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Electronic Energy Bands in Metals

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A method is presented for calculating the energy levels of a crystal. The method is based on finding a variational principle for the energy levels in terms of the Wannier functions instead of the usual Bloch wave functions. The variational principle does not give the energy $E(\mathbf{k})$ directly, but if $E(\mathbf{k})$ for a particular band is expanded in a Fourier series in $\mathbf{k}$, then the variational principle gives the Fourier coefficients of $E(\mathbf{k})$ in this expansion. The maxima and minima properties of the variational principle are investigated. The variational principle is properly modified for application to valence bands. The types of trial functions that will arise is discussed, and the method is applied to a one-dimensional crystal. Our results are compared with the results of the method of orthogonal plane waves for the same problem.

I. INTRODUCTION

The most direct method available for the calculation of the energy levels of an electron moving in a periodic potential is the cellular method; that is, we solve Schrödinger's equation within one of the atomic polyhedra for that solution which satisfies the proper boundary conditions on the surface of the polyhedron. This method is difficult to apply in practice because of the awkward shape of the surfaces of the atomic polyhedra. Slater[1] has given an approximate way of satisfying these boundary conditions, and several metals have been treated in this way.

The idea behind our approach is to find a variational principle for the energy levels of a crystal which involves only the Wannier functions instead of the usual Bloch wave functions. The hope is that such a variational principle will avoid the difficulties of having to fit the boundary conditions on the surface of the atomic polyhedra, and at the same time, the integrals arising will extend over a few cells of the crystal rather than over the entire crystal.

In the following paragraphs, such a variational principle is presented. The variational principle does not give the energy directly, but if $E(\mathbf{k})$ for a particular band is expanded in a Fourier series in $\mathbf{k}$, then our variational principle allows us to calculate the Fourier coefficients of $E(\mathbf{k})$ in this expansion.

We have applied the method to a one-dimensional crystal chosen to resemble lithium, and we have compared our results with those obtained by the method of orthogonal plane waves[2,3] when applied to the same problem.

II. THE WANNIER FUNCTION AND ITS PROPERTIES

Since we are interested in obtaining a variational principle for the energy levels of a crystal in terms of the Wannier functions, our immediate problem is to find a set of equations for the energy levels of the crystal which involve just the Wannier function; that is, the usual wave function does not occur.

For the sake of simplicity, we shall prove all our results for the one-dimensional crystal. For the most part, our results can easily be transferred to the three-dimensional crystal.

Before proceeding further, we would like to give here the definition and some of the properties of the Wannier function.

Let us consider a one-dimensional crystal whose atoms are separated by the distance a and are located at the points $x_n = na$. Let $V(x)$ be the periodic potential due to the atoms, and let $\psi_k(x)$ be the eigenfunctions of an electron moving in this potential and having the energy levels $E(k)$. Then

$$\mathcal{H}\psi_k(x) = E(k)\psi_k(x), \tag{2.1}$$

$\mathcal{H}$ being the Hamiltonian for an electron moving in a periodic potential $V(x)$.

The energy levels of the electron will occur in bands, and to each band we associate a set of Wannier functions according to the definition,

$$U_n(x) = N^{-\frac{1}{2}}\sum_k e^{-ikx_n}\psi_k(x). \tag{2.2}$$

N is the total number of atoms in the crystal and the sum over k is only over those values of k which corresponds to the particular band we are considering. For the lowest band k would go from $-\pi/a$ to $+\pi/a$.

The Wannier functions defined by (2.2) can be obtained from each other by a simple displacement,

$$U_n(x) = U_0(x - x_n), \tag{2.3}$$

and they form an orthonormal set,

$$\int dx U_0(x-x_m)U_0(x-x_n) = \delta_{nm}. \tag{2.4}$$

The Wannier function of a free particle can be easily calculated. Here $\psi_k = \exp(ikx)/L^{\frac{1}{2}}$, where $L = Na$ is the length of the crystal. Equation (2.2) gives

$$U_0 = \frac{1}{\sqrt{a}}\frac{\sin(\pi x/a)}{\pi x/a} \tag{2.5}$$

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

[2] C. Herring, Phys. Rev. 57, 1169 (1940); C. Herring and A. G. Hill, Phys. Rev. 58, 132 (1940).

[3] R. Parmenter, Phys. Rev. 86, 552 (1952).

as the Wannier function of the lowest band of a free particle.

The type of asymptotic behavior indicated by (2.5) is characteristic of the Wannier function. As x becomes large, it oscillates while its amplitude decreases like $1/x$.

It should be noted that (2.2) may be turned around and solved for $\psi_k(x)$ in terms of $U_0(x-x_n)$,

$$\psi_k(x)=N^{-\frac{1}{2}}\sum_n e^{ikx_n}U_0(x-x_n). \tag{2.6}$$

This expression may be interpreted in the following way. If we consider $\psi_k(x)$ within a single band, then within that band we can represent $\psi_k(x)$ by a Fourier series in k. Equation (2.6) is just this Fourier series for $\psi_k(x)$ and the Wannier functions $U_0(x-x_n)$ are the Fourier coefficients of the series.

Having defined the Wannier function $U_0(x)$, we may ask now for the differential equation that it must obey. This equation can be obtained from Schrödinger's equation (2.1). We substitute for $\psi_k(x)$ using Eq. (2.6) and then sum over k, which varies over a band.

We get

$$\mathcal{H}U=\sum_n \epsilon_{-n}U(x-x_n). \tag{2.7}$$

Here ϵ_n is the Fourier coefficient in the Fourier series of $E(k)$:

$$E(k)=\sum_n \epsilon_n e^{ikx_n}, \tag{2.8}$$

and

$$\epsilon_n=N^{-1}\sum_k e^{-ikx_n}E(k). \tag{2.9}$$

We have dropped the subscript zero on $U(x)$.

The variational principle we will soon derive will not give $E(k)$ directly but will be an expression for these Fourier coefficients ϵ_n. We would like to point out that ϵ_n can be expressed simply in terms of the Wannier functions,

$$\epsilon_n=\int dxU^*(x+x_n)\mathcal{H}U(x). \tag{2.10}$$

This is obtained by multiplying both sides of (2.7) by $U(x+x_n)$ and using the orthogonality property of $U(x+x_m)$.

We would like now to re-express our problem of finding the energy levels of the crystal just in terms of the Wannier functions alone, that is, to eliminate the wave function $\psi_k(x)$ entirely.

It is clear, however, that Eq. (2.7) cannot be regarded as an equivalent equation to the Schrödinger equation (2.1) for determining the energy levels of the crystal. Equation (2.7) contains a great number of unknown constants, the ϵ_n, and they cannot all be determined by a single equation.

The extra conditions on $U(x)$, which are not contained in Eq. (2.7) and which we must add so that the ϵ_n shall be completely determined, are the orthogonality conditions $\int dxU_n^*U_m=\delta_{nm}$.

A set of equations which involve only the Wannier functions and which are equivalent to the Schrödinger equation for determining the energy levels of the crystal are the following:

$$\mathcal{H}U=\sum_n \epsilon_n D^nU, \tag{2.11a}$$

$$\int dxU^*U=1, \tag{2.11b}$$

and

$$\int dxU^*D^nU=0, \quad n=\pm 1, \pm 2\cdots. \tag{2.11c}$$

Here D is the displacement operator, $D^{\pm n}f(x)=f(x\pm na)$, and has been introduced to make clear that there is but one function, $U(x)$, involved in the set of Eqs. (2.11).

In order to see that the ϵ_n are now determined, we can imagine the following procedure in solving the above equations. We can regard Eq. (2.11a) as an eigenvalue equation for ϵ_0 in which $\epsilon_{\pm 1}, \epsilon_{\pm 2}, \cdots, \epsilon_{\pm n}\cdots$ occur as parameters. Then we can solve (2.11a) to find $\epsilon_0=\epsilon_0(\epsilon_{\pm 1}, \epsilon_{\pm 2}, \cdots, \epsilon_{\pm n}, \cdots)$, and $U=U(x;\ \epsilon_{\pm 1}, \epsilon_{\pm 2}, \cdots)$. And we can take $U(x;\ \epsilon_{\pm 1}, \epsilon_{\pm 2}, \cdots)$ and put it into $\int dxU^*D^nU=0$ and thus get a set of equations for $\epsilon_{\pm 1}, \epsilon_{\pm 2}, \cdots$.

III. THE VARIATIONAL PRINCIPLE

We will now find a variational principle for the Wannier function $U(x)$ which will yield the Eqs. (2.11).

Consider the integral

$$I_0=\int dxU^*\mathcal{H}U, \tag{3.1}$$

where the function U is restricted by the conditions

$$\int dxU^*U=1 \tag{3.2a}$$

and

$$\int dxU^*D^nU=0. \tag{3.2b}$$

We will prove that the requirement that I_0 be an extremum will yield the Eqs. (2.11), that I_0 takes on a minimum value, and that this minimum value is ϵ_0. In other words, the above equations will give a variational principle for ϵ_0.

First let us prove the extremum property of I_0. Introduce the Lagrangian multipliers λ_n, $n=0, \pm 1\cdots$ for the restrictions (3.2) and compute δI_0. We get

$$\int dx\{\delta U^*(\mathcal{H}U-\sum_n \lambda_n D^nU) + ((\mathcal{H}U)^*-\sum_n \lambda_n D^{-n})\delta U\}=0, \tag{3.3}$$

so that we have

$$\mathcal{H}U=\sum_n \lambda_n D^nU, \tag{3.4}$$

which is the desired equation for U. It is clear that the Lagrangian multipliers λ_n are just the Fourier coefficient ϵ_n in the Fourier expansion of $E(k)$. Also the extremum value of I_0 is obtained when U is the Wannier function satisfying (3.4), and thus the extremum value of I_0 is ϵ_0, according to Eq. (2.10).

In the same way we can form the integrals

$$I_n=\int dxU^*\mathcal{H}D^{-n}U, \tag{3.5}$$

and with the same side conditions on U given by (3.2), these integrals have extremums when U is the Wannier function satisfying Eqs. (2.11) and the extremum value of I_n is ϵ_n.

We have therefore obtained a variational principle for the Fourier coefficients, ϵ_n, of the energy $E(k)$. We have not so far demonstrated whether the I_n have minima or not. We will do this in the next section.

It might be noted here that our variational principle seems clumsy because of the many conditions (3.2) which must be satisfied by the trial function. Actually, it is only necessary to satisfy these conditions for the first few values of n, $n=0,\ 1,\ 2\cdots$. For higher values of n, the conditions will be automatically fulfilled because the overlap between $U(x)$ and $U(x-x_n)$ will get smaller as x_n get larger.

IV. THE MINIMA PROPERTIES OF I_n

We wish to establish now the minima properties of I_n.

First let us treat I_0. To show that I_0 has a minimum, it is only necessary to show that I_0 has a lower bound; that is, that is always larger than some definite quantity when the trial function U obeys the proper restrictions.

Consider the integral

$$I=\int dx\psi^*\mathcal{H}\psi, \tag{4.1}$$

where ψ must satisfy

$$\int dx\psi^*\psi=1. \tag{4.2}$$

By the usual Rayleigh-Ritz principle, I has a minimum value and this minimum value is simply the lowest level $E(0)$ of the Hamiltonian $\mathcal{H}$.

Now consider the integral I_0. It is similar to the integral I, except that the class of functions which may be used in computing I_0 is more restrictive. We have the added restrictions $\int dxU^*D^nU=0$. Since $I\geq E(0)$, then $I_0\geq E(0)$ also. Thus, I_0 has a minimum value, and this minimum value is larger than $E(0)$; that is, we have not only shown that ϵ_0 is the minimum value of I_0 but also that $\epsilon_0\geq E(0)$.

We have shown that ϵ_0 is the minimum value of I_0, if U obeys the restrictions (3.2), but this is not true of $I_{\pm1}$, $I_{\pm2}\cdots I_{\pm n}\cdots$. These last integrals have neither minimum nor maximum. (See Appendix I, for proof.)

However, we can establish the following integrals which do not have minima:

$$I_0+\tfrac{1}{2}(I_1+I_{-1})\geq\epsilon_0+\tfrac{1}{2}(\epsilon_1+\epsilon_{-1}), \tag{4.3}$$

$$\begin{aligned}I_0+\tfrac{2}{3}(I_1+I_{-1})&+\tfrac{1}{3}(I_2+I_{-2})\\ &\geq\epsilon_0+\tfrac{1}{2}(\epsilon_1+\epsilon_{-1})+\tfrac{1}{3}(\epsilon_2+\epsilon_{-2}),\end{aligned} \tag{4.4}$$

and quite generally,

$$\begin{aligned}I_0+\frac{m-1}{m}(I_1+I_{-1})&+\frac{m-2}{m}(I_2+I_{-2})\cdots+\frac{1}{m}(I_m+I_{-m})\\ &\geq\epsilon_0+\frac{m-1}{m}(\epsilon_1+\epsilon_{-1})\cdots+\frac{1}{m}(\epsilon_m+\epsilon_{-m}).\end{aligned} \tag{4.5}$$

We shall prove (4.3) and the rest follow in the same way. We have only to prove that $I_0+\frac{1}{2}(I_1+I_{-1})$ have a lower bound. Now $I=\int dx\psi^*\mathcal{H}\psi$, where $\int dx\psi^*\psi=1$ does have a lower bound; in fact, $\int dx\psi^*\mathcal{H}\psi\geq E(0)$.

Therefore, let

$$\psi=(1/\sqrt{2})(1+D)U, \tag{4.6}$$

where U obeys at least the first two of the conditions (3.2). Then, we get for I,

$$\begin{aligned}I&=\int dxU^*[1+\tfrac{1}{2}(D^1+D^{-1})]U\\ &=I_0+\tfrac{1}{2}(I_1+I_{-1}).\end{aligned} \tag{4.7}$$

Thus, $I_0+\frac{1}{2}(I_1+I_{-1})\geq E(0)$, and it has a lower bound and also a minimum value, which must be $\epsilon_0+\frac{1}{2}(\epsilon_1+\epsilon_{-1})$.

V. THE VARIATIONAL PRINCIPLE FOR THE VALENCE BANDS

The variational principle that we have derived will give the energy levels of the lowest band. However, in practice, we are interested in finding the valence bands.

For example, suppose we wish to find the energy levels of the second band which lies above the first or lowest band. What restrictions must be put on the trial function $U(x)$ so that I_0 as calculated by Eq. (3.1) will converge to the ϵ_0 of the second band and not to the ϵ_0 of the first band?

We might guess that the trial function $U(x)$ should be orthogonal to the Wannier function $U^{(1)}(x)$ of the lowest band; that is, we should require that

$$\int dxU^*U^{(1)}=0. \tag{5.1}$$

This turns out not to be sufficient. What is required is that U should be orthogonal to *all* the Wannier functions of the lowest band, that is,

$$\int dxU^*D^nU^{(1)}=0. \tag{5.2}$$

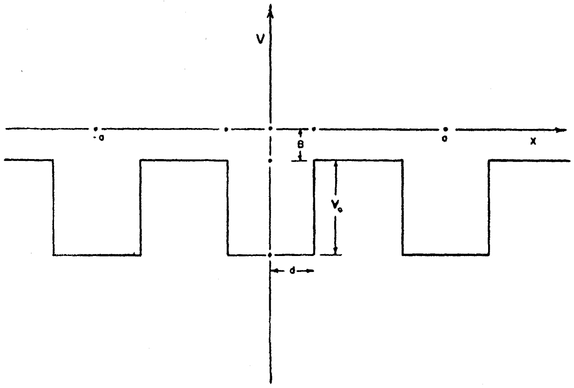

FIG. 1. The shape of the potential assumed for our one-dimensional calculation.

This result is suggested by the following. Let us expand U in the wave functions $\psi_k(x)$ of our Hamiltonian $\mathcal{H}$,

$$U=\sum_k a_k\psi_k(x). \tag{5.3}$$

Then

$$I_0=\sum_k |a_k|^2E(k). \tag{5.4}$$

If we wish (5.4) to yield the ϵ_0 of the second band, Eq. (5.4) suggests that we require $a_k=0$ for all values of k which lie in the first band; that is, $U(x)$ should be orthogonal to all the wave functions of the first band. This actually is the case and is proved in Appendix I.

Now the requirement that $a_k=0$ in the first band is equivalent to Eq. (5.2), because, as

$$U^{(1)}=\frac{1}{\sqrt{N}}\sum_{k\text{ in first band}}\psi_k(x), \tag{5.5}$$

then Eq. (5.2) gives

$$\frac{1}{\sqrt{N}}\sum_{k\text{ in first band}}a_ke^{ikx_n}=0. \tag{5.6}$$

Equation (5.6) says that the Fourier coefficients of the function a_k, where k is restricted to the lowest band, are all zero. Thus, it follows that $a_k\equiv 0$ for k is the lowest band.

VI. ON THE CHOICE OF TRIAL FUNCTIONS

Having the variational principle, we are now faced by two problems. How good is the variational principle, and what sort of functions shall we use as true functions?

Such questions cannot be answered very well without considerable calculation for the case of an actual metal. Nevertheless, we thought it might be worth while to apply our variational principle to a one-dimensional crystal which was so chosen as to resemble the metal lithium. We believe that this simple calculation will tell us how the calculation will proceed for an actual metal.

We chose our crystal potential to be made up of square wells as shown in Fig. 1. We chose the parameters, the internuclear distance a, the potential depth V_0, and the well width d, so that the first band is very narrow. An electron whose state is in the first band is essentially bound to the atom with an "orbit radius" of about d.

The ratio $a/2d$, which is the ratio of the internuclear distance to the radius of the inner a lowest band was taken fairly large; we let $a/2d=3$, 4, 5, 7, and 10. The corresponding ratio for lithium is about 15. We will see that the larger this ratio is, the better will be the trial function we will use.

Now our trial function must be orthogonal to the Wannier functions of the lowest band, as we are trying to locate the second band. Thus, if we denote by $\varphi(x)$ the Wannier function of the lowest band, we will write our trial function as

$$U(x)=u(x)-\sum_n c_n\varphi(x-x_n); \tag{6.1}$$

and we will chose c_n so as to make $U(x)$ orthogonal to $\varphi(x-x_n)$, as is required by (5.2).

Since the lowest band is very narrow, the Wannier function $\varphi(x)$ of this band is given to a good approximation by just the atomic wave function, that is, by just the bound state wave function for a well of depth V_0 and width d. (See Appendix II for discussion of this point.) Further, we also assume that the functions overlap very little and are mutually orthogonal. Thus, the coefficients c_n in (6.1) are given by

$$c_n=\int dx\varphi^*(x-x_n)u(x). \tag{6.2}$$

The only quantity as yet undetermined in our trial function (6.1) is the function $u(x)$. Now as we are finding the energy levels of a valence band, we expect the wave function of the particle to be fairly close to the free-particle wave function. Thus, we expect that $u(x)$ should resemble the free-particle Wannier function given by (2.5), that is,

$$u(x)\simeq\frac{1}{\sqrt{a}}\frac{\sin(\pi x/a)}{\pi x/a}. \tag{6.3}$$

Now, we will construct the simplest possible trial function out of (6.1), (6.2), and (6.3) by considering the case where the ratio of the interatomic distance to the radius of the inner orbit of the electrons is large. For our problem this ratio is $a/2d$. For actual metals this ratio is quite large.

From (6.2) and (6.3) one can see that the coefficient c_n decrease as n increases. In fact, as we can expect $\varphi(x)$ to have the general form $\varphi(x)\simeq\exp(-x^2/d^2)$, the c_n will decrease very fast. We will suppose that our ratio $a/2d$ is large enough so that c_1 and c_{-1} are already quite small and just the c_0 term in (6.1) is sufficient. Our trial function is then

$$U(x)=u(x)-c_0\varphi(x). \tag{6.4}$$

Now in our choice of $u(x)$, we must keep in mind that the trial function must satisfy the conditions (3.2), $\int dxU^*D^nU=0$. We see that if we choose $u(x)$ as given by the free-particle Wannier function, then (6.4) will automatically satisfy the conditions (3.2), in the sense that c_1, c_2, $\cdots$ are considered small. For since $\int dxu^*D^nu=0$, then

$$\int dxU^*DU=-(c_0{}^*c_1+c_0c_{-1}{}^*), \tag{6.5a}$$

and

$$\int dxU^*D^nU=-(c_0{}^*c_n+c_0c_{-n}{}^*), \tag{6.5b}$$

and the right band sides of (6.5) are nearly zero.

Thus, the trial function used in our calculation is

$$U=A\left\{\frac{1}{\sqrt{a}}\frac{\sin(\pi x/a)}{\pi x/a}-c_0\varphi(x)\right\}, \tag{6.6a}$$

where A is the normalization constant,

$$A=1/(1-c_0{}^2). \tag{6.6b}$$

There are no parameters left in (6.6) to vary. We will simply use (6.6) to calculate ϵ_n, the Fourier coefficients of the energy, according to $\epsilon_n\simeq\int dxU^*\mathcal{H}D^{-n}U$; and having ϵ_n, we can find the energy

$$E(k)=\textstyle\sum_n \epsilon_n \exp(ikx_n).$$

There are some properties of ϵ_n and $E(k)$ we can foresee immediately. We will write

$$\epsilon_n=\bar{\epsilon}_n+\Delta\epsilon_n, \tag{6.7}$$

where the $\bar{\epsilon}_n$ are the Fourier coefficients of a free particle, that is,

$$\hbar^2k^2/2m=\textstyle\sum_n \bar{\epsilon}_ne^{ikx_n}. \tag{6.8}$$

Then the $\bar{\epsilon}_n$ are given by

$$\bar{\epsilon}_0=(\hbar^2/2ma^2)\cdot(\pi^2/3), \tag{6.9a}$$

and

$$\bar{\epsilon}_n=\bar{\epsilon}_0((-1)^n/n^2)\cdot(3/\pi^2), \tag{6.9b}$$

for the lowest band.

Now the ϵ_n do not decrease very fast, since $\bar{\epsilon}_n$ goes like $1/n^2$; but it seems very likely that the $\Delta\epsilon_n$ do decrease very fast, and our calculation seems to verify this behavior. In fact, according to our trial function (6.6), as $a/2d$ gets larger, $c_0\rightarrow 0$ and U approaches the free Wannier function, and $\Delta\epsilon_n\rightarrow 0$.

We have supposed that our $a/2d$ is large enough so that only $\Delta\epsilon_0$ and $\Delta\epsilon_1$ are significantly different from zero. We believe this to be consistent with the approximations already made relative to $c_1, c_2\cdots c_n\cdots$.

Thus, $E(k)$ is given by

$$E(k)=(\hbar^2k^2/2m)+\Delta\epsilon_0+2\Delta\epsilon_1\cos ka. \tag{6.10}$$

Note that ϵ_1 and ϵ_{-1} are real and equal in our problem.

The position of the lowest level of the band is

$$E(0)=\Delta\epsilon_0+2\Delta\epsilon_1, \tag{6.11}$$

and the width of the band is

$$\Delta E=(\hbar^2\pi^2/2ma^2)-4\Delta\epsilon_1. \tag{6.12}$$

Using our trial function (6.6), $\Delta\epsilon_0$ and $\Delta\epsilon_1$ are found to be

$$\Delta\epsilon_0=(A^2-1)\bar{\epsilon}_0+A^2[V_{\text{Av}}-c_0{}^2E_b], \tag{6.13a}$$

and

$$\Delta\epsilon_1=(A^2-1)\bar{\epsilon}_1. \tag{6.13b}$$

Here E_b is the energy of the narrow inner band, and we have dropped terms which seemed of the same order as c_1. V_{Av} is the average value of V over a cell.

VII. COMPARISON WITH THE METHOD OF ORTHOGONAL PLANE WAVES

In the above we have presented what seems to be a suitable, yet simple, trial function for the valence band. We though it would perhaps be worthwhile to compare our results with those of some other method. We chose to compare our results with those of the method of orthogonal plane waves, because this method seems capable of some accuracy and because with our choice of trial function there is a close connection between the two methods. (See Appendix III.)

In the method of orthogonal plane waves,[4] the wave function $\psi_k(x)$ is expanded in a set of plane waves made orthogonal to wave functions of the inner bands.

For our problem, let the orthogonal plane wave ϑ_k be defined by

$$\vartheta_k(x)=e^{ikx}/L^{\frac{1}{2}}-c_k\phi_k(x), \tag{7.1a}$$

where

$$\phi_k=N^{-\frac{1}{2}}\textstyle\sum_n e^{ikx_n}\varphi(x-x_n), \tag{7.1b}$$

and

$$c_k=\frac{1}{a^{\frac{1}{2}}}\int dx\varphi^*(x)e^{ikx}. \tag{7.1c}$$

Then our trial function is

$$\psi_k=\textstyle\sum_n A_n\vartheta_{k+k_n}(x), \tag{7.2}$$

where $k_n=2\pi n/a$.

For purposes of comparison with our method, we took just one term in (7.2), since with one term the amount of labor involved in both methods will be about the same.

Thus, the orthogonal plane wave trial function was taken as

$$\psi_k=A\{e^{ikx}/L^{\frac{1}{2}}-c_k\phi_k\}, \tag{7.3}$$

where

$$A^2=1/(1-c_k{}^2).$$

With this trial function, $E(k)$ is given by

$$E(k)=\frac{1}{1-c_k{}^2}\left\{\frac{\hbar^2k^2}{2m}+V_{\text{Av}}-c_k{}^2E_b\right\}. \tag{7.4}$$

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[4] See references 2 and 3 for the details of this method.

TABLE I. A comparison of the results obtained for the valence band of a one-dimensional crystal. $E(0)$ is the lowest level of the band, and ΔE is the width of the band. Units of energy are $\hbar^2/2md^2$.

$a/2d$		Exact	Our method	OPW method
3	$E(0)$	1.00	1.06	1.24
	ΔE	0.40	0.39	0.031
4	$E(0)$	1.00	1.08	1.15
	ΔE	0.20	0.198	0.087
5	$E(0)$	1.00	1.003	1.10
	ΔE	0.12	0.12	0.049
7	$E(0)$	1.00	1.05	1.07
	ΔE	0.06	0.06	0.04
10	$E(0)$	1.00	1.04	1.04
	ΔE	0.03	0.03	0.02

VIII. THE CALCULATION AND RESULTS

For the actual calculation we chose $V_0=(\pi/2)^2\hbar^2/2md^2$, and we rather arbitrarily put $B=1\cdot\hbar^2/2md^2$. The narrow lowest band was located at $E_b=-1.59\hbar^2/2md^2$.

The atomic wave function $\varphi(x)$ associated with the lowest band was approximated by a Gaussian,

$$\varphi(x)=(2\alpha/\pi)^{\frac14}\exp(-\alpha x^2), \tag{8.1}$$

and α was chosen by minimizing the energy of a particle in a square well of depth V_0 and width d. We found $\alpha=0.510/d^2$.

The results of the calculation are given in Table I. The lowest level $E(0)$ and the width ΔE of the valence band were calculated exactly, by our method and by the method of orthogonal plane waves. The calculation was repeated for different values of $a/2d$ ($a/2d=3$, 4, 5, 7, and 10).

When $a/2d$ gets very large, our results and those of the method of orthogonal plane waves approach the correct results. However, as $a/2d$ gets smaller, it would seem that our method gives considerably better results.

The calculation was done rather roughly; the last decimal place given is somewhat uncertain. However, the accuracy is sufficient for the main purpose of this one-dimensional problem, *viz.*, to gain some understanding as to how the method is applied and what sort of trial functions should be chosen. It shows that one can expect to attain accuracy without too much labor in the three-dimensional problem, and it indicates some superiority over the method of orthogonal plane waves.

We are planning to apply our method to the calculation of the energy levels of lithium.

We would like to thank Professor Charles Mullin, Professor Eugene Guth, and Mr. Thomas Wainwright for their help and for their discussion of the problem.

APPENDIX I. THE MINIMAL PROPERTIES OF U

We will present here a different proof that I_0 has a minimum, because this proof can be easily extended to the valence or higher bands.

We wish to show that the Wannier function of the lowest band,

$$U(x)=N^{-\frac12}\textstyle\sum_k \psi_k(x), \tag{I.1}$$

is the function that minimizes the integral

$$I_0=\int dxU^*\mathcal{H}U,$$

subject to the restrictions

$$\int dxU^*U=1 \tag{I.2a}$$

and

$$\int dxU^*D^nU=0,\quad n=\pm1,\ \pm2\cdots. \tag{I.2b}$$

If we expand U in $\psi_k(x)$, $U=\sum_k a_k\psi_k(x)$, then

$$I_0=\textstyle\sum_k |a_k|^2E(k), \tag{I.3}$$

and $\sum_k |a_k|^2=1$. It is clear that to get the lowest possible value of I_0, we should make the a_k for high k equal zero. We are restricted in this by the conditions $\int dxU^*D^nU=0$. Since there are N such conditions to fulfill, N of the a_k must be different from zero. As we wish the lowest value of a_k, we will make the a_k of the N states of the lowest band different from zero, and all the other a_k equal to zero.

Condition (I.2b) now says

$$\sum_{k\text{ in lowest band}} |a_k|^2e^{ikx_n}=0,\quad n\neq0. \tag{I.4}$$

This means that $|a_k|^2$ is a constant independent of k, for k is the lowest band, since all its Fourier coefficients except the first are zero. Therefore, $|a_k|^2=1/N$, in the first band, will minimize I_0, and the minimum value of I_0 is

$$\epsilon_0=\frac{1}{\sqrt{N}}\sum_{k\text{ in lowest band}} E(k). \tag{I.5}$$

It is clear that the Wannier function (I.1) will make I_0 give this minimum value.

The above proof can be easily adapted to show that to make I_0 converge to the ϵ_0 of the second band the necessary restriction is $a_k=0$ in the first band.

To show that I_n, $n\neq0$, has no maximum nor minimum, we simply calculate I_n using as trial functions the Wannier functions of a free particle, particularly those of the higher bands. The I_n so calculated can be made as large as we please, both positively and negatively.

APPENDIX II. THE WANNIER FUNCTION OF A NARROW BAND

In Sec. VI we said that for the narrow inner bands, the Wannier function is the isolated atomic wave function $\varphi(x)$. This is a little surprising, as $\varphi(x)$ does not have the correct oscillating asymptotic behavior for a Wannier function.

A more accurate expression for the Wannier function of a narrow band is the following:

$$U=\varphi(x) \quad \text{in the first cell,} \tag{II.1a}$$

$$U=0 \ \varphi(x-x_n) \quad \text{in the } n\text{th cell.} \tag{II.1b}$$

To obtain (II.1), let us solve for the $\psi_k(x)$ of the narrow band by the cellular method. Within the first cell of the crystal, we will find $\psi_k(x)=\varphi(x)$, independent of k, because it is a narrow band. Also $\varphi(x)$ will be very nearly the isolated atomic wave function. In any other cell we can obtain $\psi_k(x)$ from its value in the first cell. Thus, in the nth cell, $\psi_k(x)=\exp(ikx)\varphi(x-x_n)$.

Now since $\psi_k(x)$, in this approximation, is given by

$$\psi_k(x)=\varphi(x) \quad \text{in the first cell,} \tag{II.2a}$$

$$\psi_k(x)=e^{ikx_n}\varphi(x-x_n) \quad \text{in the } n\text{th cell,} \tag{II.2b}$$

we can now use the definition of the Wannier function to find and obtain Eqs. (II.1).

APPENDIX III. CONNECTION WITH THE ORTHOGONAL PLANE WAVE METHOD

There is a close connection between our method and the orthogonal plane wave method. To make this connection clearer, let us take the trial function used in the OPW (orthogonal plane waves) method, and let us compute from it the Wannier function which corresponds to it and compare this result with our Wannier function.

According to (7.1), the trial function is

$$\vartheta_k=A_k(e^{ikx}/L^{\frac{1}{2}}-c_k\phi_k), \tag{III.1}$$

where $A_k=(1-c_k^2)^{-1}$.

The Wannier function which corresponds to this trial function is obtained by

$$U=N^{-\frac{1}{2}}\textstyle\sum_k \vartheta_k(x). \tag{III.2}$$

The sum over k cannot be easily done. However, there is one limit where it can be done, and this is when $a/2d\rightarrow\infty$, when the ratio of the interatomic distance to the radius of the inner orbit becomes very large. In this limit c_k becomes very small, and we will put $A_k^2=1$ independent of k. Substituting into (III.1) the proper expressions for c_k and for ϕ_k according to (7.1), and doing the sum over k in (III.2), we get

$$U=\frac{1}{a^{\frac{1}{2}}}\frac{\sin(\pi x/a)}{\pi x/a}-\sum_n c_n\varphi(x-x_n). \tag{III.3}$$

Since, when $a/2d$ is very large, only the c_0 term is significant, we see that in this limit both methods correspond to the same trial function and should lead to the same results. This is borne out by our calculation.

Of course, that the two methods become the same for very large $a/2d$ is only true for our particular choice of trial function.