Wannier Functions in a Simple Nonperiodic System

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(Received 16 March 1973)

This paper defines and analyzes in detail the Wannier functions a_l of a one-dimensional periodic lattice with a point defect. It is shown that these functions have exactly the same exponential localization as the Wannier functions of the perfect lattice and that they approach the latter exponentially as the site l recedes from the defect site. Variational methods for the calculation of the a_l are described. Eigenfunctions of the system can be obtained from the a_l by the solution of a one-band Slater-Koster-type equation, which, however, is exact in the present theory. Moments of the density of states can be obtained directly from the a_l without calculation of the eigenfunctions; so can the total electron density, $n(\mathbf{r})$, corresponding to a full "band." It is suggested that for a nonperiodic system the Wannier functions may be easier to compute directly than the eigenfunctions.

I. INTRODUCTION

The eigenfunctions of the Schrödinger equation with a periodic potential are the Bloch waves $\varphi_k^0(x)$, characterized by the wave number k and a band index. (The superscript signifies the perfectly periodic lattice, and we do not explicitly indicate the band index.) They extend quasiperiodically through the entire system. An equivalent set of functions, arising from the φ_k^0 by a unitary transformation, are the Wannier functions[1] $a_l^0(x) \equiv a^0(x - lb)$, exponentially localized[2-5] near the atomic sites lb ($l = 0, \pm 1, \pm 2, \ldots$). A serious drawback is that these functions are not eigenfunctions of the Hamiltonian. However, their localized nature has nevertheless made them useful for many theoretical discussions.[6]

When the periodicity of the potential is lost, as by the presence of an isolated defect or a surface, or in a disordered solid, the eigenfunctions are of course no longer of the quasiperiodic or Bloch character; rather, they typically include localized bound states as well as extended scattering states. It has generally been assumed that also in such nonperiodic systems there exists a complete set of well-localized Wannier functions $a_l(x)$, equivalent to the now rather complicated eigenfunctions. However, the existence and properties of these functions have not been hitherto demonstrated. Neither has there been available a constructive method for computing them.

The present paper deals with what is perhaps the simplest system with impaired periodicity, a one-dimensional periodic lattice with an isolated impurity at the origin. For this system we can rigorously establish the following results (Secs. II–IV). Let h^0 be the constant which determines the exponential decay of the Wannier functions $a_l^0(x)$ of the perfect lattice in the sense that

$$\lim_{|x-lb|\to\infty} e^{h|x-lb|} a_l^0(x) = 0, \quad h < h^0. \tag{1.1}$$

Then there exists a set of real orthonormal Wannier functions for the perturbed lattice $a_l(x)$ which has exactly the same degree of localization,

$$\lim_{|x-lb|\to\infty} e^{h|x-lb|} a_l(x) = 0, \quad h < h^0, \tag{1.2}$$

as the perfect-lattice Wannier functions. (The intuitive feeling that their range could be of the order of the bound-state range is thus not correct.) As $l \to \infty$, these perturbed Wannier functions approach those of the perfect lattice in the following exponential manner. For fixed $x - lb$,

$$\lim_{|l|\to\infty} e^{2h|l|b} [a_l(x) - a_l^0(x)] = 0, \quad h < h^0. \tag{1.3}$$

Thus only a small number of perturbed Wannier functions will differ significantly from those of the unperturbed lattice.

In Sec. V we describe a variational method for finding the a_l, without prior knowledge of the eigenstates.

Section VI deals with applications. We show how the eigenfunctions can be calculated in terms of the a_l. This procedure is similar to the one-band Slater-Koster method but, unlike the latter, is exact. Next, we show how one can obtain directly from the a_l (and without need of the eigenfunctions) the total electron density $n(\vec{\mathbf{r}})$ for a full "band," and the moments of the density of states $n(E)$.

We have shown in the present paper that the Wannier function $a_l(x)$ depends only on the immediate vicinity of the site lb where it is localized. For this reason we believe that *in the case of nonperiodic systems Wannier functions may be easier to compute than the eigenfunctions* in which the influence of a disturbance makes itself felt over large distances. Thus Wannier functions may well become increasingly useful in theories and computations relating to systems which have lost their full periodicity such as defects in crystals, surfaces, and disordered solids.

II. FORMULATION OF PROBLEM

We consider electrons in a one-dimensional perturbed periodic lattice, with Hamiltonian

$$H = -\frac{d^2}{dx^2} + V(x) + v(x); \tag{2.1}$$

here $V(x)$ is a periodic potential with the periodicity and symmetry properties

$$V(x+b) = V(x), \tag{2.2}$$

$$V(-x) = V(x); \tag{2.3}$$

and $v(x)$ is the perturbing impurity potential which also has the inversion symmetry (2.3) and is localized in the central cell, i.e.,

$$v(x) \equiv 0, \quad |x| \geq \tfrac{1}{2}b. \tag{2.4}$$

The system is taken to extend over the interval

$$-\tfrac{1}{2}d \leq x \leq \tfrac{1}{2}d \quad (d = Nb; \ N \text{ even}; \ N \gg 1). \tag{2.5}$$

(See Fig. 1.)

The eigenfunctions $\varphi(x)$ are required to satisfy the differential equation

$$H\varphi(x) = E\varphi(x) \tag{2.6}$$

and the conventional periodic boundary conditions

$$\varphi(\tfrac{1}{2}d) = \varphi(-\tfrac{1}{2}d); \quad \varphi'(\tfrac{1}{2}d) = \varphi'(-\tfrac{1}{2}d). \tag{2.7}$$

For a perfect lattice, $v \equiv 0$, these eigenfunctions are the Bloch waves

$$\varphi^0_{n,k}(x),$$

where

$$k = (2\pi/d)[-\tfrac{1}{2}N, \ \ldots, \ 0, \ \ldots, \ (\tfrac{1}{2}N - 1)] \tag{2.8}$$

and n is the band index. The corresponding eigenvalues $E^0_{n,k}$ are grouped in quasicontinuous energy bands, each containing N levels. [See Fig. 2(a).]

We now consider the perturbing potential $v(x)$, gradually being switched on. For definiteness we shall think of it as attractive. We shall also concentrate on the energy levels associated with the lowest band, $n = 0$, and from here on drop the subscript n. To simplify our proofs, we assume that the perturbing potential is not too strong. Specifically we assume that only one bound state exists below the lowest band; that no bound state is split off from the second band; and that the distance of the bound-state pole from the real k axis is smaller than that of the branchpoints connecting the lowest two bands of the perfect lattice. (See Appendices A and B.) Then, as v is switched on, the lowest-energy state of the original band splits off downwards and becomes a localized impurity state φ_0 of energy ϵ_0. See Fig. 2(b), for $N = 6$. When $N \to \infty$, φ_0 tends to the bound state φ_B, and ϵ_0 to the isolated bound-state eigenvalue ϵ_B. The other $(N-1)$ states, φ_ν, become scattering states whose energy shifts approach zero as $N \to \infty$.[7]

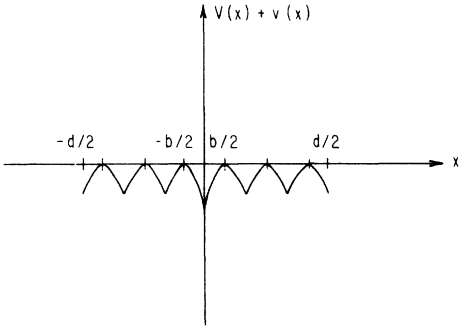

FIG. 1. Schematic plot of the potential $V(x) + v(x)$ vs x for a periodic lattice with an impurity at the center.

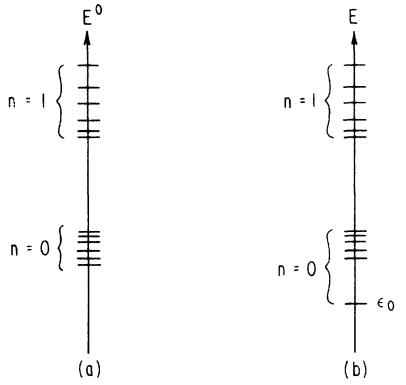

FIG. 2. Schematic plot of energy levels for $d = 6b$ for (a) periodic lattice and (b) periodic lattice with impurity at the center. (ϵ_0 is the binding energy for the impurity bound state.)

It is our primary aim to prove that the bound state φ_B and scattering states φ_ν, arising from the Bloch states of the lowest band of the perfect lattice, are equivalent, through a unitary transformation, to a set of real well-localized Wannier-like basis functions $a_l(x)$ with the properties described in Eqs. (1.2) and (1.3).

III. PROJECTION OPERATOR

Our procedure for constructing and establishing the properties of the new localized basis functions will make use of an earlier study by one of us[2] of the analytic properties of Bloch waves and Wannier functions, and of the concept of a projection operator as introduced by Des Cloizeaux[3-5] in his work on Wannier functions.

To relate the present impurity problem to this earlier work on periodic lattices, we repeat the one-impurity system of Sec. II over the entire x axis, resulting in a superlattice of unit-cell dimension d. This superlattice has the energy-band structure shown in Fig. 3. All levels which are

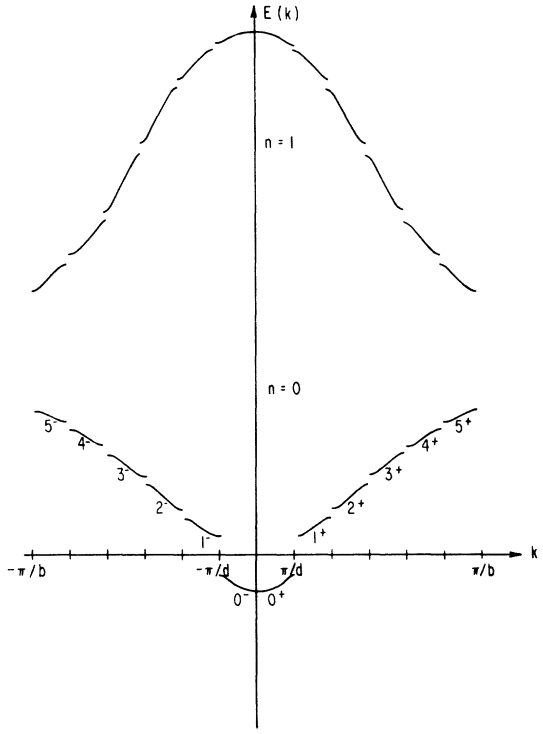

FIG. 3. Schematic plot of the splitting of the $n=0$ and $n=1$ energy bands of the perfect lattice, due to the addition of impurities. ($d=6$ b). The notation 0^+ refers to the + side of the band $m=0$, etc.

shown arise out of the original $n=0$ and 1 bands of the periodic lattice.[7] The periodic array of impurities produces a well-separated and narrow impurity band as well as a sequence of other minibands separated by minigaps which tend to zero as the impurity spacing $d\to\infty$. The fundamental zone for the superlattice is

$$-\pi/d \leq k < \pi/d\ . \tag{3.1}$$

Figure 4 shows the energy-band structure of Fig. 3 continued periodically.

We now follow Des Cloiseaux[4] in the construction of localized basis functions. First we define the projection operators $P_m(k)$ corresponding to each of the minibands m (including the impurity band) which make up the band complex arising out of the original $n=0$ band:

$$P_m(k) \equiv |\varphi_{m,k}\rangle\langle\varphi_{m,k}^*|\ , \tag{3.2}$$

where k runs over the fundamental zone (3.1). The $\varphi_{m,k}$ are normalized eigenfunctions of the superlattice satisfying the relations

$$\langle\varphi_{m,k}^*|\varphi_{m',k'}\rangle = \delta_{mm'}\delta(k-k')\ . \tag{3.3}$$

If k is real, the asterisks in (3.2) and (3.3) are of course superfluous. However, by using them as indicated, the matrix elements of $P_m(k)$ can be analytically continued into the complex k plane up to the branchpoints which connect the miniband m to its neighbors $m\pm1$. (See Appendix A.)

Next we construct the projection operator for the entire band complex arising out of the original $n=0$ band,

$$P(k) \equiv \sum_{m=0}^{M} P_m(k), \tag{3.4}$$

where m runs over all minibands. It is shown in Appendix A that $P(k)$ is analytic at all branchpoints connecting the minibands m and that the singularities nearest to the real axis are the branchpoints connecting the highest miniband belonging to $n=0$ with the lowest miniband belonging to $n=1$ [the points (*) in Fig. 5]. As $d\to\infty$, clearly the distance h_M of these branchpoints from the real k axis approaches h^0, the distance of the branchpoints connecting bands $n=0$ and 1 in the unperturbed lattice.

We now construct the total projection operator on all states of the band complex:

$$P \equiv \int_{-\pi/d}^{\pi/d} dk P(k)$$

$$\equiv \sum_m \int_{-\pi/d}^{\pi/d} dk\, |\varphi_{m,k}\rangle\langle\varphi_{m,k}^*|\ . \tag{3.5}$$

As shown in Appendix B, by shifting the k integra-

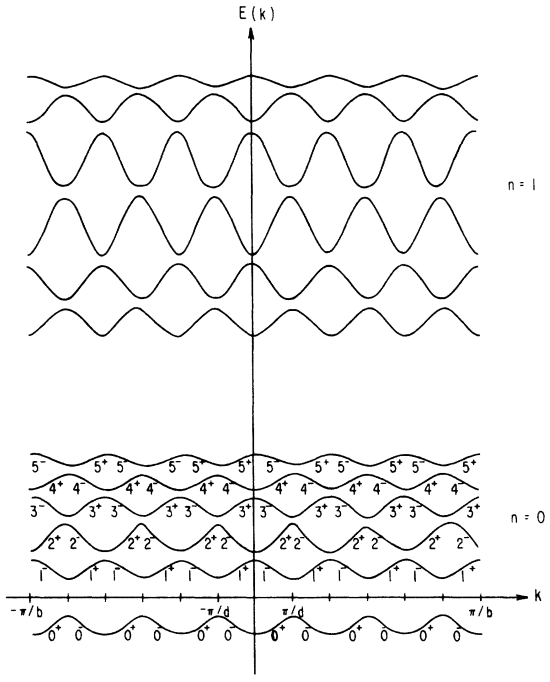

FIG. 4. Energy-band structure of Fig. 3 continued periodically.

tion to appropriate contours in the complex plane and then letting the distance d between impurities become infinite, P takes the form

$$P = P^B + P^{SC}. \tag{3.6}$$

Here P^B is the contribution from the isolated normalized bound state φ_B,

$$P^B = |\varphi_B\rangle\langle\varphi_B|; \tag{3.7}$$

and P^{SC} is the contribution from the scattering states associated with the lowest band,

$$P^{SC} = \int_{-\pi/b}^{\pi/b} dk\, P^{SC}(k) = \int_{-\pi/b}^{\pi/b} dk\, |\varphi_k^{(+)}\rangle\langle\varphi_{-k}^{(-)*}|. \tag{3.8}$$

The scattering functions $\varphi_k^{(+)}$ and $\varphi_{-k}^{(-)}$ are defined by the following conditions:

$$\begin{aligned} \varphi_k^{(+)}(x) &= [t_{22}(k)]^{-1/2}\varphi_k^0(x), \quad x \geq \tfrac{1}{2}b \\ \varphi_{-k}^{(-)}(x) &= [t_{22}(k)]^{-1/2}\varphi_{-k}^0(x), \quad x \leq -\tfrac{1}{2}b \end{aligned} \tag{3.9}$$

where $t_{22}(k)$ is a diagonal transfer matrix element of the impurity. We wish to point out, with reference to (3.8), that contrary to what might have been expected, even for real k, $\varphi_k^{(+)*} \neq \varphi_{-k}^{(-)}$.

We now consider the matrix elements of P in coordinate space, $\langle x|P|x'\rangle$. It is shown in Appendix C that these have the following short-range properties: If $h < h^0$,

$$\lim_{|x-x'|\to\infty} e^{h|x-x'|}\langle x|P|x'\rangle = 0, \tag{3.10}$$

and also, for fixed $x - x'$,

$$\lim_{(1/2)|x+x'|\to\infty} e^{2h|(x+x')/2|} \times (\langle x|P|x'\rangle - \langle x|P^0|x'\rangle) = 0, \tag{3.11}$$

where P^0 is the projection operator for the lowest band of the perfect lattice.

Equations (3.10) and (3.11) are the most important mathematical theorems of the present work. They state that $\langle x|P|x'\rangle$ decays exponentially like $e^{-h^0|x-x'|}$ and that $P \to P^0$ as $e^{-2h^0|(x+x')/2|}$. Here the exponential decay constant is the same as that of the Wannier functions in the perfect lattice, i.e., it is entirely unaffected by the presence of the impurity. We should also note that, for a weak attractive potential, where the bound state has a large orbit, the part P^B of P in Eq. (3.6) will have a much longer tail, but this tail is canceled out by a long-range part of P^{SC}.

The short-range properties, (3.10) and (3.11), of P will enable us in Sec. IV to prove corresponding short-range properties of the new localized basis functions.

IV. PROPERTIES OF LOCALIZED BASIS FUNCTIONS

In this section we shall use the projection operator P of Sec. III to construct the localized basis functions $a_l(x)$ equivalent to the eigenfunctions arising from the lowest band.

We consider first the perfect lattice. In that case, since the corresponding Wannier functions $a_l^0(x)$ are linear combinations of the Bloch waves $\varphi_k^0(x)$, it follows immediately that

$$a_l^0(x) = P^0 a_l^0(x). \tag{4.1}$$

Now, using the projection operator P of the perturbed lattice, Eqs. (3.6)–(3.9), we construct the functions

$$a_l'(x) = P a_l^0(x). \tag{4.2}$$

As shown at the end of Appendix B, the projection operator P is a continuous function of the localized perturbation. Since the $a_l^0(x)$ are orthonormal and hence independent, a comparison of Eqs. (4.1) and (4.2) and the principle of continuity shows that the $a_l'(x)$ are also independent. Since they are linear combinations of the eigenfunctions of the perturbed lattice arising out of the lowest band, and since they are equal in number to these, it follows that they span the same function space.

Now, as seen in Eq. (1.1), $a_l^0(x)$ has an exponential decay determined by the distance h^0 from the real k axis of the branchpoint connecting the lowest to the second band. Combining this with the exponential properties (3.10) and (3.11) of the projection operator P and the definition (4.2) of a_l', shows that these functions have the following properties:

$$\lim_{|x-lb|\to\infty} e^{h|x-lb|}\, a_l'(x) = 0, \quad h < h^0, \tag{4.3}$$

and that for fixed $x - lb$,

$$\lim_{|l|\to\infty} e^{2h|l|b}\,[a_l'(x) - a_l^0(x)] = 0, \quad h < h^0. \tag{4.4}$$

Equation (4.3) shows that the functions a_l' are exponentially localized with the exponential being the same as for the unperturbed Wannier functions. Equation (4.4) shows how $a_l'(x)$ approaches $a_l^0(x)$ as one moves away from the impurity.

Now the functions a_l', while constituting a set of localized functions equivalent to the eigenfunctions, unbound and bound, arising from the lowest band, are not orthonormal. Normalization can, of course, be obtained by multiplication with the correct constant. Orthogonalization is slightly more complex and is discussed in Appendix D. There it is shown that the resulting orthornormal set of functions $a_l(x)$ has the same properties (4.3) and (4.4) as the nonorthonormal functions a_l'; i.e.,

$$\lim_{|x-lb|\to\infty} e^{h|x-lb|}\, a_l(x) = 0, \quad h < h^0, \tag{4.5}$$

and, for fixed $x - lb$,

$$\lim_{|l|\to\infty} e^{2h|l|b}\,[a_l(x) - a_l^0(x)] = 0, \quad h < h^0. \tag{4.6}$$

These two properties are the chief results of our analysis.

V. *AB INITIO* VARIATIONAL CONSTRUCTION OF LOCALIZED BASIS FUNCTIONS

Now that we have established the existence of a localized basis for the eigenfunctions arising from the lowest band, it is easy to construct these functions from the energy variational principle.[8] Suppose we have altogether N cells, and hence N eigenstates arising out of the lowest band. Consider now the ground state of N spinless noninteracting fermions moving in this potential. It is given by the following equivalent expressions:

$$\Phi = (N!)^{-1/2}\det|\varphi_j(x_i)| = (N!)^{-1/2}\det|a_l(x_i)|, \tag{5.1}$$

where the φ_j are the eigenstates arising out of the lowest band and the a_l are our localized functions arising from them by a unitary transformation. We now use as trial functions

$$\Phi^t = (N!)^{-1/2}\det|a_l^t(x_i)|, \tag{5.2}$$

where the a_l^t are exponentially localized orthonormal functions approaching $a_l^0(x)$ as $|l| \to \infty$. The corresponding energy is

$$E^t = \sum_l \langle a_l^t, Ha_l^t\rangle \tag{5.3}$$

and attains its minimum when the set a_l^t is a correct set of localized functions. Of course this set is not unique, since any given set of a_l can be replaced by another set which is a suitable linear combination.

The simplest approximation is to take

$$a_l^t(x) = a_l^0(x), \quad l \neq 0$$
$$a_0^t(x) \neq a_0^0(x), \tag{5.4}$$

and then use (5.3) to determine a_0^t. If one starts with a trial function $b_0^t(x)$ which is not orthogonal to the $a_l^0(x)$ for $l \neq 0$ this can be immediately corrected by taking instead,

$$a_0^t(x) = A_0\left(b_0^t(x) - \sum_{l\neq 0}\langle b_0^t(x), a_l^0(x)\rangle a_l^0(x)\right). \tag{5.5}$$

Thus we see the important feature that one can construct the localized function *ab initio*, without first having to know the eigenfunctions of the system. In fact we think that, particularly in three-dimensional problems, it will be much easier to calculate, in the first place, these localized functions rather than the eigenfunctions; for, of the latter, the scattering states extend throughout the system and loosely bound states are also much more extended than our localized basis states. However, once the localized basis states are known, one can, as shown in Sec. VI, obtain the eigenfunctions by solving a relatively small set of linear algebraic equations.

VI. APPLICATIONS

A. Eigenfunctions

The eigenfunctions φ_j arising out of the lowest band are linear combinations of the a_l. Thus we may write, on suppressing temporarily the index j,

$$\varphi = \sum_l c_l a_l. \tag{6.1}$$

Substitution into the Schrödinger equation gives

$$\sum_{l'} H_{ll'}c_{l'} = Ec_l, \tag{6.2}$$

where

$$H_{ll'} \equiv \langle a_l, Ha_{l'}\rangle. \tag{6.3}$$

The well-known Slater-Koster theory[9] expands the eigenfunctions φ in terms of the unperturbed Wannier functions $a_{n,l}^0$, where n is the band index. In their theory the exact solution requires a summation over the site index l *and* the band index n. This latter summation is avoided in the present formulation at the expense of using the perturbed functions a_l.

To illustrate the solution of (6.2) we take H in the form given by Eqs. (2.1)–(2.4) and further assume that we can take

$$H_{ll'} \approx 0 \quad \text{for } |l-l'| > 1 \tag{6.4}$$

(tight-binding approximation), and that

$$a_l(x) \approx a_l^0(x), \quad |l| \geq 1. \tag{6.5}$$

Then (6.2) can be written as

$$\sum_{l'}[H_{ll'}^0 - E\delta_{ll'}]c_{l'} = -\sum_{l'}(H_{ll'} - H_{ll'}^0)c_{l'}, \tag{6.6}$$

where

$$H_{ll'}^0 \equiv \langle a_l^0, H^0 a_{l'}^0\rangle \tag{6.7}$$

and

$$H_{ll'} - H_{ll'}^0 = 0 \text{ if } |l| \text{ or } |l'| > 1. \tag{6.8}$$

If we now define the Green's function

$$G_{ll'}^0(E) \equiv \langle l|1/(H^0 - E)|l'\rangle, \tag{6.9}$$

then (6.6) can be rewritten as

$$c_l + \sum_{l',l''} G_{ll''}^0(E)(H_{l''l'} - H_{l''l'}^0)c_{l'} = 0. \tag{6.10}$$

In view of (6.8) the right-hand side involves only c_0 and $c_{\pm 1}$. Hence, setting l successively equal to 0, +1, and −1 gives three homogeneous linear equations. The determinental consistency condition

determines the eigenvalues E and coefficients c_0, c_1, and c_{-1}. The other coefficients are then obtained directly from (6.10).

The Green's function needed in (6.10) is given by

$$G^0_{ll'}(E) = \frac{b}{2\pi} \int \frac{e^{ik(l-l')b}}{2t\cos(kb) - (E - \bar{E})}\, dk, \qquad (6.11)$$

where

$$\bar{E} \equiv \langle a^0_l, H^0 a^0_l \rangle \qquad (6.12)$$

and t is the transfer integral

$$t \equiv \langle a^0_l, H^0 a^0_{l+1} \rangle. \qquad (6.13)$$

B. Total Electron Density

Consider a system with a defect in which all states arising from the lowest band, including any bound states, are singly occupied by spinless fermions. If Φ is the ground-state wave function, the electron density is given by

$$n(x_1) = N \int \Phi^* \Phi\, dx_2 \cdots dx_N. \qquad (6.14)$$

On using the two alternative forms (5.1) for Φ, one obtains

$$n(x_1) = \sum_j |\varphi_j(x_1)|^2 = \sum_l |a_l(x_1)|^2. \qquad (6.15)$$

For electrons with spin there is a factor of 2. Thus we see that for a calculation of the total electron density a knowledge of the a_l is sufficient; the eigenfunctions φ_j need not be solved for. The electron density is of interest for the inclusion of approximate exchange and correlation potentials,[10] for calculation of electric field gradients, etc.

C. Moments of Density of States

Let $n(E)$ be the density of states associated with the eigenfunctions, including any bound states, arising from the lowest-band. Clearly

$$n(E) = \sum_j \delta(E - E_j), \qquad (6.16)$$

where the E_j are the eigenvalues of H. The moment of order s is given by

$$M_s = \int E^s n(E)\, dE = \sum_j E_j^s = \sum_j \langle j | H^s | j \rangle = \sum_l \langle l | H^s | l \rangle, \qquad (6.17)$$

where

$$\langle l_1 | H | l_2 \rangle = \langle a_{l_1}, H a_{l_2} \rangle. \qquad (6.18)$$

Since

$$H a_l = \sum_{l'} a_{l'} \langle l' | H | l \rangle, \qquad (6.19)$$

we can use closure in (6.17) without leaving the space spanned by the N functions a_l and also write[8]

$$M_s = \sum_{l, l_1, \ldots, l_{s-1}} \langle l | H | l_1 \rangle \times \langle l_1 | H | l_2 \rangle \cdots \langle l_{s-1} | H | l \rangle. \qquad (6.20)$$

From either the last form of (6.17) or (6.20), we see that moments of the density of states can also be directly obtained from a knowledge of the a_l without having to construct the eigenfunctions φ_j. From the moments the density of states $n(E)$ can be reconstructed.[11]

APPENDIX A: REALITY, SYMMETRY, AND SINGULARITIES OF PROJECTION OPERATOR $P(k)$

For *real* k the projection operator $P_m(k)$[3-5] associated with the mth miniband can be written in the conventional form

$$P_m(k) = |\varphi_{m,k}\rangle\langle\varphi_{m,k}|, \qquad (A1)$$

where $\varphi_{m,k}$ are orthonormal Bloch waves,

$$\langle \varphi_{m,k} | \varphi_{m',k'} \rangle = \delta_{mm'} \delta(k - k'). \qquad (A2)$$

In the coordinate representation these equations read as follows:

$$\langle x | P_m(k) | x' \rangle = \varphi_{m,k}(x) \varphi^*_{m,k}(x'), \qquad (A3)$$

$$\int \varphi^*_{m,k}(x) \varphi_{m',k'}(x)\, dx = \delta_{mm'} \delta(k - k'). \qquad (A4)$$

It is evident from (A3) that $P_m(k)$ is independent of the phase of $\varphi_{m,k}$. For the following discussion it is convenient to choose this phase so that[12]

$$\varphi_{m,k}(0) = \varphi^*_{m,k}(0) = \text{real and positive}. \qquad (A5)$$

Then we clearly have the following relations:

$$\varphi_{m,-k}(x) = \varphi^*_{m,k}(x), \qquad (A6)$$

$$\varphi_{m,k}(-x) = \varphi^*_{m,k}(x). \qquad (A7)$$

Using Eqs. (A3), (A6), and (A7) we can now immediately prove the symmetry and reality properties of the projection operator for the entire mth miniband,

$$\langle x | P_m | x' \rangle \equiv \int_{-\pi/d}^{\pi/d} dk \langle x | P_m(k) | x' \rangle. \qquad (A8)$$

Clearly we have

$$\langle x | P_m(k) | x' \rangle^* = \langle x | P_m(-k) | x' \rangle, \qquad (A9)$$

$$\langle x' | P_m(k) | x \rangle = \langle x | P_m(-k) | x' \rangle, \qquad (A10)$$

$$\langle -x | P_m(k) | -x' \rangle = \langle x | P_m(-k) | x' \rangle. \qquad (A11)$$

Hence

$$\langle x | P_m | x' \rangle^* = \langle x | P_m | x' \rangle \quad \text{(reality)}, \qquad (A12)$$

$$\langle x' | P_m | x \rangle = \langle x | P_m | x' \rangle \quad \text{(symmetry)}, \qquad (A13)$$

$$\langle -x | P_m | -x' \rangle = \langle x | P_m | x' \rangle \quad \text{(inversion symmetry)}. \qquad (A14)$$

The same properties evidently hold also for the total projection operator P corresponding to all $(M+1)$ minibands arising from the $n=0$ band,

$$\langle x|P|x'\rangle = \sum_{m=0}^{M} \langle x|P_m|x'\rangle. \tag{A15}$$

We now wish to examine the singularities of the total projection operator

$$\langle x|P(k)|x'\rangle = \sum_{m=0}^{M} \langle x|P_m(k)|x'\rangle. \tag{A16}$$

The form (A3) for $\langle x|P_m(k)|x'\rangle$ is not suitable for this purpose since $\varphi^*_{m,k}(x')$ is *not* an analytic function of k (because of the *). However on the real k axis we can use the identity (A6), and rewrite (A3) and (A4) in the form

$$\langle x|P_m(k)|x'\rangle = \varphi_{m,k}(x)\varphi_{m,-k}(x') \tag{A17}$$

and

$$\int \varphi_{m,-k}(x)\varphi_{m',k'}(x)\,dx = \delta_{mm'}\delta(k-k'). \tag{A18}$$

Now it was shown in Ref. 2 that $\varphi_{m,k}$, when continued analytically into the complex plane, is regular except for branchpoints at the complex branchpoints of the multivalued energy function $E(k)$. For example, at a branchpoint k_m where bands m and $m+1$ are joined, $\varphi_{m,k}(x)$, has, for given x, the following form:

$$\varphi_{m,k} = [1/(k-k_m)^{1/4}][A + B(k-k_m)^{1/2} + C(k-k_m) + \cdots], \tag{A19}$$

and $\varphi_{m,-k}$ has the same form. From this it follows that, for fixed x and x', the projection operator $P_m(k)$ of (A8) has a square-root-type branchpoint,

$$P_m(k) = [1/(k-k_m)^{1/2}][A' + B'(k-k_m)^{1/2} + C'(k-k_m) + \cdots]. \tag{A20}$$

When the projection operator $P_{m+1}(k)$ of the next-higher miniband is analytically continued to the vicinity of the *same* branchpoint, it has the same form (A20), except with the opposite sign for all square roots. Hence the sum has the expansion

$$P_m(k) + P_{m+1}(k) = 2B' + 2D'(k-k_m) + \cdots, \tag{A21}$$

and is analytic at k_m.

From this it follows that the *total* projection operator corresponding to the original band $n=0$,

$$P(k) \equiv \sum_{m=0}^{M} P_m(k), \tag{A22}$$

is analytic at all branchpoints k_m ($m=0, \ldots, M-1$) joining the minibands $m=0, 1, \ldots, M$. Its singularities nearest to the real axis are the branchpoints k_M joining the highest miniband belonging to $n=0$ with the lowest belonging to $n=1$. As the distance d between impurities tends to infinity, these branchpoints have a distance h_M from the real axis which approaches the distance h^0 of the corresponding branchpoints connecting bands $n=0$ and 1 of the perfect lattice.

APPENDIX B: PROJECTION OPERATOR FOR A LATTICE WITH A SINGLE IMPURITY

In this Appendix we make the transition from a lattice with a periodic array of widely spaced impurities, to a lattice with a single impurity. This limiting process is somewhat subtle. We have seen that for finite impurity spacing d, the total projection operator associated with the original lowest band $n=0$ of the periodic lattice has the form

$$P = \int_{-\pi/d}^{\pi/d} P(k)\,dk, \tag{B1}$$

where

$$P(k) = \sum_{m=0}^{M} P_m(k). \tag{B2}$$

The function $P(k)$ is periodic, with period $2\pi/d$, and analytic in a strip enclosing the real axis whose boundaries, as $d\to\infty$, approach those of the perfect lattice. We shall show in this Appendix that, in the limit where $d=\infty$, P can be written in two alternative forms. One of these is

$$P = P^B + P^{SC}, \tag{B3}$$

where P^B is the projection operator on the bound impurity state, which in the coordinate representation has the form

$$P^B = \varphi_B(x)\varphi_B(x')^*, \tag{B4}$$

and P^{SC} is the projection operator on the scattering states associated with the lowest band,

$$P^{SC} = \int_C P^{SC}(k)\,dk. \tag{B5}$$

Here $P^{SC}(k)$ is a projection operator associated with scattering states characterized by momentum k and has periodicity $2\pi/b$; it has poles at $k=\pm ih_B$, where $E^0(ih_B)=\epsilon_B$, the bound-state energy, and branchpoints at the branchpoints of the perfect lattice. The integral in (B3) is along the real axis from $-\pi/b$ to π/b or any other equivalent line C which does not lie beyond the poles. (See Fig. 5.)

The second form is

$$P = \int_{C'} P^{SC}(k)\,dk, \tag{B6}$$

where C' is a contour such as shown in Fig. 5, lying between the pole ih_B and the branchpoint k^0. The form (B6) can be derived directly from (B1) and (B2); it can also be obtained starting with (B3)–(B5), and displacing C to C'. It is then found that the residue from the pole at ih_B precisely cancels the bound-state contribution P^B.

From the form (B6) we shall deduce in Appendix

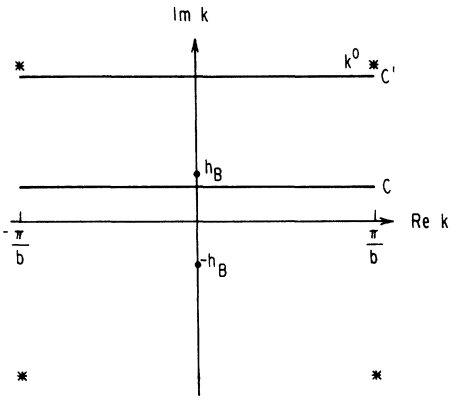

FIG. 5. Singularities of $P^{SC}(k)$ are poles at $\pm ih_B$ and branchpoints (*) at the branchpoints of the perfect periodic lattice ($k^0 = \pm\pi/b \pm ih^0$). C and C' are integration contours in Eqs. (B5) and (B6).

C the short-range properties of $\langle x|P|x'\rangle$, with characteristic length $(h^0)^{-1}$ (see Fig. 5), the same as for the underlying periodic lattice rather than the range of the bound state h_B^{-1}.

Derivation of the Form (B3) of P

We start with the projection operator for an array of impurity potentials with spacing d, Eqs. (B1) and (B2). We have seen in Appendix A that $P(k)$ is analytic in a strip of width $2h_M$. We may therefore use the integration contour C, (see Fig. 6) in Eq. (B1). This contour is chosen *beyond* the branchpoints $k_1, k_2, \ldots, k_{M-1}$, connecting the minibands other than the impurity bands, whose distance from the real axis behaves as $d^{-1/2}$. It is, however, taken *in front of* k_0, the branchpoint connecting the impurity band with the next miniband. As $d \to \infty$, the distance of this branchpoint from the real axis tends to a finite limit h_B given by the equation $E^0(ih_B) = \epsilon_B$,[2] where $E^0(k)$ refers to the perfect lattice and ϵ_B is the energy of an isolated bound state.

Along the contour C and its extension, the minibands $m = 1, 2, \ldots, M$ are all connected in the sense that, e.g.,

$$E_2(\pi/d + i\tilde{h}) = E_3(\pi/d + i\tilde{h}), \tag{B7}$$

etc., and similarly for the eigenstates. In an extended zone scheme, $E(k)$ plotted along the line $k = g + i\tilde{h}$ has the character, shown (for the sake of convenience) for $\mathrm{Re}E(k)$ in Fig. 7.

Thus, in complete equivalence to (B1) and (B2) we can write

$$P = \int_{-\pi/b}^{(\pi/b)-(2\pi/d)} P'(g + i\tilde{h})\, dg + \int_{-\pi/d}^{\pi/d} P^B(g + i\tilde{h})\, dg, \tag{B8}$$

where P' is constructed with the functions associated with the upper band in Fig. 7, while P^B is constructed from the functions associated with the lower (impurity) band.

Keeping $\tilde{h}$ and x and x' fixed, we now take the limit of (B8) as $d \to \infty$. Then (B8) takes the form

$$P = \int_{-\pi/b}^{\pi/b} P^{SC}(g + i\tilde{h})\, dg + P^B. \tag{B9}$$

The second member is

$$P^B = \varphi_B(x)\, \varphi_B^*(x'), \tag{B10}$$

which comes from an evaluation of the second integral in (B8) in the tight-binding limit, justified because $d \to \infty$. In the coordinate representation the integrand in the first term of (B9) has the form

$$P^{SC}(k) = \varphi_k^{(+)}(x)\varphi_{-k}^{(-)}(x'), \tag{B11}$$

where $\varphi_k^{(+)}$ and $\varphi_{-k}^{(-)}$ have the following forms outside the impurity cell:

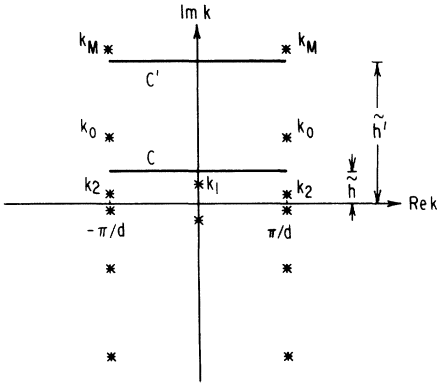

FIG. 6. Branchpoints (*) of the miniband projection operators $P_m(k)$.

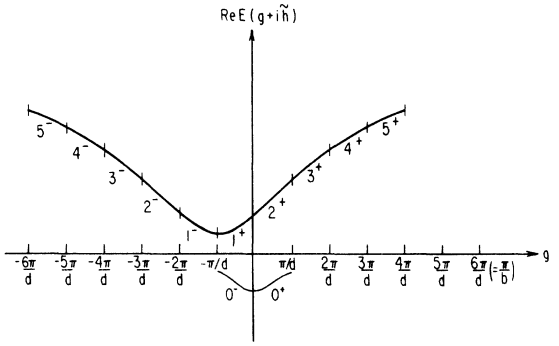

FIG. 7. ReE along the line $k = g + ih$ with $h = \tilde{h}$ (see Fig. 6). The notation 3^+ corresponds to the + side of the band $m = 3$ in Fig. 3, etc.

$$\varphi_k^{(+)}(x) = [t_{22}(k)]^{-1/2} \begin{cases} \varphi_k^0(x), & x \geq \frac{1}{2}b, \\ t_{22}(k)\varphi_k^0(x) + t_{21}(k)\varphi_{-k}^0(x), & x \leq -\frac{1}{2}b, \end{cases} \tag{B12}$$

$$\varphi_{-k}^{(-)}(x) = [t_{22}(k)]^{-1/2} \begin{cases} \varphi_{-k}^0(x), & x \leq -\frac{1}{2}b, \\ t_{22}(k)\varphi_{-k}^0(x) + t_{21}(k)\varphi_k^0(x), & x \geq \frac{1}{2}b, \end{cases} \tag{B13}$$

[Note that $\varphi_{-k}^{(-)}(x) = \varphi_k^{(+)}(-x)$.] Here $t_{ij}(k)$ is the left-to-right transfer matrix of the impurity in the representation of φ_k^0 and φ_{-k}^0, the normalized Bloch waves in the perfect crystal. Its elements satisfy the following relations:

$$\begin{aligned} &\det|t_{ij}(k)| = 1, \\ &t_{12}(k) = -t_{21}(k), \\ &t_{21}(k) = t_{12}(-k), \\ &t_{11}(k) = t_{22}(-k). \end{aligned} \tag{B14}$$

The transfer matrix elements $t_{ij}(k)$ are analytic functions of k, except for branchpoints at the branchpoints of $E(k)$. Therefore the projection operator $P^{SC}(k)$, Eq. (B11), is analytic in a strip enclosing the real axis of width $2h^0$ [the strip of analyticity of $E^0(k)$ of the perfect lattice], *except* for poles at the points k where

$$t_{22}(k) = 0. \tag{B15}$$

Thus, in particular, the integral (B9) can be performed over the real k axis where $\varphi_k^{(+)}$ and $\varphi_{-k}^{(-)}$ represent physical scattering functions. The condition (B15) is satisfied at values of k corresponding to a bound state, $k = \pm ih_B$ for which

$$E^0(ih_B) = \epsilon_B, \tag{B16}$$

the bound-state energy (see Fig. 5). In view of the analyticity of $P^{SC}(k)$ in a strip bounded by singularities at $\pm ih_B$, one can show that the projection operator $\langle x|P^{SC}|x'\rangle$ has exponential localization properties with characteristic length h_B^{-1}, just like $\langle x|P^B|x'\rangle$, Eq. (B10). For weak perturbations this can be a very great length. However, in the following paragraphs we shall see that the *sum* of P^{SC} and P^B has short-range properties of the same scale as $(h^0)^{-1}$, which determines the degree of localization of the unperturbed Wannier functions $a_i^0(x)$, and is of course independent of the strength of the perturbing potential.

Derivation of the Alternate Form (B6) of P

This form is most easily derived by starting from Eqs. (B1) and (B2) for the regularly repeated impurities. Then using the analyticity and periodicity properties of $P(k)$, we extend the integration over k over the contour C', Fig. 6, which lies between the branchpoints k_0 and k_M. Now let $d \to \infty$. Then, along the line $k = g + i\tilde{h}'$, $E(g + i\tilde{h}')$ has the same general nature as $E^0(g + i\tilde{h}')$ for the perfect lattice (see Fig. 8).

Now we let $d \to \infty$. Then we obtain Eq. (B6),

$$P = \int_{C'} P^{SC}(k)\, dk, \tag{B17}$$

where C' lies between the pole ih_B and the branchpoint k^0, and P^{SC} is defined by Eqs. (B11)–(B13).

This result can also be confirmed by starting with the form (B3) for P and replacing the integral along C by the corresponding integral along C' plus the residue at the pole ih_B. The latter can be shown to cancel precisely the bound-state portion P^B of the projection operator. For the interested reader we mention that this proof requires the following two identities:

$$\left.\frac{dt_{22}(E)}{dE}\right|_{E=E^0(ih_B)} = \frac{\int_{-\infty}^{\infty} \varphi_B^2(x)\, dx}{W(\varphi_{-ih_B}^0, \varphi_{ih_B}^0)} \tag{B18}$$

and

$$\left.\frac{dE^0}{dk}\right|_{k=ih_B} = -2\pi i W(\varphi_{-ih_B}^0, \varphi_{ih_B}^0). \tag{B19}$$

Here φ_B is the bound-state wave function with amplitude determined by the following asymptotic condition:

$$\varphi_B(x) = \varphi_{ih_B}^0(x), \quad x \geq \tfrac{1}{2}b \tag{B20}$$

and $W(f,g)$ denotes the Wronskian of the functions f and g.[13]

Continuity of $\langle x|P|x'\rangle$ as a Function of the Perturbing Potential

In Sec. IV we used the fact that P is a continuous function of the strength of the localized per-

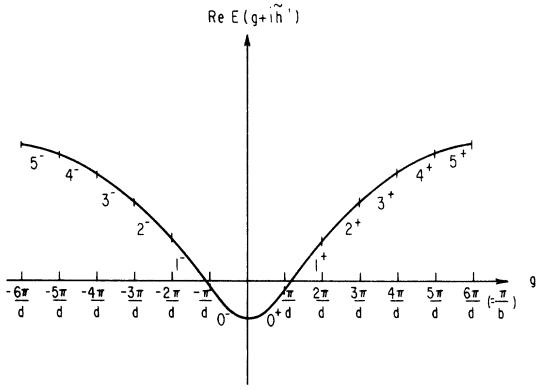

FIG. 8. ReE along the line $k = g + ih$ with $h = \tilde{h}'$ (see Fig. 6).

turbation. This will now be easily demonstrated.

For this purpose we use the form (B17) of P. On this contour the functions $\varphi_k^{(+)}(x)$ which are defined by the differential equation and the first asymptotic condition of Eq. (B13) are analytic functions of the strength of the impurity potential, say λ_v, for $0 \le \lambda_v \le 1$, provided no zeros or singularities of $E^0(k)$ cross the integration contour C'. But this latter fact is assured by our assumptions (Sec. II) that the perturbing potential is not too strong. $\varphi_{-k}^{(-)}(x)$ is similarly regular. It then follows from (B17) that P is an analytic function of λ_v, and hence of course continuous.

APPENDIX C: SHORT-RANGE PROPERTIES OF $\langle x|P|x'\rangle$

We start from the form

$$P = \int_{C'} P^{SC}(k)\, dk, \tag{C1}$$

where k runs over the values

$$k = g + i(h^0 - 0), \qquad -\pi/b \le g \le \pi/b, \tag{C2}$$

(see Fig. 5), and $P^{SC}(k)$ is defined in Eqs. (B12) and (B13).

We shall now consider $\langle x|P|x'\rangle$ for $x > x'$. From (B12) and (B13) we see that $\varphi_k^{(+)}$ and $\varphi_{-k}^{(-)}$ can be majorized as follows on the contour C':

$$|\varphi_k^{(+)}(x)| < Ae^{-h^0 x}, \tag{C3}$$

$$|\varphi_{-k}^{(-)}(x')| < Ae^{h^0 x'}, \tag{C4}$$

where A is a constant. Hence

$$|\langle x|P|x'\rangle| < (2\pi/b)A^2 e^{-h^0(x-x')}. \tag{C5}$$

But since we have shown that $\langle x|P|x'\rangle$ is symmetric in x and x', Eq. (A13), we can conclude that

$$\lim_{|x-x'|\to\infty} e^{h|x-x'|}\langle x|P|x'\rangle = 0, \quad h < h^0. \tag{C6}$$

Thus the projection operator is exponentially short ranged, *the range being the same as for the underlying periodic lattice.*

Next we wish to establish how rapidly $\langle x|P|x'\rangle$ approaches the projection operator of the perfect lattice, $\langle x|P^0|x'\rangle$, for fixed $(x-x')$ as $\frac{1}{2}|x+x'| \to \infty$. We take first x, $x' \ge \frac{1}{2}b$. Then we can write

$$\langle x|P^{SC}(k)|x'\rangle = \langle x|P^0(k)|x'\rangle + \frac{t_{21}(k)}{t_{22}(k)}\varphi_k^0(x)\varphi_k^0(x'). \tag{C7}$$

The second term may again be majorized by

$$\left|\frac{t_{21}(k)}{t_{22}(k)}\varphi_k^0(x)\varphi_k^0(x')\right| < A'e^{-h^0(x+x')}. \tag{C8}$$

Hence, we have for the total projection operator,

$$|\langle x|P|x'\rangle - \langle x|P^0|x'\rangle| < (2\pi/b)A'e^{-h^0(x+x')}. \tag{C9}$$

Finally, using the inversion symmetry (A14) we can write that, for fixed $x - x'$,

$$\lim_{|(1/2)(x+x')|\to\infty} e^{2h|(x+x')/2|} \times (\langle x|P|x'\rangle - \langle x|P^0|x'\rangle) = 0, \quad h < h^0. \tag{C10}$$

Thus we see an exponential convergence of P to P^0, as $|\frac{1}{2}(x+x')| \to \infty$. Again, it is interesting to note that the characteristic length, $(2h^0)^{-1}$, is a property of the underlying lattice and not of the impurity.

APPENDIX D: ORTHOGONALIZATION OF LOCALIZED FUNCTIONS

The localized functions a_0'; a_1', a_{-1}'; etc., obtained in Sec. V, while they span all eigenfunctions arising out of the original band $n = 0$ and are normalized, are not orthogonal except very far from the impurity. For some purposes this fact is of no consequence. But for other applications an orthogonal set is more convenient. We therefore need an algorithm for orthogonalization.[14]

In order that the following algorithm work we must start with functions which have sufficiently small overlap integrals. This may require simple preliminary rotations such as replacing

$$a_0' \to A_0[a_0' - \langle 0|1\rangle(a_1' + a_{-1}')], \tag{D1}$$

where we use the notation

$$\langle l|l'\rangle \equiv \langle a_l', a_{l'}'\rangle \tag{D2}$$

and A_0 is the appropriate normalization. We shall assume that this has been done so that

$$\langle l|l\rangle = 1$$

$$\langle l|l'\rangle \ll 1, \quad l \ne l'. \tag{D3}$$

All overlap integrals will be formally treated as quantities of the first order in smallness, and this will be made visible by affixing the coefficient λ to them (which actually has the value 1):

$$\langle l|l'\rangle \equiv \lambda\langle l|l'\rangle, \quad l \ne l'. \tag{D4}$$

Now consider the following linear transformation:

$$b_l'' = \sum_{l''} (\delta_{ll''} + \lambda S_{ll''})a_{l''}'. \tag{D5}$$

To first order in λ we have

$$\langle b_l'', b_{l'}''\rangle = \lambda[\langle l|l'\rangle + (S_{ll'} + S_{ll'})] + O(\lambda^2). \tag{D6}$$

To remove first-order overlap we choose

$$S_{ll'} = -\tfrac{1}{2}\langle l|l'\rangle(1 - \delta_{ll'}). \tag{D7}$$

We then renormalize the functions to give us the next generation of functions

$$a_l'' = \eta_l'' b_l'',$$

for which evidently

$$\langle a_l'', a_l'' \rangle = 1, \tag{D8}$$

$$\langle a_l'', a_{l'}'' \rangle = O(\lambda^2), \quad l \neq l'. \tag{D9}$$

Now we repeat this process. Clearly, after successive steps the remaining overlap integrals are of order λ, λ^2, λ^4, λ^8, etc., so that the process is very rapidly converging.

Returning now to the first stage of our procedure, we have

$$a_l'' = \eta_l'' \left(a_l' - \frac{1}{2} \sum_{l'}{}' \langle l | l' \rangle a_{l'}' \right) , \tag{D10}$$

where

$$\eta_l'' = \left(1 - \sum_{l'} \langle l | l' \rangle \langle l' | l \rangle + \frac{1}{4} \sum_{l'}{}' \sum_{l''}{}' \langle l | l' \rangle \langle l' | l'' \rangle \langle l'' | l \rangle \right)^{-1/2} . \tag{D11}$$

We have seen previously that the functions a_l' have the important exponential properties (1.2) and (1.3). [The replacement (D1) leaves these unchanged.] By (D10) and (D11) it can now be easily verified that the same is true of the a_l''s. By induction the same exponential properties pertain equally to all higher approximants, the $a_l^{(\nu)}$s and hence also to the limiting fully orthonormalized functions

$$a_l \equiv a_l^{(\infty)} . \tag{D12}$$

In practice, variational calculations may use

$$a_l' = a_l^0, \quad l > l_0, \tag{D13}$$

$$a_l' \neq a_l^0, \quad l \leq l_0. \tag{D14}$$

In this case one first exactly orthogonalizes all $a_l (l \leq l_0)$ to the $a_l (l > l_0)$ as follows:

$$b_l'' = a_l' - \sum_{l'' > l_0} \langle l | l'' \rangle a_{l''}^0, \quad l \leq l_0, \tag{D15}$$

and then orthonormalizes in an elementary fashion the finite number of $b_l''(l \leq l_0)$ among themselves.

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[12] Isolated points where $\varphi_{m,k} = 0$ are of no significance.
[13] Details of this discussion will be given in the thesis of J. R. Onffroy (University of California, San Diego, 1974).
[14] The standard Schmidt process is not suitable for the present purposes.