For large times the expression in parentheses approaches a δ-function at $E_n=E_m-\hbar\omega$. In addition, there remains the integral over the rest of the energy range, wherein one must take the principle value at the singularity $E_n=E_m-\hbar\omega$. The result is

$$\tfrac{1}{2}i\pi V_0\omega\exp(i\omega t)\int dE_m\rho(E_m)\rho(E_m-\hbar\omega)f(E_m-\hbar\omega)|\langle E_m-\hbar\omega)|Q|E_m\rangle|^2$$
$$+\tfrac{1}{2}(V_0/\hbar)\exp(i\omega t)\int\int dE_m dE_n\frac{f(E_n)\rho(E_m)\rho(E_n)(E_m-E_n)|\langle E_n|Q|E_m\rangle|^2}{E_n-E_m+\hbar\omega}.$$

Combining the results of the integrals one finally gets

$$\langle\dot{Q}\rangle=-V_0\sin\omega t\left\{\pi\omega\int\rho(E)f(E)[|\langle E+\hbar\omega|Q|E\rangle|^2\rho(E+\hbar\omega)-|\langle E-\hbar\omega|Q|E\rangle|^2\rho(E-\hbar\omega)]dE\right\}$$
$$+V_0\cos\omega t\left\{2\omega\int\int f(E_n)\rho(E_n)\rho(E_m)(E_n-E_m)|\langle E_n|Q|E_m\rangle|^2/[(E_n-E_m)^2-(\hbar\omega)^2]dE_n dE_m\right\}.$$

The expression multiplying $-V_0\sin\omega t$ is the conductance, in agreement with reference 1 and the term multiplying $V_0\cos\omega t$ is the susceptance.

It may be noted that the negative sign preceding the n-phase response is to be expected, as $\dot{Q}$ will tend to decrease in order to reduce the value of the perturbing energy term $V(t)Q(\cdots q_k\cdots p_k\cdots)$.

The extension of the fluctuation-dissipation theorem to several variables will be given in a subsequent paper by H. B. Callen, M. Barasch, and J. L. Jackson.

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Variational Methods for Periodic Lattices*

W. Kohn†
Carnegie Institute of Technology, Pittsburgh, Pennsylvania, and Institute for Theoretical Physics, Copenhagen, Denmark

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The problem of finding the propagating solutions of the Schrödinger equation in periodic lattices is formulated as a variational principle. This may be used as a starting point to establish the general properties of bands. Furthermore it is shown that by introducing various approximations into the variational principle, the chief existing approximation methods can all be derived from it. Improvements of these methods are suggested. Numerical illustrations are presented and the possibilities of the variational method for more accurate calculations of the energy bands of solids are discussed.

1. INTRODUCTION

In studying the motion of electrons in a crystal, one adopts as a starting point a picture analogous to the Hartree model for atoms. Thus to a first approximation each electron is considered as moving independently in the potential produced by the nuclei and the charge distribution of all the other electrons. Since the nuclear lattice imposes its regularity also on the electronic charge distribution, this potential has the same periodicity as the lattice.

In general, the wave equation in such a periodic potential cannot be solved exactly. For this reason various approximate methods have been devised which apply especially to this type of potential. The variational method, however, which has been so widely employed for the solution of the Schrödinger equation in other physical situations, has found no extensive application to the case of periodic lattices. To our knowledge, only the work of Slepian,[1] to which we shall come back in Sec. 2, represents a notable exception.

In the present paper a more general approach than that of Slepian will be presented which serves a fourfold purpose:

(1) It may be used as a starting point for a demonstration of the general properties of bands.

(2) It represents the analogon, for periodic potentials, of the variational principles governing bound state and scattering problems.

(3) It unifies the chief approximation methods used up to now for the periodic case. All of these may be shown to be derivable from the variational principle by introducing appropriate restrictions or approximations.

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† Postdoctoral N.R.C. Fellow, 1950–1951.

[1] D. Slepian, thesis, Harvard University (1949).

(4) It provides a new tool for the approximate solution of the Schrödinger equation in periodic lattices which suggests improvements of existing methods of calculation and may be hoped to serve as a basis for future developments.

In Part I of the present paper the variational principle is developed and applied in detail to one-dimensional lattices. The extension to three dimensions is carried out in Part II which deals also with the relationship of the existing approximation methods to the present one. Simple numerical calculations are presented in both parts, but applications to the energy bands of actual solids have not yet been made.

I. ONE-DIMENSIONAL LATTICES

2. Derivation and Discussion of the Variational Principle

In a one-dimensional lattice the Schrödinger equation takes the form

$$H\psi=E\psi,\quad H\equiv-(d^2/dx^2)+V(x), \tag{2.1}$$

where the potential $V(x)$ is periodic, with a period denoted by $2a$:

$$V(x+a)=V(x-a). \tag{2.2}$$

We look for so-called propagating solutions of (2.1). By definition these have the quasi-periodic property

$$\psi(x+a)=e^{2ika}\psi(x-a), \tag{2.3}$$

where k is some real number, which without loss of generality may be chosen between $-\pi/2a$ and $+\pi/2a$.

The quasi-periodic property (2.3) may be replaced by the boundary conditions

$$\psi(a)=e^{2ika}\psi(-a), \tag{2.4a}$$

$$\psi'(a)=e^{2ika}\psi'(-a). \tag{2.4b}$$

It is quite clear that these equations follow from (2.3) and one may also verify without difficulty that conversely (2.3) follows from (2.4a) and (2.4b). Therefore we can restrict ourselves to a solution of the boundary value problem (2.1), (2.4) in the interval $(-a, a)$.

To establish an equivalent variational principle it is natural to study the functional

$$I\equiv\int_{-a}^{a}\psi^*(H-E)\psi dx; \tag{2.5}$$

for such functionals are known to lead to stationary expressions for the energy levels of bound states as well as for the phase shifts of scattering problems.[2,3] In evaluating the first variation of I we use the Schrödinger equation (2.1) which is satisfied by both ψ and ψ^* and obtain

$$\begin{aligned}\delta I&=\int_{-a}^{a}\left(\delta\psi\frac{d^2\psi^*}{dx^2}-\psi^*\frac{d^2\delta\psi}{dx^2}\right)dx\\&=[\delta\psi\psi^{*\prime}-\psi^*\delta\psi']_{-a}^{a}.\end{aligned} \tag{2.6}$$

Thus we see that just as in the case of scattering problems, I is not stationary with respect to arbitrary variations of ψ but that on taking the first variation boundary terms are left over.[3]

Slepian[1] has based his work on the observation that if $\delta\psi$ satisfies the same periodic boundary conditions (2.4) as ψ, the boundary terms vanish through cancellation of the contributions from the two limits of integration. He therefore limits his trial functions to those which satisfy the boundary conditions (2.4) and uses the variational principle $\delta I(\psi, E)=0$ to determine E and ψ as function of k.

We shall now develop a more general variational principle in which the admissible trial functions are not subject to the boundary conditions. This is a practical advantage since, apart from plane waves, it is not easy to find simple functions which satisfy these conditions. Furthermore we shall see later (Sec. 6) how the methods of Wigner-Seitz-Bardeen and Slater can be deduced from the general form of the variational principle.

We aim to write the boundary terms in (2.6) as the first variation of a quantity, $-K_1$ say, which involves the wave function only at the boundary. This can be done by using the boundary conditions (2.4) satisfied by ψ and the corresponding boundary conditions satisfied by ψ^*. Thus, from (2.6) and (2.4) one obtains

$$\begin{aligned}\delta I&=[\psi^{*\prime}(a)\delta\psi(a)-\psi^{*\prime}(-a)\delta\psi(-a)]\\&\qquad-[\psi^*(a)\delta\psi'(a)-\psi^*(-a)\delta\psi'(-a)]\\&=\{\psi^{*\prime}(a)[\delta\psi(a)-\delta\psi(-a)e^{2ika}]\\&\qquad-\psi^*(a)[\delta\psi\ (a)-\delta\psi\ (-a)e^{2ika}]\}\\&=\delta\{\psi^{*\prime}(a)[\psi(a)-\psi(-a)e^{2ika}]\\&\qquad-\psi^*(a)[\psi'(a)-\psi'(-a)e^{2ika}]\}\\&=-\delta K_1,\end{aligned} \tag{2.7}$$

where K_1 can also be written as

$$\begin{aligned}K_1=&-\psi^{*\prime}(a)e^{ika}[\psi(a)e^{-ika}-\psi(-a)e^{ika}]\\&+\psi^*(a)e^{ika}[\psi'(a)e^{-ika}-\psi'(-a)e^{ika}].\end{aligned} \tag{2.8}$$

Thus we have the variational principle $\delta(I+K_1)=0$ which, however, suffers from the blemish of not being symmetrical in the points a and $-a$. However, a derivation exactly similar to the above gives the alternative result

$$\delta I=-\delta K_2, \tag{2.9}$$

where

$$\begin{aligned}K_2=&-\psi^*(-a)e^{-ika}[\psi(a)e^{-ika}-\psi(-a)e^{-ika}]\\&+\psi^*(-a)e^{-ika}[\psi'(a)e^{-ika}-\psi'(-a)e^{ika}].\end{aligned} \tag{2.10}$$

Hence we can write down the following symmetrical

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[2] L. Hulthén, Arkiv Mat. Astr. Fys. **35A**, No. 25 (1948).

[3] W. Kohn, Phys. Rev. **74**, 1763 (1948).

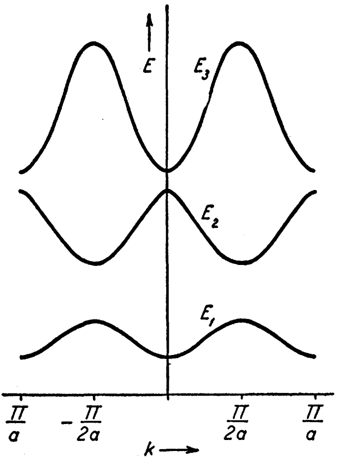

FIG. 1. A typical energy band diagram.

variational principle:

$$J(\psi, k, E) \equiv I + \tfrac{1}{2}(K_1 + K_2) = \text{stationary}. \tag{2.11}$$

For the correct ψ, k, and E, J clearly has the value 0.

We have shown that the solution of the boundary value problem (2.1), (2.4) satisfies the variational principle (2.11). We shall now prove, conversely, that a function satisfying the variational principle is also a solution of the boundary value problem. This will establish the complete equivalence of (2.11) with (2.1) and (2.4).

We consider first a variation $\delta\psi$ which is zero except near an arbitrary point x' in the interior of the interval $(-a, a)$. Then $\delta K_1 = \delta K_2 = 0$ and we find from (2.11)

$$\begin{aligned} 0 = \delta J &= \delta I \\ &= \int_{-a}^{a} \{\delta\psi^*(H-E)\psi + \psi^*(H-E)\delta\psi\} dx \\ &= \int_{-a}^{a} \{\delta\psi^*(H-E)\psi + \delta\psi(H-E)\psi^*\} dx \\ &= 2\,\mathrm{Re} \int_{-a}^{a} \delta\psi^*(H-E)\psi dx, \end{aligned} \tag{2.12}$$

where we have performed an integration by parts and discarded the boundary terms because of the assumed vanishing of $\delta\psi$ at the boundary. By choosing $\delta\psi$ to be real and imaginary in turn, we find that both the real and imaginary parts of $(H-E)\psi$ vanish at every interior point x'. This proves (2.1).

Next we consider an arbitrary variation $\delta\psi$. Using the already established Eq. (2.1) we find

$$\delta I = [\delta\psi(x)\psi^{*\prime}(x) - \delta\psi'(x)\psi^*(x)]_{-a}^{a}. \tag{2.13}$$

When this is combined with $\delta\frac{1}{2}(K_1+K_2)$ and conveniently grouped, one obtains

$$\begin{aligned} \delta J = \mathrm{Re}[&(\delta\psi(a)e^{-ika} + \delta\psi(-a)e^{ika})(\psi^{*\prime}(a)e^{ika} \\ &- \psi^{*\prime}(-a)e^{-ika}) - (\delta\psi'(a)e^{-ika} + \delta\psi'(-a)e^{ika}) \\ &\times(\psi^*(a)e^{ika} - \psi^*(-a)e^{-ika})]. \end{aligned} \tag{2.14}$$

Since $\delta\psi$ and $\delta\psi'$ are entirely arbitrary, it is possible to make the first factor of the first term vanish, while giving the first factor of the second term real and imaginary values in turn. The condition $\delta J = 0$ then shows that the real and imaginary parts of $\psi^*(a)e^{ika} - \psi^*(-a)e^{-ika}$ vanish, which establishes the boundary condition (2.4a). Similarly one can show that ψ must satisfy the other boundary condition (2.4b) which completes our proof.

It should be noted that the functional J is real for arbitrary ψ. For

$$\begin{aligned} \mathrm{Im} I = \tfrac{1}{2}(I - I^*) &= \tfrac{1}{2}\int_{-a}^{a}\left(\psi\frac{d^2}{dx^2}\psi^* - \psi^*\frac{d^2}{dx^2}\psi\right)dx \\ &= \tfrac{1}{2}[\psi\psi^{*\prime} - \psi^*\psi']_{-a}^{a} \end{aligned} \tag{2.15}$$

and this may be seen to cancel $\mathrm{Im}\frac{1}{2}(K_1+K_2)$. It follows that E, evaluated from the equation $J=0$, will correctly be real, no matter what ψ is used in the construction of J.

Since the imaginary part of J vanishes identically in ψ, (2.11) may be written in the equivalent form

$$\begin{aligned} J(\psi, k, E) \equiv \mathrm{Re}\Bigg[&\int_{-a}^{a} \psi^*(H-E)\psi dx \\ &+ (\psi(-a)\psi^{*\prime}(a)e^{2ika} - \psi(a)\psi^{*\prime}(-a)e^{-2ika})\Bigg] \\ &= \text{stationary}, \end{aligned} \tag{2.16}$$

which is more compact and convenient for practical applications.

Finally it should be remarked that approximate values of E obtained from the variational principle (2.11) or (2.16) do not in general represent upper or lower bounds to the true energy, as may be seen from the numerical example worked out in Sec. 4.

3. General Properties of Bands Deduced from the Variational Principle

In periodic lattices every value of k together with the Schrödinger equation constitutes a boundary value problem with an energy spectrum $E_n(k)$. Basing his investigations on the differential equation (2.1), Kramers[4] has shown that the $E_n(k)$ curves have the general features indicated in Fig. 1. It is of some interest to see how these features may also be deduced from the variational principle.

We begin with two very simple propositions:

Periodicity

If (k, E) is a point on the $E_n(k)$-curves, so is $(k+2\pi/2a, E)$. Proof: Let ψ be the wave function corresponding to (k, E). Then

$$0 = \delta J(\psi, k, E) = \delta J(\psi, k+2\pi/2a, E), \tag{3.1}$$

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[4] H. A. Kramers, Physica 2, 483 (1935).

since J, Eq. (2.16), is invariant under the transformation $k \rightarrow k+2\pi/2a$. Hence ψ is also a solution corresponding to $(k+2\pi/2a, E)$.

Symmetry

If (k, E) is a point on the (k, E) curves, so is $(-k, E)$. Proof: Again let ψ correspond to (k, E). Then

$$0=\delta J(\psi, k, E)=\delta J(\psi^*, -k, E), \tag{3.2}$$

since J is invariant under the transformation $\psi \rightarrow \psi^*$, $k \rightarrow -k$. Hence ψ^* is a solution corresponding to $(-k, E)$.

Next we turn to the most interesting property, namely, allowed and forbidden energy ranges.

Allowed and Forbidden Energy Ranges

Propagating wave functions exist only in those so-called allowed energy ranges in which a certain inequality is satisfied. (Energy ranges in which no propagating solutions exist are called forbidden.)

Proof: We consider a given E and examine under what conditions there are propagating solutions corresponding to this value of E. Now every solution of the Schrödinger equation (2.1) must be a linear combination of a pair of two linearly independent solutions φ_1 and φ_2 which we choose real for convenience:

$$\psi=c_1\varphi_1+c_2\varphi_2, \quad c_i=a_i+ib_i. \tag{3.3}$$

We shall try to determine k and c_1, c_2 from the condition

$$\delta J(\psi, k, E)=0, \tag{3.4a}$$

where we consider only variations of the coefficients c_1 and c_2, i.e.,

$$\delta\psi=\delta c_1\varphi_1+\delta c_2\varphi_2. \tag{3.4b}$$

If there is no real k for which (3.4) can be satisfied, then evidently there exist no propagating solutions corresponding to the given E, which is therefore forbidden.

On the other hand, if (3.4) can be satisfied with a real k, then E is allowed. This statement, however, requires special justification since (3.4) shows the stationary character of J only under the limited variations (3.4b).

Suppose then that a real k and corresponding c_i have been determined from (3.4). Then δJ is given by (2.14), where only the differential equation (2.1) has been assumed which is satisfied by our ψ. Let us denote the four parentheses in (2.14) by δ_1, B_1 and δ_2, B_2, respectively. We may now choose a $\delta\psi$ of the type (3.4b) which makes $\delta_1=0$. If it also makes $\delta_2=0$ then this $\delta\psi$ satisfies not only the Schrödinger equation (2.1) but also periodic boundary conditions of the type (2.4) with $k'=k+\pi/2a$, which are represented by the equations $\delta_1=0$, $\delta_2=0$. Thus E is allowed in this case. If, however, $\delta_2 \neq 0$ the condition $\delta J=0$ implies $B_2=0$ which is just the boundary condition (2.4b). Similarly, unless there is a $\delta\psi$ for which both δ_1 and δ_2 are zero, we can prove (2.4b). Thus we see that if (3.4) is satisfied with a real k, E is allowed, and there exists a propagating solution corresponding either to k or to $k+\pi/2a$.

The problem of ascertaining under which conditions (3.4) leads to real k's is quite straightforward. We form the quantity J, Eq. (2.16), with the function (3.3) which by construction satisfies the Schrödinger equation (2.1). Hence

$$J=\mathrm{Re}(\psi(-a)\psi^{*\prime}(a)e^{2ika}-\psi(a)\psi^{*\prime}(-a)e^{-2ika}). \tag{3.5}$$

The conditions $\partial J/\partial a_i=\partial J/\partial b_i=0$ lead to four homogeneous linear equations for the a_i and b_i which are compatible only if the determinant of the coefficients vanishes. This condition is found to be

$$\tan^2 2ka=(E_{11}E_{22}-E_{12}^2)/F_{12}^2, \tag{3.6}$$

where

$$\begin{aligned} E_{ij}&=[\varphi_i(-a)\varphi_j'(a)-\varphi_i(a)\varphi_j'(-a)]+[i\rightleftarrows j] \\ F_{ij}&=[\varphi_i(-a)\varphi_j'(a)+\varphi_i(a)\varphi_j'(-a)]-[i\rightleftarrows j] \end{aligned} \tag{3.7}$$

(the symbol $i\rightleftarrows j$ indicates an interchange of i and j). We see that (3.6) leads to real k's if and only if

$$E_{11}E_{22}-E_{12}^2 \geqslant 0, \tag{3.8}$$

which is the required condition for the allowed energies. It is easy to verify that this condition is equivalent to Kramers' conditions.[5]

4. Practical Use of the Variational Method

As in the case of bound state and scattering problems the variational method may be used to obtain approximate solutions of the boundary value problem (2.1) and (2.4).

In the first place, if an approximate wave function φ for (2.1), (2.4) has been obtained in some independent way (by analogy, ingenious guess-work, etc.), this function may be substituted into the stationary equation

$$J(\varphi, k, E)=0, \tag{4.1}$$

which relates E and k with high accuracy, the error being of the order of (error of $\varphi)^2$.

Secondly, (2.16) can be used for the systematic construction of the solution, most conveniently by the method of Rayleigh and Ritz.[6] We shall not discuss this well known method in detail here, but only remark on some points specific to the present problem.

One takes as an approximate solution

$$\psi=\sum_{i=1}^{n} c_i\varphi_i, \quad c_i=\text{real}, \tag{4.2}$$

where, to obtain good answers, the φ_i must be judiciously chosen. One now substitutes this ψ in (2.16) and satisfies the stationary property approximately by

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[5] See reference 4, conditions (2) and (3), pp. 484–485.

[6] W. Ritz, J. reine angew. Math. **135**, 1 (1909); for application to wave mechanics, see, e.g., L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935).

TABLE I. Numerical results for $E(k)$ for Kronig-Penney potential.

Number of trial functions	$2ka=0$	$2ka=\pi/2$	$2ka=\pi$
	Lowest band		
1	0.25	0.25	3.00
2	0.24	1.00	2.47
3	0.24	0.87	2.47
Exact functions	0.23	0.84	2.47
	Second band		
2	11.20		3.01
3	9.88	8.43	2.96
4		6.33	
5		5.85	
Exact functions	9.87	5.80	2.94

demanding that

$$\partial J/\partial c_i=0, \quad i=1, 2, \cdots n, \tag{4.3}$$

which gives n linear homogeneous equations for the c_i. The corresponding compatibility equation has the form

$$\Delta_n(k, E)=0 \tag{4.4}$$

and defines an approximate (real) E-spectrum for a given k or approximate k's for a given E. The stationary property of (4.4) implies that the error of (4.4) is of the order of $(\delta\psi)^2$. If the φ_i are a set of differentiable functions, complete in the sense that any continuous function on $(-a, a)$ can be arbitrarily approximated by a suitable linear combination, then as $n\rightarrow\infty$, Eq. (4.4) represents the complete band structure of the lattice. Once (4.4) is solved one can substitute a k and the corresponding E in (4.3) and solve for the c_i, thus obtaining an approximate wave function.

It should again be remarked that in contrast to the usual case of bound state problems the lowest, second-lowest, etc., values of E calculated from (4.4) for a given k do not necessarily represent upper bounds to the true eigenvalues E_1, E_2, etc. (see the second entry of 0.25 in Table I). This is due to the fact that in (2.16) we admit variations of ψ which do not satisfy the boundary conditions.

As a concrete illustration we consider the simple case originally discussed by Kronig and Penney[7] where the potential has the form

$$V(x)=V\sum_{n=-\infty}^{\infty}\delta(x-2na). \tag{4.5}$$

We set $V=\frac{1}{2}$ and $a=1$ and use trial functions of the form

$$\psi_k(x)=(c_0+c_2x^2+\cdots)+i(c_1x+c_3x^3+\cdots). \tag{4.6}$$

The c_i are real, for whenever $V(x)=V(-x)$, then $\psi_k(-x)=\psi_{-k}(x)=\psi_k{}^*(x)$ so that $\mathrm{Re}\psi_k=$ even, $\mathrm{Im}\psi_k=$ odd. It is now quite easy to express J as a quadratic form in the c_i and to determine E as a function of k from the usual secular equation coming from the conditions $\partial J/\partial c_i=0$. The approximate results obtained for the lowest two bands with an increasing number of trial functions as well as the exact values of E are given in Table I. (For $2ka=0$ or π, the true wave functions are either even or odd, so that we have used only even or odd trial functions.)

The convergence may be considered satisfactory. It is relatively slowest at $2ka=\pi/2$, since the corresponding wave functions are complex and therefore require a larger number of parameters for accurate fitting.

II. THREE-DIMENSIONAL LATTICES

5. The Variational Principle

The ideas of the preceding paragraphs can be easily generalized to three dimensions. Here one surrounds each nucleus by identically shaped polyhedra, as illustrated schematically in Fig. 2. Selecting anyone of these for our further considerations, we note that to every boundary point $\mathbf{r}$ there corresponds a conjugate point $\mathbf{r}'$, also on the boundary, such that $\mathbf{r}'-\mathbf{r}$ is a fundamental translation vector $\boldsymbol{\tau}_\mathbf{r}$. It will be seen that $\boldsymbol{\tau}_\mathbf{r}$ is constant on each face and that $\boldsymbol{\tau}_{\mathbf{r}'}=-\boldsymbol{\tau}_\mathbf{r}$.

We now state the boundary value problem which we wish to formulate as a variational principle:

$$[-\nabla^2+V(\mathbf{r})-E]\psi(\mathbf{r})=0 \quad \text{for all } \mathbf{r} \text{ inside the polyhedron,} \tag{5.1}$$

$$\psi(\mathbf{r}')=\exp(i\mathbf{k}\boldsymbol{\tau}_\mathbf{r})\psi(\mathbf{r}) \quad \text{for all } \mathbf{r} \text{ on the surface of the polyhedron,} \tag{5.2a}$$

$$\partial\psi(\mathbf{r}')/\partial n=-\exp(i\mathbf{k}\boldsymbol{\tau}_\mathbf{r})\partial\psi(\mathbf{r})/\partial n \quad \text{for all } \mathbf{r} \text{ on the surface of the polyhedron.} \tag{5.2b}$$

Here $\mathbf{k}$ is the wave vector and $\partial/\partial n$ denotes differentiation along the outward normal at the point in question. The minus sign in (5.2b) is due to the fact that the outward normals at r and r' have opposite directions.

To obtain an equivalent variational principle, we consider the functional

$$I\equiv\int_\Omega\psi^*[-\nabla^2+V(\mathbf{r})-E]\psi d\omega, \tag{5.3}$$

where Ω denotes the interior of the polyhedron. Its first variation can, with the aid of (5.1), be written as an integral over the bounding surface S of the polyhedron:

$$\delta I=\int_S\left(\delta\psi\frac{\partial}{\partial n}\psi^*-\psi^*\frac{\partial}{\partial n}\delta\psi\right)dS. \tag{5.4}$$

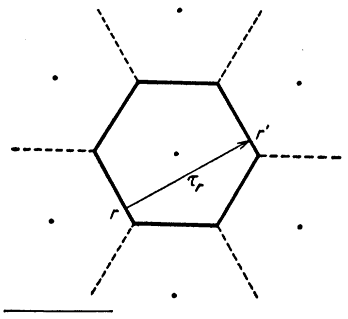

FIG. 2. Conjugate boundary points.

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[7] R. de L. Kronig and W. G. Penney, Proc. Roy. Soc. (London) **130**, 499 (1931).

By proceeding in analogy with our treatment of the one-dimensional problem (Sec. 2), with pairs of conjugate faces corresponding to our previous end points $\pm a$, we could transform the right-hand side of (5.4) into the first variation of a surface integral. This would lead to the form of the variational principle corresponding to (2.11). However, instead of repeating this rather lengthy process a second time we shall derive directly the form of the variational principle corresponding to (2.16).

For this purpose, we consider the real part of I, which we aim to write as the first variation of a surface integral. Beginning with the first term on the right-hand side of (5.4) we make the following transformations:

$$\begin{aligned}\operatorname{Re}\int_S \delta\psi(\mathbf{r})\frac{\partial}{\partial n}\psi^*(\mathbf{r})dS &= \operatorname{Re}\int_S \frac{\partial}{\partial n}\psi(\mathbf{r})\delta\psi^*(\mathbf{r})dS \\ &= \operatorname{Re}\int_S \frac{\partial}{\partial n}\psi(\mathbf{r}')\delta\psi^*(\mathbf{r}')dS \\ &= \operatorname{Re}\int_S -\frac{\partial}{\partial n}\psi(\mathbf{r})\delta\psi^*(r')\exp(i\mathbf{k}\tau_r)dS, \qquad (5.5)\end{aligned}$$

where the last step involves the boundary condition (5.2b). The second term of (5.4) can, in virtue of (5.2a), be written as

$$\begin{aligned}\operatorname{Re}\int_S -\frac{\partial}{\partial n}\delta\psi(\mathbf{r})\psi^*(\mathbf{r})dS &= \operatorname{Re}\int_S -\frac{\partial}{\partial n}\delta\psi(\mathbf{r})\psi^*(\mathbf{r}')\exp(i\mathbf{k}\tau_r)dS. \qquad (5.6)\end{aligned}$$

Combining (5.5) and (5.6) we thus obtain

$$\delta(\operatorname{Re} I) = -\delta\left[\operatorname{Re}\int \frac{\partial}{\partial n}\psi(\mathbf{r})\psi^*(\mathbf{r}')\exp(i\mathbf{k}\tau_r)dS\right]. \qquad (5.7)$$

The desired variational principle can now be written in the following form:

$$J(\psi, k, E) \equiv \operatorname{Re}\left[\int_\Omega \psi^*(-\nabla^2+V-E)\psi d\omega + \int_S \frac{\partial\psi(\mathbf{r})}{\partial n}\psi^*(\mathbf{r}')\exp(i\mathbf{k}\tau_r)dS\right] = \text{stationary}, \qquad (5.8)$$

which may be compared with (2.16). Clearly, for the correct ψ, $\mathbf{k}$, and E, the functional J vanishes.

The proof that a solution of (5.8) also solves the boundary value problem (5.1), (5.2) is exactly analogous to that given for one dimension and therefore need not be repeated here.

Finally we may note two special forms of (5.8). If the admitted trial functions all satisfy the boundary conditions (5.2), we have

$$I \equiv \int_\Omega \psi^*(-\nabla^2+V-E)\psi d\omega = \text{stationary} \qquad (5.9)$$

(see reference 1), while if the trial functions satisfy the wave equation (5.1) we obtain

$$K \equiv \operatorname{Re}\int_S \frac{\partial\psi(\mathbf{r})}{\partial n}\psi^*(\mathbf{r}')\exp(i\mathbf{k}\tau_r) = \text{stationary}. \qquad (5.10)$$

6. The Approximate Methods of Wigner-Seitz-Bardeen, Kuhn-Van Vleck, and Slater

It is a gratifying feature of the variational approach that it serves as common basis for the various approximation procedures which have been used in the past. In addition, the variational formulation suggests ways in which these methods may be further developed.

The Method of Wigner-Seitz-Bardeen[8,9]

In their classical work on metallic sodium and lithium Wigner and Seitz,[8] in order to simplify their calculations, replaced the actual polyhedron, in which the boundary value problem (5.1) and (5.2) was to be solved, by a sphere of equal volume. Thus they addressed themselves to the solution of the following simpler problem,

$$(-\nabla^2+V-E)\psi(\mathbf{r})=0, \quad r<r_s, \qquad (6.1)$$

$$\psi(\mathbf{r})=e^{-2i\mathbf{k}\mathbf{r}}\psi(-\mathbf{r}), \quad r=r_s, \qquad (6.2\text{a})$$

$$\partial\psi(\mathbf{r})/\partial r = -e^{-2i\mathbf{k}\mathbf{r}}\partial\psi(-\mathbf{r})/\partial r, \quad r=r_s, \qquad (6.2\text{b})$$

where $r=|\mathbf{r}|$ and r_s is the radius of the equivalent sphere. Even these simplified equations could be only approximately solved. A particularly attractive method was given by Bardeen[9] who obtained a solution of (6.1), (6.2) in the form of a power series in k. Bardeen's original derivation is somewhat lengthy and can be simplified with the aid of the variational theory which also suggests further developments.

The problem (6.1), (6.2) is equivalent to the variational problem

$$J_s(\psi, k, E) = \operatorname{Re}\left[\int_{\Omega_s}\psi^*(-\nabla^2+V-E)\psi d\omega + \int_{S_s}\frac{\partial\psi(\mathbf{r})}{\partial r}\psi^*(-\mathbf{r})e^{-2i\mathbf{k}\mathbf{r}}dS\right] = \text{stationary}, \qquad (6.3)$$

where the subscript s refers to the equivalent sphere.

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[8] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); E. Wigner, Phys. Rev. **46**, 1002 (1934); F. Seitz, Phys. Rev. **47**, 400 (1935).

[9] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

This is in complete analogy with our previous variational principle (5.8).

Since $V(r)$ has spherical symmetry, the direction of k is immaterial and we may for convenience choose it along the z axis. The solution of (6.3) has axial symmetry and hence, for a given E may be expanded in spherical harmonics as

$$\psi = a_0R_0(r;E)+ia_1R_1(r;E)P_1(\cos\theta) + a_2R_2(r;E)P_2(\cos\theta)+\cdots. \tag{6.4}$$

Here θ is the polar angle and the successive terms are the solutions of the Schrödinger equation (6.1) corresponding to angular momenta 0, 1, 2, etc. If V is given, these solutions can be easily calculated by numerical methods.

For $k=0$, the solution of (6.1) and (6.2) is spherically symmetrical and must satisfy the boundary condition

$$[\partial R_0(r;E)/\partial r]_{r=r_s}=0, \tag{6.5}$$

which determines the ground-state energy $E=E_0$.

Next we calculate E for small values of k. Symmetry considerations show that if $a_0\sim 1$, then $a_1\sim k$, $a_2\sim k^2$, etc., that the a_i are real and that

$$E=E_0+E_2k^2+E_4k^4+\cdots. \tag{6.6}$$

Hence a wave function correct to order k inclusive is

$$\psi = c_0R_0(r;E_0)+ikc_1R_1(r;E_0)P_1(\cos\theta), \tag{6.7}$$

where the c_i and R_i are independent of k. Substitution of this function into the variational principle (6.3) must give E correct to order k^2. Now when we reject terms of higher order, we find that

$$J_s=k^2\left[-c_0^2E_2\int_{\Omega_s}R_0^2d\omega+2c_0c_1\frac{4\pi}{3}r_s^3R_0\frac{\partial R_1}{\partial r} - c_1^2\frac{4\pi}{3}r_s^2R_1\frac{\partial R_1}{\partial r}\right], \tag{6.8}$$

where the common argument $E=E_0$ has been suppressed and in the second and third terms $r=r_s$ is understood. The corresponding determinantal equation,

$$\begin{vmatrix} -E_2\int_{\Omega_s}R_0^2d\omega & \frac{4\pi}{3}r_s^3R_0\frac{\partial R_1}{\partial r} \\ \frac{4\pi}{3}r_s^3R_0\frac{\partial R_1}{\partial r} & -\frac{4\pi}{3}r_s^2R_1\frac{\partial R_1}{\partial r} \end{vmatrix}=0, \tag{6.9}$$

gives at once Bardeen's result

$$E_2=r_s\left[\frac{R_0^2}{\int_{\Omega_s}R_0^2d\omega\Big/\frac{4\pi}{3}r_s^3}\right]\frac{\partial R_1/\partial r}{R_1}. \tag{6.10}$$

The coefficients E_4, E_6, etc., in (6.6) can be calculated in an analogous way.[10]

Finally, it may be remarked that trial-functions up to a certain angular momentum, of the form (6.4), can be used in the variational principle (6.3), without expansion in powers of k. It should be observed that the volume integral in (6.3) vanishes for these functions. Since the $R_i(r_s;E)$ may be normalized to 1, it is clear that the result of making (6.3) stationary with respect to variations of the a_i in (6.4) can depend only on the logarithmic derivatives of the R_i at the surface. We illustrate this by considering, for simplicity, only S and P functions corresponding to energy E; this gives

$$J_s=2\pi\left[a_0^2\frac{\partial R_0}{\partial r}R_0I_0+a_0a_1\left(R_0\frac{\partial R_1}{\partial r}+R_1\frac{\partial R_0}{\partial r}\right)I_1 - a_1^2\frac{\partial R_1}{\partial r}R_1I_2\right], \tag{6.11}$$

where

$$\begin{aligned} I_0&=\int_0^\pi e^{-2ikr_s\cos\theta}\sin\theta d\theta=\sin(2kr_s)/(kr_s), \\ I_n&=-\frac{1}{2i}\frac{\partial}{\partial(kr_s)}I_{n-1}. \end{aligned} \tag{6.12}$$

The corresponding compatibility equation can be written as follows:

$$L(R_1)/L(R_0)+L(R_0)/L(R_1)=4I_0I_2/I_1^2-2, \tag{6.13}$$

where we have used the notation

$$L(R_i)\equiv\left.\frac{\partial R_i(r;E)/\partial r}{R_i}\right|_{r=r_s} \tag{6.14}$$

for the logarithmic derivative at $r=r_s$. Equation (6.13) has the form $f(E)=g(k)$, whose solution gives the required dependence of E on k.

The Method of Kuhn and Van Vleck[11]

In the spherical approximation, the energy of the ground state of metallic electrons is defined by Eq. (6.5), which may also be written as $L(R_0)=0$. Kuhn and Van Vleck have now made the interesting observation that the experimental term values of the valence electron in the metallic atom allow one to obtain L as a function of E by means of inter- and extrapolation. Thus they are able to find the energy E_0 where $L=0$, without requiring a knowledge of the potential or the wave function inside the ion.

In the expression (6.10) for E_2, $\{(\partial R_1/\partial r)/R_1\}_{E=E_0}$ can similarly be found by extrapolation. The square bracket which has the value 1 for a constant wave

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[10] R. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950); R. Silverman, Phys. Rev. **85**, 227 (1952).

[11] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950).

function, differs only slightly from 1 for the alkalis and can be rather accurately estimated without requiring a very exact knowledge of $V(r)$. Apart from this slight incompleteness, both E_0 and E_2 are thus directly obtained from the atomic spectra.

Let us now discuss these ideas from the point of view of the variational principle (6.3). We note that if we admit only trial functions of the type (6.4) which satisfy the Schrödinger equation (5.1), the volume integral in (6.3) vanishes and we have, corresponding to (5.10), the variational principle

$$K_s \equiv \int_{S_s} \frac{\partial\psi(\mathbf{r})}{\partial r}\psi^*(-\mathbf{r})e^{-2ikr\cos\theta} = \text{stationary}. \quad (6.15)$$

Thus the values and radial derivatives of the R_i are required only at the boundary $r=r_s$. Since as remarked before one may arbitrarily normalize the functions such that $R_i(r_s;E)=1$, the only quantities really needed in (6.15) are the logarithmic derivatives $L(R_i)$, and these are at least in principle obtainable from the atomic spectra.

Why then does an integral over the interior occur in Eq. (6.10) used by Kuhn and Van Vleck? To resolve this apparent contradiction we expand (6.13), in which only logarithmic derivatives at the boundary occur, in powers of k. This gives

$$E_2 = -\tfrac{1}{3}r_s^2 L(R_1) \Big/ \left[\frac{d}{dE}L(R_0)\right]_{E=E_0}, \quad (6.16)$$

which involves only surface quantities and which is equivalent with (6.9) if the equation

$$4\pi r_s^2\left[\frac{d}{dE}L(R_0)\right]_{E=E_0} = -\int_{\Omega_s} R_0^2 d\omega/R_0^2 \quad (6.17)$$

holds. The truth of this equation follows by Green's theorem from the Schrödinger equation

$$(-\nabla^2+V-E)R_0(r;E)=0, \quad (6.18)$$

which is satisfied identically in E, and its derivative with respect to E. Thus we see that the volume integral occurring in (6.9) can in fact be expressed as a boundary term. It remains to be seen, however, whether $(d/dE)L(R_0)$ can be obtained with sufficient accuracy from the atomic spectra to make the calculation of E_2 from (6.16) practical.

It will be obvious how the method of Kuhn and Van Vleck can be extended by means of (6.15) to include also higher angular momenta. It should again be remarked that the expansion in powers of k can be avoided by introducing the exact solutions of the Schrödinger equation into (6.15) [see Eq. (6.13)].

Another possible extension should also be noted, which consists of the removal of the spherical approximation used by Kuhn and Van Vleck. We return to the boundary value problem (5.1) and (5.2) in the actual polyhedron and consider the solution ψ corresponding to a certain $\mathbf{k}$ and E. Within the inscribed sphere of the polyhedron, ψ can be expanded in a series of spherical harmonics,

$$\psi = \sum_l \sum_m c_{l,m}\psi_{l,m}, \quad (6.19)$$

where each $\psi_{l,m}$ is a solution of the Schrödinger equation (5.1) corresponding to the energy E. There is no guarantee that this series will also converge in the space between the inscribed sphere and the boundary of the polyhedron. However, one may hope that the true wave function can at least be well approximated by a series of this kind in the entire polyhedron.[12]

For a given energy, let us then take a finite series of the type (6.19) as approximation to the true wave function. Since each term satisfies the Schrödinger equation, the appropriate variational principle is (5.10), which requires the wave functions $\psi_{l,m}$ and their normal derivatives only at the boundary of the polyhedron.

Calling the radial part of $\psi_{l,m}$, R_l, the procedure of Kuhn and Van Vleck will give us the logarithmic derivative of R_l at a point $r=a$ such that the sphere $r<a$ contains essentially the entire metal ion. This method further presupposes that this sphere lies inside the polyhedron. For $r>a$, the potential is hydrogenic so that there R_l is that radial hydrogenic function whose logarithmic derivative at $r=a$ has the given value. In this way R_l and hence also $\psi_{l,m}=R_lY_l^m$ are obtained at and near the surface of the polyhedron entirely from information derived from the atomic spectra.

Using these $\psi_{l,m}$ in (5.10) leads to homogeneous linear equations for the coefficients $c_{l,m}$ which are compatible only for certain vectors $\mathbf{k}$. Thus the desired relationship between k and E is established.

The Method of Slater[13]

Much information about the band structure of metals has been obtained by means of a method due to Slater which, unlike that of Wigner and Seitz, takes into account the actual (nonspherical) shape of the crystal polyhedra.

Briefly, the idea of this method is as follows: Since the potential in each cell may be taken to be spherical, the Schrödinger equation (5.1) has, for a given E, the spherical solutions $\psi_{l,m}(\mathbf{r})$. Once the potential is known, these functions are easily obtained by numerical integration of the radial equation.

As approximate solution ψ of the boundary value problem (5.1), (5.2), Slater uses a linear combination, of the type (6.19), of a finite number of $\psi_{l,m}$. This ψ satisfies the Schrödinger equation (5.1) exactly and can be made to comply with the boundary conditions

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[12] It is reassuring that for the plane wave solutions, corresponding to $V=0$, the expansion (6.19) is valid everywhere.

[13] J. C. Slater, Phys. Rev. **45**, 794 (1934).

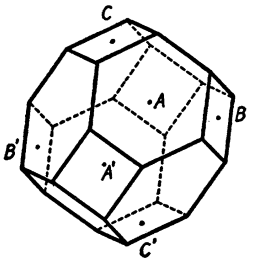

FIG. 3. Unit cell of a body centered cubic lattice.

(5.2) at a finite number of conjugate points:

$$\psi(\mathbf{r}_i')=\exp(i\mathbf{k}\boldsymbol{\tau}_i)\psi(\mathbf{r}_i) \tag{6.20a}$$

$$\partial\psi(\mathbf{r}_i')/\partial n=-\exp(i\mathbf{k}\boldsymbol{\tau}_i)\partial\psi(\mathbf{r}_i)/\partial n, \tag{6.20b}$$

there $\boldsymbol{\tau}_i$ is the translation vector at the point $\mathbf{r}_i$.

Each pair of conjugate boundary points leads to two complex linear equations, involving the unknown vector **k**, for the coefficients $c_{l,m}$. Now if the total number of independent real linear equations is less than the number of real coefficients in (6.21), these equations can be satisfied for all **k**, if greater they cannot be satisfied for any **k**. However, if the number of equations equals the number of unknown coefficients, a solution will exist if and only if the determinant of the set of equations vanishes. This condition has the form of an equation restricting the vector **k** to lie on a surface in **k** space, which may be taken to be an approximation to the correct **k** surface belonging to the given E.

The fact that Slater's method leads to a compatibility equation strongly suggests that it may be derivable from our variational principle (5.8). This will now be shown.

We use as trial function corresponding to energy E, the expression (6.19), which satisfies the Schrödinger equation so that the relevant form of the variational principle is again (5.10). This leads to the equation

$$0=\delta K=\mathrm{Re}\int_S\left[\frac{\partial}{\partial n}\delta\psi(\mathbf{r})\psi^*(\mathbf{r}')+\frac{\partial}{\partial n}\psi(\mathbf{r})\delta\psi(\mathbf{r}')\right]\exp(i\mathbf{k}\boldsymbol{\tau}_r)dS$$

$$=\int\left\{\delta\psi(\mathbf{r})\left[\frac{\partial}{\partial n}\psi^*(\mathbf{r})+\frac{\partial}{\partial n}\psi^*(\mathbf{r}')\exp(i\mathbf{k}\boldsymbol{\tau}_r)\right]+\frac{\partial}{\partial n}\delta\psi(\mathbf{r})\left[-\psi^*(\mathbf{r})+\psi^*(\mathbf{r}')\exp(i\mathbf{k}\boldsymbol{\tau}_r)\right]\right\}dS, \tag{6.21}$$

where in passing to the last line we have added two terms which cancel one another in virtue of Green's theorem and the Schrödinger equation satisfied by $\delta\psi$ and ψ^*. If we substitute for ψ^* from (6.19) and use $\delta\psi=\delta c_{l,m}\psi_{l,m}$ we get a set of linear equations leading to a compatibility equation which defines a surface in **k** space corresponding to the given E.

This is not quite Slater's surface. The latter is obtained only after making the further approximation of replacing (6.21) by

$$0=\mathrm{Re}\sum_i\alpha_i\left\{\delta\psi(\mathbf{r}_i)\left[\frac{\partial}{\partial n}\psi^*(\mathbf{r}_i)+\frac{\partial}{\partial n}\psi^*(r_i')\exp(i\mathbf{k}\boldsymbol{\tau}_i)\right]+\frac{\partial}{\partial n}\delta\psi(\mathbf{r}_i)\left[-\psi^*(\mathbf{r}_i)+\psi^*(\mathbf{r}_i')\exp(i\mathbf{k}\boldsymbol{\tau}_i)\right]\right\}, \tag{6.21$'$}$$

where the α_i are numerical weight-factors and the $\mathbf{r}_i$ are the points at which Slater satisfies the boundary conditions. For it is clear that Slater's solutions, which satisfy (6.20) also satisfy the approximate variational principle (6.21′).

Now the transition from (6.21) to (6.21′) is just the usual procedure of numerical integration, where the integrand is evaluated at a finite number of points and summed with appropriate weight-factors. It should be noted, however, that in (6.21′), which is equivalent to Slater's procedure, the number of points used in the numerical integration is limited by the number of trial functions, whereas to take full advantage of the accuracy offered by (5.10) or the equivalent (6.21), enough points should be taken to make the error of the numerical integration negligible.

In the next section we shall, in a numerical example, examine the difference between the results obtained by Slater's method and the more accurate variational principle (5.10).

7. The Variational Method as a New Tool for the Calculation of Energy Bands

From a practical point of view the variational principle (5.8) can be regarded as a framework, within which judiciously selected wave functions are to be employed.

At present, it may be said that a completely satisfactory way of determining the solutions of the Schrödinger equation in three-dimensional periodic lattices is not yet known. The methods of Wigner-Seitz-Bardeen and Kuhn-Van Vleck approximate the actual polyhedron by a spherical cell, which must be expected to lead to appreciable errors near the top of the zones. On the other hand, the method of Slater which takes the actual shape of the polyhedron into account has been found to be rather slowly convergent.[14] Furthermore, it assumes implicitly that due to the spherical symmetry of the potential, the wave function can be expanded in spherical harmonics inside the entire polyhedron. However, we have already noted that such an expansion may not converge outside the inscribed sphere of the polyhedron.

In addition, since all the above mentioned methods use expansions in spherical harmonics, they are very

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[14] W. Shockley, Phys. Rev. **52**, 866 (1937).

slowly convergent and hence not practical for high-lying bands. For this reason other ways of approximating the wave function should be investigated.

For problems of this kind the variational principle (5.8) may be expected to be a useful aid but no such analysis is attempted in the present paper. We shall merely describe a very simple, exploratory application of the variational method to a three-dimensional problem.

We consider a body-centered cubic lattice, of fundamental cube edge=2, whose cell is shown in Fig. 3. We take the potential to vanish everywhere, in which case the solutions of the boundary value problem (5.1), (4.2) are known to be plane waves with $E=k^2$. In this case one knows further that an expansion in spherical harmonics is possible. Following Shockley,[14] we shall first check the accuracy of Slater's method against the exact result by using as approximate function a linear combination of the S and P solutions of the wave equation. Next we shall use the same trial functions in the variational principle (5.10), which is the special form of (5.8) for trial functions which satisfy the wave equation. This will give us an opportunity to compare our results both with those obtained by Slater's method and with the exact results.

We shall look for E as a function of k, where for simplicity we take k to lie along the line BB' of Fig. 3. We chose this line as polar axis and write

$$\psi=c_0 j_0(E^{\frac{1}{2}}r)+ic_1 j_1(E^{\frac{1}{2}}r)\cos\theta, \qquad (7.1)$$

where symmetry considerations show that c_0 and c_1 can be taken as real.

Following the method of Slater, we can satisfy the boundary conditions (6.20) with the function (7.1) at any pair of conjugate points (and all other pairs which for symmetry reasons are equivalent to it), but only for a particular value of k. This gives us a relationship between E and k. If the pair of points is chosen as AA', located at the centers of two conjugate hexagons in Fig. 3, one obtains the curve labeled AA'. For small k, this is seen to be in good agreement with the exact relation, $E=k^2$, but for k near the zone boundary, the error becomes quite serious. If the pair of points is chosen less favorably, namely, as BB' or CC', Fig. 4 shows that the results are quite meaningless.

The same wave function (7.1), substituted in the variational principle (5.10) gives the curve labeled "Variational." This is seen to be a significant improvement over the best curve obtained by Slater's method. Furthermore, the arbitrariness which, in Slater's approach, is connected with the choice of boundary points is here avoided. It should be remarked, however, that for the same trial function the application of the variational principle which involves the evaluation of the surface integrals in (5.10) is more laborious than Slater's method. In the latter the surface integrals are effectively replaced by the sum of the integrands at the usually small number of chosen boundary points (see Sec. 6).

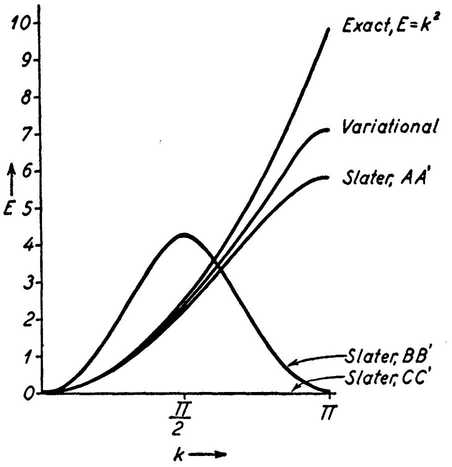

FIG. 4. The variational and Slater's method compared for the case of an "empty" lattice.

CONCLUSION

We have attempted, in this paper, to survey the possibilities offered by the variational method for the solution of the Schrödinger equation in periodic lattices. It is hoped that with the aid of this method, which has been so useful in many other fields of wave mechanics, more accurate calculations of the band structures of solids will become possible.

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