{1}{a} 2\pi(400)$

The Brillouin Zone for a F.C.C. reciprocal space is a rhombododecahedron; in fig.4 we show the BZ and the symmetry points.

The main symmetry points are

$$\Gamma = 2\pi/a (000)$$

$$\Delta = 2\pi/a (00\zeta) ; 0 < \zeta < 1$$

$$H = 2\pi/a (001)$$

$$\Sigma = 2\pi/a (\zeta\zeta 0) ; 0 < \zeta < \frac{1}{2}$$

$$N = 2\pi/a (\frac{1}{2}\frac{1}{2}0)$$

$$\Lambda = 2\pi/a (\zeta\zeta\zeta) ; 0 < \zeta < \frac{1}{2}$$

$$P = 2\pi/a (\frac{1}{2}\frac{1}{2}\frac{1}{2})$$

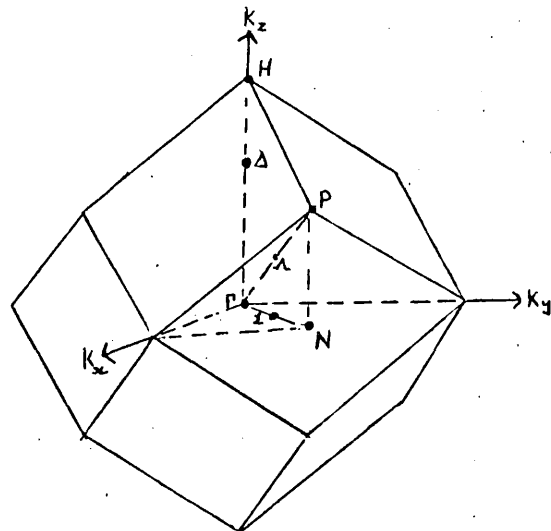


Fig.4. The BZ of the B.C.C. crystal

2- The Crystal Potential

Our starting point in constructing the potential for our problem is the potential as given by the Hartree-Fock (H.F.) equation I(13), except that we apply the Slater approximation to the exchange term. Slater [23] replaced the exchange term by an exchange potential, which is the same as the average exchange potential of a free-electron gas having the same local charge density at all points of space as the crystal. In the derivation of the H.F. equation given in section 4 of chapter I, we have assumed the widely accepted approximation that a valence electron in a solid moves in the field of the ionic cores -formed of the nuclei and the inner electrons- and of the valence electrons present. Since this approximation reduces the effect of the interaction between the inner electrons and the valence electrons we are trying to describe, we felt that it might affect the potential considerably and therefore we decided to reject it and consider the valence electron to be moving in the field of the nuclei plus the field of the other electrons. This modification does not require too much additional computational effort because of the rather special case of the Li. atom containing a few electrons. We assume the crystal to contain N primitive unit cells, i.e. each contains one atom only. Since the atomic number of Li. is three, we have $3N$ electrons. From what we have said above the crystal potential takes the form

$$V(\underline{r}) = -6 \sum_n^N \frac{1}{|\underline{r} - \underline{R}_n|} + 2 \sum_{j=1}^{3N} \int \frac{\Psi_j^*(\underline{r}') \Psi_j(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' - 6 \left\{ \frac{3}{8\pi} \sum_{j=1}^{3N} \Psi_j^*(\underline{r}) \Psi_j(\underline{r}) \right\}^{1/3}$$

The first term represents the nuclei coulomb potential, the second the electronic coulomb potential, and the third the electronic exchange potential as given by Slater's free-electron approximation.

The functions Ψ appearing in this equation are the wave functions of the electrons in the crystal, which are the solutions of the crystal Hamiltonian with $V(\underline{r})$ representing the potential energy. In other words, the wave functions and the crystal potential have to be calculated self consistently. However, we approximate the expression for $V(\underline{r})$ by substituting atomic wave functions $U(\underline{r})$ for the Ψ 's. We split the summation over the $3N$ electrons into two sums, the first running over the electrons of one atom and the other over all atoms. Moreover, we simplify the last term by taking the summation over the N atoms outside the bracket which is raised to the power of one third.

Hence we get

$$\begin{aligned}
 V(\underline{r}) = & -6 \sum_{n=1}^N \frac{1}{|\underline{r} - \underline{R}_n|} + 2 \sum_{n=1}^N \sum_{j=1}^3 \int \frac{U_j^*(\underline{r}' - \underline{R}_n) U_j(\underline{r}' - \underline{R}_n)}{|\underline{r} - \underline{r}'|} d\underline{r}' \\
 & -6 \sum_{n=1}^N \left\{ \frac{3}{8\pi} \sum_j U_j^*(\underline{r} - \underline{R}_n) U_j(\underline{r} - \underline{R}_n) \right\}^{1/3} \quad (1)
 \end{aligned}$$

This is the final form of our crystal potential; however, in an orthogonalized plane wave calculation one employs the Fourier coefficients of the potential not the potential itself. The method by which we obtain the Fourier coefficients of the potential $V(\underline{r})$ as defined by equation (1) will be described in section 4.

3- Atomic Eigenvalues and Eigenfunctions

From equation (1) defining the crystal potential we observe that we can write it as the sum of potential functions each located around one of the atoms present, viz.

$$V(\underline{r}) = \sum_{n=1}^N V_a(\underline{r} - \underline{R}_n) \quad (2)$$

where

$$V_a(\underline{r}) = -\frac{6}{|\underline{r}|} + 2 \sum_{j=1}^3 \int \frac{U_j^*(\underline{r}') U_j(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' - 6 \left\{ \frac{3}{8\pi} \sum_{j=1}^3 U_j^*(\underline{r}) U_j(\underline{r}) \right\}^{1/3} \quad (3)$$

Since the crystal core functions are assumed to be solutions of the crystal Hamiltonian, then from equations (2), I(28), and from the simplest form of the tight binding approximation, we deduce that the atomic wave functions $U(\underline{r})$ should satisfy the equation

$$[-\nabla^2 + V_a(\underline{r})] U_j(\underline{r}) = \epsilon_j U_j(\underline{r}) \quad (4)$$

Before continuing to describe the procedure for obtaining the atomic wave functions and the corresponding energy values we shall simplify the terms occurring in $V_a(\underline{r})$

$$\sum_{j=1}^3 U_j^*(\underline{r}) U_j(\underline{r}) = 2 [U_{1s}(\underline{r})]^2 + [U_{2s}(\underline{r})]^2 = \rho_a^e(\underline{r}) \quad (5)$$

where $\rho_a^e(\underline{r})$ denotes the electronic charge density in the isolated atom.

Also,

$$2 \sum_{j=1}^3 \int_c^{\infty} \frac{U_j^*(\underline{r}') U_j(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' = 2 \int_c^{\infty} \frac{\rho_a^e(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}'$$

$$= \frac{2}{r} \int_0^r 4\pi r'^2 \rho_a^e(r') dr' + 2 \int_r^{\infty} 4\pi r'^2 \frac{\rho_a^e(r')}{r'} dr'$$

Hence we get

$$V_a(\underline{r}) \equiv V_a(r) = -\frac{6}{r} + \frac{2}{r} \int_0^r 4\pi r'^2 \rho_a^e(r') dr' + 2 \int_r^{\infty} 4\pi r' \rho_a^e(r') dr'$$

$$- 6 \left\{ \frac{3}{8\pi} \rho_a^e(r) \right\}^{1/3} \quad (6)$$

We have started by the wave functions of the free Li. atom given by Holöien [11], namely

$$U_{1s} = A[\exp.(-2ar) + h \exp.(-4ar)] \quad (7)$$

$$U_{2s} = B[r \exp.(-kr) - \frac{1}{a} \exp.(-ar)] + DU_{1s}$$

where

$$A = 1.990740 \quad ; \quad a = 1.233120$$

$$B = .128134 \quad ; \quad h = .323568$$

$$D = -.094727 \quad ; \quad k = .672$$

Hence, substituting in equation (5)

$$\rho_a^e(r) = \sum_{j=1}^{10} F_j r^{n_j} \exp.(-\alpha_j r) \quad (8)$$

where

$F_1 = .833555$;	$n_1 = 0$;	$\alpha_1 = 9.86496$
$F_2 = 5.152271$;	$n_2 = 0$;	$\alpha_2 = 7.39872$
$F_3 = .012681$;	$n_3 = 0$;	$\alpha_3 = 6.16560$
$F_4 = 7.961651$;	$n_4 = 0$;	$\alpha_4 = 4.93248$
$F_5 = .039190$;	$n_5 = 0$;	$\alpha_5 = 3.69936$
$F_6 = .010797$;	$n_6 = 0$;	$\alpha_6 = 2.46624$
$F_7 = -.026629$;	$n_7 = 1$;	$\alpha_7 = 1.90512$
$F_8 = -.048326$;	$n_8 = 1$;	$\alpha_8 = 3.13824$
$F_9 = -.015637$;	$n_9 = 1$;	$\alpha_9 = 5.60448$
$F_{10} = .016418$;	$n_{10} = 2$;	$\alpha_{10} = 1.34400$

We re-write equation (6)

$$V_a(r) = - \left\{ \frac{6}{r} + 3 \left[\frac{3}{\pi} \right]^{1/3} \left[\rho_a^e(r) \right]^{1/3} \right\} + \frac{8\pi}{r} [I + \text{II}] \quad (9)$$

where

$$I = \int_0^r r'^2 \rho_a^e(r') dr' = \sum_{j=1}^{10} F_j \int_0^r r^{n_j + 2} \exp.(-\alpha_j r) dr$$

$$\begin{aligned}
 I &= \sum_{j=1}^6 F_j \int_0^r r^2 \exp.(-\alpha_j r) dr + \sum_{j=7}^9 F_j \int_0^r r^3 \exp.(-\alpha_j r) dr \\
 &\quad + F_{10} \int_0^r r^4 \exp.(-\alpha_{10} r) dr \\
 &= \sum_{j=1}^6 F_j \left\{ \frac{2}{\alpha_j^3} - [2(\alpha_j^3)^{-1} + 2r(\alpha_j^2)^{-1} + r^2(\alpha_j)^{-1}] \exp.(-\alpha_j r) \right\} \\
 &\quad + \sum_{j=7}^9 F_j \left\{ 6(\alpha_j)^{-4} - [6\alpha_j^{-4} + 6r\alpha_j^{-3} + 3r^2\alpha_j^{-2} + r^3\alpha_j^{-1}] e^{-\alpha_j r} \right\} \\
 &\quad + F_{10} \left\{ 24\alpha_{10}^{-5} - [24\alpha_{10}^{-5} + 24r\alpha_{10}^{-4} + 12r^2\alpha_{10}^{-3} + 4r^3\alpha_{10}^{-2} + r^4\alpha_{10}^{-1}] e^{-\alpha_{10} r} \right\} \\
 &= \sum_{j=1}^6 F_j \alpha_j^{-3} [2 - (2+2\alpha_j r + \alpha_j^2 r^2) e^{-\alpha_j r}] + \sum_{j=7}^9 F_j \alpha_j^{-4} [6 - (6+6\alpha_j r + \\
 &\quad 3\alpha_j^2 r^2 + \alpha_j^3 r^3) e^{-\alpha_j r}] + F_{10} \alpha_{10}^{-5} [24 - (24+24\alpha_{10} r + 12\alpha_{10}^2 r^2 + \\
 &\quad 4\alpha_{10}^3 r^3 + \alpha_{10}^4 r^4) \exp.(-\alpha_{10} r)]
 \end{aligned}$$

and

$$\begin{aligned}
 II &= \int_r^\infty r' \rho(r') dr' = \sum_{j=1}^{10} F_j \int_r^\infty r'^{n_j+1} e^{-\alpha_j r'} dr' \\
 &= \sum_{j=1}^6 F_j \int_r^\infty r' e^{-\alpha_j r'} dr' + \sum_{j=7}^9 F_j \int_r^\infty r'^2 e^{-\alpha_j r'} dr' + F_{10} \int_r^\infty r'^3 e^{-\alpha_{10} r'} dr' \\
 &= \sum_{j=1}^6 F_j \alpha_j^{-2} (1 + \alpha_j r) e^{-\alpha_j r} + \sum_{j=7}^9 F_j \alpha_j^{-3} (2 + 2\alpha_j r + \alpha_j^2 r^2) e^{-\alpha_j r} \\
 &\quad + F_{10} \alpha_{10}^{-4} (6 + 6\alpha_{10} r + 3\alpha_{10}^2 r^2 + \alpha_{10}^3 r^3) e^{-\alpha_{10} r}
 \end{aligned}$$

Now we can re-write equation (9) in the form:

$$V_a(r) = -\left[\frac{6}{r} + 3\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3} \right] + V_1 \quad (10)$$

where

$$V_1 = \frac{8\pi}{r} \sum_{j=1}^{10} F_j \Theta(\alpha_j) \quad (11)$$

and

$$\Theta(\alpha_j) = \alpha_j^{-3} [2 - (2 + \alpha_j r) e^{-\alpha_j r}] \quad \text{for } j=1 \rightarrow 6$$

$$= \alpha_j^{-4} [6 - (6 + 4\alpha_j r + \alpha_j^2 r^2) e^{-\alpha_j r}] \quad \text{for } j=7 \rightarrow 9$$

$$= \alpha_j^{-5} [24 - (24 + 18\alpha_j r + 6\alpha_j^2 r^2 + \alpha_j^3 r^3) e^{-\alpha_j r}] \quad \text{for } j=10$$

By the aid of equations (10) and (11), we were able to solve equation (4) numerically. The eigenvalue obtained is $E_{1s} = -4.53$ Ryd., which is comparable to the experimental value -4.03 [15]. As to the core wave function needed in applying the OPW method, we used the U_{1s} given by equation (7).

4- Fourier Coefficients of The Crystal Potential

We write the crystal potential

$$V(\underline{r}) = V_c(\underline{r}) + V_e(\underline{r})$$

where $V_c(\underline{r})$ and $V_e(\underline{r})$ denote respectively the Coulomb, and the exchange parts. We Fourier analyse each of the two terms of the crystal potential separately, viz.

$$V_c(\underline{r}) = \sum_m W_c(\underline{K}_m) e^{-i\underline{K}_m \cdot \underline{r}} \quad (a) \quad (12)$$

$$V_e(\underline{r}) = \sum_m W_e(\underline{K}_m) e^{-i\underline{K}_m \cdot \underline{r}} \quad (b)$$

so that the Fourier coefficient of the crystal potential is

$$W(\underline{K}_m) = W_c(\underline{K}_m) + W_e(\underline{K}_m) \quad (13)$$

We shall first calculate the Coulomb potential Fourier coefficient $W_c(\underline{K}_m)$.

Poisson's equation is

$$\nabla^2 V_c(\underline{r}) = 8\pi\rho(\underline{r}) \quad (14)$$

We write the total charge density

$$\rho(\underline{r}) = \rho^n(\underline{r}) + \rho^e(\underline{r}) \quad (15)$$

where $\rho^n(\underline{r})$ and $\rho^e(\underline{r})$ are respectively the total nuclear and electronic charge densities in the crystal.

Thus

$$\rho^n(\underline{r}) = 3 \sum_{n=1}^N \delta(\underline{r} - \underline{R}_n) \quad (a)$$

and

$$\rho^e(\underline{r}) = - \sum_{n=1}^N \rho_a^e(|\underline{r} - \underline{R}_n|) \quad (b) \quad (16)$$

Fourier analysing the components of the total charge density, we get

$$\rho^n(\underline{r}) = \sum_m \sigma^n(\underline{K}_m) e^{-i\underline{K}_m \cdot \underline{r}} \quad (a) \quad (17)$$

$$\rho^e(\underline{r}) = \sum_m \sigma^e(\underline{K}_m) e^{-i\underline{K}_m \cdot \underline{r}} \quad (b)$$

hence the Fourier analysis of the total charge density is

$$\rho(\underline{r}) = \sum_m [\sigma^n(\underline{K}_m) + \sigma^e(\underline{K}_m)] e^{-i\underline{K}_m \cdot \underline{r}} \quad (18)$$

substituting from equations (12a) and (18) in (14), we get

$$W_c(\underline{K}_m) = -8\pi/K_m^2 [\sigma^n(\underline{K}_m) + \sigma^e(\underline{K}_m)] \quad (19)$$

Now we shall proceed to calculate the charge density;

from equation (17a), we have

$$\begin{aligned}
 \sigma^n(\underline{K}_m) &= [N\Omega]^{-1} \int \rho^n(\underline{r}) e^{i\underline{K}_m \cdot \underline{r}} d\underline{r} \\
 &= [N\Omega]^{-1} \int \left\{ 3 \sum_{n=1}^N \delta(\underline{r} - \underline{R}_n) \right\} e^{i\underline{K}_m \cdot \underline{r}} d\underline{r} \\
 &= 3[N\Omega]^{-1} \sum_{n=1}^N \int e^{i\underline{K}_m \cdot (\underline{r} - \underline{R}_n)} \delta(\underline{r} - \underline{R}_n) d\underline{r} \\
 &= \frac{3}{\Omega} \quad (20)
 \end{aligned}$$

similarly from equation (17b) we have

$$\sigma^e(\underline{K}_m) = [N\Omega]^{-1} \int \rho^e(\underline{r}) e^{i\underline{K}_m \cdot \underline{r}} d\underline{r}$$

substituting for ρ^e from equation (16b)

$$\begin{aligned}
 \sigma^e(\underline{K}_m) &= -[N\Omega]^{-1} \int \left\{ \sum_{n=1}^N \rho_a^e(|\underline{r} - \underline{R}_n|) \right\} e^{i\underline{K}_m \cdot \underline{r}} d\underline{r} \\
 &= -4\pi[\Omega K_m]^{-1} \int \rho_a^e(r) \sin(K_m r) r dr
 \end{aligned}$$

substituting for ρ_a^e from equation (8)

$$\sigma^e(\underline{K}_m) = -\frac{4\pi}{\Omega K_m} \sum_{j=1}^{10} F_j \int r^{n_j+1} e^{-\alpha_j r} \sin(K_m r) dr \quad (21)$$

using the mathematical relation

$$\int_0^{\infty} r^p e^{-qr} \sin(dr) dr = (d^2 + q^2)^{-\frac{[p+1]}{2}} \Gamma(p+1) \sin[(p+1) \tan^{-1} \frac{d}{q}]$$

equation (21) becomes

$$\sigma^e(K_m) = -\frac{4\pi}{\Omega K_m} \sum_{j=1}^{10} F_j(K_m^2 + \alpha_j^2)^{-\frac{[n_j+2]}{2}} (n_j+1)! \sin[(n_j+2) \tan^{-1} \frac{K_m}{\alpha_j}] \quad (22)$$

By calculating the right hand side of equation (22) and substituting it together with equation (20) in equation (19), we obtain the Fourier coefficients of the Coulomb part of the crystal potential.

Similarly from equation (12b), we obtain for the Fourier coefficients of the exchange potential

$$\begin{aligned} W_e(K_m) &= [N\Omega]^{-1} \int v_e(\underline{r}) e^{iK_m \cdot \underline{r}} d\underline{r} \\ &= [N\Omega]^{-1} \int \left\{ \sum_n \left[\frac{3}{8\pi} \sum_j U_j^*(\underline{r}-\underline{R}_n) U_j(\underline{r}-\underline{R}_n) \right]^{1/3} \right\} e^{iK_m \cdot \underline{r}} d\underline{r} \\ &= -6[N\Omega]^{-1} \sum_n \int \left\{ \frac{3}{8\pi} \rho_a^e(|\underline{r}-\underline{R}_n|) \right\}^{1/3} e^{iK_m \cdot \underline{r}} d\underline{r} \\ &= -\frac{24\pi}{\Omega K_m} \int \left\{ \frac{3}{8\pi} \rho_a^e(r) \right\}^{1/3} \sin(K_m r) r dr \quad (23) \end{aligned}$$

The integral in the right hand side of equation (23) has been calculated numerically for every reciprocal lattice vector needed. In each case the integral was taken over the unit cell. The treatment just applied fails when we are dealing with the average potential Fourier coefficient i.e. $W(000)$; hence we have to consider this case separately.

For the Coulomb Fourier coefficient we use the relation given by Woodruff [25], namely

$$W_c(000) = - \frac{16\pi^2}{3\Omega} \int_0^\infty r^4 \rho_a^e(r) dr \quad (24)$$

substituting for $\rho_a^e(r)$ from equation (8)

$$\begin{aligned} W_c(000) &= - \frac{16\pi^2}{3\Omega} \int_0^\infty \left\{ r^4 \sum_j F_j r^{n_j} e^{-\alpha_j r} \right\} dr \\ &= - \frac{16\pi^2}{3\Omega} \sum_j \int F_j r^{4+n_j} e^{-\alpha_j r} dr \end{aligned}$$

using the mathematical relation

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}} \quad ; n > -1, a > 0$$

we get

$$W_c(000) = - \frac{16\pi^2}{3\Omega} \sum_j F_j \frac{(n_j + 4)!}{\alpha_j^{n_j+5}} \quad (25)$$

Now, to obtain the exchange Fourier coefficient for the average potential, we take the limit of equation (23) as $\underline{K}_m \rightarrow 0$. Hence

$$\begin{aligned} W_e(000) &= \lim_{K_m \rightarrow 0} W_e(K_m) \\ &= -\frac{24\pi}{\Omega} \int_0^\infty \left\{ \frac{3}{8\pi} \rho_a^e(r) \right\}^{1/3} \lim_{K_m \rightarrow 0} \left\{ \frac{\text{Sin}(K_m r)}{K_m} \right\} r dr \\ &= -\frac{12\pi}{\Omega} \int_0^\infty \left\{ \frac{3}{\pi} \rho_a^e(r) \right\}^{1/3} r^2 dr \quad (26) \end{aligned}$$

The Fourier coefficients of the potential as calculated by the procedure described in this section are listed in table 1 .

Table 1: Fourier coefficients of the crystal potential

$\underline{K}_m = \frac{2\pi}{a}(m_1 m_2 m_3)$		$-W(\underline{K}_m)$
$m_1 m_2 m_3$	m^2	
0,0,0	0	1.039575197
1,1,0	2	.183726855
2,0,0	4	.075644488
2,1,1	6	.076228281
2,2,0	8	.075829212
3,1,0	10	.062300727
2,2,2	12	.044942192
3,2,1	14	.031788743
4,0,0	16	.025324893
411;330	18	.024129932
4,2,0	20	.025395408
3,3,2	22	.026662782
4,2,2	24	.026554485
510;431	26	.024790762
5,2,1	30	.015395227
4,4,0	32	.013168823
441;433;530	34	.011966883
442;600	36	.011708036
611;532	38	.012123981
6,2,0	40	.012885006

5- The Orthogonality Coefficients

From the general discussion given in chapter I about the orthogonalized plane wave method, we find that equation I(35) defining the orthogonality coefficients takes, in the case of Li, the form

$$\mu(1s, \underline{k}_m) = [\Omega]^{-\frac{1}{2}} \int e^{i\underline{k}_m \cdot \underline{r}} U_{1s}(r) d\underline{r} \quad (27)$$

where $U_{1s}(r)$ is given by equation (7).

We shall take \underline{k}_m in the z direction

$$\begin{aligned} e^{i\underline{k}_m \cdot \underline{r}} &= e^{ik_m r \cos\theta} \\ &= \sum_{\ell=0}^{\infty} [4\pi(2\ell+1)]^{\frac{1}{2}} i^{\ell} J_{\ell}(k_m r) Y_{\ell 0}(\theta, \phi) \end{aligned} \quad (28)$$

where the J 's and the Y 's are respectively spherical Bessel functions, and spherical harmonics.

If we write

$$U_{1s}(r) = \frac{1}{r} R_{10}(r) Y_{00}(\theta, \phi) \quad (29)$$

then by substituting from the above two relations in equation (27), we get

$$\mu(1s, \underline{k}_m) = [\Omega]^{-\frac{1}{2}} \sum_{l=0}^{\infty} [4\pi(2l+1)]^{\frac{1}{2}} i^l \int J_l(k_m r) \frac{R_{10}(r)}{r} r^2 dr \int Y_{l0} Y_{00} d\omega$$

where $\int \dots d\omega = \int_0^{2\pi} \dots d\phi \int_0^{\pi} \dots \sin\theta d\theta$

$$\begin{aligned} \mu(1s, \underline{k}_m) &= \frac{1}{\sqrt{\Omega}} \sum_{l=0}^{\infty} [4\pi(2l+1)]^{\frac{1}{2}} i^l \int J_l(k_m r) R_{10}(r) r dr \delta_{l0} \\ &= [\Omega]^{-\frac{1}{2}} [4\pi]^{\frac{1}{2}} \int J_0(k_m r) R_{10}(r) r dr \\ &= [\Omega]^{-\frac{1}{2}} \frac{4\pi}{k_m} \int U_{1s}(r) \sin(k_m r) r dr \end{aligned} \quad (30)$$

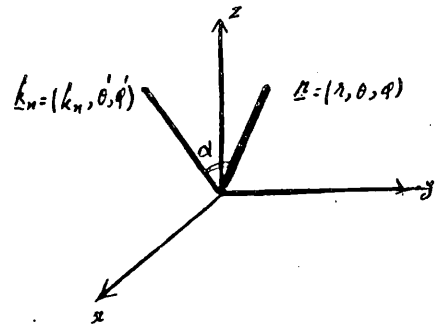
The last step follows upon substituting from equation (29) and by using the relation

$$J_0(k_m r) = \sqrt{4\pi} \frac{\sin(k_m r)}{k_m r}$$

Now to get a general expression for μ , we consider the vector \underline{k}_n whose coordinates are (k_n, θ, ϕ) as shown in the figure

$$e^{i \underline{k}_n \cdot \underline{r}} = e^{i k_n r \cos\alpha}$$

where α is the angle between the two vectors \underline{r} and \underline{k}_n



$$e^{i\mathbf{k}_n \cdot \mathbf{r}} = \sum_{l=0}^{\infty} (2l+1) i^l J_l(k_n r) P_l(\cos\alpha)$$

using the addition theorem of spherical harmonics

$$\begin{aligned} e^{i\mathbf{k}_n \cdot \mathbf{r}} &= \sum_{l=0}^{\infty} (2l+1) i^l J_l(k_n r) \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') \\ &= \sum_{l=0}^{\infty} \sum_{m=-l}^l (4\pi) i^l J_l(k_n r) Y_{lm}(\theta, \phi) Y_{lm}^*(\theta', \phi') \end{aligned}$$

hence

$$\begin{aligned} \mu(1s, \mathbf{k}_n) &= [\Omega]^{-\frac{1}{2}} \int e^{i\mathbf{k}_n \cdot \mathbf{r}} U_{1s}(r) d\mathbf{r} \\ &= [\Omega]^{-\frac{1}{2}} \sum_{l=0}^{\infty} \sum_{m=-l}^l (4\pi) i^l Y_{lm}^*(\theta', \phi') \int J_l(k_n r) \frac{R_{10}(r)}{r} r^2 dr \\ &\quad \times \int Y_{lm}(\theta, \phi) Y_{00}(\theta, \phi) d\omega \\ &= [\Omega]^{-\frac{1}{2}} 4\pi Y_{00}(\theta', \phi') \int J_0(k_n r) \frac{R_{10}(r)}{r} r^2 dr \\ &= [\Omega]^{-\frac{1}{2}} 4\pi [4\pi]^{-\frac{1}{2}} \int J_0(k_n r) R_{10}(r) r dr \\ &= [\Omega]^{-\frac{1}{2}} \frac{4\pi}{k_n} \int U_{1s}(r) \sin(k_n r) r dr \quad (31) \end{aligned}$$

From equation (30) and equation (31) we deduce that for any \mathbf{k} -vector \mathbf{k}_m the orthogonality coefficient is given by the relation

$$\mu(1s, \underline{k}_m) \equiv \mu(1s, k_m) = [\Omega]^{-\frac{1}{2}} \frac{4\pi}{k_m} \int U_{1s}(r) \sin(k_m r) r dr \quad (32)$$

Now substituting for U_{1s} from equation (7)

$$\mu(1s, k_m) = 4\pi[\Omega]^{-\frac{1}{2}} \frac{A}{k_m} \int (e^{-br} + h e^{-2br}) \sin(k_m r) r dr \quad (33a)$$

where $b=2a=2.46624$; finally we get

$$\begin{aligned} \mu(1s, k_m) = [\Omega]^{-\frac{1}{2}} \frac{4\pi A}{k_m} \left\{ (k_m^2 + b^2)^{-1} \sin[2 \tan^{-1}(k_m/b)] \right. \\ \left. + h(k_m^2 + 4b^2)^{-1} \sin[2 \tan^{-1}(k_m/2b)] \right\} \quad (33b) \end{aligned}$$

From equation (33b) we obtain the orthogonality coefficients needed in our calculations; they are listed in table 2.

The orthogonality coefficient for the vector $\underline{k}_m=0$ needs special treatment

$$\begin{aligned} \mu(1s, 0) &= \lim_{k_m \rightarrow 0} \mu(1s, k_m) \\ \text{substituting from (33a)} \\ \mu(1s, 0) &= [\Omega]^{-\frac{1}{2}} 4\pi A \int (e^{-br} + h e^{-2br}) \lim_{k_m \rightarrow 0} \left\{ \frac{\sin(k_m r)}{k_m} \right\} r dr \\ &= [\Omega]^{-\frac{1}{2}} 4\pi A \int (e^{-br} + h e^{-2br}) r^2 dr \\ &= .287372 \end{aligned}$$

Table 2: Orthogonality coefficients

a) along the Δ axis ; $k = \frac{2\pi}{a} (00\zeta)$

k_m	$k+k_m$	$\mu(k+k_m)$					
		$\zeta=.01$	$\zeta=.125$	$\zeta=.25$	$\zeta=.5$	$\zeta=.75$	$\zeta=.875$
000	0,0, ζ	.287364	.286090	.282295	.267863	.246203	.233533
101	1,0, $\zeta-1$.175106	.183661	.192373	.207074	.216741	.219266
110	1,1, ζ	.174339	.173748	.171981	.165184	.154740	.148488
101	1,0, $\zeta+1$.173578	.164636	.154740	.135063	.116399	.107669
002	0,0, $\zeta-2$.118524	.128481	.140029	.165184	.192373	.206298
200	2,0, ζ	.117687	.117365	.116399	.112658	.106824	.103278
002	0,0, $\zeta+2$.116859	.107669	.098415	.082114	.068510	.062609

Table 2: Orthogonality coefficients (cont.)

b) along the Σ axis ; $\underline{k} = \frac{2\pi}{a} (\zeta\zeta_0)$

\underline{K}_m	$\underline{k}+\underline{K}_m$	$\mu(\underline{k}+\underline{K}_m)$			
		$\zeta=.01$	$\zeta=.125$	$\zeta=.25$	$\zeta=.375$
000	$\zeta, \zeta, 0$.287356	.284816	.277354	.265567
110	$\zeta-1, \zeta-1, 0$.175873	.193769	.213443	.232600
101	$\zeta-1, \zeta, 1$.175102	.183016	.189626	.193769
110	$\zeta-1, \zeta+1, 0$.174335	.173156	.169668	.164091
101	$\zeta+1, \zeta, 1$.173574	.164091	.152774	.140884
110	$\zeta+1, \zeta+1, 0$.172818	.155738	.138343	.122382
200	$\zeta-2, \zeta, 0$.118522	.128110	.138343	.148024

c) along the Λ axis ; $\underline{k} = \frac{2\pi}{a} (\zeta\zeta\zeta)$

\underline{K}_m	$\underline{k}+\underline{K}_m$	$\mu(\underline{k}+\underline{K}_m)$			
		$\zeta=.01$	$\zeta=.125$	$\zeta=.25$	$\zeta=.375$
000	ζ, ζ, ζ	.287348	.283552	.272545	.255604
110	$\zeta-1, \zeta-1, \zeta$.175869	.193069	.210221	.224455
110	$\zeta+1, \zeta-1, \zeta$.174332	.172567	.167403	.159310
110	$\zeta+1, \zeta+1, \zeta$.172814	.155238	.136688	.119333
200	$\zeta-2, \zeta, \zeta$.118520	.127740	.136688	.143941
200	$\zeta+2, \zeta, \zeta$.116855	.107104	.096473	.086174

6- The Trial Wave Function

When dealing with a \underline{k} vector having high symmetry we use, as basis functions, a set of symmetrized combinations of OPW's that transform according to the particular irreducible representation we are interested in. Thus instead of writing the trial wave function as a linear combination of OPW's, as we did in the general case (cf. eq. I31), we expand it in a series of symmetrized linear combination of OPW's, namely,

$$\Psi_{\underline{k}} = \sum_{\underline{m}} A(\underline{k} + \underline{K}_m) \Phi(\underline{k} + \underline{K}_m) \quad (34)$$

where

$$\begin{aligned} \Phi(\underline{k} + \underline{K}_m) &= \sum_{\underline{j}} C(\underline{j}) \chi(\underline{k} + \underline{K}_m^{\underline{j}}) \\ &= [N_m]^{-1} \left\{ [N\Omega]^{-\frac{1}{2}} \sum_{\underline{j}} C_{\underline{j}} e^{i(\underline{k} + \underline{K}_m^{\underline{j}}) \cdot \underline{r}} \right. \\ &\quad \left. - [N]^{-\frac{1}{2}} \mu(\underline{k} + \underline{K}_m) \sum_{\underline{i}} e^{i\underline{k} \cdot \underline{R}_i} U(\underline{r} - \underline{R}_i) \right\} \quad (35) \end{aligned}$$

The summation over \underline{j} in the first term runs over selected reciprocal lattice vectors as is done in a symmetrized

combination of plane waves (cf. page 31); the coefficients C in this combination are exactly the same as the coefficients in the symmetrized combination of plane waves. N_m is a normalization factor calculated so as to normalize Φ over the volume of the crystal.

$$N_m = \left\{ \sum_j C_j^2 + \mu^2 (k+K_m) [1 - 2 \sum_j C_j] \right\} \quad (36)$$

The coefficients A in equation (34) satisfy the set of equations

$$\sum_n \left\{ \int \Phi^*(\underline{k} + \underline{K}_m) H \Phi(\underline{k} + \underline{K}_n) d\underline{r} - E \int \Phi^*(\underline{k} + \underline{K}_m) \Phi(\underline{k} + \underline{K}_n) d\underline{r} \right\} A(\underline{k} + \underline{K}_n) = 0 \quad (37)$$

for $m=0,1,\dots,p$. This set of equations has a solution if

$$\det \left| \int \Phi^*(\underline{k} + \underline{K}_m) H \Phi(\underline{k} + \underline{K}_n) d\underline{r} - E \int \Phi^*(\underline{k} + \underline{K}_m) \Phi(\underline{k} + \underline{K}_n) d\underline{r} \right| = 0 \quad (38)$$

To solve this determinant we have to find the matrix elements of both the identity and the Hamiltonian, which we now proceed to calculate.

7- Matrix Elements of Unity

$$\int \Phi^*(\underline{k}+\underline{K}_m)\Phi(\underline{k}+\underline{K}_n)d\underline{r} = [N_m N_n]^{-1} [I + II + III + IV]$$

where

$$I = [N\Omega]^{-1} \sum_{j,j'} C_j C_{j'} \int e^{i(\underline{K}_n^{j'} - \underline{K}_m^j) \cdot \underline{r}} d\underline{r}$$

$$= \sum_j C_j C_j \delta_{mn} \delta_{jj'}$$

$$II = [N]^{-1} \mu(k+K_m)\mu(k+K_n) \sum_{i,i'} e^{i\underline{k} \cdot (\underline{R}_i' - \underline{R}_i)} \int U(\underline{r}-\underline{R}_i') U^*(\underline{r}-\underline{R}_i) d\underline{r}$$

$$= \mu(k+K_m)\mu(k+K_n)$$

$$III = [N]^{-1} [\Omega]^{-\frac{1}{2}} \mu(k+K_n) \sum_j \sum_{i'} C_j \int e^{-i(\underline{k}+\underline{K}_m^j) \cdot \underline{r}} U(\underline{r}-\underline{R}_i') d\underline{r}$$

$$= [N]^{-1} [\Omega]^{-\frac{1}{2}} \mu(k+K_n) \sum_j \sum_{i'} C_j e^{-i\underline{K}_m^j \cdot \underline{R}_i'} \int e^{-i(\underline{k}+\underline{K}_m^j) \cdot \underline{r}} U(\underline{r}) d\underline{r}$$

$$= \mu(k+K_m)\mu(k+K_n) \sum_j C_j$$

$$\begin{aligned} \text{IV} &= [N]^{-1} [\Omega]^{-\frac{1}{2}} \mu(\mathbf{k}+\mathbf{K}_m) \sum_{j'} \sum_i C_j e^{i\mathbf{K}_n^{j'} \cdot \mathbf{R}_i} \int e^{i(\mathbf{k}+\mathbf{K}_n^{j'}) \cdot \mathbf{r}} U(\mathbf{r}) d\mathbf{r} \\ &= \mu(\mathbf{k}+\mathbf{K}_m) \mu(\mathbf{k}+\mathbf{K}_n) \sum_{j'} C_j \end{aligned}$$

hence

$$\begin{aligned} \int \Phi^*(\mathbf{k}+\mathbf{K}_m) \Phi(\mathbf{k}+\mathbf{K}_n) d\mathbf{r} &= \frac{1}{N_m N_n} \left\{ \delta_{mn} \sum_{j, j'} C_j C_{j'} \delta_{j j'} \right. \\ &\quad \left. + \mu(\mathbf{k}+\mathbf{K}_m) \mu(\mathbf{k}+\mathbf{K}_n) [1 - \sum_j C_j - \sum_{j'} C_{j'}] \right\} \quad (39) \end{aligned}$$

In particular

$$\int \Phi^*(\mathbf{k}+\mathbf{K}_m) \Phi(\mathbf{k}+\mathbf{K}_m) d\mathbf{r} = \frac{1}{N_m} \left\{ \sum_j C_j^2 + \mu^2(\mathbf{k}+\mathbf{K}_m) [1 - 2 \sum_j C_j] \right\} = 1$$

8- Matrix Elements of The Hamiltonian

$$\int \Phi^*(\mathbf{k}+\mathbf{K}_m) H \Phi(\mathbf{k}+\mathbf{K}_n) d\mathbf{r} = \frac{1}{N_m N_n} [\text{I} + \text{II} + \text{III} + \text{IV}]$$

where

$$\text{I} = [N\Omega]^{-1} \int \left[\sum_j C_j e^{-i(\mathbf{k}+\mathbf{K}_m)^j \cdot \mathbf{r}} \right] H \left[\sum_{j'} C_{j'} e^{i(\mathbf{k}+\mathbf{K}_n)^{j'} \cdot \mathbf{r}} \right] d\mathbf{r}$$

$$\begin{aligned}
 \text{I} &= [\text{N}\Omega]^{-1} \left\{ \sum_{j,j'} \text{C}_j \text{C}_{j'} [|\underline{k} + \underline{K}_n^{j'}|^2] \int e^{i(\underline{K}_n^{j'} - \underline{K}_m^j) \cdot \underline{r}} d\underline{r} \right. \\
 &\quad \left. + \text{N}\Omega \sum_{j,j'} \text{C}_j \text{C}_{j'} W(\underline{K}_n^{j'} - \underline{K}_m^j) \right\} \\
 &= \sum_{j,j'} \text{C}_j \text{C}_{j'} [|\underline{k} + \underline{K}_n^{j'}|^2] \delta_{mn} \delta_{jj'} \sum_{j,j'} \text{C}_j \text{C}_{j'} W(\underline{K}_n^{j'} - \underline{K}_m^j) \\
 \text{II} &= [\text{N}]^{-1} \mu(\underline{k} + \underline{K}_m) \mu(\underline{k} + \underline{K}_n) \int \left\{ \sum_{\underline{i}} e^{-i\underline{k} \cdot \underline{R}_i} U(\underline{r} - \underline{R}_i) \right\} \text{H} \left\{ \sum_{\underline{i}'} e^{i\underline{k} \cdot \underline{R}_{i'}} U(\underline{r} - \underline{R}_{i'}) \right\} \\
 &= [\text{N}]^{-1} \mu(\underline{k} + \underline{K}_m) \mu(\underline{k} + \underline{K}_n) \sum_{\underline{i}, \underline{i}'} e^{i\underline{k} \cdot (\underline{R}_{i'} - \underline{R}_i)} E_{1s} \delta_{\underline{i} \underline{i}'} \\
 &= \mu(\underline{k} + \underline{K}_m) \mu(\underline{k} + \underline{K}_n) \\
 \text{III} &= [\text{N}]^{-1} [\Omega]^{-\frac{1}{2}} \mu(\underline{k} + \underline{K}_n) \int \left\{ \sum_j \text{C}_j e^{-i(\underline{k} + \underline{K}_m^j) \cdot \underline{r}} \right\} \text{H} \left\{ \sum_{\underline{i}'} e^{i\underline{k} \cdot \underline{R}_{i'}} U(\underline{r} - \underline{R}_{i'}) \right\} d\underline{r} \\
 &= [\text{N}]^{-1} [\Omega]^{-\frac{1}{2}} \mu(\underline{k} + \underline{K}_n) E_{1s} \sum_j \sum_{\underline{i}'} \text{C}_j \int e^{-i(\underline{k} + \underline{K}_m^j) \cdot \underline{r}} e^{i\underline{k} \cdot \underline{R}_{i'}} U(\underline{r} - \underline{R}_{i'}) d\underline{r} \\
 &= [\text{N}]^{-1} [\Omega]^{-\frac{1}{2}} \mu(\underline{k} + \underline{K}_n) E_{1s} \sum_j \sum_{\underline{i}'} \text{C}_j \\
 &\quad \int e^{-i(\underline{k} + \underline{K}_m^j) \cdot (\underline{r} - \underline{R}_{i'})} e^{i\underline{K}_m^j \cdot \underline{R}_{i'}} U(\underline{r} - \underline{R}_{i'}) d\underline{r} \\
 &= [\text{N}]^{-1} \mu(\underline{k} + \underline{K}_n) E_{1s} \sum_{\underline{i}'} e^{i\underline{K}_m^j \cdot \underline{R}_{i'}} \sum_j \text{C}_j [\Omega]^{-\frac{1}{2}} \int e^{-i(\underline{k} + \underline{K}_m^j) \cdot \underline{r}} U(\underline{r}) d\underline{r} \\
 &= \mu(\underline{k} + \underline{K}_n) \mu(\underline{k} + \underline{K}_m) E_{1s} \sum_j \text{C}_j
 \end{aligned}$$

$$\begin{aligned} \text{IV} &= [N]^{-1} [\Omega]^{-\frac{1}{2}} \left\{ \sum_i e^{-i\mathbf{k} \cdot \mathbf{R}_i} U^*(\mathbf{r} - \mathbf{R}_i) \right\} \text{H} \left\{ \sum_{j'} C_{j'} e^{i(\mathbf{k} + \mathbf{K}_n^{j'}) \cdot \mathbf{r}} \right\} d\mathbf{r} \\ &= \mu(\mathbf{k} + \mathbf{K}_m) \mu(\mathbf{k} + \mathbf{K}_n) E_{1s} \sum_{j'} C_{j'} \end{aligned}$$

Hence, finally we get

$$\begin{aligned} \int \Phi^*(\mathbf{k} + \mathbf{K}_m) \text{H} \Phi(\mathbf{k} + \mathbf{K}_n) d\mathbf{r} &= \frac{1}{N_m N_n} \left\{ \sum_j \sum_{j'} C_j C_{j'} [|\mathbf{k} + \mathbf{K}_n^{j'}|^2] \delta_{jj'} \delta_{mn} \right. \\ &\quad + \sum_j \sum_{j'} C_j C_{j'} W(\mathbf{K}_n^{j'} - \mathbf{K}_m^j) \\ &\quad \left. + \mu(\mathbf{k} + \mathbf{K}_m) \mu(\mathbf{k} + \mathbf{K}_n) E_{1s} [1 - \sum_j C_j - \sum_{j'} C_{j'}] \right\} \quad (40) \end{aligned}$$

9- The Secular Determinant

We are now in a position to calculate the elements of the secular determinant. Substituting from equations (39) and (40) in equation (38), we get for the mn element

$$\begin{aligned} D_{mn} &= \frac{1}{N_m N_n} \left\{ \sum_{j, j'} [|\mathbf{k} + \mathbf{K}_n^{j'}|^2 - E] C_j C_{j'} \delta_{jj'} \delta_{mn} + \sum_j \sum_{j'} W(\mathbf{K}_n^{j'} - \mathbf{K}_m^j) C_j C_{j'} \right. \\ &\quad \left. - \mu(\mathbf{k} + \mathbf{K}_m) \mu(\mathbf{k} + \mathbf{K}_n) (E - E_{1s}) [1 - \sum_j C_j - \sum_{j'} C_{j'}] \right\} \quad (41) \end{aligned}$$

Once the elements of the determinant of a particular \mathbf{k} vector in the BZ are calculated we solve the determinantal eq. and thereby obtain the energy values.

10- Difficulties in Applying the OPW Method

To obtain satisfactory results, one would wish to use something around 60 OPW's. At a \underline{k} -vector with high symmetry, the symmetry required for the wave function has the consequence that many of the coefficients of the OPW's will be dependant. Therefore the degree of the secular equation will be reduced, say, to the order of 6 or 7, and hence the labour needed in solving the problem will be within a reasonable limit. However, for a general \underline{k} -vector, all the coefficients are independant, and so the secular equation will have the same order as the number of OPW's included. This makes the OPW method impracticable for such points. We have compensated for not considering any general \underline{k} -vector by calculating at many points with high symmetry. Apart from the points $\Gamma, H, N,$ and $P,$ we calculated for 6 points on the Δ axis, and for 4 points on each of the Σ and Λ axes.

Another difficulty arises when the wave function of the state we are considering, is, by reason of symmetry, automatically orthogonal to the core wave functions, and hence the orthogonality coefficients will be identically zero. In this case the OPW

expansion will reduce to a plane wave expansion, with the possible consequence of a poor convergence.

Callaway [4] has suggested that in such cases, instead of calculating the orthogonality coefficients, we choose them so that Ψ_k would have a form near the nuclei, as one would expect the crystal wave function to have. Obviously this is not a rigorous treatment, and one has to judge it by the merit of the convergence achieved. In our calculation we came across this difficulty at the points H,P, and N, where for the valence band the wave functions there are p-type, and therefore orthogonal to the core wave functions. However, we found that the convergence at these points, using a plane wave expansion, was so good that it did not seem necessary to apply the correction mentioned.

11- Numerical Calculations

Most of the calculations that we had to perform in this work, have been carried out on the University of London ATLAS computer using the EXCHLF language. To give an example of a computer program we write below the program used for finding the eigenvalues and eigenvectors of the secular equation (37). Before doing so we shall put the problem in a form suitable for numerical computation.

The secular equation has the form

$$\begin{aligned} [H_{11}-B_{11}E]A_1+[H_{12}-B_{12}E]A_2+\dots+[H_{1n}-B_{1n}E]A_n &= 0 \\ [H_{21}-B_{21}E]A_1+[H_{22}-B_{22}E]A_2+\dots+[H_{2n}-B_{2n}E]A_n &= 0 \\ \vdots & \\ [H_{n1}-B_{n1}E]A_1+[H_{n2}-B_{n2}E]A_2+\dots+[H_{nn}-B_{nn}E]A_n &= 0 \end{aligned}$$

which can be written in the matrix form

$$[H-EB]A = 0$$

or

$$HA = EBA \quad (42)$$

where both H and B are symmetric and $B_{ii} = 1$ for all i.

It was noted that there was a library routine, R925, which finds the solutions of an eigenvalue problem of the form

$$SA = EA \quad (43)$$

where the matrix S is symmetric. It is clear that equation (43)

is a special case of equation (42), which one obtains when the basis functions employed are mutually orthogonal. In this case the matrix B reduces to the identity matrix. We tried to put equation (42) in the form (43) so that the library routine could be utilized. This was possible as shown in the following analysis.

If the matrix B is a positive definite matrix (i.e. $Z^t B Z > 0$ where $Z \neq 0$; the suffix t denotes the transpose) then it can be written as a product of an upper triangular matrix** and its transpose, viz.

$$B = U^t U \quad (44)$$

conversely, if it is possible to put the matrix B in this form then it is a positive definite matrix.

All the matrices B that we had to deal with were found to be positive definite since they could be written in the form (44). This was achieved by applying another library routine, R900 ; actually only a part of this routine was used.

Now substituting from (44) in (42)

$$HA = EU^t UA \quad (45)$$

If we write

$$X = UA \quad (46)$$

** An upper triangular matrix is a matrix for which the element $U_{ij} = 0$ for $i > j$

equation (45) becomes

$$HU^{-1}X = EU^tX$$

multiplying by $[U^t]^{-1}$ from left

$$[U^t]^{-1}HU^{-1}X = EX \quad (47)$$

Since

$$[U^t]^{-1} = [U^{-1}]^t$$

equation (47) can be written

$$[U^{-1}]^tH[U^{-1}]X = EX$$

or

$$PX = EX \quad (48)$$

where

$$P = [U^{-1}]^tH[U^{-1}] \quad (49)$$

The matrix P is symmetric i.e. equation (48) is just the same as equation (43), and so we can apply the library routine R925 .

It is clear that the eigenvalues will not be effected by the transformation applied, however, the eigenvectors of equation (42) can be readily obtained from those of equation (48) using relation (46), viz.

$$A = U^{-1}X$$

Besides the two library routines mentioned above, the program consists of the two chapters following.

CHAPTER 1

A->44
F->320
B->117
U->9
V->81
Y->9
W->9

3) I=N
M=1
E=.01N
JUMPDOWN (R025)

NEWLINE
J=1(1)N
PRINT (UJ, 0, 8)
REPEAT
*7(300)V(1), N
350=*26(0, 300, N, 1, N)
*6(350)W(1), N
Z=0
J=1(1)N
Z=Z+WJWJ
REPEAT

Z=*SQRT(Z)
NEWLINE
J=1(1)N
WJ=WJ/Z
PRINT (WJ, 0, 8)
REPEAT
UP
CLOSE

CHAPTER 0

A->44
R->44
D->44
E->44
C->80
G->80


```
K'=1(1)3
J=0(1)44
READ (DJ)
REPEAT
J=0(1)44
READ (EJ)
REPEAT
```

```
L=0
N=3(1)L
M=-1
Q=L+2
P=-L-1
J=N
J'=1(1)N
Q=Q-1
P=P+Q
I'=P-1
J=J-1
K=0(1)J
M=M+1
I'=I'+1
BM=FI'
AM=DI'
REPEAT
REPEAT
```

JUMPDOWN (R900)

```
K=0
I=1(1)N
I'=I-1
M=NI'
J=I(1)N
C(M+J-1)=BK
G(M+J-1)=AK
K=K+1
REPEAT
JUMP 2, I=1
Q=I-1
R=0
S=N
J=1(1)Q
C(M+J-1)=B(I+R-1)
G(M+J-1)=A(I+R-1)
S=S-1
R=R+S
REPEAT
2)REPEAT
```

Q'=NN

*7(0)C(0), Q'
*7(50)G(0), Q'
100=*16(0, N, N)
150=*26(50, 0, N, N, N)
200=*26(100, 150, N, N, N)
*6(200)G(0), Q'
I=0
J=0
M'=S'

I'=0(1)S'
I=I+I'
K=0(1)M'
AJ=GI
I=I+1
J=J+1
REPEAT
M'=M'-1
FPEAT
DOWN 3/1

REPEAT
REPEAT
END
CLOSE

III: RESULTS AND DISCUSSION

1- Survey of Previous Work

Due to the fact that the Li atom has only three electrons attached to it, the band structure of the Li crystal has been a subject of many investigations, using the different methods proposed to solve the one-electron equation. The earlier work, [19,14, 1,21,22, 10,20, 2], has been mostly concerned with the cohesive energy of Li. Apart from Millman, [14] who used a free atom potential and proceeded to integrate Schrodinger's equation numerically, they use the Seitz semi-empirical potential [19]. This potential reproduces the observed spectrographic energy values of the free atom.

Parmenter [16] constructed an approximately self-consistent potential which he took to be the sum of atomic potentials. The atomic potential had the form $V = -2 \frac{Z_p(r)}{r}$, where Z_p is an effective charge determined on the basis of an electronic configuration $(1s)^2 (2s)^{5/8} (2p)^{3/8}$, and was calculated using the self-consistent wave functions of the free atom given by Fock and Petrashen [4]. He also took account of the exchange effects by including Slater's free-electron exchange potential. The OPW method was employed and,

for the 1s core function needed in this type of calculation, he used a single exponential. The corresponding energy E_{1s} was obtained by numerical integration and was found to be -4.57 Ryd. which is quite close to the value -4.53 Ryd. which we obtained. Although Parmenter's procedure is the nearest to our's, unfortunately we can not compare our results for the eigenvalues with his because whereas his results are qualitatively correct they have no quantitative significance. This is because his crystal potential contained two terms, the first is small and dependent on position, and the other large and independent of position; whereas this latter term was not accurate he did not attempt to correct it because he was mainly interested in the shape and separation of the energy bands which are not effected by the presence of a constant term in the potential. Parmenter obtained for the width of the filled portion of the band the value $.304$ Ryd. and for the effective mass the value $.808$.

Wainwright and Parzen [24] used the corrected form of the Seitz potential [12]. They employed a variational method based on the Wannier functions of the crystal, their results do not compare well with those obtained by other methods using the same potential.

Schiff [18] calculated a semi-empirical potential using the method of Prokofiev. His potential is weaker near the nucleus than the Seitz potential, and therefore probably less accurate. He used the improved cellular method of Howorth and Jones, and obtained the eigenvalues for the states $\Gamma_1, N_1', H_{15}, N_1, H_{12}$, and H_1 ; these are respectively $-.615, -.304, -.120, -.114, .202$, and $.55$ Ryd. The energy gap at the centre of a face of the zone is

$$E(N_1) - E(N_1') = .190 \text{ Ryd.}$$

Kohn and Rostoker [12] employed a variation-iteration method (Green's function method) which requires the potential to be spherically symmetric within the inscribed spheres of the atomic polyhedron and constant in the space between them. Since the Seitz potential does not fulfil the second of these requirements they had to modify it to suit the restrictions of the method. Thus their potential had the form

$$\begin{aligned} V'(r) &= V(r) & \text{for } r \leq r_i \\ &= V_0 & \text{for } r > r_i \end{aligned}$$

where r_i is the radius of the inscribed sphere, and $V(r)$ is the Seitz potential, and V_0 is the average value of $V(r)$ in the region between the inscribed sphere and the boundaries of the polyhedron. This method requires a great deal of labour ; however it must be noted that most

of the labour required is spent in calculating certain geometrical structure constants which need to be found once and for all for each type of lattice.

Brown and Krumhansl [3] apply a variational procedure which does not specify at the outset the core functions to which the plane waves are to be orthogonalized. Thus one can consider the OPW method to be a special case of it. The freedom of not specifying the core functions at the beginning makes it possible to choose them such that the valence electron wave function is expressed as a linear combination of mutually orthogonal functions. Thus the matrix equation will contain the eigenvalues on the main diagonals only. Hence the calculations for this method will be simpler than the calculations for the OPW method, in which the matrix equations have E along the off diagonals because the different OPW's are not orthogonal. In view of the fact that most calculations nowadays are carried out by electronic computers, this simplification does not seem important.

Glasser and Callaway [6] use the Seitz potential and the OPW method to find the energy values at the symmetry points Γ, H, N , and P of the Brillouin zone. Callaway [5] has extended these calculations to points

on the symmetry axes Δ , Σ , and Λ , after slightly modifying the Seitz potential so as to take into account the fact that the normal component of the gradient of the crystal potential must vanish at many points on the surface of the atomic polyhedron.

Ham [8] recently studied the whole group of the alkali metals using the Green's function method. Because he wanted to avoid using an explicit potential, he had to determine the values of the logarithmic derivatives on the inscribed sphere as required by the method and this he did by the Quantum Defect method.

2- Eigenvalues and Constant Energy Surfaces

We have calculated the energy for states corresponding to the lowest band of the conduction electrons. In table 3 we list our results for the states Γ_{11} , H_{15} , N'_1 , and P_4 (cf. p.42). In table 3 we also list for comparison the results reported by Glasser and Callaway [6], Callaway [5], and Ham [8].

We have also calculated the energy for 6 points on the $\Delta \equiv 2 \frac{\pi}{a}(0,0,\zeta)$ axis for $\zeta = .01, .125, .25, .5, .75, \text{ and } .875$. Also for 4 points on each of the $\Sigma \equiv \frac{2\pi}{a}(\zeta, \zeta, 0)$ and $\Lambda \equiv \frac{2\pi}{a}(\zeta, \zeta, \zeta)$ axes for $\zeta = .01, .125, .25, \text{ and } .375$. The results for these points are shown in table 4 together

with Callaway's [5] results for comparison. Callaway had actually calculated the energy at points whose parameter ζ is different from our's; however to facilitate comparison we interpolated his results so as to correspond to our points. The convergence for all the points considered was very good. In the table given below we show the convergence for some of the points considered

Point	3x3	4x4	5x5	6x6	7x7
$\Delta=(0,0,\zeta) ; \zeta=.5$	-.541	-.543	-.547	-.552	-.552
$\Sigma=(\zeta,\zeta,0) ; \zeta=.25$	-.632	-.632	-.633	-.634	-.640
$\Lambda=(\zeta,\zeta,\zeta) ; \zeta=.25$	-.589	-.590	-.602	-.605	-.606

It is clear from tables 3 and 4 that our energy values differ for all points, from those obtained by the others by approximately .05 Ryd. This difference is well within what we would expect, regarding the fact that we used a different potential and a different value for the cube edge. Also, one should bear in mind that the degree of accuracy of the calculations based on the Seitz potential is $\pm .05$ Ryd. This is due to the fact that whereas the crystal potential is required by symmetry to have a vanishing normal derivative on the surface of the atomic polyhedron the Seitz potential does not have this property.

We draw below constant energy contours in the xy plane of reciprocal space, for $E = -.636$, $-.506$, and $-.477$. The last value is the Fermi energy obtained by interpolating Ham's results to fit our calculated bands. Although the contour for $E = -.636$ is almost spherical, those for higher *energies* become more and more distorted in the 110 direction. From the Fermi energy contour we see that the bulge does not touch the zone, in agreement with previous predictions.

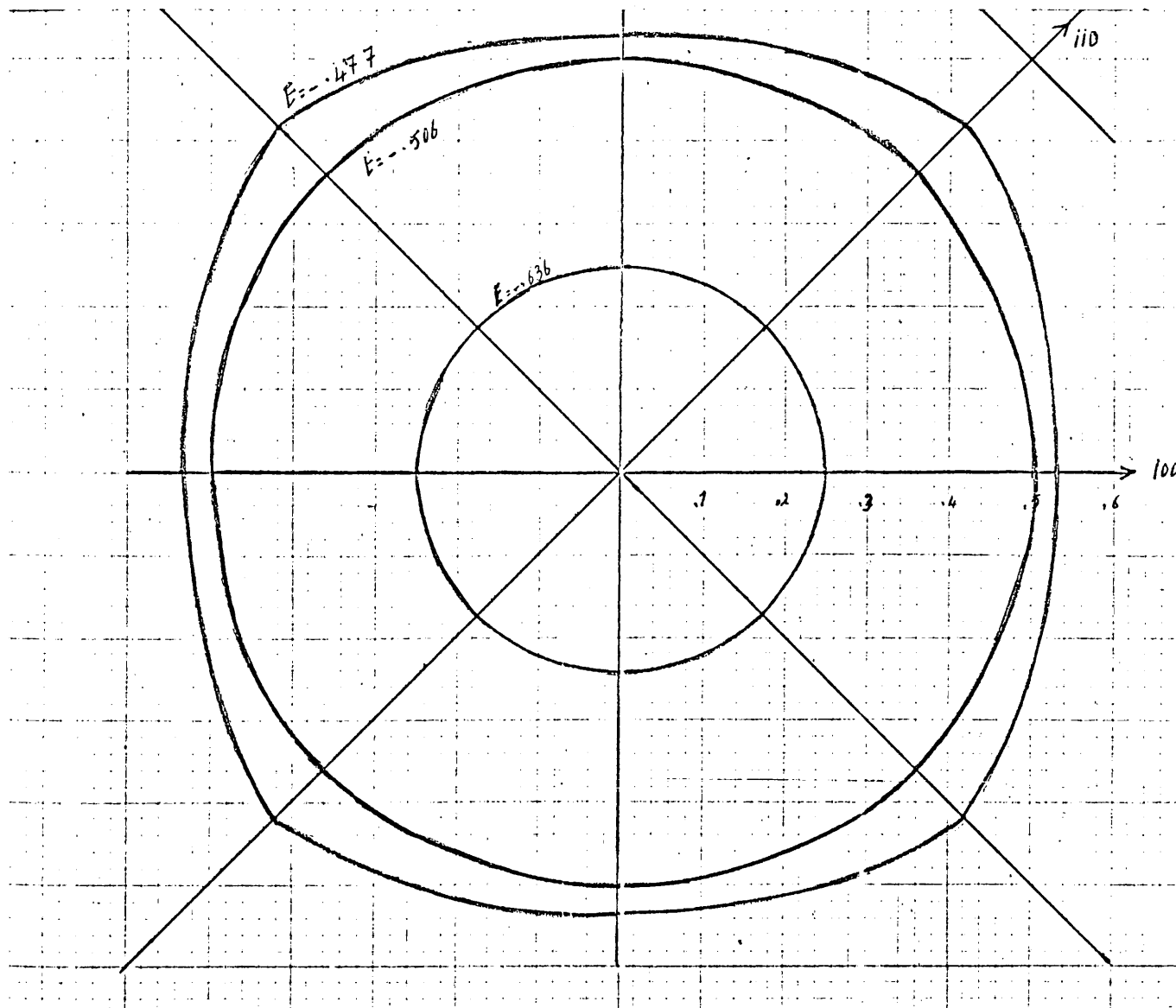


Table 3: Energy values at symmetry points

	Glasser	Callaway	Callaway	Ham	Present
Method					
Potential	OPW	OPW	OPW	Green's fn.	OPW
Cube Side	Seitz	Seitz	Seitz	Semi-empirical	Self-consistent
E_{1s}	6.5183	6.5183	6.5183	6.5183	6.6317 (a)
Γ_1	-3.765	-3.765	-3.765		-4.53
H_{1s}	-0.6832	-0.685	-0.685	-0.685	-0.744
N'_1	-0.092	-0.009	-0.009	-0.047	-0.126
P_4	-0.404	-0.413	-0.413	-0.411	-0.448
	-0.189	-0.179	-0.179	-0.182	-0.228

(a) Wyckoff; Crystal Structure, Vol. I, Chap. II, table p.9

Table 4: Energy values for points on symmetry axes

axis	ζ	present	Callaway
$\Delta \equiv \frac{2\pi}{a}(0,0,\zeta)$.01	-.733	
	.125	-.723	
	.25	-.688	-.636
	.5	-.552	-.506
	.75	-.359	-.276
	.875	-.280	
$\Sigma \equiv \frac{2\pi}{a}(\zeta,\zeta,0)$.01	-.728	
	.125	-.707	-.658
	.25	-.640	-.592
	.375	-.530	-.494
$\Lambda \equiv \frac{2\pi}{a}(\zeta,\zeta,\zeta)$.01	-.730	
	.125	-.701	-.645
	.25	-.606	-.545
	.375	-.464	-.387

3- Momentum Eigenfunctions

The momentum eigenfunctions - i.e. the coefficients A in the expansion II(34) - which correspond to the energy values $E_{\underline{k}}$ at the vector \underline{k} , are obtained by substituting for $E_{\underline{k}}$ in the set of equations II(37), and solving this set subject to the condition that

$$\sum [A_{\underline{l}}^{\underline{k}}]^2 = 1$$

The momentum eigenfunctions thus obtained are listed in tables 5,6, and 7, for the vectors along the 001, 110, and 111 axes respectively. First we give a few remarks on the tables. In table 5, we observe that the vectors obtained by permutation and/or change of sign of the first two coordinates of the vectors listed, are equivalent. We also notice that for the different combinations of the vectors \underline{k} and \underline{K}_m which have the same modulus, the coefficient $A(\underline{k} + \underline{K}_m)$ has the same value. For example, the value of A when \underline{k} is 001 and \underline{K}_m is 000, is the same as when \underline{k} is 001 and \underline{K}_m is 002. This shows that our calculation of the momentum eigenfunctions is self consistent. The reciprocal lattice vectors that differ from those listed in table 6 by permutation of the first two arguments and/or a change in the sign of the third

argument, are equivalent.

In fig.5 we plot the momentum eigenfunctions in the extended zone scheme for vectors along both the 001 and the 110 directions. The curve along the 001 direction starts at the centre of the zone with a value almost equal to one, and maintains it until about $3/4$ of the way towards the end of the first zone. Then it drops quite quickly, becoming zero at the end of the first zone.

The second peak on the curve occurs as soon as we enter the second zone, and again there is a maximum at the end of the second zone. In the third zone the curve has many fluctuations.

The curve along the 110 direction behaves in a similar manner.

Table 5: Momentum eigenfunctions along the 001 axis

K_m	Γ	$\Delta \equiv \frac{2\pi}{a}(0,0,\zeta)$						$H \equiv \frac{2\pi}{a}(0,0,1)$
		$\zeta=0.01$	$\zeta=0.125$	$\zeta=0.25$	$\zeta=0.5$	$\zeta=0.75$	$\zeta=0.875$	
000	-.976	-.997	-.997	-.995	-.984	-.489	-.314	0
101	.196	.029	.049	.077	.164	.831	.937	.984
110	.196	.032	.030	.028	.023	.174	.151	.142
101	.196	.030	.011	-.004	-.025	.033	.021	.020
002	.091	.017	.030	.029	.044	-.171		0
200	.091	.043	.042	.041	.040	.093		.095
002	.091	.018	.012	.007	.001	.005		0

Table 6: Momentum eigenfunctions along the 110 axis

\underline{K}_m	Γ	$\Sigma \equiv \frac{2\pi}{a} (\zeta, \zeta, 0)$			$N \equiv \frac{2\pi}{a} (\frac{1}{2}, \frac{1}{2}, 0)$
		$\zeta = .01$	$\zeta = .25$		
			$\zeta = .125$	$\zeta = .375$	
000	-.976	-.999	-.998	-.994	-.979
110	.196	.009	.030	.072	.180
101	.196	.021	.038	.054	.058
110	.196	.012	.010	.002	-.015
101	.196	.018	.002	-.015	-.035
110	.196	.003	-.009	-.018	-.024
200	.091	.028	.037	.049	.061

Table 7: Momentum eigenfunctions along the 111 axis

K_m	Γ	$\Lambda = \frac{2\pi}{a}(\zeta, \zeta, \zeta)$				$P = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
		$\zeta = .01$	$\zeta = .125$	$\zeta = .25$	$\zeta = .375$	
000	-.976	-.998	-.994	-.998	-.838	.986
110	.196	.028	.079	.183	.522	.986
110	.196	.035	.047	.051	.092	.148, -.017
110	.196	.016	.001	.010	-.005	.060, .033
200	.091	.037	.054	.078	.126	0
200	.091		.027	.033	.022	.018

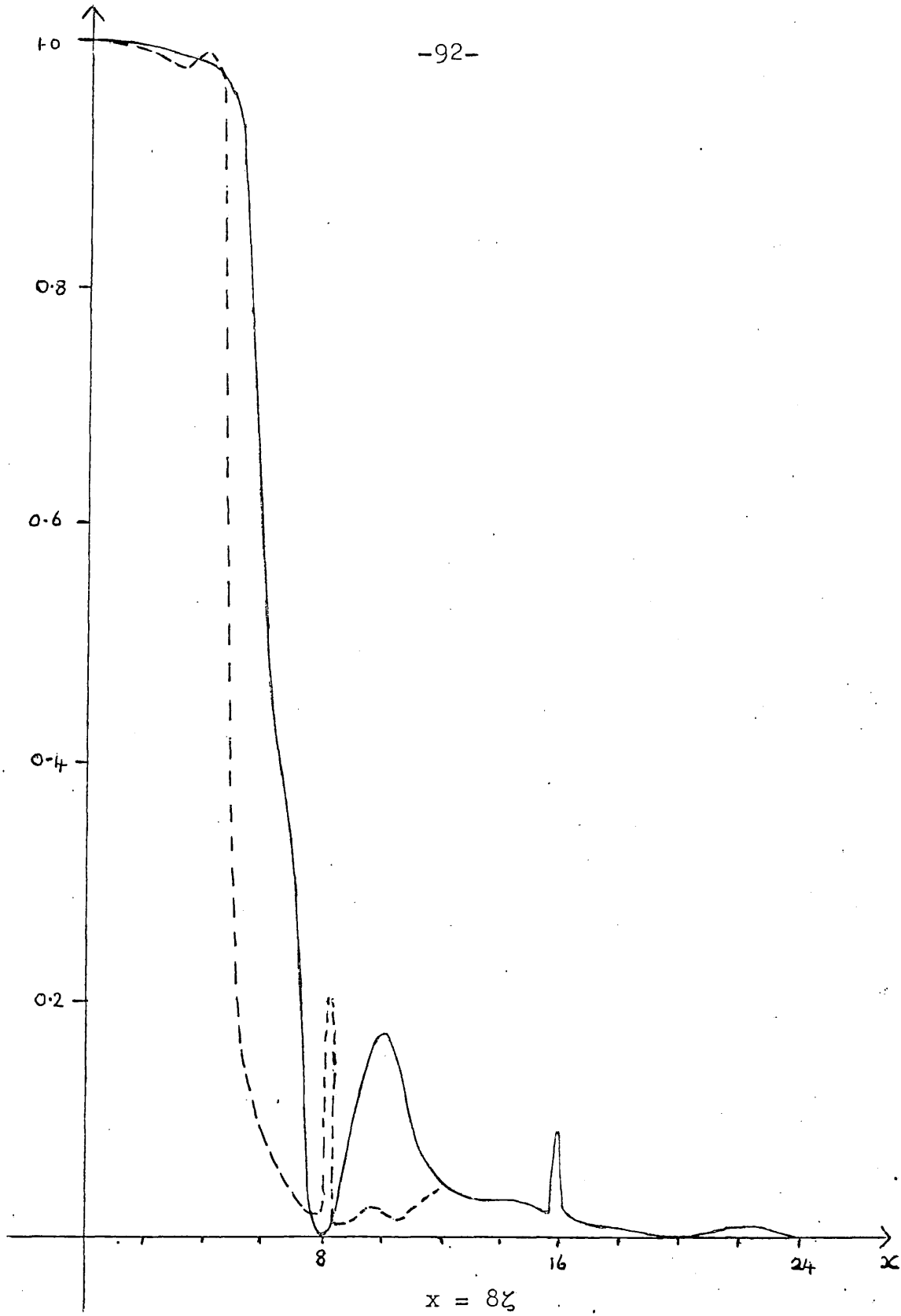


Fig .5. Momentum eigenfunctions along the 001 axis (continuous line), and the 110 axis (dotted line).

4- Wave Functions

In spite of the fact that the band structure of metallic Li has been studied extensively (cf. p.79) yet the wave functions have been scarcely obtained.

It is important to obtain the wave functions because they are employed in the theoretical evaluation of some of the properties that can be experimentally observed, such as the Knight shift. Moreover, in order to compare the wave functions obtained by different methods, one has to evaluate them explicitly. This comparison is particularly desirable in view of the fact pointed out by Pincherle [17] that since most of the methods applied in solving the one-electron equations involve using a variational procedure, there is no guarantee that the correct energy values obtained will necessarily bring about with them the correct set of wave functions.

We express the wave function as a function of inter-nuclear distances, i.e. we draw a line through the direct lattice and find the real and imaginary parts of the complex wave function at points along this line, drawing separate curves for each of them. We take the lines, along the three edges of the cube and along its diagonal; the reason for choosing the latter is that the atoms are closely packed in this direction for the lattice structure we are investigating.

The wave functions plotted in figures 6-17 correspond to different \underline{k} -vectors taken along the axes of symmetry in the BZ. We shall first point out the common features among the curves. The most striking feature is the complete resemblance of the wave functions, in the region between the atomic cores, to plane waves having \underline{k} -vectors in the first BZ. As one would expect, the wave functions near the cores fluctuate violently to take an atomic function shape. Here again one finds a feature which occurs in most of the curves, namely, that the same crystal wave function may have near one nucleus an s-like character and near another nucleus a p-like character. The occurrence of both of these forms for the same function indicates clearly that the crystal wave function is actually a mixture of atomic wave functions having different angular momentum quantum numbers.

Now we consider the curves separately. In fig. 6a,b we draw respectively the real and imaginary parts of the wave function corresponding to a \underline{k} -vector on the Δ axis, whose parameter $\zeta=.25$. The plotting is done along the z direction of the direct lattice. In 6a, we can see clearly the phenomenon already mentioned concerning the presence of both the s and p-like types of the wave function near the nuclei. Around the first nucleus on the left of the curve the wave function has s-like properties, whereas around the second it

has p-like properties. In fig. 6b - the imaginary part of the wave ^{function} for which fig.6a is the real part - we find that the s and p-like types have interchanged their roles. The function represented in fig.7 differs from that represented in fig.6 in that the value of ζ in the former is .5. We observe that the real part of fig.7 has extra nodes midway between the nuclei. These nodes are not due to the 2s atomic functions, since each of these has only one node; they are due to the modulating plane wave. Figs.10-13 show wave functions with \underline{k} -vectors along the Σ axis. In 10 and 11 the function is plotted along a cube edge, and, in 12 and 13, along a cube diagonal. The parameter ζ is .25 in 10 and 12, and is .375 in 11 and 13. We observe that the wave functions, corresponding to the same parameter, exhibit the same behaviour when plotted along either a cube edge or diagonal.

Finally, figs.14-17 express the wave functions having wave vectors along the Λ axis. The value of ζ is .25 in 14 and 16, and is .375 in 15 and 17. The plotting is along a cube edge in figs.14-15, and along a cube diagonal in figs.16-17. As we approach the zone surface, we note that the wave functions lose, to some extent, their resemblance to a plane wave.

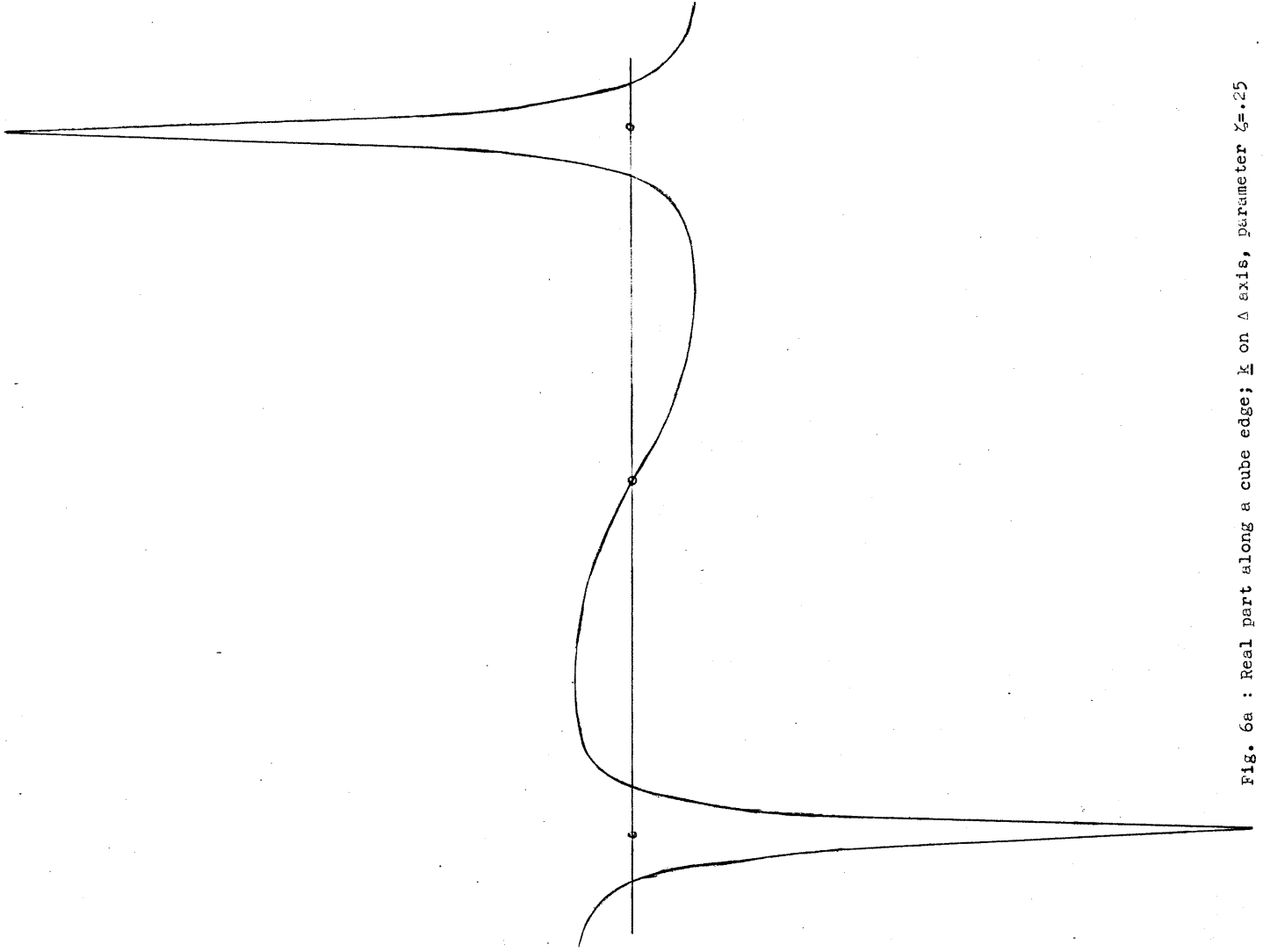


Fig. 6a : Real part along a cube edge; k on Δ axis, parameter $\zeta=0.25$

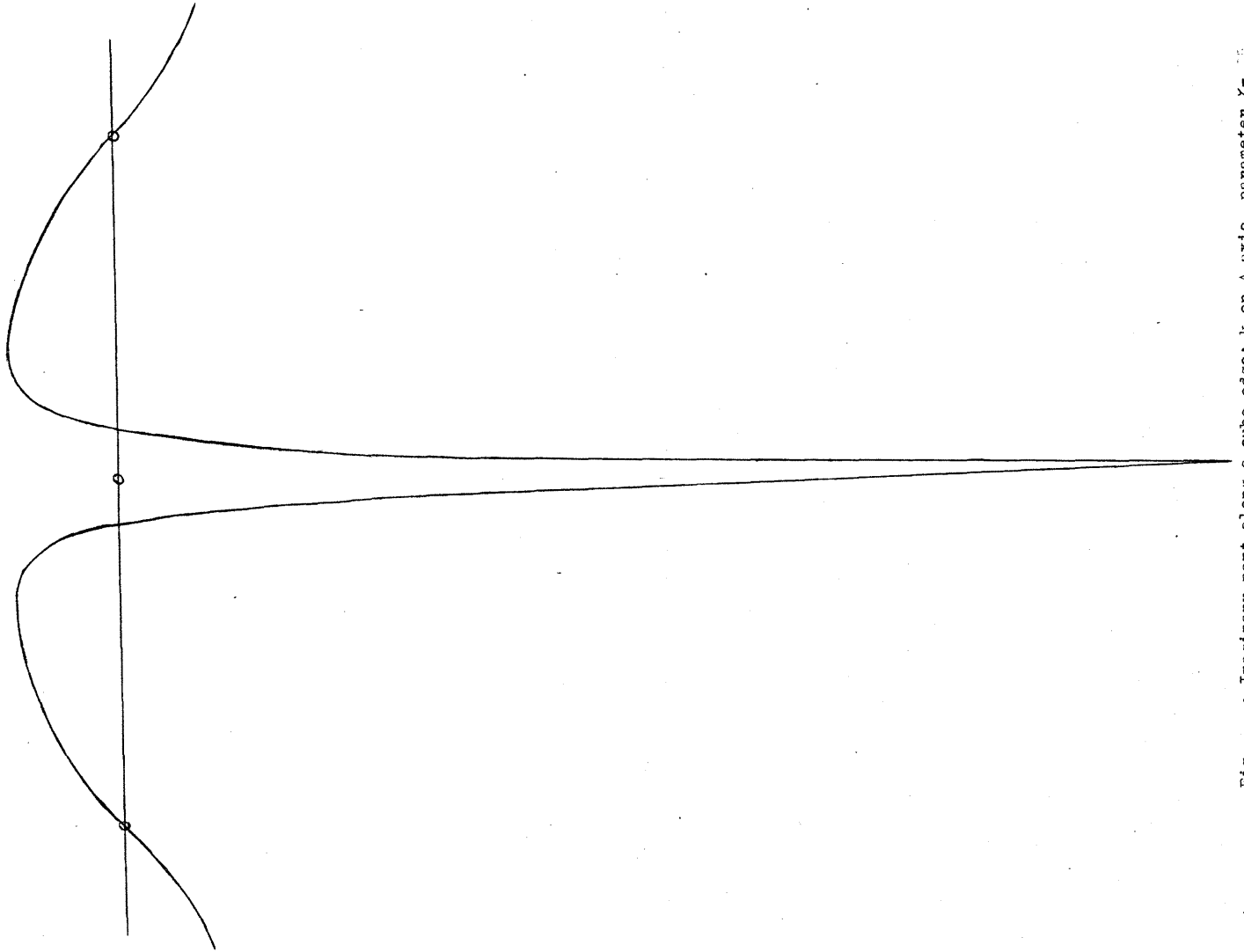


Fig. 1.1 : Imaginary part along a cube edge; k on Δ axis, parameter $\zeta = 1.5$

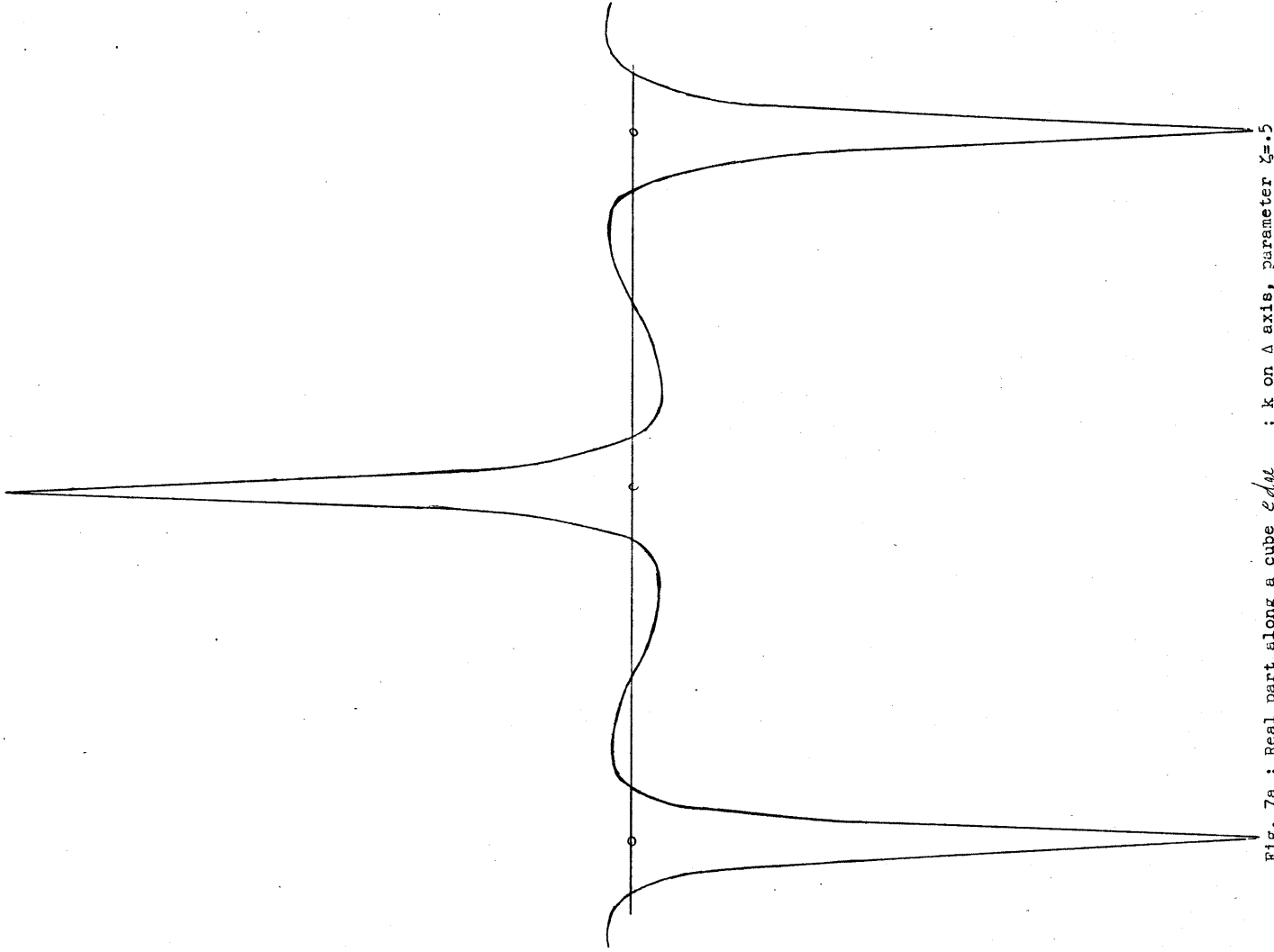


FIG. 7a : Real part along a cube edge ; κ on Δ axis, parameter $\zeta=5$

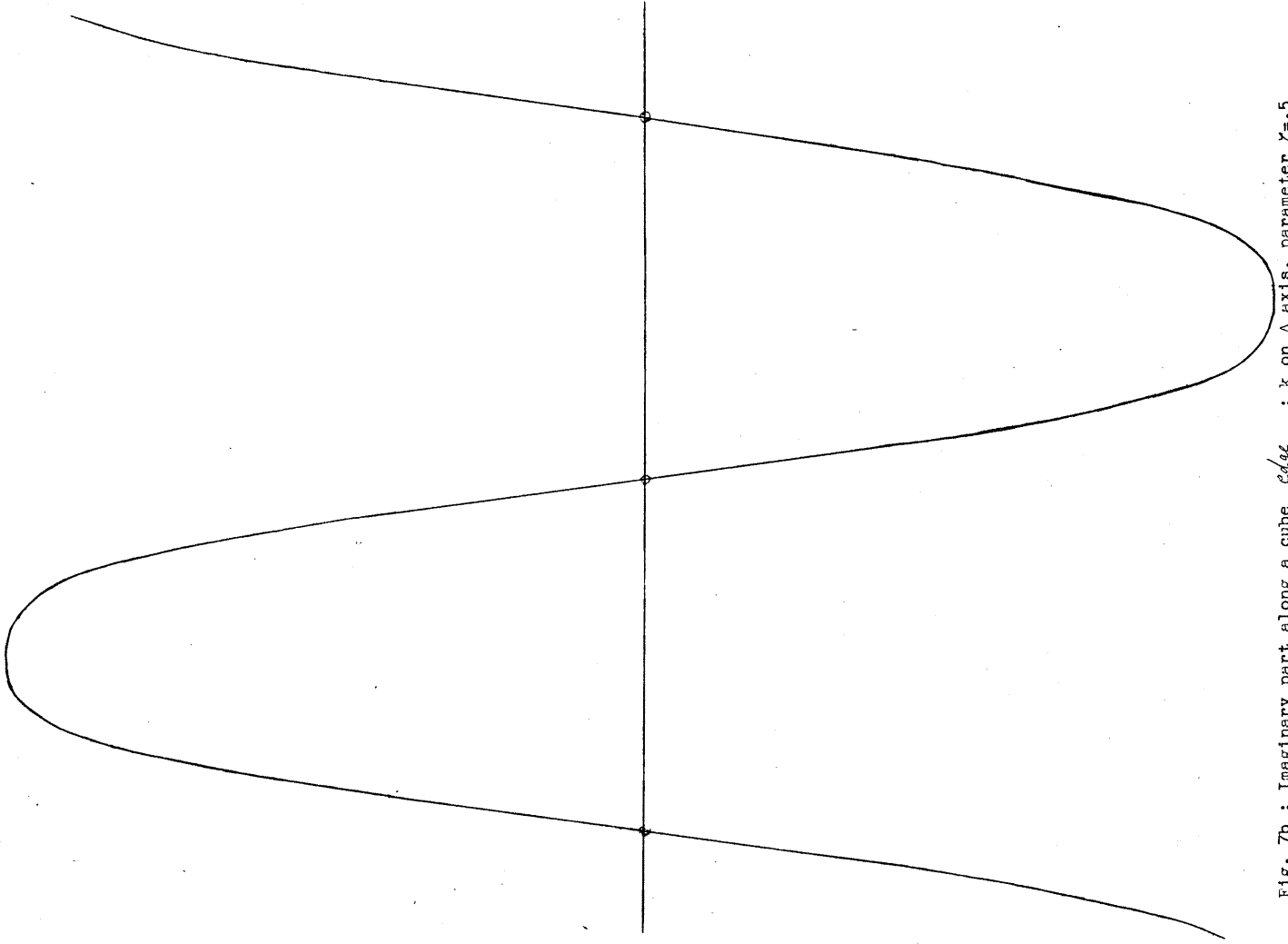


Fig. 7b : Imaginary part along a cube edge ; k on Δ axis, parameter $\zeta=5$

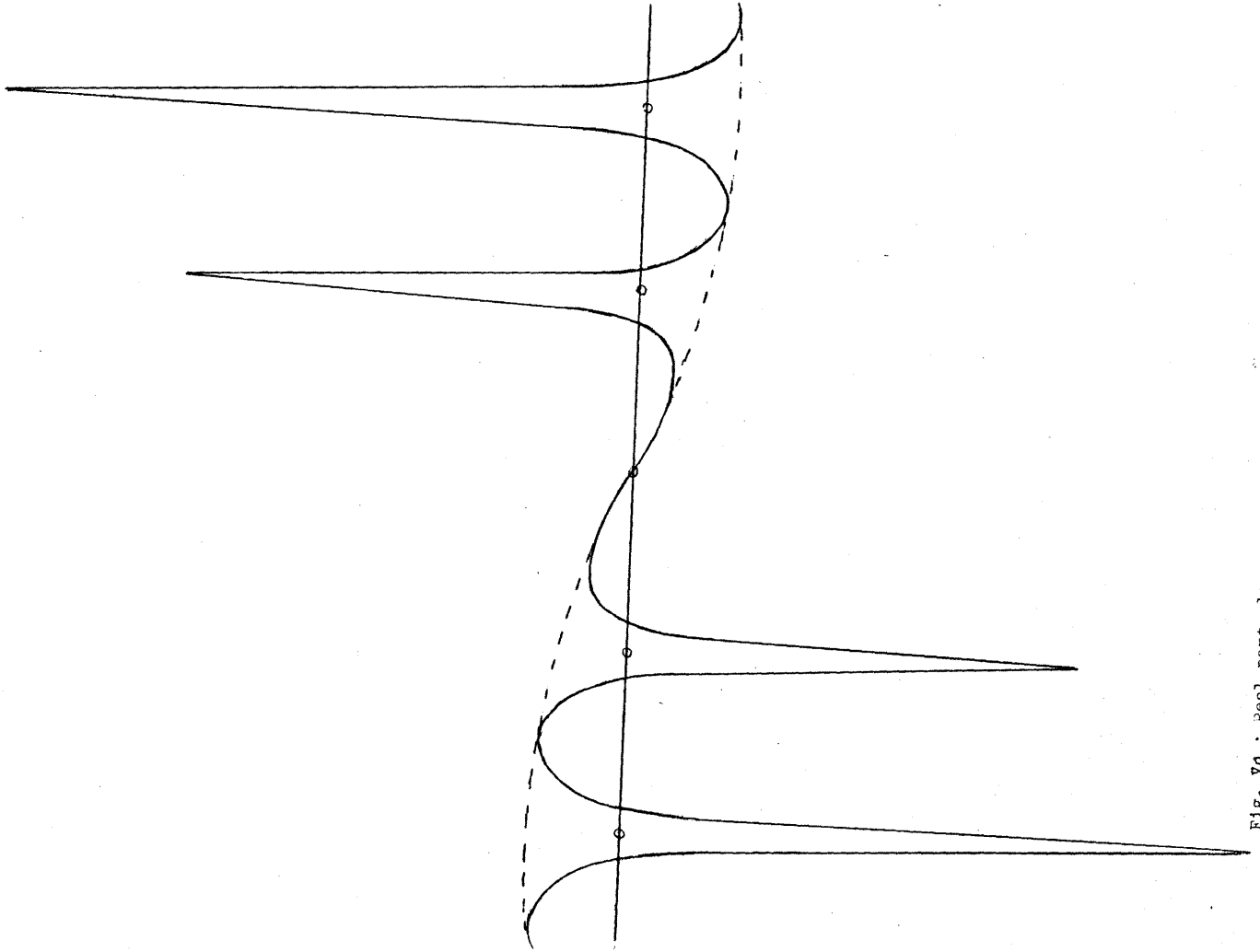


Fig. 8A : Real part along a cube diagonal; Δ on Δ axis, parameter $\zeta=.25$

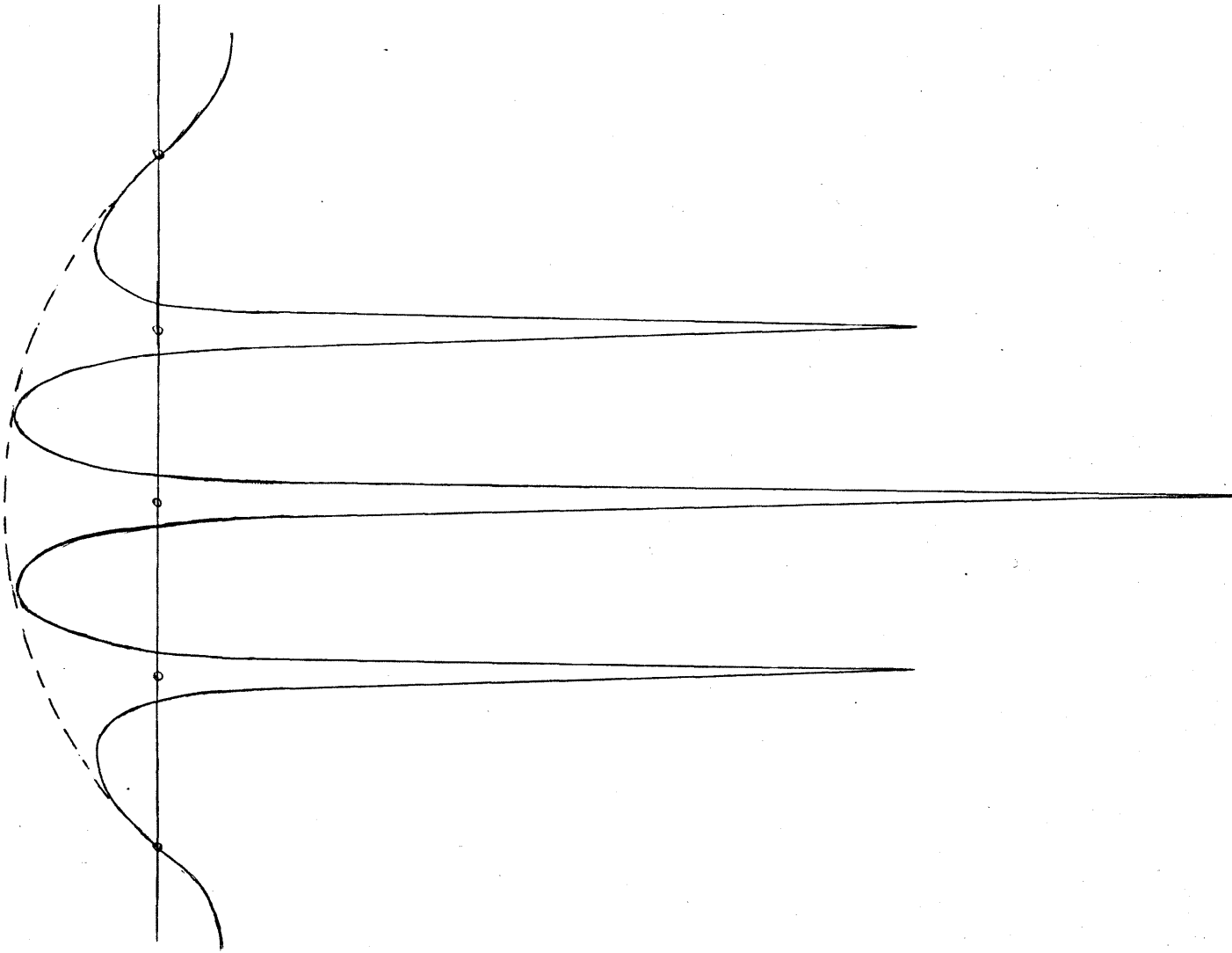


Fig. 8b : Imaginary part along a cube diagonal; k on Δ axis, parameter $\zeta = .25$

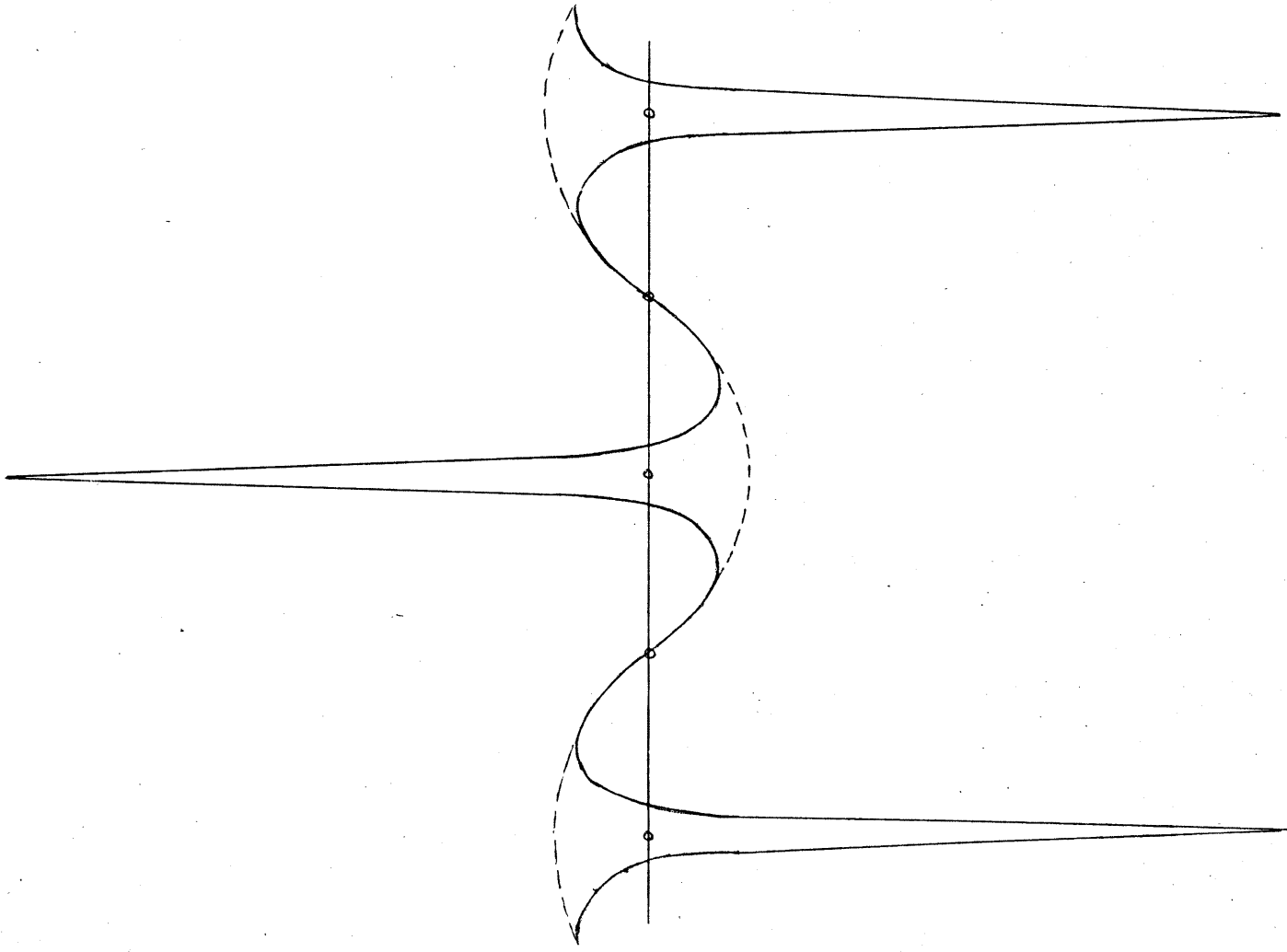


Fig. 9a : Real part along a cube diagonal; k on Δ axis, parameter $\zeta=5$

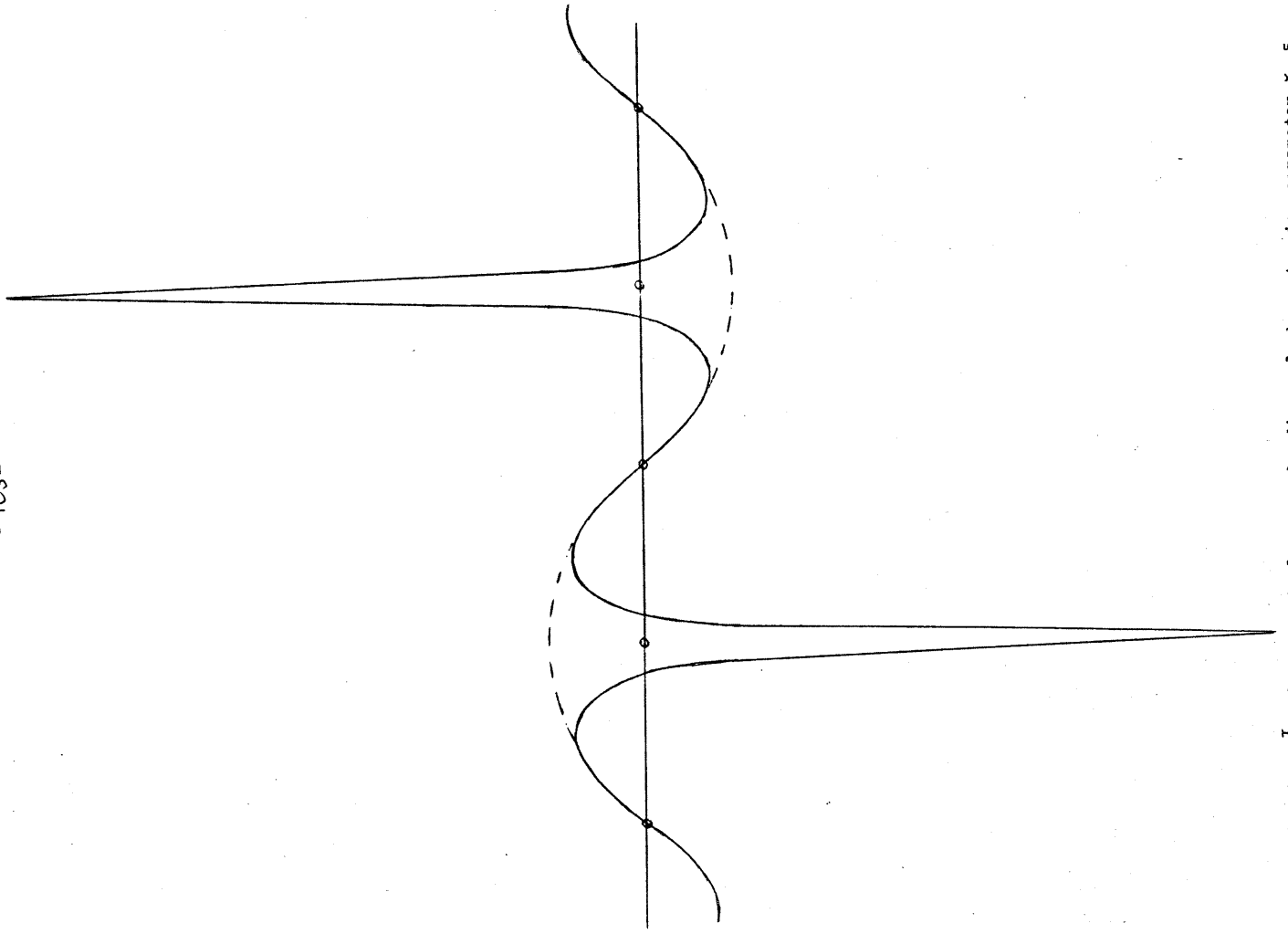


Fig. 9b : Imaginary part along a cube diagonal; k on Δ axis, parameter $\zeta=0.5$

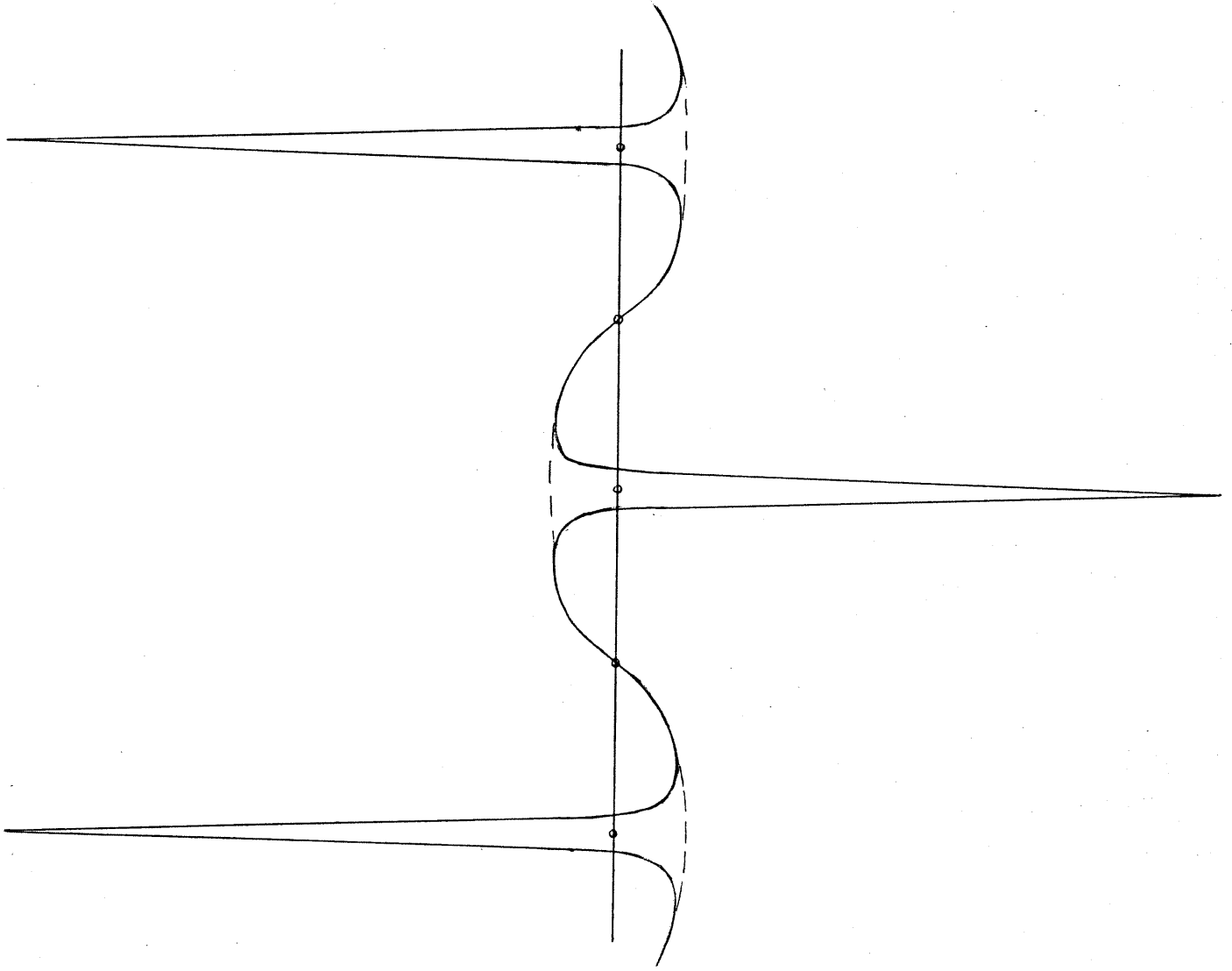


Fig. 10a : real part along a cube edge; \bar{k} on Σ axis, parameter $\zeta=0.25$

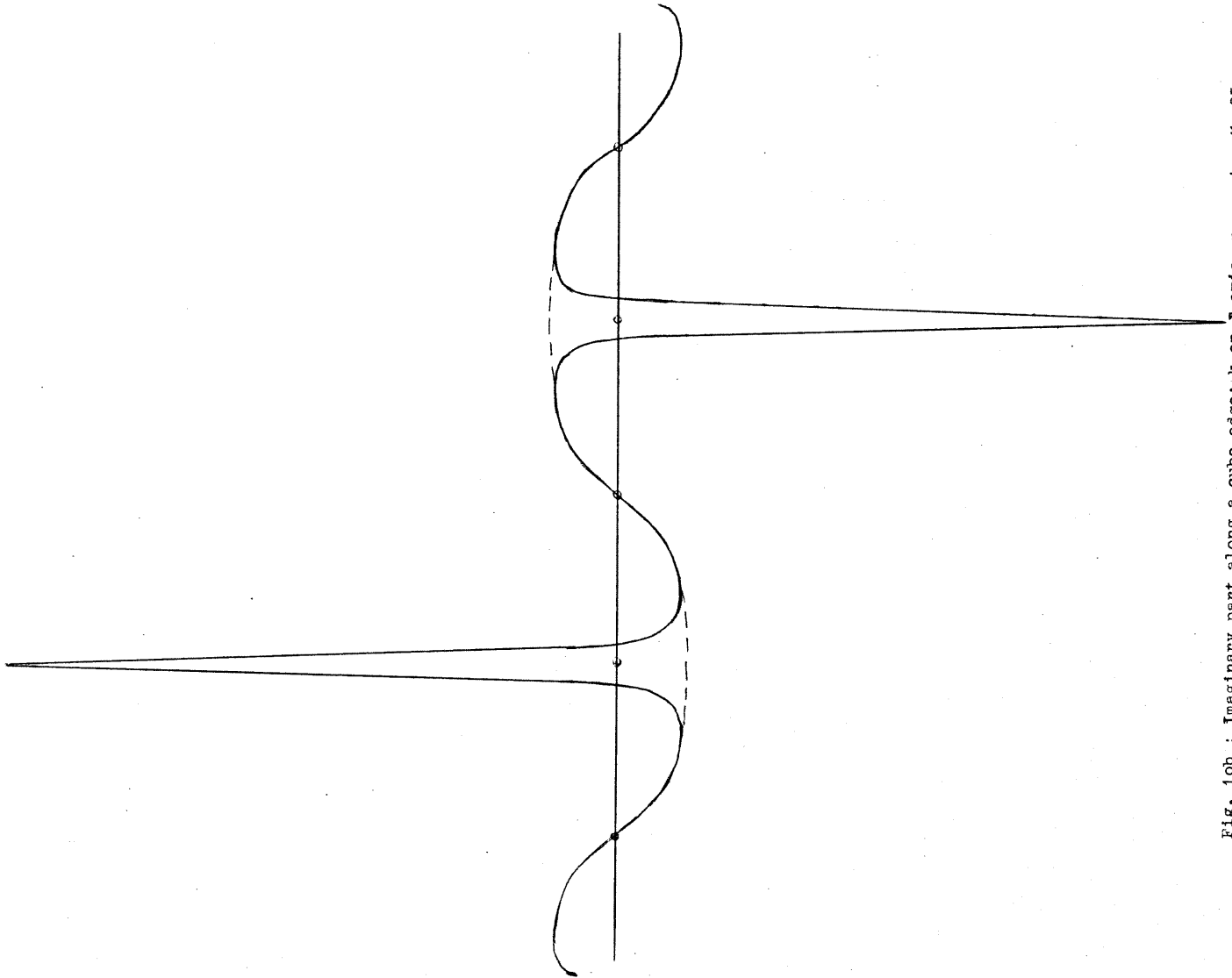


Fig. 10b : Imaginary part along a cube edge; k on z axis, parameter $\zeta = .25$

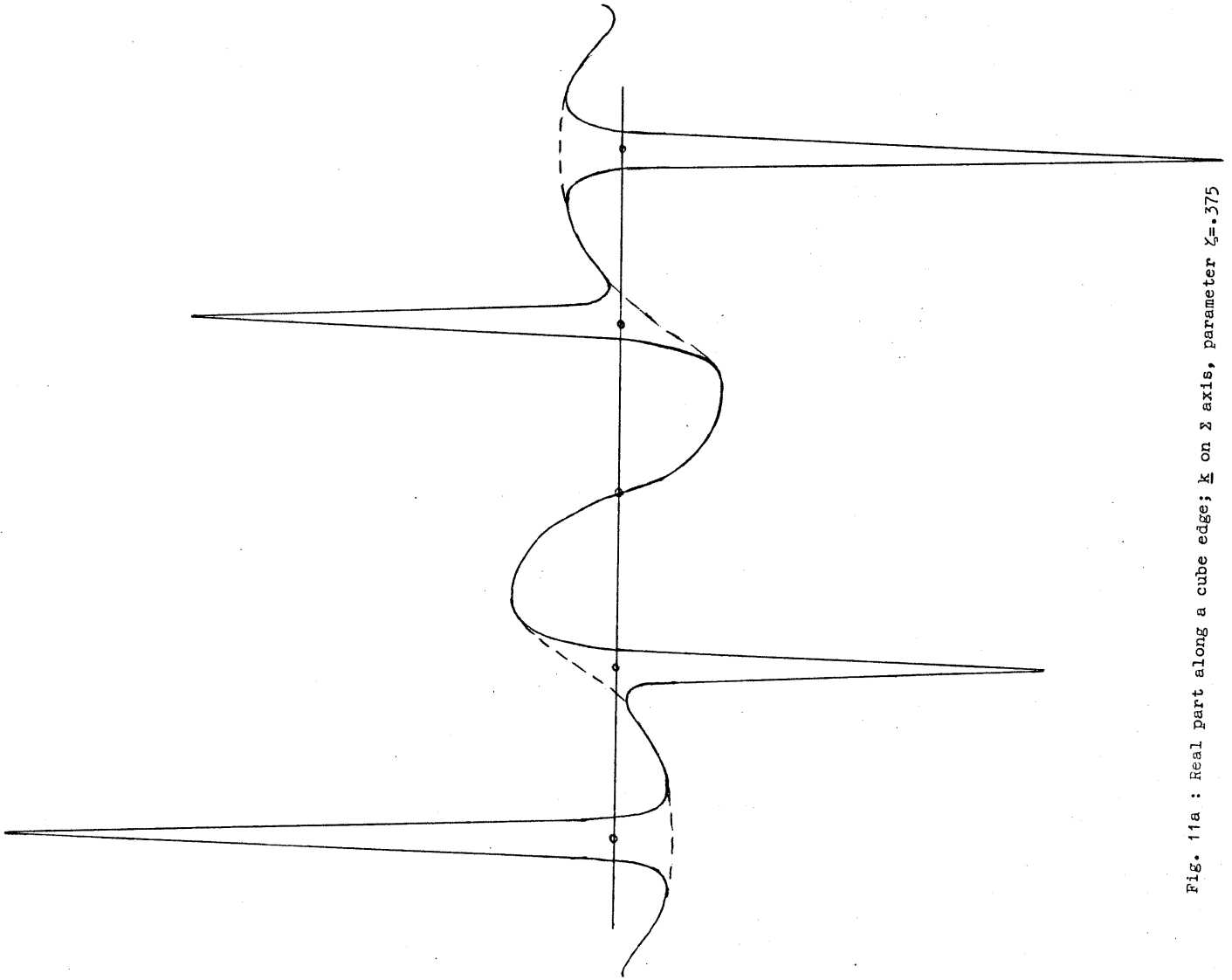


Fig. 11a : Real part along a cube edge; k on Σ axis, parameter $\zeta = .375$

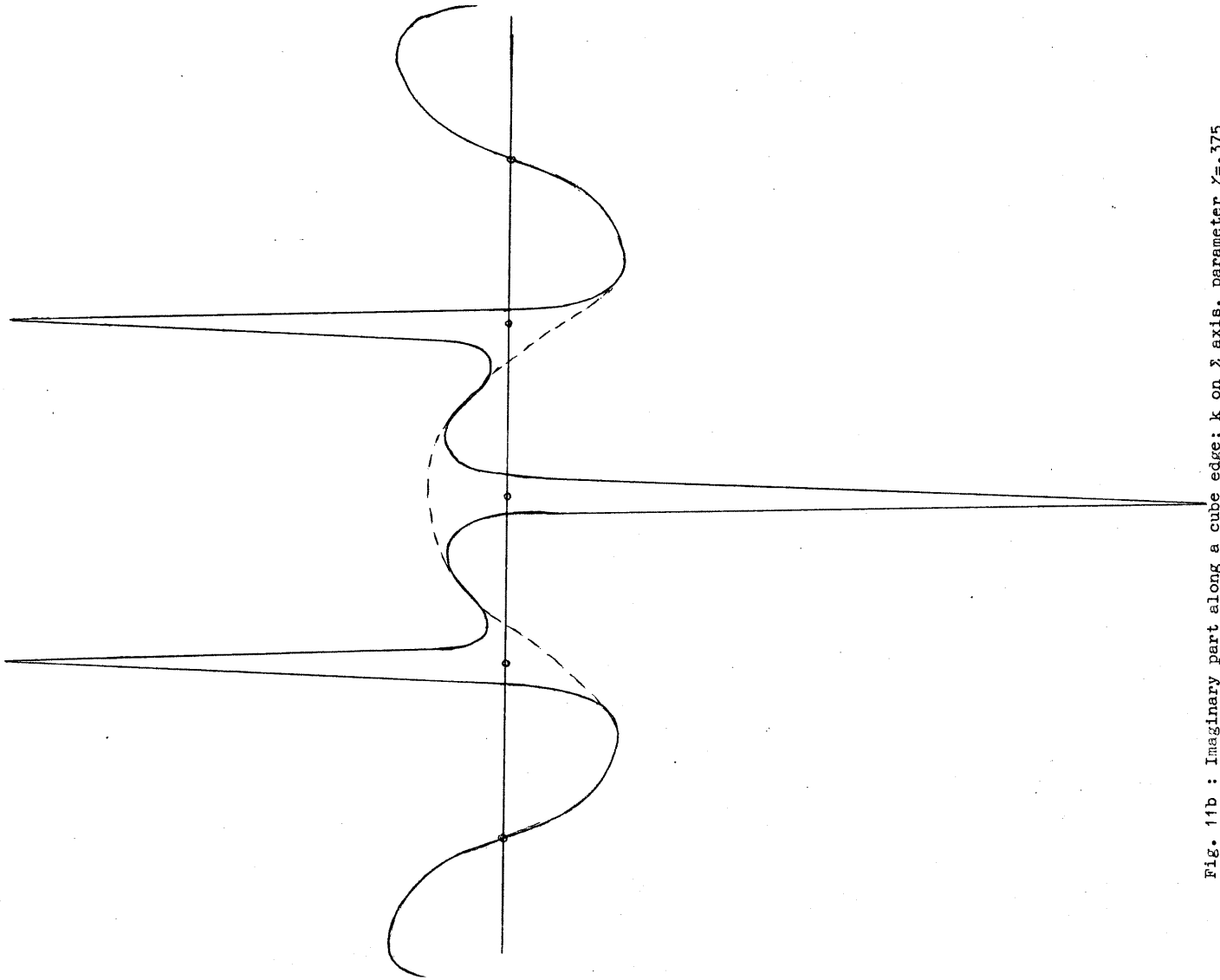


Fig. 11b : Imaginary part along a cube edge; k on z axis, parameter $\zeta=0.375$

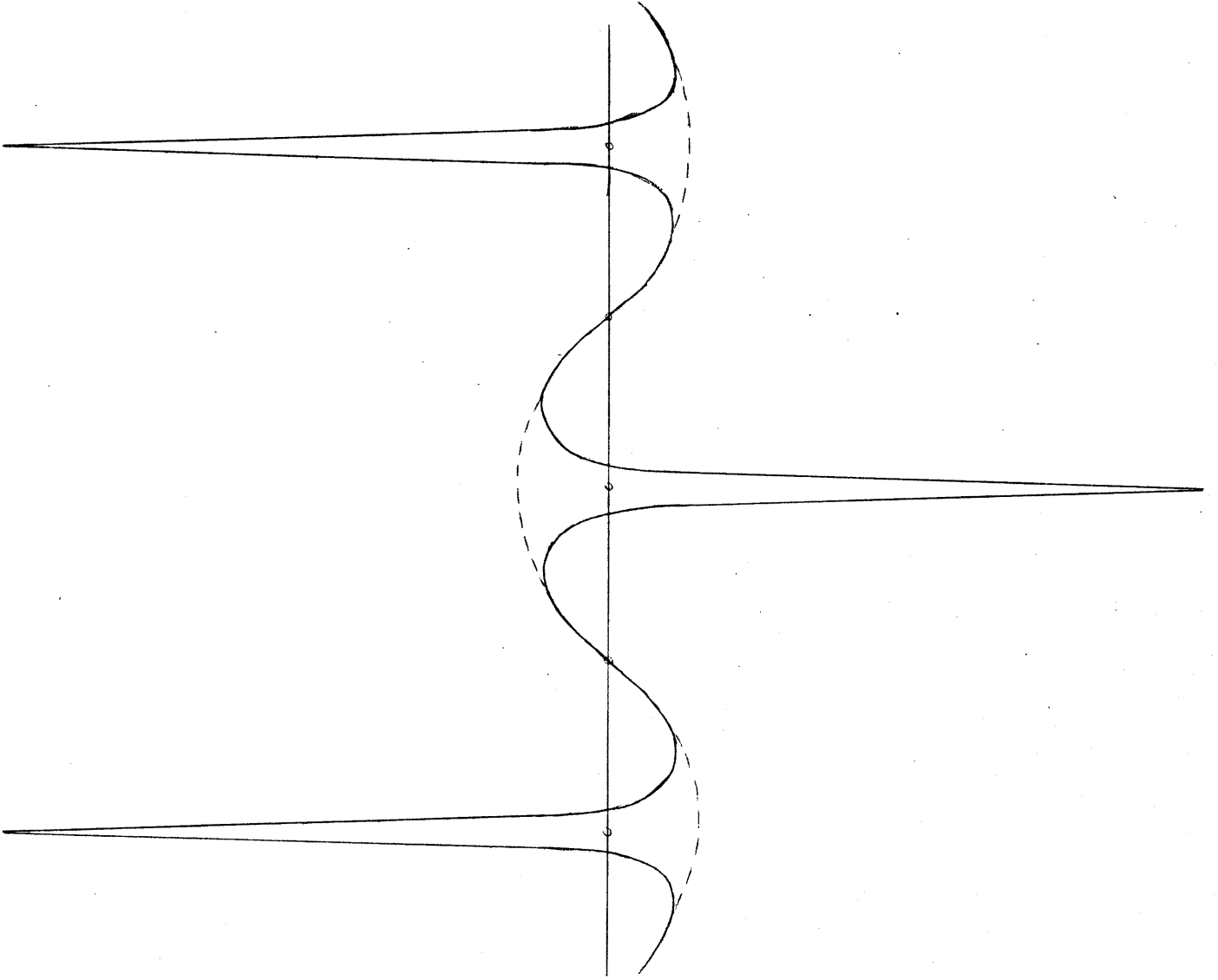


Fig. 12a : real part along a cube diagonal; \bar{k} on Σ axis, parameter $\chi=0.25$

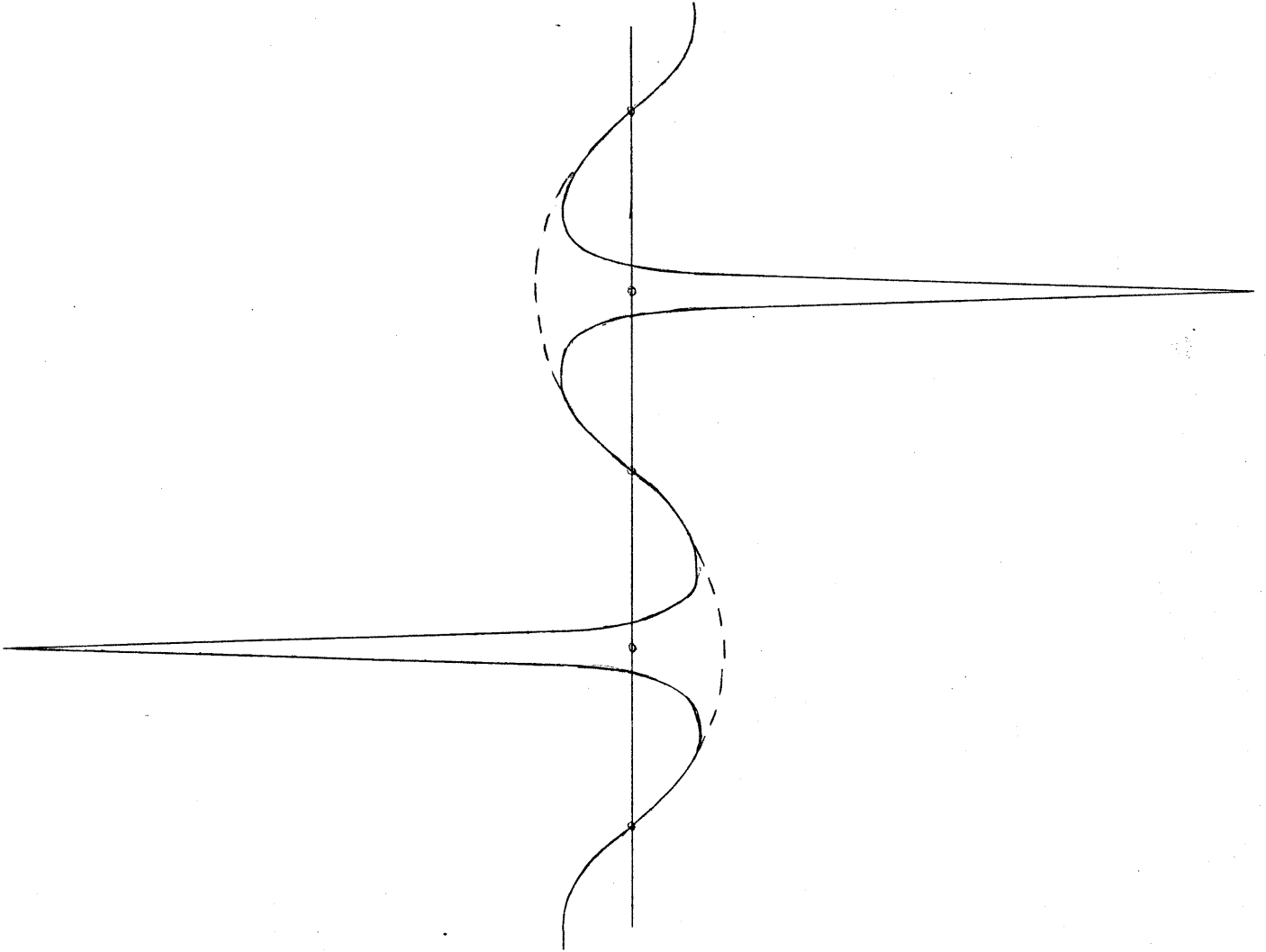


Fig. 12b : Imaginary part along a cube diagonal; \bar{k} on \bar{x} axis, parameter $\zeta = .25$

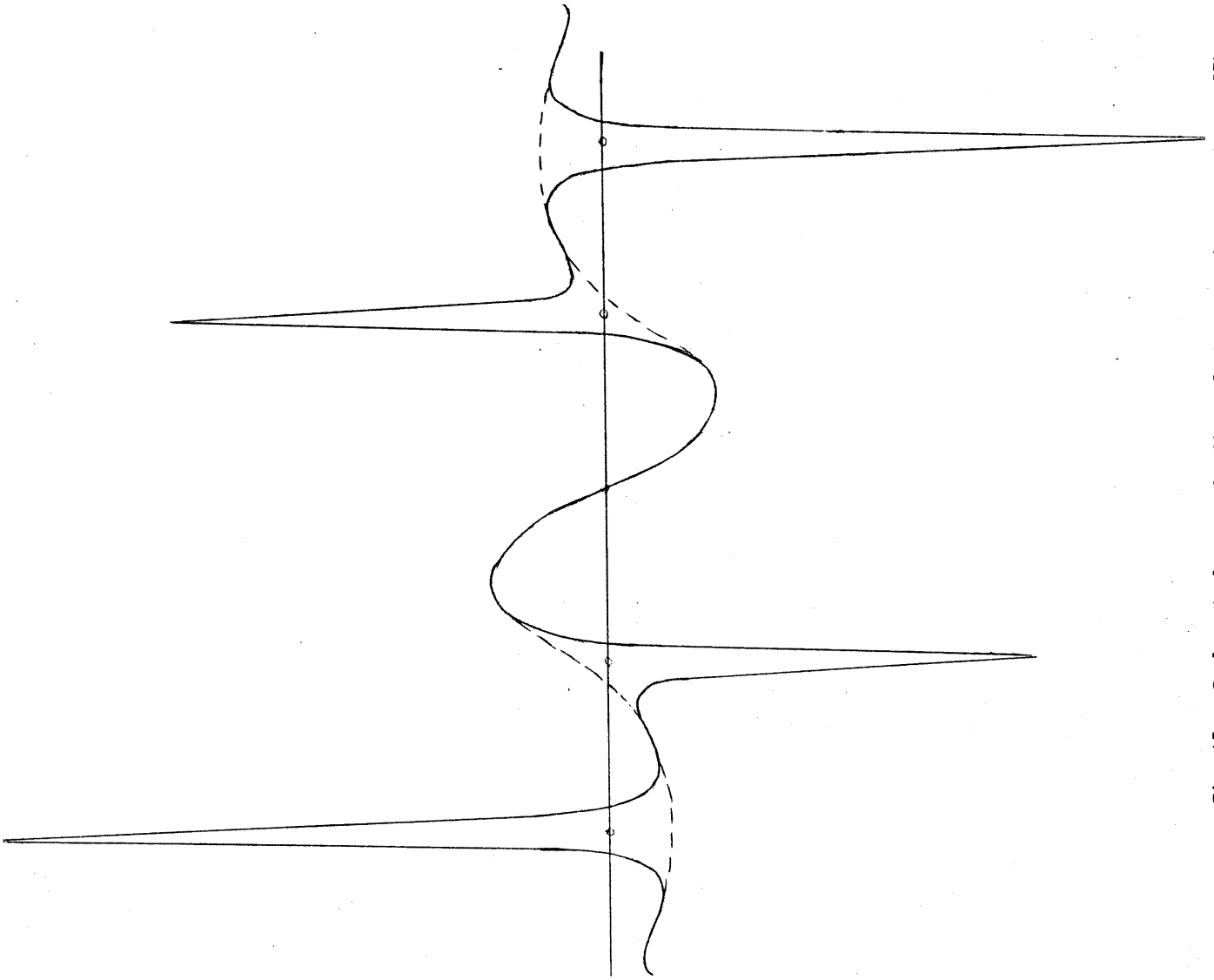


Fig. 13e : Real part along a cube diagonal; $\frac{1}{2}$ on X axis, parameter $\zeta = .375$

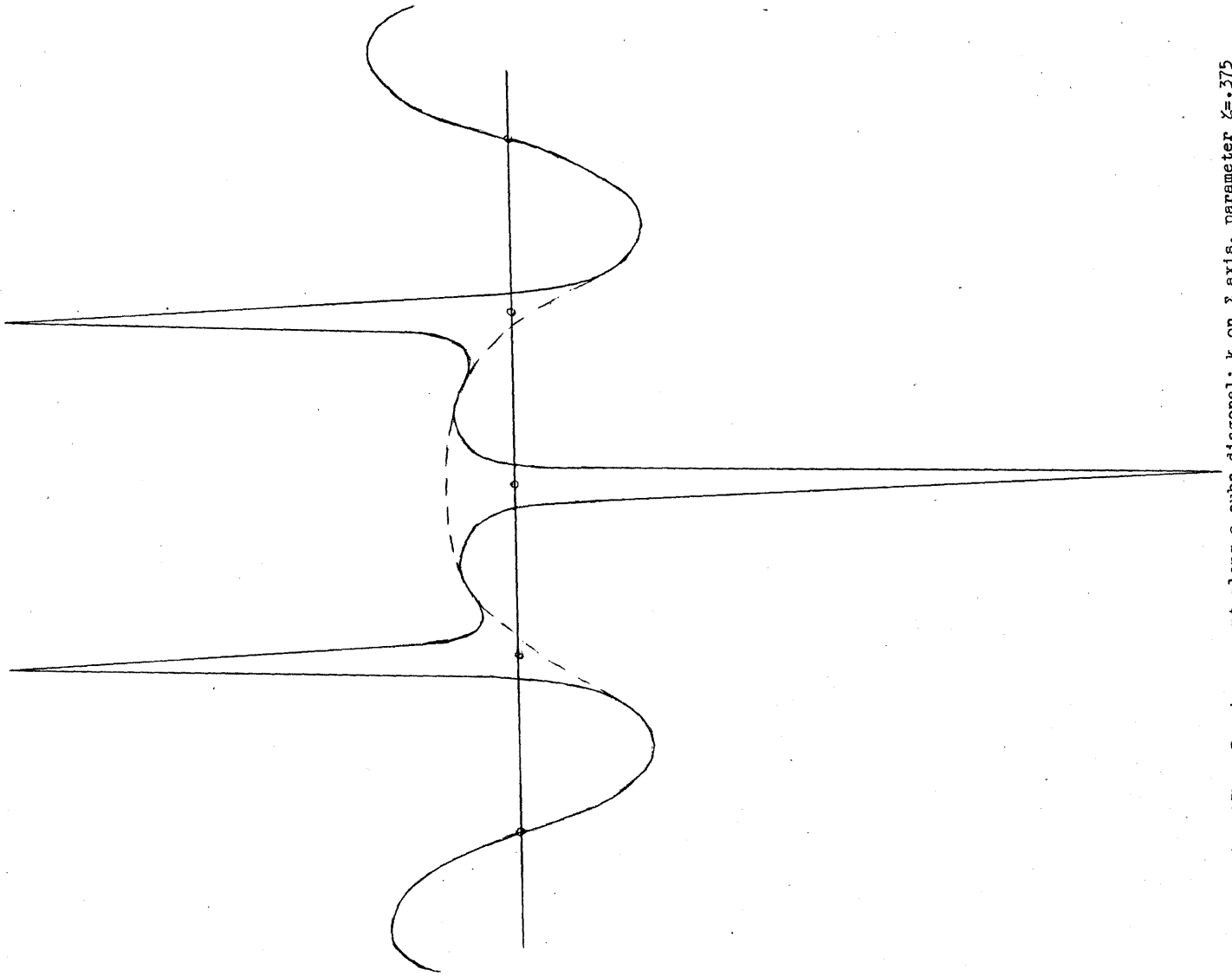


Fig. 13b : Imaginary part along a cube diagonal; k on z axis, parameter $z = 0.375$

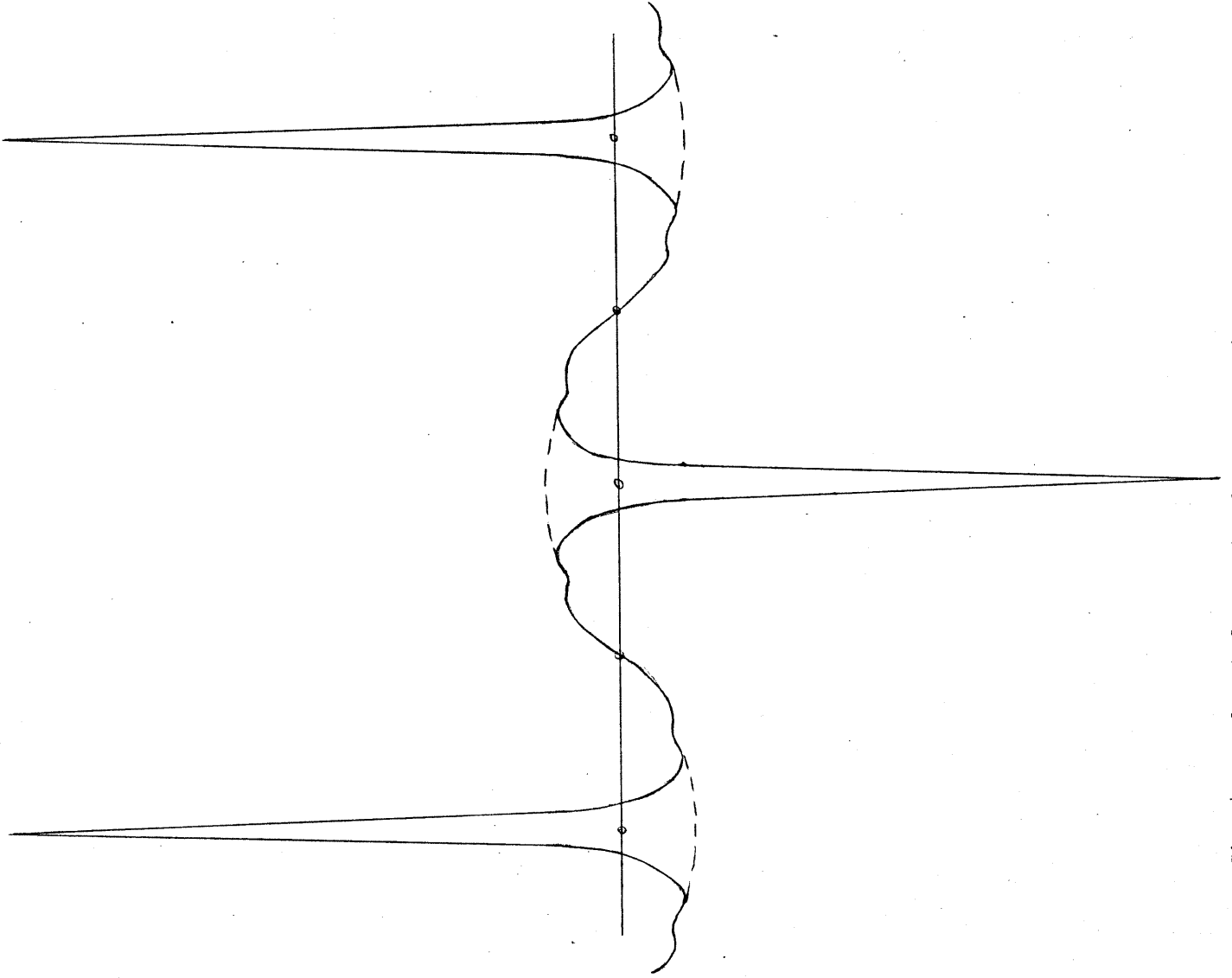


Fig. 14a : Real part along a cube edge ; \bar{k} on Λ axis, parameter $\zeta=0.25$

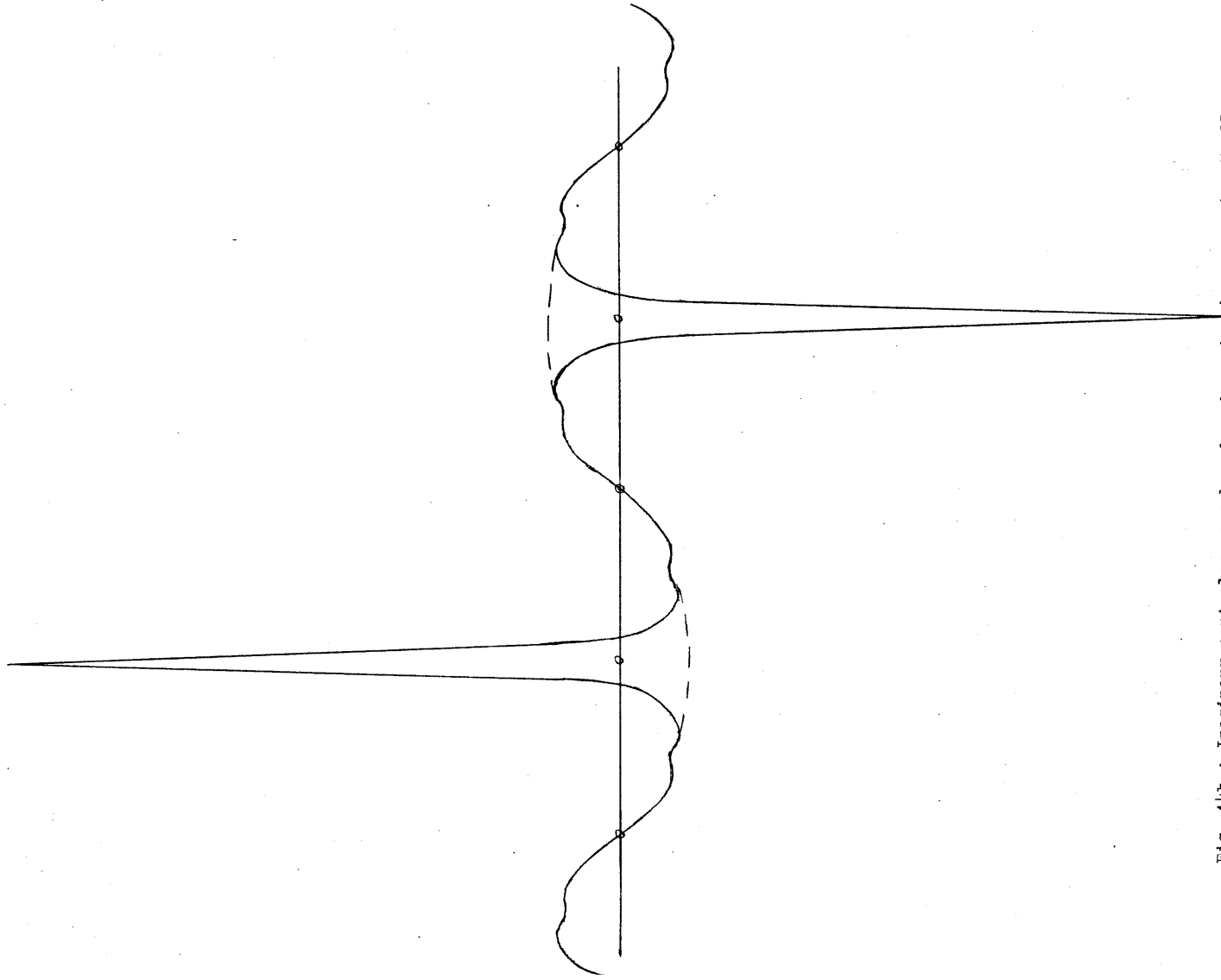


Fig. 14b : Imaginary part along a cube edge; λ on Λ axis, parameter $\zeta = .25$

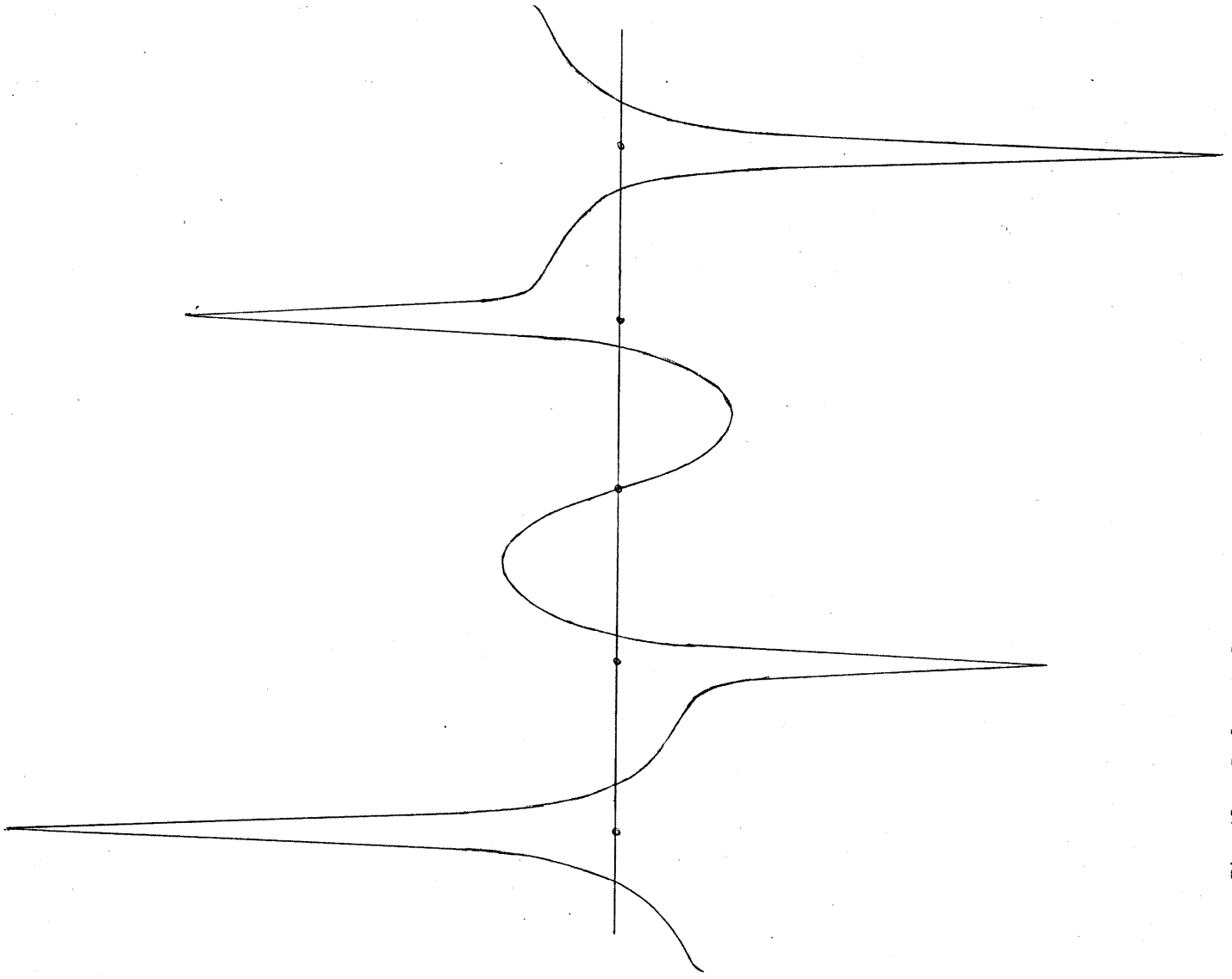


Fig. 15a : Real part along a cube edge; λ on Λ axis, parameter $\zeta = .375$

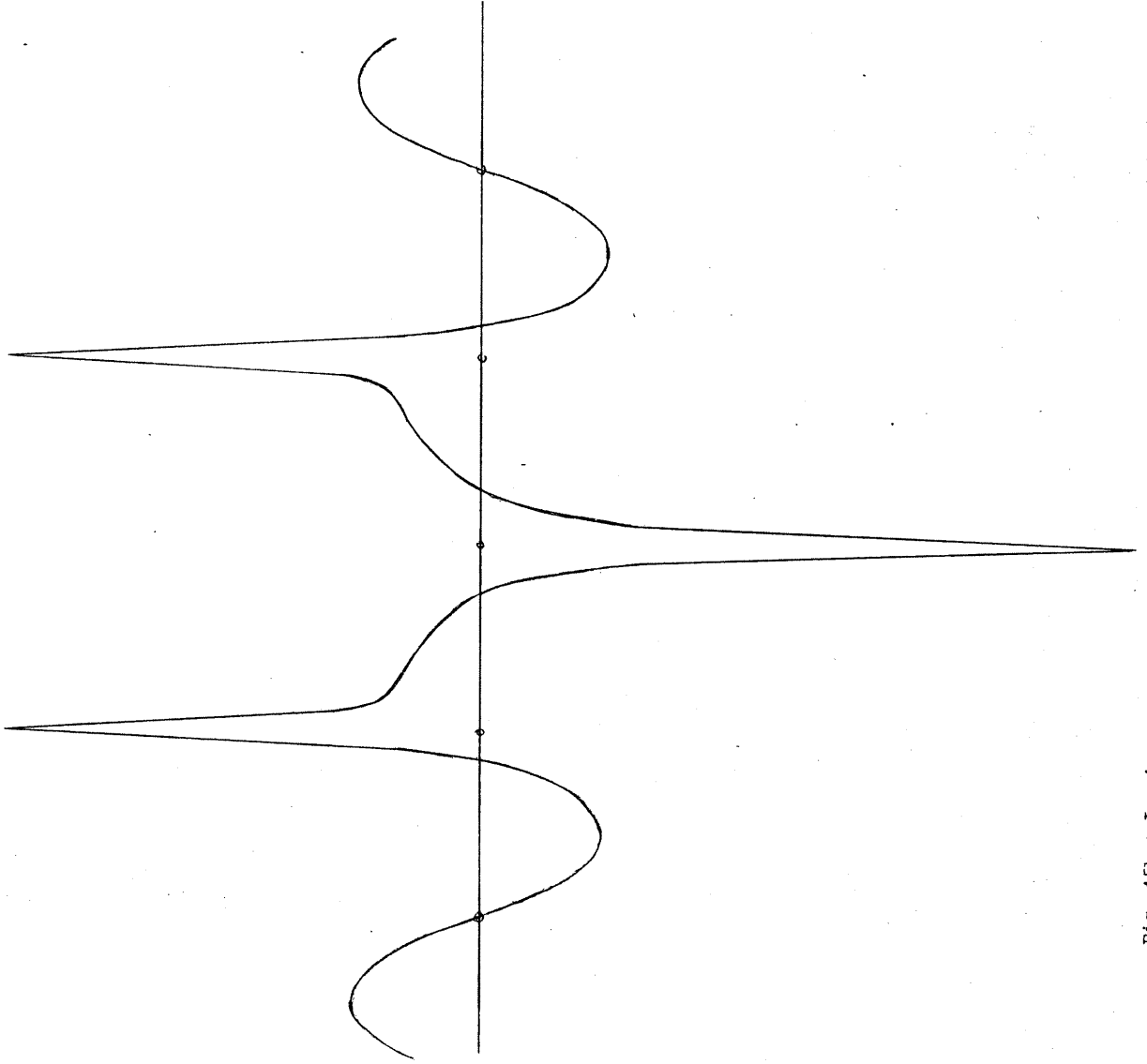


Fig. 15b : Imaginary part along a cube edge; k on Λ axis; parameter $\zeta = .375$

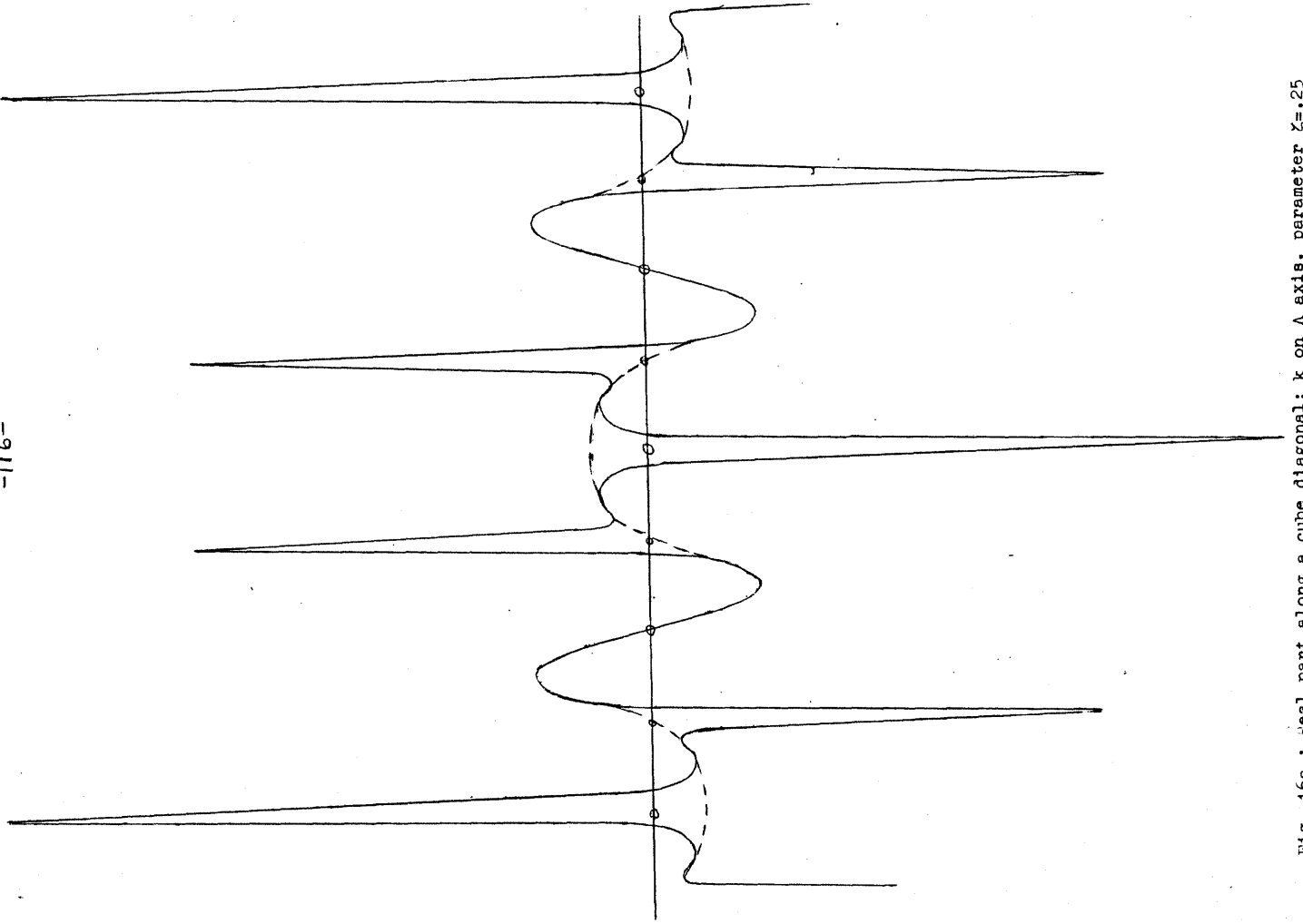


Fig. 16a : Real part along a cube diagonal; λ on Λ axis, parameter $\chi = .25$

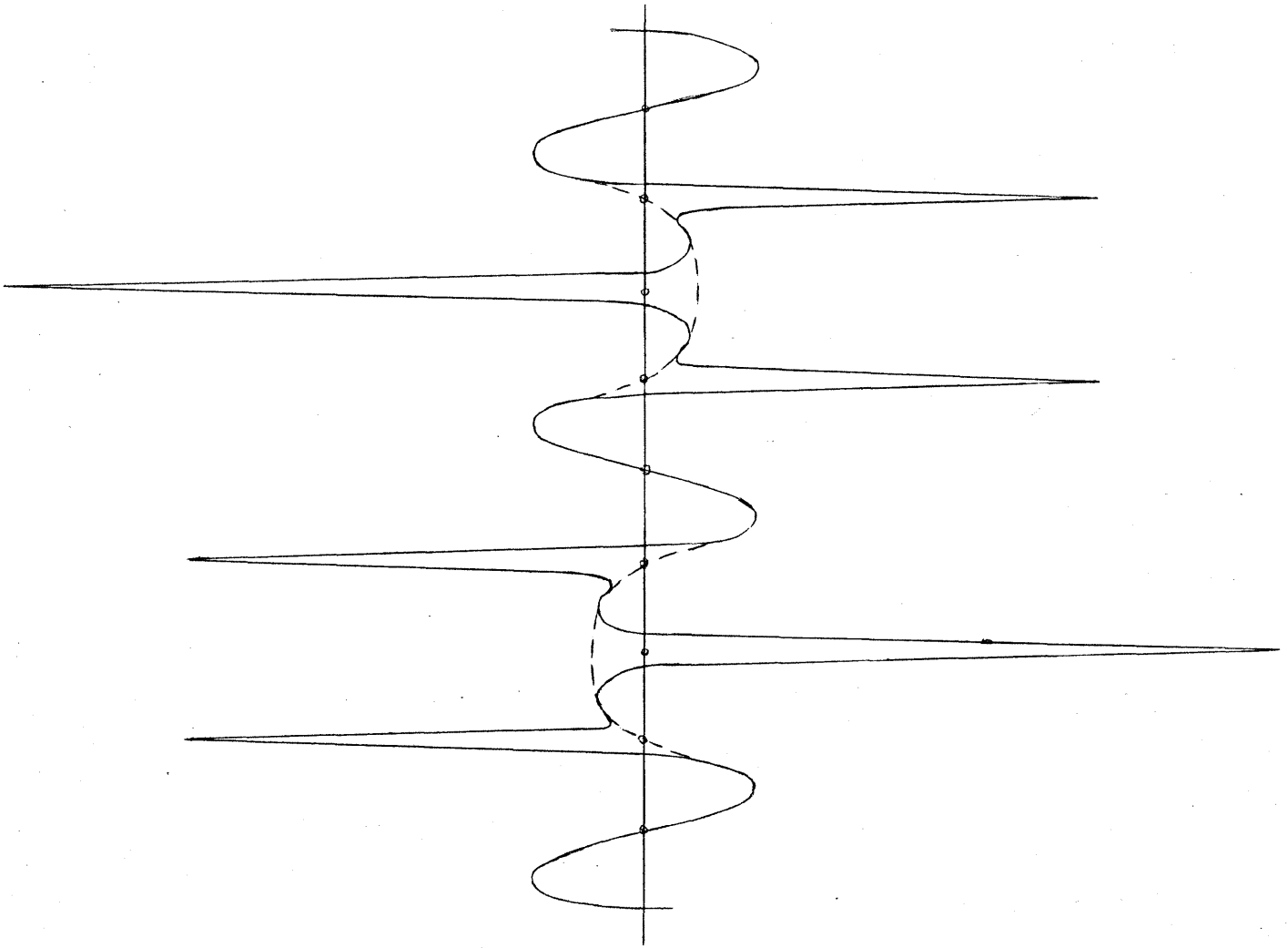


Fig. 16b : Imaginary part along a cube diagonal; k on Λ axis, parameter $\zeta=0.25$

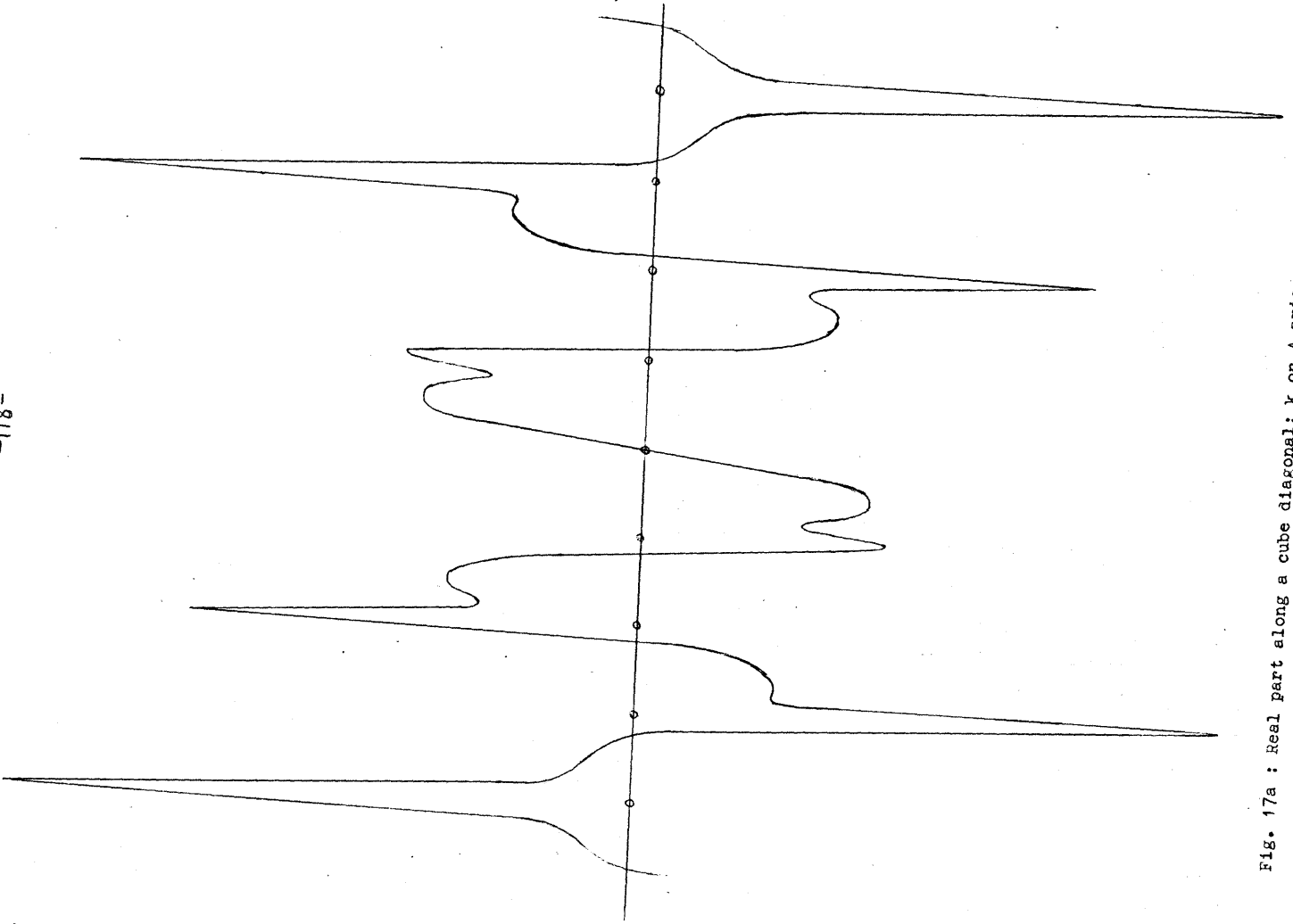


Fig. 17a : Real part along a cube diagonal; λ on Δ axis, parameter $\zeta=0.375$

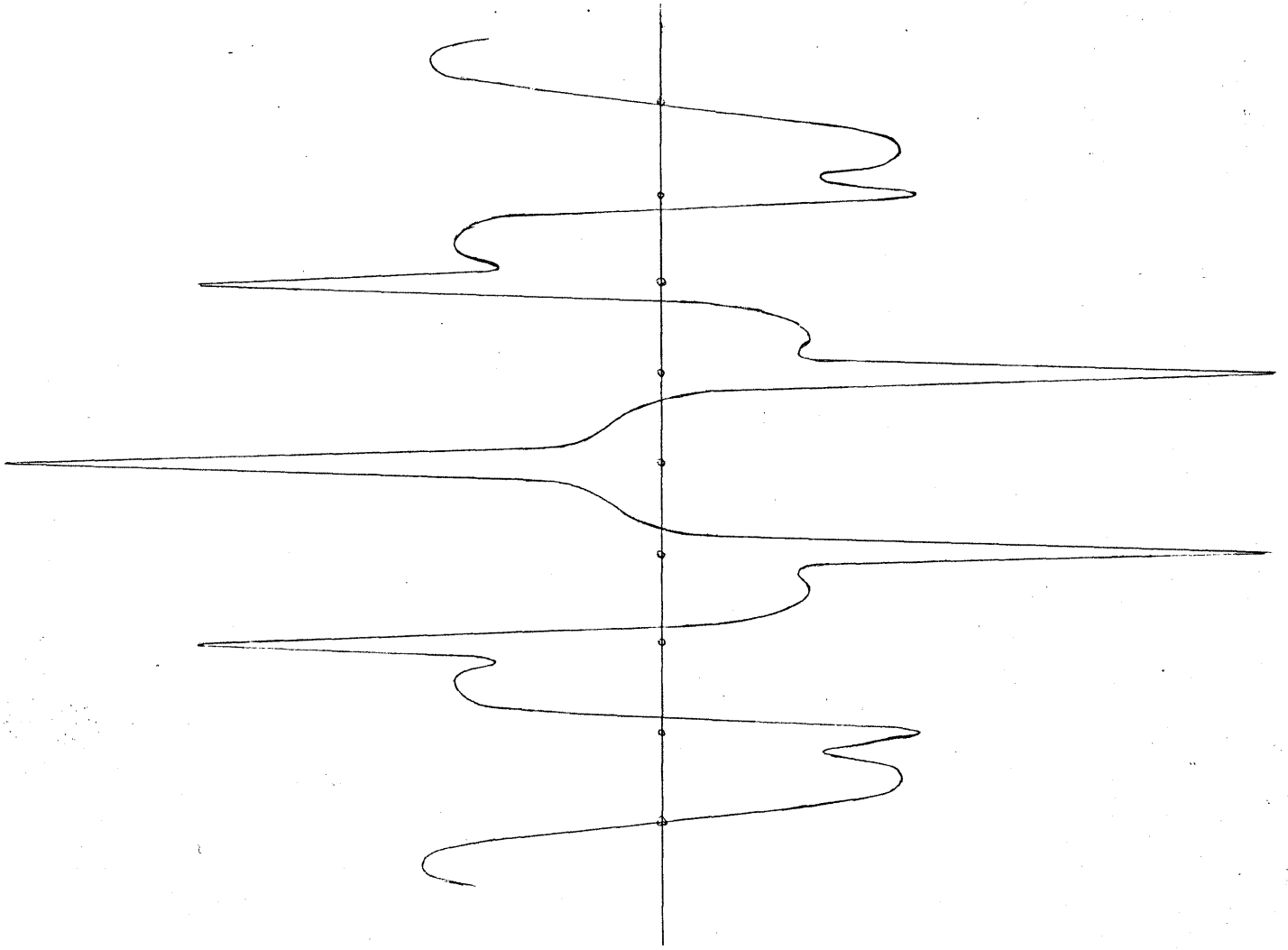


Fig. 17b : Imaginary part along a cube diagonal; k on Λ axis, parameter $\zeta = .375$

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