INVESTIGATION OF ELECTRICAL CONDUCTIVITY IN AMORPHOUS SEMICONDUCTORS

BY
EARL L. COOK AND A. T. FROMHOLD, JR.

SEMI-ANNUAL REPORT

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DEPARTMENT OF PHYSICS
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TO
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ABSTRACT

Several electron transport mechanisms in amorphous solids have been investigated. The field-assisted nonlinear diffusion of charged particles in the presence of a concentration gradient and homogeneous electric field has been considered. An expression for the steady-state current has been derived including explicitly the effects due to the lattice discreteness. The results of this research have been presented for publication.[1] The transport of electrons by Schottky emission from a metal into an oxide has been treated. This transport mechanism has resulted in a new model for the thermal oxidation of metals. A preliminary report has appeared in the literature.[2]

The role of periodicity in the electronic band structure of solids has been examined. A careful examination of periodicity and Bloch's theorem is presented. It is shown that perfect periodicity allows the electronic wave function to be simultaneously an eigenfunction of the Hamiltonian and the translation operator. The periodic solid is treated in terms of tunneling. This investigation shows the allowed energy bands result from complete transparency of the solid to electrons. The aperiodic solid is treated by calculating the wave functions and determining the distribution of allowed energy states by a node counting method. The model employed in these calculations assumes square wells of finite width with the spacings between adjacent wells being chosen at random from a Gaussian distribution. The results indicate that the band edges become diffuse for small degrees of aperiodicity and that the bands merge as the aperiodicity becomes large. For large periodicity the density of states approaches that of the free-electron model.

I. Introduction

The quantum-mechanical treatment of the motion of electrons in crystalline solids has resulted in the highly successful band theory. This theory is evoked in essentially all considerations of the electrical properties of solids and has quantitatively correlated a large body of experimental data. The conventional development of this theory is based on Bloch's theorem which states the relation between the perfect periodicity of the lattice and the electronic wave functions. This relation allows a mathematically rigorous determination of certain general properties of the electronic wave functions; specifically, the electrons may be described by modulated plane waves. Further, the values of the total energy for which this type of solution exists fall into bands. Such a description implies a free motion of the electrons through the lattice subject to the condition that the electrons do not respond to external forces the same as if they were free. This leads to the assignment of an effective mass which is generally different from the free electron mass.

It appears that the band theory is inseparably connected to the condition of perfect periodicity and that a band structure would not exist for a system which is aperiodic, i.e., disordered. Such conclusions, however, are not supported experimentally.[3] Liquid metals are not periodic yet the electrical properties of liquid metals are not very different from those of the solid metals. The similiarity of electrical properties of molten and solid semiconductors offers strong evidence since the electrical properties of a semiconductor are extremely sensitive to changes in the band structure. Many amorphous systems exhibit semi-conducting properties. Alloys and crystalline solids with randomly distributed impurities are, with respect to the question of validity of a band theory, comparable to liquids and amorphous solids. Although the electrical properties of these systems indicate the existence of a band structure, there is, as yet, no theoretical justification for the application of the present band theory to systems which are not strictly periodic.

The investigation of disordered systems has taken two approaches: (1) perturbation methods, (2) numerical methods. In the perturbation approaches, disorder is assumed to be a perturbation on an ordered system. The results indicate that bands should exist but this is not conclusive since the band structure arises from the unperturbed (ordered) system. Further, it is not clear that disorder may be treated as a true perturbation in all cases. The numerical approach assumes extremely simple models for disordered systems and the resulting Schrodinger equations are solved numerically. This method does not lend itself to generalization and no significant results have been achieved. At present, it appears that the disordered system is intractable to rigorous treatment.

The present communication is concerned with the numerical investigation of an aperiodic linear chain. The general approach is one of operator algebra. In Section II, Bloch's theorem is considered and carefully examined. The operator technique is used to solve the well-known Kronig-Penney model (perfect periodicity). In Section III, the periodic chain is treated in terms of the tunneling phenomena and the results suggest a method of attack for the aperiodic case. Finally, in Section IV, the aperiodic linear chain is treated using the operator technique.

II. The Perfect Solid and Bloch's Theorem

The band theory of crystalline solids is based on the results of Bloch's theorem. This theorem relates the periodicity of the lattice to the electronic wave functions. In order to ascertain this connection, it is necessary to examine Bloch's theorem in detail. Although the proof may be found in many places,[4] it is given here for its pedagogical value. Further, it establishes the framework for succeeding considerations.

Operator algebra is the basis of the proof. The two operators of interest are the translation operator and the Hamiltonian or energy operator. The translation operator is defined by:

$$T_{\pm d}\ \psi(x) = \psi(x\pm d) \quad . \tag{2.1}$$

In other words, the operation of $T_{\pm d}$ on the wave function evaluated at the point x yields the value of the wave function of the point $x\pm d$. For the present, d will be taken as the lattice parameter. Applying $T_{\pm d}$ N times yields

$$T^{N}_{\pm d}\ \psi(x) = \psi(x\pm Nd) \quad . \tag{2.2}$$

The Hamiltonian operator is of the form

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \quad . \tag{2.3}$$

If ψ is an eigenfunction of H, then the operation of H yields the total energy of the electron;

$$H\psi(x) = E\psi(x) \quad , \tag{2.4}$$

i.e., Schroedinger's equation holds.

Consider the operator obtained by combining $T_{\pm d}$ and H;

$$T_{\pm d}H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\,T_{\pm d} + T_{\pm d}V(x) \quad . \tag{2.5}$$

For the case of perfect lattice periodicity,

$$T_{\pm d}V(x) = V(x\pm d)T_{\pm d} = V(x)T_{\pm d} \quad , \tag{2.6}$$

and

$$T_{\pm d}H = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \right] T_{\pm d}$$

or (2.7)

$$[T_{\pm d}, H] = 0 \quad .$$

Here [ ] denotes the commutator of $T_{\pm d}$ and H.

The desired electronic wave functions must be eigenfunctions of H; i.e., Eq. (2.4) must hold. If both sides of Eq. (2.4) are operated upon by $T_{\pm d}$

$$T_{\pm d}H\psi = ET_{\pm d}\psi \quad , \tag{2.8}$$

the commutation relation, Eq. (2.7), implies

$$H \{T_{\pm d}\psi\} = E \{T_{\pm d}\psi\} \quad . \tag{2.9}$$

In other words, the function $T_{\pm d}\psi$ is also an eigenfunction of H with the same eigenvalue E. Moreover, the function ψ may be chosen to be an eigenfunction of $T_{\pm d}$[5]:

$$T_{\pm d}\psi = \lambda_{\pm}\psi \quad , \tag{2.10}$$

where $\lambda_{\pm}$ is the eigenvalue.

In addition to the condition that the wave function be an eigenfunction of H, it is also required that ψ remain finite as x tends to infinity. This condition is satisfied if the eigenvalue of $T_{\pm d}$ has a magnitude of unity; i.e., $x \rightarrow \pm\infty$ is equivalent to $N \rightarrow \infty$ in Eq. (2.2) and for

$$\underset{N\rightarrow\infty}{\text{Limit}} \, (\lambda_{\pm}^{N}) \tag{2.11}$$

to remain finite , $|\lambda_{\pm}|$ must be unity. This restriction suggests redefining the eigenvalue $\lambda_{\pm}$ as

$$\lambda_{\pm} = e^{\pm i\theta} \quad , \tag{2.12}$$

where θ is a real quantity.

Further algebraic manipulation will show that the general form of the electronic wave function for a perfectly periodic system is

$$\psi(x) = \exp(ikx)U_k(x) \quad , \tag{2.13}$$

where $kd = \Theta$, and $U_k(x)$ is a periodic function with period d. The electronic wave function as given by Eq. (2.13) is known as a Bloch function. This form is a direct consequence of the lattice periodicity.

This derivation indicates that the periodicity of the crystal allows the wave function to be simultaneously an eigenfunction of both the Hamiltonian operator and the translation operator. Further, Eq. (2.13) shows that the wave function differs from cell to cell by only a phase factor. The implication is that the probability of finding an electron within a cell is the same in all cells. This follows since $\psi^*\psi$, interpreted as the probability density, is the same at equivalent points in all cells. Apparently the electrons experience no difficulty in moving through the lattice.

Any aperiodicity of the potential will produce a non-vanishing commutator of $T_{\pm d}$ and H. Consequently, the wave function cannot be simultaneously eigenfunctions of both $T_{\pm d}$ and H and the wave function cannot be represented as a modulated plane wave. In general, the probability density integrated over a unit cell will depend on the cell.

The existence of energy bands for a perfect lattice is not the subject of Bloch's theorem but may be obtained by using Bloch's theorem. The development of the bands is easily seen by example. Consider the potential function shown in Fig. 1. This is the model of Kronig and Penney.[6] The procedure for determining the "Band Structure" is to explicitly determine a representation of the translation operator by solving the appropriate Schroedinger equation. The wave functions which are eigenfunctions of the translation operator are then determined by finding the transformation which diagonalizes the translation operator. The present considerations will be restricted to negative energies

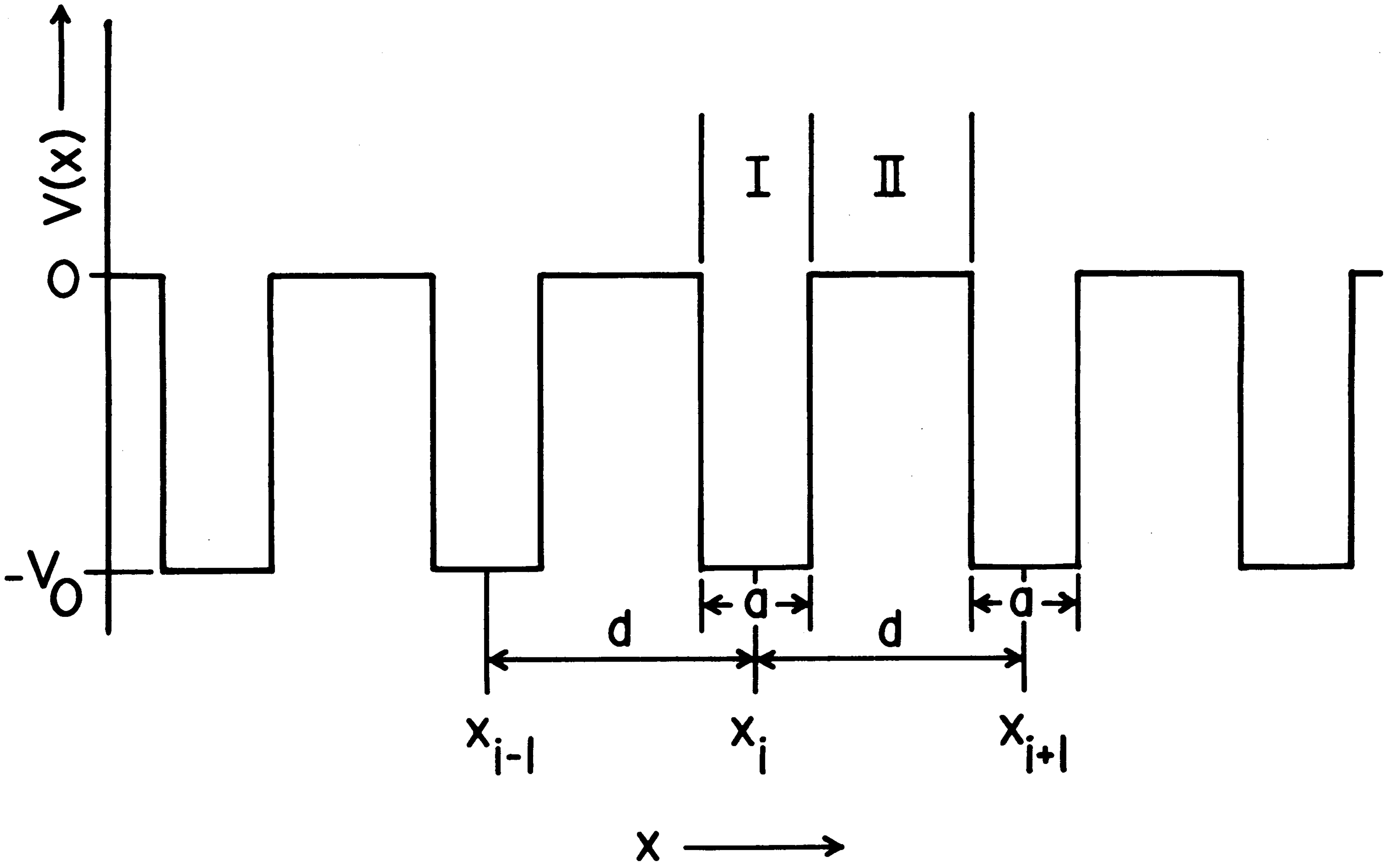

Figure 1. Potential for Kronig-Penney Model.

(See Fig. 1). The development for positive energies follows an identical procedure with the initial wave functions being slightly different.

Consider the i^{th} well and let the quantity x_i be the position of the center of this well. The well width is denoted by a and the well spacing by d. In region I (See Fig. 1), the wave function may be written as

$$\psi(x) = A_i \sin[\beta(x-x_i)] + B_i \cos[\beta(x-x_i)] \quad ,$$

where (2.14)

$$\beta^2 = \frac{2m}{\hbar^2}(V_0+E) \quad .$$

In region II, the wave function may be written as

$$\psi(x) = C_i \exp[\alpha(x-x_i)] + D_i \exp[-\alpha(x-x_i)]$$

where (2.15)

$$\alpha^2 = -\frac{2m}{\hbar^2}E \quad .$$

The continuity of the wave function and its derivative at $x = x_i+a/2$ yields the equations

$$A_i \sin(\beta a/2) + B_i \cos(\beta a/2) = C_i \exp(\alpha a/2) + D_i \exp(-\alpha a/2)$$

(2.16)

$$\beta\{A_i \cos(\beta a/2) - B_i \sin(\beta a/2)\} = \alpha\{C_i \exp(\alpha a/2) - D_i \exp(-\alpha a/2)\}$$

The continuity of the wave function and its derivative at $x = x_i+d-a/2 = x_{i+1}-a/2$ i.e., Eq. (2.14) for the $i+1^{st}$ well matched with Eq. (2.15) for the i^{th} well, yields the two equations

$$-A_{i+1}\sin(\beta a/2) + B_{i+1}\cos(\beta a/2) = C_i \exp[\alpha(d-a/2)] + D_i \exp[-\alpha(d-a/2)]$$

(2.17)

$$\beta\{A_{i+1}\cos(\beta a/2) + B_{i+1}\sin(\beta a/2)\} = \alpha\{C_i \exp[\alpha(d-a/2)] - D_i \exp[-\alpha(d-a/2)]\} \quad .$$

Equations (2.16) may be used to eliminate C_i and D_i from Eq. (2.17). The resulting two equations, relating A_{i+1}, B_{i+1}, A_i, and B_i constitute a representation of the operator T_{+d}. When cast into matrix notation

$$\begin{pmatrix} A_{i+1} \\ \\ B_{i+1} \end{pmatrix} = T_{+d} \begin{pmatrix} A_i \\ \\ B_i \end{pmatrix} \qquad (2.18)$$

the operator T_{+d} is represented by a 2 x 2 matrix. The elements of this matrix are:

$$(T_{+d})_{1,1} = (T_{+d})_{2,2} = \cos(\beta a) \cosh[\alpha(d-a)] + \frac{\alpha^2-\beta^2}{2\alpha\beta} \sin(\beta a) \sinh[\alpha(d-a)]$$

$$\begin{aligned} (T_{+d})_{1,2} = & -\frac{1}{2} \exp[\alpha(d-a)]\{\sin(\beta a) - \frac{\alpha^2+\beta^2}{2\alpha\beta} - \frac{\alpha^2-\beta^2}{2\alpha\beta} \cos(\beta a)\} \\ & -\frac{1}{2} \exp[-\alpha(d-a)]\{\sin(\beta a) + \frac{\alpha^2+\beta^2}{2\alpha\beta} - \frac{\alpha^2-\beta^2}{2\alpha\beta} \cos(\beta a)\} \quad . \qquad (2.19 \\ (T_{+d})_{2,1} = & \ \frac{1}{2} \exp[\alpha(d-a)]\{\sin(\beta a) + \frac{\alpha^2+\beta^2}{2\alpha\beta} - \frac{\alpha^2-\beta^2}{2\alpha\beta} \cos(\beta a)\} \\ & +\frac{1}{2} \exp[-\alpha(d-a)]\{\sin(\beta a) - \frac{\alpha^2+\beta^2}{2\alpha\beta} - \frac{\alpha^2-\beta^2}{2\alpha\beta} \cos(\beta a)\} \quad . \end{aligned}$$

A representation for T_{-d} may be obtained from the identity

$$T_{-d} = T_{+d}^{-1} \quad . \qquad (2.20)$$

In order that ψ be an eigenfunction of T_{+d}, a transformation

$$\begin{pmatrix} A_i' \\ \\ B_i' \end{pmatrix} = Q \begin{pmatrix} A_i \\ \\ B_i \end{pmatrix} \qquad (2.21)$$

must be found such that the transformed T_{+d} representation,

$$T_{\pm d}' = Q^{-1} T_{\pm d} Q \qquad (2.22)$$

is diagonal. Such a transformation[7] is assured provided the secular equation

$$\begin{vmatrix} (T_{\pm d})_{1,1} - e^{\pm i\Theta} & (T_{\pm d})_{1,2} \\ (T_{\pm d})_{2,1} & (T_{\pm d})_{2,2} - e^{\pm i\Theta} \end{vmatrix} = 0 \qquad (2.23)$$

is satisfied. Thus the wave function is simultaneously an eigenfunction of $T_{\pm d}$ and H whenever

$$\cos \Theta = \cos(\beta a) \cosh[\alpha(d-a)] + \frac{\alpha^2-\beta^2}{2\alpha\beta} \sin(\beta a) \sinh[\alpha(d-a)] \quad . \qquad (2.24)$$

The fact that Det $T_{\pm d} = 1$ has been used to obtain this equation. Since Θ is a real quantity, the allowed energy values, contained in α and β, are given by the equation

$$|\cos \Theta| < 1 \qquad (2.25)$$

The function cos Θ is shown in Fig. 2. Those energies for which Eq. (2.25) is satisfied are seen to fall into bands. It is interesting to note that these bands develop around the bound levels of an isolated well.[8] The bound levels are given by the equation

$$\tan (\beta a) = - \frac{2\alpha\beta}{\alpha^2-\beta^2} \quad . \qquad (2.26)$$

This corresponds approximately to the point cos $\Theta = 0$ of Eq. (2.25). The positions of the bound levels are shown in Fig. 2.

The electronic dispersion is usually given by the dependence of the energy on the wave-vector of the Bloch functions. Such a representation for the Kronig-Penney model is shown in Fig. 3. The extension of this approach leads to the theory of Brillouin Zones. It is important to realize that Brillouin zones are a direct consequence of perfect lattice periodicity. This follows since the Bloch wave-vector k is essentially the eigenvalue of the translation operator. In instances where the translation operator does not commute with the Hamiltonian operator, i.e., aperiodic systems, the Brillouin zone scheme

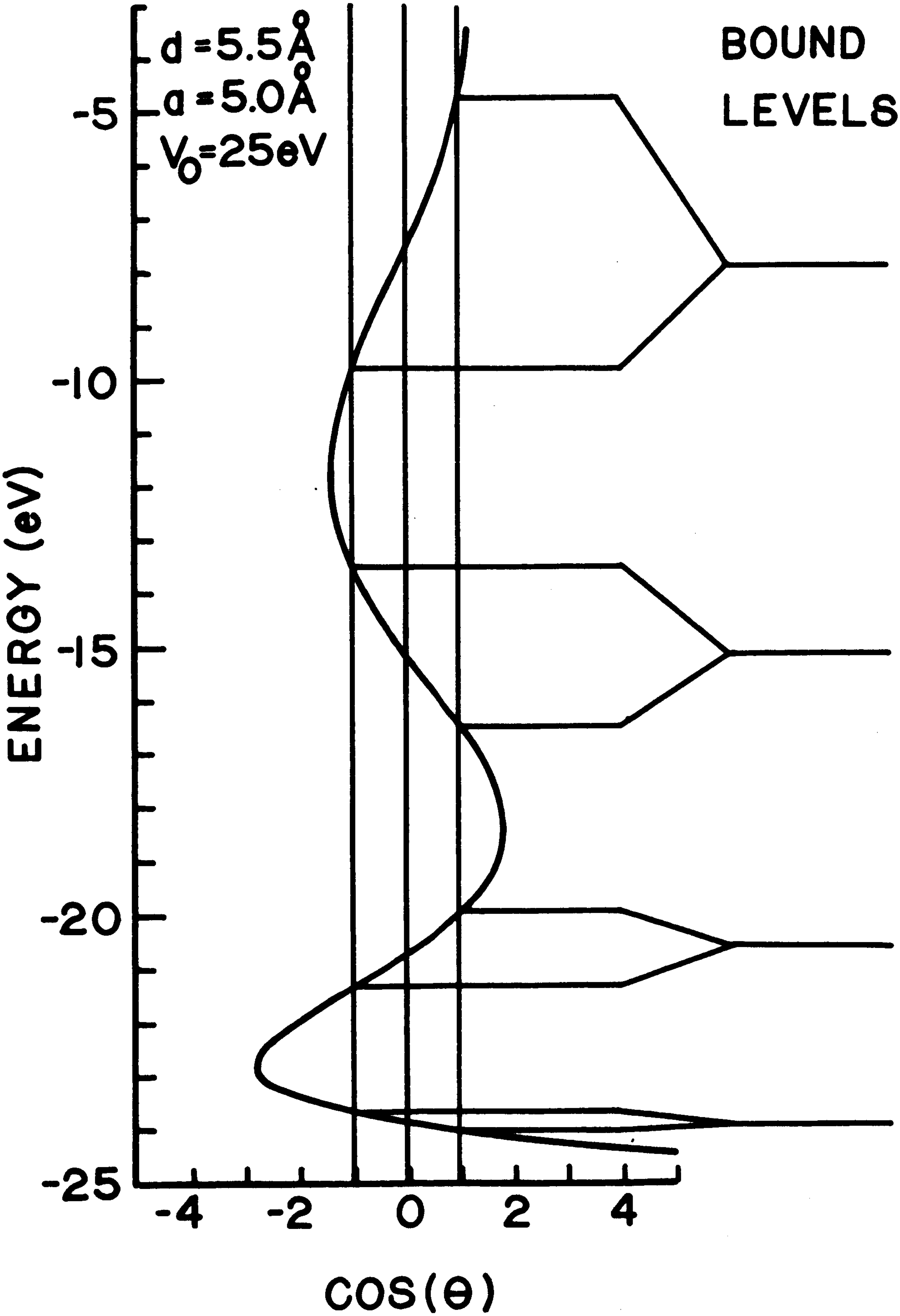

Figure 2. Allowed Energies for Kronig-Penney Model.

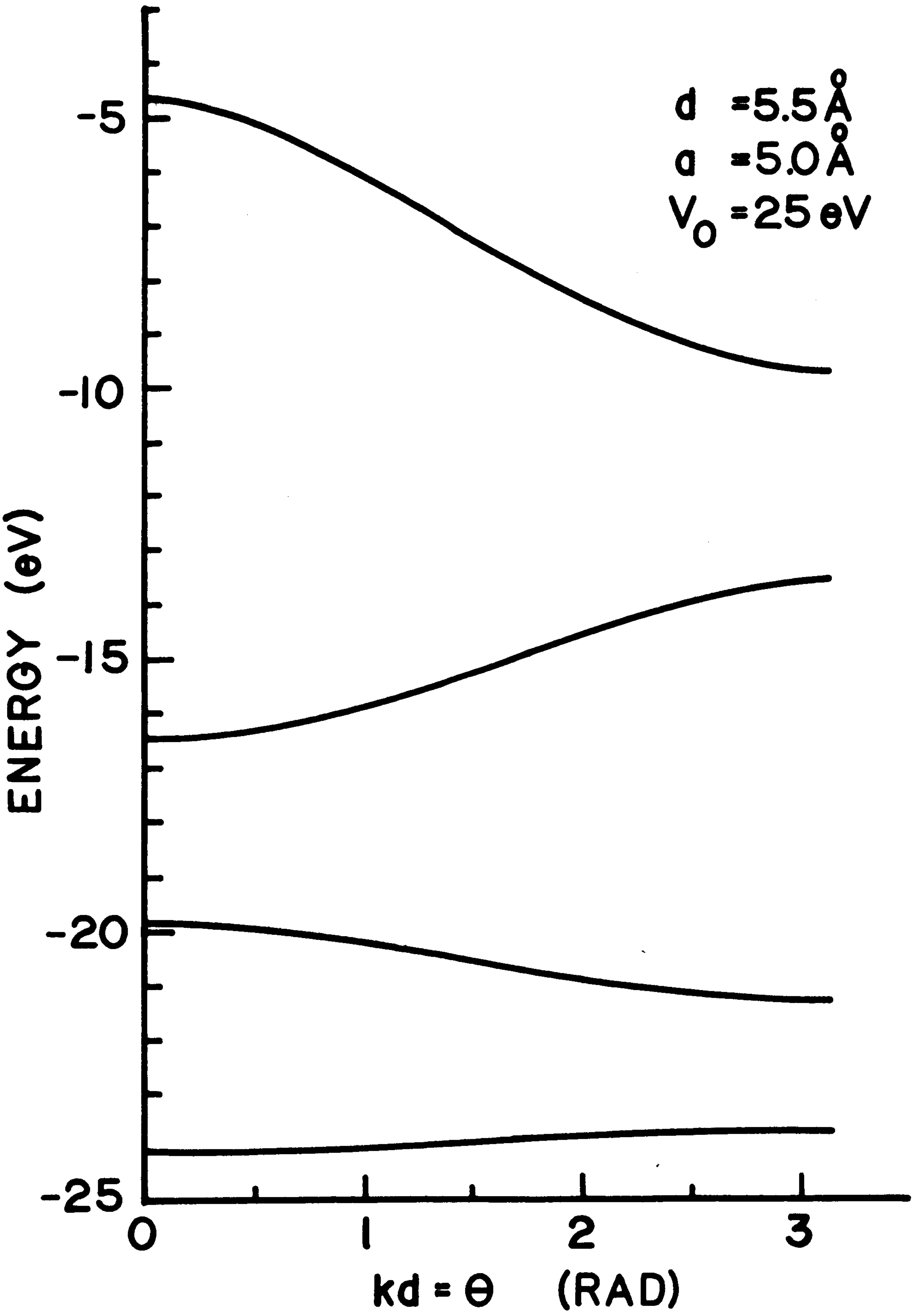

Figure 3. Energy versus Bloch wave-vector.

has no validity and the dispersion relation cannot be represented by E versus k. In this event, the density of states is a convenient representation of the dispersion relation.

III. Physical Interpretation of Bloch's Theorem

Bloch's Theorem as presented in the previous section provides the necessary formalism for treating the electrons in a periodic solid. It does not, however, offer much in the way of understanding of the physics involved. The purpose of this section is to treat the perfect solid in a rather unconventional way and to show the intimate connection between Bloch's theorem and the phenomenon of electron tunneling.

A very important aspect of quantum mechanics is that it predicts that particles of energy E will penetrate a potential barrier $V(x)$ where $E-V(x)$ is locally negative.[9] This situation is without classical analogue and corresponds to particles appearing on the other side of the barrier without "going over the top"; i.e., they tunnel through. An analogous situation occurs over a potential well; the electrons are reflected when classically no reflection should occur. These effects are a direct consequence of the wave nature of matter and are operative phenomena in electron transport in solids.

The connection of Bloch's theorem and the tunnel effect is best seen by considering an electron in a given well and calculating the probability of this electron tunneling through the barriers between the wells and appearing in another well. It is supposed that an electron in the zeroth well is traveling to the right and incident on the barrier system formed by the succeeding atoms. The electron wave function is calculated in the N^{th} well and the ratio of the transmitted electron flux to the incident electron flux then gives the transmission coefficient for the intervening barrier system. The transmission coefficient thus calculated in a measure of the ease with

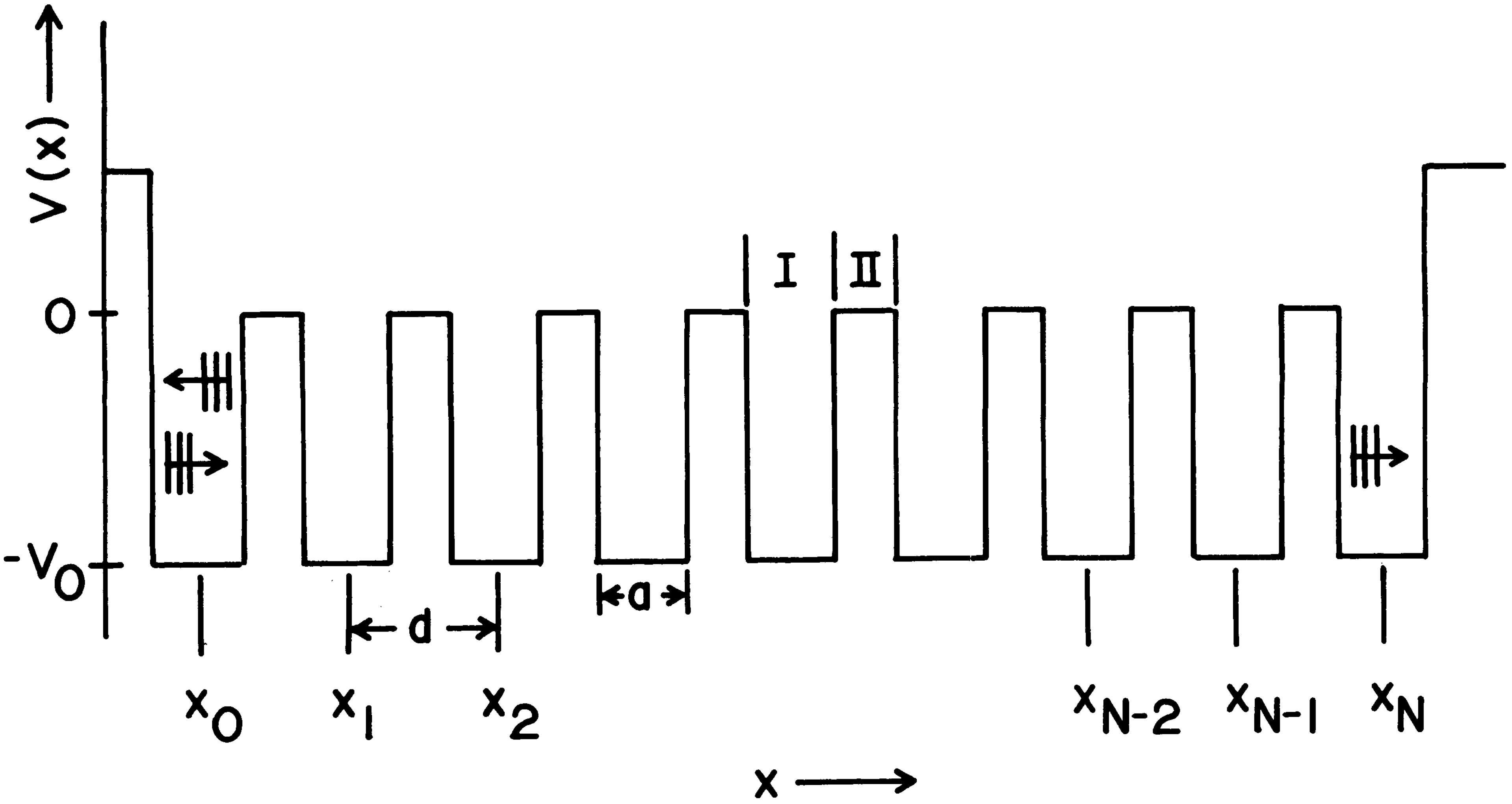

Figure 4. Potential for tunneling considerations.

which the electron moves through the lattice. This situation is shown diagramatically in Fig. 4.

The wave function in the zeroth well is considered to be composed of two parts: (1) plane wave moving to the right, the incident wave, (2) a plane wave moving to the left, the reflected wave. The wave function may be written as

$$\psi(x) = A_o' \exp[i\beta(x-x_o)] + B_o' \exp[-i\beta(x-x_o)] \quad . \tag{3.1}$$

The wave function in Nth cell is composed of only a transmitted wave moving to the right. Thus

$$\psi(x) = A_N' \exp[i\beta(x-x_N)] + B_N' \exp[-i\beta(x-x_N)]$$

with (3.2)

$$B_N' = 0 \quad .$$

The transmitted wave may be related to the incident wave by using the translation operator. If it is assumed that the wells are perfectly periodic with a spacing d, then

$$\begin{pmatrix} A_i' \\ B_i' \end{pmatrix} = T_{-d}' \begin{pmatrix} A_{i+1}' \\ B_{i+1}' \end{pmatrix} \tag{3.3}$$

Note that the operator $T_{\pm d}'$ performs the same function as $T_{\pm d}$ in the previous section. However, in the present treatment the wave functions are slightly different and consequently the representation of $T_{\pm d}'$ is different. This is explicitly denoted by the prime. The $T_{\pm d}'$ representation may be related to the $T_{\pm d}$ representation by noting the relation between the amplitudes A_i', B_i', A_i, and B_i:

$$\begin{pmatrix} A_i \\ B_i \end{pmatrix} = Q \begin{pmatrix} A_i' \\ B_i' \end{pmatrix} , \qquad Q = \begin{pmatrix} i & -i \\ 1 & 1 \end{pmatrix} . \tag{3.4}$$

The $T_{\pm d}$ matrix, Eq. (2.19), transforms according to the similarity transformation

$$T_{\pm d}' = Q^{-1} T_{\pm d} Q . \tag{3.5}$$

Evaluation of Eq. (3.5) using the transformation as defined by Eq. (3.4) yields

$$(T_{-d}')_{1,1} = \frac{\exp(-i\beta a)}{4i\alpha\beta} \{(\alpha-i\beta)^2 \exp[\alpha(d-a)] - (\alpha+i\beta)^2 \exp[-\alpha(d-a)]\}$$

$$(T_{-d}')_{1,2} = \frac{\alpha^2+\beta^2}{2i\alpha\beta} \sinh[\alpha(d-a)] . \tag{3.6}$$

It is easily shown that the remaining elements of T_{-d}' are related to those of Eq. (3.6) by

$$\begin{aligned} (T_{-d}')_{2,2} &= (T_{-d}')^*_{1,1} \\ (T_{-d}')_{2,1} &= (T_{-d}')^*_{1,2} \end{aligned} \tag{3.7}$$

The transmission coefficient, defined by

$$\tau_N = \left| \frac{A_N'^{\,2}}{A_o'^{\,2}} \right| \tag{3.8}$$

becomes

$$\tau_N = \left| \frac{A_N'}{(T_{-d}')_{1,1} A_N' + (T_{-d}'^{N})_{2,1} B_N'} \right|^2$$

$$= \left| (T_{-d}'^{N})_{1,1} \right|^{-2} , \tag{3.9}$$

since it is assumed that $B_N' = 0$; i.e., there is no electron traveling to the left in well N.

The evaluation of the N^{th} power of the operator T_{-d}' as given by Eqs.(3.6) and (3.7) will then yield the transmission coefficient. This evaluation is most easily performed by using a theorem from matrix algebra known as the idempotent theorem.[10] Suppose that f(A) is any polynominal function of the matrix A. Then, for the case of a 2 x 2 matrix, this matrix function may be written as

$$f(A) = \frac{\lambda_2 f(\lambda_1) - \lambda_1 f(\lambda_2)}{\lambda_2 - \lambda_1} I_2 - \frac{f(\lambda_2) - f(\lambda_1)}{\lambda_2 - \lambda_1} A \tag{3.10}$$

provided

$$\lambda_1 \neq \lambda_2 \quad .$$

Here λ_1 and λ_2 are the eigenvalues of the matrix A, I_2 is the 2 x 2 identity matrix and $f(\lambda)$ is the scalar obtained by evaluating the function f(A) with the eigenvalues λ_1 and λ_2 replacing the matrix A. Using this theorem, the transmission coefficient becomes

$$\tau_N = \left| \frac{\lambda_2 \lambda_1^N - \lambda_1 \lambda_2^N}{\lambda_2 - \lambda_1} - \frac{\lambda_2^N - \lambda_1^N}{\lambda_2 - \lambda_1} (T'_{-d})_{1,1} \right|^{-2} \quad . \tag{3.11}$$

The eigenvalues of the A matrix are given by the equation

$$[(T'_{-d})_{1,1} - \lambda][(T'_{-d})_{2,2} - \lambda] - (T'_{-d})_{2,1} (T'_{-d})_{1,2} = 0 \quad . \tag{3.12}$$

Using the identities

$$\mathrm{Det}(T'_{-d}) = 1$$

and (3.13)

$$(T'_{-d})_{2,2} = (T'_{-d})^*_{1,1} \quad ,$$

Eq. (3.12) becomes

$$\lambda^2 - 2\mathrm{Re}[(T'_{-d})_{1,1}]\lambda + 1 = 0 \quad . \tag{3.14}$$

Equation (3.14) is a quadratic equation with real coefficients. The theory of algebraic equations indicates either both roots are real or are complex and conjugate. Further, the roots must be reciprocals of each other and the two complex roots therefore have a magnitude of unity. For real roots

$$\mathrm{Re}^2[(T'_{-d})_{1,1}] > 1 \quad ,$$

$$\lambda_1 + \lambda_2 = 2\mathrm{Re}[(T'_{-d})_{1,1}] \quad , \tag{3.15}$$

$$\lambda_1 = 1/\lambda_2 \quad ,$$

and for imaginary roots

$$\mathrm{Re}^2(T'_{-d})_{1,1} < 1 \quad ,$$

$$\lambda_1 = \lambda_2^* \quad ,$$

$$|\lambda_1| = |\lambda_2| = 1 \quad , \tag{3.16}$$

$$\mathrm{Re}(\lambda_1) = \mathrm{Re}(\lambda_2) = \mathrm{Re}[(T'_{-d})_{1,1}] \quad .$$

Consider the case of real roots. By direct substitution of Eq. (3.15) into Eq. (3.11) it can be shown that

$$\begin{aligned} \tau_N &\propto \lambda_1^{2(N-2)} & \lambda_1 &< 1 \quad , \\ \tau_N &\propto \lambda_1^{-2(N-2)} & \lambda_1 &> 1 \quad , \end{aligned} \tag{3.17}$$

for large values of N. Thus the transmission coefficient is always less than unity and becomes vanishingly small as N becomes large. The interpretation is that the electron does not move readily through the lattice, since the probability of finding the electron monotonically decreases with distance from the original well, i.e., $\tau_N \to 0$ as $N \to \infty$.

Consider the case of complex roots. By substituting Eq. (3.16) into Eq. (3.11) the transmission coefficient becomes

$$\tau = \left| - \frac{\sin(N-1)\theta}{\sin\theta} + \frac{\sin N\theta}{\sin\theta} \left(T'_{-d}\right)_{1,1} \right|^{-2} , \qquad (3.18)$$

where θ is defined by

$$\lambda_1 = e^{i\theta} \qquad 0 < \theta < \pi \quad . \qquad (3.19)$$

Note the restriction that θ be in the first or second quadrant follows from the conjugate relation between λ_1 and λ_2. From the last of Eq. (3.16) the equation

$$\cos\theta = \cos(\beta a) \cosh[\alpha(d-a)] + \frac{\alpha^2-\beta^2}{2\alpha\beta} \sin(\beta a) \sinh[\alpha(d-a)] \quad . \qquad (3.20)$$

results. Algebraic manipulation of Eqs. (3.18) and (3.20) yields the expression

$$\tau_N = \left|\cos^2 N\theta + \frac{\sin^2 N\theta}{\sin\theta} \mathrm{Im}^2[(T'_{-d})_{1,1}]\right|^{-1} . \qquad (3.21)$$

This equation shows that the transmission coefficient becomes unity wherever

$$\theta = \frac{n\pi}{N} \quad , \quad n = 1,2, \ . \ . \ . \ N-1 \quad . \qquad (3.22)$$

The special case $\theta = 0$ is easily shown to yield a transmission coefficient less than unity. Hence, the N-1 values of θ given by Eq. (3.22) yield all the unit transmission peaks.

The transmission coefficient as given by Eq. (3.21) is readily evaluated numerically. The evaluation obtained for N=6 is shown in Fig. 5. The results are in accord with the predictions of the above derivation: whenever the eigenvalues of T are real the transmission coefficient is small, and in the range where the eigenvalues are complex there are N-1=5 unit transmission peaks.

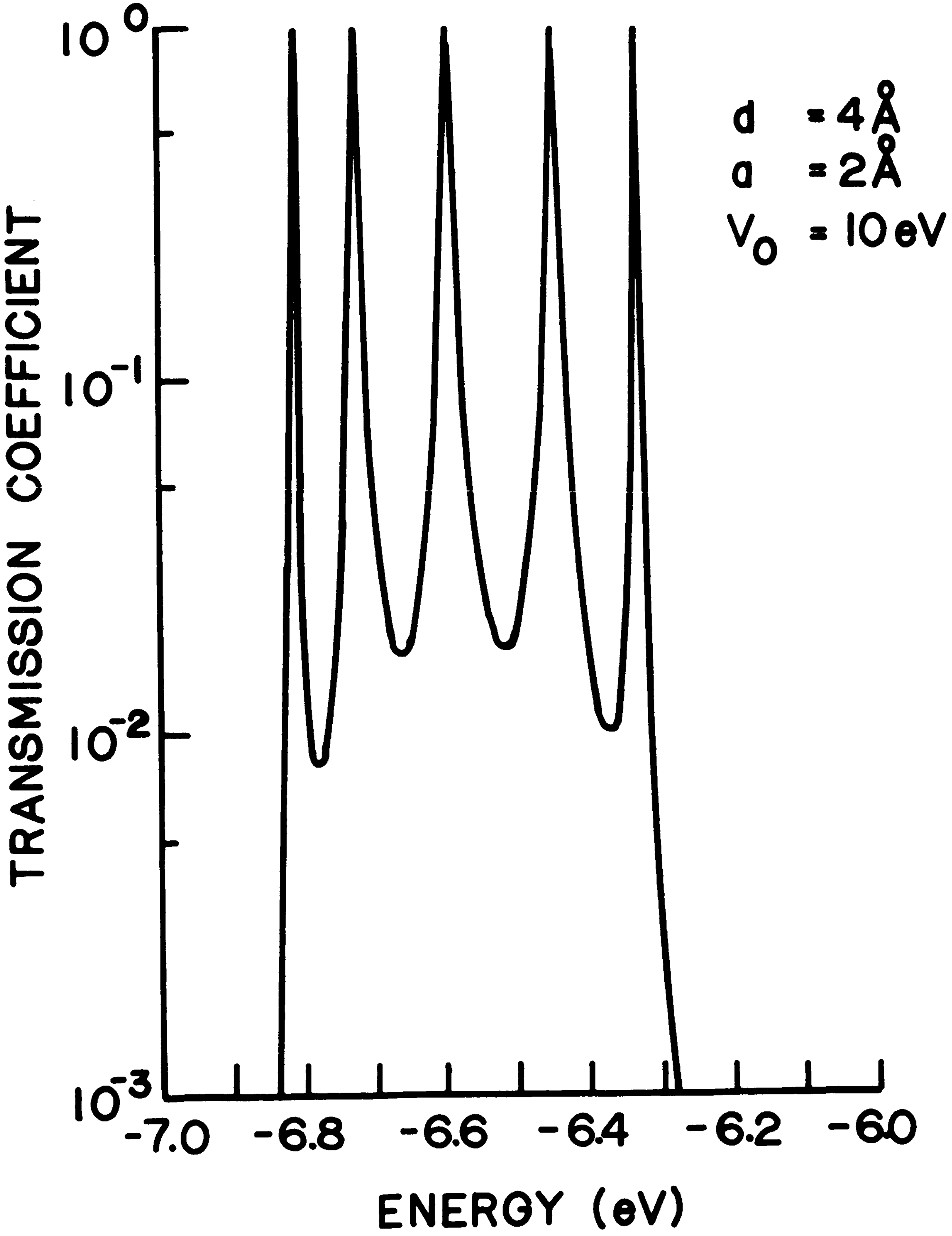

Figure 5. Transmission coefficient versus energy.

The most noteworthy aspect of the above approach is that electrons with energies (contained in α and β) satisfying Eqs. (3.20) and (3.22) are essentially free. In other words, a unit transmission coefficient implies that the barrier system is ineffective in blocking the electrons and the crystal is completely transparent to the electrons. This is essentially the result predicted by Bloch's Theorem as contained in the statement that the electron may be described by a modulated plane wave. Indeed, the relation between the energies of the unit transmission peaks and the eigenvalues Θ is identical with that of the Kronig-Penney model (Compare Eqs. (2.24) and (3.20)). Further, there is a one-to-one correspondence between the values of Θ for the two cases provided the appropriate boundary conditions are imposed on the Kronig-Penney model.

This treatment clearly indicates the way in which the bands of a crystal are generated: As more and more atoms are added to the crystal, the number of unit transmission peaks increases. As N tends to infinity, the density of unit transmission peaks becomes quasi-continuous and a band of allowed energies is formed. It should be noted that the energy range for which the eigenvalues of the T' operator are complex does not depend on the number of wells. Consequently, the band width is independent of the number of wells, in agreement with the Kronig-Penney result.

The perfect periodicity of the lattice in the tunnel treatment is used at only one point, Eq. (3.9). If the lattice were aperiodic, this equation would be replaced by

$$\tau_N = \left| \left(\prod_{i=1}^{N} T'_{-d_i} \right)_{1,1} \right|^{-2} \tag{3.23}$$

In other words, the translation operator T' depends upon the cell index and the result of the N translations produces a product of N 2 x 2 matrices and this may not be written as the N^{th} power of a single 2 x 2 matrix. Obviously the reduction of the matrix product cannot be performed using the idempotent theorem. This however, does not rule out the existence of unit transmission coefficients and consequently, energies for which the crystal is transparent.

The argument presented above must be interpreted with reservation. At present, it appears to be an acceptable plausability argument for the existence of bands in aperiodic systems but is by no means definitive. Perhaps the greatest merit lies in the physical interpretation given to electronic motion in solids. Also, this approach minimizes the role of periodicity. It is hoped that this understanding will eventually be beneficial in the development of a rigorous aperiodic band theory.

IV. Aperiodic Linear Chain

Attention is now directed to the aperiodic linear chain. A very simple model will be considered and discussed in detail. Although the extension of the results is not evident it is hoped that the understanding of the one-dimensional model will be beneficial in developing more realistic models.

There have been several pertinent investigations utilizing numerical techniques reported in the literature: of particular interest are reports of James and Ginzbarg,[11] Landauer and Helland[12] and Makinson and Roberts.[13] James and Ginzbarg[11] treated the cases of one-dimensional disordered alloy and impurity semi-conductor. They found that the sharply defined impurity band of a crystal with regularly spaced impurities becomes smeared out as the distribution of impurities become random. Landauer and Helland[12] treated the disordered chain by considering a series of identical wells separated by a random well-to-well spacing and found that disorder narrowed the forbidden gaps and a disappearance of the forbidden band for large degrees of disorder. However, Allen and Shockley[14] have suggested that the pecularities of the delta-well model may make it unsuitable for band calculations.

Accordingly, the present investigation attempts to unify and extend these calculations by considering statistically acceptable aperiodic chains composed of square wells. The spacings between the wells are chosen at random from a Gaussian distribution. The band structure is determined by calculating the wave functions using the translation operator and determining density of allowed electronic states using a node counting method.

The model for the aperiodic linear chain is essentially that of Gubanov[15] which assumes a Gaussian distribution of lattice spacings. The probability of choosing a spacing between x and x + dx is given by f(x) dx, where

$$f(d) = (2\pi)^{-\frac{1}{2}} \sigma^{-1} \exp[-(d-d_o)^2/2\sigma^2] \quad . \tag{4.1}$$

Here σ is the variance which is assumed to be a measure of aperiodicity, and d_o is the mean spacing.

The physical properties of the chains may be calculated from the distribution of spacings. By using the central limit theorem of statistics,[16] it is found that the probability of an N + 1 particle chain having a total length between L and L + dL is F(L)dL, where

$$F(L) = (2\pi N)^{-\frac{1}{2}} \sigma^{-1} \exp[-(L-Nd_o)^2/2N\sigma^2]$$

and (4.2)

$$L = \sum_{i=1}^{N} d_i \quad .$$

Accordingly, the average or most probable length of a N + 1 atom chain is

$$L = \int_{-\infty}^{+\infty} L\, F(L)dL = Nd_o \quad . \tag{4.3}$$

This implies that the mean density of particles of the aperiodic chain is the same as the corresponding periodic chain. This agrees with the observation that the particle density of a solid form of a substance (periodic) is very nearly equal to that of the liquid form (aperiodic). In other words melting does not produce a marked density change.

The order may be investigated by determining the distribution of particles relative to a given particle. Let the function $\rho(x)$ denote the probability of finding a particle a distance x from a given particle. This is equivalent to the probability of finding a chain of length x composed of any number of particles. From Eq. (4.2), it follows that

$$\rho(x) = \sum_{N=1}^{\infty} (2\pi N)^{-\frac{1}{2}} \sigma^{-1} \exp[-(L-Nd_o)^2/2N\sigma^2] \quad . \qquad (4.4)$$

The evaluation of this function for two values of σ with d_o = 4 Å is shown in Fig. 6. For small values of x, the particles are most probably at perfect lattice sites. Consequently, the lattice exhibits short-range order. On the other hand, when x becomes large the probability approaches a constant indicating that particles are equally probable at any point. Thus, there is no statistical relation between the position of the particles and consequently, no long-range order. This agrees with the results of x-ray diffraction experiments which show that liquids and amorphous solids exhibit a degree of short-range order but no long-range order.

An estimate of the degree of order may be obtained from Eq. (4.2). An N + 1 atom chain is assumed to be ordered whenever the N + 1st particle is located within one half of a mean lattice spacing of the corresponding position in a perfect lattice, i.e., whenever

$$(N-1/2)d_o < \sum_{i=1}^{N} d_i < (N+1/2)d_o$$

or $\qquad (4.5)$

$$(L-Nd_o)^2 < \frac{d_o^2}{4} \quad .$$

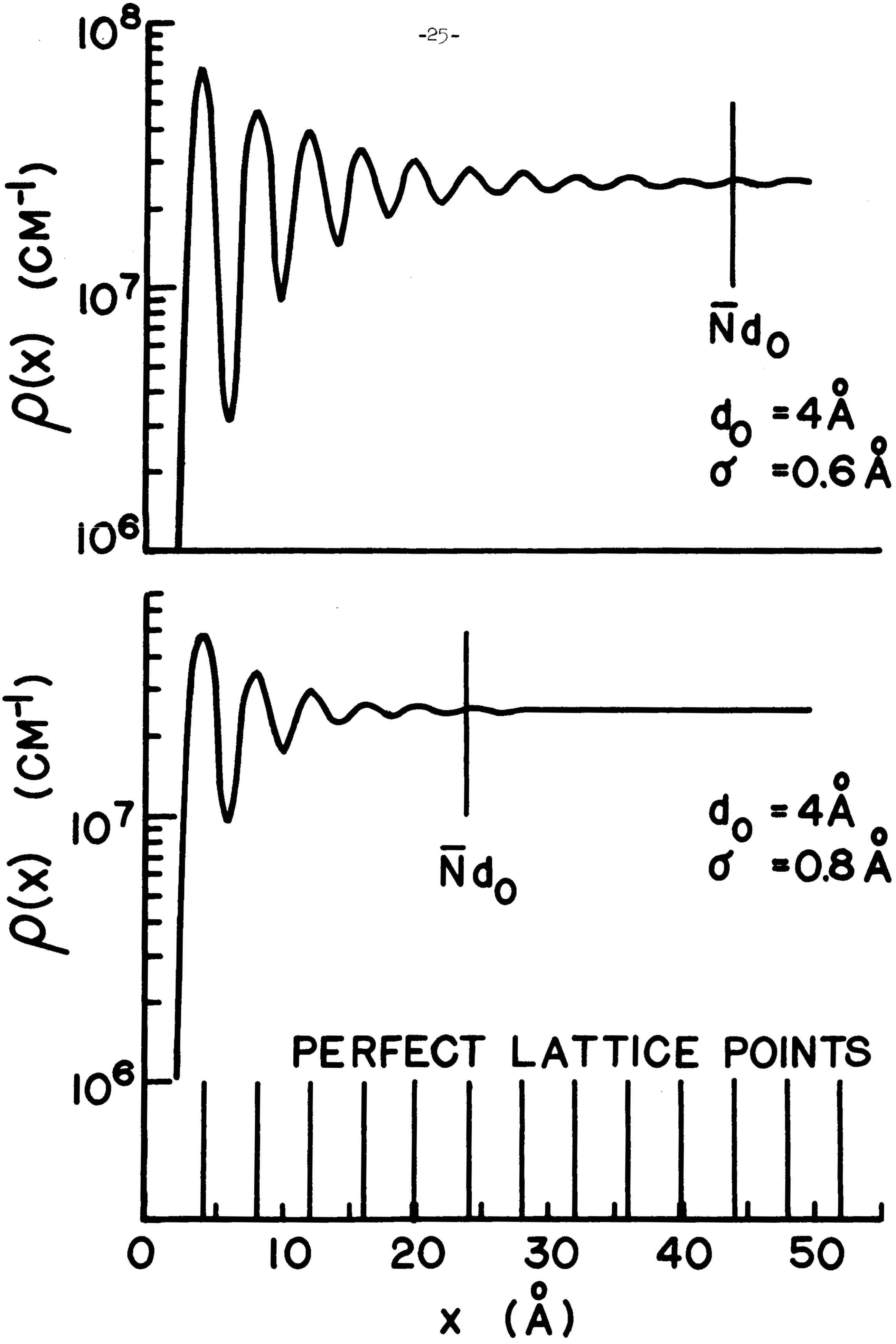

Figure 6. Density function for aperiodic chain.

The left hand side of Eq. (4.5), averaged over the distribution of Eq. (4.2), becomes

$$(L-Nd_o)^2 = \int_{-\infty}^{+\infty} (L-Nd_o)^2 F(L)\,dL = N\sigma^2 \quad . \tag{4.6}$$

Hence, the chain is ordered whenever

$$N < \frac{1}{4}\,(d_o/\sigma)^2 \tag{4.7}$$

The degree of order $\bar{N}$ is defined for the case of the equality in Eq. (4.7). If a disordered chain is considered, $N > \bar{N}$, the above result is interpreted as a statement that the largest sequence of ordered particles contains $\bar{N}$ particles and that no longer sequences are ordered.

The wave functions for the aperiodic chain may be calculated using the translation operator. For the chain, indexed as shown in Fig. 7 and for $E < 0$, the wave function may be written as:

$$\psi(x) = A_i \sin[\beta(x-x_i)] + B_i \cos[\beta(x-x_i)]$$

in Region I, and

$$\psi(x) = C_i \exp[\alpha(x-x_i)] + D_i \exp[-\alpha(x-x_i)] \tag{4.8}$$

in Region II.

Proceeding as in the Kronig-Penney derivation, the matrix equation

$$\begin{pmatrix} A_{i+1} \\ B_{i+1} \end{pmatrix} = T_{+d_{i+1}} \begin{pmatrix} A_i \\ B_i \end{pmatrix} \tag{4.9}$$

may be used to calculate the wave function in any well in terms of the wave function in some arbitrary well. Here $T_{+d_{i+1}}$ is given by Eq. (2.19) with d replaced by d_{i+1}. Eq. (4.9) is suitable for evaluation of the density of states using the tunnel approach. However, in order to obtain statistically significant results a large number of wells must be considered. Consequently,

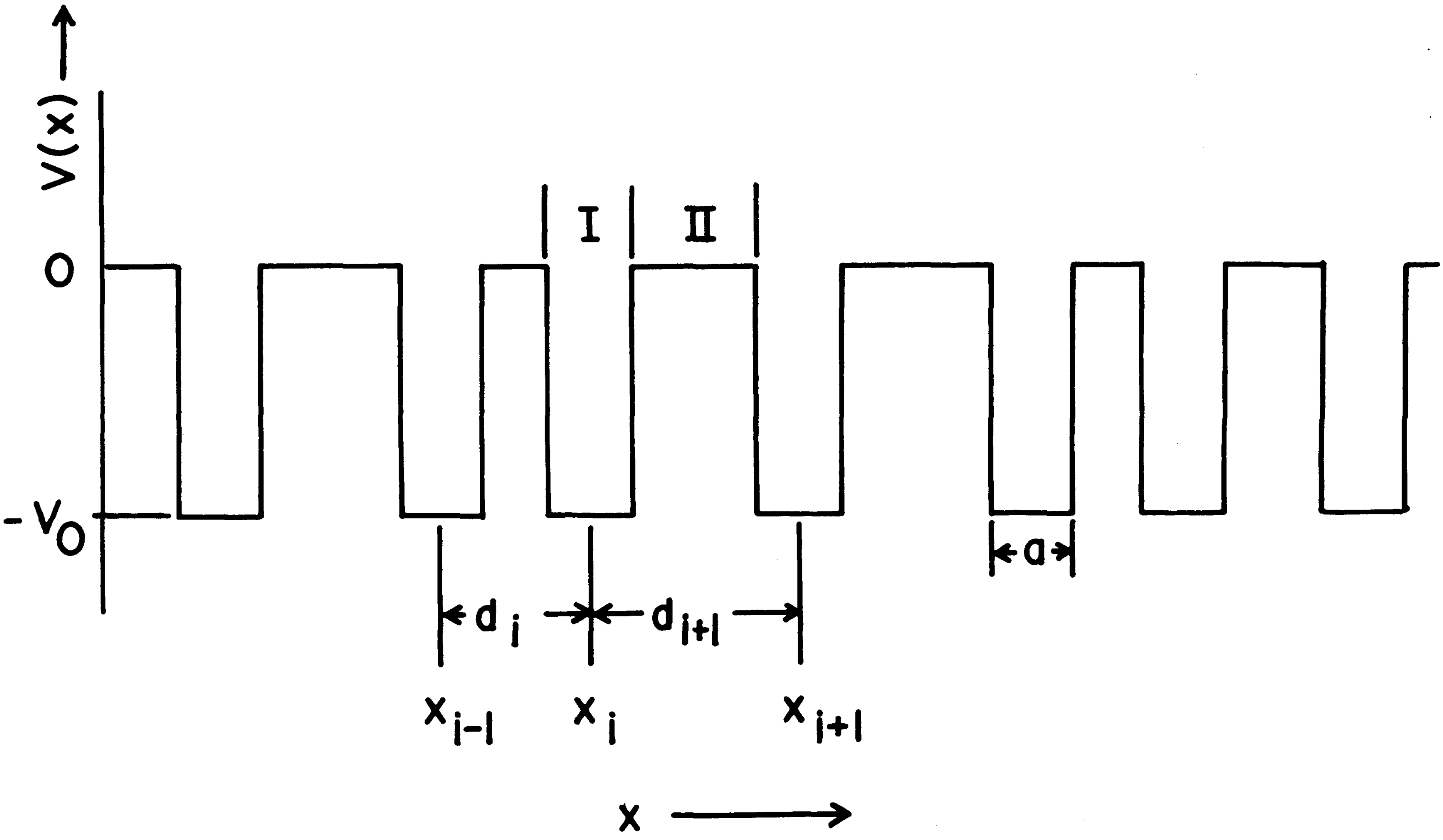

Figure 7. Potential for the aperiodic chain.

each band will contain a large number of unit transmission peaks and the resolution of individual peaks is extremely difficult. This difficulty is overcome by using a node counting technique.

The node counting method is based on a well-known theorem of quantum mechanics;[17] the p^{th} eigenfunction of the Hamiltonian for a one-dimensional problem contains p-1 nodes within the domain of x. Let $N_M(E)$ denote the number of nodes in the wave function over M cells for the energy E. According to the above theorem, there are then $N_M(E)$ allowed states with energy less than E. The integrated density of states becomes

$$G(E) = \underset{M\to\infty}{\text{Limit}} \; (N_M(E)/M) \qquad (4.10)$$

and is related to the density of states by

$$G(E) = \int_0^E g(E')dE'$$

or $\qquad (4.11)$

$$g(E) = \frac{\partial G(E)}{\partial E} \quad .$$

Thus, the average number of nodes per cell is a direct measure of the integrated density of states. This method is the one used in the investigations mentioned earlier.[9-11]

Since the wave function in the entire cell is required, the representation of the $T_{+d_{i+1}}$ operator given by Eq. (4.9) may be written as

$$T_{+d_{i+1}} = R_{i+1}Q \quad . \qquad (4.12)$$

The amplitudes become

$$\begin{pmatrix} C_i \\ \\ D_i \end{pmatrix} = Q \begin{pmatrix} A_i \\ \\ B_i \end{pmatrix}$$

and

$$\begin{pmatrix} A_{i+1} \\ \\ B_{i+1} \end{pmatrix} = R_{i+1} \begin{pmatrix} C_i \\ \\ D_i \end{pmatrix} \qquad (4.13)$$

where

$$Q_{1,1} = \frac{1}{2} \exp(-\alpha a/2)\{\sin(\beta a/2) + \beta/\alpha \cos(\beta a/2)\}$$

$$Q_{1,2} = \frac{1}{2} \exp(-\alpha a/2)\{\cos(\beta a/2) - \beta/\alpha \sin(\beta a/2)\}$$

$$Q_{2,1} = \frac{1}{2} \exp(\alpha a/2)\{\sin(\beta a/2) - \beta/\alpha \cos(\beta a/2)\}$$

$$Q_{2,2} = \frac{1}{2} \exp(\alpha a/2)\{\cos(\beta a/2) + \beta/\alpha \sin(\beta a/2)\}$$

$$R_{1,1} = -\exp[\alpha(d_{i+1}-a/2)]\{\sin(\beta a/2) - \alpha/\beta \cos(\beta a/2)\}$$

$$R_{1,2} = -\exp[-\alpha(d_{i+1}-a/2)]\{\sin(\beta a/2) + \alpha/\beta \sin(\beta a/2)\}$$

$$R_{2,1} = \exp[\alpha(d_{i+1}-a/2)]\{\cos(\beta a/2) + \alpha/\beta \sin(\beta a/2)\}$$

$$R_{2,2} = \exp[-\alpha(d_{i+1}-a/2)]\{\cos(\beta a/2) - \alpha/\beta \sin(\beta a/2)\} \quad . \qquad (4.14)$$

The number of nodes $N_M(E)$ is obtained by calculating the wave function for M consecutive wells and determining the solutions to the equation

$$\psi(x) = 0 \quad . \qquad (4.15)$$

Inside the i^{th} well, the wave function is given by the first of Eq. (4.8). The nodes occur at the points

$$x-x_i = \beta^{-1} \tan^{-1}(-B_i/A_i) \qquad (4.16)$$

subject to the restriction that

$$-a/2 < (x-x_i) < a/2 \quad . \qquad (4.17)$$

Thus, the number of nodes in the i^{th} well may be expressed in the following way

$$N = 0$$

for $\phi_i > \beta a/2$ and (4.18)

$$N = 1 + \mathrm{Ip}[(\beta a - \phi_i)/2\pi] + \mathrm{Ip}[(\beta a + \phi_i)/2\pi]$$

for $\phi_i < a/2$. Here

$$\phi_i = \tan^{-1}(-B_i/A_i) \quad ,$$

and is restricted to the first or fourth quadrant. The symbol Ip denotes the integer part.

Between the i^{th} and $i + 1^{st}$ wells, the wave function is given by the second of Eqs. (4.8). The solution to Eq. (4.15) in this region yields

$$x - x_i = (2\alpha)^{-1} \mathrm{Ln}(-D_i/C_i) \quad . \tag{4.19}$$

Clearly, there is only one node possible and this node occurs whenever

$$-D_i/C_i > 0$$

and (4.20)

$$a/2 < (x - x_i) < d_{i+1} - a/2 \quad .$$

The following procedure is employed in numerically evaluating the number of nodes $N_M(E)$: The wave function is arbitrarily chosen in the first well (e.g., $A_1 = 1$ and $B_1 = 0$). Then, the amplitudes C_1 and D_1 are calculated using the Q matrix and the number of nodes in the first well calculated using Eqs. (4.18) and (4.20). Finally, the amplitudes A_2 and B_2 are determined using the R matrix and the above procedure repeated. The total number of nodes after treating M cells gives the quantity $N_M(E)$.

Extensive numerical investigation showed that the number of cells counted must be sufficiently large to assure a good statistical sample of the lattice spacing distribution. It was found that counting the nodes in 1000 cells satisfied this requirement. Further, this number is considerably larger than the largest degree of order (See Eq. (4.7)) considered and consequently, the short range order is breached many times in the sample.

The above derivation is applicable for energies $E < 0$. The derivation for $E > 0$ follows an analogous procedure and will not be given. The results differ in the expressions for the Q and R operators and in the solution for the nodes.

The numerical evaluation of the integrated density of states for the aperiodic chain has been performed. In all calculations, the chain parameters were taken as $d_o = 4$ Å, $a = 2$ Å, and $V_o = 10$ ev with σ the variable parameter. The calculation for $\sigma = 0$ results in the periodic case and provides a check on the method since this case may be determined analytically. The results are shown in Fig. 8; these compare well with those of the Kronig-Penney model.

The interpretation of the integrated density as a function of energy is derived from Eq. (4.11). The flat regions in Fig. 8 correspond to the forbidden energy bands since the slope vanishes and consequently $g(E) \doteq 0$. The non-zero slope regions correspond to allowed bands. Thus, the results shown in Fig. 8 contain 3 allowed energy bands. The first band (the integer part of $G(E)$ plus 1 gives the band index) lies entirely in the negative energy range and corresponds to tightly bound electrons. The band is seen to be quite narrow compared to the forbidden region between the first and second bands and to the width of higher bands. The second and third bands are in the positive energy range and correspond to nearly-free electrons.

The effect of aperiodicity on the first band is shown in Fig. 9. These curves are for $\sigma = 0$, 0.2, 0.4, 0.6, and 0.8 Å corresponding to variances of 0, 5, 10, 15, and 20% of the mean lattice spacing respectively. It is seen

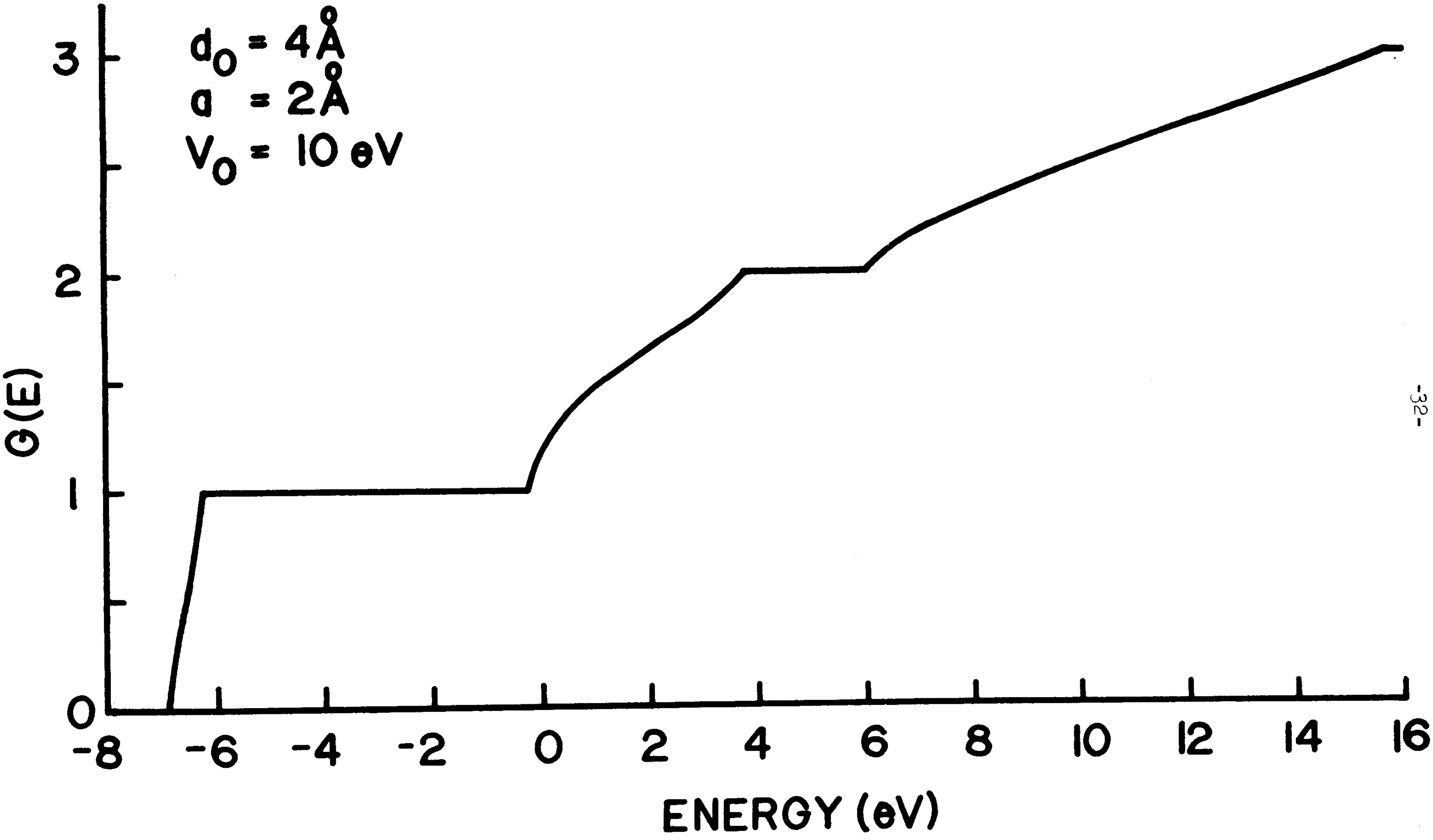

Figure 8. Integrated density of states of the periodic chain.

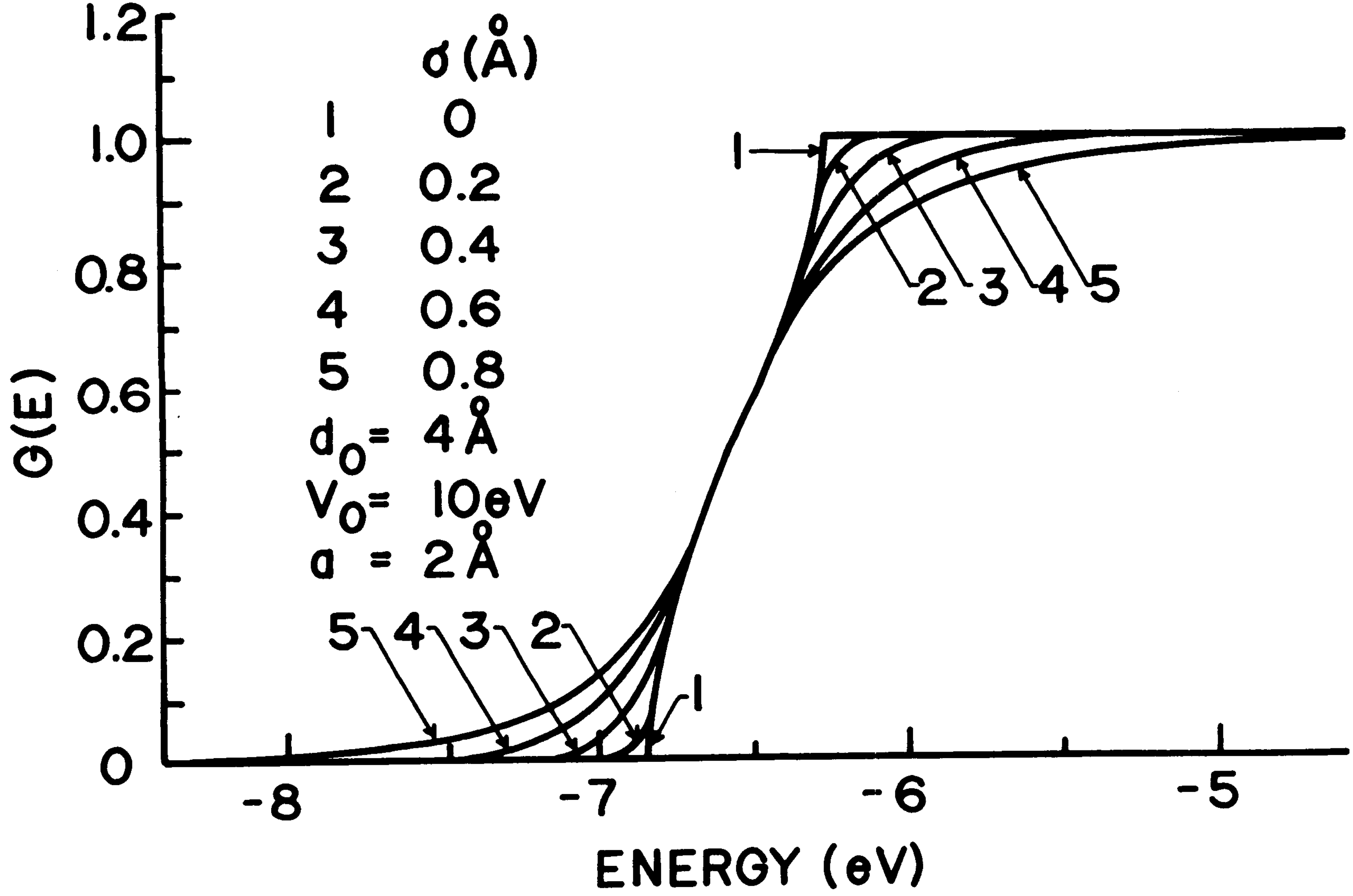

Figure 9. Integrated density of states for the first allowed band of the aperiodic chain.

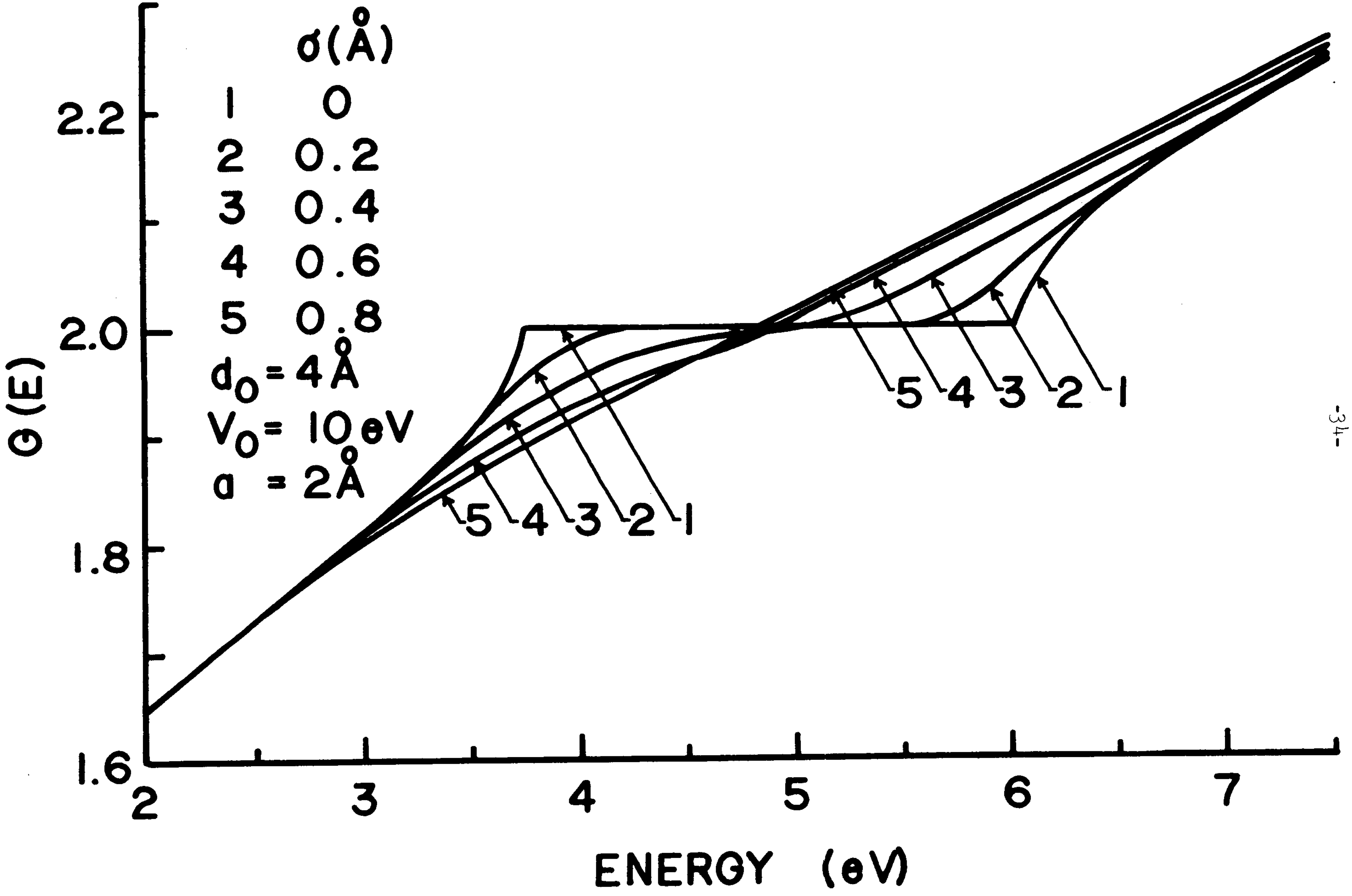

Figure 10. Integrated density of states for second band gap of the aperiodic chain.

that the aperiodicity affects only the band edges with the center of the band remaining unaffected. The greater the aperiodicity, the more diffuse are the band edges. Further, the bands seem to be smeared equally at both the upper and lower edges. Since the tightly-bound band is separated from the next higher band by a very large band gap, the narrowing of the gap by the smearing of the band edges is not appreciable.

The second and third bands are quite wide but separated by a relatively small gap. In this case the region of the forbidden band is of primary interest. Fig. 10 shows the results of aperiodicity on this gap. The values of the parameters are the same as those in Fig. 9. Again, the aperiodicity is seen to affect only the band edges. For $\sigma = 0.2$ Å, the band edges are spread by a small amount but a definite forbidden region remains. However, for $\sigma = 0.4$ Å the spread is sufficient to populate the entire forbidden region with levels; the density of states is small but nonetheless non-vanishing. Finally, for $\sigma \geq 0.6$ Å all traces of the forbidden band vanish and the density of states is approximately uniform throughout the energy range considered.

The present results are in qualitative agreement with those of Makinson and Roberts[12] and Landaver and Helland,[13] and must be considered a verification of their work.

V. Summary

The investigations presented in this communication have been very beneficial in understanding aperiodic systems. An understanding of the role of periodicity in the conventional development of the band structure has been achieved. It was seen that Bloch functions are a direct consequence of periodicity and are eigenfunctions of the translation operator. The tunnel considerations indicated that this situation results from the condition of transparency. This second approach minimized the role of periodicity and indicated that transparency is expected in the aperiodic case. Clearly, Bloch functions are not applicable for the aperiodic case. The numerical treatment of the aperiodic Kronig-Penney model served to solidify these insights.

Present plans are to continue the numerical evaluation of the aperiodic Kronig-Penney model. Further, it is planned to investigate the various perturbation approaches to the problem of aperiodicity.

A paper is being prepared for publication[18] on the tunneling of electrons through thin oxide films. This transport mechanism is of particular interest in the theory of the thermal oxidation of metals. The investigation of electron transport by Schottky emission from the metal into the oxide will be continued. Further, an investigation into the role of space-charge on the transport of electrons has been initiated.

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