PHYSICAL REVIEW VOLUME 86, NUMBER 4 MAY 15, 1952

Electronic Energy Bands in Crystals*

R. H. PARMENTER
Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received February 6, 1952)

A study is made of the feasibility of calculating valence and excited electronic energy bands in crystals by making use of one-electron Bloch wave functions. The elements of the secular determinant for this method consist of Bloch sums of overlap and energy integrals. Although often used in evaluating these sums, the approximation of tight binding, which consists of neglecting integrals between non-neighboring atoms of the crystal, is very poor for metals, semiconductors, and valence crystals. By partially expanding each Bloch wave function in a three-dimensional Fourier series, these slowly convergent sums over ordinary space can be transformed into extremely rapidly convergent sums over momentum space. It can then be shown that, to an excellent approximation, the secular determinant vanishes identically. This peculiar behavior results from the poorness of the atomic correspondence for valence electrons. By a suitable transformation, a new secular determinant can be formed which does not vanish identically and which is suitable for numerical calculations. It is found that this secular determinant is identical with that obtained in the method of orthogonalized plane waves (plane waves made orthogonal to the inner-core Bloch wave functions).

Calculations are made on the lithium crystal in order to test how rapidly the energy converges to its limiting value as the order of the secular determinant is increased. For the valence band, this convergence is rapid. The effective mass of the electron at the bottom of the valence band is found to be closer to that of the free electron than are those of previous calculations on lithium. This is probably because of the use of a crystal potential here rather than an atomic potential. The former varies less rapidly than the latter over most of the unit cell of the crystal, and thus should result in a value of effective mass more nearly free-electron-like. Unlike previous calculations on lithium, the computed value of the width of the filled portion of the valence band agrees excellently with experiment. By making use of calculated transition probabilities between the valence band and the 1*s* level, a theoretical curve is drawn of the shape of the soft x-ray *K* emission band of lithium. The comparison with the shape of the experimental curve is only fair.

I. INTRODUCTION

In this paper we will study the properties of electrons in unbounded, crystalline solids. We will assume that any given electron of the crystal can be considered to move in the electric field resulting from fixed nuclei plus the time-averaged charge distribution of all the other electrons of the crystal. It is well known that such an assumption neglects correlation and exchange between the electrons of the crystal. No attempt will be made to correct for correlation directly, but an approximate method of correcting for exchange will be included (see Appendix A).

Within the framework of the above assumption there are great difficulties involved in solving Schrödinger's equation for an electron in a crystal. A number of approximate methods have been introduced.[1] Here we will be concerned with two such methods, the method of Bloch waves[2,3] and the method of orthogonalized plane waves.[4] In connection with these two methods, it might be appropriate to indicate how the work here reported actually developed. It was originally planned to make a study of the Bloch method. As a test of the method's practicability for numerical calculation, it was planned to calculate electronic energy bands in the lithium crystal. Such a procedure was in fact carried out, but only after mathematical manipulation had been made in the Bloch method for the purposes of convenience in the numerical computations. It was later realized by the writer that the secular equation obtained from the Bloch method by means of this mathematical manipulation was identical with the secular equation which could be obtained from the orthogonalized plane wave method in a more straightforward fashion. For this reason, after having shown that the Bloch method is equivalent to the orthogonalized plane wave method, we will consider only the latter method in obtaining explicit results for the lithium crystal.

II. METHOD OF BLOCH WAVES

Let us consider an unbounded crystalline solid, which can be divided into a set of identical unit cells. We may define an enumerable, infinite set of displacement vectors, $\mathbf{r}_n$, where the nth vector is drawn from an origin of coordinates to the center of the nth unit cell. For convenience, the origin will be taken at the center of one of the unit cells. It is now possible to form an unbounded reciprocal lattice which can be divided into a set of identical unit cells. (We will pick each cell such that it is equivalent to the first Brillouin zone.) This reciprocal lattice is defined such that the quantity $\mathbf{K}_i\cdot\mathbf{r}_n/2\pi$ is some integer for all values of i and n, where the $\mathbf{K}_i$'s form an enumerable, infinite set of reciprocal vectors drawn from an origin of coordinates (centered on one of the unit cells) to the center of the ith unit cell in reciprocal space. The factor $1/2\pi$ appears since atomic units are being used; e.g., energy is expressed in units of the Rydberg energy, distance in units of the Bohr radius, etc.

---

* Part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate School of the Massachusetts Institute of Technology. This work was supported by the ONR.

[1] For a survey of such methods, see F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapter IX.

[2] F. Bloch, Z. Physik **52**, 555 (1928).

[3] Jones, Mott, and Skinner, Phys. Rev. **45**, 379 (1934).

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

It can be shown that the wave functions in a crystal must satisfy Bloch's theorem; namely, that any such wave function $\Psi(\mathbf{r})$ must be of the form[5]

$$\Psi_{\mathbf{k}}(\mathbf{r}+\mathbf{r}_n)=e^{i\mathbf{k}\cdot\mathbf{r}_n}\Psi_{\mathbf{k}}(\mathbf{r}). \tag{1}$$

Let us define

$$\mathbf{k}_i=\mathbf{k}+\mathbf{K}_i. \tag{2}$$

Then (1) can be written in the form

$$\Psi_{\mathbf{k}_i}(\mathbf{r}+\mathbf{r}_n)=e^{i\mathbf{k}\cdot\mathbf{r}_n}\Psi_{\mathbf{k}_i}(\mathbf{r}),$$

so that, as far as the translational properties of the Ψ's are concerned, all the different $\mathbf{k}_i$'s corresponding to a given $\mathbf{k}$ are equivalent, and we need consider only values of $\mathbf{k}$ lying in the first Brillouin zone. It was first pointed out by Bloch[2] that such a wave function can be formed by a spacial Bloch sum of atomic or molecular wave functions, $\psi(\mathbf{r})$,

$$\Psi_{\mathbf{k}}(\mathbf{r})=\sum\nolimits_n e^{i\mathbf{k}\cdot\mathbf{r}_n}\psi(\mathbf{r}-\mathbf{r}_n). \tag{3}$$

In the discussion to follow, it will be assumed that there is only one atom in the unit cell of the crystal. The discussion can be generalized to the case of many atoms per unit cell, however, simply by everywhere replacing the word atomic by the word molecular, the molecule in question being that formed by the atoms of the unit cell.

If the crystal potential, $\mathrm{V}(\mathbf{r})$ is essentially the same as the potential, $V(\mathbf{r})$, of the isolated atom in the vicinity of each nucleus, then $\Psi(\mathbf{r})$ will be an approximate solution for the crystal potential if $\psi(\mathbf{r})$ is a solution for the atomic potential. This approximation will be good for the ion-core electrons but poor for the valence electrons. Thus, if $u_s(\mathbf{r})$ is the set of isolated-atom wave functions for the ion-core electrons, then

$$\Phi_s(\mathbf{r})=\sum\nolimits_n e^{i\mathbf{k}\cdot\mathbf{r}_n}u_s(\mathbf{r}-\mathbf{r}_n) \tag{4}$$

is the set of ion-core Bloch wave functions for the crystal. If $v_s(\mathbf{r})$ is the set of isolated-atom valence and excited wave functions, then the two sets $u_s(\mathbf{r})$ and $v_s(\mathbf{r})$ combine to form $\psi_s(\mathbf{r})$, the complete set of solutions to the Schrödinger equation for the isolated atom potential. For reasons that will be discussed in Sec. III, it is convenient to work with valence and excited Bloch wave functions that are orthogonal to the ion-core Bloch wave functions, Φ_s. In order to obtain these, we define

$$w_s=v_s-\sum\nolimits_t \sigma_{st}u_t, \tag{5}$$

where

$$\sigma_{st}=\frac{\sum_n e^{-i\mathbf{k}\cdot\mathbf{r}_n}\int_\infty u_t^*(\mathbf{r}-\mathbf{r}_n)v_s(\mathbf{r})d\tau}{\int_\infty u_t^*(\mathbf{r})u_t(\mathbf{r})d\tau}. \tag{6}$$

(Here $\int_\infty d\tau$ represents an integral over the entire crystal.) We now define

$$\Psi_s(\mathbf{r})=\sum\nolimits_n e^{i\mathbf{k}\cdot\mathbf{r}_n}w_s(\mathbf{r}-\mathbf{r}_n) \tag{7}$$

as the set of valence and excited Bloch wave functions. Assume that

$$\int_\infty u_s^*(\mathbf{r}-\mathbf{r}_n)u_t(\mathbf{r})d\tau=\delta_{st}\delta_{n0}\int_\infty u_s^*(\mathbf{r})u_s(\mathbf{r})d\tau; \tag{8}$$

i.e., the ion-core atomic wave functions are mutually orthogonal and the overlap integrals between ion-core wave functions on different atoms are negligible. It now follows immediately that

$$\int_\infty \Psi_s^*\Phi_t d\tau=0, \tag{9}$$

for all the values of s and t.

Assume that the exact Bloch wave function, Ψ, for a valence or an excited electron can be expanded in terms of the Ψ_t's,

$$\Psi=\sum\nolimits_t \alpha_t\Psi_t. \tag{10}$$

Let us define as energy and overlap integrals, respectively,

$$\begin{aligned} H_{stn}&=\int_\infty w_t^*(\mathbf{r})Hw_s(\mathbf{r}-\mathbf{r}_n)d\tau,\\ I_{stn}&=\int_\infty w_t^*(\mathbf{r})w_s(\mathbf{r}-\mathbf{r}_n)d\tau, \end{aligned} \tag{11}$$

where H is the one-electron Hamiltonian for the crystal. If we require that (10) satisfies Schrödinger's equation, then by making use of the usual variation method we get the set of equations,

$$\sum\nolimits_s \alpha_s\sum\nolimits_n e^{i\mathbf{k}\cdot\mathbf{r}_n}(H_{stn}-EI_{stn})=0. \tag{12}$$

The corresponding secular equation is

$$\det[\sum\nolimits_n e^{i\mathbf{k}\cdot\mathbf{r}_n}(H_{stn}-EI_{stn})]=0. \tag{13}$$

The elements of the secular determinant are thus Bloch sums of overlap and energy integrals.

A major problem of the method of Bloch waves is the accurate evaluation of these Bloch sums. The approximation of "tight binding" has been used extensively in the past in obtaining these sums.[3] This approximation consists of neglecting all integrals between non-neighboring atoms of the crystal. This approximation is usually excellent for ion-core wave functions ([Eq. (8)] is a strengthened version of this approximation), but the approximation may be very bad for valence and excited wave functions, whence the corresponding Bloch sums converge very slowly. An accurate method of calculating such Bloch sums will be discussed in Sec. IV.

---

[5] Actually this theorem holds only for wave functions satisfying periodic boundary conditions. Other types of wave functions may be used when phenomena at the surface of the crystal are being studied. For an excellent proof of Bloch's theorem, see W. Shockley, *Electron and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

III. METHOD OF ORTHOGONALIZED PLANE WAVES

One of the earliest methods of treating valence electrons in a crystal involved expanding the wave function in plane waves.[6] This method is not accurate, however, for the following reason. When using a small number of plane waves, the lowest root of the secular equation gives an energy in the region of the valence band, but, of necessity, if a complete set of plane waves were used, the lowest root should give the energy of the lowest ion-core band. This indicates that a very large number of plane waves is necessary to represent accurately the wave function, a fact which results from the rapid variation with position of the wave function close to each nucleus.

Herring[4] has shown that this difficulty can be removed by expanding the valence wave function in terms of orthogonalized plane waves. An orthogonalized plane wave, by definition, is a plane wave which has been made orthogonal to the ion-core Bloch wave functions by the Schmidt orthogonalization procedure. It is well known that the complete set of plane waves for an unbounded crystal is $e^{i\mathbf{k}_i\cdot\mathbf{r}}$. (The symbols used here have the same meaning as in Sec. II.) The corresponding set of orthogonalized plane waves is

$$\mathrm{X}_i(\mathbf{r})=e^{i\mathbf{k}_i\cdot\mathbf{r}}-\sum_j \mu_{ij}\Phi_j(\mathbf{r}), \tag{14}$$

$$\mu_{ij}=\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}u_j^*(\mathbf{r})d\tau\bigg/\int_\infty u_j^*(\mathbf{r})u_j(\mathbf{r})d\tau. \tag{15}$$

It is easily shown that

$$\int_\infty \mathrm{X}_i^*\Phi_j d\tau=0 \tag{16}$$

for all the values of i and j.

Assume that the exact Bloch wave function, Ψ, for a valence or an excited electron can be expanded in terms of the X_i's,

$$\Psi=\sum_i \beta_i\mathrm{X}_i. \tag{17}$$

Define

$$D_{ij}=(1/\Omega N)\int_\infty \mathrm{X}_j^*(H-E)\mathrm{X}_i d\tau, \tag{18}$$

where Ω is the volume of the unit cell and N is the number of unit cells in the crystal, so that ΩN is the volume of the crystal. Making use of the variation method, we get the set of equations

$$\sum_i \beta_i D_{ij}=0. \tag{19}$$

The corresponding secular equation is

$$\det D_{ij}=0. \tag{20}$$

Let us assume that the Hamiltonian is of the form

$$H=-\nabla^2+\mathbf{V}(\mathbf{r}), \tag{21}$$

where the crystal potential $\mathbf{V}$ is a spacial sum of atomic-like potentials, V, i.e.,

$$\mathbf{V}(\mathbf{r})=\sum_n V(\mathbf{r}-\mathbf{r}_n). \tag{22}$$

(See Appendix A for the determination of V.) D_{ij} can now be put in a form more convenient for numerical computation, namely,

$$\begin{aligned}D_{ij}=(k_i^2-E)\delta_{ij}-\Omega^{-1}\sum_s\Big[&(k_i^2+k_j^2-E)\mu_{is}\mu_{js}^*\\&\times\int_\infty u_s^*(\mathbf{r})u_s(\mathbf{r})d\tau-\mu_{is}\mu_{js}^*\int_\infty \nabla u_s^*(\mathbf{r})\\&\cdot\nabla u_s(\mathbf{r})d\tau\Big]+\Omega^{-1}\int_\infty V(\mathbf{r})e^{i\mathbf{K}_{ij}\cdot\mathbf{r}}d\tau\\&-\Omega^{-1}\sum_{s,n}\Big[\mu_{is}\int_\infty e^{-i\mathbf{k}_j\cdot\mathbf{r}}u_s(\mathbf{r})V(\mathbf{r}-\mathbf{r}_n)d\tau\\&+\mu_{js}^*\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}u_s^*(\mathbf{r})V(\mathbf{r}-\mathbf{r}_n)d\tau\\&-\mu_{is}\mu_{js}^*\int_\infty u_s^*(\mathbf{r})u_s(\mathbf{r})V(\mathbf{r}-\mathbf{r}_n)d\tau\Big].\end{aligned} \tag{23}$$

Here we have used the shortened notation $\mathbf{K}_i-\mathbf{K}_j\equiv\mathbf{K}_{ij}$.

As Herring has pointed out, by using a set of orthogonalized plane waves, X_i, rather than a set of ordinary plane wave, $e^{i\mathbf{k}_i\cdot\mathbf{r}}$, the energy of the lowest root of the secular equation converges to the energy of the lowest valence band (rather than to the energy of the lowest ion-core level) as the order of the secular determinant is increased (in the approximation that the Φ_i's are the exact solutions for the ion-core levels). Therefore it might be expected that the series in Eq. (17) would be much more rapidly convergent than a similar series using ordinary plane waves. This expectation will be shown to be justified in the case of the lithium crystal. It was for essentially the same reason that we went to the trouble of insuring orthogonality between the ion-core and the valence Bloch functions in Sec. II.

An alternative, but equivalent, method of explaining the rapid convergence of the series in Eq. (17) is the following. The reason that an ordinary Fourier expansion of the valence Bloch wave function does not converge rapidly lies in the fact that the wave function varies rapidly with position in the vicinity of each atomic nucleus—this rapid variation requiring plane waves of short wavelength for the accurate representation of the wave function. The mathematical necessity for this rapid variation with position arises from the requirement that the valence Bloch wave function be orthogonal to the ion-core Bloch wave functions combined with the fact that the latter vary rapidly with position near each nucleus. If we use orthogonalized plane waves in place of simple plane

---

[6] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag J. Springer, Berlin, Germany, 1933), Vol. 24, No. 2, p. 385.

waves for expanding the wave function, however, the Schmidt orthogonalization procedure insures that the rapidly varying portion of the wave function is *not* expanded in plane waves but is kept in its unexpanded form. Thus we break up Ψ into two parts, Ψ' and Ψ'', where

$$\Psi'=\sum_i \beta_i e^{i\mathbf{k}_i\cdot\mathbf{r}}$$

is that portion which *is* expanded in plane waves, while

$$\Psi''=\sum_{i,j} \beta_i \mu_{ij} \Phi_j(\mathbf{r})$$

is that portion which is not expanded in plane waves. There is no reason why the expansion of Ψ' should not converge rapidly.

IV. TRANSFORMATION FROM THE METHOD OF BLOCH WAVES TO THE METHOD OF ORTHOGONALIZED PLANE WAVES

It was pointed out in Sec. II that a major problem in the method of Bloch waves is the accurate evaluation of the Bloch sums of energy and overlap integrals. For ionic and molecular crystals, where the approximation of "tight binding" is valid, these sums can be evaluated in a straightforward manner. For metals, semiconductors, and valence crystals, however, any attempt at evaluation in a straightforward manner is discouraging, since the sums converge very slowly. Henceforth, we shall consider only crystals where such a situation holds.

The following device is effective under such a situation. Expand in three-dimensional Fourier series that portion of each Bloch wave function which contains an isolated-atom valence or excited wave function, $v_s(\mathbf{r})$. A corresponding portion of each Bloch sum over crystal space can thereby be transformed into a Bloch sum over reciprocal space. Recalling the uncertainty principle, we would expect that a slow convergence over crystal space would correspond to a rapid convergence over reciprocal space. Such is the case. This is equivalent to the fact that a valence electron in a crystal will have a very sharply defined momentum when it has a very poorly defined position.

In obtaining the Fourier series, the correct set of expansion functions to use is the set of ordinary plane waves, $e^{i\mathbf{k}_i\cdot\mathbf{r}}$, already discussed in Sec. III. If we define the coefficients, A_{si}, by the equation

$$\sum_i A_{si} e^{i\mathbf{k}_i\cdot\mathbf{r}}=\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n} v_s(\mathbf{r}-\mathbf{r}_n), \tag{24}$$

then it immediately follows that

$$A_{si}=\Omega^{-1}\int_\infty e^{-i\mathbf{k}_i\cdot\mathbf{r}} v_s(\mathbf{r})d\tau. \tag{25}$$

The coefficients σ_{st} and μ_{it}, used in the Schmidt orthogonalization procedures for the Bloch waves and the orthogonalized plane waves, respectively, can be related through the equation,

$$\sigma_{st}=\sum_i A_{si}\mu_{it}. \tag{26}$$

Combining Eqs. (4), (5), (7), (14), (24), and (26), we get

$$\Psi_s(\mathbf{r})=\sum_i A_{si}\mathrm{X}_i(\mathbf{r}). \tag{27}$$

Thus our device of expanding only a portion of the Bloch wave function in a Fourier series is equivalent to expanding the entire Bloch wave function in orthogonalized plane waves. It is interesting that the Eq. (27) is exact despite the fact that the set X_i is not a complete set. (27) holds since the set X_i may be considered a complete set for the purpose of expanding any function which is orthogonal to the set of ion-core Bloch wave functions, Φ_s.

It is possible to write the Bloch sums of overlap and energy integrals in the form

$$\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}(H_{stn}-EI_{stn})=N^{-1}\int_\infty \Psi_t^*(H-E)\Psi_s d\tau. \tag{28}$$

Substituting (18) and (27) into (28), we get

$$\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}(H_{stn}-EI_{stn})=\Omega\sum_{ij} A_{si}A_{tj}^*D_{ij}. \tag{29}$$

Thus the secular equation in the Bloch method can be written

$$\det[\Omega\sum_{ij} A_{si}A_{tj}^*D_{ij}]=0. \tag{30}$$

Applying the law of determinant multiplication, we get

$$\det[\sum_{ij} A_{si}A_{tj}^*D_{ij}] =(\det A_{si})(\det A_{tj}^*)(\det D_{ij}), \tag{31}$$

so that (30) is equivalent to

$$\det D_{ij}=0. \tag{32}$$

Since Eqs. (32) and (20) are identical, we have shown that the Bloch method is equivalent to the orthogonalized plane wave method.

Let us now study the practicability of the Bloch method for numerical calculation. We will show that while Eq. (29) is a very useful way of evaluating Bloch sums of overlap and energy integrals, Eq. (30) is absolutely useless for calculating energy bands. To do this we must determine A_{si}, which depends upon $v_s(\mathbf{r})$. In the types of crystals under consideration, the atomic correspondence is very poor for valence electrons, so that it is not necessary to use accurate analytic approximations to the true set, $v_s(\mathbf{r})$, of isolated-atom valence and excited wave functions when making numerical calculations. Indeed, it is not even necessary that the analytic approximations to $v_s(\mathbf{r})$ have radial nodes. When we form $w_s(\mathbf{r})$ from $v_s(\mathbf{r})$ by the Schmidt orthogonalization procedure [Eq. (5)], we automatically insure that $w_s(\mathbf{r})$ has the proper number of nodes. We will approximate $v_s(\mathbf{r})$ by a set of Gaussian functions,[7]

$$v_{lm}(\mathbf{r})=i^l P_l^{|m|}(\cos\theta)e^{im\varphi}r^l \exp(-b_l r^2). \tag{33}$$

---

[7] The use of Gaussians in place of the more conventional exponential wave functions in problems involving many atoms was first suggested by S. F. Boys, Proc. Roy. Soc. (London) **200**, 542 (1950). Boys pointed out that energy and overlap integrals could be obtained much more easily by using Gaussians rather than exponentials.

Substituting (33) into (25), we get

$$A_{lmi}=\Omega^{-1}(\pi/b_l)^{\frac{3}{2}}(k_i/2b_l)^l P_l^{|m|}(\cos\theta_i)e^{im\varphi_i} \times\exp[-(k_i^2/4b_l)], \quad (34)$$

where θ_i and φ_i give the orientation of $\mathbf{k}_i$. We can see the relative magnitudes of the various A's by considering the example of lithium. For a $2p$ Gaussian wave function in an isolated lithium atom, the values of b_l obtained by minimizing the one-electron energy can be shown to be $b_1=0.0557$. (The atomic potential, $V(r)$, used in such a calculation is that obtained in Appendix A.) In the crystal b_1 is probably still smaller, since the wave function is probably more spread out in the crystal than it is in an isolated atom. For the lithium crystal $\mathbf{K}_i$ is the form

$$\mathbf{K}_{n_1n_2n_3}=K(\mathbf{i}_1n_1+\mathbf{i}_2n_2+\mathbf{i}_3n_3),$$

where $\mathbf{i}_1$, $\mathbf{i}_2$, and $\mathbf{i}_3$ are fixed, mutually orthogonal unit vectors, $(n_1+n_2+n_3)$ is an arbitrary even integer (face-centered-cubic reciprocal lattice), and $K=0.957$. Since k_i usually increases with i (by convention), we can see that, because of the factor $\exp[-(k_i^2/4b_l)]$ in A_i, the ration A_{i+1}/A_i will usually be a very small number, often smaller than one millionth. Because of this fact, the double series on the right-hand side of Eq. (29) will converge extremely rapidly. This situation will hold in general provided that the Bloch sums on the left-hand side are slowly convergent. It is thus usually a very good approximation to replace Eq. (29) by

$$\textstyle\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}(H_{stn}-EI_{stn})\cong\Omega A_{s0}A_{t0}{}^*D_{00} \quad (35)$$

when the Bloch sums converge slowly. (Here we have replaced the double series over reciprocal space by its leading term.) If we attempt to use this approximation in Eq. (30), however, we find that the secular determinant vanishes identically (since the rows and columns are mutually proportional), so that it is impossible to solve for the energy eigenvalues. This is a convincing demonstration of the fact that it is necessary to determine the Bloch sums extremely accurately, since the solution to the secular equation depends upon the minute deviations from proportionality of the rows and columns of the secular determinant.

It is now apparent that Eq. (30) is not practical for numerical calculations. The key to this lack of usefullness of the Bloch method lines in Eq. (27). Just as we approximated Eq. (29) by Eq. (35), we may approximate Eq. (27) by

$$\Psi_s(\mathbf{r})\cong A_{s0}\mathrm{X}_0(\mathbf{r}). \quad (36)$$

We thus see that in Eq. (10) we are attempting to expand the exact crystal wave function, Ψ, in terms of a set of wave functions, Ψ_s, the members of this set all being, to an excellent approximation, numerical multiples of a single function, X_0. In other words, Ψ_s is an extremely poor set to use in expanding Ψ. Disregarding numerical factors, we see that Ψ_s depends almost entirely on X_0 and almost not at all on v_s. Because of the large amount of overlapping of valence atomic wave functions centered on different nuclei of the crystal, the valence atomic correspondence of Ψ_s is almost completely lost.

It is possible to reformulate the Bloch method in order to remove the difficulty of a secular determinant which vanishes identically (for practical purposes). This reformulation is rather unwieldy for numerical computations, however. From the set of valence Bloch wave functions, $\Psi_s(\mathbf{r})$, let us form the set of doubly orthogonal valence Bloch wave functions, $\boldsymbol{\Psi}_s(\mathbf{r})$, where

$$\boldsymbol{\Psi}_s(\mathbf{r})=\Psi_s(\mathbf{r})-\sum_{\nu<s}\xi_{s\nu}\boldsymbol{\Psi}_\nu(\mathbf{r}) \quad (37)$$

and

$$\xi_{s\nu}=\int_\infty \boldsymbol{\Psi}_\nu{}^*\Psi_s d\tau \bigg/ \int_\infty \boldsymbol{\Psi}_\nu{}^*\boldsymbol{\Psi}_\nu d\tau. \quad (38)$$

As well as being orthogonal to the ion-core Bloch waves, the $\boldsymbol{\Psi}_s(\mathbf{r})$ are mutually orthogonal. Similarly, let us form the set of doubly orthogonalized plane waves, $\mathbf{X}_i(\mathbf{r})$, where

$$\mathbf{X}_i(\mathbf{r})=\mathrm{X}_i(\mathbf{r})-\sum_{j<i}\eta_{ij}\mathbf{X}_j(\mathbf{r}) \quad (39)$$

and

$$\eta_{ij}=\int_\infty \mathbf{X}_j\mathrm{X}_i d\tau \bigg/ \int_\infty \mathbf{X}_j\mathbf{X}_j d\tau. \quad (40)$$

As well as being orthogonal to the ion-core Bloch waves, the $\mathbf{X}_i(\mathbf{r})$ are mutually orthogonal. As might be expected, it is possible to expand $\boldsymbol{\Psi}_s(\mathbf{r})$ in terms of the $\mathbf{X}_i$'s.

$$\boldsymbol{\Psi}_s(\mathbf{r})=\textstyle\sum_i B_{si}\mathbf{X}_i(\mathbf{r}). \quad (41)$$

It can be shown that

$$B_{si}=\textstyle\sum_{\mu,\nu}\gamma_{s\mu}A_{\mu\nu}\eta_{\nu i}, \quad (42)$$

where

$$\textstyle\sum_\nu \gamma_{s\nu}\xi_{\nu t}=\delta_{st}. \quad (43)$$

Using the fact that $A_{\mu\nu}\gg A_{\mu,\nu+1}$, we can show that $B_{ss}\gg B_{s,s\pm1}\gg B_{s,s\pm2}\cdots$, so that, to a very good approximation, we have

$$\boldsymbol{\Psi}_s(\mathbf{r})\cong B_{ss}\mathbf{X}_s(\mathbf{r}). \quad (44)$$

Equation (44) should be contrasted with Eq. (36). Associated with each doubly orthogonal valence Bloch function there is a particular doubly orthogonalized plane wave—the two being very nearly proportional—so that there are no difficulties with vanishing secular determinants. Just as with $\Psi_s(\mathbf{r})$, the valence atomic correspondence of $\boldsymbol{\Psi}_s(\mathbf{r})$ is almost completely lost.

V. APPLICATION TO LITHIUM

We shall now apply the method of orthogonalized plane waves to the case of the lithium crystal. The calculations are simplified by the fact that there is only one type of ion-core atomic wave function, namely, a $1s$ wave function, u_{1s}. We approximate this by the exponential

$$u_{1s}=e^{-ar}. \tag{45}$$

a is determined by minimizing the expectation value of the $1s$ energy in the isolated lithium atom; i.e., we solve the equation

$$\partial E_{1s}'/\partial a=0,$$

where

$$E_{1s}'=\int_{\infty} u_{1s}H'u_{1s}d\tau \bigg/ \int_{\infty} u_{1s}u_{1s}d\tau, \tag{46}$$

$$H'=-\nabla^2+V(r), \tag{47}$$

$V(r)$ being the atomic potential determined in Appendix A; i.e.,

$$V(r)=-\frac{2}{r}\sum_{\nu=1}^{4} C_\nu \exp(-c_\nu r^2) \tag{48}$$

(the C's and c's being suitably chosen constants). The results obtained are $a=2.788$ and $E_{1s}'=-4.572$ (to be compared with the experimental value of $E_{1s}'=-4.799$).

By substituting Eqs. (45) and (48) into Eq. (23), we can explicitly evaluate the integrals occurring in the expression for D_{ij}. After considerable mathematical manipulation it is possible to obtain an approximate but numerically accurate expression from which D_{ij} may easily be calculated as a function of $\mathbf{k}_i$ and $\mathbf{k}_j$.

When we approximate Ψ by the first n terms of the series in Eq. (17), then we obtain in Eq. (20) an nth order secular determinant. For example, if we use only the leading term of the series in (17), then (20) becomes

$$D_{00}=0, \tag{49}$$

and we get a single solution for E *versus* $\mathbf{k}$, this solution being independent of the direction of $\mathbf{k}$. For higher approximations, involving a secular determinant of order greater than the first, the energy will not be completely independent of the direction of $\mathbf{k}$. If the crystal wave function in the lowest valence band can be closely approximated by a single orthogonalized plane wave, however, then the energy will be nearly independent of direction. That such is the case for lithium can be seen from an examination of the results given in Table I, where it is apparent that as the order of the secular determinant is increased, E converges rapidly to its limiting value. It is this behavior which makes the orthogonalized plane wave method useful for numerical calculation.

Knowing E as a function of $\mathbf{k}$, we can find the ratio of free to effective electronic mass in the valence band. For $\mathbf{k}$ along a symmetry axis of the reciprocal lattice, the ratio is given by

$$m/m^*=\tfrac{1}{2}d^2E/dk^2.$$

TABLE I. E *versus* $\mathbf{k}$ for the valence band of lithium. For convenience, $E+(4\pi C_1/\Omega c_1)$ has been denoted simply by E. The number in the parentheses after E refers to the order of the secular determinant used in solving for E.

110 direction			
k	$E(1)$	$E(2)$	
0.0	0.188567	0.188527	
0.2	0.222039	0.221287	
0.4	0.330156	0.326336	
0.6	0.509509	0.487387	
0.67675	0.598254	0.527035	
111 direction			
k	$E(1)$	$E(2)$	$E(4)$
0.0	0.188567	0.188527	0.188437
0.2	0.222039	0.221456	0.220183
0.4	0.330156	0.328368	0.324709
0.6	0.509509	0.504317	0.495564
0.67675	0.598254	0.589861	0.578193
0.75	0.693473	0.677700	0.663656
0.82885	0.807631	0.756032	0.756032
100 direction			
k	$E(1)$	$E(2)$	$E(5)$
0.0	0.188567	0.188527	0.188394
0.2	0.222039	0.221674	0.220513
0.4	0.330156	0.329050	0.325783
0.6	0.509509	0.507119	0.501071
0.67675	0.598254	0.595096	0.587910
0.75	0.693473	0.689234	0.681002
0.82885	0.807631	0.801213	0.792210
0.9	0.921154	0.909060	0.901722
0.95707	1.019513	0.985029	0.994526

We obtain as values along the 110, 111, and 100 directions at the bottom of the band

$$(m/m^*)_{110}=0.8190,$$

$$(m/m^*)_{111}=0.7936,$$

$$(m/m^*)_{100}=0.8030,$$

$$\langle m/m^*\rangle_{\text{Av}}=0.8075.$$

(The directional average is obtained in an approximate fashion by averaging the values for the three symmetry directions—weighting these values according to the fact that there are six 110 axes, four 111 axes, and three 100 axes.) Silverman and Kohn[8] computed $(m/m^*)=0.727$ at the bottom of the band. The difference is probably because of their use of an atomic rather than a crystal potential. The latter varies less rapidly than the former over most of the unit cell, and thus should result in a value of m^* more nearly "free-electron-like" (see Appendix A).

Knowing E as a function of $\mathbf{k}$, we can compute the energy-width of the filled portion of the valence band, obtaining a value of 4.06 electron volts. By means of the soft x-ray K emission band of lithium, Skinner[9] measured this to be 4.1±0.3 volts. This excellent comparison is in contrast with the results of previous calculations on lithium.[8,10] For example, the results of Silverman and Kohn, who use the Wigner-Seitz ap-

---

[8] R. A. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950).

[9] H. W. B. Skinner, Reports on Progress in Physics, **V** (1938).

[10] J. Millman, Phys. Rev. **47**, 286 (1935); F. Seitz, Phys. Rev. **47**, 400 (1935); J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

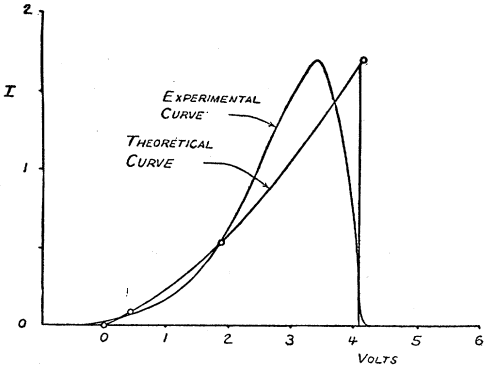

FIG. 1. Soft x-ray K emission band of lithium.

proximation, would predict the filled portion of the band to have a width of only 3.51 volts.

It is instructive to compute the $1s$ energy level in the lithium crystal; i.e.,

$$E_{1s}=\int_{\infty}\Phi_{1s}^{*}H\Phi_{1s}d\tau\Big/\int_{\infty}\Phi_{1s}^{*}\Phi_{1s}d\tau, \tag{50}$$

where

$$\Phi_{1s}(\mathbf{r})=\textstyle\sum_{n}e^{i\mathbf{k}\cdot\mathbf{r}_n}u_{1s}(\mathbf{r}-\mathbf{r}_n), \tag{51}$$

and H is given by Eq. (21). (Note the distinction between Eqs. (50) and (46)—the former holding for the crystal and the latter for the isolated atom.) Having done this, we can compute the energy-difference between the Fermi level and the $1s$ level in the crystal to be 57.8 volts. This should be compared with the experimental value of 54.8±0.6 volts.[11]

Let us now compute the shape of the soft x-ray K emission band of lithium. The experimental shape of the emission band will be proportional to the optical transition probability between the valence band and the $1s$ level and proportional to the density of filled states per unit energy range in the valence band. In the approximation of E being independent of the direction of $\mathbf{k}$ in the valence band, then k^2dk/dE is proportional to the density of states per unit energy range. The optical transition probability between a $1s$ wave function Φ_{1s} and a valence wave function Ψ is proportional to the quantity P, defined as

$$P=\left|\int_{\infty}\Phi_{1s}^{*}\nabla\Psi d\tau\right|^{2}\Big/\left(\int_{\infty}\Phi_{1s}^{*}\Phi_{1s}d\tau\int_{\infty}\Psi^{*}\Psi d\tau\right). \tag{52}$$

If we define the quantity

$$I=Pk^2dk/dE, \tag{53}$$

then, for energies below the Fermi level, I should be proportional to the experimental shape of the emission band. As can be seen from Fig. 1, the comparison between theory and experiment[9] is only fair. The computed values of I are roughly proportional to $E^{\frac{3}{2}}$. The reason for the drop in the experimental curve at high energies is not known.

VI. CONCLUSION

Let us briefly recapitulate the basic results of this paper. For ion-core electrons (i.e., electrons associated with a given nucleus), the crystal wave functions can be conveniently expressed as Bloch wave functions formed from the appropriate atomic wave functions. As is shown in Appendix B, it is permissible to use simple analytic approximations for these atomic wave functions if our primary interest lies in the valence and excited bands.

For valence and excited electrons (i.e., electrons which cannot be associated with any given nucleus), the ordinary Bloch method leads to computational difficulties. The elements of the secular determinant involve slowly convergent spacial sums of overlap and energy integrals between the various atoms of the crystal. An approximation often used, that of tight binding, which consists of neglecting integrals between non-neighboring atoms of the crystal, is quite unjustified because of the slow convergence of these sums. By expanding each valence Bloch wave function in terms of orthogonalized plane waves, however, these slowly convergent sums over ordinary space are transformed into extremely rapidly convergent sums over reciprocal space. It thereupon becomes apparent that, for the purpose of numerical computation, the secular determinant occurring in the Bloch method will vanish identically. This difficulty is caused by the fact that, to a good approximation, all the valence Bloch wave functions (in terms of which we attempt to expand the true wave function) differ among themselves only by a multiplicative constant. By a simple process, however, the secular equation of the Bloch method can be transformed into the secular equation of the method of orthogonalized plane waves. The latter equation is quite suitable for numerical computations. Thus we see that the valence and excited wave functions are most conveniently expressed in terms of orthogonalized plane waves. The latter have most of the advantages and none of the overwhelming disadvantages of ordinary plane waves.

There are, of course, electrons which fall into neither of the two general classes considered in the last two paragraphs (e.g., the $3d$ electrons in the transition elements). About such electrons nothing can be said here.

Concerning the crystal potential, two important facts stand out, as is shown in Appendix A. In the first place, within a given unit cell of the crystal, the crystal potential is not approximately the same as the corresponding potential for the isolated atom. As we have seen for the case of lithium, the two give significantly different answers to the same problem, so that one should not be used in place of the other. Secondly,

---

[11] H. M. O'Bryan and H. W. B. Skinner, Phys. Rev. **45**, 370 (1934).

Slater's method of including exchange in a one-electron approximation (by using an effective potential) seems to be well-suited for the calculation of energy bands in crystals.

The writer is indebted to the members of the Solid-State and Molecular Theory Group at MIT for their helpful discussion and criticism during the course of the investigation reported herein. In particular, the writer is indebted to the director of the group, Professor John C. Slater, for much-needed advice and encouragement.

APPENDIX A

Determination of the Crystal Potential

First we shall justify Eq. (22),

$$\mathbf{V}(\mathbf{r})=\sum_n V(\mathbf{r}-\mathbf{r}_n), \tag{1a}$$

which states that the crystal potential, $\mathbf{V}(\mathbf{r})$, can be taken as a spacial sum of atomic-like potentials. This is certainly true for that part of the crystal potential resulting from the ion-cores of the various atoms of the crystal, since the charge distributions of different ion-cores do not overlap. We now show that the same is true for that portion of the crystal potential resulting from valence electrons. The exact (one-electron) wave function $\Psi(\mathbf{r})$ for the valence electrons can be written in the form

$$\Psi(\mathbf{r})=\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}a(\mathbf{r}-\mathbf{r}_n), \tag{2a}$$

where (2a) may be taken as an implicit definition of the Wannier function, $a(\mathbf{r})$.[12] This function is similar to an atomic wave function, a fact which might be suspected by comparing Eqs. (2a) and (3). If we define

$$\rho(\mathbf{r})=\sum_n e^{i\mathbf{k}\cdot\mathbf{r}_n}a^*(\mathbf{r})a(\mathbf{r}-\mathbf{r}_n), \tag{3a}$$

then it follows that

$$\Psi^*\Psi=\sum_n \rho(\mathbf{r}-\mathbf{r}_n). \tag{4a}$$

We have now fully justified (1a), since (4a) shows that that portion of the crystal potential arising from the valence electrons can be taken as a spacial sum of atomic potentials, the atomic potential being that arising from the atomic-like charge distribution, $\rho(\mathbf{r})$.

We shall use the spherical average of $\rho(\mathbf{r})$, rather than $\rho(\mathbf{r})$ itself, in computing $V(r)$—this approximation being used universally in atomic problems. We will make the further approximation of replacing the series in (3a) by its leading term; i.e.,

$$\rho(\mathbf{r})=a^*(\mathbf{r})a(\mathbf{r}). \tag{5a}$$

These two approximations tremendously simplify the calculations. Incidentally, it can be shown that (5a) follows from the spherical averaging unless $a(\mathbf{r})$ has the character of an s wave function.

In order to include electron exchange in our one-electron Hamiltonian, we will form our potential by a method introduced by Slater.[13] If we define $\mathcal{V}(\mathbf{r})$ as the conventional potential of an electron in the field of the neutral crystal, then $\mathbf{V}(\mathbf{r})$, the potential including exchange, is given by

$$\mathbf{V}=\mathcal{V}+(3/2)(3/\pi^2)^{\frac{1}{3}}(\nabla^2\mathcal{V})^{\frac{1}{3}}. \tag{6a}$$

It follows from the previous discussion that we may decompose $\mathcal{V}(\mathbf{r})$ into a spacial sum of atomic potentials; i.e.,

$$\mathcal{V}(\mathbf{r})=\sum_n \mathcal{W}(\mathbf{r}-\mathbf{r}_n), \tag{7a}$$

where[14]

$$\mathcal{W}(r)=-(2/r)Z_p(r) \tag{8a}$$

serves to define the effective atomic number $Z_p(r)$. Instead of properly applying the exchange correction to the crystal potential as is done in Eq. (6a), we will adopt the approximate procedure of applying it to the atomic potential $\mathcal{W}(r)$. Thus we take

$$\begin{aligned} V(r)&=-(2/r)Z_{p1}(r),\\ Z_{p1}(r)&=Z_p+3(3/32\pi^2)^{\frac{1}{3}}(r^2d^2Z_p/dr^2)^{\frac{1}{3}}, \end{aligned} \tag{9a}$$

where $V(r)$ and $\mathbf{V}(\mathbf{r})$ are related by Eq. (22). The second term in Z_{p1} results from a free-electron approximation to the exchange hole correction.

In computing Z_p for lithium, isolated-atom wave functions (with exchange) for lithium were taken from Fock and Petrashen.[15] It was assumed that the appropriate configuration to use for the neutral lithium atom in computing Z_p is $(1s)^2(2s)^{5/8}(2p)^{3/8}$. This assumption is based on the following approximate calculation. Let the valence atomic wave function for lithium be of the form,

$$\psi=a_s(\mathbf{k})\psi_{2s}+a_p(\mathbf{k})\psi_{2p}.$$

Following Jones, Mott, and Skinner,[3] we assume that $|a_p|=k/K_1$, where $\mathbf{k}=\mathbf{K}_1$, at the edge of the first Brillouin zone. Denote by Ω_K the volume of the first Brillouin zone, so that approximately $\Omega_K=(4/3)\pi K_1^3$. Two valence electrons would fill the valence band. Since for lithium there is only one valence electron per atom, the band is exactly half full, and $\frac{1}{2}\Omega_K=(4/3)\pi k_1^3$, k_1 being defined as the maximum value of k associated with an occupied state. We now find that

$$\langle a_p^2\rangle_k=\int_0^{k_1}4\pi k^2a_p^2dk\Big/\int_0^{k_1}4\pi k^2dk$$

$$=\tfrac{3}{5}(\tfrac{1}{2})^{\frac{2}{3}}=0.3780\cong\tfrac{3}{8}$$

is the fraction of $2p$ electrons in the valence band of the lithium crystal.

It was found that Z_{p1} could be very closely approximated by a sum of Gaussians,

$$Z_{p1}(r)=\sum_{\nu=1}^{4}C_\nu\exp(-c_\nu r^2), \tag{10a}$$

---

[12] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

[13] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[14] It should be emphasized that $\mathcal{W}(r)$ is the conventional potential energy of an electron in the field of the neutral, isolated atom.

[15] V. Fock and M. J. Petrashen, Physik. Z. Sowjetunion **8**, 547 (1935).

where

$C_1=0.9256,\quad C_2=1.2278,\quad C_3=0.5901,\quad C_4=0.2369,$
$c_1=0.014408,\quad c_2=1.0642,\quad c_3=11.939,\quad c_4=107.37.$

If we define

$$V_\nu(r)=-(2/r)C_\nu \exp(-c_\nu r^2), \tag{11a}$$

then

$$V(r)=\sum_{\nu=1}^{4} V_\nu(r). \tag{12a}$$

It is convenient to speak of V_1, as the long-range part of the atomic potential and $(V_2+V_3+V_4)$ as the short-range portion. Similarly, we call $\sum_n V_1(\mathbf{r}-\mathbf{r}_n)$ the long-range portion of the crystal potential and

$$\sum_n \sum_{\nu=2}^{4} V_\nu(\mathbf{r}-\mathbf{r}_n)$$

the short-range portion. Because of the values of c_2, c_3, and c_4, it can be seen that the short-range portion of the crystal potential near a given nucleus is the same as the short-range portion of the atomic potential centered on the given nucleus. Because of the smallness of c_1, this is not true of the long-range portion. By expanding the long-range crystal potential in a Fourier series, it can be shown that near a given nucleus the long-range crystal potential acts like the long-range atomic potential (centered on the given nucleus) multiplied by a screening factor, $S(r)$, of the form

$$S(r)=\left[1-(2/\pi)\int_0^{K_1 r} x^{-1}\sin x dx\right], \tag{13a}$$

K_1 having already been defined such that $\Omega_K=(4/3)\pi K_1^3$. This screening factor has the important effect of making a crystal potential more "free-electron-like" than is the corresponding atomic potential.

The long-range crystal potential further contains a small term not strongly dependent on position and a very large term independent of position. This latter is called the divergence term and has the value $-(4\pi C_1/\Omega c_1)$ $(-77.6$ volts for lithium). (Ω is the volume of the polyhedral cell of the crystal.) Apart from this divergence term, $\mathbf{V}(\mathbf{r})$ is rather insensitive to changes in c_1. This means that the variation with position of the crystal potential is insensitive to the value of the corresponding atomic potential at large distances (large r) since the latter is largely dependent on c_1. Such a situation is fortunate, since the atomic potential we are using is clearly incorrect at large distances; i.e., Z_{p1} approaches zero whereas it should approach unity as $r\rightarrow\infty$. This incorrect behavior is a result of the free-electron approximation to the exchange hole correction in (9a), and is the cause of the excessively large value of the divergence term. Since our primary interest lies in energy bands, then an error in the divergence term is unimportant, for the shape and relative separation of the bands are independent of any constant terms in the potential.

APPENDIX B

The Use of Approximate Ion-Core Wave Functions

Let us investigate the error in the lithium valence band resulting from the approximation of the $1s$ atomic wave function by a single exponential. We do this in the following way. Consider the approximation of a first-order secular determinant, so that the secular equation is given by Eq. (49). In this approximation we can expand E in powers of k^2,

$$E=E_0+E_2k^2+E_4k^4+\cdots. \tag{1b}$$

Solving for the coefficients, we get

$$E_0+(4\pi C_1/\Omega c_1)=0.1886,\ E_2=0.8792,\ E_4=0.0199. \tag{2b}$$

If we approximate our $1s$ wave function by a Gaussian, $\exp(-a'r^2)$, rather than by an exponential, e^{-ar}, and then repeat the above calculation, we get

$$E_0+(4\pi C_1/\Omega c_1)=0.1905,\ E_2=0.8751,\ E_4=0.0224. \tag{3b}$$

There is some work involved in getting (3b). First we must obtain the best value of a' from the equation

$$\partial E_{1s}'/\partial a'=0,$$

where E_{1s}' is given by Eq. (46), where now

$$u_{1s}=\exp(-a'r^2). \tag{4b}$$

The results obtained are $a'=2.076$ and $E_{1s}'=-3.248$. Comparing this energy with those given in the discussion following Eq. (46), we can see that a Gaussian is a decidedly poorer approximation to the $1s$ wave function than is an exponential. Substituting (4b) into Eq. (23) we can evaluate D_{00} and thus obtain (3b). The point that should be made is that (3b) is remarkably similar to (2b), despite the fact that a much poorer $1s$ wave function was used in obtaining (3b). This leads us to hope that the error resulting from approximating the $1s$ wave function by a single exponential will be negligible.