ognized that they may be difficult to distinguish from other effects, as for example, changes in mobility.

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Solution of Schrödinger Equation for a Periodic Lattice

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We present a new method for solving the problem of one electron in a periodic potential; it is discussed in this paper mainly for $\mathbf{k}=0$, although it can be generalized to other $\mathbf{k}$. The periodic potential is considered to be generated by spherically symmetric "atomic" potentials at each lattice site; this does not mean of course that the total potential near a lattice site need be spherically symmetric. The method has its origin in the observation that (for $\mathbf{k}=0$) the equation for $C(\mathbf{K}_i)$, the Fourier coefficient of the wave function, becomes just the momentum-space Schrödinger equation when the lattice spacing becomes infinite. This latter equation is separable into a radial part, and an angle-dependent part expressible in spherical harmonics. This suggests that it would be advantageous to expand the $C(\mathbf{K}_i)$ for finite lattice spacing similarly, into radial functions $C_l(K_m)$, where K_m is the magnitude of the mth smallest reciprocal lattice vector, and into an angle-dependent part expressible (for cubic lattices) by Kubic harmonics. We do this and the Schrödinger equation for the system becomes a set of homogeneous linear equations for the $C_l(K_m)$, with a corresponding secular determinant for the eigenvalues.

We have tested the method numerically, as a function of lattice spacing and potential strength, for S-like states, when the "atomic" potentials are exponential ones, and the lattice is body-centered cubic. In many cases it turns out that one can solve the periodic potential case more easily and more accurately than one can solve for the isolated atom. This is because as the lattice spacing gets large the successive K_m became more and more closely spaced and this leads to larger and larger secular equations. The wave functions as well as energies are given for most lattice spacings to considerable accuracy (three to seven significant figures).

When the lattice spacing gets large and the equations approach those for the isolated atom, we show how one can use the atomic momentum space functions as variational functions, in the same spirit as the usual tight-binding approximation (as applied for $\mathbf{k}=0$). The present method has the considerable advantage that it bypasses the usual difficulties with that approximation—near-neighbor approximations and calculation of overlap integrals—and permits an easy and accurate evaluation of the variational expression as a sum over the K_m.

I. INTRODUCTION AND THE BASIC EQUATIONS

THE one-electron band structure problem, i.e., the problem of solving the Schrödinger equation for an electron in a periodic lattice, is an old one with an extensive literature.[1] In this paper, we look at some old equations for this problem in a new light, and are led to a new and accurate method for solving it. We are also led to a new way of doing the "tight-binding" approximation which bypasses the multi-center integrals that occur in the usual formulation of this method.

To begin, we consider a monatomic periodic lattice at each lattice site of which there is an "atomic" potential; this gives rise, of course, to a periodic space potential. For simplicity, we shall assume that these "atomic" potentials are spherically symmetric, although one can generalize to potentials which are not spherically symmetric in a straightforward way. This assumption does *not* mean, of course, that an electron sees a spherically symmetric *total* potential, for near any lattice site it will see the local "atomic" potential plus the tails of the potentials that are at other sites. We choose an origin of coordinates at one of the potentials and in this coordinate system let $\mathbf{r}$ be a position vector to a point $\mathbf{P}$ in space. The site of the ith potential is specified by a vector $\mathbf{d}_i$ of the form

$$\mathbf{d}_i=i_1\mathbf{a}_1+i_2\mathbf{a}_2+i_3\mathbf{a}_3,$$

where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are three basis vectors for the crystal and i_1, i_2, i_3 are integers. At each lattice site, we set up a coordinate system oriented similarly to the coordinate system at the origin, and let $\mathbf{r}_i$ be the position vector in the ith system to the point $\mathbf{P}$ in space. Then obviously we have

$$\mathbf{d}_i+\mathbf{r}_i=\mathbf{r}.$$

As usual, we define the basis vectors $\mathbf{b}_j$ of the reciprocal lattice by

$$\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij}$$

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[1] For a review article with extensive references to the literature see, for example: Joseph Callaway, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 7.

and define a reciprocal lattice vector $\mathbf{K}_j$,

$$\mathbf{K}_j = 2\pi(j_1\mathbf{b}_1 + j_2\mathbf{b}_2 + j_3\mathbf{b}_3).$$

There are two standard formulas[2] that have to do with the reciprocal lattice which we quote here for future use. First is the well-known equation

$$\textstyle\sum_i \exp(i\boldsymbol{\sigma}\cdot\mathbf{d}_i) = (2\pi)^3\Omega_b \sum_j \delta(\boldsymbol{\sigma} - \mathbf{K}_j), \tag{1}$$

where δ is the usual Dirac delta function and Ω_b is the volume of the unit cell of the reciprocal lattice. Of course, this has meaning only if it is used as a factor in an integrand. The second formula is this. Suppose for a given space lattice we wish to sum some function $F(\mathbf{K}_j)$ over the reciprocal lattice. If the lattice constant of the space lattice is large, then the points of the reciprocal lattice are very close and the summation can be approximated by an integration

$$\sum_j F(\mathbf{K}_j) \sim \frac{1}{(2\pi)^3\Omega_b}\int F(\mathbf{K})d\mathbf{K}. \tag{2}$$

The total potential of the problem is $V_c(\mathbf{r})$, the crystal potential. It is the sum of the "atomic" potentials,

$$V_c(\mathbf{r}) = \textstyle\sum_i V^a(r_i). \tag{3}$$

The Schrödinger equation is then

$$(\nabla^2 + \beta)\Psi(\mathbf{r}) = v_c(\mathbf{r})\Psi(\mathbf{r}), \tag{4}$$

where

$$v_c(\mathbf{r}) = \frac{2m}{\hbar^2}V_c(\mathbf{r}), \quad v^a(\mathbf{r}_i) = \frac{2m}{\hbar^2}V^a(\mathbf{r}_i), \quad \beta = \frac{2mE}{\hbar^2}, \tag{5}$$

and E is the energy. Since $v_c(\mathbf{r})$ is periodic in $\mathbf{r}$, we can expand it in Fourier series,

$$v_c(\mathbf{r}) = \textstyle\sum_j w(\mathbf{K}_j)\exp(i\mathbf{K}_j\cdot\mathbf{r}). \tag{6}$$

Moreover, we know by Bloch's theorem that the wave function can be written in the form

$$\Psi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\textstyle\sum_j C(\mathbf{K}_j)\exp(i\mathbf{K}_j\cdot\mathbf{r}). \tag{7}$$

If we put (6) and (7) into (4), we get a standard equation for the coefficients $C(\mathbf{K}_i)$.

$$[\beta - (\mathbf{K}_i + \mathbf{k})^2]C(\mathbf{K}_i) = \textstyle\sum_j C(\mathbf{K}_j)w(\mathbf{K}_i - \mathbf{K}_j). \tag{8}$$

Equation (8) is our basic equation. It is really an infinite homogeneous set of equations in an infinite number of unknowns. If there were a single practical method of solving them, or of evaluating the infinite secular determinant that pertains to them, the problem would be closed. Of course there is no such method; but the point of this paper is that one can treat them much more efficaciously than has been done heretofore.

In this paper we mainly discuss the case $\mathbf{k}=0$; we intend to treat the general case in a later publication.

The work that follows is motivated by the following observation. We consider Eq. (8) for $k=0$. Now in Appendix I it is shown that if we define the Fourier transform $w^a(\boldsymbol{\sigma})$ of the atomic potential $v^a(r_i)$,

$$w^a(\boldsymbol{\sigma}) = \frac{1}{(2\pi)^3}\int v^a(r)\exp(i\boldsymbol{\sigma}\cdot\mathbf{r})d\mathbf{r}, \tag{9}$$

and evaluate it at $\boldsymbol{\sigma} = \mathbf{K}_j$, then it is essentially identical to $w(\mathbf{K}_j)$.

$$w^a(\mathbf{K}_j) = w(\mathbf{K}_j)/(2\pi)^3\Omega_b. \tag{10}$$

Thus for $\mathbf{k}=0$, Eq. (8) can be written

$$C(\mathbf{K}_i) = \frac{(2\pi)^3\Omega_b \sum_j C(\mathbf{K}_j)w^a(\mathbf{K}_i - \mathbf{K}_j)}{\beta - K_i^2}. \tag{11}$$

If we now imagine the lattice to expand uniformly, the points of the reciprocal lattice become closer and closer, and we can replace the summation by an integration, according to Eq. (2). Then Eq. (11) becomes ($\mathbf{K}_i$ and $\mathbf{K}_j$ pass over to continuous variables $\mathbf{K}$ and $\mathbf{K}'$)

$$C(\mathbf{K}) = \frac{\int C(\mathbf{K}')w^a(\mathbf{K} - \mathbf{K}')d\mathbf{K}'}{(\beta - K^2)}. \tag{12}$$

Now, Eq. (12) is simply the Schrödinger equation in momentum space, and like the corresponding equation in coordinate space, it is *separable* if the potential $v^a(\mathbf{r})$ to which it pertains is spherically symmetric. The fact of separability enormously simplifies the solution of the equation, for it means that instead of considering one equation in three variables, we can consider one at a time an (infinite) set of equations, but each in one variable.

One point of these remarks is that, however else one treats Eq. (11), it now appears reasonable to expand the $C(\mathbf{K}_i)$ which occurs in it in spherical harmonics,[3] for we now know that at least in the limit of large separation, this leads to an exact separation of variables. We hope, of course, that even when the separation is not large, and the equations are only "approximately separable," that even this approximate separability makes the equations easier to handle than they would be if we simply tried to solve the single equation (11) as a function of the vector variable $\mathbf{K}$.

If we expand Eqs. (11) they become a set of homogeneous equations for the radial parts of the amplitudes $C(\mathbf{K}_i)$, evaluated at the different absolute magnitudes of the reciprocal lattice vectors. The work of Sec. II is devoted to solving these equations and to investigating

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[2] When we write $\mathbf{d}_i$ and $\mathbf{K}_j$, the subscripts i and j on these *vectors* should be understood to stand for the triad of integers i_1, i_2, i_3 and j_1, j_2, j_3. This is to be contrasted later with the notation K_j, in which j stands for a single integer which labels the *magnitude* of the jth smallest reciprocal lattice vector.

[3] Actually, we shall deal with cubic lattices for which the appropriate functions are not spherical harmonics, but Kubic harmonics.

the practical questions of convergence that arise. In Sec. III we show how Eq. (11) can be used in a "tight-binding" method which has appreciable advantages over the usual method.

Before we proceed, there is one point that needs discussion. We are accustomed to expanding continuous functions of angle in spherical harmonics and using the orthogonality relations which are predicated on the fact of continuous functions. Is there any difficulty in expanding the $C(\mathbf{K}_i)$, which are *not* continuous functions, but are defined only at points of the reciprocal lattice? In fact, there is not, as we can see by introducing the basic equation (8) in a different way, a way which justifies this kind of expansion, as well as one which is interesting in its own right.

To discuss this, suppose we wanted to represent the wave function $\Psi(\mathbf{r})$ not using Fourier series, but rather writing the periodic part as a series of "orbital" functions,

$$\Psi(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})\textstyle\sum_i\psi(\mathbf{r}_i). \tag{13}$$

We introduce the Fourier transorm $\phi(\lambda)$ of the "orbital" function $\psi(\mathbf{r}_i)$,

$$\phi(\lambda)=\frac{1}{(2\pi)^3}\int\psi(r)\exp(i\lambda\cdot\mathbf{r})d\mathbf{r}, \tag{14}$$

in which, of course, λ is a continuous variable. Now we know from the theorem of Appendix I that if we set $\lambda=\mathbf{K}_j$

$$\phi(\mathbf{K}_j)=C(\mathbf{K}_j)/(2\pi)^3\Omega_b,$$

i.e., at the reciprocal lattice points, the function $\phi(\lambda)$ coincides (except for a factor) with the Fourier coefficients function $C(\mathbf{K}_j)$. But this does not tell us how to calculate the function $\phi(\lambda)$ at points other than reciprocal lattice ones. To do this, we must have some supplementary formula which enables us to calculate $\phi(\lambda)$ at all points, as a function of the continuous variable λ. We derive such a formula now.

We put Eqs. (3) and (13) into the Schrödinger equation (4) and get

$$\begin{aligned}(\nabla^2+\beta)\{\textstyle\sum_i\psi(\mathbf{r}_i)\exp[i\mathbf{k}\cdot(\mathbf{r}_i+\mathbf{d}_i)]\}\\ =[\textstyle\sum_l v^a(r_l)]\{\textstyle\sum_i\psi(r_i)\exp[ik(\mathbf{r}_i+\mathbf{d}_i)]\}.\end{aligned} \tag{15}$$

In this equation we sum over all values[2] of i. But it is clear that this equation will be satisfied if we can satisfy it for a single *arbitrary* lattice, i.e., site, if we can solve

$$\begin{aligned}(\nabla^2+\beta)\{\psi(\mathbf{r}_i)\exp[i\mathbf{k}\cdot(\mathbf{r}_i+\mathbf{d}_i)]\}\\ =[\textstyle\sum_l v^a(r_l)]\psi(\mathbf{r}_i)\exp[ik\cdot(\mathbf{r}_i+\mathbf{d}_i)].\end{aligned} \tag{16}$$

If we transform Eq. (16) to momentum space, we get the following equation for $\phi(\lambda)$:

$$\begin{aligned}&[\beta-(\lambda+\mathbf{k})^2]\phi(\lambda)\\ &\qquad=\int\phi(\boldsymbol{\sigma})w^a(\boldsymbol{\sigma}-\lambda)[\textstyle\sum_l\exp(i\boldsymbol{\sigma}\cdot\mathbf{d}_l)]d\boldsymbol{\sigma}.\end{aligned} \tag{17}$$

This equation for $\phi(\lambda)$ bears a word of comment. On the left-hand side we have $\phi(\lambda)$, a function of the continuous variable λ. The function $\phi(\boldsymbol{\sigma})$ in the integrand on the right-hand side is ostensibly also a function of the continuous variable $\boldsymbol{\sigma}$, but in reality this is not so. For, using Eqs. (1) and (10) we see that the right-hand side is nothing but

$$\textstyle\sum_j\phi(\mathbf{K}_j)w(\mathbf{K}_j-\lambda),$$

essentially the same as the right-hand side of Eq. (8). Thus Eq. (17) has to be interpreted in the following way. If in it we set $\lambda=\mathbf{K}_i$, and let $\mathbf{K}_i$ run over all reciprocal lattice vectors we get a homogeneous set of equations, identical with Eqs. (8), and the energy eigenvalues are determined by the vanishing of its (infinite) determinant. Once these eigenvalues are determined, however, and the function $\phi(\mathbf{K}_i)$ is found we can, if we want to write $\psi(r)$ in the orbital description (13), get ϕ as a function of the continuous variable λ by using Eq. (17) as a kind of interpolation formula.

II. SOLUTION OF THE EQUATIONS

A. General Discussion

In this section, we discuss in a general fashion the direct solution[4] of Eq. (8) which for the case we consider, $\mathbf{k}=0$, becomes

$$(\beta-K_i^2)C(\mathbf{K}_i)=\textstyle\sum_j C(\mathbf{K}_j)w(\mathbf{K}_i-\mathbf{K}_j). \tag{18}$$

We shall deal with a cubic space lattice; hence the reciprocal lattice is also cubic. Then, as we have mentioned, the appropriate functions for expanding the $C(\mathbf{K}_i)$ are not spherical harmonics but Kubic harmonics. This can be seen as follows. Let $\hat{R}$ be one of the rotation-inversion operations of the cubic group. Then obviously we can rewrite Eq. (18) as follows:

$$\beta C(\mathbf{K}_i)=K_i^2C(\mathbf{K}_i)+\textstyle\sum_j C(\hat{R}\mathbf{K}_j)w(\mathbf{K}_i-\hat{R}\mathbf{K}_j). \tag{19}$$

Now operate with $\hat{R}$ on this equation, and get

$$\beta C(\hat{R}\mathbf{K}_i)=K_i^2C(\hat{R}\mathbf{K}_i)+\textstyle\sum_j C(\hat{R}\mathbf{K}_j)w(\hat{R}(\mathbf{K}_i-\mathbf{K}_j)).$$

For spherically symmetric atomic potentials, w depends only on the magnitude of $\mathbf{K}_i-\mathbf{K}_j$, hence we can replace $w(\hat{R}(\mathbf{K}_i-\mathbf{K}_j))$ in the last equation by $w(\mathbf{K}_i-\mathbf{K}_j)$. We see then that if $C(\mathbf{K}_i)$ is a solution of Eq. (18) with a given energy, $C(\hat{R}\mathbf{K}_i)$ is also a solution. In other words, all the operators of the cubic group "commute with the Hamiltonian." Hence, the functions $C(K_i)$ must transform as base functions for the irreducible representations of the cubic group, i.e., as Kubic harmonics.

In Eq. (18) then, we can expand the $C(\mathbf{K}_i)$ in Kubic harmonics of a given "type."[5] For our example, we shall

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[4] An attempt to solve Eq. (18) directly as a matrix equation, but without breaking up the $C(\mathbf{K}_i)$ into radial and angular parts has been reported on briefly: P. A. Marcus and H. Schlosser, Bull. Am. Phys. Soc. 4, 276 (1959).

[5] See Appendix III for a summary of notation for Kubic harmonics.

do this for α type. We would emphasize, however, that any other type could be done as well and that the procedure is basically the same. It may be, of course, that the various convergence problems are worse with other types, but in general the convergence properties are satisfactory enough for the α type that even if they should turn out to be somewhat worse for other types, they would still be adequate. Also the α type is especially interesting in that the lowest level of this type goes over into the ground state of the isolated atom when the lattice spacing goes to infinity.

Instead of choosing some special substance and an approximate or phenomenological potential known only numerically, it is much more useful for our purposes to try to keep the work analytic as long as possible; this facilitates both the exposition of the method and the estimation of the errors in the approximations we make. To this end, we have chosen the individual potential to be an exponential one. This has the advantage that the atomic case (for S states) can be solved exactly, and the resultant wave functions and energies can be compared with the band case; this yields an illuminating comparison of the way the wave functions and energies change as the lattice is formed by bringing up the individual potentials from infinity.

We expand then the $C(\mathbf{K}_i)$ in Kubic harmonics of α type,

$$C(\mathbf{K}_i)=\sum_{l'} C_{l'}(K_i)H_{l'}{}^{(\alpha)}(\Omega_i), \quad l'=0,\ 4,\ 6,\ \cdots, \tag{20}$$

and put Eqs. (A.6) and (A.8) together to get an expansion for $w(\mathbf{K}_i-\mathbf{K}_j)$ in Kubic harmonics:

$$w(\mathbf{K}_i-\mathbf{K}_j)=\sum_{l''}\sum_{\nu}\sum_{s} w_{l''}(K_i,K_j) \times H_{l''s}{}^{(\nu)}(\Omega_i)H_{l''s}{}^{(\nu)}(\Omega_j). \tag{21}$$

Using these expansions in (18), it becomes

$$(\beta-K_i^2)\sum_{l'} C_{l'}(K_i)H_{l'}{}^{(\alpha)}(\Omega_i) =\sum_j\sum_{l'}\sum_{l''}\sum_{\nu}\sum_{s} C_{l'}(K_j)H_{l'}{}^{(\alpha)}(\Omega_j) \times w_{l''}(K_i,K_j)H_{l''s}{}^{(\nu)}(\Omega_i)H_{l''s}{}^{(\nu)}(\Omega_j). \tag{22}$$

Now we multiply Eq. (22) by $H_l{}^{(\alpha)}(\Omega_i)$ $l=0,\ 4,\ 6,\ \cdots$ and we *integrate* over the solid angle of Ω_i, i.e., we can consider for the moment, for the reasons given in Sec. I, that Ω_i is a continuous variable. We get the fundamental set of coupled equations,

$$(\beta-K_i^2)C_l(K_i)=\sum_j\sum_{l'=0,4,6\cdots} w_l(K_i,K_j) \times C_{l'}(K_j)H_{l'}{}^{(\alpha)}(\Omega_i)H_l{}^{(\alpha)}(\Omega_j). \tag{23}$$

In this equation the sum[6] over j can be considered to be a sum over all the $\mathbf{K}_j$ of a given magnitude (which sum we denote by $\sum_{\Omega_j}$) plus one over all the different magnitudes of the $\mathbf{K}_j$ (which sum we denote by $\sum_{K_j}$). Symbolically

$$\sum_j\rightarrow\sum_{K_j}\sum_{\Omega_j}. \tag{24}$$

Finally then, we can write Eq. (23) as

$$(\beta-K_i^2)C_l(K_i)=\sum_{K_j}\sum_{l'=0,4,6\cdots}^{\infty} C_{l'}(K_j)w_l(K_i,K_j) \times\left(\sum_{\Omega_j} H_{l'}{}^{(\alpha)}(\Omega_j)H_l{}^{(\alpha)}(\Omega_j)\right). \tag{25}$$

This is the basic set of homogeneous equations for the amplitudes $C_l(K_i)$.

For the numerical example we shall, for reasons discussed above, choose the exponential potential

$$v^a(r)=-b^2e^{-r/d}. \tag{26}$$

We consider a bcc lattice of lattice constant a, so the reciprocal lattice is face centered, and treat the states that become pure s states when a becomes infinite. When a is infinite, Eqs. (25) can be "truncated" without approximation, i.e., as we have pointed out before, they break up into a set of *separated* equations for the amplitudes C_0, C_4, $C_6\cdots$ and of course it is the equation for C_0 which defines the s-state wave function. In the present case, the equations are coupled, and we must make the approximation of truncating them. We shall begin as simply as possible by assuming that on the right-hand side of Eq. (25) C_0 is large and all the other C_l are small; we later check this assumption using the approximate solution for C_0 that we derive, and find that it is an excellent one. The equation for C_0 is then

$$(\beta-K_i^2)C_0(K_i) =\sum_{K_j} w_0(K_i,K_j)C_0(K_j)\sum_{\Omega_j}\left[H_0{}^{(\alpha)}(\Omega_j)\right]^2. \tag{27}$$

For the exponential potential we have from Appendix II

$$w_0(K_i,K_j)=-\frac{8\pi\Omega_b b^2d^3}{[1+d^2(K_i-K_j)^2][1+d^2(K_i+K_j)^2]}.$$

Now consider in Eq. (27) the sum over Ω_j. Since $(H_0{}^{(\alpha)})^2$ is unity, the sum is, for a given magnitude K_j, just the number of lattice vectors with that magnitude. We call this number n_j.

$$n_j=\sum_{\Omega_j}(H_0{}^{(\alpha)})^2$$

$$\equiv\text{number of lattice vectors with magnitude } K_j.$$

n_j can be calculated in a straightforward way; we outline the calculation now. For a bcc lattice with basis vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ defined by

$$\mathbf{a}_1=\tfrac{1}{2}a(-\mathbf{i}+\mathbf{j}+\mathbf{k}),\quad \mathbf{a}_2=\tfrac{1}{2}a(\mathbf{i}-\mathbf{j}+\mathbf{k}),\quad \mathbf{a}_3=\tfrac{1}{2}a(\mathbf{i}+\mathbf{j}-\mathbf{k}),$$

the basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ of the reciprocal lattice are

$$\mathbf{b}_1=a^{-1}(\mathbf{j}+\mathbf{k}),\quad \mathbf{b}_2=a^{-1}(\mathbf{i}+\mathbf{k}),\quad \mathbf{b}_3=a^{-1}(\mathbf{i}+\mathbf{j}),$$

The volume Ω_b of the unit cell of the reciprocal lattice is then $2/a^3$ and the magnitude of the reciprocal lattice vector $\mathbf{K}_j$ is

$$|\mathbf{K}_j|=2\sqrt{2}\pi\gamma/a,$$

where

$$\gamma^2=(j_1^2+j_2^2+j_3^2+j_1j_2+j_1j_3+j_2j_3).$$

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[6] This is still a vector sum, of course. That is, j stands for the triad of integers j_1, j_2, j_3. See reference 2.

We put in different integral values for j_1, j_2, j_3 to find the different magnitudes that the vector $\mathbf{K}_j$ may have. We call these magnitudes[2] K_j, and label the smallest value ($j_1=j_2=j_3=0$) by $j=1$. This is simply for convenience later in computer programming. There are twelve vectors for which $\gamma^2=1$ and hence for which $|\mathbf{K}_j|=2\sqrt{2}\pi/a$; these correspond to ($j_1$, j_2, j_3) having values (0,0,1), (0, 0, −1) (0, 1, −1) plus cyclical permutations of the numbers in parentheses. At least up to $j=18$, γ^2 increases by integral steps so we can write for the magnitudes K_j that will be of interest to us

$$K_j=(2\pi/a)[2(j-1)]^{\frac{1}{2}},\quad j=1,\,2,\,3,\,\cdots. \tag{28}$$

The number of different vectors associated with a given magnitude K_j can be counted up, with results which follow.

j	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
n_j	1	12	6	24	12	21	8	48	6	36	24	21	24	66	3	48	12	39

Now we return to Eq. (27). In it, we introduce dimensionless variables

$$x_j=K_jd,$$

and it becomes

$$(\beta d^2-x_i^2)C_0(x_i)=-16\pi(bd)^2\left(\frac{d}{a}\right)^3 \times\sum_{j=1}^{\infty}\frac{n_jC_0(x_j)}{[1+(x_i-x_j)^2][1+(x_i+x_j)^2]}. \tag{29}$$

For computation, it is convenient to write (29) in a more symmetric form. To this end, we define a new variable D_i:

$$D_i=C_0(x_i)\sqrt{n_i}, \tag{30}$$

and find that (29) can be written in the standard form for a linear eigenvalue problem

$$\sum_{j=1}^{\infty}H_{ij}D_j=\lambda D_i, \tag{31}$$

where now H_{ij} is symmetric

$$H_{ij}=H_{ji}=-16\pi(bd)^2\left(\frac{d}{a}\right)^3 \times\frac{(n_in_j)^{\frac{1}{2}}}{[1+(x_i-x_j)^2][1+(x_i+x_j)^2]}+x_ix_j\delta_{ij},$$

and

$$\lambda=\beta d^2.$$

Of course, Eq. (31) is formally of infinite order; to solve it in practice, we must truncate it. The reason we expect this to work is that, as we have mentioned, we know the qualitative behavior of the function $C_0(x_i)$: It resembles the momentum-space wave function for an isolated atom, and as such, it becomes negligibly small after some moderate value of x_i. Because of the factor $\sqrt{n_i}$, D_i decreases less rapidly for large x_i, but it decreases nonetheless and is also negligible for large values of x_i, which again suggests that we can neglect the D_i for large i.

Obviously, it would be very useful if one could estimate in advance at just what point to truncate the equations; this can be done by using the atomic momentum space function as a qualitative guide. For if it is true that the atomic function resembles $C_0(x_i)$, we have simply to look at the atomic function and find at what value of x we can consider it as negligible for practical purposes. Then, for a given lattice spacing, we ask how many values of x_i there are below this value, and this is the order of the secular equation we must solve.[7]

A remarkable feature about this procedure is that it often makes the periodic potential *easier* to solve than the isolated atom. For whereas the allowed values of x_i in the atomic case are continuously distributed, for the periodic lattice they are discrete. Moreover, successive x_i become more widely separated as the lattice spacing decreases, so that the *smaller the lattice spacing, the fewer values of x_i that we must consider*. We state this slightly differently: The periodic case differs from the atomic case in two ways. The integral equation for the atom becomes a set of linear equations for the periodic potential; this tends to make the periodic case easier to solve. On the other hand, in the periodic potential, we cannot in principle confine ourselves to only one value of l, corresponding to a single spherical harmonic, but must expand in Kubic harmonics of a given type in each of which there appears an infinite number of l values. If, however, it should turn out in practice that the values of the lattice spacing we are interested in are such that the higher order partial waves are still negligible, but at the same time we are led to a secular equation of reasonable order, then it will indeed be easier to solve the periodic potential than the atomic one. This is often so, as we shall see.

Thus the cases we must consider often divide conveniently into two. If the lattice spacing is small, the reciprocal lattice spacing is large, and we are led to secular equations of small order. When the spacing gets large, we are led back to many points and secular equations of a high order. But for the latter case, the solutions that we find are so closely approximated by the atomic wave function itself that we can, as we point out in Sec. III, use it as a variational function to good accuracy. Of course, this division is not always so neat. It will turn out that there are intermediate lattice spacings for which the equations are of uncomfortably high order, and yet the spacings are not quite large enough that the atomic functions are a good approximation. For these, the treatment can be modified so that one can still solve with high accuracy using secular

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[7] This assumes that $C_0(x_i)$ resembles the atomic function closely enough. This turns out to be so for most cases.

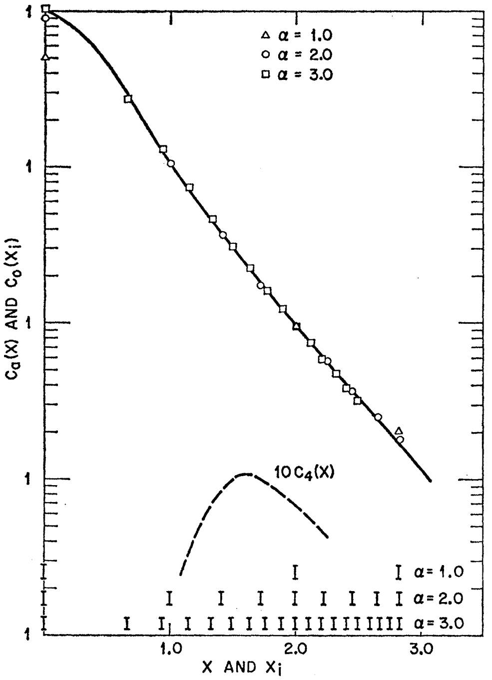

FIG. 1. Wave functions $C_0(x_i)$ for the "1S" state, the solutions of Eq. (29) for $bd=1.916$, for different values of the lattice spacing parameter $\alpha=a/\sqrt{2}\pi d$. The solid line is the momentum space radial 1S wave function $C_a(x)$ for the isolated atom. For the lattice, the wave function is defined at points $x_i=K_id$, where K_i is one of the allowed magnitudes of a reciprocal lattice vector. To show vividly how the spacing between successive x_i decreases as the lattice expands, with a consequent increase of the number of points that one must consider, we indicate the allowed values of x_i by the vertical lines at the bottom of the graph, for the three different lattice spacings. The dashed curve is the estimate from Eq. (32) of $C_4(x)$ for $\alpha=1$, which amplitude we assumed initially to be negligible. Note that $C_4(x)$ is so small that we have plotted $10C_4(x)$ to get it on the same graph with C_0.

equations of reasonable order. This is discussed in Sec. III.B and in the last section.

There is one final point that we must consider. We have neglected $C_4(K_i)$ in the above solution; it remains to estimate it. This can be done, as we have remarked before, by using Eq. (25) to roughly calculate C_4 from the (approximately) known C_0. From this equation we get, setting $l=4$ and keeping only the term with $l'=0$ on the right-hand side

$$(\beta-K_i^2)C_4(K_i)\approx\sum_{K_j} C_0(K_j)w_4(K_i,K_j)\sum_{\Omega_j} H_4^{(\alpha)}(\Omega_j).$$

If we use the expression for $w_4(K_i,K_j)$ derived in Appendix II, we get, in dimensionless variables

$$C_4(x_i)\approx-\frac{1024\pi(bd)^2}{63(\lambda-x_i^2)}\left(\frac{d}{a}\right)^3\sum_{j=1}^{\infty}\frac{x_i^4x_j^4}{(1+x_i^2+x_j^2)^6}\times C_0(x_j)\left(1+\frac{84}{11}\frac{x_i^2x_j^2}{(1+x_i^2+x_j^2)^2}+\cdots\right)\times\sum_{\Omega_j} H_4^{(\alpha)}(\Omega_j).\quad(32)$$

From this expression we see that for given bd the magnitude of C_4 is dominated by two different factors. First is the factor $(d/a)^3$ on the right-hand side. When a becomes much larger than d, that is, when the lattice spacing is such that near one site the tails of the potentials at the other sites become negligible, then C_4 becomes small. The other essential factor is the magnitude over the sum over j. This will be large if the "overlap" of $C_0(x_j)$ and $x_i^4x_j^4/(1+x_i^2+x_j^2)^6$ is large. Now for small x_j, this last factor is very *small*, so that if $C_0(x_j)$ drops rapidly to zero, the sum will be small. This will tend to be the case for the ground state and low excited states, but less so for the higher excitations for which the $C_0(x_i)$ acquire more nodes and are more extended functions.

B. Numerical Results

We shall discuss the solution of Eq. (29), for both ground and excited states, as a function of the potential strength parameter bd and of lattice spacing. To do this we have chosen three different values of bd which successively allow one, two, and three bound states for the isolated atom.

We begin with the solution for $bd=1.916$, a value which we choose because with it the wave function in coordinate space involves a Bessel function of order unity, and not the nonintegral order which occurs in general. This choice simplifies the computation of the ground-state momentum space wave function for the isolated atom, which is useful to us in that it is the solution of Eq. (29) in the limit of infinite lattice spacing; hence it gives a qualitative idea of the behavior of $C_0(x_i)$. We plot it in Fig. 1. In the same figure, we indicate the different magnitudes of the reciprocal lattice parameter $x_i=K_id$ that must be considered for three different values of the lattice spacing a. We see that for the smallest lattice spacing, we need only consider four or five values of x_i before we come to a point where the atomic function has dropped to a very small fraction of its maximum value. This suggests, as we have mentioned, that in solving Eq. (29) we can truncate it and drop all x_i greater than some x_N, thereby reducing the secular determinant to one of the Nth order. We have tried this, using the IBM 709 to find the eigenvalues and eigenfunctions of Eq. (29) for different values of N, to examine the convergence questions discussed above.[8] The results are given in Table I.

We see that out expectations are confirmed. For the smaller values of lattice spacing, we get good results by truncating at relatively small N. In fact, one can do even better than is indicated there: For small lattice spacing one can often get 1S energies accurate to a percent or so by taking only $N=2$, and solving a quadratic equation.

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[8] The programming for this was done by Mrs. Virginia Johnson, to whom I am much indebted for her help. Her program incorporated a matrix diagonalization subroutine due to Fred Quelle: Programming Note No. 16, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished).

TABLE I. The two lowest "energy" eigenvalues $\lambda=2mEd^2/\hbar^2$ of Eq. (29) for s-like states for a bcc lattice of lattice constant a, at each lattice point of which there is an exponential potential $v^a(r)=-b^2e^{-r/d}$. In the limit $a\rightarrow\infty$, i.e., for the isolated exponential potential, $\lambda=-\frac{1}{4}$. The results as a function of N are those obtained by truncating the formally infinite secular equation at that value of N. The lattice spacings a are given by $a=\alpha\sqrt{2}\pi d$, and $bd=1.916$.

		N			
α	State[a]	6	9	12	15
1.00	"1S"	−2.124024	−2.124056	−2.124064	−2.124066
	"2S"	2.47449	2.47388	2.47375	2.47372
1.500	"1S"	−0.68568	−0.68611	−0.68623	−0.68626
	"2S"	0.80590	0.80276	0.80198	0.80176
2.000	"1S"	−0.37085	−0.37356	−0.37448	−0.37474
	"2S"	0.3301	0.3227	0.3204	0.3196
2.500	"1S"	−0.2731	−0.2819	−0.2854	−0.2868
	"2S"	0.1617	0.1515	0.1477	0.1463
∞	1S	Isolated atom: −0.2500			
	2S	This state not bound for isolated atom			

[a] The quotation marks around the 1S and 2S mean that, strictly speaking, these are not pure S states, except in the limit when α becomes infinite.

The wave functions $C_0(x_i)$ that we find are plotted in Fig. 1. We would expect that for large values of x_i, which of course correspond to small spatial distances, the $C_0(x_i)$ would closely approximate to the atomic functions. As the figure shows, this turns out to be strikingly true. It is only when the energy differs by a factor of almost ten from that for the isolated atom, that the tails of the wave functions fail to fall closely on the atomic function. For the other cases it is only for the first few reciprocal lattice points that the function $C_0(x_i)$ differs from the atomic one. Potentially, this agreement makes Eq. (29) even easier to solve than we have indicated, for it is clear that for most lattice spacings only the first few values of the $C_0(x_i)$ are truly unknown. It might well be that a method could be devised that exploits this fact, although we have not pursued it any further.

TABLE II. Results for $bd=3.5001$. Other parameters and notation are the same as in Table I.

		N		
α	State	10	14	18
0.500	"1S"	−56.180585	−56.180586	−56.180586
	"2S"	5.53320	5.53316	5.53315
	"3S"	29.2382	29.2381	29.2381
1.00	"1S"	− 7.20613	− 7.20631	− 7.20634
	"2S"	− 1.3438	− 1.3457	− 1.3460
	"3S"	6.0847	6.0799	6.0794
1.50	"1S"	− 3.2782	− 3.2928	− 3.2954
	"2S"	− 1.2366	− 1.2462	− 1.2479
	"3S"	+ 2.0032	+ 1.9677	1.9620
2.00	"1S"	− 2.9673	− 3.0437	− 3.0620
	"2S"	− 0.55864	− 0.57818	− 0.58286
	"3S"	0.87105	0.79620	0.77875
∞	1S	Energy of isolated atom: − 3.0625		
	2S	Energy of isolated atom: − 0.2500		
	3S	Not a bound state for isolated atom		

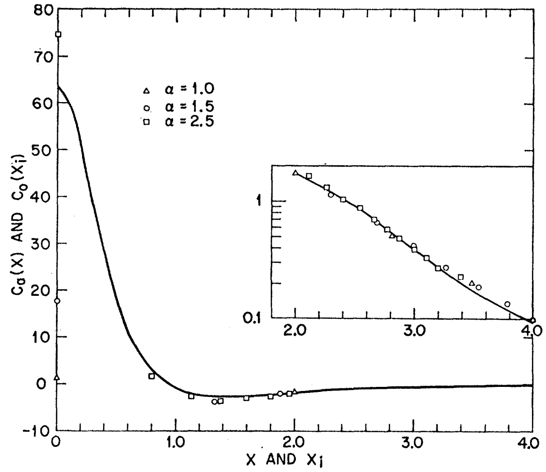

FIG. 2. Wave functions $C_0(x_i)$ for the "2S" state for $bd=3.5001$ for different values of $\alpha=a/\sqrt{2}\pi d$. The solid line is the momentum space radial wave function $C_a(x)$ for the 2S state of the isolated atom. In the inset, we replot on a semilogarithmic scale the negative of the tails of the wave functions shown on the main graph, to show how closely these tails coincide over a large range of the variable. The wave functions are not normalized.

It remains only to estimate $C_4(x_i)$. We do this for $\alpha=1$, which we expect will lead to the largest values of C_4, and hence provide us with an upper bound for the other cases. For $C_0(x_i)$ normalized to unity at $x_i=0$, we get from Eq. (32), using the parameters pertinent to this case,

$$C_4(x_i)\approx\frac{13.2x_i^4}{(x_i^2+2.12)(5+x_i^2)^6}.$$

This function is plotted (for convenience as a continuous function of x_i) in Fig. 1, where we see it is very small indeed compared with C_0.

We now consider a stronger potential, $bd=3.5001$, for which value the isolated atom has *two* bound states. Similarly to the last section, we study how the energies and the wave functions of these states change as the lattice is built up from atomic potentials. We have again solved the truncated Eq. (29), this time for values of N equal to 10, 14, 18. The results are given in Table II.

Table II is like Table I and is self-explanatory, so we shall concentrate on discussing the wave function. Moreover, the results for the 1S wave function as compared to the atomic function are so similar to those for the previous case, $bd=1.916$, that we omit them here and give instead the results for the 2S state. In Fig. 2 then, we plot the atomic wave function $C_a(x)$ and the corresponding functions $C_0(x_i)$ for various values of α, the lattice parameter spacing. As expected, for large α the $C_0(x_i)$ agree fairly closely everywhere with the atomic function evaluated at the appropriate points, but as α gets smaller, they begin to differ appreciably for small values of x_i. On the other hand, for large values of the

TABLE III. Results for $bd=5.500$. Other parameters and notation are the same as in Table I.

		N		
α	State	10	14	18
0.500	"1S"	-138.7275	-138.7275	-138.7275
	"2S"	-10.0708	-10.0712	-10.0713
	"3S"	23.4124	23.4108	23.4107
	"4S"	32.1528	32.1513	32.1512
1.000	"1S"	-18.211	-18.215	-18.216
	"2S"	-10.178	-10.213	-10.218
	"3S"	$+0.10512$	$+0.005789$	-0.007512
	"4S"	7.1985	7.1594	7.1544
1.500	"1S"	-11.68	-11.95	-12.02
	"2S"	-4.732	-4.868	-4.908
	"3S"	-1.611	-1.923	-1.998
	"4S"	2.963	2.685	2.596
∞	$1S$	Energy of isolated atom:		-11.98
	$2S$	Energy of isolated atom:		-3.84
	$3S$	Energy of isolated atom:		-0.616
	$4S$	Not a bound state for isolated atom		

x_i the tails of the functions remain strikingly similar. This cannot be seen readily on the linear plot which it is necessary to use for the $2S$ function (which changes sign), so we have plotted these separately on a semi-logarithmic scale. We see that even for lattice spacings which correspond to energies almost ten times that of the isolated atom, the tails of the wave functions differ at most by a few percent over a range in which the function itself changes by a factor of 50. A rough calculation of the amplitude C_4 analogous to that for $bd=1.916$ indicates that for the values of α we consider it is negligible for our purposes.

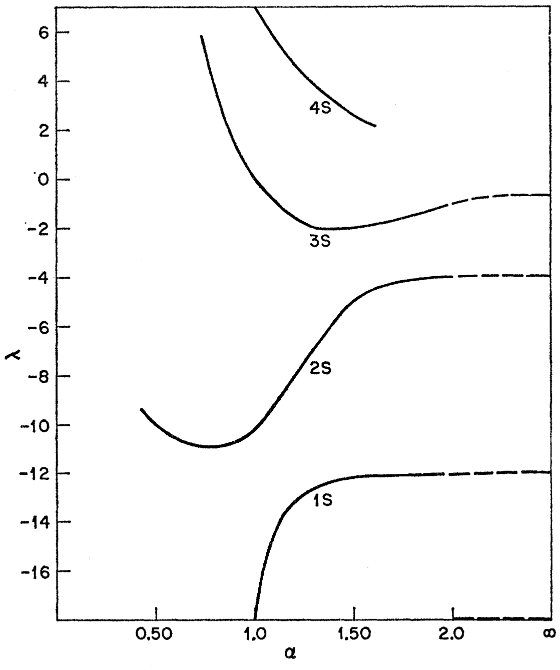

FIG. 3. "Energy" eigenvalues $\lambda=2mEd^2/\hbar^2$ of the first four "s" states as functions of the lattice spacing parameter $\alpha=a/\sqrt{2}\pi d$ for $bd=5.500$. The atomic energies ($\alpha\rightarrow\infty$) are also indicated.

Finally, we give results in Table III for the solution of Eq. (29) for $bd=5.5000$, a value which allows three bound S states for the isolated atom.

The results are similar[9] to the previous cases, but there is one new feature. The eigenvalues for the $3S$ state for $\alpha=1$ converge less well than the others. This seems to be connected with the fact that the eigenvalue is quite close to zero.

We represent these results graphically in Fig. 3, where we plot energy versus α; in these graphs we have used more points than given in Table III. It is interesting to plot the results for the wave functions as well, and we do this in Fig. 4. The $1S$ and $2S$ functions are similar to those we have presented previously, so for clarity we present only the $3S$ and $4S$ functions.

From Table III we see that for the larger values of α and higher states (e.g., the $3S$ and $4S$ states for $\alpha=1.500$) we begin to run into poor convergence as a function of N. We would like to present a proposal here which may overcome this difficulty, and enable us to increase the accuracy for the states for which we have already calculated, and also to calculate still higher states.

This proposal is based on the fact, which was quite unexpected, that all the oscillations in the functions C_0 occur for the first few K_m; after that they are smooth, monotonically decreasing functions. Now as we have observed, the points K_m get closer and closer together as m gets larger, so that after some moderate N we gain accuracy very slowly by increasing N. That is, to increase the accuracy appreciably we must calculate accurately the long tails of the wave functions, and when N gets large a given increase in the number of points takes us relatively less far out on the tails.

The point we wish to make is that it is really unnecessary to suffer this disadvantage that successive x_i get closer and closer for large i. For in order to define the shape of the tails to good accuracy we do not really need the x_i spaced so closely. If we had values of x_i which are not successive ones, but are such that there is moderate variation of the function between them, then we could find the intermediate values of x_i by interpolation. This idea, as applied to Eq. (29), suggests that we do not consider all possible x_i as the unknowns in this equation. Rather, it suggests that we first consider enough values of i to take us past the nodes of the function we seek, and then for larger i we consider as unknowns not *successive* x_i but a selected set which are farther apart, but not so far that we cannot interpolate satisfactorily between them. Having done this we must write the sum on the right-hand side in terms of the chosen set of x_i and their interpolated values, and doing this we are led back to a homogeneous set of equations with a square matrix, which we must solve numerically,

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[9] In calculating these eigenvalues we have again assumed C_4 is negligible.

but whose solution will define the wave function out to long distances in momentum space.

III. A VARIATIONAL METHOD—"TIGHT BINDING"

As we have seen, when the lattice spacing gets large and the reciprocal lattice points get close, the order of secular equation that must be solved gets impractically large. On the other hand, in this limit the eigenvalues and eigenfunctions approach the atomic ones; it is then an obvious course to try to exploit this, and to use the atomic functions as trial or variational functions. This is not a new idea, of course; it is essentially the well-known "tight-binding" approximation, as applied for $\mathbf{k}=0$. But we shall see that, in practice, the present formalism has appreciable advantages over the conventional scheme.

The equation we need for the variational formalism is derived directly from Eq. (8). Actually, it is as easy to write down for general $\mathbf{k}$, so we shall do that, although in this paper we shall only *apply* it for $\mathbf{k}=0$. Equation (8) shows that if $C(\mathbf{K}_i)$ is an eigenfunction, we can calculate β from[10]

$$\beta=\frac{\sum_i C^2(\mathbf{K}_i)(\mathbf{K}_i+\mathbf{k})^2+\sum_i\sum_j C(\mathbf{K}_i)C(\mathbf{K}_j)w(\mathbf{K}_i-\mathbf{K}_j)}{\sum_i C^2(\mathbf{K}_i)}. \tag{33}$$

If $C(\mathbf{K}_i)$ is not the exact eigenfunction, then the above expresssion for β has variational properties,[10] i.e., if we put into it a $C(\mathbf{K}_i)$ correct to "first order" then the value of β we calculate is good to "second order." This property follows essentially from the fact that the numerator in Eq. (33) is symmetric with respect to the interchange of i and j; this fact is obvious if we write the first term in the form

$$\sum_i\sum_j C(\mathbf{K}_i)C(\mathbf{K}_j)(\mathbf{K}_i+\mathbf{k})\cdot(\mathbf{K}_j+\mathbf{k})\delta_{ij}.$$

The double sum in Eq. (33) can be simplified considerably if we break up the sum over $\mathbf{K}_i$ in the manner expressed by Eq. (24), and use a theorem about the product of two Kubic harmonics summed over the reciprocal lattice. We derive this theorem now.

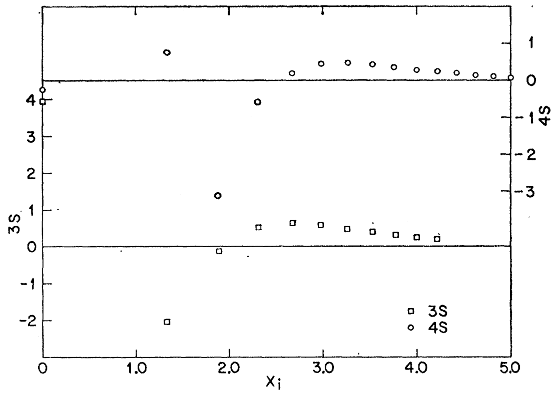

FIG. 4. The wave functions $C_0(x_i)$ for the $3S$ and $4S$ states for $bd=5.5000$ and $\alpha=1.50$.

Consider the sum σ defined by

$$\sigma=\sum\nolimits_{\Omega_i} H_{ls}{}^{(\nu)}(\Omega_i)H_{l's'}{}^{(\nu')}(\Omega_i).$$

Instead of writing σ as a sum over Ω_i, we observe that it is proportional to a sum over the group operations, a representative one of which we call $\hat{G}$. Thus

$$\sigma\propto\sum\nolimits_G[\hat{G}H_{ls}{}^{(\nu)}(\Omega_i)][\hat{G}H_{l's'}{}^{(\nu')}(\Omega_i)].$$

But we know that $\hat{G}$ operating on H_{ls} generates a linear combination of Kubic harmonics of the same order and type

$$\hat{G}H_{ls}{}^{(\nu)}=\sum\nolimits_t G_{st}{}^{(\nu)}H_{lt}{}^{(\nu)},$$
$$\hat{G}H_{l's'}{}^{(\nu')}=\sum\nolimits_{t'} G_{s't'}{}^{(\nu')}H_{l't'}{}^{(\nu')},$$

so we can write

$$\sigma\propto\sum\nolimits_t\sum\nolimits_{t'} H_{lt}{}^{(\nu)}H_{l't'}{}^{(\nu')}\sum\nolimits_G G_{st}{}^{(\nu)}G_{s't'}{}^{(\nu')}.$$

But according to one of the basic orthogonality relations of group theory, this last sum over G vanishes unless $\nu=\nu'$: the sum σ is identically zero unless both Kubic harmonics that enter into it are of the same type.

We apply these results (now we set $\mathbf{k}=0$) to the S-like states we have discussed in the previous sections. The variational wave function is then just the atomic momentum space radial wave function $C_a(K)$, evaluated at appropriate K_i. If we put this into (33) and use the expansions (A.6) and (A.8) we get

$$\beta=\Big[\sum_{K_i} C_a{}^2(K_i)K_i{}^2n_i+\sum_{K_i}\sum_{K_j}\sum_{\Omega_i}\sum_{\Omega_j} C_a(K_i)C_a(K_j)\sum_{l=0}^{\infty} w_l(K_i,K_j)\sum_{s,\nu} H_{ls}{}^{(\nu)}(\Omega_i)H_{ls}{}^{(\nu)}(\Omega_j)\Big]\Big/\sum_{K_i} C_a{}^2(K_i)n_i. \tag{34}$$

Now the sum over Ω_i of $H_{ls}{}^{(\nu)}(\Omega_i)$ [which we can consider to be the sum over Ω_i of the product $H_{ls}{}^{(\nu)}(\Omega_i)H_0{}^{(\alpha)}(\Omega_i)$] is, from the theorem above, zero unless the type ν is the type α. But α-type harmonics only occur for $l=0, 4, 6, \cdots$ so this breaks up the sum over l and we can write

$$\beta=\Big[\sum_{K_i} C_a{}^2(K_i)K_i{}^2n_i+\sum_{K_i}\sum_{K_j} C_a(K_i)C_a(K_j)\sum_{l=0,4,6,\cdots} w_l(K_i,K_j)H_l{}^{(\alpha)}(\Omega_i)H_l{}^{(\alpha)}(\Omega_j)\Big]\Big/\sum_{K_i} C_a{}^2(K_i)n_i. \tag{35}$$

It is interesting to compare this formula for the energy with the analogous one for the atomic s state for which

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[10] Equation (33) is, of course, just the momentum space counterpart of $E=\int\Psi^*H\Psi d\tau/\int\Psi^*\Psi d\tau$, and can be directly derived from this last equation using the formulas of Sec. I.

$C_a(K)$ is the solution. The latter is

$$\beta=\left[\int_0^\infty C_a^2(K)K^2dK+\int_0^\infty\int_0^\infty C_a(K)C_a(K')w_0^a(K,K')K^2K'^2dKdK'\right]\Big/\int_0^\infty C_a^2(K)K^2dK. \tag{36}$$

To give an idea of the accuracy to be had from Eq. (35) we have applied it to the $1S$ states for $bd=1.916$, for which we have the "exact" results of Table I. Using the atomic function plotted in Fig. 1, we get for $\alpha=1.000$ the value $\beta d^2=-2.119$, to compare with the exact result -2.124. For $\alpha=1.500$ the variational result is -0.6812 and the exact one -0.6863.

The above treatment runs into difficulty when the unperturbed atomic state is degenerate, since it is then not clear which of the unperturbed degenerate functions to use as a variational function. To resolve this, it is useful to regard this calculation in another way, not as a variational one but as a perturbation one. To do this, we write the Schrödinger equation (12) for the isolated atom as a matrix equation for a (continuous) matrix $\mathbf{H}_a(\mathbf{K},\mathbf{K}')$ and a column vector $C(\mathbf{K})$:

$$\mathbf{H}_a(\mathbf{K},\mathbf{K}')\mathbf{C}(\mathbf{K}')=\beta\mathbf{C}(\mathbf{K}),$$

where

$$\mathbf{H}_a(\mathbf{K},\mathbf{K}')=\mathbf{K}\cdot\mathbf{K}'\delta(\mathbf{K}-\mathbf{K}')+w^a(\mathbf{K}-\mathbf{K}')$$

and the subscript a stands for atomic. Similarly, we can write the equation for the periodic potential as

$$\mathbf{H}_p(\mathbf{K}_i,\mathbf{K}_j)C(\mathbf{K}_j)=\beta C(\mathbf{K}_i),$$

where

$$\mathbf{H}_p(\mathbf{K}_i,\mathbf{K}_j)=\mathbf{K}_i\cdot\mathbf{K}_j\delta(\mathbf{K}_i-\mathbf{K}_j)+(2\pi)^3\Omega_bw^a(\mathbf{K}_i-\mathbf{K}_j).$$

Now we write[11]

$$\mathbf{H}_p=\mathbf{H}_a+(\mathbf{H}_p-\mathbf{H}_a).$$

When the lattice spacing gets large, $(\mathbf{H}_p-\mathbf{H}_a)$ gets small, and we can consider it as a perturbation on the unperturbed Hamiltonian $\mathbf{H}_a$. Of course, the variational calculation done above is, from this point of view, simply first-order perturbation theory as applied to $\mathbf{H}_p-\mathbf{H}_a$.

This observation makes it clear how to handle the degenerate case. An atomic eigenfunction of energy E_0,

$$C_l(K)Y_{lm}(\Omega_k)$$

is $(2l+1)$-fold degenerate. This degeneracy is split up, at least partially, in the crystal, and to calculate how it is we must solve the secular equation for the perturbation theory of degenerate states. For this case it becomes

$$|H_{st}-(E_0-E)\delta_{st}|=0,$$

where a typical matrix element is

$$H_{mm'}=\sum_i\sum_j C_l(K_i)Y_{lm}(\Omega_i)\times H_p(\mathbf{K}_i,\mathbf{K}_j)C_{lm'}(K_j)Y_{lm}^*(\Omega_j).$$

This sum can be simplified in practice by using the theorem above on the product of two Kubic harmonics when summed over the lattice, and the secular equation will, of course, factor in many cases into equations of smaller order.

We end with a brief comment on the method of this section: It is a variational method which uses the free-atom solutions to calculate an approximate value for the energy, and as such, it is in the same spirit as the usual tight-binding approximation. That approximation is bedeviled by the fact that to apply it, one must calculate a difficult succession of overlap integrals. But in the formulation above, all these integrals are effectively done automatically, when we sum as indicated over the magnitudes K_i. The only approximation we use is to take the atomic functions as the variational functions.

IV. FINAL COMMENTS

In this section we make a few remarks on the method as we have presented it, and on possible generalizations.

First, it may be worth pointing out that our results for a single exponential above can be extended, without further analytic work, to any potential which can be represented as the sum of exponential potentials, for in that case the function $w(\mathbf{K}-\mathbf{K}')$ and related ones will simply be sums of the functions we have evaluated for a single exponential.

In this paper we have found, as we would expect, that the convergence problems get worse and the accuracy poorer as we consider higher and higher excited states. The problem is essentially that the tails of the wave functions become very long, and superficially at least, this demands high-order secular equations. Here we would simply call attention to the remarks at the end of Sec. II.B, where we suggest a way for overcoming this difficulty, since we feel they show good promise of enabling us to calculate high S states (and other states as well) without being driven to secular equations of impractically large order.

In the last analysis, the method we present in this paper is an expansion of the wave functions in plane waves with amplitudes $C(\mathbf{K}_i)$. One may well ask why it is advantageous to expand the wave function in just the way we have done, that is, by separating the $C(\mathbf{K}_i)$ into radial and angle-dependent parts. The answer is that this is the only way that takes full advantage of all the symmetries present in the problem. These are the translational symmetry of the lattice, the rotation-inversion symmetry of the lattice as a whole, *and* the rotational symmetry of the individual potentials. Now one can take the first two symmetries into account by writing the wave function in Bloch form and expanding

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[11] There is a possible formal objection here in that the $C(\mathbf{K})$ for the atom and the $C(\mathbf{K}_i)$ for the periodic potential are not in the same Hilbert space, but this causes no real difficulty.

the wave function in symmetrized plane waves without breaking the $C(\mathbf{K}_i)$ into radial and angle-dependent parts. This has the disadvantage that one cannot make the natural separation of the $C(\mathbf{K}_i)$ into large and small radial parts, i.e., one cannot drop the small partial waves of high order. For example, as we have pointed out in the text, if one does not make this separation, one is essentially trying, in the limit of large lattice spacing, to solve a spherically symmetric problem without making the crucial simplifying step of separating variables.

In the present method, which does take this crucial step, one tends to have advantages always compensating disadvantages. Thus when the lattice spacing gets large, there is the computational disadvantage that the reciprocal lattice points get close, but this is compensated for by the fact that we have to take into account essentially only one partial wave, whose form we know pretty well from the atomic solution. When the lattice spacing gets small, it may well be (especially for other than S waves) that we have to consider simultaneously coupled equations for partial wave amplitudes, but this is compensated for by the fact that the reciprocal lattice points get farther apart, tending to make for secular equations of smaller order.

APPENDIX I. RELATION BETWEEN ORBITAL AND FOURIER REPRESENTATION OF A PERIODIC FUNCTION

Suppose we have a function $f(\mathbf{r})$ which is periodic with the periodicity of the lattice. We can then express it in two different ways. First, we can write it as an infinite series of "orbitals"

$$f(\mathbf{r})=\sum_i f_o(\mathbf{r}_i), \tag{A.1}$$

the subscript "o" standing for "orbital," this being a function which obviously has lattice periodicity. Alternatively, we can express it as a Fourier series in reciprocal space

$$f(\mathbf{r})=\sum_j g(\mathbf{K}_j)\exp(i\mathbf{K}_j\cdot\mathbf{r}). \tag{A.2}$$

There is a relation between these two superficially different ways of writing the same function. To show this, we Fourier-transform each of the orbital functions

$$f_o(\mathbf{r}_i)=\int g_o(\boldsymbol{\sigma})\exp(i\boldsymbol{\sigma}\cdot\mathbf{r}_i)d\boldsymbol{\sigma}, \tag{A.3}$$

$$g_o(\boldsymbol{\sigma})=\frac{1}{(2\pi)^3}\int f_o(\mathbf{r}_i)\exp(-i\boldsymbol{\sigma}\cdot\mathbf{r}_i)d\mathbf{r}_i. \tag{A.4}$$

Putting (A.3) into (A.1) and using $\mathbf{d}_i+\mathbf{r}_i=\mathbf{r}$, we get

$$f(\mathbf{r})=\int g_o(\boldsymbol{\sigma})\exp(i\boldsymbol{\sigma}\cdot\mathbf{r})\big(\sum_i\exp(-i\boldsymbol{\sigma}\cdot\mathbf{d}_i)\big)d\boldsymbol{\sigma}.$$

But using Eq. (1) of the text this is

$$f(\mathbf{r})=(2\pi)^3\Omega_b\sum_j g_o(\mathbf{K}_j)\exp(i\mathbf{K}_j\cdot\mathbf{r}),$$

from which we conclude that

$$g(\mathbf{K}_j)=(2\pi)^3\Omega_b g_o(\mathbf{K}_j). \tag{A.5}$$

APPENDIX II. CALCULATION OF $w(\mathbf{K}-\mathbf{K}')$ AND $w_l(\mathbf{K},\mathbf{K}')$

We have from Eqs. (9) and (10) of the text

$$w(\mathbf{K}-\mathbf{K}')=\Omega_b\int v^a(r)\exp[i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}]d\mathbf{r}$$

$$=4\pi\Omega_b\int_0^\infty v^a(r)j_0(|\mathbf{K}-\mathbf{K}'|r)r^2dr.$$

We use the addition theorem for $j_0(|\mathbf{K}-\mathbf{K}'|r)$ to get

$$w(\mathbf{K}-\mathbf{K}')=\sum_{l=0}^{\infty}(2l+1)w_l(K,K')P_l(\cos\gamma), \tag{A.6}$$

where

$$w_l(K,K')=4\pi\Omega_b\int_0^\infty v^a(r)j_l(Kr)j_l(K'r)r^2dr. \tag{A.7}$$

For the exponential potential

$$v^a(r)=-b^2e^{-r/d}$$

we then have

$$w_l(K,K')=-4\pi b^2\Omega_b\int_0^\infty e^{-r/d}j_l(Kr)j_l(K'r)r^2dr$$

$$=4\pi b^2\Omega_b(\partial I_l/\partial\zeta)_{\zeta=1/d},$$

where

$$I_l=\int_0^\infty e^{-\zeta r}j_l(Kr)j_l(K'r)rdr.$$

The integral I_l is a standard one[12]:

$$I_l=(1/2KK')Q_l(y),$$

where $y=(\zeta^2+K^2+K'^2)/2KK'$ and where $Q_l(y)$ is the Legendre polynomial of the second kind. The first few polynomials are (for $y>1$)

$$Q_0=\tfrac{1}{2}\ln[(y+1)/(y-1)],$$
$$Q_1=yQ_0(y)-1,$$
$$Q_2=P_2(y)Q_0(y)-3y/2,$$
$$Q_3=P_3(y)Q_0(y)-5y^2/2+2/3,$$
$$Q_4=P_4(y)Q_0(y)-35y^3/8+55y/24.$$

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[12] P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 1575.

From the expression for Q_0 we find

$$w_0(K,K')=-\frac{2\pi b^2 d\Omega_b}{KK'}\times\left(\frac{1}{1+d^2(K-K')^2}-\frac{1}{1+d^2(K+K')^2}\right).$$

From the expression above for Q_4, we could of course write down a similar formula for the function $w_4(K,K')$ which is needed in the text, but it is a fairly clumsy expression. More suitable for our purposes is a series expansion which can be got by expanding $\ln[(y+1)/(y-1)]$ in the expression for Q_4 in powers of $1/y$,

$$Q_4(y)=\frac{8}{5\times 7\times 9}\left[\frac{1}{y^5}+\frac{15}{11y^7}+\cdots\right].$$

This leads to

$$w_4(K,K')=-\left(\frac{1024\pi b^2 d^3\Omega_b}{63}\right)\frac{(Kd)^4(K'd)^4}{[1+(K^2+K'^2)d^2]^6}\times\left\{1+\frac{84}{11}\frac{(Kd)^2(K'd)^2}{[1+(K^2+K'^2)d^2]^2}+\cdots\right\}.$$

APPENDIX III. KUBIC HARMONICS

We introduce a notation for the Kubic harmonics, which generically we call $H(\Omega)$. There are ten types corresponding to the ten different classes of operations of the cubic group. To keep to a minimum the number of numerical superscripts and subscripts, we label the types with the original notation of Van der Lage and Bethe,[13] i.e., as α, β, γ, δ, ϵ, α', β', γ', δ', ϵ'. The type label is put as a superscript and the order as subscript. For example, the function α_l in the original notation becomes $H_l{}^{\alpha}$:

$$\alpha_l\rightarrow H_l{}^{(\alpha)}.$$

If a function is one of a degenerate set, we add an additional subscript s, which takes the value 1 or 2 for doubly degenerate functions, and 1, 2, or 3 for triply degenerate, with the connection x, y, $z\rightarrow 1$, 2, 3. Strictly, s should have a subscript ν attached to it, to show that it takes on different sets of values, according to the type (ν) of the Kubic harmonic, but it is easier to simply bear this fact in mind than to continually write subscripts of subscripts. If there is more than one function of a given type and given order, we put a prime over the *order* number. Examples of the correspondence between the notation of Van der Lage and Bethe and the present one are

$$(\gamma_6)_1\rightarrow H_{61}{}^{(\gamma)},\quad(\delta_5)_z\rightarrow H_{53}{}^{(\delta)},\quad(\delta_{5'})_z\rightarrow H_{5'3}{}^{(\delta)}.$$

Finally, we write the analog for Kubic harmonics of the addition theorem of spherical harmonics. If γ is the angle between a vector specified in a spherical coordinate system by θ, ϕ (which we jointly symbolize as Ω) and one specified by θ', ϕ' (Ω'), then

$$P_l(\cos\gamma)=\frac{1}{2l+1}\sum_{\nu,s}H_{ls}{}^{(\nu)}(\Omega)H_{ls}{}^{(\nu)}(\Omega').\qquad\text{(A.8)}$$

The summation over ν is taken over all types which contain Kubic harmonics of order l, and the summation over s is taken over all the degenerate functions which may belong to a given type and order. For example, we have

$$P_0(\cos\gamma)=H_0{}^{(\alpha)}(\Omega)H_0{}^{(\alpha)}(\Omega')\equiv 1,$$

$$P_1(\cos\gamma)=\tfrac{1}{3}\sum_{s=1}^{3}H_{1s}{}^{(\delta)}(\Omega)H_{1s}{}^{(\delta)}(\Omega'),$$

$$P_2(\cos\gamma)=\tfrac{1}{5}\Big(\sum_{s=1}^{3}H_{2s}{}^{(\epsilon)}(\Omega)H_{2s}{}^{(\epsilon)}(\Omega')+\sum_{s=1}^{2}H_{2s}{}^{(\gamma)}(\Omega)H_{2s}{}^{(\gamma)}(\Omega')\Big).$$

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[13] F. C. Van der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).