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Electronic Energy Bands in Crystals*

THOMAS WAINWRIGHT AND GEORGE PARZEN
University of Notre Dame, Notre Dame, Indiana

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In a previous paper, a variational principle was derived for the energy levels of a crystal. The variational principle was stated in terms of the Wannier functions of the crystal instead of the more usual Bloch waves. In this paper, the variational principle has been applied to two problems, to the one-dimensional cosine potential, and to the energy levels of the valence band of lithium. The method of forming the trial function is discussed. It was found more convenient to use the Wannier function in momentum space rather than in configuration space. In the lithium case, our results are compared with those obtained by the Wigner-Seitz spherical approximation.

I. INTRODUCTION

In a previous paper[1] we have derived a variational principle for the energy levels of a crystal. The characteristic feature of this variational principle was that it was expressed in terms of the Wannier functions of the crystal instead of the more usual Bloch wave functions.[2] In this paper we will apply the variational principle to two problems. We shall treat the problem of an electron moving in a one-dimensional cosine potential. This problem has been treated in some detail by Slater,[3] and it is a problem for which the Wannier function has been explicitly calculated. We shall also calculate the energy levels of the valence band of lithium. This problem was chosen with the idea of testing the possible advantages of our method over other available methods. For this purpose, the choice of lithium has turned out to be not too fortunate. The reason for this is that for Li the method of orthogonalized plane waves, introduced by Herring,[4] seems to give quite good results with rather few parameters and our method is about equivalent in labor and accuracy to the method of OPW (abbreviation for orthogonalized plane waves) in this case. However, Li does serve very well as an illustration of the method and as an indication of which problems may find the method advantageous. We shall also compare our results with calculations based on the Wigner-Seitz spherical approximation.[5]

We would like to restate here our variational principle in the form that we have found most useful. All the properties of a particular energy band of a crystal are contained in a single function, the Wannier function, $U(x)$, of the band. From the Wannier function, we can compute the wave functions of the band according to the formula

$$\psi_k(x)=N^{-\frac{1}{2}}\sum_n \exp(ikx_n)U(x-x_n), \tag{1.1}$$

where N is the total number of atoms in the lattice and x_n locates the atoms in the lattice. Having found $\psi_k(x)$, we can compute the energy levels $E(k)$ of the band by the equation

$$E(k)=\int dx\psi_k^*H\psi_k \bigg/ \int dx\psi_k^*\psi_k, \tag{1.2}$$

where H is the Hamiltonian of the crystal.

Thus from this point of view the entire problem is to calculate the Wannier function and we shall have all the information we require. To calculate the Wannier function we have the variational principle I, Eqs. (3.1) and (3.2). The Wannier function $U(x)$ is that function which minimizes the integral

$$I_0=\int dxU^*HU, \tag{1.3a}$$

where U is restricted by the conditions

$$\int dxU^*U=1, \tag{1.3b}$$

and

$$\int dxU^*D^nU=0, \quad n\neq 0. \tag{1.3c}$$

The operator D^n is the displacement operator, $D^nf(x)=f(x+x_n)$.

In applying this variational principle it is difficult to find trial functions which satisfy all the side conditions (1.3c); that is, that $U(x)$ shall be orthogonal to $U(x-x_n)$ for all x_n different from zero. We shall therefore choose our trial function so that $U(x)$ and $U(x-x_n)$ are orthogonal for the smaller x_n, for the x_n to the nearest and next nearest neighbors say. For the larger x_n, the overlap between $U(x)$ and $U(x-x_n)$ becomes smaller as $U(x-x_n)$ is concentrated about the point x_n.

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[1] G. Parzen, Phys. Rev. **89**, 237 (1953). This paper will be denoted by I. We shall use the same notation in the present paper. In describing general results we will use a one-dimensional notation, and we will go over to the three-dimensional notation when applying the general results to a particular problem.

[2] The same variational principle has also been derived by G. F. Koster, Phys. Rev. **89**, 67 (1953).

[3] J. C. Slater, Phys. Rev. **87**, 807 (1952).

[4] C. Herring, Phys. Rev. **57**, 1169 (1940).

[5] R. Parmenter, Phys. Rev. **86**, 552 (1952), has calculated the energy levels of Li using the method of OPW. However, as he did not use the Seitz potential and as his potential allowed him to compute only energy differences within the band, he was not able to make a complete comparison of his results with those based on the Wigner-Seitz spherical approximation.

The Wannier function $U(x)$ does not really fall off very rapidly as x becomes large. However the overlap between $U(x)$ and $U(x-x_n)$ seems to become smaller with increasing x_n more rapidly than the behavior of $U(x)$ would indicate. This is because $U(x)$ tends to have a node at the point x_n where $U(x-x_n)$ has its maximum.

Since in using the variational principle (1.3) for the Wannier function we shall not in general satisfy all the side conditions on $U(x)$, it would seem that we have thus lost one of the advantages of a variational principle, that our result for $E(k)$ will not be an upper bound for $E(k)$. This turns out not to be the case. If we take the Wannier function $U(x)$ that we calculate from the variational principle and calculate from it $\psi_k(x)$ according to Eq. (1.1), and then calculate the energy $E(k)$ according to Eq. (1.2), the $E(k)$ so calculated will still be an upper bound for the energy levels although the Wannier function we have used does not satisfy all the side conditions (1.3c).

This result may be understood as follows. Equation (1.2) is a variational principle for $E(k)$ and will give an upper bound on $E(k)$ provided $\psi_k(x)$ obeys the following two conditions. $\psi_k(x)$ must have the form of a Bloch wave, $\psi_k(x)=\exp(ikx)u(x)$, where $u(x)$ is periodic; this makes $\psi_k(x)$ orthogonal to all the other levels in the band in particular to those levels below the one being calculated. This requirement is guaranteed by the form of Eq. (1.1) without any restrictions on $U(x)$. The second condition is that $\psi_k(x)$ must be orthogonal to the wave functions of any lower band if there are any. This requirement is met if $U(x-x_n)$ is made orthogonal to the Wannier function of the lower band and the $U(x)$ we shall use shall be so constructed. Thus it is seen that it is not necessary for $U(x)$ to satisfy all the side conditions (1.3c) for Eq. (1.2) to give an upper bound for $E(k)$.

By substituting Eq. (1.1) into Eq. (1.2), we find the following variational result for $E(k)$ stated directly in terms of the Wannier function $U(x)$,

$$E(k)\leq\sum_s I_s \exp(ikx_s)/\sum_s \Delta_s \exp(ikx_s), \tag{1.4}$$

where

$$I_s=\int dxU^*HD^sU, \tag{1.5}$$

and

$$\Delta_s=\int dxU^*D^sU. \tag{1.6}$$

If our Wannier function $U(x)$ satisfied all the side conditions (1.3c), then we should have $\Delta_0=1$, $\Delta_s=0$ for $s\neq 0$. For the case of Li it turned out that enough of the side conditions were satisfied that Δ_s does have these values to the accuracy of the calculation.

We would like to remark that an important characteristic of the method is that it calculates the entire energy band and not each energy level separately. We must minimize just the one integral I_0 in contrast to, say, the method of OPW in which the energy integral must be minimized for each energy level that one desires to calculate.

II. APPLICATION TO THE COSINE POTENTIAL

In this section we will apply the variational principle to a one dimensional lattice; the atoms are located at the points $x_n=na$ and give rise to the potential

$$V(x)=V_0+2V_1\cos(k_1x), \tag{2.1}$$

where $k_1=2\pi/a$ defines the reciprocal lattice, and we make $V(0)=0$ by putting $V_1=-\frac{1}{2}V_0$.

We feel that this example may be instructive, as in choosing our trial functions we shall make certain assumptions as to the behavior of the Wannier function, which assumptions can be verified for the simple cosine potential.

We have adjusted the peak of the potential to correspond to the case which Slater[3] denotes by $s=1$. This corresponds to a weakly bound electron. For this problem we shall calculate the lowest band only and avoid the extra complications of the valence band.

In choosing our trial function, we have come to the conclusion that the Wannier function in momentum space is a considerably simpler function than the Wannier function in coordinate-space and has certain advantages which we will point out. Thus we will Fourier transform the Wannier function and introduce the function $b(k)$ defined by

$$U(x)=N^{-\frac{1}{2}}\sum_k b(k)\exp(ikx)/L^{\frac{1}{2}}, \tag{2.2}$$

where L is the length of the crystal.

In terms of $b(k)$ our side conditions (1.3b) and (1.3c) become

$$N^{-1}\sum_k |b(k)|^2\exp(ikx_s)=\delta_{s0}. \tag{2.3}$$

It is very often convenient not to have k range from $-\infty$ to $+\infty$, but to restrict k to varying over the lowest zone from $-\pi/a$ to $+\pi/a$. We can then write (2.3) as

$$N^{-1}\sum_{kn}|b(k-k_n)|^2\exp(ikx_s)=\delta_{s0}, \tag{2.4}$$

where it is understood that k ranges over the lowest zone only and we also sum over k_n, the vectors of the reciprocal lattice.

The integral we must minimize can be written in terms of $b(k)$ as

$$I_0=\frac{1}{N}\sum_{kn}\frac{\hbar^2}{2m}(k+k_n)^2|b(k+k_n)|^2$$
$$+\frac{1}{N}\sum_{knm}V_nb^*(k+k_n+k_m)b(k+k_m). \tag{2.5}$$

To evaluate $E(k)$ according to (1.2) we will need $\sum_s I_s \exp(ikx_s)$ which can be written

$$\sum_s I_s \exp(ikx_s) = \sum_n \frac{\hbar^2}{2m}(k+k_n)^2|b(k+k_n)|^2 + \sum_{nm} V_n b^*(k+k_n+k_m)b(k+k_m). \quad (2.6)$$

The Wannier function in k space for the cosine potential has been considerably discussed by Slater.[3] We would just like to repeat here a few of his results. In Fig. 1 we have plotted the Wannier function in k space for the lowest band of a weakly bound electron, $s=1$, and for a strongly bound electron, $s=100$. It will be noted that for the weakly bound case, the Wannier function is different from zero only in the first few zones of k space. It is quite flat in the first zone and drops very sharply in the next zone. On the other hand the Wannier function of a strongly bound electron drops to zero very slowly and varies slightly within a zone.

For the valence bands the above behavior is complicated by the fact that the Wannier function must be orthogonal to the Wannier functions of the lower bands, which introduces further wiggles in the Wannier function. We shall see in the case of Li how the above behavior of the Wannier functions is maintained provided we subtract out the part that makes it orthogonal to the Wannier function of the lower band. This is the same trick as is used in the method of orthogonal plane waves by Herring.[4]

In this case, as we are calculating the lowest band, it is possible for us to construct a wave function that fulfills all the side conditions (2.3). Consider $b(k)$ in the lowest zone where k ranges from $-\pi/a$ to $+\pi/a$. In this region of k space, we can expand $b(k)$ in a Fourier series and write

$$b(k) = \sum_j a_{0,j} \exp(ikx_j). \quad (2.7)$$

We can break up k space into zones obtained by translating the lowest zone by k_n, and in each of these zones[6] express $b(k)$ as a Fourier series. Thus in the k_n zone,

$$b(k-k_n) = \sum_j a_{n,j} \exp(ikx_j). \quad (2.8)$$

In (2.8), and in all such similar formulas, k varies only over the lowest zone.

In terms of the new parameters $a_{n,j}$, our side conditions (2.4) become

$$\sum_{jn} a_{n,j+s}{}^* a_{n,j} = \delta_{s0}, \quad (2.9)$$

where $a_{n,j}{}^*$ is the complex conjugate of $a_{n,j}$. It will be seen that it is possible to satisfy all the side conditions by just keeping a few of the parameters different from zero.

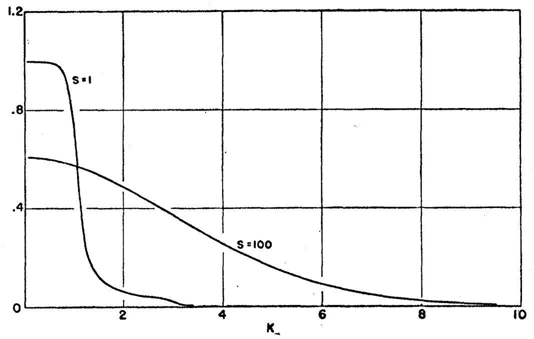

FIG. 1. The Wannier function for the lowest band of a weakly bound electron, $s=1$, and for a strongly bound electron, $s=100$, plotted in k space. k is measured in units of π/a. These curves are taken from Slater (reference 3).

We would like now to discuss a few of the simpler trial functions which arise from this Fourier series breakdown of the Wannier function in momentum space.

The simplest trial function is

$$b(k) = a_{0,0}, \quad (2.10)$$

and

$$b(k-k_n) = 0 \quad k_n \neq 0,$$

where k ranges over just the lowest zone; that is, $b(k)$ is constant in the lowest zone and zero elsewhere.

For this trial function, the side conditions (2.7) reduce to $|a_{0,0}|^2 = 1$ and the parameter is fixed. This trial function is equivalent to the OPW method using just one plane wave.

A second trial function is

$$b(k) = a_{0,0}, \quad (2.11a)$$

$$b(k-k_{\pm 1}) = a_{1,0}, \quad (2.11b)$$

and

$$b(k-k_n) = 0, \text{ all other zones.} \quad (2.11c)$$

For this trial function, the side conditions (2.9) reduce to

$$|a_{0,0}|^2 + 2|a_{1,0}|^2 = 1. \quad (2.12)$$

Thus we have two parameters and just one condition, which leaves one parameter to vary.

A third trial function is

$$b(k) = a_{0,0} + a_{0,1} \exp(ikx_1) + a_{0,-1} \exp(ikx_{-1}), \quad (2.13a)$$

$$b(k-k_1) = a_{1,0} + a_{1,1} \exp(ikx_1) + a_{1,-1} \exp(ikx_{-1}), \quad (2.13b)$$

$$b(k-k_{-1}) = a_{1,0} + a_{1,1} \exp(-ikx_1) + a_{1,-1} \exp(-ikx_{-1}), \quad (2.13c)$$

and

$$b(k-k_n) = 0 \text{ all other zones.} \quad (2.13d)$$

To make $b(k)$ real, $a_{1,-1} = a_{1,1}{}^*$ and $a_{0,0}$ and $a_{1,0}$ are real. As $b(k)$ is even in the lowest zone $a_{0,1}$ is real. This leaves us with five parameters in (2.13). For this trial

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[6] We should like to point out that these zones are not identical with the Brillouin zones.

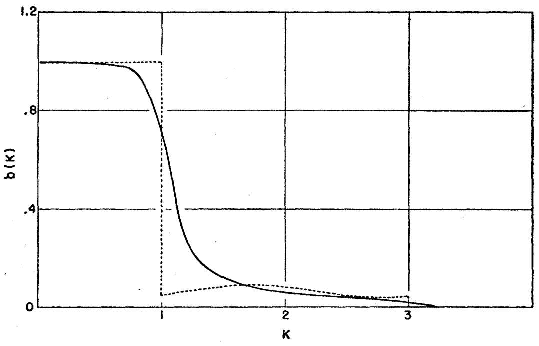

FIG. 2. Our calculated Wannier function compared with the exact Wannier function for the lowest band of cosine potential in the weakly bound $s=1$ case. The dashed curve is the calculated curve. k is measured in units of π/a.

function the side conditions become.

$$|a_{0,0}|^2+2|a_{1,0}|^2+2|a_{0,1}|^2+4|a_{1,1}|^2=1, \quad (2.14a)$$

$$a_{0,0}a_{0,1}+a_{1,0}(a_{1,1}+a_{1,-1})=0, \quad (2.14b)$$

and

$$a_{0,1}^2+a_{1,1}^2+a_{1,-1}^2=0. \quad (2.14c)$$

Thus we have five parameters and 3 conditions, leaving us two free parameters to vary.

This last trial function was used to compute the lowest band of the cosine potential for the weakly bound $s=1$ case.

In Fig. 2 we have compared the Wannier function we have calculated by minimizing I_0 using the trial function (2.13) with the exact Wannier function.[7]

In Fig. 3 we have plotted $E(k)$, which we calculated using the Wannier function found by minimizing I_0 and Eq. (1.4), and we have also plotted the exact $E(k)$. The agreement is good and our result is above the exact result as it should be. The agreement gets worse towards the top of the band, which seems to be a characteristic result of the method. This is probably due to the fact that the energy $E(k)$ near the top of the band becomes more sensitive to the behavior of $b(k)$ near the edge of the central zone.

We should remark that the method of orthogonalized plane waves using three plane waves and thus three parameters will give somewhat better results, particularly at the top of the band. This is due, in part, to the fact that in the OPW method we must minimize the energy integral for each energy level in the band we wish to find, whereas in the present method the minimizing process is carried out just once in for the entire band. Since I_0 can be shown to be the average energy level of the band, our results are probably best near the middle of the band.

We might add that for this one-dimensional problem the OPW method involves solving a third-order determinant, and minimizing the energy for each level in the band is no great hardship. Thus, for this problem, the OPW method seems the better. However in a problem where the number of parameters may become quite large, it seems to us that the present method may have considerable advantages.

III. APPLICATION TO Li

For this calculation we used the Seitz potential[8] in order to be able to compare our results with those based on the Wigner-Seitz spherical approximation.

In this case we are calculating the valence band so our Wannier function must be orthogonal to the Wannier function of the lower 1s band.[9] Let $\varphi(r)$ be the 1s atomic wave function of the Seitz potential. If the 1s band is very narrow, then the atomic wave function is very nearly the Wannier function of the 1s band. We then write our Wannier function for the valence band as

$$U(\mathbf{r})=\mathcal{V}(\mathbf{r})-\sum_j c_j\varphi(\mathbf{r}-\mathbf{r}_j), \quad (3.1)$$

where $\mathbf{r}_j$, are the vectors of the lattice and the c_j are chosen so that $U(\mathbf{r})$ and $\varphi(\mathbf{r}-\mathbf{r}_j)$ are orthogonal. Thus

$$c_j=\int d\tau\varphi(\mathbf{r}-\mathbf{r}_j)\mathcal{V}(\mathbf{r}). \quad (3.2)$$

The c_j decrease with increasing $\mathbf{r}_j$ as the overlap between $\varphi(\mathbf{r}-\mathbf{r}_j)$ and $\mathcal{V}(\mathbf{r})$ gets smaller. For the case of Li, it was only necessary to include c_0, c_1, and c_2. c_1 is defined by (3.2), where $\mathbf{r}_1$ is the vector to one of the

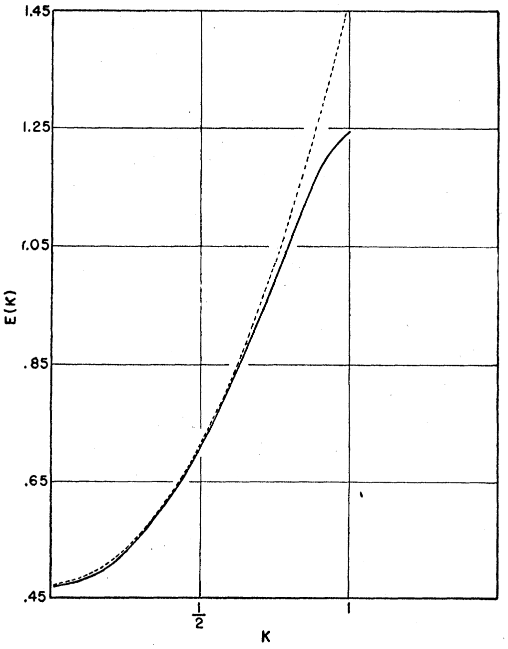

FIG. 3. The calculated $E(k)$ compared with the exact $E(K)$. The calculated curve is dashed. k is measured in units of π/a.

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[7] We would like to thank Dr. Slater for sending us a table of the exact Wannier function.

[8] F. Seitz, Phys. Rev. **47**, 400 (1935). We would like to thank Dr. C. Herring for sending us the corrected version of this potential.

[9] See reference 1.

nearest-neighbor atoms in the lattice and c_2 corresponds to a second-nearest neighbor.

We determined $\varphi(\mathbf{r})$ by numerical integration. The $1s$ level was found to have the energy[10] $E_{1s}=-5.352$ Ry.

In determining $\mathcal{V}(\mathbf{r})$, it seems more convenient to go over to momentum space as we did in the one-dimensional case. So we introduce the function $b(\mathbf{k})$ defined by

$$\mathcal{V}(\mathbf{r})=N^{-\frac{1}{2}}\sum_k b(k)\exp(i\mathbf{k}\cdot\mathbf{r})/\Omega^{\frac{1}{2}}, \tag{3.3}$$

where Ω is the volume of the crystal.

The integral we must minimize can now be written in terms of $b(\mathbf{k})$ as

$$\begin{aligned} I_0=\frac{1}{N}\sum_{\mathbf{k}n}\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{k}_n)^2|b(\mathbf{k}+\mathbf{k}_n)|^2 \\ +\frac{1}{N}\sum_{\mathbf{k}nm} V_n b^*(\mathbf{k}+\mathbf{k}_n+\mathbf{k}_m)b(\mathbf{k}+\mathbf{k}_m) \\ -E_{1s}\sum_j|c_j|^2. \end{aligned} \tag{3.4}$$

In (3.4) k ranges over the lowest zone in k-space; the sum over n or m is over $\mathbf{k}_n$ or $\mathbf{k}_m$, the vectors of the reciprocal lattice. The V_n are the Fourier coefficients of the potential,[11]

$$V(\mathbf{r})=\sum_n V_n\exp(i\mathbf{k}_n\cdot\mathbf{r}). \tag{3.5}$$

Our side conditions (1.3) now take the form

$$N^{-1}\sum_{\mathbf{k}n}|b(\mathbf{k}-\mathbf{k}_n)|^2-\sum_j|c_j|^2=1, \tag{3.6a}$$

and

$$N^{-1}\sum_{\mathbf{k}n}|b(\mathbf{k}-\mathbf{k}_n)|^2-\sum_j c_j^* c_{j+s}=0,\quad s\neq 0. \tag{3.6b}$$

We follow the same procedure as for the one-dimensional problem of breaking k space up into zones, and in each zone we expand $b(\mathbf{k})$ in a Fourier series. Thus we write in the $\mathbf{k}_n$ zone,

$$b(\mathbf{k}-\mathbf{k}_n)=\sum_j a_{n,j}\exp(i\mathbf{k}\cdot\mathbf{r}_j). \tag{3.7}$$

In terms of the new parameters $a_{n,j}$, our side conditions become

$$\sum_{jn} a_{n,j+s}^* a_{n,j}-\sum c_{j+s}c_j=\delta_{s0}. \tag{3.8}$$

It is not easy in this case to satisfy all the side conditions (3.8) so we content ourselves with satisfying them for $\mathbf{r}_s=0$, for the $\mathbf{r}_s$ to the nearest neighbors and to the second-nearest neighbors.

In the trial function we used, we assumed $b(\mathbf{k})$ was different from zero only in the central zone of $\mathbf{k}$ space and in the 12 nearest-neighbor zones; and in each of these zones we expressed $b(\mathbf{k})$ as a Fourier series according to (3.7).

Our trial function was

$$b(\mathbf{k})=a_{0,0}+a_{0,1}\sum_{j'}\exp(i\mathbf{k}\cdot\mathbf{r}_{j'}), \tag{3.9a}$$

$$b(\mathbf{k}-\mathbf{k}_{n'})=a_{1,0}+a_{1,1}\sum_{j'}\exp(i\mathbf{k}\cdot\mathbf{r}_{j'}), \tag{3.9b}$$

and $b(\mathbf{k}-\mathbf{k}_n)=0$ in all other zones.

In (3.9) the $\mathbf{r}_{j'}$ are the 8 vectors to the 8 nearest neighbors in the lattice and the $\mathbf{k}_{n'}$ are the 12 vectors to the 12 nearest neighbors in the reciprocal lattice.

With this trial function, the side conditions become

$$\begin{aligned} a_{0,0}^2+12a_{1,0}^2+8a_{0,1}^2+96a_{1,1}^2 \\ =1+c_0^2+8c_1^2+6c_2^2, \end{aligned} \tag{3.10a}$$

$$a_{0,1}a_{0,0}+12a_{1,0}a_{1,1}=c_0c_1+3c_1c_2 \tag{3.10b}$$

$$a_{0,1}^2+12a_{1,1}^2=\tfrac{1}{2}c_0c_2+c_1^2. \tag{3.10c}$$

These are just the side conditions up to the second-nearest neighbor, and we have neglected the c_j above c_2 which our results seem to justify. It is also necessary to compute c_0, c_1, and c_2 in terms of the $a_{n,j}$. This computation is done in Appendix I.

Subject to the side conditions (3.10) we must minimize the integral I_0 as given by (3.4). This integral can be written in terms of the $a_{n,j}$ as

$$\begin{aligned} I_0-E_{1s}=a_{0,0}^2(\epsilon_0-E_{1s}+V_0) \\ +a_{0,1}^2 8(\epsilon-E_{1s}+V_0) \\ +a_{1,0}^2 12(\epsilon_0-E_{1s}+\hbar^2k_1^2/2m+V) \\ +a_{1,1}^2 96(\epsilon-E_{1s}+\hbar^2k_1^2/2m+V) \\ +a_{0,0}a_{0,1}16\epsilon_1+a_{0,0}a_{1,0}24V_1 \\ +a_{1,1}a_{1,0}192\epsilon_1+a_{1,1}a_{0,1}192V_1. \end{aligned} \tag{3.11}$$

In (3.11) the ϵ_j are Fourier coefficients in the expansion for the $E(k)$ of a free particle,

$$\hbar^2k^2/2m=\sum_j\epsilon_j\exp(i\mathbf{k}\cdot\mathbf{r}_j). \tag{3.12}$$

The first five ϵ_j for a body-centered lattice are given in Appendix I. The quantity ϵ is defined as

$$\epsilon=\epsilon_0+3\epsilon_2+3\epsilon_3+\epsilon_5,$$

and

$$V=V_0+4V_1+2V_2+4V_3+V_4.$$

$\mathbf{k}_1$ is one of the vectors to a nearest neighbor in the reciprocal lattice.

For calculating $E(k)$ from (1.2) one needs $\sum_s I_s \times\exp(i\mathbf{k}\cdot\mathbf{r}_s)$, which can be written in terms of $b(k)$ as

$$\begin{aligned} \sum_s I_s\exp(i\mathbf{k}\cdot\mathbf{r}_s)=\sum_n\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{k}_n)^2|b(\mathbf{k}+\mathbf{k}_n)|^2 \\ +\sum_{nm}V^n b^*(\mathbf{k}+\mathbf{k}_n+\mathbf{k}_m)b(\mathbf{k}+\mathbf{k}_m) \\ -E_{1s}\left|\sum_s c_s\exp(i\mathbf{k}\cdot\mathbf{r}_s)\right|^2. \end{aligned} \tag{3.13}$$

IV. RESULTS OF THE Li CALCULATION

In Table I, we have tabulated $E(k)$ in three directions in K space, the 100, 101, and 111 directions.

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[10] It might be noted that the $1s$ wave function calculated here is not the true Li $1s$ wave function. It is the solution of the Seitz potential and has no direct physical significance.

[11] We found the V_n difficult to calculate for the Seitz potential, which is defined as spherically symmetric within each atomic polyhedron. This difficulty seems somewhat artificial to us, as the Seitz potential was devised with the idea of applying the Wigner-Seitz method for which it is convenient. We estimated the V_n as best as we could so that our results would be in error by at most 0.01 Rydberg.

TABLE I. The energy levels $E(k)$ for the valence band of Li as a function of k in the 100, 110, and 111 directions in k space. Atomic units are used.

100		110		111	
k	$E(k)$	k	$E(k)$	k	$E(k)$
0	−0.735	0	−0.735	0	−0.735
0.2	−0.703	0.2	−0.704	0.2	−0.704
0.4	−0.590	0.4	−0.596	0.4	−0.601
0.6	−0.371	0.6	−0.396	0.6	−0.415
0.8	−0.056	0.6816	−0.287	0.8	−0.135
0.9639	0.250			0.8348	−0.076

In Table II, we have compared several of our results with the corresponding results of previous calculations on Li. It might be noted that our result for the lowest level of the band $E(0)$ is -0.735 Ry, compared with -0.6635 Ry obtained by the Wigner-Seitz method and the value of -0.68 Ry obtained by Millman[12] using Slater's method. Since our result is obtained from a variational principle and it is the lower result, it is necessarily closer to the correct answer.

Our result for the width of the filled partition of the band is considerably larger than the Wigner-Seitz result. Soft x-ray measurements[13] indicate the width of the filled portion of the band to be 0.30 ± 0.02 Ry.

It may be noted that though our values for $E(0)$ and ΔE differ by 0.07 Ry and 0.08 Ry from the Wigner-Seitz values, the results for the cohesive energy differ by only about 0.01 Ry/atom. The differences in $E(0)$ and ΔE cancel each other in computing the cohesive energy.

In conclusion, we think that in the case of Li our method has no advantages over the method of OPW and the two methods are about equivalent. However, for those cases where the method of OPW would require a large number of parameters, we feel our method may have some advantages. There is greater freedom in choosing the trial function and the number of undetermined parameters does not rise as quickly as it does in the OPW method. Also, our method treats the entire band at once and requires only one integral to be minimized, which should reduce the labor involved.

APPENDIX I

In this appendix we will calculate the c_j as defined by (3.2). More than one approach is possible. We chose to take advantage of the fact that the Wannier function of the $1s$ band is concentrated in a relatively small region compared to the size of the crystal cell. Let a_s be the radius of the $1s$ orbit and a the linear size of the crystal cell, then we shall find an expansion for c_j in powers of $(a_s/a)^2$. For lithium, a_s/a is about one-tenth.

In formula (3.2) for c_j, since $\mathcal{V}(\mathbf{r})$ varies slowly compared to $\varphi(\mathbf{r})$, we expand $\mathcal{V}(\mathbf{r})$ in a power series about $\mathbf{r}_j$ and obtain

$$c_j=\mathcal{V}(\mathbf{r}_j)\int d\tau\varphi(\mathbf{r})+\tfrac{1}{6}\nabla^2\mathcal{V}|_{r_j}\int d\tau\mathbf{r}^2\varphi(\mathbf{r})+\cdots. \quad \text{(A.1)}$$

Now replacing $\mathcal{V}(\mathbf{r})$ by its expression in terms of $b(\mathbf{k})$ and then in terms of the $a_{n,j}$, we get the result

$$c_j=\sum\nolimits_n a_{n,j}(\alpha-k_n{}^2\beta^2)-\beta^2\sum\nolimits_{ns}a_{n,s}\epsilon_{s+j}, \quad \text{(A.2)}$$

where

$$\alpha=\Delta^{-\frac{1}{2}}\int d\tau\varphi(\mathbf{r}), \quad \text{(A.3)}$$

and

$$\beta^2=\tfrac{1}{6}\Delta^{-\frac{1}{2}}\int d\tau r^2\varphi(\mathbf{r}). \quad \text{(A.4)}$$

TABLE II. $E(0)$ is the lowest level in the band; ΔE is the width of the filled portion of the band.

	$E(0)$ Ry	ΔE Ry	Cohesive energy kcal/mol	Effective mass m/m^*
Present method	−0.735	0.339	40.2	0.788
Wigner-Seitz[a]	−0.6635	0.258	35	0.727
Parmenter[b]		0.304		0.808

[a] The Wigner-Seitz type of approximation was first used by Seitz (reference 8) and was later improved by J. Bardeen [J. Chem. Phys. **6**, 367 (1938)] and by R. A. Silverman and W. Kohn [Phys. Rev. **80**. 912 (1950)].
[b] See reference 5.

Δ is the size of the crystal cell. α and β were found by numerical integration. The ϵ_j are defined by (3.12). The first few ϵ_j for a body-centered lattice are, in units of $\hbar^2/ma^2$,

$$\epsilon_0=3\pi^2/16, \qquad \epsilon_3=1/16,$$
$$\epsilon_1=-8/3\pi^2, \qquad \epsilon_4=8/45\pi^2,$$
$$\epsilon_2=-1/\pi^2, \qquad \epsilon_5=1/3\pi^2,$$

where a is one-half the edge of the cube that defines the body-centered lattice. $a=1.7246A^0$ for Li.

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[12] J. Millman, Phys. Rev. **47**, 286 (1935).
[13] H. W. B. Skinner, Repts. Progr. Phys. **5**, 257 (1938).