

## LATTICE DYNAMICS PROGRAM

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SUBROUTINE PRDOS(NH,NWMAX,N,NMAX,DCYSC,DOSXSC)
  INTEGER I,L,CHK(120),DCYSC,DOSXSC,XAXIS,YAXIS,SPACE,CROSS,
1      INT2,SUB,NOUGHT,ONE,TWO,THREE,FOUR,FIVE,
2      SIX,SEVEN,EIGHT,NINE,DCYSC2,SCALE,K
  REAL NW(6,200),NWMAX,N(200),NMAX
  COMMON CH
  DATA XAXIS,YAXIS,SPACE,CROSS/1H1,1H-,1H ,1H+/
  DATA NOUGHT,ONE,TWO,THREE,FOUR/1H0,1H1,1H2,1H3,1H4/
  DATA FIVE,SIX,SEVEN,EIGHT,NINE/1H5,1H6,1H7,1H8,1H9/
C
C   THIS SUBROUTINE PRODUCES ON THE LINEPRINTER GRAPHS OF THE DENSITY
C   OF STATES FOR EACH POLARIZATION, AND THE TOTAL DENSITY OF STATES.
C
  WRITE(2,1200)
1200 FORMAT(//////41H DENSITY OF STATES FOR EACH POLARIZATION)
  DCYSC2=DCYSC+2
  DO 201 L=1,DCYSC2,1
201   CHK(L)=SPACE
      CHK(2)=NOUGHT
      CHK(12)=ONE
      CHK(22)=TWO
      CHK(32)=THREE
      CHK(42)=FOUR
      CHK(52)=FIVE
      CHK(62)=SIX
      CHK(72)=SEVEN
      CHK(82)=EIGHT
      CHK(92)=NINE
      CHK(102)=NOUGHT
      CHK(112)=ONE
      WRITE(2,1201) (CHK(K),K=1,DCYSC2)
      DO 202 L=2,DCYSC2,1
202   CHK(L)=YAXIS
      CHK(1)=NOUGHT
      WRITE(2,1201) (CHK(K),K=1,DCYSC2)
1201 FORMAT(1H ,120A1)
      DOSXSC=DOSXSC+2
      DO 203 I=1,DOSXSC,1
        DO 204 L=1,DCYSC2,1
204   CHK(L)=SPACE
          INT2=DCYSC/3
          DO 205 L=1,3,1
            SUB=IFIX(NW(L,I+1)*FLOAT(INT2)/NWMAX+1.5)+INT2*(L-1)
            CHK(SUB)=CROSS
205   CONTINUE
          CHK(1)=XAXIS
          CHK(INT2+1)=XAXIS
          INT2=2*INT2
          CHK(INT2+1)=XAXIS
          SCALE=I/10
          IF(SCALE*10.EQ,I) GOTO 206
          WRITE(2,1202) (CHK(K),K=1,DCYSC2)
1202  FORMAT(2H ,120A1)
          GOTO 203
206   IF(SCALE.LT.10) GOTO 207
        SCALE=SCALE-10

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## LATTICE DYNAMICS PROGRAM

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      GOTO 206
207   WRITE(2,1203)SCALE, (CH(K),K=1,DCYSC2)
1203  FORMAT(1H ,I1,120A1)
203  CONTINUE
      WRITE(2,1300)
1300  FORMAT(//////25H TOTAL DENSITY OF STATES)
      DO 301 L=1,DCYSC2,1
301   CH(L)=SPACE
      CH(2)=NOUGHT
      CH(12)=ONE
      CH(22)=TWO
      CH(32)=THREE
      CH(42)=FOUR
      CH(52)=FIVE
      CH(62)=SIX
      CH(72)=SEVEN
      CH(82)=EIGHT
      CH(92)=NINE
      CH(102)=NOUGHT
      CH(112)=ONE
      WRITE(2,1301) (CH(K),K=1,DCYSC2)
      DO 302 L=2,DCYSC2,1
302   CH(L)=YAXIS
      CH(1)=NOUGHT
      WRITE(2,1301) (CH(K),K=1,DCYSC2)
1301  FORMAT(1H ,120A1)
      DO 303 I=1,DOSXSC,1
      DO 304 L=1,DCYSC2,1
304   CH(L)=SPACE
      SUB=IFIX(N(I+1)*FLOAT(DCYSC)/NMAX+1.5)
      CH(SUB)=CROSS
      CH(1)=XAXIS
      SCALE=I/10
      IF(SCALE*10.EQ.I) GOTO 305
      WRITE(2,1302) (CH(K),K=1,DCYSC2)
1302  FORMAT(2H ,120A1)
      GOTO 303
305   IF(SCALE.LT.10) GOTO 306
      SCALE=SCALE-10
      GOTO 305
306   WRITE(2,1303)SCALE, (CH(K),K=1,DCYSC2)
1303  FORMAT(1H ,I1,120A1)
303  CONTINUE
      RETURN
      END

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## CHAPTER 10

# *Electron Energy Bands in a One-dimensional Periodic Potential*

R. D. CLARKE and D. J. MARTIN

### 1. INTRODUCTION

A particularly demanding area encountered in any course on solid-state physics is that of the energies of electrons in crystals.<sup>1</sup> Familiarity with this material is basic to a proper understanding of electrical phenomena in metals and semiconductors; perhaps the most significant difficulty that arises is that any realistic treatment necessitates the use of numerical methods. Commonly, however, only qualitative arguments or rather unrealistic models, such as the Kronig–Penney model,<sup>2</sup> are presented. The computer program presented here enables the user to investigate electron energies in a system where the form, magnitude, and period of the potential can be specified by the user. The results can be compared with those derived from approximate analytic treatments for certain ranges of the parameters. Exercises of this kind can supplement more conventional presentations and give students some familiarity with the basic methods employed in band structure calculations.

Any system involving particles will exhibit quantum-mechanical features if the de Broglie wavelength associated with the momentum of the particles is of the same order of magnitude or greater than a typical length over which the potential acting on the particles changes significantly. It is easy to show that this is the case for conduction electrons in a solid by the following considerations.

In the case of metals a typical free electron density ( $N$ ) is  $\sim 4 \times 10^{28} \text{ m}^{-3}$ . An ideal Fermi–Dirac gas of this density would have kinetic energy ( $E$ ) per particle  $\sim \hbar^2(3\pi^2N)^{2/3}/2m_e \sim 7 \times 10^{-19} \text{ J}$ , a velocity ( $v$ )  $\sim \sqrt{2E/m_e} \sim 1.2 \times 10^6 \text{ m s}^{-1}$ , and a corresponding wavelength  $\lambda = h/m_e v \sim 6 \times 10^{-10} \text{ m}$ . For a semiconductor  $E \sim k_B T \sim 10^{-21} \text{ J}$ , so  $v \sim 10^5 \text{ m s}^{-1}$  and  $\lambda \sim 7 \times 10^{-9} \text{ m}$ .

The potential acting on the electrons will vary significantly over the

interatomic spacing  $\sim 3 \times 10^{-10}$  m. It follows that quantum-mechanical methods are essential to tackle the problem.

The computer program presented here solves the Schrödinger equation to an accuracy of  $\sim 1$  per cent for electrons in a one-dimensional potential, the form, magnitude, and period of which can be set by the user.

This study was limited to the one-dimensional case because it is designed as an aid to learning and deliberately avoids the numerical and conceptual complications of the three-dimensional case. It should, however, be noted that there are in fact some systems such as 'KCP' ( $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ ) where the electron motion is in reality effectively confined to one dimension.<sup>3</sup>

One of the most significant factors influencing the behaviour of electrons in a typical metal or semiconductor is the fact that the potential to which they are subject is *periodic*. The reason for the periodicity is that the atoms are arranged in a regular crystal lattice. (Amorphous—randomized—metals and semiconductors exist but a rather different theoretical approach is then necessary.) The potential is periodic over many thousands of atoms, even if the material as a whole is polycrystalline.

## 2. ELECTRONS IN A PERIODIC POTENTIAL

### 2.1 Brillouin zones

It is not difficult to appreciate that the periodic potential due to the regular crystal lattice will affect the electron energies, and indeed to see in general terms what the effect will be. Electrons in free space have kinetic energy  $E = \frac{1}{2}m_e v^2$ . Knowing that for electrons in a solid quantum effects are important we can use the de Broglie relationship to express this as

$$E = \frac{h^2}{2m_e \lambda^2} \quad \text{or} \quad E = \frac{\hbar^2 k^2}{2m_e}$$

where  $k (= 2\pi/\lambda)$  is called the wave number. The corresponding wave function in free space is  $\psi(x) = \exp(ikx)$ . In the case of a crystalline solid, states are specified by  $n$  (the band index) and  $k$  (the 'crystal momentum').

For a weak potential of period  $a$ ,  $E = \hbar^2 k^2 / 2m_e$  except when  $k$  is close to  $n\pi/a$  ( $n = \pm 1, \pm 2, \dots$ )—the Brillouin zone boundaries. The reason why deviations always occur in these regions is that a wave function of the form  $\psi(x) = \exp(ikx)$  represents a *travelling* wave in the  $+x$ -direction, of wavelength  $2\pi/k$ . From the condition for Bragg reflection:  $2a \sin \theta = n\lambda$  (where  $a$  is the interplane spacing) we might expect the travelling electron wave to be strongly affected in our one-dimensional case (for which  $\sin \theta = 1$ ) when  $2a = n\lambda$ , i.e.  $2a = n \cdot 2\pi/k$ , i.e.  $k = n\pi/a$ . The electron waves cannot propagate at the zone boundaries and a discontinuity occurs in the  $E$ - $k$

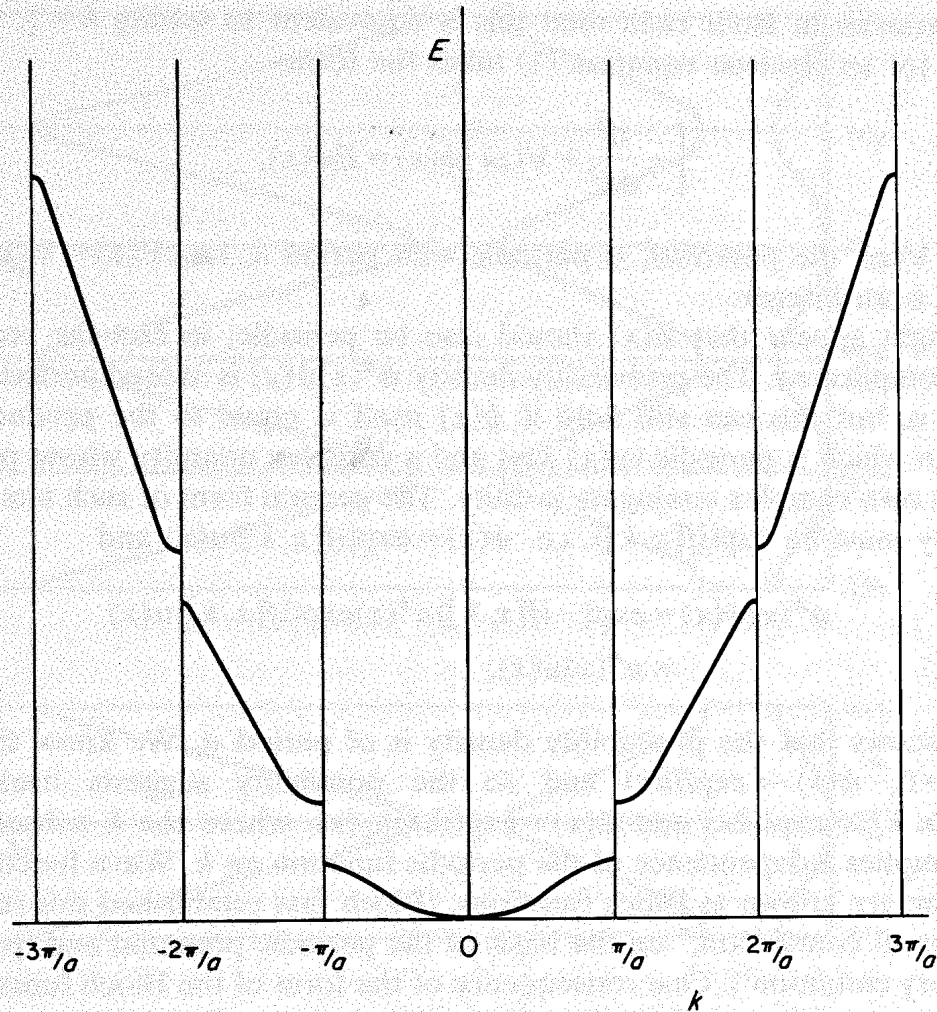


Figure 1. A typical  $E$ - $k$  relationship for a weak potential. Discontinuities in  $E$  occur at  $k = n\pi/a$  ( $n = \pm 1, \pm 2, \dots$ )

relationship (see Figure 1). The region for  $0 < |k| < \pi/a$  is called the first Brillouin zone,  $\pi/a < |k| < 2\pi/a$  the second Brillouin zone, etc.

While these general arguments give a qualitative picture, a determination of the details of the variation of  $E$  with  $k$  depends on solving the Schrödinger equation for the particular periodic potential involved.

## 2.2 Bloch functions

The time-independent Schrödinger equation for an electron in one dimension is

$$\left[ -\frac{\hbar^2}{2m_e} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x). \quad (1)$$

If we use atomic units (see Chapter 9) and measure energies in Rydbergs

and distances in Bohr radii then this is equivalent to setting  $\hbar = 1$ ,  $m_e = \frac{1}{2}$ . Hence for an electron equation (1) takes the form:

$$\left[ -\frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x), \quad (2)$$

where  $V(x)$ , the potential, is periodic with period  $a$ , i.e.  $V(x) = V(x + ma)$  and  $m$  is an integer.

It might appear that  $\psi(x)$  should also be periodic; in fact the reality is more complicated. The probability density  $\psi^*(x)\psi(x)$  is indeed periodic with period  $a$ , but this can still hold if  $\psi(x)$  itself is equal to the product of a function which is periodic ( $u(x)$  say) and a complex quantity whose product with its own complex conjugate is unity. The general form of such a complex quantity must be  $\exp(if[x, k])$ , i.e.  $\psi(x) = \exp(if[x, k])u(x)$  and

$$\begin{aligned} \psi^*(x)\psi(x) &= \exp(-if[x, k])u^*(x)\exp(if[x, k])u(x) \\ &= u^*(x)u(x), \end{aligned} \quad (3)$$

which shows that the probability density is of period  $a$ . We know that for  $V(x) \rightarrow 0$ ,  $\psi(x) \rightarrow \exp(ikx)$  and so the possibility suggests itself that  $\exp(if[x, k]) = \exp(ikx)$  and  $\psi(x) = \exp(ikx)u_k(x)$ , where the  $k$  subscript on  $u_k(x)$  implies a dependence of the periodic function on  $k$ . Wave functions of this form are known as Bloch functions. (Bloch first established this result in the present connection,<sup>4</sup> on the basis of the periodic potential and 'periodic boundary condition'). One consequence of the form of the Bloch functions is that there are states at  $k + 2n\pi/a$  ( $n = \pm 1, \pm 2, \dots$ ) with the same energy as a state at  $k$ . Consider the state  $\psi_k(x) = \exp(ikx)u_k(x)$  and the state at  $k' = k + 2n\pi/a$ ;

$$\begin{aligned} \psi_{k'}(x) &= \exp(ik'x)u_{k'}(x) \\ &= \exp(ikx)\exp(i2n\pi x/a)u_{k'}(x), \end{aligned} \quad (4)$$

where  $\exp(i2n\pi x/a)$  is of period  $a$  so that  $\exp(i2n\pi x/a)u_{k'}(x)$  is of period  $a$ . A possible form for this function, which will certainly correspond to a solution of equation (1) is

$$\exp(i2n\pi x/a)u_{k'}(x) = u_k(x), \quad (5)$$

in which case

$$\psi_k(x) = \psi_{k'}(x), \quad (6)$$

i.e. the two states are the same.

There are, in consequence, three entirely equivalent ways in which the  $E-k$  relationship can be presented (see Figure 2):



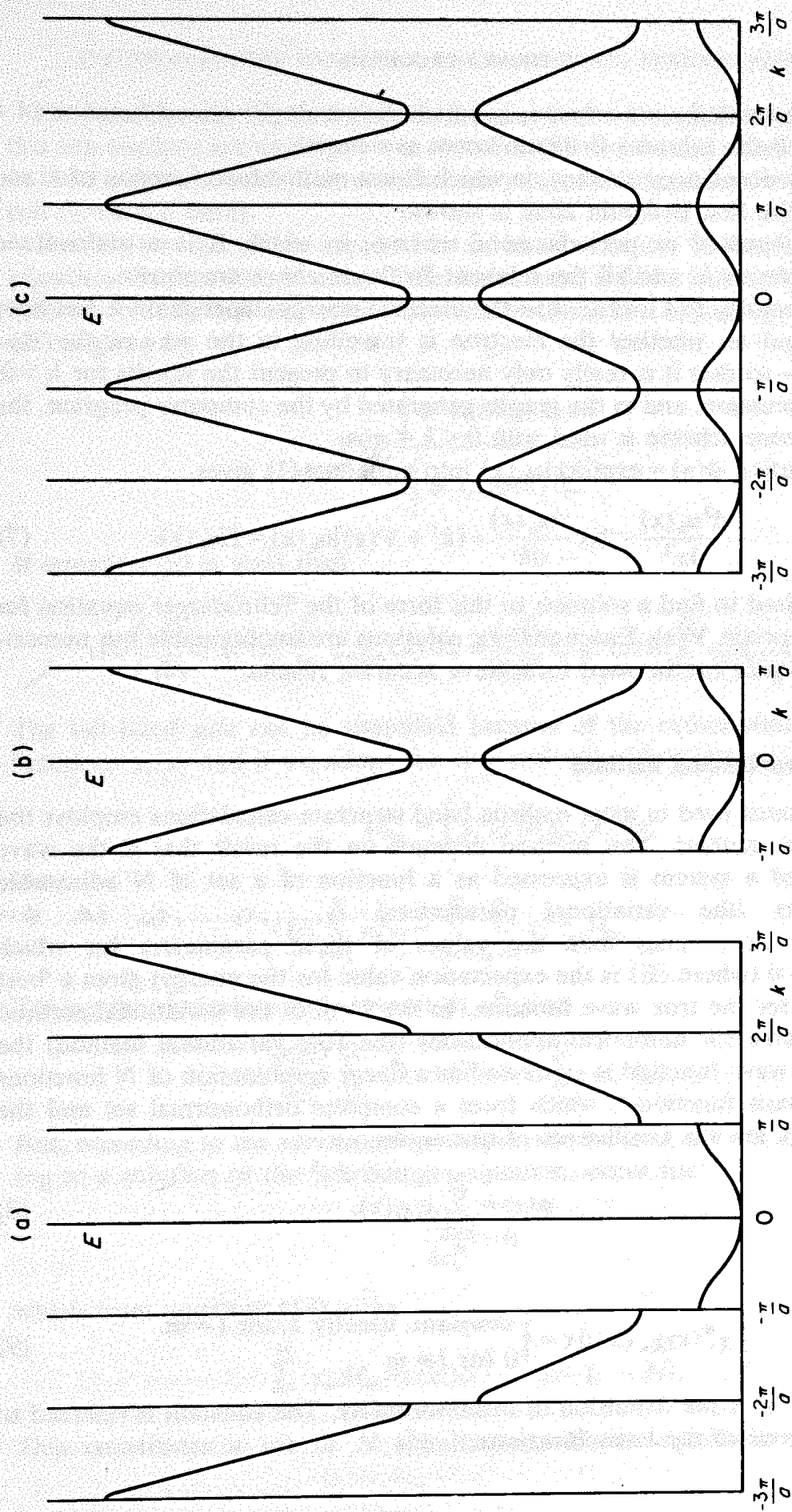


Figure 2. The three equivalent zone schemes: (a) the extended zone scheme; (b) the reduced zone scheme; and (c) the repeated or periodic zone scheme

- (a) The extended zone scheme, in which  $E$  is a single-valued function of  $k$  and all the relevant Brillouin zones are shown.
- (b) The reduced zone scheme, in which  $E$  is a multivalued function of  $k$  and only the first Brillouin zone is shown.
- (c) The repeated or periodic zone scheme, in which  $E$  is a multivalued function of  $k$ , and all the relevant Brillouin zones are shown.

Furthermore,  $E(k) = E(-k)$ —the electron energy depends on  $k$  but does not depend on whether the electron is travelling in the  $+x$ - or the  $-x$ -direction—so that it is really only necessary to present the results for  $k > 0$ . In this discussion, and in the graphs generated by the computer program, the reduced zone scheme is used with  $0 < k < \pi/a$ .

Substituting  $\psi(x) = \exp(ikx)u_k(x)$  into equation (1) gives

$$-\frac{d^2 u_k(x)}{dx^2} - 2ik \frac{du_k(x)}{dk} + [k^2 + V(x)]u_k(x) = Eu_k(x). \quad (7)$$

It is required to find a solution to this form of the Schrödinger equation for the appropriate  $V(x)$ . Exact analytic solutions are unobtainable but numerical techniques can be used to achieve accurate results.

### 2.3 The variational method

The approach used in most realistic band structure calculations employs the variational method. This method depends on the result that if the wave function of a system is expressed as a function of a set of  $N$  adjustable parameters (the variational parameters)  $c_1, \dots, c_b, \dots, c_N$ , i.e.  $\psi = \psi(x, c_1, \dots, c_b, \dots, c_N)$  then the values of these parameters for which  $\partial \langle E \rangle / \partial c_i = 0$  (where  $\langle E \rangle$  is the expectation value for the energy) gives a 'best estimate' for the true wave function. In the form of the variational method most suitable for numerical applications (the Ritz variational method) the unknown wave function is expressed as a linear combination of  $N$  functions  $\chi_l$  (the 'basis functions') which form a complete orthonormal set and the chosen  $c_l$ 's are the coefficients of this series, i.e.

$$\psi(x) = \sum_{l=1}^N c_l \chi_l(x), \quad (8)$$

where

$$\int \chi_l^*(x) \chi_m(x) dx = \begin{cases} \text{constant, usually 1, for } l = m. \\ 0 \text{ for } l \neq m \end{cases} \quad (9)$$

Equation (9) is the definition of orthonormality. The constant is referred to as the 'norm' of the basis functions.



For bound states the limits of this integral (and subsequent integrations in this sub-section) are usually  $-\infty$  to  $+\infty$ . For the non-bound states of interest in band structure work it is usual to carry out the integration over the unit cell ( $0 \leq x \leq a$  here).

For  $N \rightarrow \infty$  the series approaches an exact solution to the Schrödinger equation. In practice, of course, the series used is finite but is chosen to be sufficiently long that any errors due to truncation are negligibly small. Now  $\langle E \rangle$  is given by

$$\langle E \rangle = \frac{\int \psi^*(x) \mathcal{H} \psi(x) dx}{\int \psi^*(x) \psi(x) dx}. \quad (10)$$

If equation (8) is used then

$$\langle E \rangle \int \sum_{l=1}^N c_l^* \chi_l^*(x) \sum_{m=1}^N c_m \chi_m(x) dx = \int \sum_{l=1}^N c_l^* \chi_l^*(x) \mathcal{H} \sum_{m=1}^N c_m \chi_m(x) dx. \quad (11)$$

The left-hand side can be simplified because of the orthonormality of the functions  $\chi_l(x)$  and if we adopt the conventional abbreviation

$$H_{lm} = \int \chi_l^*(x) \mathcal{H} \chi_m(x) dx, \quad (12)$$

then

$$\langle E \rangle \sum_{l=1}^N c_l^* c_l = \sum_{l=1}^N \sum_{m=1}^N c_l^* c_m H_{lm}. \quad (13)$$

Taking the derivative with respect to  $c_l^*$  gives

$$\frac{\partial \langle E \rangle}{\partial c_l^*} \sum_{l=1}^N c_l^* c_l + \langle E \rangle c_l = \sum_{m=1}^N c_m H_{lm}. \quad (14)$$

But, according to the variational principle, the value of the  $c_l$ 's, corresponding to a solution of the Schrödinger equation, occur for

$$\frac{\partial \langle E \rangle}{\partial c_l^*} = 0, \quad (15)$$

which from equation (14) gives

$$\sum_{m=1}^N c_m H_{lm} = \langle E \rangle c_l \quad (l = 1 \dots N). \quad (16)$$

This constitutes a set of  $N$  simultaneous linear equations which have

non-trivial solutions if

$$\begin{vmatrix} H_{11} - \langle E \rangle & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} - \langle E \rangle & & \vdots \\ \vdots & & \ddots & \vdots \\ H_{N1} & \cdots & \cdots & H_{NN} - \langle E \rangle \end{vmatrix} = 0. \quad (17)$$

This equation has  $N$  roots for  $\langle E \rangle$  and can be solved by standard numerical techniques. The  $N$  roots constitute a 'best estimate' of the  $N$  lowest energy levels of the system, for the chosen basis functions. The corresponding values for the  $c_i$ 's, and hence  $\psi(x)$ , can also be found.

A key issue is therefore the choice of a suitable set of basis functions  $\chi(x)$  and the central problem of the subsequent analysis is the evaluation of

$$H_{lm} = \int \chi_l^*(x) \mathcal{H} \chi_m(x) dx. \quad (18)$$

One noteworthy feature of the variational method is that the results for  $\langle E \rangle$  are generally more accurate than the results for  $\psi(x)$  because a first-order error in  $\psi(x)$  only leads to a second-order error in  $\langle E \rangle$ .

## 2.4 The basis functions

To apply the Ritz variational method we must express  $u_k(x)$  as a linear combination of complete orthonormal functions. The fact that  $u_k(x)$  is periodic, of period  $a$ , suggests the possibility of expressing  $u_k(x)$  as a Fourier series:

$$u_k(x) = \frac{a_0}{2} + \sum_{l=1}^N a_l \cos\left(\frac{2\pi lx}{a}\right) + \sum_{l=1}^N b_l \sin\left(\frac{2\pi lx}{a}\right). \quad (19)$$

(The terms of a Fourier series form a complete orthonormal set.) This approach was adopted in the present work and is useful for a general-purpose treatment. In fact, as we shall see, there are better ways of expanding  $u_k(x)$  for the case of realistic potentials.

Rather than employing explicit cosine and sine terms it is more convenient to use  $\chi_l(x) = \exp[i(2\pi lx/a)]$  and to express the Fourier series as

$$u_k(x) = \sum_{l=-N}^{+N} c_l \exp\left(\frac{i2\pi lx}{a}\right), \quad (20)$$

where the  $c_l$ 's are in general complex. These functions are normalized to 'a' rather than 1 over the unit cell, but this factor subsequently cancels.

The potential  $V(x)$  is also periodic and can likewise be expanded as a Fourier series:

$$V(x) = \frac{d_0}{2} + \sum_{j=1}^N d_j \cos\left(\frac{2\pi jx}{a}\right) + \sum_{j=1}^N e_j \sin\left(\frac{2\pi jx}{a}\right). \quad (21)$$

Many crystals possess what is called an 'inversion centre' and if such a point is chosen as the origin of coordinates then  $V(\mathbf{r}) = V(-\mathbf{r})$ . Symmetry of this kind leads to a considerable reduction in the computing involved and for all the potentials investigated here we can choose an origin such that  $V(x) = V(-x)$ . Now  $\cos(ax) = \cos(-ax)$  but  $\sin(ax) = -\sin(-ax)$  so, if we make this choice of origin, all the  $e_j$ 's are zero. It is again more convenient to write

$$V(x) = \sum_{j=-N}^{+N} f_j \exp\left(\frac{i2\pi jx}{a}\right). \quad (22)$$

Because the sine terms are absent

$$f_j = f_{-j} = \frac{d_j}{2}, \quad (23)$$

and, since  $V(x)$  is real, all the  $f_j$ 's are real.

The Hamiltonian operator takes the form

$$\begin{aligned} \mathcal{H} &= -\frac{d^2}{dx^2} - 2ik \frac{d}{dx} + k^2 + V(x) \\ &= -\frac{d^2}{dx^2} - 2ik \frac{d}{dx} + k^2 + \sum_{j=-N}^{+N} f_j \exp\left(\frac{i2\pi jx}{a}\right). \end{aligned} \quad (24)$$

Hence

$$\begin{aligned} H_{lm} &= \frac{1}{a} \int_0^a \exp\left(\frac{-i2\pi lx}{a}\right) \left[ \frac{4\pi^2 m^2}{a^2} + \frac{4\pi mk}{a} \right. \\ &\quad \left. + k^2 + \sum_{j=-N}^N f_j \exp\left(\frac{i2\pi jx}{a}\right) \right] \exp\left(\frac{i2\pi mx}{a}\right) dx. \end{aligned} \quad (25)$$

The integration is over the unit cell and the factor of  $1/a$  cancels with the norm of the basis functions. Because of the orthogonality of the basis functions over the unit cell, equation (25) becomes

$$H_{lm} = \begin{cases} f_{l-m} & (l \neq m) \\ \left(k + \frac{2\pi m}{a}\right)^2 + f_0 & (l = m). \end{cases} \quad (26)$$

Hence, using equation (23) the matrix Hamiltonian is

$$\mathcal{H} = \begin{bmatrix} \left(k - \frac{2N\pi}{a}\right)^2 + \frac{d_0}{2} & \dots & \dots & \dots & \frac{d_{2N}}{2} \\ \vdots & \left(k - \frac{2\pi}{a}\right)^2 + \frac{d_0}{2} & \frac{d_1}{2} & \frac{d_2}{2} & \vdots \\ \vdots & \frac{d_1}{2} & k^2 + \frac{d_0}{2} & \frac{d_1}{2} & \vdots \\ \vdots & \frac{d_2}{2} & \frac{d_1}{2} & \left(k + \frac{2\pi}{a}\right)^2 + \frac{d_0}{2} & \vdots \\ \frac{d_{2N}}{2} & \dots & \dots & \dots & \left(k + \frac{2N\pi}{a}\right)^2 + \frac{d_0}{2} \end{bmatrix}. \quad (27)$$

The task therefore reduces to Fourier analysing  $V(x)$ , setting up the Hamiltonian matrix  $\mathcal{H}$  (27) and then employing numerical techniques to determine the energies (diagonalization) and, if required, the corresponding wave functions.

## 2.5 The periodic potential

In a real crystal the periodic potential arises from the Coulomb interaction of the electron with all of the atomic nuclei and all of the other electrons. In the computer program presented here the user can choose between a number of potentials which have been selected principally with a view to their heuristic value rather than to their similarity to real crystal potentials. The potentials are of period  $a$  which is set by the user. The origin is an inversion centre, i.e.  $V(x) = V(-x)$  so that it is only necessary to specify them for  $0 \leq x \leq a/2$ . The potentials are (see Figure 3):

(i) A rectangular potential

$$V(x) = \begin{cases} 0 & 0 \leq x < \left(\frac{a}{2} - \frac{b}{2}\right) \\ V_0 & \left(\frac{a}{2} - \frac{b}{2}\right) < x \leq \frac{a}{2}. \end{cases} \quad (28)$$

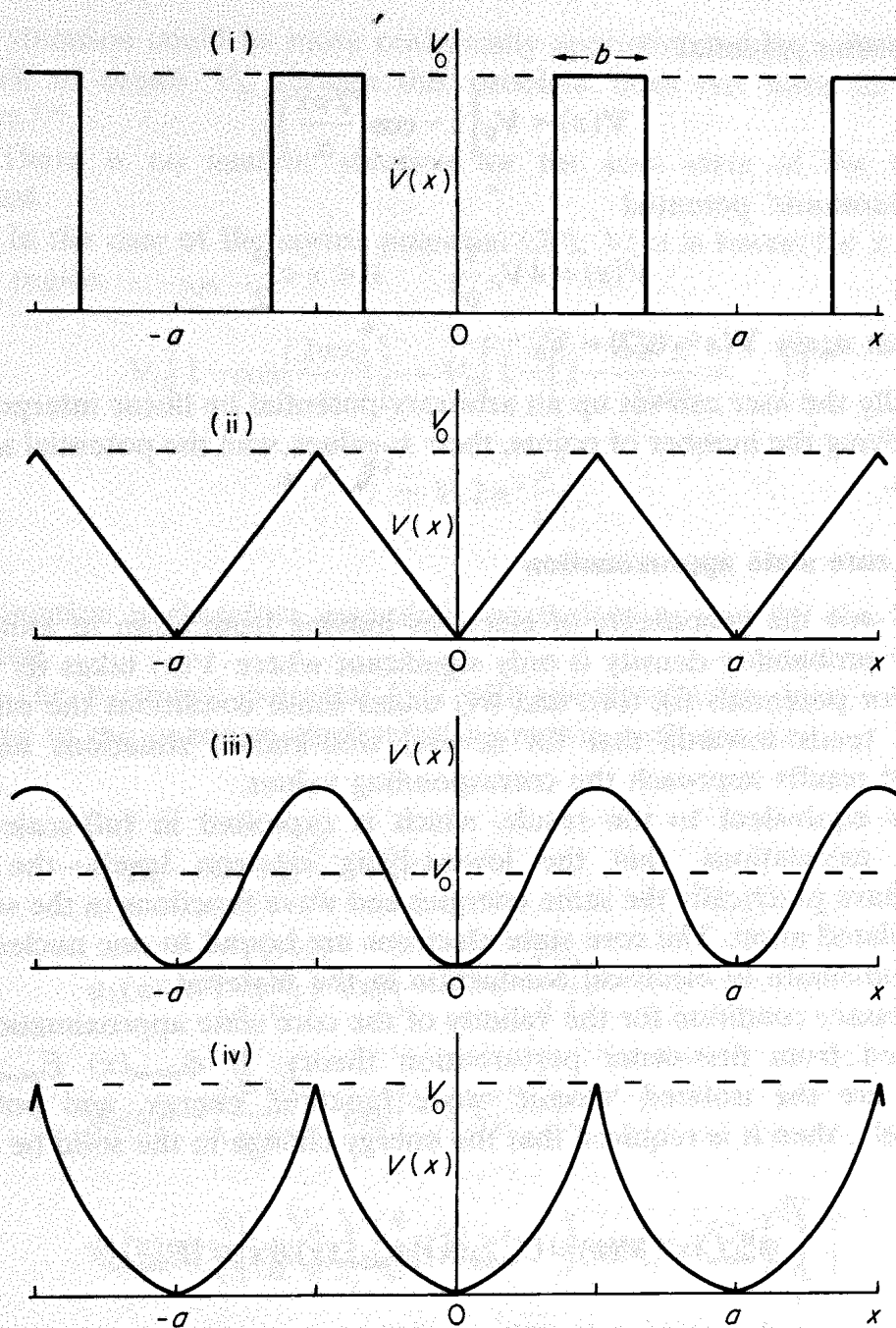


Figure 3. The potential options: (i) the rectangular potential; (ii) the sawtooth potential; (iii) the cosine potential; and (iv) the harmonic potential. (An arbitrary potential can also be set up by linear interpolation)

(ii) A 'sawtooth' potential

$$V(x) = 2V_0 \frac{x}{a}, \quad 0 < x < \frac{a}{2}. \quad (29)$$

This form is used so that  $V(x = a/2) = V_0$ .

(iii) A cosine potential

$$V(x) = V_0 \left\{ 1 - \cos\left(\frac{2\pi x}{a}\right) \right\}. \quad (30)$$

(iv) A 'harmonic' potential

$$V(x) = 4V_0 \frac{x^2}{a^2} \quad 0 < x < \frac{a}{2}, \quad (31)$$

so that again  $V(x = a/2) = V_0$ .

(v) Finally the user can set up an arbitrary potential by linear interpolation specifying the number of points, their  $x$ -values, and the potential at each point.

## 2.6 The core state approximation

For  $V_0 a \rightarrow \infty$  the probability of elections moving from atom to atom falls and their probability density is only significant where  $V(x)$  takes its lowest values. For potentials (i), (iii), and (iv) under these conditions the effective potential tends towards that for several well-known situations and the computed results approach the corresponding values.

This is equivalent to the result, which is exploited in full-scale band structure calculations, that the lowest-lying electron levels—the 'core states'—have practically the same energies and wave functions in the solid as in the isolated atom. The core state electrons are bound to one nucleus and do not contribute to electrical conduction in the material.

A necessary condition for the validity of the core state approximation can be derived from first-order perturbation theory. If  $\phi_{\text{atom}}(x)$ ,  $E_{\text{atom}}$  and  $U_{\text{atom}}(x)$  are the isolated 'atomic' wave function, energy, and potential respectively, then it is required that the energy change in the solid be small, i.e.

$$\left| \int_{-\infty}^{+\infty} \phi_{\text{atom}}^*(x) [V(x) - U_{\text{atom}}(x)] \phi_{\text{atom}}(x) dx \right| \ll |E_{\text{atom}}|. \quad (32)$$

For  $V_0 a \rightarrow \infty$  the potentials (28) to (31) lead to the following limiting energies and normalized wave functions in atomic units (for  $-a/2 < x < a/2$ ):

(i) For  $V_0 > 0$  and  $V_0 a \rightarrow \infty$  the rectangular potential (28) tends towards an infinite potential well of width  $(a - b)$ .

$$E_n \rightarrow \frac{\pi^2 n^2}{(a - b)^2}, \quad n = 1, 2, 3, \dots, \quad (33)$$

$$\psi_n \rightarrow \frac{1}{\sqrt{a - b}} \cos\left(\frac{n\pi x}{a - b}\right), \quad n = 1, 3, \dots, \quad (34)$$

$$\psi_n \rightarrow \frac{1}{\sqrt{a - b}} \sin\left(\frac{n\pi x}{a - b}\right), \quad n = 2, 4, \dots \quad (35)$$



The situation could be more realistically approximated by a finite potential well of depth  $V_0$ , though this problem does not have an analytic solution.<sup>5,6</sup>

(ii) There is no analytic solution for the core state of the sawtooth potential.

(iii) In the case of the cosine potential (30),  $V(x)$  is lowest for  $x \rightarrow 0$  and in this region

$$\begin{aligned} V_0 \left[ 1 - \cos\left(\frac{2\pi x}{a}\right) \right] &\rightarrow V_0 \left[ 1 - \left( 1 - \frac{4\pi^2 x^2}{2!a^2} + \dots \right) \right] \\ &\approx V_0 2\pi^2 \frac{x^2}{a^2}. \end{aligned} \quad (36)$$

The situation is therefore essentially equivalent to that for the harmonic potential.

(iv) The harmonic potential (31) will give results for  $V_0 a \rightarrow \infty$  corresponding to the quantum-mechanical harmonic oscillator, i.e.

$$E_n \rightarrow (n + \frac{1}{2}) \frac{4}{a} \sqrt{V_0}, \quad (37)$$

$$\psi_1(x) \rightarrow \left( \frac{4V_0^{\frac{3}{8}}}{a^2 \pi^2} \right)^{\frac{1}{2}} \exp\left( -\sqrt{V_0} \cdot \frac{x^2}{a} \right), \quad (38)$$

$$\psi_2(x) \rightarrow \left( \frac{2^{\frac{5}{4}} V_0^{\frac{3}{8}}}{a^{\frac{3}{2}} \pi^{\frac{1}{2}}} \right) x \exp\left( -\sqrt{V_0} \frac{x^2}{a} \right), \quad (39)$$

$$\psi_3(x) \rightarrow \frac{1}{2^{\frac{1}{4}}} \left( \frac{V_0}{a^2 \pi^2} \right)^{\frac{1}{8}} \left( \frac{4}{a} \sqrt{V_0} x^2 - 1 \right) \exp\left( -\sqrt{V_0} \frac{x^2}{a} \right). \quad (40)$$

In all cases, as  $V_0 a$  is increased, the lowest energy state will approach the core state limit soonest because, having less energy, it is more closely confined to the regions where  $V(x)$  is low.

As an example of the application of the core state approximation the data points in Figure 4 shows the results of a series of runs of the computer program for the energies at  $k = 0$  employing the cosine potential for a wide range of values of  $V_0$ . The solid lines show the energies of the three lowest energy states of an electron as predicted by the core state approximation (i.e.  $E_n = (n + \frac{1}{2})(2\pi/a)\sqrt{2V_0}$ ), for the cosine potential. Note that agreement deteriorates for low  $V_0$ , particularly for the third band.

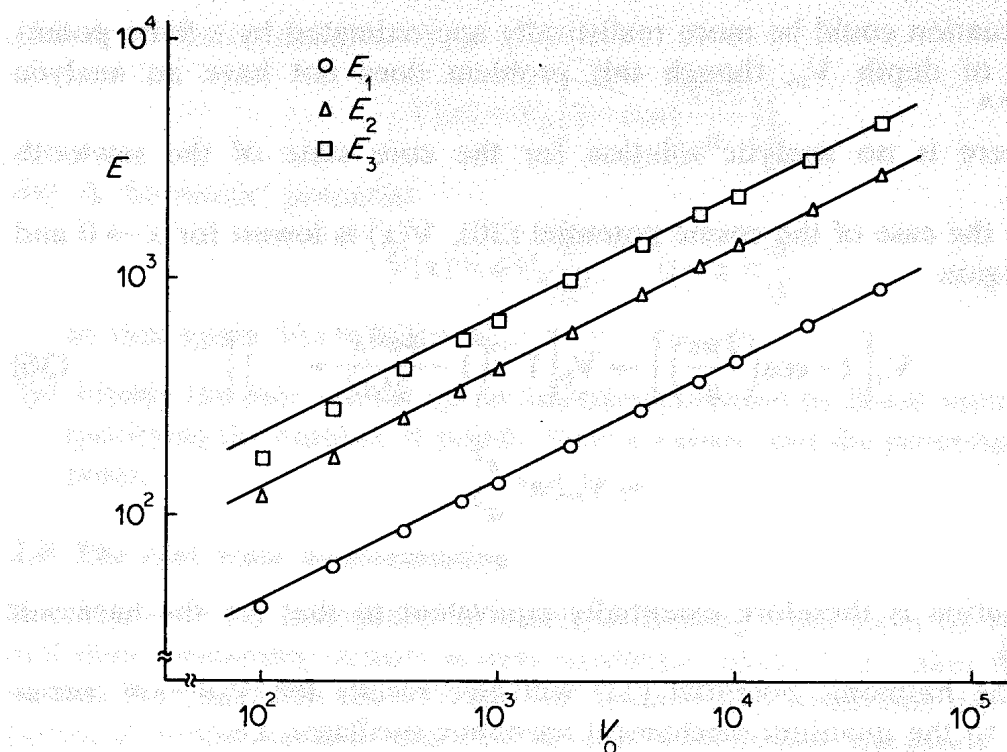


Figure 4. The results of the computer program employing the cosine potential with a period of 1.0 showing the energies at  $k=0$  as a function of  $V_0$ :  $E_1(\circ)$ ,  $E_2(\triangle)$ , and  $E_3(\square)$ . The straight lines show the predictions of the core state approximation

The computer program also finds the probability density  $\psi^*(x)\psi(x)$ . In Figure 5 the data points show the computed results for  $k=0$  with the cosine potential; the solid curves are the predictions of the core state approximation (which are simple analytic expressions). Agreement is poorest at larger  $|x|$  where the difference between

$$V_0 \left\{ 1 - \cos\left(\frac{2\pi x}{a}\right) \right\} \quad \text{and} \quad V_0 \left( \frac{2\pi^2 x^2}{a^2} \right)$$

is greatest.

## 2.7 The nearly-free electron approximation

The opposite extreme of very low values of  $V_0 a$  can be treated using the nearly-free approximation. If  $V(x)=0$  then  $\psi(x)=\exp(ikx)$  and  $E=k^2$ . If  $V(x)$  is small we can treat it as a perturbation and from the usual expression

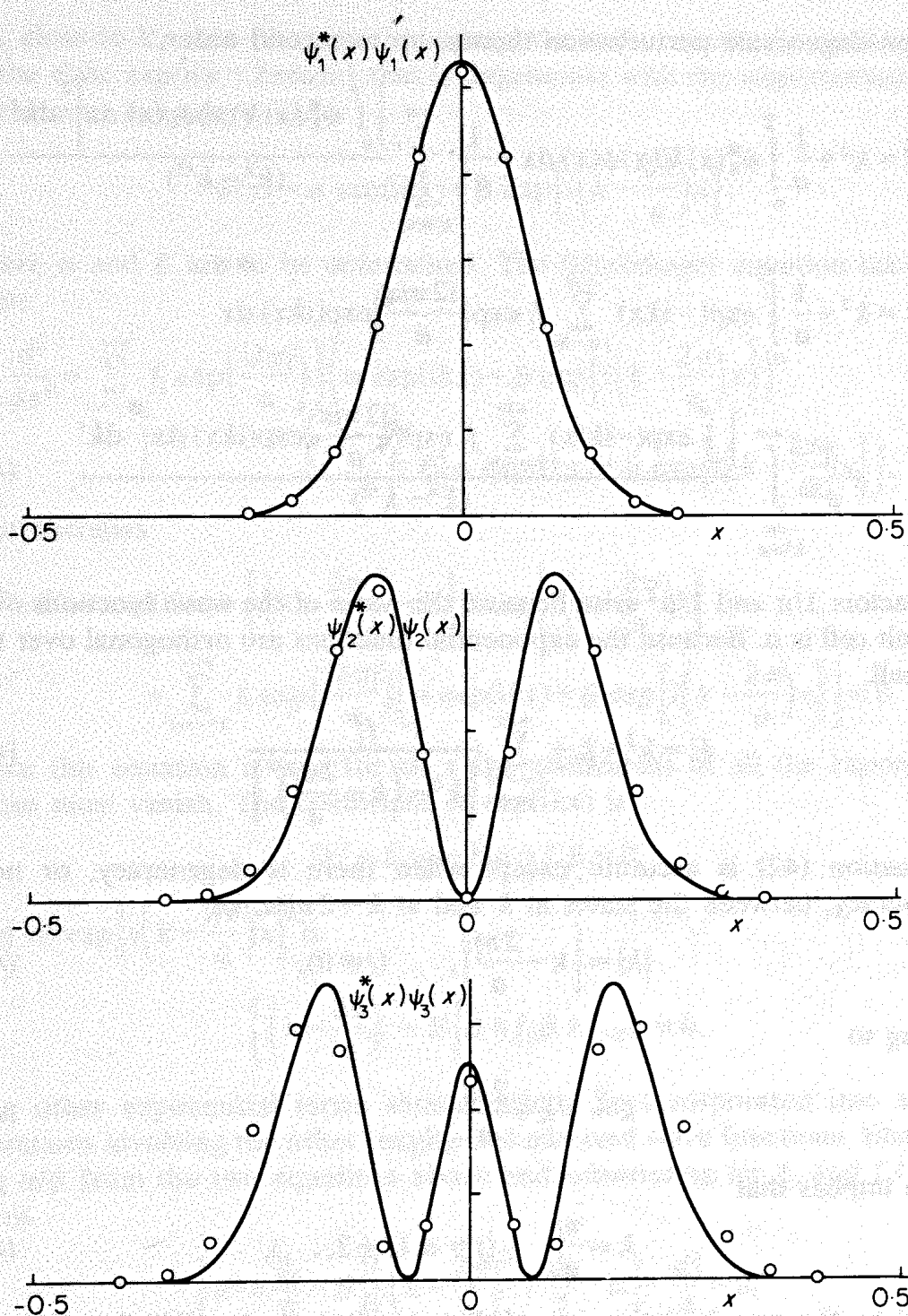


Figure 5. The circles are the results of the computer program for the probability density when the cosine potential is employed with a period of 1.0,  $V_0=400$  and  $k=0$ . The curves show the predictions of the core state approximation

for non-degenerate perturbation theory, up to second order,

$$\begin{aligned}
 E &= k^2 + \frac{1}{a} \int_0^a \psi_k^*(x) V(x) \psi(x) dx + \frac{1}{a^2} \int_{-\infty, k' \neq k}^{+\infty} \frac{\left| \int_0^a \psi_k^*(x) V(x) \psi_{k'}(x) dx \right|^2 dk'}{(k^2 - k'^2)} \\
 &= k^2 + \frac{1}{a} \int_0^a \exp(-ikx) \sum_{j=-N}^{+N} f_j \exp\left(\frac{i2\pi jx}{a}\right) \exp(ikx) dx \\
 &\quad + \frac{1}{a^2} \int_{-\infty, k' \neq k}^{+\infty} \frac{\left| \int_0^a \exp(-ik'x) \sum_{j=-N}^{+N} f_j \exp\left(\frac{i2\pi jx}{a}\right) \exp(ikx) dx \right|^2 dk'}{(k^2 - k'^2)}. \quad (41)
 \end{aligned}$$

The factors  $1/a$  and  $1/a^2$  arise because the norm of the wave functions over the unit cell is  $a$ . Because the exponential functions are orthogonal over the unit cell,

$$E = k^2 + f_0 + \sum_{\substack{j=-N \\ j \neq 0}}^{+N} \frac{f_j^2}{\left\{ k^2 - \left( k - \frac{2\pi j}{a} \right)^2 \right\}}. \quad (42)$$

Equation (42) is accurate except when there is degeneracy, or near degeneracy, between the states at  $k$  and at  $k - 2\pi j/a$ , i.e.

$$|k| \approx \left| k - \frac{2\pi j}{a} \right|, \quad (j \neq 0), \quad (43)$$

leading to

$$k \approx -k + \frac{2\pi j}{a}, \quad (44)$$

which implies that

$$k \approx \frac{\pi j}{a} \quad (j = \pm 1, \pm 2, \dots), \quad (45)$$

as will be the case in the region of the zone boundaries. We then need to consider the explicit form of the wave functions.

As an example of the approach consider the lowest energy band. The unperturbed wave function  $\psi(x) = \exp(ikx)$ . The perturbation  $V(x)$  will 'mix in' states with wave functions

$$\exp\left\{i\left(k - \frac{2\pi j}{a}\right)x\right\} \quad j = \pm 1, \pm 2, \dots$$

but, close to  $k = \pi/a$  (the zone boundary) the main contribution will be due to the state  $\exp\{i(k - 2\pi/a)x\}$  that is degenerate with the unperturbed state at the zone boundary, i.e.

$$\psi(x) \approx \alpha \exp(ikx) + \beta \exp\left\{i\left(k - \frac{2\pi}{a}\right)x\right\}, \quad (46)$$

where  $\alpha$  and  $\beta$  are to be determined. The Schrödinger equation takes the form:

$$\left[ -\frac{d^2}{dx^2} + \sum_{j=-N}^{+N} f_j \exp\left(\frac{i2\pi j}{a}\right) \right] \left( \alpha \exp(ikx) + \beta \exp\left\{i\left(k - \frac{2\pi}{a}\right)x\right\} \right) = E \left( \alpha \exp(ikx) + \beta \exp\left\{i\left(k - \frac{2\pi}{a}\right)x\right\} \right), \quad (47)$$

that becomes

$$(k^2 - E)\alpha \exp(ikx) + \left[ \left(k - \frac{2\pi}{a}\right)^2 - E \right] \beta \exp\left\{i\left(k - \frac{2\pi}{a}\right)x\right\} + \sum_{j=-N}^{+N} f_j \exp\left(\frac{i2\pi j}{a}\right) \left[ \alpha \exp(ikx) + \beta \exp\left\{i\left(k - \frac{2\pi}{a}\right)x\right\} \right] = 0. \quad (48)$$

Since this equation is true for all  $x$  the coefficients of all the exponential terms must vanish. The coefficient of  $\exp(ikx)$  is

$$(k^2 - E)\alpha + f_0\alpha + f_1\beta = 0, \quad (49)$$

and of  $\exp\left\{i\left(k - \frac{2\pi}{a}\right)x\right\}$  is

$$\left[ \left(k - \frac{2\pi}{a}\right)^2 - E \right] \beta + f_0\beta + f_{-1}\alpha = 0. \quad (50)$$

The other exponential terms should strictly be incorporated into similar equations involving the other (negligible) admixed wave functions. Eliminating  $\alpha/\beta$  from the two equations above and substituting for  $f_0$  and  $f_1 (= f_{-1})$  gives

$$\left[ k^2 + \frac{d_0}{2} - E \right] \left[ \left(k - \frac{2\pi}{a}\right)^2 + \frac{d_0}{2} - E \right] - \frac{d_1^2}{4} = 0, \quad (51)$$

which has the roots

$$E = k^2 + \frac{d_0}{2} + \frac{2\pi}{a} \left[ \frac{\pi}{a} - k \pm \sqrt{\left(\frac{\pi}{a} - k\right)^2 + \left(\frac{ad_1}{4\pi}\right)^2} \right]. \quad (52)$$

The lower root applies to the lowest energy band. The higher root applies to the second energy band close to the first zone boundary.