

ON THE MOMENTUM EIGENFUNCTIONS

FOR THE PERIODIC PROBLEM

A thesis submitted for the Degree  
of Master of Science in the  
University of London

by

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## INTRODUCTION

The problem of calculating the electronic energy levels in solids has attracted great interest, because of its considerable practical importance for a good understanding of the properties of metals and semi-conductors.

Among the methods derived for this purpose, many are based on a plane wave expansion of the electronic wavefunction. With such methods energy and wavefunctions are usually calculated only for a few values of the crystal momentum of the electron. It was pointed out that, from the computation required to find the energy - that is the solution of a determinantal equation - it is possible to derive with little labour the rate of change with crystal momentum, of the energy and wavefunctions, at least for a certain direction of the momentum.

The calculation of these derivatives has not been carried out so far, and the purpose of the present work is to perform it for a simple one-dimensional case, and try to assess the value of the method for a band structure calculation of an actual substance.

CHAPTER I

PRELIMINARY SURVEY

1. The One-Electron Approximation

The need of a method dealing with systems of many electrons has led to the one-electron approximation. This approximation is based on the assumption that the Schrödinger's equation of a system of N electrons can be separated into N Schrödinger's equations of the form:

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + V_i(\underline{r}_i) \right] \psi_i = \epsilon_i \psi_i \quad (1.1)$$

where the function  $V_i(\underline{r}_i)$  is the potential of the  $i$ th electron due to the field of the other electrons. So, each electron is considered as moving in a self-consistent field which takes into account the nuclear attraction and the averaged repulsions of the other electrons.

Hartree has taken the potential  $V_i(\underline{r}_i)$  to be the field of the average charge distribution of the other electrons and given by the formula:

$$V_i(\underline{r}_i) = e^2 \sum_{j \neq i}^N \int \frac{|\psi_j(\underline{r}_j)|^2}{r_{ij}} d\underline{r}_j \quad (1.2)$$

The function  $V_i(\underline{r}_i)$  is a spherically symmetrical one for the atoms, but not for the molecules and solids.

Substituting the value of the potential  $V_i(\underline{r}_i)$  into equation (1.1) the Hartree form of the Schrödinger's equation is obtained:

$$\left[ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + e^2 \sum_{j \neq i}^N \int \frac{|\psi_j(r_j)|^2}{r_{ij}} d\tau_j \right] \psi_i(r_i) = \epsilon_i \psi_i(r_i) \quad (1.3)$$

where  $i = 1, 2, 3, \dots, N$

Now an atom is considered, and a set of approximate wavefunctions  $\psi_i$  is chosen, with which the  $N$  spherically symmetrical potential functions  $V_i(r_i)$  are calculated. Then the Hartree equations can be solved by numerical methods, and with the so found new wave functions the whole procedure is repeated until self-consistency is reached.

Therefore the total wave function  $\Psi$  is written as the product of the calculated eigenfunctions, that is

$$\Psi = \psi_1(r_1) \psi_2(r_2) \dots \psi_N(r_N) \quad (1.4)$$

Considering that this total wave function  $\Psi$  is normalized, the total energy is:  $E = \int \Psi^* H \Psi d\tau$  (1.5)

where the Hamiltonian for the atom is:

$$H = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + \frac{1}{2} \sum_{i \neq j}^N \sum_{j=1}^N \frac{e^2}{r_{ij}} \quad (1.6)$$



Using equations (4) and (6), equation (5) becomes:

$$E = \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{i \neq j}^N \sum_{j=1}^N \iint \frac{e^2}{r_{ij}} |\psi_i(\underline{r}_i)|^2 |\psi_j(\underline{r}_j)|^2 d\underline{r}_i d\underline{r}_j \quad (1.7)$$

that is the total energy of the electrons is the sum of the one-electron eigenvalues, minus the interaction energy of the electrons.

Fock gave another form to the Hartree's equations, by taking into account the Pauli principle, according to which the total wave function must be antisymmetric, that is, it can be expressed in the following determinantal form:

$$\Psi = \begin{vmatrix} \phi_1(\underline{x}_1) & \phi_1(\underline{x}_2) & \dots & \phi_1(\underline{x}_N) \\ \phi_2(\underline{x}_1) & \phi_2(\underline{x}_2) & \dots & \phi_2(\underline{x}_N) \\ \dots & \dots & \dots & \dots \\ \phi_N(\underline{x}_1) & \phi_N(\underline{x}_2) & \dots & \phi_N(\underline{x}_N) \end{vmatrix} \quad (18)$$

where  $\phi_i(\underline{x}_i) = \psi_i(\underline{r}_i) \alpha(j_i)$

is the one-electron wave function, consisting of an orbital and a spin function.



The new equations are called Hartree-Fock equations, and they include an additional term, the exchange term.

The Hartree-Fock equations, in the case of a metal, are:

$$(1.9) \quad \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + \sum_{\alpha} V_{\alpha}(z_i) + e^2 \sum_j^N \left[ \frac{|\psi_j(z_j)|^2}{r_{ij}} \right] \right] \psi_i(z_i) - e^2 \sum_j^N \left[ \frac{\psi_j^*(z_j) \psi_j(z_j) \psi_i(z_i)}{r_{ij} \psi_i(z_i)} \right] \psi_i(z_i) = \epsilon_i \psi_i(z_i)$$

From these equations the total energy of the electrons and nuclei in the metal is found to be:

$$\begin{aligned} E = & \sum_i^N \epsilon_i - \frac{1}{2} \sum_i^N \sum_j^N \iint \frac{e^2}{r_{ij}} |\psi_j(z_j)|^2 |\psi_i(z_i)|^2 dz_i dz_j \\ & + \frac{1}{2} \sum_i^N \sum_j^N \iint \frac{e^2}{r_{ij}} \psi_i^*(z_i) \psi_j^*(z_j) \psi_i(z_i) \psi_j(z_j) dz_i dz_j \\ & + \frac{1}{2} \sum_{a \neq b}^N \sum_{a \neq b}^N \frac{e^2}{R_{ab}} \end{aligned} \quad (1.10)$$

Here it is necessary to say that we are not interested in the total energy but only in its difference from the energy of a system of free atoms. This difference is called cohesive energy and is defined, as the energy required to dissociate a given mass of the solid metal

at the absolute zero of temperature, into free atoms.

Comparing equations (1.7) and (1.10) we notice that equation (1.10) contains two additional terms. The appearance of the fourth term, which gives the potential energy for the Coulomb interaction of the nuclei, is simply due to the fact that we have considered a metal in obtaining the Hartree-Fock energy, and not an atom as we have done for the Hartree energy. But the existence of the third term which is called exchange energy, shows the main difference between the two methods. The exchange energy arises through the use of an antisymmetrical wave function, as we have mentioned before.

Although the Hartree-Fock method is an improvement on the Hartree method for the calculation of the cohesive energy, it still lacks an energy term representing the effects of proper Coulomb correlations. This term, which is called correlation energy, takes into account the correlation between the positions of two electrons with antiparallel spins, while the correlation in the motion of electrons with parallel spins is taken into account automatically by the Pauli principle.

The calculation of the correlation energy is a difficult one. It has been done at first by Wigner using semi-empirical methods.

Pines improved Wigner's results by using the following interpolation formula:

$$W = - \frac{0.88}{r_s + 7.8} \text{ ryd} \quad (1.11)$$

Also Pines, using the idea of plasma oscillations, obtained the formula:

$$W = 0.031 \ln r_s - 0.225 \text{ ryd} \quad (1.12)$$

The quantity  $r_s$  is the so-called atomic radius which is defined by the relation:

$$\frac{4\pi}{3} r_s^3 = \frac{U}{N}$$

where  $U$  is the volume of the metal and  $N$  the number of atoms in the metal.

## 2. The Bravais Lattice

The atoms in a crystal are arranged periodically so that the position of each one (called lattice point) may be obtained from the position of any other by a linear combination of three non-coplanar vectors  $\underline{a}_1$ ,  $\underline{a}_2$  and  $\underline{a}_3$ , that is by the following translation operation:

$$\underline{R}_n = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3 \quad (1.13)$$

where  $\underline{a}_1$  is the shortest translation of an atom's position,  $\underline{a}_2$  the shortest translation not parallel to  $\underline{a}_1$  and  $\underline{a}_3$  the shortest translation not coplaner to  $\underline{a}_1$ ,  $\underline{a}_2$ .

The vectors  $\underline{R}_n$  are called the fundamental vectors

of the lattice. The infinite three-dimensional array of points, thus derived, is called space-lattice, or Bravais lattice after the name of the scientist who has proved that there are only fourteen such lattices. A crystal can be divided into unit cells each one containing either one atom (nonatomic lattice) or more than one atom (polyatomic lattice). Strictly the unit cell is the parallelepiped constructed of  $\underline{a}_1$ ,  $\underline{a}_2$ ,  $\underline{a}_3$ . The polyatomic lattice is described as a Bravais lattice with a "basis" which gives the positions of the atoms.

An alternative construction for the unit cell has been made by Wigner and Seitz in the following way: We draw lines connecting an atom to its nearest and next nearest neighbour and consider the planes bisecting these lines perpendicularly. Now the smallest polyhedron surrounding the central atom and bounded by these planes is the Wigner-Seitz cell. This definition applies to monatomic substances.

The simplest crystal structure is the simple cubic lattice whose W-S cell is a cube. It was believed that no metal crystallizes in this structure, but now it seems demonstrated that Polonium must be classified in the simple cubic lattice.

A lot of metals have the crystal structure of the face centred and body centred cubic lattices. The first



one, whose Wigner-Seitz cell is a rhombododecahedron, is described as a Bravais lattice having edges

$$\begin{aligned}\underline{a}_1 &= \frac{a}{2}(\underline{i} + \underline{j}) \\ \underline{a}_2 &= \frac{a}{2}(\underline{j} + \underline{k}) \\ \underline{a}_3 &= \frac{a}{2}(\underline{k} + \underline{i})\end{aligned}\tag{1.14}$$

and the second, where Wigner-Seitz cell is a truncated octahedron, is described as a Bravais lattice having edges

$$\begin{aligned}\underline{a}_1 &= \frac{a}{2}(-\underline{i} + \underline{j} + \underline{k}) \\ \underline{a}_2 &= \frac{a}{2}(\underline{i} - \underline{j} + \underline{k}) \\ \underline{a}_3 &= \frac{a}{2}(\underline{i} + \underline{j} - \underline{k})\end{aligned}\tag{1.15}$$

In the fcc lattice each atom has twelve nearest neighbours at distance  $a/\sqrt{2}$  and in the bcc lattice each atom has eight nearest neighbours at distance  $\frac{\sqrt{3}}{2}a$  and six next nearest neighbours at distance  $a$ , where  $a$  is the length of the cube's edge.

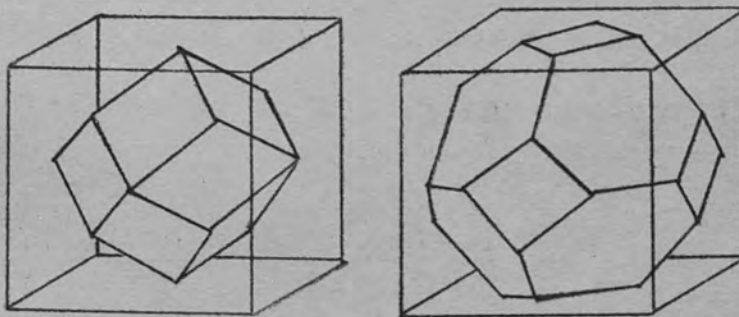


Fig. 1

W.-S. cells for (a) fcc str., and (b) for bcc str. enclosed in non-primitive unit cells of side  $2a$ .



### 3. Periodic Boundary Conditions and Form of the Wave Functions

Considering the periodic electrostatic field in which an electron moves within a crystal and neglecting any surface effects, the potential energy of the electron is periodic with the periodicity of the lattice, that is

$$V(\underline{r}) = V(\underline{r} + \underline{R}n) \quad (1.16)$$

Schrodinger's equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(\underline{r})] \psi = 0 \quad (1.17)$$

can be solved after applying periodic boundary conditions. These consist of the requirement that every admissible wave function shall be periodic of the following form:

$$\psi(\underline{r}) = \psi(\underline{r} + N_1 \underline{a}_1) = \psi(\underline{r} + N_2 \underline{a}_2) = \psi(\underline{r} + N_3 \underline{a}_3) \quad (1.18)$$

where  $\underline{a}_1$ ,  $\underline{a}_2$  and  $\underline{a}_3$  are the edges of the unit cell and  $N_1$ ,  $N_2$  and  $N_3$  are integers whose values are taken large so that the intensive properties of the crystal are independent of the particular value of them.

Block proved that the assumption of periodic boundary conditions leads to a solution of Schrodinger's equation of the form,

$$\psi_{\underline{k}}(\underline{r}) = e^{i \underline{k} \cdot \underline{r}} u_{\underline{k}}(\underline{r}) \quad (1.19)$$

which is of the running wave type and where  $\underline{k}$  is called the crystal momentum considered as a triplet of quantum numbers. The function  $U_{\underline{k}}(\underline{r})$  is periodic with the

periodicity of the lattice, that is

$$U_{\underline{k}}(\underline{r}) = U_{\underline{k}}(\underline{r} + \underline{R}n) \quad (1.20)$$

Obviously the same consideration applies to the one-dimensional case. So we shall give a proof of Bloch's theorem in one dimension. Schrödinger's equation is now

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (1.21)$$

where the potential energy is periodic with period the distance  $a$  between the atoms, that is

$$V(x) = V(x + a) \quad (1.22)$$

In order to shorten the algebra we can make the substitution

$$\frac{2m}{\hbar^2} (E - V) = f(x) \quad (1.23)$$

$$\text{where } f(x) = f(x + a) \quad (1.24)$$

Now equation (1.21) becomes

$$\frac{d^2\psi}{dx^2} + f(x)\psi = 0 \quad (1.25)$$

Equation (1.25), as a second order linear differential one, has two independent solutions  $\psi_1(x)$  and  $\psi_2(x)$  and the general solution is of the form

$$\psi(x) = K_1\psi_1(x) + K_2\psi_2(x) \quad (1.26)$$

By putting  $\psi_1$  and  $\psi_2$  in (1.25) and multiplying by  $\psi_2, \psi_1$  one obtains

$$\begin{aligned}\psi_1 \psi_2'' + f \psi_1 \psi_2 &= 0 \\ \psi_2 \psi_1'' + f \psi_2 \psi_1 &= 0\end{aligned}\tag{1.27}$$

Then subtracting

$$\psi_1 \psi_2'' - \psi_2 \psi_1'' = 0\tag{1.28}$$

and integrating

$$W = \begin{vmatrix} \psi_1 & \psi_2 \\ \psi_1' & \psi_2' \end{vmatrix} = \text{constant}\tag{1.29}$$

Now if  $\psi(x)$  is a solution of (1.25),  $\psi(x+a)$  is also a solution which can be expressed as a linear combination of  $\psi_1(x)$  and  $\psi_2(x)$ , therefore

$$\begin{aligned}\psi_1(x+a) &= A \psi_1(x) + B \psi_2(x) \\ \psi_2(x+a) &= C \psi_1(x) + D \psi_2(x)\end{aligned}\tag{1.30}$$

By repeating the same procedure as before we find

$$W = \begin{vmatrix} A \psi_1 + B \psi_2 & C \psi_1 + D \psi_2 \\ A \psi_1' + B \psi_2' & C \psi_1' + D \psi_2' \end{vmatrix} = \begin{vmatrix} \psi_1 & \psi_2 \\ \psi_1' & \psi_2' \end{vmatrix} \times \begin{vmatrix} A & C \\ B & D \end{vmatrix}\tag{1.31}$$

and since  $W$  has the same value at both  $x$  and  $x+a$  we obtain

$$AD - BC = 1\tag{1.32}$$

In order to find the suitable independent solutions, equations (1.30) are written

$$\begin{aligned}A \psi_1 + B \psi_2 &= \lambda \psi_1 \\ C \psi_1 + D \psi_2 &= \lambda \psi_2\end{aligned}\tag{1.33}$$

where  $\lambda$  is a constant.

For non zero solutions of the system (1.33) we must have

$$\begin{vmatrix} A - \lambda & B \\ C & D - \lambda \end{vmatrix} = 0 \quad (1.34)$$

and using (1.32) we get

$$\lambda^2 - (A + D)\lambda + 1 = 0 \quad (1.35)$$

Now we put  $\lambda = e^\alpha$  so equation (1.35) becomes

$$\cos h\alpha = \frac{1}{2} (A + D) \quad (1.36)$$

For  $\frac{1}{2} (A + D) > 1$   $\alpha$  is real and the independent solutions are

$$\begin{aligned} \psi_1(x + a) &= e^\alpha \psi_1(x) \\ \psi_2(x + a) &= e^{-\alpha} \psi_2(x) \end{aligned} \quad (1.37)$$

For  $\frac{1}{2} (A + D) < 1$ ,  $\alpha$  is pure imaginary and writing  $\alpha = ika$  where  $k$  is real, the independent solutions are

$$\begin{aligned} \psi_1(x + a) &= e^{ika} \psi_1(x) \\ \psi_2(x + a) &= e^{-ika} \psi_2(x) \end{aligned} \quad (1.38)$$

The solutions (1.37) are not bounded and so they do not correspond to stationary states of electrons in the lattice. On the contrary the solutions (1.38) are bounded and therefore they have a physical meaning, corresponding to stationary states.

The solutions (1.38) are put in the equivalent form

$$\psi_k(x) = e^{\pm ikx} u_k(x) \quad (1.39)$$

which clearly satisfies (1.38) where  $u_k(x) = u_k(x + a)$  and which expresses the Bloch's theorem in one dimension known to the mathematicians as Floquet's theorem.



#### 4. The Reciprocal Lattice and the Brillouin Zones

In the previous Section a new vector  $\underline{k}$  has been introduced, as a set of 3 quantum numbers. This vector belongs to the space of the reciprocal lattice which is defined as follows.

A set of vectors  $\underline{b}_1, \underline{b}_2, \underline{b}_3$  and the primitive translations  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  of the Bravais lattice are required to satisfy the following condition:

$$\underline{a}_i \cdot \underline{b}_j = 2\pi \delta_{ij} \quad (i, j = 1, 2, 3) \quad (1.39)$$

where  $\delta_{ij}$  is the Kronecker's delta.

The meaning of the relation (1.39) is that the vectors  $\underline{b}_1, \underline{b}_2, \underline{b}_3$  are perpendicular to the planes of the axes  $\underline{a}_1, \underline{a}_2, \underline{a}_3$ . The vectors  $\underline{b}_1, \underline{b}_2, \underline{b}_3$  are called reciprocal vectors and the linear combination of them:

$$\underline{K}_m = m_1 \underline{b}_1 + m_2 \underline{b}_2 + m_3 \underline{b}_3 \quad (1.40)$$

defines a set of points which forms what is called reciprocal lattice, with  $\underline{K}_m$  the fundamental vector of this lattice.

As it happens to the ordinary space, elementary cells are defined in the reciprocal space as well. The cell analogous to the Wigner-Seitz cell is called first Brillouin zone, and remains invariant under the symmetry operations of the crystal.



In order to consider the reciprocal lattice, for the face-centred and body-centred cubic lattices, equation (1.39) is written in the equivalent forms:

$$\underline{b}_1 = \frac{2\pi}{D} \underline{a}_2 \times \underline{a}_3, \quad \underline{b}_2 = \frac{2\pi}{D} \underline{a}_3 \times \underline{a}_1, \quad \underline{b}_3 = \frac{2\pi}{D} \underline{a}_1 \times \underline{a}_2 \quad (1.41)$$

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

Then substituting  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  from equations (1.14) and (1.15) in equations (1.43) we find that,

$$\underline{b}_1 = \frac{2\pi}{a} (-\underline{i} + \underline{j} + \underline{k}), \quad \underline{b}_2 = \frac{2\pi}{a} (\underline{i} - \underline{j} + \underline{k}), \quad \underline{b}_3 = \frac{2\pi}{a} (\underline{i} + \underline{j} - \underline{k}) \quad (1.42)$$

for the face-centred lattice, and

$$\underline{b}_1 = \frac{2\pi}{a} (\underline{j} + \underline{k}), \quad \underline{b}_2 = \frac{2\pi}{a} (\underline{k} + \underline{i}), \quad \underline{b}_3 = \frac{2\pi}{a} (\underline{i} + \underline{j}) \quad (1.43)$$

for the body-centred lattice.

This means that to a face-centred Bravais lattice corresponds a body-centred reciprocal lattice and vice versa. So the first Brillouin zone for a body-centred cubic lattice is a rhombododecahedron and for a face-centred cubic lattice a truncated octahedron, while for a simple cubic lattice is also a cube. (Figures)1.

In the one-dimensional case the periodicity  $a$  for the ordinary space becomes  $\frac{2\pi}{a}$  for the reciprocal space. So the first Brillouin zone in one dimension can be represented by a segment on which  $k$  varies from  $k = -\pi/a$  to  $k = \pi/a$ . In the same way one can define a second, third, etc. Brillouin zone as it is shown in figure 2.

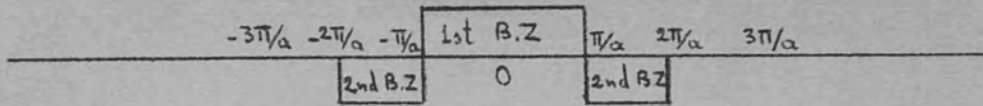


Figure 2.

We can also define 2nd, 3rd, etc. Brillouin zones in the three dimensions by considering the volumes in the reciprocal space bounded by the surfaces which are the perpendicular bisectors of all vectors  $\underline{K}_m$ . These zones are identical to the first Brillouin zone, since any point of reciprocal space may be obtained by a lattice translation from a point in the first Brillouin zone. So they all have the same volume  $\Omega_B$  which, due to the definition of reciprocal lattice (equation (1.39)), satisfies the following condition:

$$\Omega \Omega_B = (2\pi)^3 \quad (1.44)$$

where  $\Omega$  is the volume of the elementary cell in ordinary space.

## 5. Reduced and Extended k -space

The most important problem of band theory is to find the relation between  $E$  and  $\underline{k}$ . There are two different ways to approach this problem. The first is to restrict the  $\underline{k}$  vectors to the first Brillouin zone and add to the solution of Schrodinger's equation a suffix  $\ell$  denoting

the energy states, that is

$$\psi_{\underline{k}l}(\underline{r}) = e^{i\underline{k}\underline{r}} U_{\underline{k}l}(\underline{r}) \quad (1.45)$$

The energy is then a multivalued function of  $\underline{k}$ . This method is called "reduced zone scheme" and can be used for either a free or a bound electron.

The second way is to make the energy a single-valued function of  $\underline{k}$  by letting  $\underline{k}$  be extended throughout the 1st, 2nd, 3rd, etc. Brillouin zones. Now the energy has a discontinuity on the boundaries of each Brillouin zone. This procedure is called "extended zone scheme" and it seems to apply only to the free electron case.

In order to show the difference of the two schemes in a simple way, we shall consider the one-dimensional case for the nearly free electron approximation. Schrödinger's equation gives for the energies the following solutions

$$E_e(\underline{k}) = \frac{\hbar^2}{2m} \left( k + \frac{2\pi l}{a} \right)^2 + V_0 \quad (1.46)$$

where  $l$  takes the values  $0, 1, 2, \dots$  and  $V_0$  is a small periodic potential. Using equation (1.46) one can find the following diagrams of  $E_q(k)$  for the two schemes.

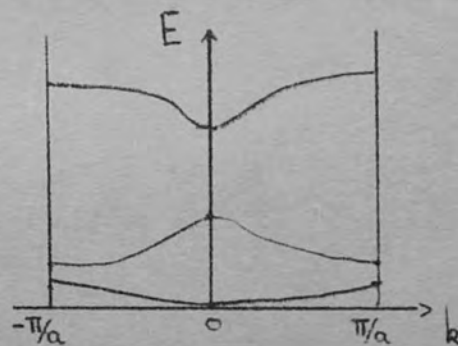


Fig 3 (a)

Fig 3 (b)

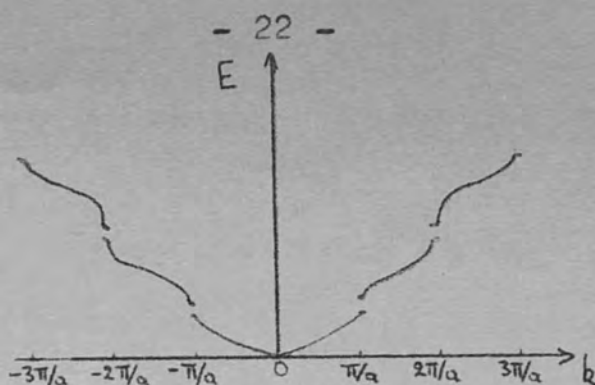


Diagram (a) shows that the energy distribution is broken into continuous bands of energy levels separated by forbidden energy regions. Diagram(b) shows a discontinuity on the boundaries of each Brillouin zone.

Both the reduced and extended zone schemes are equally valid and which one is used is a matter of convenience. We often jump from the one scheme to the other as we are going to do in the present work. When the approximation of nearly free electrons is not valid, it is not possible to assign a given band to a given Brillouin zone; the energy is then multivalued in each zone and there is great advantage in using the reduced zone scheme.

## 6. The Operations of the Point Group

In addition to the translation, crystals possess the symmetry operations of the point group, which consist of rotations and reflections that leave the crystal invariant. With respect to the operations of



the point group we are able to classify the electronic states.

Since the electronic states of the crystals are identified by  $\underline{k}$ -vectors, we shall investigate the symmetry operations which leave the given  $\underline{k}$  invariant. These operations form the point group of the given  $\underline{k}$ , and their number varies for the different  $\underline{k}$ -points. For the cubic structures at  $\underline{k} = 0$ , there are 48 operations which transform a cube into itself. These operations form the full cubic group and are the following:

- 1) The identity E which leaves the cube in its original position.
- 2) Six rotations of  $\pi/2$  about an axis of fourfold symmetry. Class  $C_4$ .
- 3) Three rotations of  $\pi$  about the same axis. Class  $C_4^2$ .
- 4) Six rotations of  $\pi$  about an axis of twofold symmetry. Class  $C_2$ .
- 5) Eight rotations of  $2\pi/3$  about an axis of threefold symmetry. Class  $C_3$ .
- 6) The inversion with respect to the origin J.
- 7) Combination of (2) with the inversion. Class  $JC_4$ .
- 8) " " (3) " " " "  $JC_4^2$ .
- 9) " " (4) " " " "  $JC_2$ .
- 10) " " (5) " " " "  $JC_3$ .

Therefore the 48 operations of the full cubic group are divided into 10 classes.

The Hamiltonian operator commutes with each operation of the point group, though these operators do not all commute with each other. This leads to the conclusion that the energy must have full cubic symmetry in  $\underline{k}$ -space. So we need to determine the E- $\underline{k}$  relations in only the 1/48 of the first Brillouin zone.

In the case of a one-dimensional periodic chain of atoms, there are two types of symmetry operations which leave the potential unchanged. These are indicated by the linear transformations.

$$x' = x \pm ma$$

$$x' = -x \pm ma$$

where  $a$  is the distance between two successive atoms of the chain and  $m$  an arbitrary integer.

Therefore the group of operations that leaves the lattice invariant includes the identity and the inversion. So by the inversion operation we obtain that the energy is an even function of  $k$ , as it will be proved in Chapter II. We shall also see in the next chapter that what we define there as momentum eigenfunctions, are even functions of  $k$  for odd order of bands and are odd functions of  $k$  for even order of bands.

In writing this chapter we had in mind the following references 3, 4, 5, 8, 9, 10, 12, 13, 14.

CHAPTER II

1. Schrödinger's equation in momentum space

There are three approaches to the problem of solving the Schrödinger's equation for an electron moving in a periodic potential. The first is the well known cellular method of Wigner and Seitz. The second is the atomic orbitals approximation which considers the electrons as tightly bound and their wave functions only slightly overlapping, and the third is the nearly free-electron approximation which assumes that the electrons' wave functions can be represented, as a first approximation, by plane waves.

In the following work we shall adopt the standpoint of the free-electron approximation and shall be concerned with the study of certain properties of the so-called momentum eigenfunctions, which are defined in the following way:

Schrödinger's equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V(\underline{r})] \psi = 0 \quad (2.1)$$

with the potential  $V(\underline{r}) = V(\underline{r} + \underline{R}_n)$  (2.2)

has, according to Bloch's theorem, the solution of the form

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\underline{r}} U_{\underline{k}}(\underline{r}) \quad (2.3)$$

The function  $U_{\underline{k}}(\underline{r})$  is periodic with the periodicity of the lattice, that is

$$U_{\underline{k}}(\underline{r}) = U_{\underline{k}}(\underline{r} + \underline{R}_n) \quad (2.4)$$

Therefore  $U_{\underline{k}}(\underline{r})$  can be expanded in a Fourier series in ordinary space and in terms of the reciprocal lattice vectors  $\underline{K}_n$ , that is

$$U_{\underline{k}}(\underline{r}) = \sum_{\underline{K}_n} v_{\underline{k}}(\underline{K}_n) e^{i\underline{K}_n \cdot \underline{r}} \quad (2.5)$$

with 
$$v_{\underline{k}}(\underline{K}_n) = \frac{1}{\Omega} \int_{\text{unit cell}} U_{\underline{k}}(\underline{r}) e^{-i\underline{K}_n \cdot \underline{r}} d\underline{r} \quad (2.6)$$

The integration is over the unit cell of volume  $\Omega$  in ordinary space, because the definition of  $\underline{K}_n$  (Chapter I, eq. (4.1)) provides that the waves  $e^{i\underline{K}_n \cdot \underline{r}}$  form a complete orthogonal system within the unit cell.

Using equations (2.3) and (2.5) the Fourier expansion of the wave function  $\psi_{\underline{k}}(\underline{r})$  is obtained, that is

$$\psi_{\underline{k}}(\underline{r}) = \sum_{\underline{K}_n} v(\underline{k} + \underline{K}_n) e^{i(\underline{k} + \underline{K}_n) \cdot \underline{r}} \quad (2.7)$$

with 
$$v(\underline{k} + \underline{K}_n) = \frac{1}{\Omega} \int_{\text{unit cell}} \psi_{\underline{k}}(\underline{r}) e^{-i(\underline{k} + \underline{K}_n) \cdot \underline{r}} d\underline{r} \quad (2.8)$$

where  $\underline{k}$  is a particular point in reciprocal space.

$\underline{K}_n$  are the fundamental vectors of the reciprocal lattice and  $\Omega$  is the volume of the unit cell in ordinary space.

The Fourier coefficients  $v(\underline{k} + \underline{K}_n)$  is what we call



momentum eigenfunctions. They represent the probability of finding the electron with a given momentum, in the same way as the ordinary eigenfunction is the probability of finding the electron with a given coordinate.

The functions  $V(\underline{k} + \underline{K}n)$  may be considered centred at any lattice point  $\underline{K}n$  but they are all identical for the same band. Therefore  $V$  is considered as a continuous function of  $\underline{k}$ , defining completely the electronic properties at any band.

We ignore here questions of degeneracy since we shall be dealing with a one-dimensional case when all the bands are non-degenerate when spin is neglected.

There is also a normalization condition for the momentum eigenfunctions, that is

$$\sum_{\underline{K}n} V^*(\underline{k} + \underline{K}n)V(\underline{k} + \underline{K}n) = \frac{1}{\Omega} \quad (2.9)$$

or

$$\int_{-\infty}^{+\infty} V^2(\underline{k})d\underline{k} = \frac{8\pi^3}{\Omega^2}$$

which is found from equation (2.8) after normalizing to 1, in the unit cell, the wave function  $\psi_{\underline{k}}(\underline{r})$ .

The periodic potential  $V(\underline{r})$ , exactly as the function  $U_{\underline{k}}(\underline{r})$ , may be expanded in a Fourier series in ordinary space and in terms of the reciprocal

lattice vectors  $\underline{K}_n$  that is,

$$V(\underline{r}) = \sum_{\underline{K}_n} W(\underline{K}_n) e^{i\underline{K}_n \cdot \underline{r}} \quad (2.10)$$

with 
$$W(\underline{K}_n) = \frac{1}{\Omega} \int_{\text{unit cell}} V(\underline{r}) e^{-i\underline{K}_n \cdot \underline{r}} d\underline{r} \quad (2.11)$$

Using modified atomic units, that is, for the energy 1 rydberg =  $\frac{me^4}{2\hbar^2}$  and for the length 1 Bohr unit =  $\frac{\hbar^2}{me^2}$ , Schrödinger's equation (2.1) is written in the form

$$-\nabla^2 \psi + V\psi = E\psi \quad (2.12)$$

Now substituting equations (2.7) and (2.10) into equation (2.12) multiplying by  $e^{-i(\underline{k} + \underline{K}_i) \cdot \underline{r}}$  and integrating over the unit cell, we obtain

$$\left[ |\underline{k} + \underline{K}_i|^2 - E \right] V(\underline{k} + \underline{K}_i) + \sum_{\underline{K}_m} W(\underline{K}_m) V(\underline{k} + \underline{K}_i - \underline{K}_m) = 0 \quad (2.13)$$

which is called Schrödinger's equation in momentum space and is, in fact, a system of homogeneous algebraic equations for the  $V(\underline{k} + \underline{K}_i)$ . Therefore this system has non-zero solutions only if the determinant of the coefficients  $V(\underline{k} + \underline{K}_i)$  vanishes. This determinant gives an equation of infinite degree, determining the energies  $E_n(\underline{k})$  for a given  $\underline{k}$ .

The solutions depend on the lattice of points  $\underline{k} + \underline{K}_i$  where  $\underline{K}_i$  takes all values of the reciprocal

lattice. Considering a new  $\underline{k}$ , given by  $\underline{k}' = \underline{k} + \underline{K}n$ , the lattice of points  $\underline{k}' + \underline{K}i$  comprises the same points as the lattice  $\underline{k} + \underline{K}n$ . Using Bloch's theorem we prove that the solutions of Schrödinger's equation for  $\underline{k}'$  must be identical with those of  $\underline{k}$ , that is for  $\underline{k}' = \underline{k} - \underline{K}n$

$$\begin{aligned} \psi_{\underline{k}}(\underline{r}) &= e^{i\underline{k}\underline{r}} U_{\underline{k}}(\underline{r}) = e^{i(\underline{k}-\underline{K}n)\cdot\underline{r}} U_{\underline{k}}(\underline{r}) e^{i\underline{K}n\cdot\underline{r}} = \\ &e^{i\underline{k}'\cdot\underline{r}} U_{\underline{k}}(\underline{r}) = \psi_{\underline{k}'}(\underline{r}) \end{aligned} \quad (2.14)$$

Hence the energy  $E_n(\underline{k})$  must be a periodic function of  $\underline{K}_i$  that is,  $E_n(\underline{k}) = E_n(\underline{k} + \underline{K}_i)$  (2.15)

The energy is also an even function of  $\underline{k}$ , that is  $E_n(\underline{k}) = E_n(-\underline{k})$ . This follows from the observation that the function  $\psi_{\underline{k}}^*(\underline{r}) = e^{-i\underline{k}\cdot\underline{r}} U_{\underline{k}}^*(\underline{r})$  is also a solution of Schrödinger's equation. The suffix  $n$  denotes that the energy is a multivalued function of  $\underline{k}$ , and for a tight bound electron is analogous to the quantum number  $l$  of an atom. In our case of the nearly free electron  $n$  coincides with one of the  $\underline{K}$ 's.

Having found the energies  $E_n(\underline{k})$  from the determinant we substitute into the equations of the system any value of them and after using a normalization condition,

one obtains the momentum eigenfunctions  $V$  at the points  $\underline{k} + \underline{K}_n$  corresponding to any band. This is repeated for all  $\underline{k}$  points of interest within the first Brillouin zone. The lowest roots will be given with sufficient approximation even by cutting down to an arbitrary finite number the equations considered.

The approximation is generally estimated by finding the energies of interest from the system with  $n$  equations and then from the system with  $n + 1$  equations, though this does not guarantee that some higher Fourier coefficients of the potential may not have a marked effect on some eigenvalues or eigenvectors.

## 2. One-dimensional Application of Schrödinger's Equation in Momentum Space

We are going to deal with a special case of the potential

$$V(\underline{r}) = \sum_{\underline{K}_n} W(\underline{K}_n) e^{i\underline{K}_n \cdot \underline{r}} \quad (2.16)$$

in which only a few coefficients  $W(\underline{K}_n)$  are different from zero. A simple cubic structure is considered with a potential,

$$V(\underline{r}) = -3\cos \frac{2\pi x}{a} - 3\cos \frac{2\pi y}{a} - 3\cos \frac{2\pi z}{a} \quad (2.17)$$



After writing the cosines in exponential form the potential is put in the required form (2.16), that is

$$V(r) = -\frac{3}{2} e^{2\pi i x/a} - \frac{3}{2} e^{-2\pi i x/a} - \frac{3}{2} e^{2\pi i y/a} - \frac{3}{2} e^{-2\pi i y/a} - \frac{3}{2} e^{2\pi i z/a} - \frac{3}{2} e^{-2\pi i z/a} \quad (2.18)$$

With this potential Schrödinger's equation can be separated into three one-dimensional equations each one having the potential,

$$V(x) = -\frac{3}{2} e^{2\pi i x/a} - \frac{3}{2} e^{-2\pi i x/a} \quad (2.19)$$

and the general form of the Mathieu's equation.

It is very convenient for the calculations to choose the period in ordinary space equal to  $\pi$ . This, from the definition of reciprocal lattice (eq.(1.39)) gives the value  $K_n = 2$  for the period in reciprocal space. Also the fundamental vectors of the reciprocal lattice are 2, 4, 6, 8, etc., and the first Brillouin zone extends now from  $k = -1$  to  $k = 1$ .

It is obvious that the Fourier coefficients of the expansion of the periodic potential are

$$W(2) = W(-2) = -\frac{3}{2} \quad (2.20)$$

The Schrodinger's equation in momentum space is now going to be solved in succession for  $|K| < 0, 2, 4, 6, 8$ . It is arbitrarily assumed that all coefficients with  $|K| > 0, 2, 4, 6, 8$  are negligible.

So according to this approximation the Schrödinger's equation gives the following systems of algebraic equations for the several values of  $K$ .

$(k^2 - E)V_0 = 0$	(I)	Assuming that only $V_0$ exists
$[(k - 2)^2 - E] V_2 - 1.5 V_0 = 0$	}	(II) Assuming that all $V$ with $ K  > 2$ can be neglected
$-1.5V_2 + [k^2 - E] V_0 - 1.5 V_2 = 0$		
$-1.5V_0 + [(k + 2)^2 - E] V_2 = 0$		
$[(k - 4)^2 - E] V_4 - 1.5 V_2 = 0$	}	(III) Assuming that $V$ 's with $ K  > 4$ neglected
$-1.5V_4 + [(k - 2)^2 - E] V_2 - 1.5V_0 = 0$		
$-1.5V_2 + [k^2 - E] V_0 - 1.5V_2 = 0$		
$-1.5V_0 + [(k + 2)^2 - E] V_2 - 1.5V_4 = 0$		
$-1.5V_2 + [(k + 4)^2 - E] V_4 = 0$		
$[(k - 6)^2 - E] V_6 - 1.5V_4 = 0$	}	(IV) $V$ 's with $ K  > 6$ neglected
$-1.5V_6 + [(k - 4)^2 - E] V_4 - 1.5V_2 = 0$		
$-1.5V_4 + [(k - 2)^2 - E] V_2 - 1.5V_0 = 0$		
$-1.5V_2 + [k^2 - E] V_0 - 1.5V_2 = 0$		
$-1.5V_0 + [(k + 2)^2 - E] V_2 - 1.5V_4 = 0$		
$-1.5V_2 + [(k + 4)^2 - E] V_4 - 1.5V_6 = 0$		
$-1.5V_4 + [(k + 6)^2 - E] V_6 = 0$		

$$\begin{array}{l}
 \left. \begin{array}{l}
 \left[ (k - 8)^2 - E \right] V_8 - 1.5V_6 = 0 \\
 -1.5V_8 + \left[ (k - 6)^2 - E \right] V_6 - 1.5V_4 = 0 \\
 -1.5V_6 + \left[ (k - 4)^2 - E \right] V_4 - 1.5V_2 = 0 \\
 -1.5V_4 + \left[ (k - 2)^2 - E \right] V_2 - 1.5V_0 = 0 \\
 -1.5V_2 + \left[ k^2 - E \right] V_0 - 1.5V_2 = 0 \\
 -1.5V_0 + \left[ (k + 2)^2 - E \right] V_2 - 1.5V_4 = 0 \\
 -1.5V_2 + \left[ (k + 4)^2 - E \right] V_4 - 1.5V_6 = 0 \\
 -1.5V_4 + \left[ (k + 6)^2 - E \right] V_6 - 1.5V_8 = 0 \\
 -1.5V_6 + \left[ (k + 8)^2 - E \right] V_8 = 0
 \end{array} \right\} \text{(V) Assuming that} \\
 \left. \begin{array}{l}
 \\
 \\
 \\
 \\
 \\
 \\
 \\
 \\
 \end{array} \right\} \text{V's with } |k| > 8 \\
 \left. \begin{array}{l}
 \\
 \\
 \\
 \\
 \\
 \\
 \\
 \\
 \end{array} \right\} \text{neglected}
 \end{array}$$

As it has been written in section 1 of this chapter, these systems of algebraic equations are linear homogeneous ones. Hence they have a non-zero solution only when the determinant of the coefficients of V's vanish.

The above determinants lead to equations by which the energy E is determined. Then adding to the systems the equation of a normalization condition

$$\sum_{|k|} V_{|k|}^2 = \frac{1}{\pi} = 0.31830988 \quad (2.21)$$

the values of the momentum eigenfunctions V can be found.

Each of the systems I, II, III, IV and V has been solved for the values of  $k = 0, 0.25, 0.50, 0.75, 1.$

Since  $V$  is either symmetrical or antisymmetrical this determines  $V$ 's between  $-8$  and  $8$  at  $0.25$  interval.

The calculations have been carried out for the first three bands, and the results are shown in tables 1, 2, 3 and 4. For the points  $k = 0.75, 1$  we have omitted the first equation of each system considering 2, 4, 6 and 8 equations instead of 3, 5, 7 and 9 equations, as we did for  $k = 0, 0.25, 0.50$ .

We noticed that the results for 7 or 9 equations do not differ from each other, and therefore we assume that these are the exact values, with the given number of decimals.

Instead of finding the energies from the determinants and then solving the systems, which both are a laborious work, in this particular case it is possible to apply a simple numerical method which can be carried out using a desk computer. We write down the general form of the equations of the considered systems, that is

$$-1.5V_{n-2} + \left[ (k+n)^2 - E \right] V_n - 1.5V_{n+2} = 0 \quad (2.22)$$

where  $n$  takes the values  $n = \pm 8, \pm 6, \pm 4, \pm 2, 0$ .

Then we start the calculation by choosing



arbitrarily  $V_{-8} = 0$  and  $V_{-6} = 1$ . We also choose the value of the energy to be near the value which we can easily find for three equations. So the value for  $V_{-4}$  is found. Then we repeat the same using  $V_{-6} = 1$  and then found  $V_{-4}$ , and so  $V_{-2}$  is found. We carry on this way until we find  $V_8$ . By comparing the values of  $V_6$  and  $V_8$  ( $V_8$  must be much smaller than  $V_6$ ) we can see whether the chosen energy is the exact one or not. If not we change the energy and we start the same procedure from the beginning until  $V_8 \ll V_6$ . The exact value of the energy is generally obtained to 6 or 7 decimal figures. Finally we normalize the  $V$ 's by using equation (2.21).

In the following pages we have listed the results and plotted the curves  $E_n(k)$  and  $V_n(k)$  for the first three bands.

A similar calculation has been done by J.C. Slater (Reference 11, page 84), who considered a periodic potential of the same form and calculated the momentum eigenfunctions for the first fourteen bands. Slater found that the momentum eigenfunctions are similar to Hermite functions for the tightly-bound levels but very different for free-electron like levels.

Also Eyges (Ref.2) suggested a method for calculating the momentum eigenfunctions in three dimensions.

In the next chapter we shall discuss a method of finding the derivatives  $\frac{dE}{dk^n}$ ,  $\frac{dV}{dk^n}$ . If this method shows satisfactory results, it makes it possible to reduce the number of k-points at which the calculations need be performed.

In writing section 1 of this chapter we had in mind the following references: 6, 9, 11, 12.

Table 1

Energy values for the first three bands  
(by solving the determinantal equations)

k	No. of equations considered	$E_1$	$E_2$	$E_3$
0	1	0	-	-
0	3	-0.9155	4	4.9155
0	5	-0.93675	3.81533	4.74783
0	7	-0.9368185	3.814291	4.746779
0	9	-0.93681849	3.81429087	4.74677947
0.25	1	0.0625	-	-
0.25	3	-0.8850	3.5181	5.5542
0.25	5	-0.91043	3.33195	5.38973
0.25	7	-0.910530	3.330716	5.388846
0.25	9	-0.91052981	3.33071608	5.38884605
0.50	1	0.25	-	-
0.50	3	-0.8055	2.9217	6.6337
0.50	5	-0.84247	2.72956	6.47851
0.50	7	-0.8426695	2.727965	6.477781
0.50	9	-0.84266958	2.727965	6.477781
0.75	2	0.2545	-	7.8705
0.75	4	-0.7052	2.5040	7.7445
0.75	6	-0.766795	2.31618	7.73898
0.75	8	-0.7672475	2.314250	7.738351
0.75	10	-0.76724811	2.314250	7.73835066
1	2	0.72795	-	9.27205
1	4	-0.6226	2.3383	9.1440
1	6	-0.73224	2.16823	9.12694
1	8	-0.73326339	2.165947	9.092609
1	10	-0.73326515	2.165947	9.09260861

The energies  $E_1$  and  $E_3$  for the 9 X 9 determinant have been found on an automatic computer.



TABLE 2

Momentum eigenfunctions for the first band

k	No. of eqs.	V <sub>8</sub>	V <sub>-6</sub>	V <sub>-4</sub>	V <sub>-2</sub>	V <sub>0</sub>	V <sub>2</sub>	V <sub>4</sub>	V <sub>6</sub>	V <sub>8</sub>
0	3	-	-	-	0.158	0.518	0.158	-	-	-
0	5	-	-	0.01426	0.16101	0.51566	0.16101	0.01426	-	-
0	7	-	0.000578	0.014227	0.160058	0.512560	0.160058	0.014227	0.000578	-
0	9	0.000013	0.000578	0.014227	0.160058	0.512560	0.160058	0.014227	0.000578	0.000013
0.25	3	-	-	-	0.1950	0.5134	0.1950	-	-	-
0.25	5	-	-	0.02007	0.20034	0.51055	0.20034	0.02007	-	-
0.25	7	-	0.000891	0.020158	0.200328	0.510448	0.200328	0.020158	0.000389	-
0.25	9	0.000022	0.000891	0.020158	0.200328	0.510448	0.200328	0.020158	0.000389	0.000022
0.50	3	-	-	-	0.2442	0.4974	0.2442	-	-	-
0.50	5	-	-	0.02897	0.25286	0.49234	0.25286	0.02897	-	-
0.50	7	-	0.001407	0.029132	0.252869	0.492229	0.252869	0.029132	0.000262	-
0.50	9	0.000037	0.001407	0.029132	0.252869	0.492229	0.252869	0.029132	0.000262	0.000037
0.75	2	-	-	-	0.30797	(0.5526)	(0.1134)	-	-	-
0.75	4	-	-	-	0.30797	0.46513	0.08444	0.00544	-	-
0.75	6	-	-	0.042425	0.320430	0.455159	0.082931	0.005343	0.000168	-
0.75	8	-	0.002265	0.042718	0.320389	0.454899	0.082879	0.005340	0.000173	0.000003
0.75	10	0.000064	0.002265	0.042718	0.320389	0.454899	0.082879	0.005340	0.000173	0.000003
1	2	-	-	-	0.38045	(0.5552)	(0.1007)	-	-	-
1	4	-	-	-	0.38045	0.41155	0.06473	0.00372	-	-
1	6	-	-	0.06074	0.394091	0.394366	0.061334	0.003578	0.000108	-
1	8	-	0.003579	0.06130	0.394189	0.394189	0.06130	0.003579	0.000108	0.000002
1	10	0.000108	0.003579	0.061300	0.394189	0.394189	0.061300	0.003579	0.000108	0.000002



**TABLE 3**  
Momentum eigenfunctions for the second band

k	No. of eqs.	V <sub>8</sub>	V <sub>6</sub>	V <sub>4</sub>	V <sub>2</sub>	V <sub>0</sub>	V <sub>2</sub>	V <sub>4</sub>	V <sub>6</sub>	V <sub>8</sub>
0	3	-	-	-	0.39894	0	0.39894	-	-	-
0	5	-	-	-	0.39592	0	0.39592	0.04874	-	-
0	7	-	0.002284	-	0.395848	0	0.395848	0.049008	-	-
0	9	0.000056	0.002284	0.049008	0.395848	0	0.395848	0.049008	-	-
0.25	3	-	-	-	0.5195	-0.1578	0.5195	-	-	-
0.25	5	-	-	-	0.51185	-0.16349	0.51185	0.07156	-	-
0.25	7	-	0.003635	-	0.511848	-0.163574	0.511848	0.07205	-	-
0.25	9	0.000096	0.003635	0.07205	0.511848	-0.163574	0.511848	0.07205	-	-
0.50	3	-	-	-	0.5065	-0.2268	0.5065	-	-	-
0.50	5	-	-	-	0.49531	-0.23639	0.49531	0.07804	-	-
0.50	7	-	0.004288	-	0.495151	-0.236453	0.495151	0.078676	-	-
0.50	9	0.000120	0.004288	0.078676	0.495151	-0.236453	0.495151	0.078676	-	-
0.75	4	-	-	-	0.47194	-0.29623	0.47194	-	-	-
0.75	6	-	-	-	0.45440	-0.31097	0.45440	0.08265	-	-
0.75	8	-	0.004960	-	0.454124	-0.311079	0.454124	0.083487	-	-
0.75	10	0.000148	0.004960	0.083487	0.454124	-0.311079	0.454124	0.083487	-	-
1	4	-	-	-	0.41603	-0.37176	0.41603	-	-	-
1	6	-	-	-	0.38982	-0.38919	0.38982	0.08559	-	-
1	8	-	0.005696	-	0.389351	-0.389350	0.389351	0.086708	-	-
1	10	0.000182	0.005696	0.086708	0.389351	-0.389350	0.389351	0.086708	-	-

TABLE 4

Momentum eigenfunctions for the third band

k	No. of eqs.	V <sub>8</sub>	V <sub>6</sub>	V <sub>4</sub>	V <sub>2</sub>	V <sub>0</sub>	V <sub>2</sub>	V <sub>4</sub>	V <sub>6</sub>	V <sub>8</sub>
0	3	-	-	-	0.3660	-0.2234	0.3660	-	-	-
0	5	-	-	0.04820	0.361568	-0.22846	0.361568	0.04820	-	-
0	7	-	0.002328	0.048505	0.361564	-0.228510	0.361564	0.048505	0.002328	-
0	9	0.000059	0.002330	0.048499	0.361518	-0.228482	0.361518	0.048499	0.002330	0.000059
0.25	3	-	-	-	0.1039	-0.1727	0.5268	-	-	-
0.25	5	-	-	0.0176	0.10193	-0.17578	0.52234	0.06183	-	-
0.25	7	-	0.000964	0.017785	0.101876	-0.175784	0.522317	0.062147	0.002772	-
0.25	9	0.000026	0.000965	0.017786	0.101881	-0.175793	0.522342	0.062150	0.002771	0.000066
0.50	3	-	-	-	0.0477	-0.1393	0.5446	-	-	-
0.50	5	-	-	0.01193	0.04590	-0.14133	0.54095	0.05892	-	-
0.50	7	-	0.000764	0.012108	0.045829	-0.141279	0.540739	0.059165	0.002485	-
0.50	9	0.000023	0.000766	0.012112	0.045843	-0.141323	0.540909	0.059184	0.002484	0.000057
0.75	2	-	-	-	-	-0.1134	0.55248	-	-	-
0.75	4	-	-	-	0.02814	-0.11861	0.55087	0.05630	-	-
0.75	6	-	-	0.01369	0.025769	-0.119799	0.547389	0.055397	0.00220	-
0.75	8	-	0.001074	0.014194	0.025650	-0.119802	0.547469	0.055620	0.002207	0.000048
0.75	10	0.000036	0.001077	0.014202	0.025661	-0.119854	0.547708	0.055644	0.002208	0.000048
1	2	-	-	-	-	-0.1007	0.5552	-	-	-
1	4	-	-	-	0.01937	-0.10515	0.55153	0.05220	-	-
1	6	-	-	0.17417	-0.01474	-0.09431	0.52570	0.4982	0.00151	-
1	8	-	0.036831	0.390590	-0.060946	-0.061783	0.394271	0.037441	0.00140	0.000029
1	10	0.001396	0.037137	0.392440	-0.061366	-0.061366	0.392440	0.037137	0.001396	0.000029

TABLE 5

k	$V_1$	$V_2$	$V_3$
	1st band	2nd band	3rd band
0	0.512560	0	-0.228482
0.25	0.510448	0.163574	-0.175793
0.50	0.492229	0.236453	-0.141323
0.75	0.454899	0.311079	-0.119854
1.00	0.394189	0.389350	-0.061366
1.25	0.320389	0.454124	0.025661
1.50	0.252869	0.495151	0.045843
1.75	0.200328	0.511848	0.101881
2.00	0.160058	0.395848	0.361518
2.25	0.130793	0.155452	0.522342
2.50	0.105693	0.104536	0.540909
2.75	0.082879	0.090835	0.547708
3.00	0.061300	0.086710	0.392440
3.25	0.042718	0.083487	0.014202
3.50	0.029132	0.078676	0.012112
3.75	0.020158	0.072050	0.017786
4.00	0.014227	0.049008	0.048499
4.25	0.010371	0.015898	0.062150
4.50	0.007535	0.009001	0.059184
4.75	0.005340	0.006738	0.055644
5.00	0.003579	0.005703	0.037137
5.25	0.002265	0.004960	0.001077
5.50	0.001407	0.004288	0.000766
5.75	0.000891	0.003635	0.000965
6.00	0.000578	0.002284	0.002330
6.25	0.000389	0.000691	0.002771
6.50	0.000262	0.000608	0.002484
6.75	0.000173	0.000187	0.001208
7.00	0.000108	0.000182	0.001396
7.25	0.000064	0.000148	0.000036
7.50	0.000037	0.000120	0.000023
7.75	0.000022	0.000096	0.000026
8.00	0.000013	0.000056	0.000059

From the tables on the previous pages we notice that the first and third bands have even  $V$  functions while the second band has odd  $V$  functions.

So using the "extended zone scheme" we construct Table 5 giving the values of  $V$  as a function of  $k$  without being specified in the 1st Brillouin zone. (See curves)



$E_1$  ↑  
E.S.A., LONDON.

$E(k)$  for the first band.

-0.725

-0.770

-0.815

-0.860

-0.905

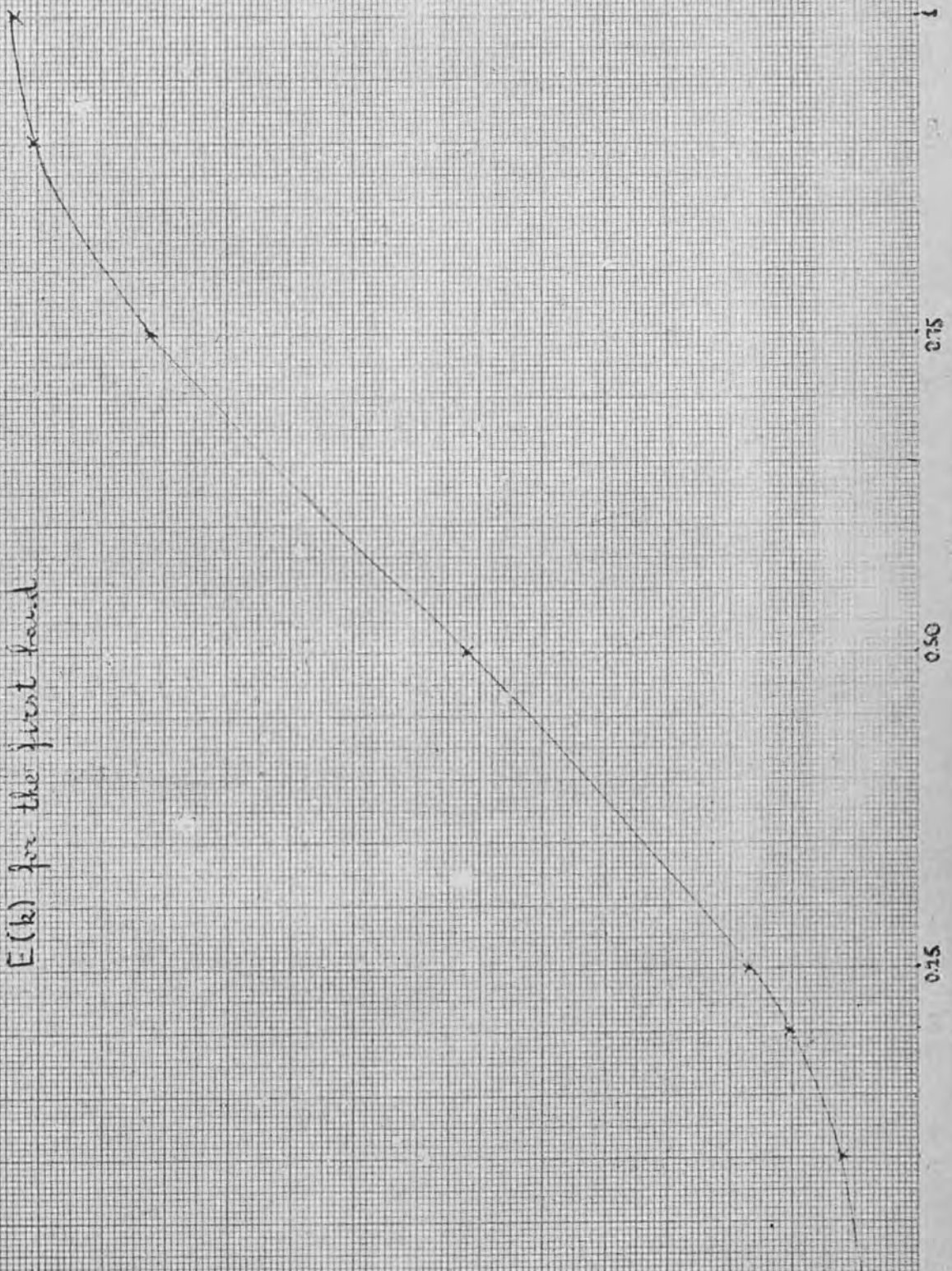
-0.950

0.125

0.50

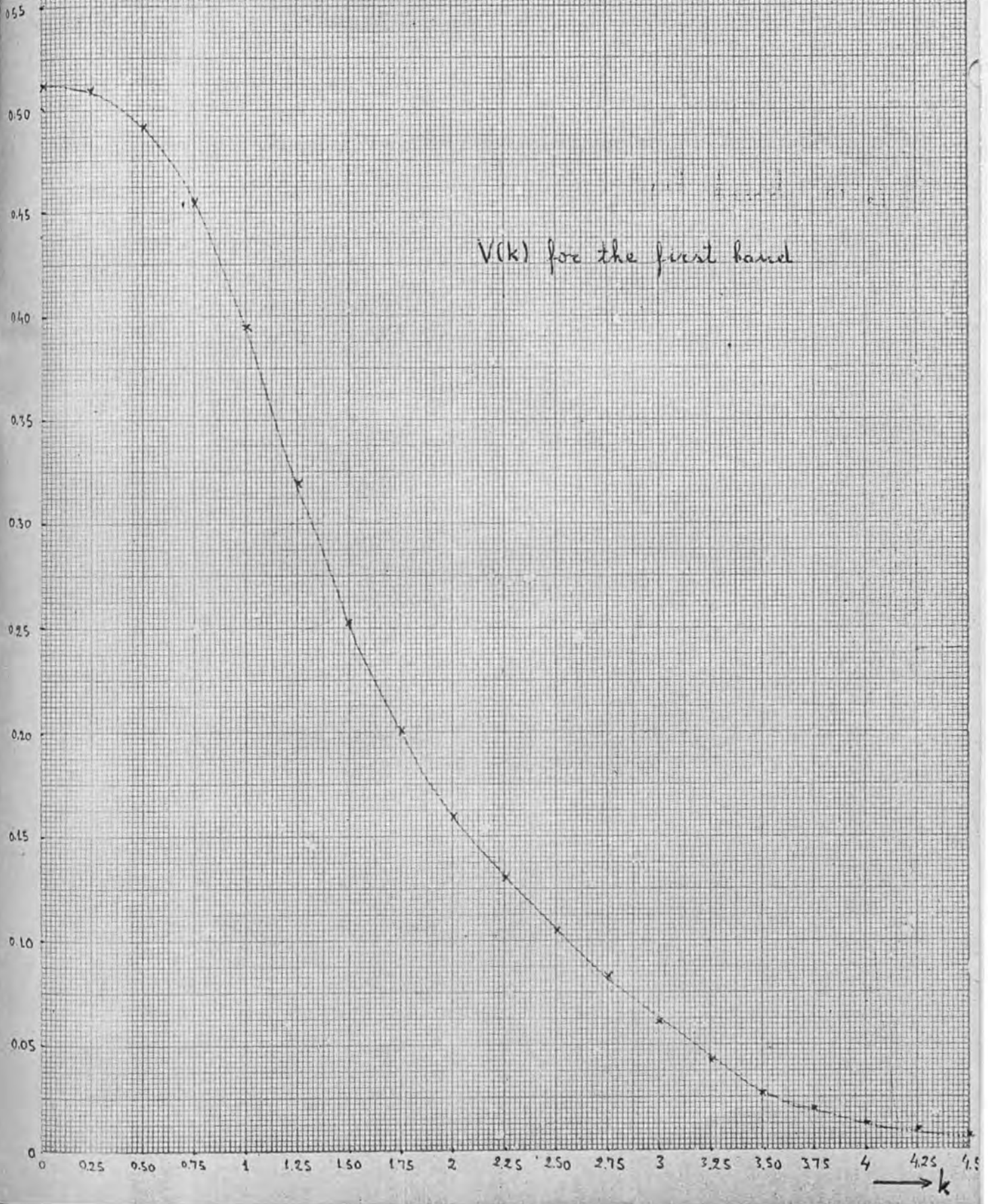
0.875

↑  
→  $k$

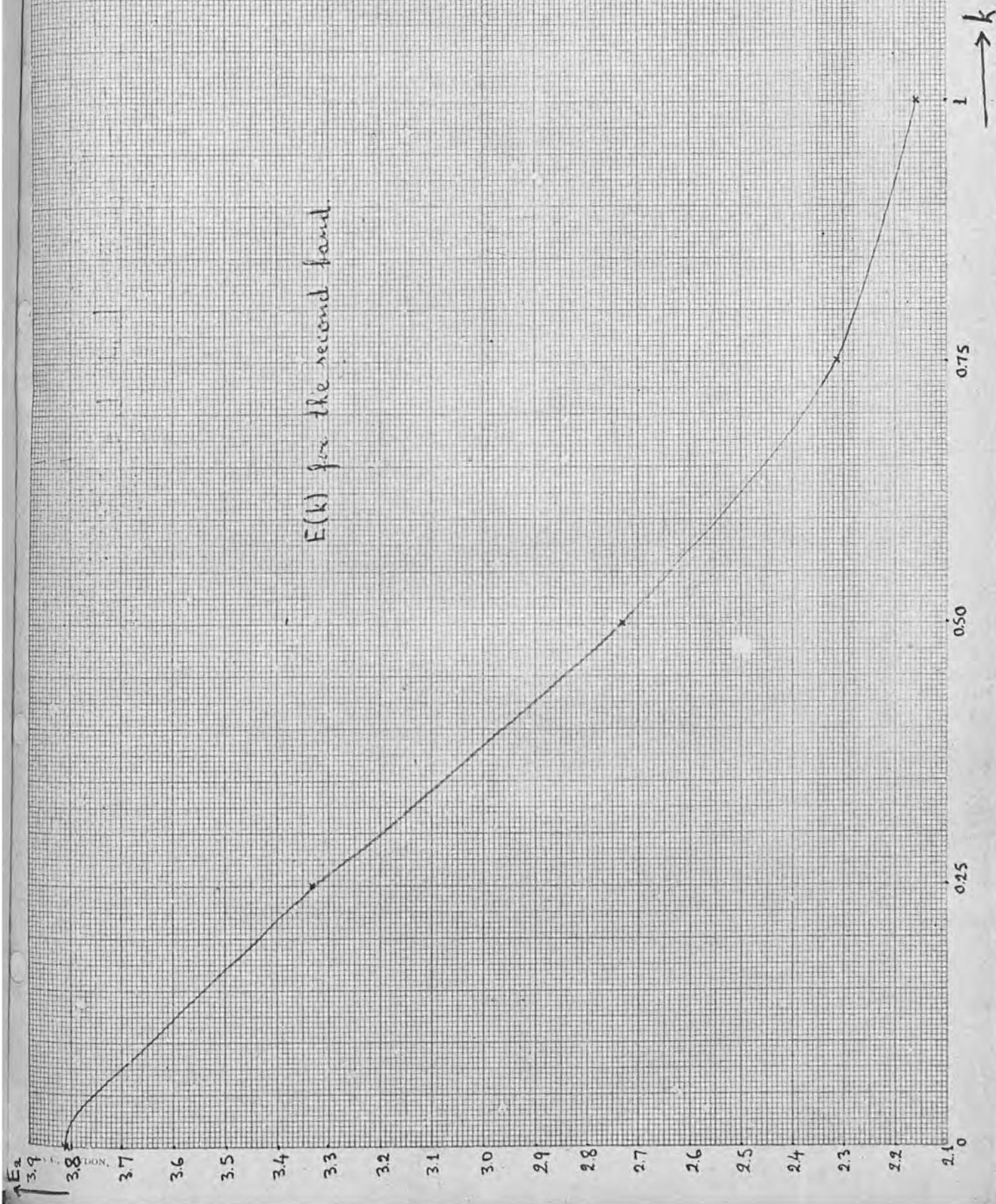




$V(k)$  for the first band

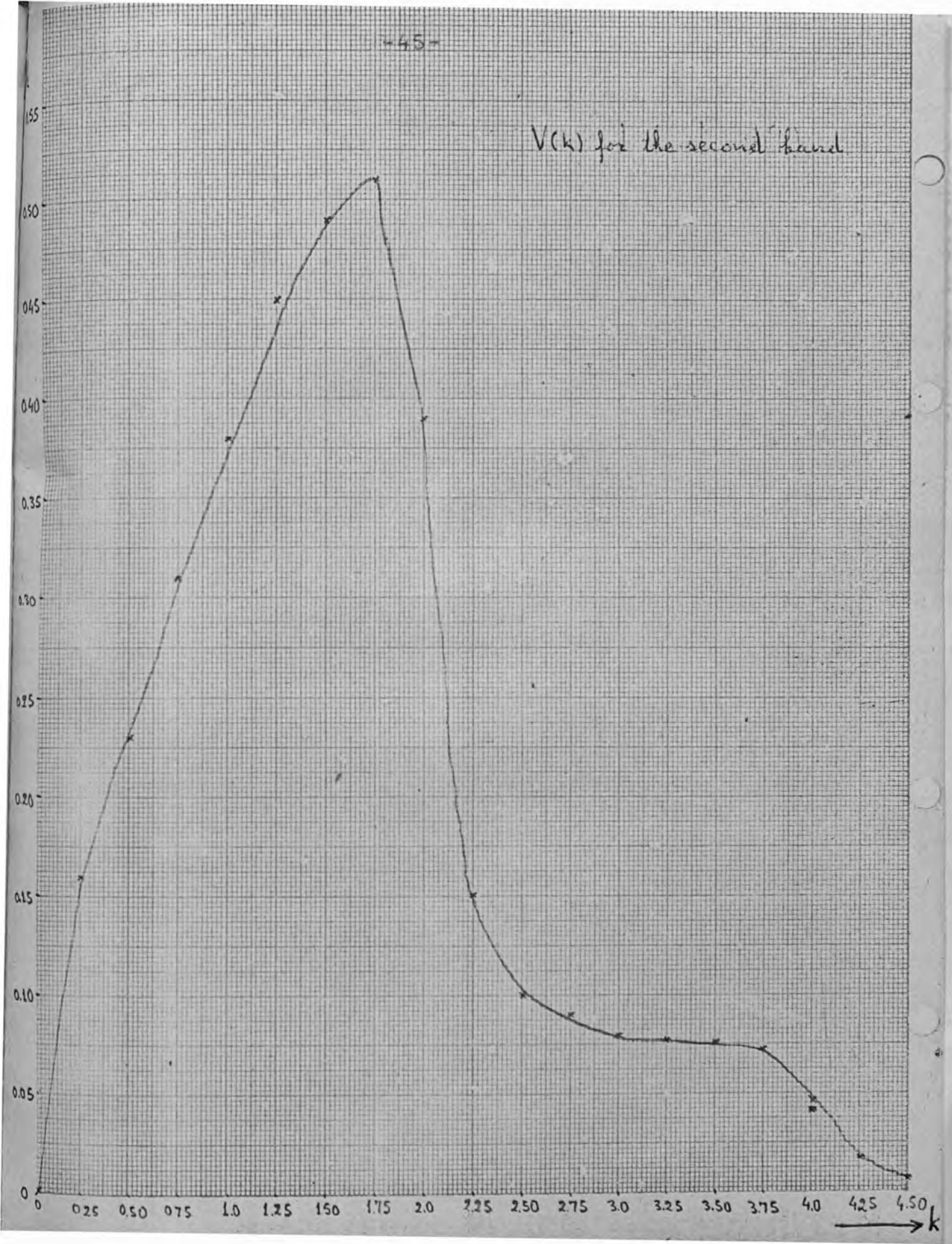


$E(k)$  for the second band.





$V(k)$  for the second band

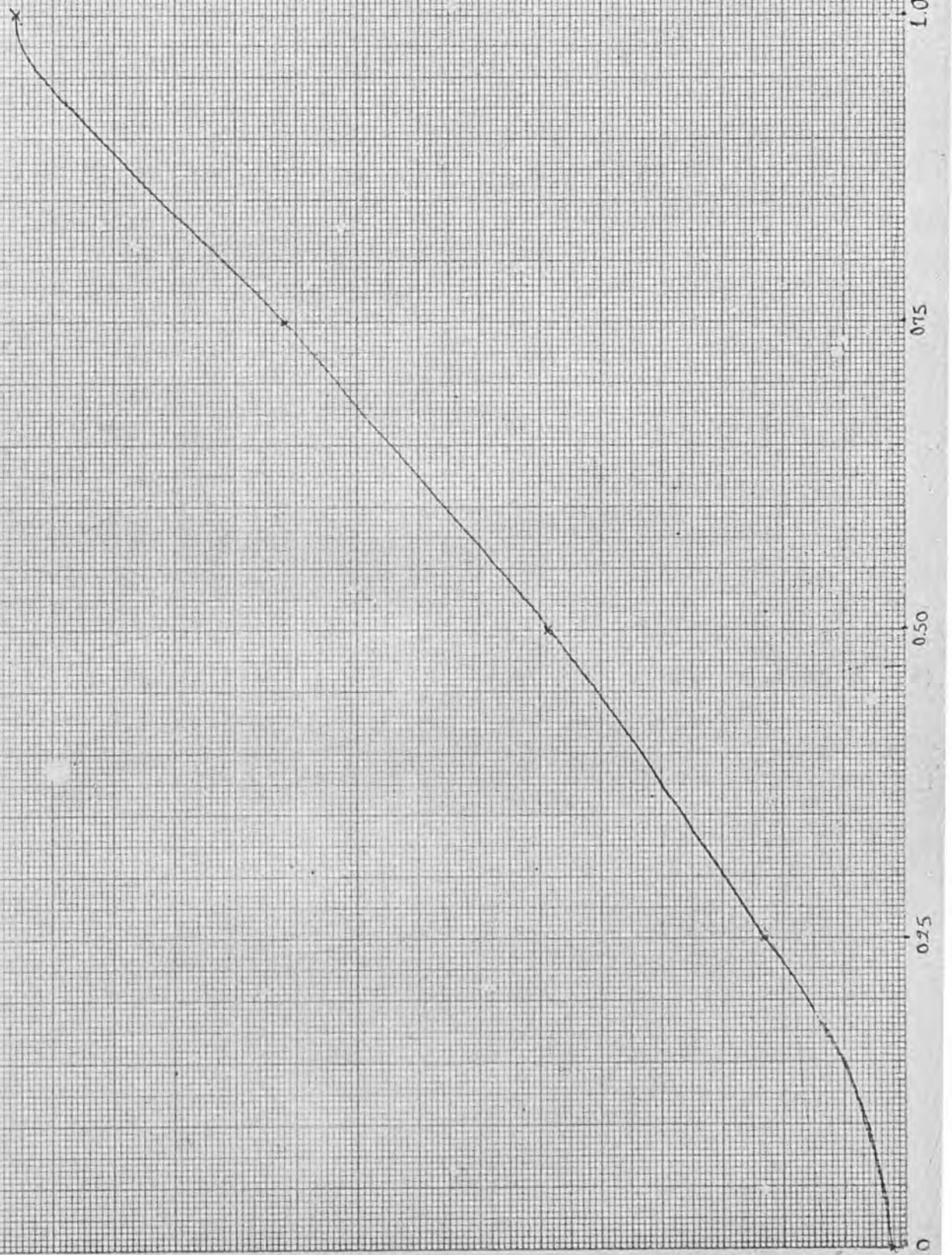


$E(k)$  for the blind band

ESA, LONDON.

$E_3$  ↑

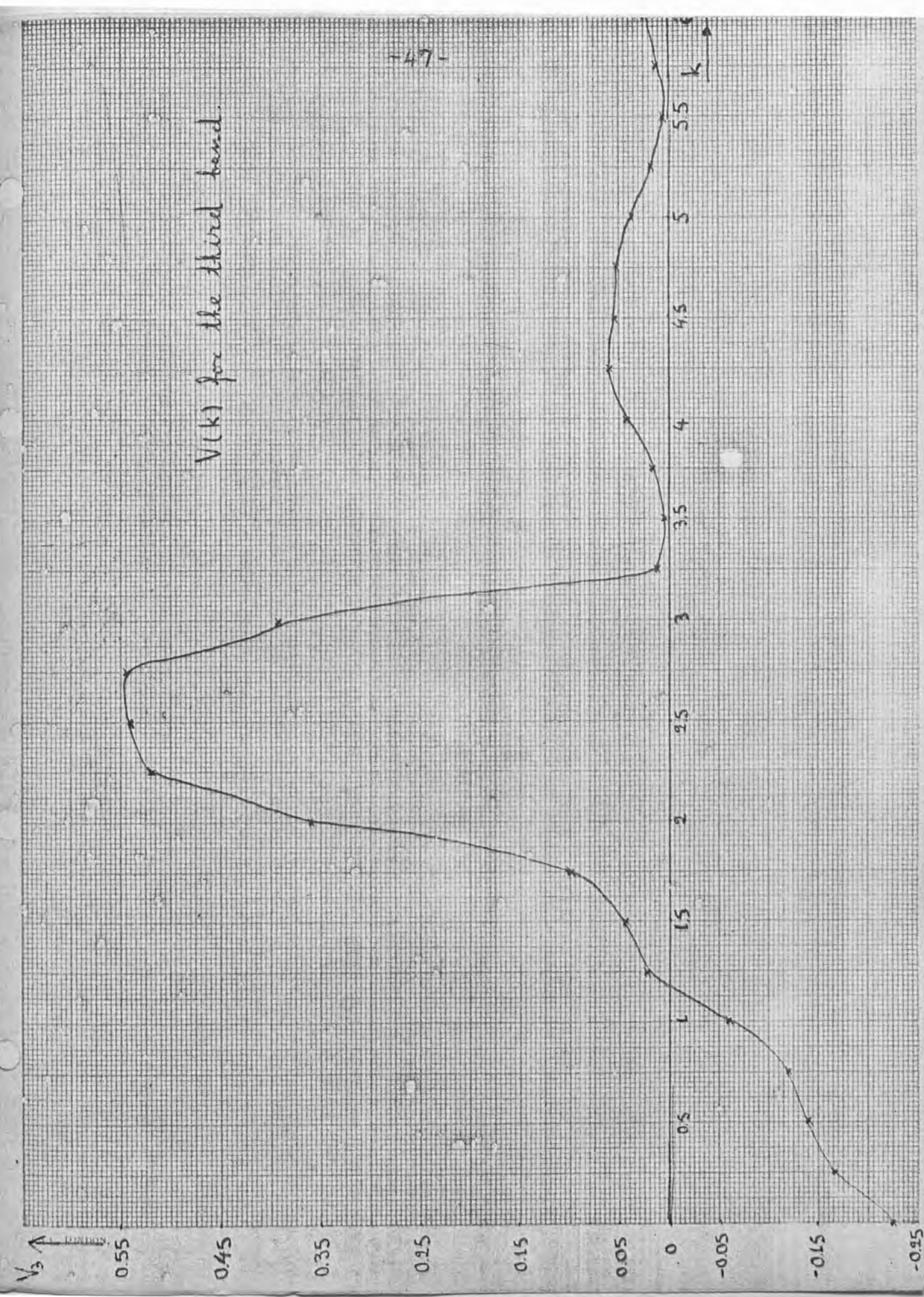
92 89 86 83 80 77 74 71 68 65 62 59 56 53 50 47 0



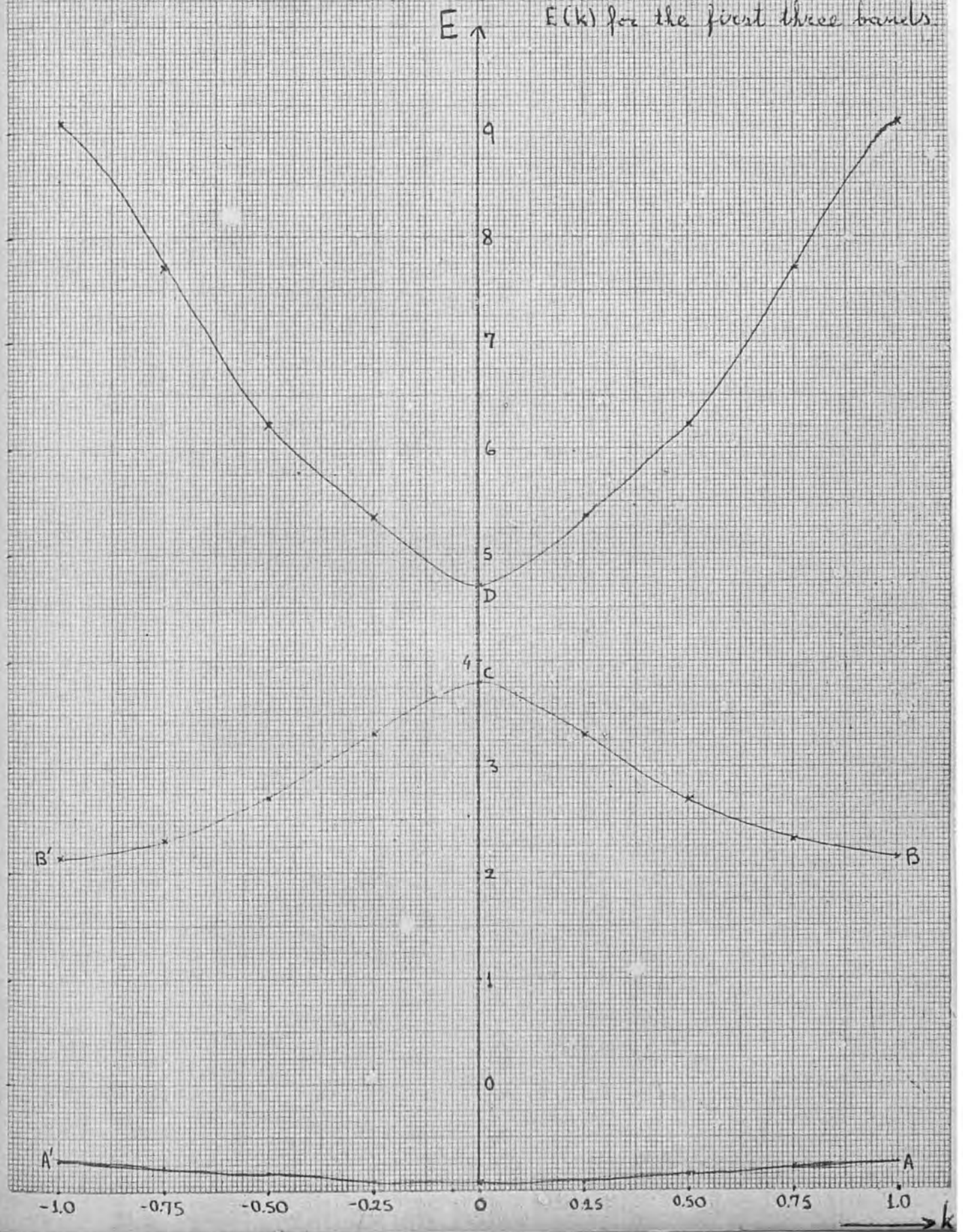
→ k



$V(k)$  for the third band.



$E(k)$  for the first three bands





### 3. Comments on the Curves

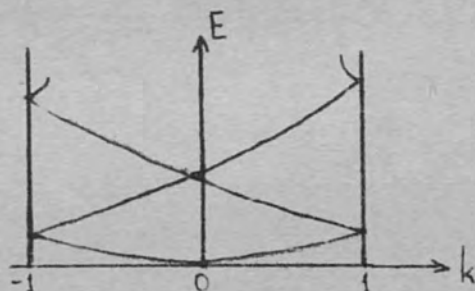
If we plot the curves  $E(k)$  considering that  $E(k) = E(-k)$  on the same diagram we can see (page 48) that they have the form of the "reduced zone scheme" discussed at page 21.

We notice that at the boundaries of the first Brillouin zone there are energy gaps (AB and CD). It is interesting to consider the free-electron case where the energy is given by the formula

$$E(k) = (k + K_n)^2 \quad (2.23)$$

where  $K_n$  takes the values  $0, \pm 2, \pm 4, \dots$

Equation (2.23) leads to the following diagram



Now there are no energy gaps and the curves join at the boundaries of the first Brillouin zone.

Comparing the two cases we draw the conclusion that the smaller the periodic potential is the nearer to the free-electron model we are.

The curves  $V(k)$  are plotted on the "extended zone scheme". It is again interesting to compare them with the curves of a completely free electron case ( $\psi_k(\tau) = e^{ik \cdot \tau}$ ) which have the following forms for the first three bands:

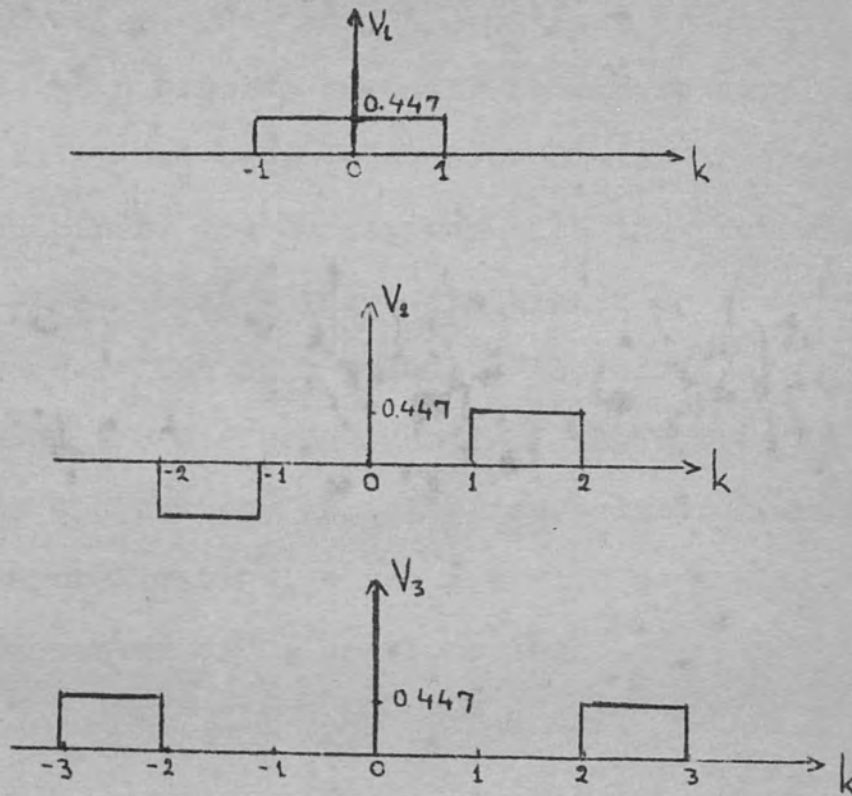


Fig. 5

$V$ 's are normalized to 2, in the same way as in the nearly free-electron consideration.

In the curves which we have found using a periodic potential, we notice the following. In the first band  $V$  takes its maximum value at  $k = 0$  and then reduces from both sides, having its higher values at  $-1 < k < 1$ . In the second band (where  $V(k) = -V(-k)$ )  $V$  takes its higher and lower values at  $1 < k < 2$ , and  $-2 < k < -1$  respectively.



Finally in the third band  $V$  takes its higher values at  $2 < k < 3$  and  $-3 < k < -2$ . In this band we have the appearance of second and third maxima, and if we calculate higher bands we shall find more complicated curves, as it has been pointed by Slater in the already mentioned paper. By comparison with the free electron's curves, we see that  $V$  takes its higher or lower values in the same region of  $k$  values. Therefore by considering the different shape of the curves in the two cases one can say that the free electron model is a rough approximation, which can give us a hint as to how the momentum eigenfunctions look.

CHAPTER III

1. The differentiated Schrödinger's equation in momentum space

It is desirable to extract as much information as possible out of the calculations performed at any  $\underline{k}$ -point. For this purpose a suggestion was made\* that  $\text{grad}_{\underline{k}} E$  may be found as well from the calculation and also  $\text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_n)$ . This can be done by differentiating Schrödinger's equation in momentum space (1.13) with respect to  $\underline{k}$ . We assume here that  $\psi_{\underline{k}}$  is a differentiable function of  $\underline{k}$ . This has been proved by Blount to be the case except at points of degeneracy. (Ref.1) So a new system of algebraic equations is found.

$$\left[ |\underline{k} + \underline{K}_i|^2 - E \right] \text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_i) + \sum_{\underline{K}_m} W(\underline{K}_m) \text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_i - \underline{K}_m) = \left[ \text{grad}_{\underline{k}} E - 2(\underline{k} + \underline{K}_i) \right] V(\underline{k} + \underline{K}_i) \quad (3.1)$$

Considering as unknown quantities the derivatives of  $V$ 's the system (3.1) is a linear non-homogeneous one. Therefore the values of each  $\text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_n)$  are given by a ratio of determinants in which the denominator is the determinant of the coefficients of  $\text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_n)$  and the numerator the same determinant, but with the constant coefficients replacing the column, which corresponds to each particular  $\text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_n)$ .

The denominator is, in fact, the same determinant which we put equal to zero in order to solve the system (2.13). Hence the solutions of the system (3.1)

\* Ref. 7.

must have the undetermined value  $\frac{0}{0}$ . So by setting the determinant of the numerator equal to 0 one obtains an algebraic equation of first degree for  $\text{grad}_{\underline{k}} E$ .

Then substituting into the equations of the system (3.1) the so found  $\text{grad}_{\underline{k}} E$  and adding the differentiated normalization condition, one has the corresponding values of  $\text{grad}_{\underline{k}} V(\underline{k} + \underline{K}_n)$ . We follow the same procedure, as we have done in Chapter II, limiting the number of rows and columns in the determinantal equation.

It is not clear how good an approximation this method will provide to such quantities and, as stated in the introduction, the purpose of the present work is to bring light on this question by treating a one-dimensional example for which exact solutions can be found with little labour.

## 2. One-dimensional Application

The differentiated Schrödinger's equation in momentum space is going to be solved in succession for  $|K| < 0, 2, 4, 6, 8$ . Making the same assumption as in Chapter II, that is that all coefficients with  $|K| > 0, 2, 4, 6, 8$  are negligible, the following systems are to be solved:



$$(k^2 - E) \frac{dV_0}{dk} = \left( \frac{dE}{dk} - 2k \right) V_0 \quad \text{I}$$

$$\left[ (k-2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_0}{dk} = \left[ \frac{dE}{dk} - 2(k-2) \right] V_2$$

$$-1.5 \frac{dV_2}{dk} + (k^2 - E) \frac{dV_0}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2k \right] V_0 \quad \text{II}$$

$$-1.5 \frac{dV_0}{dk} + \left[ (k+2)^2 - E \right] \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2(k+2) \right] V_2$$

$$\left[ (k-4)^2 - E \right] \frac{dV_4}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2(k-4) \right] V_4$$

$$-1.5 \frac{dV_4}{dk} + \left[ (k-2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_0}{dk} = \left[ \frac{dE}{dk} - 2(k-2) \right] V_2$$

$$-1.5 \frac{dV_2}{dk} + \left[ k^2 - E \right] \frac{dV_0}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2k \right] V_0 \quad \text{III}$$

$$-1.5 \frac{dV_0}{dk} + \left[ (k+2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_4}{dk} = \left[ \frac{dE}{dk} - 2(k+2) \right] V_2$$

$$-1.5 \frac{dV_2}{dk} + \left[ (k+4)^2 - E \right] \frac{dV_4}{dk} = \left[ \frac{dE}{dk} - 2(k+4) \right] V_4$$

$$\begin{aligned}
 & \left[ (k-6)^2 - E \right] \frac{dV_6}{dk} - 1.5 \frac{dV_4}{dk} = \left[ \frac{dE}{dk} - 2(k-6) \right] V_6 \\
 - 1.5 \frac{dV_6}{dk} & + \left[ (k-4)^2 - E \right] \frac{dV_4}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2(k-4) \right] V_4 \\
 - 1.5 \frac{dV_4}{dk} & + \left[ (k-2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_0}{dk} = \left[ \frac{dE}{dk} - 2(k-2) \right] V_2 \\
 - 1.5 \frac{dV_2}{dk} & + \left[ k^2 - E \right] \frac{dV_0}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2k \right] V_0 \\
 - 1.5 \frac{dV_0}{dk} & + \left[ (k+2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_4}{dk} = \left[ \frac{dE}{dk} - 2(k+2) \right] V_2 \\
 - 1.5 \frac{dV_2}{dk} & + \left[ (k+4)^2 - E \right] \frac{dV_4}{dk} - 1.5 \frac{dV_6}{dk} = \left[ \frac{dE}{dk} - 2(k+4) \right] V_4 \\
 - 1.5 \frac{dV_4}{dk} & + \left[ (k+6)^2 - E \right] \frac{dV_6}{dk} = \left[ \frac{dE}{dk} - 2(k+6) \right] V_6
 \end{aligned}
 \tag{IV}$$

$$\begin{aligned}
 & \left[ (k-8)^2 - E \right] \frac{dV_8}{dk} - 1.5 \frac{dV_6}{dk} = \left[ \frac{dE}{dk} - 2(k-8) \right] V_8 \\
 - 1.5 \frac{dV_8}{dk} + & \left[ (k-6)^2 - E \right] \frac{dV_6}{dk} - 1.5 \frac{dV_4}{dk} = \left[ \frac{dE}{dk} - 2(k-6) \right] V_6 \\
 - 1.5 \frac{dV_6}{dk} + & \left[ (k-4)^2 - E \right] \frac{dV_4}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2(k-4) \right] V_4 \\
 - 1.5 \frac{dV_4}{dk} + & \left[ (k-2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_0}{dk} = \left[ \frac{dE}{dk} - 2(k-2) \right] V_2 \\
 + 1.5 \frac{dV_2}{dk} + & \left[ k^2 - E \right] \frac{dV_0}{dk} - 1.5 \frac{dV_2}{dk} = \left[ \frac{dE}{dk} - 2k \right] V_0 \\
 - 1.5 \frac{dV_0}{dk} + & \left[ (k+2)^2 - E \right] \frac{dV_2}{dk} - 1.5 \frac{dV_4}{dk} = \left[ \frac{dE}{dk} - 2(k+2) \right] V_2 \\
 - 1.5 \frac{dV_2}{dk} + & \left[ (k+4)^2 - E \right] \frac{dV_4}{dk} - 1.5 \frac{dV_6}{dk} = \left[ \frac{dE}{dk} - 2(k+4) \right] V_4 \\
 - 1.5 \frac{dV_4}{dk} + & \left[ (k+6)^2 - E \right] \frac{dV_6}{dk} - 1.5 \frac{dV_8}{dk} = \left[ \frac{dE}{dk} - 2(k+6) \right] V_6 \\
 - 1.5 \frac{dV_6}{dk} + & \left[ (k+8)^2 - E \right] \frac{dV_8}{dk} = \left[ \frac{dE}{dk} - 2(k+8) \right] V_8
 \end{aligned}$$

V

Considering as unknown quantities the derivatives of the V's the above systems are linear non-homogeneous ones. So we follow the procedure stated in the previous section finding first the derivative of the energy  $\frac{dE}{dk}$  and then by adding the differentiated normalization



condition.

$$\sum_{|K|} v_{|K|} \dot{v}_{|K|} = 0 \quad (3.2)$$

we obtain the derivatives  $\frac{dV}{dk}$  of the momentum eigenfunctions.

The calculations have been performed using a desk computer, by the method explained in Chapter II, and the results are given in tables 6, 7, 8, 9.

TABLE 6

Derivatives of the Energies

k	Number of equations considered	$dE_1/dk$	$dE_2/dk$	$dE_3/dk$
0	3	0	0	0
0	5	0	0	0
0	7	0	0	0
0	9	0	0	0
0.25	3	0.2327	-2.5968	3.8569
0.25	5	0.2034	-2.6108	3.8870
0.25	7	0.20311	-2.61325	3.88756
0.25	9	0.20311	-2.61325	3.88756
0.50	3	0.3909	-2.0915	4.6991
0.50	5	0.3175	-2.0966	4.7347
0.50	7	0.31687	-2.09421	4.73484
0.50	9	0.31687	-2.09421	4.73484
0.75	4	0.3998	-1.1964	5.3386
0.75	6	0.2524	-1.1615	5.3351
0.75	8	0.25106	-1.16374	5.33428
0.75	10	0.25106	-1.16374	5.33428
1	4	0.22	-0.0837	5.8860
1	6	0.003	0.0017	4.7485
1	8	0	0	0
1	10	0	0	0

TABLE 7

Derivatives of the Momentum Eigenfunctions for the First Band

k	No. of Eqs.	$dV_3/dk$	$dV_4/dk$	$-dV_5/dk$	$dV_6/dk$	$dV_7/dk$	$dV_8/dk$	$dV_9/dk$	$dV_{10}/dk$	$dV_{11}/dk$	$dV_{12}/dk$	$dV_{13}/dk$
0	3	-	-	0.1286	0	-0.1286	-	-	-	-	-	-
0	5	-	0.01879	0.13617	0	-0.13617	-0.01879	-	-	-	-	-
0	7	-	0.01880	0.13540	0	-1.3540	-0.01880	-0.00100	-0.00100	-	-	-
0	9	0.00000	0.01880	0.13540	0	-1.3540	-0.01880	-0.00100	-0.00100	-0.00100	-0.00100	0
0.25	3	-	-	0.1698	-0.0385	-0.1026	-	-	-	-	-	-
0.25	5	-	0.02844	0.18087	-0.04401	-0.10844	-0.01309	-	-	-	-	-
0.25	7	-	0.02875	0.18094	-0.04407	-0.10846	-0.01315	-0.00061	-0.00061	-	-	-
0.25	9	0.00006	0.02875	0.18094	-0.04407	-0.10846	-0.01315	-0.00061	-0.00061	-0.00061	-0.00001	-
0.50	3	-	-	0.2258	-0.0921	-0.0886	-	-	-	-	-	-
0.50	5	-	0.04381	0.24109	-0.10601	-0.09429	-0.00984	-	-	-	-	-
0.50	7	-	0.04419	0.24101	-0.10601	-0.09432	-0.00983	-0.00042	-0.00042	-	-	-
0.50	9	0.00009	0.04419	0.24101	-0.10601	-0.09432	-0.00983	-0.00042	-0.00042	-0.00042	-0.00001	-
0.75	4	-	-	0.2535	-0.2125	-0.0919	-0.0080	-	-	-	-	-
0.75	6	-	0.06414	0.29352	-0.19631	-0.08901	-0.00785	-0.00030	-0.00030	-	-	-
0.75	8	-	0.06489	0.29356	-0.19655	-0.08903	-0.00786	-0.00030	-0.00030	-0.00030	0	-
0.75	10	0.00014	0.06489	0.29356	-0.19655	-0.08903	-0.00786	-0.00030	-0.00030	-0.00030	0	-
1	4	-	-	0.28202	-0.28148	-0.08213	-0.00618	-	-	-	-	-
1	6	-	0.08093	0.18199	-0.28194	-0.08219	-0.00619	-0.00021	-0.00021	-0.00021	0	-
1	8	-	0.08221	0.18199	-0.28199	-0.08219	-0.00619	-0.00021	-0.00021	-0.00021	0	-
1	10	0.00021	0.08221	0.18199	-0.28199	-0.08219	-0.00619	-0.00021	-0.00021	-0.00021	0	-





TABLE 2

Derivatives of the Momentum Eigenfunctions for the Third Band

k	No. of Eqs.	$dV_3/dk$	$dV_4/dk$	$dV_5/dk$	$dV_6/dk$	$dV_7/dk$	$dV_8/dk$	$dV_9/dk$	$dV_{10}/dk$	$dV_{11}/dk$	$dV_{12}/dk$	$dV_{13}/dk$	$dV_{14}/dk$
0	3	-	-	-1.5991	0	1.5991	-	-	-	-	-	-	-
0	5	-	-0.17638	-1.58018	0	1.58018	0.17638	-	-	-	-	-	-
0	7	-	-0.007619	-1.580478	0	1.580478	0.007619	0.007619	0.007619	0.007619	0.007619	0.007619	0.007619
0	9	-0.000177	-0.177206	-1.580478	0	1.580478	0.177206	0.177206	0.177206	0.177206	0.177206	0.177206	0.000177
0.25	3	-	-	-0.4150	0.1797	0.1408	-	-	-	-	-	-	-
0.25	5	-	-0.04830	-0.41288	0.18692	0.14575	-0.00526	-	-	-	-	-	-
0.25	7	-	-0.048413	-0.412903	0.187024	0.145789	-0.005479	-0.000954	-0.000954	-0.000954	-0.000954	-0.000954	-
0.25	9	-0.000046	-0.048413	-0.412903	0.187024	0.145789	-0.005479	-0.000954	-0.000954	-0.000954	-0.000954	-0.000954	-0.000036
0.50	3	-	-	-0.1180	0.1001	0.0358	-	-	-	-	-	-	-
0.50	5	-	-0.00654	-0.11345	0.10377	0.03885	-0.01401	-	-	-	-	-	-
0.50	7	-	-0.006164	-0.113584	0.104024	0.038944	-0.014317	-0.002132	-0.002132	-0.002132	-0.002132	-0.002132	-
0.50	9	0.000012	-0.006164	-0.113584	0.104014	0.038944	-0.014317	-0.002132	-0.002132	-0.002132	-0.002132	-0.002132	0.000060
0.75	4	-	-	-0.06379	0.12487	0.03152	-0.01336	-	-	-	-	-	-
0.75	6	-	0.01725	-0.05671	0.07166	0.01907	-0.01374	-0.00101	-0.00101	-0.00101	-0.00101	-0.00101	-
0.75	8	-	0.030658	-0.057503	0.071080	0.019071	-0.013809	-0.001026	-0.001026	-0.001026	-0.001026	-0.001026	-0.000037
1	4	-	-	-0.0285	0.0532	0.0123	-0.0124	-	-	-	-	-	-
1	6	-	10.65317	-2.14959	1.05958	-3.36779	-0.33596	-0.01299	-0.01299	-0.01299	-0.01299	-0.01299	-
1	8	-	22.47006	-5.09144	5.07986	-22.24943	-2.12918	-0.08107	-0.08107	-0.08107	-0.08107	-0.08107	-0.00167

CHAPTER IV

Verification of the Results by Using an Interpolation  
Formula

As a check on the method suggested in Chapter III, we are going to calculate the same derivatives from exact values of  $E$  and  $V$  at a number of points, using a simple interpolation formula. For example, we find the exact values of the energy and the momentum eigenfunctions at the points  $k \pm 0.01$ , using again the same technique as in Chapter II. The results for the first band are listed in Table 10.

Now we apply to the energies corresponding to each triplet of points  $k-0.01$ ,  $k$ ,  $k+0.01$  an interpolation formula of the type

$$E = E_0 + X\Delta E + \frac{X(X-1)}{2}\Delta^2 E \quad (4.1)$$

where  $E_0$  is the energy at  $k-0.01$ ,  $X = \frac{k - k_0}{0.01}$   
 $\Delta E = E(k) - E(k - 0.01)$  and  $\Delta^2 E = [E(k + 0.01) - E(k)] - \Delta E$ .

This formula leads to an equation of the form

$$E(k) = A + Bk + Ck^2 \quad (4.2)$$

from which we obtain the derivatives  $\frac{dE}{dk}(k)$ .

Using exactly the same interpolation formula we find

the derivatives  $\frac{dV}{dk}(k)$ .

Before we give the full results we write down as an example the procedure of finding the  $\frac{dE}{dk}(0.5)$ .



From table 10 we obtain.

k	E	$\Delta E$	$\Delta^2 E$
0.49	-0.8458303		
0.50	-0.8426695	0.0031608	0.000015
0.51	-0.8394937	0.0031758	

$$\text{Now } X = \frac{k - k_0}{0.01} = \frac{k - 0.49}{0.01} = 100k - 49$$

$$\text{and } X - 1 = 100k - 50$$

$$\text{Hence } E = E_0 + (100k - 49)\Delta E + \frac{(100k - 49)(100k - 50)}{2} \Delta^2 E$$

or after the substitutions

$$E(k) = -0.8458303 + 0.31608k - 49\Delta E + 0.075k^2 - 0.07425k + 1225\Delta^2 E$$

$$\text{or } E(k) = \text{constant} + 0.24183k + 0.075k^2$$

Taking the derivative

$$\frac{dE}{dk}(k) = 0.24183 + 2 \times 0.075k$$

For  $k = 0.5$  we have

$$\frac{dE}{dk}(0.5) = 0.24183 + 0.075 = 0.31683$$

which is in complete agreement with the value which we have found from the system.

In the same way we have obtained the results of Table 11 and compare them with the results of Chapter III written using the extended zone scheme.

The agreement of these results leads to the conclusion that the suggested method is successful.

What we have succeeded by the method of Chapter III, is to obtain the derivatives of  $E(k)$  or  $V(k)$  without knowing the values of these functions in a very close region of  $k$ 's. This involves less computational labour and probably more accuracy. The computer time is substantially reduced, because in this section we solved the system three times for each  $k$  region (i.e. for  $k-0.01$ ,  $k$ ,  $k+0.01$ ) and then we used interpolation formulae to find the required results; while in the suggested method we have to solve a little more complicated system, but only once for each  $k$ .

We also have better accuracy in the suggested method because of the fact that in this paragraph we calculated the derivatives at points  $k \pm 0.01$  which can always be improved by setting  $k \pm 0.001$ ,  $k \pm 0.0001$ , etc.

The suggested method is expected to be more valuable for the higher bands where the curves have more complicated form than the curves of the 1st band.

TABLE 10

k	E	V <sub>6</sub>	V <sub>4</sub>	V <sub>2</sub>	V <sub>0</sub>	V <sub>2</sub>	V <sub>4</sub>	V <sub>6</sub>
-0.01	-0.9367755	0.000572	0.014131	0.159738	0.515868	0.162464	0.014510	0.000599
0.00	-0.9368190	0.000578	0.014227	0.160058	0.512560	0.160058	0.014227	0.000578
0.01	-0.9367755	0.000591	0.014506	0.162424	0.515743	0.159700	0.014128	0.000580
0.24	-0.9125260	0.000874	0.019863	0.198421	0.510600	0.131810	0.010498	0.000396
0.25	-0.9105300	0.000891	0.020158	0.200328	0.510448	0.130793	0.010371	0.000389
0.26	-0.9084640	0.000906	0.020449	0.202168	0.510047	0.129725	0.010242	0.000387
0.49	-0.8458303	0.001379	0.018689	0.250429	0.493195	0.106621	0.007633	0.000269
0.50	-0.8426695	0.001407	0.029132	0.252869	0.492229	0.105693	0.007535	0.000262
0.51	-0.8394937	0.001435	0.029637	0.255807	0.492142	0.104962	0.007452	0.000260
0.74	-0.7697921	0.002219	0.042068	0.317427	0.456799	0.083761	0.005418	0.000180
0.75	-0.7672475	0.002265	0.042718	0.320389	0.454899	0.082879	0.005340	0.000173
0.76	-0.7647720	0.002305	0.043368	0.323315	0.452893	0.081985	0.005261	0.000171
0.99	-0.73332227	0.003512	0.060485	0.391389	0.397029	0.062130	0.003642	0.000113
1.00	-0.73326339	0.003579	0.061300	0.394189	0.394189	0.061300	0.003579	0.000108
1.01	-0.73332211	0.003635	0.062118	0.396963	0.391325	0.060476	0.003518	0.000108



TABLE 11

Derivatives of the Energy and Momentum Eigenfunctions for the First Band

k	<u>By solving system (3.1)</u>		<u>By interpolation formula</u>	
	dE/dk	dV/dk	dE/dk	dV/dk
0	0	0	0	0.00625
0.25	0.20311	0.04407	0.20310	0.03908
0.50	0.31687	0.10602	0.31683	0.10868
0.75	0.25106	0.19655	0.25100	0.19530
1.00	0	0.28199	0	0.28475
1.25		0.29356		0.29440
1.50		0.24101		0.24211
1.75		0.18094		0.18001
2.00		0.13540		0.13430
2.25		0.10846		0.10722
2.50		0.09432		0.09484
2.75		0.08903		0.08980
3.00		0.08219		0.08270
3.25		0.06489		0.06450
3.50		0.04419		0.04447
3.75		0.02875		0.02835
4.00		0.01880		0.01875
4.25		0.01315		0.01315
4.50		0.00983		0.00905
4.75		0.00786		0.00785
5.00		0.00619		0.00620
5.25		0.00430		0.00430
5.50		0.00265		0.00265
5.75		0.00257		0.00280
6.00		0.00100		0.00096
6.25		0.00061		0.00063
6.50		0.00042		0.00043
6.75		0.00030		0.00030
7.00		0.00021		0.00019

CHAPTER V

1. Further Differentiation of Schrödinger's Equation in Momentum Space

By successive differentiations of equations (3.1) with respect to  $k$ , we obtain for the one-dimensional case the following systems of equations:

For the second derivative

$$\left[ (k + K_1)^2 - E \right] \frac{d^2 V_{K_1}}{dk^2} + \sum_{K_m} W(K_m) \frac{d^2 V_{(K_1 - K_m)}}{dk^2} = \left[ \frac{d^2 E}{dk^2} - 2 \right] V_{K_1} + 2 \left[ \frac{dE}{dk} - 2(k + K_1) \right] \frac{dV_{K_1}}{dk} \quad (5.1)$$

For the third derivative

$$\left[ (k + K_1)^2 - E \right] \frac{d^3 V_{K_1}}{dk^3} + \sum_{K_m} W(K_m) \frac{d^3 V_{(K_1 - K_m)}}{dk^3} = \frac{d^3 E}{dk^3} V_{K_1} + 3 \left[ \frac{d^2 E}{dk^2} - 2 \right] \frac{dV_{K_1}}{dk} + 3 \left[ \frac{dE}{dk} - 2(k + K_1) \right] \frac{d^2 V_{K_1}}{dk^2} \quad (5.2)$$

For the fourth derivative

$$\left[ (k + K_1)^2 - E \right] \frac{d^4 V_{K_1}}{dk^4} + \sum_{K_m} W(K_m) \frac{d^4 V_{(K_1 - K_m)}}{dk^4} = \frac{d^4 E}{dk^4} V_{K_1} + 4 \frac{d^3 E}{dk^3} \frac{dV_{K_1}}{dk} + 6 \left[ \frac{d^2 E}{dk^2} - 2 \right] \frac{d^2 V_{K_1}}{dk^2} + 4 \left[ \frac{dE}{dk} - 2(k + K_1) \right] \frac{d^3 V_{K_1}}{dk^3} \quad (5.3)$$

For the  $n^{\text{th}}$  derivative

$$\left[ \right] \frac{d^n V_{K_1}}{dk^n} + \sum_{K_m} \dots = \frac{d^n E}{dk^n} V_{K_1} + \binom{n}{1} \frac{d^{n-1} E}{dk^{n-1}} \frac{dV_{K_1}}{dk} + \binom{n}{2} \frac{d^{n-2} E}{dk^{n-2}} \frac{d^2 V_{K_1}}{dk^2} + \dots + \binom{n}{1} \left[ \frac{dE}{dk} - 2(k + K_1) \right] \frac{d^{n-1} V_{K_1}}{dk^{n-1}}$$

Using the corresponding normalization conditions, obtained by successive differentiations of equation (3.2), that is

$$\sum_{K_i} \left[ \left( \frac{dV_{K_i}}{dk} \right)^2 + V_{K_i} \frac{d^2 V_{K_i}}{dk^2} \right] = 0 \quad (5.4)$$

$$\sum_{K_i} \left[ 3 \frac{dV_{K_i}}{dk} \frac{d^2 V_{K_i}}{dk^2} + V_{K_i} \frac{d^3 V_{K_i}}{dk^3} \right] = 0 \quad (5.5)$$

$$\sum_{K_i} \left[ 3 \left( \frac{d^2 V_{K_i}}{dk^2} \right)^2 + 4 \frac{dV_{K_i}}{dk} \frac{d^3 V_{K_i}}{dk^3} + V_{K_i} \frac{d^4 V_{K_i}}{dk^4} \right] = 0 \quad (5.6)$$

$$\sum_{K_i} \left[ V_{K_i} \frac{d^n V_{K_i}}{dk^n} + \binom{n}{1} \frac{d^{n-1} E}{dk^{n-1}} \frac{dV_{K_i}}{dk} + \dots + \frac{1}{2} \binom{n}{n/2} \left( \frac{d^{n/2} V_{K_i}}{dk^{n/2}} \right)^2 \right] = 0$$

$n$  is even  
 if  $n$  is odd, we have all the binomial coefficients.

One can solve the above systems, by the same method which we applied for finding the functions  $E(k)$  and  $V(k)$ , and their first derivatives.

Therefore we are able to calculate these functions and their derivatives at any point  $k_0$ . So  $E(k)$  and  $V(k)$  can be expanded in a Taylor's series of the form,

$$E(k) = E(k_0) + (k - k_0) E^{(1)}(k_0) + \frac{(k - k_0)^2}{2!} E^{(2)}(k_0) + \frac{(k - k_0)^3}{3!} E^{(3)}(k_0) + \dots \quad (5.7)$$

## 2. Application using a 5 X 5 determinant

Considering the same potential  $V(x) = -3 \cos 2x$  on which we have based all our previous calculations, we apply equations (5.1), (5.2) and (5.3) at  $k = 0$  for the first band. If we let  $K_1$  to take the values  $0, \pm 2, \pm 4$  we have the following systems of equations (Using the previous results for 5 equations):

From (5.1)

$$\left. \begin{aligned} 16.93675 \frac{dV_4}{dk^2} - 1.5 \frac{dV_2}{dk^2} &= 0.01426 \frac{dE}{dk^2} + 0.27212 \\ -1.5 \frac{dV_4}{dk^2} + 4.93675 \frac{dV_2}{dk^2} - 1.5 \frac{dV_0}{dk^2} &= 0.16101 \frac{dE}{dk^2} + 0.76734 \\ -3 \frac{dV_2}{dk^2} + 0.93675 \frac{dV_0}{dk^2} &= 0.51566 \frac{dE}{dk^2} - 1.03132 \end{aligned} \right\} \quad (5.8)$$

This system should contain 5 equations, but it has been reduced to a three equations one, because at  $k = 0$  the functions  $\frac{dV}{dk^2}$  are even. From (5.8) using (5.4) we have



found

$$\begin{aligned} \frac{d^2 E}{dk^2} &= 0.87045, & \frac{d^2 V_0}{dk^2} &= -0.16413 \\ \frac{d^2 V_2}{dk^2} &= \frac{d^2 V_4}{dk^2} = 0.14290, & \frac{d^2 V_4}{dk^2} &= \frac{d^2 V_2}{dk^2} = 0.02945 \end{aligned} \quad (5.9)$$

From (5.2) we obtain, for the odd functions  $\frac{d^3 V}{dk^3}$ , the following system:

$$\begin{aligned} 16.93675 \frac{d^3 V_4}{dk^3} - 1.5 \frac{d^3 V_2}{dk^3} &= 0.01426 \frac{d^3 E}{dk^3} + 0.64313 \\ -1.5 \frac{d^3 V_4}{dk^3} + 4.93675 \frac{d^3 V_2}{dk^3} - 1.5 \frac{d^3 V_0}{dk^3} &= 0.16101 \frac{d^3 E}{dk^3} + 1.25337 \\ 0.93675 \frac{d^3 V_0}{dk^3} &= 0.51566 \frac{d^3 E}{dk^3} \end{aligned} \quad (5.10)$$

Which gives the following values:

$$\begin{aligned} \frac{d^3 E}{dk^3} &= 0 & \frac{d^3 V_0}{dk^3} &= 0 \\ \frac{d^3 V_4}{dk^3} = -\frac{d^3 V_2}{dk^3} &= 0.06212, & \frac{d^3 V_2}{dk^3} = -\frac{d^3 V_4}{dk^3} &= 0.27276 \end{aligned} \quad (5.11)$$

From (5.3), since the functions  $\frac{d^4 V}{dk^4}$  are even, we obtain a system of three equations, that is:

$$\begin{aligned} 16.93675 \frac{d^4 V_4}{dk^4} - 1.5 \frac{d^4 V_2}{dk^4} &= 0.01426 \frac{d^4 E}{dk^4} + 1.78825 \\ -1.5 \frac{d^4 V_4}{dk^4} + 4.93675 \frac{d^4 V_2}{dk^4} - 1.5 \frac{d^4 V_0}{dk^4} &= 0.16101 \frac{d^4 E}{dk^4} + 3.39568 \\ -3 \frac{d^4 V_2}{dk^4} + 0.93675 \frac{d^4 V_0}{dk^4} &= 0.51566 \frac{d^4 E}{dk^4} + 1.11236 \end{aligned} \quad (5.12)$$

This system, using (5.6), gives the following solutions,

$$\begin{aligned} \frac{d^4 E}{dk^4} &= -5.40021, & \frac{d^4 V_0}{dk^4} &= -1.13262 \\ \frac{d^4 V_2}{dk^4} = \frac{d^4 V_4}{dk^4} &= 0.20376, & \frac{d^4 V_4}{dk^4} = \frac{d^4 V_2}{dk^4} &= 0.11908 \end{aligned} \quad (5.13)$$

Now with the values of  $E(0)$ ,  $\frac{dE}{dk}(0)$ ,  $\frac{d^2E}{dk^2}(0)$ ,  $\frac{d^3E}{dk^3}(0)$ ,  $\frac{d^4E}{dk^4}(0)$  we can find an analytical form for the function  $E(k)$ . This analytical form is, in fact, a Maclaurin's series with five terms, that is:

$$E(k) = E(0) + k \frac{dE}{dk}(0) + \frac{k^2}{2!} \frac{d^2E}{dk^2}(0) + \frac{k^3}{3!} \frac{d^3E}{dk^3}(0) + \frac{k^4}{4!} \frac{d^4E}{dk^4}(0) \quad (5.14)$$

Applying (5.14) for  $k = 0, 0.25, 0.50, 0.75, 1$ , we have found the following results for the energy in the first band:

	<u>Values from table 1</u>
$E(0.25) = -0.91043$	$E(0.25) = -0.91043$
$E(0.50) = -0.84201$	$E(0.50) = -0.84247$
$E(0.75) = -0.76313$	$E(0.75) = -0.76679$ (6 waves)
$E(1) = -0.72654$	$E(1) = -0.73224$ (6 waves)

which are in a very good agreement with the results of table 1. (page 37).

A similar calculation can be done for the functions  $V_0$ ,  $V_2$  and  $V_4$ .

Hence the conclusion is that in order to plot the curves  $E(k)$ , or  $V(k)$  we can calculate  $E(k)$ ,  $V(k)$  and its derivatives at the point  $k = 0$  and find the rest of the values from Maclaurin's series. We probably obtain more accurate results if we do the same at the point  $k = 1$  using now Taylor's expansion. It is expected to have, in this particular example, the exact solutions

using a system of 9 equations and calculating the derivatives of sixth order as well. Since the functions  $V$  are not at all smooth functions (see e.g.  $V_3$  - page 47) it is not expected that this favourable state of affairs holds in general.

The practical use of the method we have investigated when one performs a full three dimensional calculation for a real substance, will lie in allowing a fairly accurate plotting of the bands along a direction (such as the (100) direction or the (111) direction in a cubic crystal ) of which the wavefunction belongs at all points to the same irreducible representation of the same point group. So far, in many calculations, the  $E-k$  curves have been calculated only at widely separated points (e.g. at the centre and boundary of the Brillouin zone) and the curves have been sketched in between, following more or less plausible assumptions. In other words, the present method is designed to remove, in a large number of cases, the ambiguities that a simple application of the compatibility relations generally leaves in deciding which level at the centre is joined to which level at the boundary.



CHAPTER VI

1. The Wannier functions

We have seen in Chapter I that by expanding in a Fourier series the function  $\psi_{\underline{k}}(\underline{r})$  in ordinary space, we define the momentum eigenfunctions. Now we consider the expansion of  $\psi_{\underline{k}}(\underline{r})$  in a Fourier series, in  $\underline{k}$ -space, that is:

$$\psi_{\underline{k}}(\underline{r}) = \sum_{\underline{R}_i} a(\underline{r} - \underline{R}_i) e^{i\underline{R}_i \cdot \underline{k}} \quad (6.1)$$

The functions  $a(\underline{r} - \underline{R}_i)$  are called Wannier functions and are the exact atomic orbitals to insert in Bloch's formula. The Wannier functions, being Fourier coefficients in the expansion (6.1), are given by the relation

$$a(\underline{r} - \underline{R}_i) = \frac{1}{\Omega_B} \int_{\text{B.Z.}} \psi_{\underline{k}}(\underline{r}) e^{-i\underline{R}_i \cdot \underline{k}} d\underline{k} \quad (6.2)$$

where  $\Omega_B$  is the volume of the first Brillouin zone within which the above integration is being extended. These functions centred on different lattice sites are all identical, so it is enough to calculate  $a(\underline{r})$ .

We are now going to find a similar system of equations as we did for the momentum eigenfunctions.

So we calculate the matrix elements of the Hamiltonian

$H = -\nabla^2 + V$ . It is

$$H_{ij} = \int_{\text{all space}} a^*(\underline{r} - \underline{R}_i) \left[ -\nabla^2 + V \right] a(\underline{r} - \underline{R}_j) d\underline{r} \quad (6.3)$$

From equation (6.2) we get

$$Ha(\underline{r} - \underline{R}_i) = \frac{1}{\Omega_B} \int_{\text{unit cell}} H \psi_{\underline{k}}(\underline{r}) e^{-i\underline{R}_i \cdot \underline{k}} d\underline{k} \quad (6.4)$$

and because  $H\psi = E(\underline{k})\psi$  we have,

$$Ha(\underline{r} - \underline{R}_i) = \frac{1}{\Omega_B} \int_{\text{unit cell}} \psi_{\underline{k}}(\underline{r}) e^{-i\underline{R}_i \cdot \underline{k}} E(\underline{k}) d\underline{k} \quad (6.5)$$

Then substituting (6.1) into (6.5) we obtain the system of differential equations for the Wannier functions:

$$Ha(\underline{r} - \underline{R}_i) = \sum_{\underline{R}_j} a(\underline{r} - \underline{R}_i + \underline{R}_j) \epsilon(\underline{R}_j) \quad (6.6)$$

$$\text{where } \epsilon(\underline{R}_j) = \frac{1}{\Omega_B} \int_{\text{unit cell}} E(\underline{k}) e^{-i\underline{R}_j \cdot \underline{k}} d\underline{k} \quad (6.7)$$

and thus the  $E(\underline{k})$  relation is given by,

$$E(\underline{k}) = \sum_{\underline{R}_i} \epsilon(\underline{R}_i) e^{i\underline{R}_i \cdot \underline{k}} \quad (6.8)$$

There is a variational procedure to solve the system (6.6) and determine directly the Wannier functions, but it appears of difficult practical application and so we have decided to calculate the Wannier functions indirectly using the fact that they are Fourier transforms of the momentum eigenfunctions. This can be proved as follows:

In equation (6.2) substituting  $\psi$  as given by equation (2.7) we obtain

$$a(\underline{r} - \underline{R}_i) = \frac{1}{\Omega_B} \int_{\text{B.Z.}} e^{-i\underline{R}_i \cdot \underline{k}} d\underline{k} \sum_{\underline{K}_n} V(\underline{k} + \underline{K}_n) e^{i(\underline{k} + \underline{K}_n) \cdot \underline{r}} \quad (6.9)$$

or since  $\underline{K}_n \cdot \underline{R}_i = 2\pi m$

$$a(\underline{r} - \underline{R}_i) = \frac{1}{\Omega_B} \int_{\text{B.Z.}} d\underline{k} \sum_{\underline{K}_n} V(\underline{k} + \underline{K}_n) e^{i(\underline{k} + \underline{K}_n) \cdot (\underline{r} - \underline{R}_i)} \quad (6.10)$$

But the summation over all the Brillouin zones means integration over the whole  $\underline{k}$ -space. So we have

$$a(\underline{r} - \underline{R}_i) = \frac{1}{\Omega_B} \int_{\substack{\text{whole} \\ \underline{k}\text{-space}}} V(\underline{k}) e^{i\underline{k} \cdot (\underline{r} - \underline{R}_i)} d\underline{k} \quad (6.11)$$

In particular for  $\underline{R}_i = 0$  we get,

$$a(\underline{r}) = \frac{1}{\Omega_B} \int_{\substack{\text{whole} \\ \underline{k}\text{-space}}} V(\underline{k}) e^{i\underline{k} \cdot \underline{r}} d\underline{k} \quad (6.12)$$

Hence  $a(\underline{r})$  is the Fourier integral transform of  $V(\underline{k})$ .

In the same way we can prove that

$$V(\underline{k}) = \frac{1}{\Omega} \int_{\substack{\text{whole} \\ \text{ordinary space}}} a(\underline{r}) e^{-i\underline{k} \cdot \underline{r}} d\underline{r} \quad (6.13)$$

Thus  $a(\underline{r})$  and  $V(\underline{k})$  are Fourier transforms one another.



2. One-dimensional Application

For the one-dimensional case, formula (6.12) can be written as

$$a(x) = \frac{1}{2} \int_{-\infty}^{+\infty} V(k) \cos kx \, dk \quad (6.14)$$

In Chapter II we have found the values of  $V(k)$  for  $k = 0$  to  $k = 8$ . So integral (6.14) is approximately equivalent to the following.

$$a(x) = \int_0^8 V(k) \cos kx \, dk \quad (6.15)$$

which can be solved by applying Simpson's formula,

$$\int_a^b f(x) dx \approx \frac{h}{3} \left[ f(a) + 4f(a+h) + 2f(a+2h) + 4f(a+3h) + 2f(a+4h) + \dots + 2f\{a + (2n-2)h\} + 4f\{a + (2n-1)h\} + f(b) \right] \quad (6.16)$$

where  $h = \frac{b-a}{2n}$

Hence after calling  $V(k)\cos kx = f(kx)$ , we obtain,

$$a(x) = \frac{1}{12} \left[ f(0) + 4f(0.25x) + 2f(0.50x) + 4f(0.75x) + 2f(x) + 4f(1.25x) + 2f(1.50x) + 4f(1.75x) + 2f(2x) + 4f(2.25x) + 2f(2.5x) + 4f(2.75x) + 2f(3x) + 4f(3.25x) + 2f(3.50x) + 4f(3.75x) + 2f(4x) + 4f(4.25x) + 2f(4.50x) + 4f(4.75x) + 2f(5x) + 4f(5.25x) + 2f(5.50x) + 4f(5.75x) + 2f(6x) + 4f(6.25x) + 2f(6.50x) + 4f(6.75x) + 2f(7x) + 4f(7.25x) + 2f(7.50x) + 4f(7.75x) + f(8x) \right] \quad (6.17)$$

This formula has been applied on the following points  
 $x = 0, \frac{\pi}{8}, \frac{\pi}{4}, \frac{3\pi}{8}, \frac{\pi}{2}, \frac{3\pi}{4}, \pi, \frac{5\pi}{4}, \frac{3\pi}{2}, \frac{7\pi}{4}, 2\pi$

The results for the first band are listed in tables 13

For the free-electron case the Wannier functions *for the first*  
*band* have the form

$$a(x) = A \frac{\sin x}{x} \quad (6.18)$$

where A is a normalization factor which can be found using the results of the nearly free-electron case. Table 12 shows the values of the Wannier functions for the two cases. Plotting the corresponding curves we notice that in both cases we have the same sort of oscillation.

TABLE 12

Wannier functions for the first band

<u>x</u>	<u>a(x) (free electron)</u>	<u>a(x) (nearly free electron)</u>
0	0.64459	0.89062
$\frac{\pi}{8}$	0.62550	0.75572
$\frac{\pi}{4}$	0.57932	0.45204
$\frac{3\pi}{8}$	0.50513	0.24356
$\frac{\pi}{2}$	0.41036	0.11471
$\frac{3\pi}{4}$	0.19311	0.02485
$\pi$	0	-0.01298
$\frac{5\pi}{4}$	-0.11586	-0.01458
$\frac{3\pi}{2}$	-0.13679	-0.00498
$\frac{7\pi}{4}$	-0.08276	-0.00175
$2\pi$	0	0.00019



Calculation of the Wannier Functions

k	x=0		x=π/8			
	kx=0	coskx=1	f(kx)=V(k)	kx=kπ/8	cos kπ/8	f(kπ/8)
0			0.51256	0	1	0.51256
0.25			0.51045	π/32	0.99509	0.50794
0.50			0.49223	2π/32	0.98079	0.48277
0.75			0.45490	3π/32	0.95717	0.43542
1.00			0.39419	4π/32	0.92321	0.36392
1.25			0.32039	5π/32	0.88147	0.28242
1.50			0.25287	6π/32	0.83147	0.21025
1.75			0.20033	7π/32	0.77351	0.15496
2.00			0.16006	8π/32	0.70587	0.11298
2.25			0.13079	9π/32	0.63365	0.08287
2.50			0.10569	10π/32	0.55557	0.05872
2.75			0.08288	11π/32	0.47209	0.03913
3.00			0.06130	12π/32	0.38107	0.02336
3.25			0.04272	13π/32	0.28937	0.01236
3.50			0.02913	14π/32	0.19509	0.00568
3.75			0.02016	15π/32	0.09880	0.00199
4.00			0.01423	16π/32	0	0
4.25			0.01037	17π/32	-0.09880	-0.00102
4.50			0.00753	18π/32	-0.19509	-0.00147
4.75			0.00534	19π/32	-0.28937	-0.00154
5.00			0.00358	20π/32	-0.38107	-0.00136
5.25			0.00226	21π/32	-0.47209	-0.00107
5.50			0.00141	22π/32	-0.55557	-0.00078
5.75			0.00089	23π/32	-0.63365	-0.00056
6.00			0.00058	24π/32	-0.70587	-0.00041
6.25			0.00039	25π/32	-0.77351	-0.00030
6.50			0.00026	26π/32	-0.83147	-0.00022
6.75			0.00017	27π/32	-0.88147	-0.00015
7.00			0.00011	28π/32	-0.92321	-0.00010
7.25			0.00006	29π/32	-0.95711	-0.00006
7.50			0.00004	30π/32	-0.98079	-0.00004
7.75			0.00002	31π/32	-0.99509	-0.00002
8.00			0.00001	π	-1	-0.00001

$a(0) = 0.89062$

$a(\pi/8) = 0.75572$

Calculation of the Wannier functions

k	x = $\pi/4$			x = $3\pi/8$			x = $\pi/2$		
	$kx = k\frac{\pi}{4}$	$\cos k\frac{\pi}{4}$	$f(k\frac{\pi}{4})$	$kx = k\frac{3\pi}{8}$	$\cos k\frac{3\pi}{8}$	$f(k\frac{3\pi}{8})$	$kx = k\frac{\pi}{2}$	$\cos k\frac{\pi}{2}$	$f(k\frac{\pi}{2})$
0	0	1	0.51256	0	1	0.51256	0	1	0.51256
0.25	$\pi/16$	0.98079	0.50064	$3\pi/32$	0.95717	0.48859	$\pi/8$	0.92321	0.47125
0.50	$2\pi/16$	0.92321	0.45443	$6\pi/32$	0.83147	0.40927	$2\pi/8$	0.70587	0.34745
0.75	$3\pi/16$	0.83147	0.37823	$9\pi/32$	0.63365	0.28825	$3\pi/8$	0.38107	0.17335
1.00	$4\pi/16$	0.70587	0.27825	$12\pi/32$	0.38107	0.15021	$4\pi/8$	0	0
1.25	$5\pi/16$	0.55557	0.17800	$15\pi/32$	0.09880	0.03165	$5\pi/8$	-0.38107	-0.12209
1.50	$6\pi/16$	0.38107	0.09636	$18\pi/32$	-0.19509	-0.04933	$6\pi/8$	-0.70587	-0.17849
1.75	$7\pi/16$	0.19509	0.03908	$21\pi/32$	-0.47209	-0.09457	$7\pi/8$	-0.92321	-0.18495
2.00	$8\pi/16$	0	0	$24\pi/32$	-0.70587	-0.11298	$8\pi/8$	-1	-0.16006
2.25	$9\pi/16$	-0.19509	-0.03123	$27\pi/32$	-0.88147	-0.11529	$9\pi/8$	-0.92321	-0.12075
2.50	$10\pi/16$	-0.38107	-0.04984	$30\pi/32$	-0.98079	-0.10366	$10\pi/8$	-0.70587	-0.07460
2.75	$11\pi/16$	-0.55557	-0.05872	$33\pi/32$	-0.99509	-0.08247	$11\pi/8$	-0.38107	-0.03158
3.00	$12\pi/16$	-0.70587	-0.05850	$36\pi/32$	-0.92321	-0.05659	$12\pi/8$	0	0
3.25	$13\pi/16$	-0.83147	-0.05097	$39\pi/32$	-0.77351	-0.03304	$13\pi/8$	-0.38107	0.01628
3.50	$14\pi/16$	-0.92321	-0.03944	$42\pi/32$	-0.55557	-0.01618	$14\pi/8$	0.70587	0.02056
3.75	$15\pi/16$	-0.98079	-0.02857	$45\pi/32$	-0.28937	-0.00583	$15\pi/8$	0.92321	0.01861
4.00	$16\pi/16$	-1	-0.02016	$48\pi/32$	0	0	$16\pi/8$	1	0.01423
4.25	$17\pi/16$	-0.98079	-0.01396	$51\pi/32$	0.28937	0.00300	$17\pi/8$	0.92321	0.00957
4.50	$18\pi/16$	-0.92321	-0.00957	$54\pi/32$	0.55557	0.00418	$18\pi/8$	0.70587	0.00531
4.75	$19\pi/16$	-0.83147	-0.00626	$57\pi/32$	0.77351	0.00413	$19\pi/8$	0.38107	0.00203
5.00	$20\pi/16$	-0.70387	-0.00377	$60\pi/32$	0.92321	0.00330	$20\pi/8$	0	0
5.25	$21\pi/16$	-0.55557	-0.00199	$63\pi/32$	0.99509	0.00225	$21\pi/8$	-0.38107	-0.00086
5.50	$22\pi/16$	-0.38107	-0.00086	$66\pi/32$	0.98079	0.00138	$22\pi/8$	-0.70587	-0.00099
5.75	$23\pi/16$	-0.19509	-0.00027	$69\pi/32$	0.88147	0.00078	$23\pi/8$	-0.92321	-0.00082
6.00	$24\pi/16$	0	0	$72\pi/32$	0.70587	0.00041	$24\pi/8$	-1	-0.00058
6.25	$25\pi/16$	0.19509	0.00011	$75\pi/32$	0.47209	0.00018	$25\pi/8$	-0.92321	-0.00036
6.50	$26\pi/16$	0.38107	0.00015	$78\pi/32$	0.19509	0.00005	$26\pi/8$	-0.70587	-0.00018
6.75	$27\pi/16$	0.55557	0.00014	$81\pi/32$	-0.09880	-0.00002	$27\pi/8$	-0.38107	-0.00006
7.00	$28\pi/16$	0.70587	0.00012	$84\pi/32$	-0.38107	-0.00004	$28\pi/8$	0	0
7.25	$29\pi/16$	0.83147	0.00009	$87\pi/32$	-0.63365	-0.00004	$29\pi/8$	0.38107	0.00002
7.50	$30\pi/16$	0.92321	0.00005	$90\pi/32$	-0.83147	-0.00003	$30\pi/8$	0.70587	0.00003
7.75	$31\pi/16$	0.98079	0.00004	$93\pi/32$	-0.95717	-0.00002	$31\pi/8$	0.92321	0.00002
8.00	$2\pi$	1	0.00001	$96\pi/32$	-1	-0.00001	$32\pi/8$	1	0.00001

$a(\pi/4) = 0.45204$

$a(3\pi/8) = 0.24356$

$a(\pi/2) = 0.11471$

Calculation of the Wannier functions

k	x = 3π/4			x = π		
	kx=k <sup>3π</sup> / <sub>4</sub>	cosk <sup>3π</sup> / <sub>4</sub>	f(k <sup>3π</sup> / <sub>4</sub> )	kx=kπ	coskπ	f(kπ)
0	0	1	0.51256	0	1	0.51256
0.25	3π/16	0.83147	0.42442	π/4	0.70587	0.36031
0.50	6π/16	0.38107	0.18757	2π/4	0	0
0.75	9π/16	-0.19509	-0.08875	3π/4	-0.70587	-0.32110
1.00	12π/16	-0.70587	-0.27825	4π/4	-1	-0.39419
1.25	15π/16	-0.98079	-0.31423	5π/4	-0.70587	-0.22615
1.50	18π/16	-0.92321	-0.23345	6π/4	0	0
1.75	21π/16	-0.55557	-0.11130	7π/4	0.70587	0.14141
2.00	24π/16	0	0	8π/4	1	0.16006
2.25	27π/16	0.55557	0.07266	9π/4	0.70587	0.09232
2.50	30π/16	0.92321	0.09757	10π/4	0	0
2.75	33π/16	0.98079	0.08129	11π/4	-0.70587	-0.05850
3.00	36π/16	0.70587	0.04327	12π/4	-1	-0.06130
3.25	39π/16	0.19509	0.00833	13π/4	-0.70587	-0.03015
3.50	42π/16	-0.38107	-0.01110	14π/4	0	0
3.75	45π/16	-0.83147	-0.01676	15π/4	0.70587	0.01423
4.00	48π/16	-1	-0.01423	16π/4	1	0.01423
4.25	51π/16	-0.83147	-0.00862	17π/4	0.70587	0.00732
4.50	54π/16	-0.38107	-0.00287	18π/4	0	0
4.75	57π/16	0.19509	0.00104	19π/4	-0.70587	-0.00377
5.00	60π/16	0.70587	0.00253	20π/4	-1	-0.00358
5.25	63π/16	0.98079	0.00222	21π/4	-0.70587	-0.00159
5.50	66π/16	0.92321	0.00130	22π/4	0	0
5.75	69π/16	0.55557	0.00049	23π/4	0.70587	0.00063
6.00	72π/16	0	0	24π/4	1	0.00058
6.25	75π/16	-0.55557	-0.00022	25π/4	0.70587	0.00027
6.50	78π/16	-0.92321	-0.00024	26π/4	0	0
6.75	81π/16	-0.98079	-0.00017	27π/4	-0.70587	-0.00012
7.00	84π/16	-0.70587	-0.00008	28π/4	-1	-0.00011
7.25	87π/16	-0.19509	-0.00001	29π/4	-0.70587	-0.00004
7.50	90π/16	0.38107	0.00001	30π/4	0	0
7.75	93π/16	0.83147	0.00002	31π/4	0.70587	0.00001
8.00	96π/16	1	0.00001	32π/4	1	0.00001

a(3π/4) = 0.02485

a(π) = -0.01298



Calculation of the Wannier Functions

k	$x = 5\pi/4$			$x = 3\pi/2$		
	$kx = k\frac{5\pi}{4}$	$\cos k\frac{5\pi}{4}$	$f(k\frac{5\pi}{4})$	$kx = k\frac{3\pi}{2}$	$\cos k\frac{3\pi}{2}$	$f(k\frac{3\pi}{2})$
0	0	1	0.51256	0	0	0.51256
0.25	$5\pi/16$	0.55557	0.28359	$3\pi/8$	0.38107	0.19452
0.50	$10\pi/16$	-0.38107	-0.18757	$6\pi/8$	-0.70587	-0.34745
0.75	$15\pi/16$	-0.98079	-0.44616	$9\pi/8$	-0.92321	-0.41997
1.00	$20\pi/16$	-0.70587	-0.27825	$12\pi/8$	0	0
1.25	$25\pi/16$	0.19509	0.06250	$15\pi/8$	0.92321	0.29579
1.50	$30\pi/16$	0.92321	0.23345	$18\pi/8$	0.70587	0.17849
1.75	$35\pi/16$	0.83147	0.16657	$21\pi/8$	-0.38107	-0.07634
2.00	$40\pi/16$	0	0	$24\pi/8$	-1	-0.16006
2.25	$45\pi/16$	-0.83147	-0.10875	$27\pi/8$	-0.38107	-0.04984
2.50	$50\pi/16$	-0.92321	-0.09757	$30\pi/8$	0.70587	0.07460
2.75	$55\pi/16$	-0.19509	-0.01617	$33\pi/8$	0.92321	0.07651
3.00	$60\pi/16$	0.70587	0.04327	$36\pi/8$	0	0
3.25	$65\pi/16$	0.98079	0.04190	$39\pi/8$	-0.92321	-0.03944
3.50	$70\pi/16$	0.38107	0.01110	$42\pi/8$	-0.70587	-0.02056
3.75	$75\pi/16$	-0.55557	-0.01120	$45\pi/8$	0.38107	0.00768
4.00	$80\pi/16$	-1	-0.01423	$48\pi/8$	1	0.01423
4.25	$85\pi/16$	-0.55557	-0.00576	$51\pi/8$	0.38107	0.00395
4.50	$90\pi/16$	0.38107	0.00287	$54\pi/8$	-0.70587	-0.00531
4.75	$95\pi/16$	0.98079	0.00524	$57\pi/8$	-0.92321	-0.00493
5.00	$100\pi/16$	0.70587	0.00253	$60\pi/8$	0	0
5.25	$105\pi/16$	-0.19509	-0.00044	$63\pi/8$	0.92321	0.00209
5.50	$110\pi/16$	-0.92321	-0.00130	$66\pi/8$	0.70587	0.00099
5.75	$115\pi/16$	-0.83147	-0.00074	$69\pi/8$	-0.38107	-0.00034
6.00	$120\pi/16$	0	0	$72\pi/8$	-1	-0.00058
6.25	$125\pi/16$	0.83147	0.00032	$75\pi/8$	-0.38107	-0.00015
6.50	$130\pi/16$	0.92321	0.00024	$78\pi/8$	0.70587	0.00018
6.75	$135\pi/16$	0.29509	0.00003	$81\pi/8$	0.92321	0.00016
7.00	$140\pi/16$	-0.70587	-0.00008	$84\pi/8$	0	0
7.25	$145\pi/16$	-0.98079	-0.00006	$87\pi/8$	-0.92321	-0.00005
7.50	$150\pi/16$	-0.38107	-0.00001	$90\pi/8$	-0.70587	-0.00003
7.75	$155\pi/16$	0.55557	0.00001	$93\pi/8$	0.38107	0.00001
8.00	$160\pi/16$	1	0.00001	$96\pi/8$	1	0.00001

$a(5\pi/4) = -0.01458$

$a(3\pi/2) = -0.00498$

Calculation of the Wannier Functions

k	$x = \frac{7\pi}{4}$			$x = 2\pi$		
	$kx = k\frac{7\pi}{4}$	$\cos k\frac{7\pi}{4}$	$f(k\frac{7\pi}{4})$	$kx = k2\pi$	$\cos k2\pi$	$f(k2\pi)$
0	0	1	0.51256	0	1	0.51256
0.25	$7\pi/16$	0.19509	0.09958	$2\pi/4$	0	0
0.50	$14\pi/16$	-0.92321	-0.45443	$4\pi/4$	-1	-0.49223
0.75	$21\pi/16$	-0.55557	-0.25273	$6\pi/4$	0	0
1.00	$28\pi/16$	0.70587	0.27825	$8\pi/4$	1	0.39419
1.25	$35\pi/16$	0.83147	0.26639	$10\pi/4$	0	0
1.50	$42\pi/16$	-0.38107	-0.09636	$12\pi/4$	-1	-0.25287
1.75	$49\pi/16$	-0.98079	-0.19648	$14\pi/4$	0	0
2.00	$56\pi/16$	0	0	$16\pi/4$	1	0.16006
2.25	$63\pi/16$	0.98079	0.12828	$18\pi/4$	0	0
2.50	$70\pi/16$	0.38107	0.04027	$20\pi/4$	-1	-0.10569
2.75	$77\pi/16$	-0.83147	-0.06891	$22\pi/4$	0	0
3.00	$84\pi/16$	-0.70587	-0.04327	$24\pi/4$	1	0.06130
3.25	$91\pi/16$	0.55557	0.02373	$26\pi/4$	0	0
3.50	$98\pi/16$	0.92321	0.02689	$28\pi/4$	-1	-0.02913
3.75	$105\pi/16$	-0.19509	-0.00393	$30\pi/4$	0	0
4.00	$112\pi/16$	-1	-0.01423	$32\pi/4$	1	0.01423
4.25	$119\pi/16$	-0.19509	-0.00202	$34\pi/4$	0	0
4.50	$126\pi/16$	0.92321	0.00695	$36\pi/4$	-1	-0.00753
4.75	$133\pi/16$	0.55557	0.00297	$38\pi/4$	0	0
5.00	$140\pi/16$	-0.70587	-0.00253	$40\pi/4$	1	0.00358
5.25	$147\pi/16$	-0.83147	-0.00188	$42\pi/4$	0	0
5.50	$154\pi/16$	0.38107	0.00054	$44\pi/4$	-1	-0.00141
5.75	$161\pi/16$	0.98079	0.00087	$46\pi/4$	0	0
6.00	$168\pi/16$	0	0	$48\pi/4$	1	0.00058
6.25	$175\pi/16$	-0.98079	-0.00038	$50\pi/4$	0	0
6.50	$182\pi/16$	-0.38107	-0.00010	$52\pi/4$	-1	-0.00026
6.75	$189\pi/16$	0.83147	0.00014	$54\pi/4$	0	0
7.00	$196\pi/16$	0.70587	0.00008	$56\pi/4$	1	0.00011
7.25	$203\pi/16$	-0.55557	-0.00003	$58\pi/4$	0	0
7.50	$210\pi/16$	-0.92321	-0.00004	$60\pi/4$	-1	-0.00004
7.75	$217\pi/16$	0.19509	0	$62\pi/4$	0	0
8.00	$224\pi/16$	1	0.00001	$64\pi/4$	1	0.00001

$a(7\pi/4) = -0.00175$

$a(2\pi) = 0.00019$

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