

Role of Orthogonalization in the Determination of Valence States in Crystals

E. BROWN

Rensselaer Polytechnic Institute, Troy, New York

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The orthogonalization process used in the method of orthogonalized plane waves (OPW) and in the pseudopotential method of Phillips and Kleinman (PK) is investigated. It is shown that the sole effect of this procedure is the introduction of proper core behavior into the wave function. A more direct method is shown to give the same result more simply than OPW and with better accuracy in the case that the core functions are not well known. The alternative formulation can also be used to derive the PK pseudopotential and leads to a deeper insight into its meaning.

I. INTRODUCTION

ONE of the more successful methods for the calculation of valence states in crystals has been the method of orthogonalized plane waves (OPW).¹ The method makes use of an expansion in plane waves which have been orthogonalized to appropriate core states. The convergence of this expansion is extremely rapid when compared with a simple plane wave expansion. A more recent method introduced by Phillips and Kleinman (PK)²⁻⁵ also makes use of the idea of orthogonalization to core states. In this method they show that the orthogonalization terms lead to a repulsive potential which largely cancels the effect of the atomic potential in the atomic cores. Although this potential actually depends on the valence function of interest, its dependence is primarily through the l value of the dominant spherical harmonic.

The approximate cancellation of the potentials is beneficial in that the eigenfunction of this modified Hamiltonian may be well approximated by a relatively smooth function. Only a few plane waves are required to give a good approximation to it.

Cohen and Heine⁶ have shown that the PK wave function is not uniquely defined. They have made use of this property to put auxiliary conditions on the function so as to simplify the application of the method to special problems. For example, one may pick that function which minimizes the expectation value of the kinetic-energy operator in hope that such a function may be well represented by only a few terms in an expansion. In addition, they show that, strictly speaking, the repulsive potential is really a nonlocal operator. Only when the valence function is known can this operator be properly replaced by a potential. Because of this feature, and the related fact that the potential changes for different states, the method is difficult to apply accurately. However, the approximate cancellation of potentials seems to explain the qualitative

free-electron character shown by energy bands in metals.

Although the OPW and PK methods seem to be based on the orthogonalization process, it turns out that this is somewhat illusory. A considerable insight can be gained by deriving the basic equations of these methods without recourse to orthogonalization. It can then be seen how important simplifications can be made without sacrificing the benefits previously obtained.

In Sec. II the OPW and PK methods are derived in the conventional way; an alternative derivation is given in Sec. III. The repulsive potential of PK is examined in some detail in Sec. V, where it is shown how the cancellation with the core potential comes about. Finally the problem of inaccurate core functions is examined. It will be shown that convergence to the correct valence state can still be guaranteed.

II. THE ORTHOGONALIZATION CONDITION

It is assumed that a one-electron Hamiltonian with a self-consistent periodic potential is given:

$$\mathbf{H} = -\nabla^2 + V(\mathbf{r}), \quad (1)$$

and that there are M core states and eigenvalues, $|\phi_i\rangle$ and E_i , respectively, which are known.⁷

The projection operator

$$\mathbf{Q} = \sum_{i=1}^M |\phi_i\rangle \langle \phi_i|, \quad (2)$$

when applied to an arbitrary state, projects it into the space of the core states. Define

$$\mathbf{P} = \mathbf{1} - \mathbf{Q}. \quad (3)$$

This operator projects an arbitrary vector into the space of the remaining states, and thereby orthogonalizes it to core states,

$$\langle \phi_i | \mathbf{P} | \chi \rangle = 0, \quad i = 1, 2, \dots, M \quad (4)$$

for arbitrary χ . Thus the orthogonalization procedure applied to any state is simply accomplished by operating with \mathbf{P} .

⁷ In a periodic potential we may restrict our attention only to states of a given k . The eigenvalues are then discrete, and M is generally a small number.

¹ T. O. Woodruff, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4.

² J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959).

³ L. Kleinman and J. C. Phillips, *Phys. Rev.* **116**, 880 (1959).

⁴ L. Kleinman and J. C. Phillips, *Phys. Rev.* **117**, 460 (1960).

⁵ L. Kleinman and J. C. Phillips, *Phys. Rev.* **118**, 1153 (1960).

⁶ M. H. Cohen and V. Heine, *Phys. Rev.* **122**, 1821 (1961).

The equation

$$\mathbf{H}\mathbf{P}|\phi\rangle = E\mathbf{P}|\phi\rangle, \quad (5)$$

in which $\mathbf{P}|\phi\rangle$ is assumed nontrivial, has for its eigenvalues all those of \mathbf{H} , except those of the core states.

The state $|\phi\rangle$ is not determined completely by Eq. (5) since we could add $\mathbf{Q}|\chi\rangle$ without any effect. However, $\mathbf{P}|\phi\rangle$ is uniquely determined, and is the proper eigenstate of the Hamiltonian. From (3) we get for any state $|\phi\rangle$ which satisfies Eq. (5),

$$\mathbf{H}|\phi\rangle + (E - \mathbf{H})\mathbf{Q}|\phi\rangle = E|\phi\rangle. \quad (6)$$

The operator $(E - \mathbf{H})\mathbf{Q}$ is seen to be the nonlocal potential operator \mathbf{V}_r discussed by Cohen and Heine:

$$\mathbf{V}_r = (E - \mathbf{H}) \sum_i |\phi_i\rangle\langle\phi_i| = \sum_i (E - E_i) |\phi_i\rangle\langle\phi_i|. \quad (7)$$

In a spatial representation $\mathbf{V}_r|\phi\rangle$ becomes

$$\mathbf{V}_r\phi = \int V(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') d\mathbf{r}', \quad (8)$$

where

$$V(\mathbf{r}, \mathbf{r}') = \sum_i (E - E_i) \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}'). \quad (9)$$

The local repulsive potential of PK is then

$$V_r(\mathbf{r}) = (\mathbf{V}_r\phi)/\phi(\mathbf{r}),$$

an operator which depends on ϕ . In these terms, Eq. (6) becomes

$$-\nabla^2\phi + (V + V_r)\phi = E\phi. \quad (10)$$

This is the fundamental equation of the PK method.

The OPW equations can be obtained similarly. The functional which, when extremalized, leads to Eq. (5) is

$$\Lambda = \langle\phi|\mathbf{H}\mathbf{P}|\phi\rangle / \langle\phi|\mathbf{P}|\phi\rangle = \langle\mathbf{P}\phi|\mathbf{H}|\mathbf{P}\phi\rangle / \langle\mathbf{P}\phi|\mathbf{P}\phi\rangle. \quad (11)$$

If $|\chi_n\rangle$ is a plane wave, then $\mathbf{P}|\chi_n\rangle$ is an OPW. It then follows that variation of Λ in terms of the amplitudes of a plane wave expansion for ϕ leads to the secular equations of OPW.

III. ALTERNATIVE DERIVATION

Let $|\psi\rangle$ be a valence eigenstate of \mathbf{H} and write

$$|\psi\rangle = \sum_{i=1}^M a_i |\phi_i\rangle + |\phi\rangle. \quad (12)$$

We then get, on substituting in the Schrödinger equation,

$$\mathbf{H}|\phi\rangle + \sum_i a_i (E_i - E) |\phi_i\rangle = E|\phi\rangle. \quad (13)$$

In Eq. (12) and Eq. (13) the coefficients a_i are arbitrary, so that $|\phi\rangle$ is not uniquely determined. However, since the coefficients a_i and $|\phi\rangle$ are related, we can express the a_i in terms of $|\phi\rangle$. We will use Eq. (13) for this purpose by dotting both sides through with $\langle\phi_j|$:

$$\langle\phi_j|E|\phi\rangle + \sum_i a_i (E_i - E) \langle\phi_j|\phi_i\rangle = E \langle\phi_j|\phi\rangle. \quad (14)$$

Using

$$\langle\phi_j|\phi_i\rangle = \delta_{i,j}, \quad (15)$$

we get

$$a_j = -\langle\phi_j|\phi\rangle. \quad (16)$$

Putting this result into Eq. (12) and Eq. (14) yields

$$|\psi\rangle = \mathbf{P}|\phi\rangle \quad (17)$$

and

$$\mathbf{H}\mathbf{P}|\phi\rangle = E\mathbf{P}|\phi\rangle \quad (5)$$

which is the starting point of Sec. II and establishes the equivalence.

In one respect this is a trivial result. The coefficients a_i determined by Eq. (16) are just those which orthogonalize $|\psi\rangle$ to the core states. It is well known that this must be the case, as a consequence of the Hermitian property of H . The point to note is that *the orthogonalization condition need not be invoked a priori*. [Use was made, however, of the orthonormal property of core states, Eq. (15), in the derivation.]

This point becomes important when approximation methods, based on the variational principle, are used. It has already been noted² that for certain choices of the a_i in Eq. (12), ϕ can be closely approximated by a few plane waves. Thus a trial function is suggested, of the form

$$\psi_t = \sum_{i=1}^M a_i \phi_i + \sum_n b_n (PW)_n, \quad (18)$$

in which a_i and b_n are determined variationally.

Omitting the orthogonality conditions achieves a great simplification in form without any loss of accuracy. This point will be discussed further in Sec. V.

IV. THE NATURE OF THE WAVE FUNCTION IN THE CORE REGION

Sufficiently close to a nucleus the potential in the solid is almost spherically symmetric. The wave function is conveniently expressed in a series of spherical harmonics times radial functions in this region.

$$\psi(\mathbf{r}) = r^{-1} \sum_{l,m} u_l(r) C_{l,m} Y_{l,m}(\theta, \phi). \quad (19)$$

The radial functions satisfy the equation,

$$u_l'' = [V + l(l+1)/r^2 - E] u_l, \quad (20)$$

with inner boundary condition:

$$u_l(0) = 0. \quad (21)$$

Over most of the core region the coefficient of u_l in Eq. (20) is insensitive to the energy. For this reason, states of a given l are very similar in form in the core region. This point is illustrated in Fig. 1 for the case of atomic hydrogen. The eigenfunctions have been adjusted in amplitude so that the coefficient of the leading term in the power series expansion is unity.

It should be noted that (1) the functions "track" best near the origin, and (2) the tracking between adjacent eigenstates becomes better, and over a more

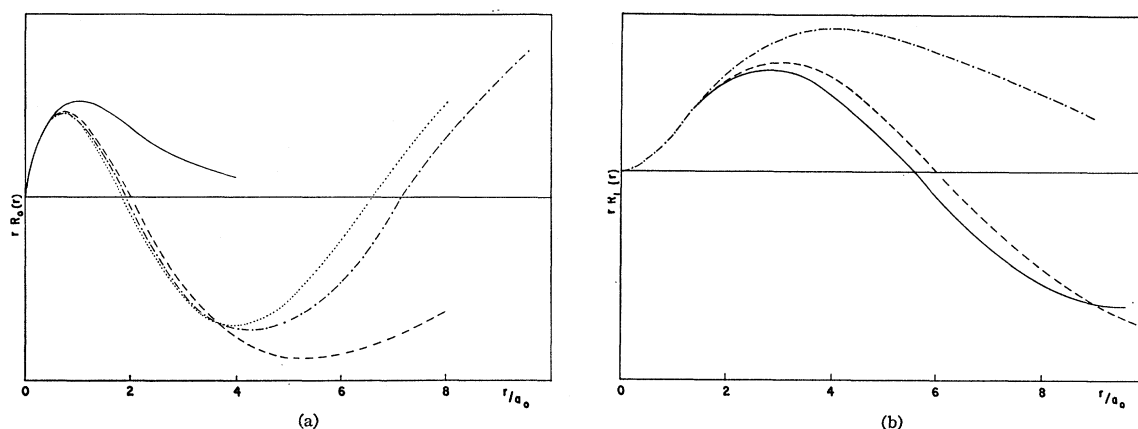


FIG. 1. Radial part of hydrogen wave functions. Amplitudes have been adjusted to display the tracking of the functions near the origin. (a) s functions; solid curve $n=1$; dashed curve $n=2$; dot-dashed curve $n=3$; dotted curve $n=4$. (b) p functions; dot-dashed curve $n=2$; dashed curve $n=3$; solid curve $n=4$.

extended region, as n increases. These observations are to be expected from Eq. (20) since (1) the coefficient of u_l is insensitive to E near the origin, (2) it is less sensitive to E over a larger region for high E , especially for $l=0$, and (3) adjacent states become closer in energy as n increases. It is to be expected that $l=0$ states would track best, in general, since there is no inner turning point (i.e., the coefficient has only one zero). The tracking is expected to become poor near the turning points, as is illustrated in Fig. 1. (The turning points can easily be estimated by noting where the functions change character between oscillatory and exponential behavior.) Thus, a valence function may be well approximated by an appropriate linear combination of core orbitals and a smooth function. Without core orbitals a large number of terms in a plane wave

expansion are necessary to represent the rapid oscillations in the core. With the core orbitals included in the expansion, only a few additional plane waves are necessary. As will be shown, it is this fact alone that makes the OPW and PK methods work as well as they do. The point is best illustrated by consideration of the Fourier integral transforms of the hydrogenic functions. These have the same angular symmetry in momentum space as the spatial functions. Figure 2 shows the radial parts in k space, as determined by Podolsky and Pauling.⁸ The amplitudes have been adjusted in this case to yield the same asymptotic form for each type of symmetry. It is seen that these transforms differ appreciably only at low wave numbers. Thus only a few plane waves of low wave number, are needed to approximate the difference between one hydrogenic

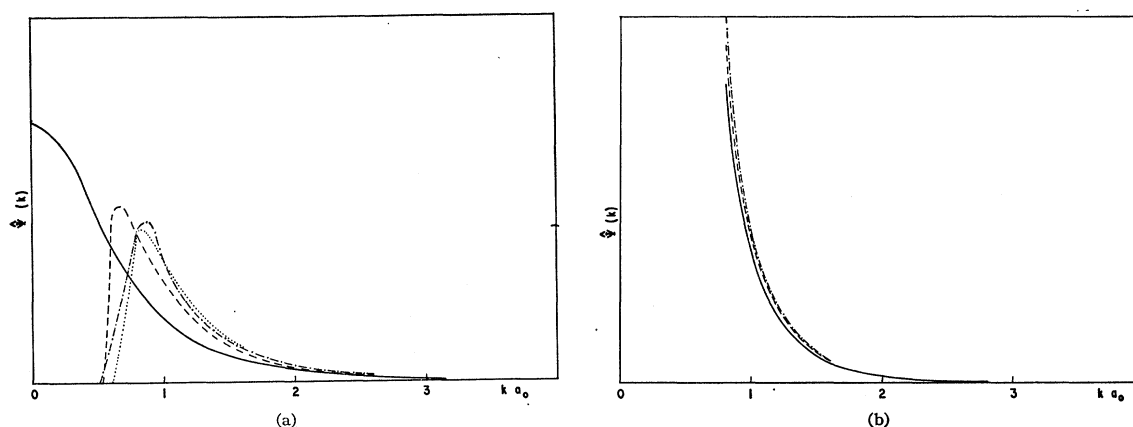


FIG. 2. Asymptotic part of Fourier integral transforms of hydrogen wave functions. The complete transform is $\hat{\psi}(k, \Theta, \Phi) = \hat{\psi}(k) Y_{l,m}(\Theta, \Phi)$. Functions have been normalized to show similar asymptotic form. The functions which are not shown at low wave number oscillate off scale. (The number of radial nodes is the same as that of the corresponding spatial function.) Labeling corresponds to that of Fig. 1.

⁸ B. Podolsky and L. Pauling, Phys. Rev. **34**, 109 (1929).

function and another of the same symmetry type.⁹ In this connection, it is noted that mixing several core states does not help much, as the functions are highly redundant for this purpose.

It may appear somewhat coincidental that the amplitudes of the core orbitals introduced by the orthogonalization process are just those which require only a few terms in an OPW expansion. It is not a coincidence, as can be shown with reference to the expansion of ψ , of Eq. (18). The secular determinant resulting from this expansion has for its first- M eigenvalues the M -core eigenvalues. By a well-known theorem,

$$E_{M+1} = \min(\langle \psi_i | \mathbf{H} | \psi_i \rangle / \langle \psi_i | \psi_i \rangle), \quad (22)$$

subject to the condition

$$\langle \phi_i | \psi_i \rangle = 0, \quad i = 1, 2, \dots, M. \quad (23)$$

The linear combination of plane waves and core functions which yields this minimum value, is, in a sense, "the best available approximation" to the valence state. In this sense the function $\phi(\mathbf{r}) = \psi(\mathbf{r}) - \sum a_i \phi_i(\mathbf{r})$, in which the a_i are determined by Eq. (22), is the one best approximated by the available plane waves. The OPW expansion must yield exactly the same result since Eq. (22) and Eq. (23) are equivalent to

$$E_{M+1} = \min(\langle \mathbf{P}\psi_i | \mathbf{H} | \mathbf{P}\psi_i \rangle / \langle \mathbf{P}\psi_i | \mathbf{P}\psi_i \rangle), \quad (24)$$

where

$$\mathbf{P}|\psi_i\rangle = \sum_{n=1}^N b_n(\text{OPW})_n. \quad (25)$$

The important points will be summarized. The function $\phi(\mathbf{r})$ depends parametrically on the coefficients of core states. Although ϕ will be smooth only for certain choices of these coefficients, it is not necessary to select an optimum choice by special conditions on ϕ , if a variational method is used. Such a method will select an optimum linear combination, if the coefficients are variationally determined. This is the case for the expansion of Eq. (18), or that of OPW. In the latter method these coefficients do not appear explicitly but are buried in the orthogonalization terms. Thus, if one were to take the linear combination of orthogonalized plane waves which correspond to the valence state, and express them as plane waves and Bloch sums of core orbitals, the results would be identical with the variationally determined coefficients of Eq. (18).

V. CANCELLATION OF POTENTIALS

Given an arbitrary well-behaved function, it is always possible to concoct a Schrödinger equation for which the given function is a solution. Letting $f(\mathbf{r})$ be the given function and E a specified eigenvalue, we

define a potential

$$V'(\mathbf{r}) = \nabla^2 f / f + E, \quad (26)$$

so that rearranging terms we get

$$-\nabla^2 f + V' f = E f. \quad (27)$$

The potential V' will be spherically symmetric in the region where f can be written as a product of a radial function and a single spherical harmonic. Letting f be written

$$f = r^{-1} u(r) Y_{l,m}(\theta, \phi), \quad (28)$$

we find

$$V' = u''/u - l(l+1)/r^2 + E. \quad (29)$$

In the region where u''/u is small the effective potential V' depends on $f(\mathbf{r})$ primarily through the angular momentum quantum number l . It is now relatively easy to understand why the repulsive potential introduced by Phillips and Kleinman almost cancels out the effect of the core potential for s states and leaves a residue of $-l(l+1)/r^2$ for other states. For the purpose of clarifying this point we assume we know the correct valence state of symmetry type l , $\psi(v, l)$, and the corresponding energy, E_l . We assume that $\psi(1, l)$, $\psi(2, l)$, \dots , $\psi(M, l)$ are core states of the same symmetry. Now, by our previous arguments, some linear combination of these will differ from the correct valence state in a very smooth way, having no nodes. Let ϕ_l be the smoothest of such functions,¹⁰

$$\phi_l = \psi(v, l) - \sum a_m \psi(m, l) \quad (30)$$

where the a_m are fixed by the smoothness condition. It is obvious that applying the projection operator \mathbf{P} to ϕ leaves us with the correct valence state, since the core states are removed thereby.

As in Eq. (27), we now form a Schrödinger equation for ϕ_l with eigenvalue $E_{v,l}$:

$$-\nabla^2 \phi_l + V \phi_l + V_r \phi_l = E_{v,l} \phi_l, \quad (31)$$

where $V + V_r = V' = u''/u - l(l+1)/r^2 + E_{v,l}$ as in Eq. (29).

The function u is the difference between the correct radial function and a linear combination of core radial functions. The first two terms in the expansion of each of these comes from the terms $l(l+1)/r^2 - 2Z/r$ in the effective potential. Unless the leading terms are cancelled in the subtraction process, we get $u''/u = l(l+1)/r^2 - 2Z/r$ for very small r . For larger r , $-u''/u$ should be of the order of the square of a reciprocal lattice vector,¹¹ since ϕ may be roughly approximated by a single symmetrized plane wave.

⁹ Strictly speaking, a discrete expansion in plane waves is appropriate only for a Bloch sum of such orbitals. In that case the Fourier coefficients are proportional to the Fourier integral transform sampled at a lattice of points.

¹⁰ The term "smooth" roughly implies the requirement of only a few symmetrized plane waves in the expansion. As with Cohen and Heine, we may pick the function that minimizes $\langle \phi | -\nabla^2 | \phi \rangle / \langle \phi | \phi \rangle$ as being the smoothest.

¹¹ The reciprocal lattice vectors are defined by $\mathbf{\kappa}_i \cdot \mathbf{\tau}_j = 2\pi \delta_{i,j}$.

Thus we can expect V_r to be small very close to the origin, giving negligible cancellation. For larger r , but still in the core, we may expect cancellation of the Coulomb part, but also a term $-l(l+1)/r^2$, which tends to cancel the repulsive potential in the radial equation. Except for the behavior very near the origin, it is qualitatively correct to think of V_r as a repulsive potential which cancels out the effect of the actual potential for S -like states and leaves the residual effect of $-l(l+1)/r^2$ for others. This is the result found by Phillips and Kleinman.

VI. BOUNDEDNESS OF EIGENVALUES

One of the well-known difficulties of the OPW method is that the core functions must be known with a great deal of accuracy. In most problems they are fairly easily found since there is usually negligible overlap between core orbitals on different atoms. It should be noted, in passing, that these core orbitals must be the proper eigenfunctions of the one electron Hamiltonian used in computing valence states, rather than some more appropriate Hamiltonian for the core states of the crystal. If, in the interest of simplicity, approximate functions are used to approximate the core functions, serious errors may result.¹² These errors reflect the fact that the trial function is restricted to the wrong subspace of Hilbert space. The mathematics is equivalent to the geometrical problem of finding the principal axes of an ellipsoid. Assume the direction of one axis is precisely known: One then merely has to examine the ellipse formed by the intersection of the ellipsoid with the plane normal to the given direction through the center. The largest diameter is one principal axis, and the smallest is the other. The error which results from using an incorrect plane may easily be visualized.

The minimum eigenvalue of the secular determinant in OPW will, in case of error, approach a value lower than the correct valence eigenvalue as the size of the matrix increases without limit. Moreover, for a finite truncation there is no criterion for the sign of the error. Secular methods based on the expansion of Eq. (18) have no such drawback. As is shown in the Appendix, the approximate eigenvalues will approach the correct eigenvalues monotonically from above, even if the core functions are only approximately known. The reason for the difference in the two approaches can be understood qualitatively from the fact that Eq. (18) yields core states which are an improvement over the original approximations. In the limit of an infinite expansion, the core states, as well as the valence states will be correctly given.

Consideration of Figs. 1 and 2 indicates that little is gained by incorporating all the core states of a given

symmetry in Eq. (18). In principle it should suffice to incorporate only the one of neighboring energy. If this is done, not only will the valence state be given reasonably accurately with the addition of a few plane waves, but so will the remaining core states. The monotonic nature of the approach of the eigenvalues to the correct ones, as the matrix size increases, still is valid.

VII. DISCUSSION AND SUMMARY

The reason that methods which utilize the orthogonalization procedure converge rapidly is due solely to the incorporation of core behavior into the wave function. In several respects this procedure is an unnecessarily clumsy and unreliable way of accomplishing this end: (1) It fails completely when there are no core orbitals of appropriate symmetry, (2) accurate calculations must be based on accurately known core orbitals, and (3) expansion methods, such as OPW, make use of highly redundant and unnecessarily complicated functions, each of which incorporate the core behavior.

Incorporation of core behavior can be accomplished in a very straightforward way. An expansion, such as Eq. (18), utilizing functions with the proper core behavior is all that is required.¹³ These may be eigenfunctions of lower energy, but they need not be. Orbitals which satisfy Eq. (20) for small r and join on smoothly to a smooth function which goes to zero at a radius of half the interatomic distance might also be used. These would be valuable when there are no core states of appropriate symmetry. It is an oversimplification to describe states in terms of a single angular momentum quantum number. In practice, for any given state several spherical harmonics should be considered. The considerations already given suggest an expansion such as Eq. (18) with one orbital for each l value considered.

It doesn't seem likely that many l values need be explicitly introduced. For one thing it is well known that the amplitudes of higher l functions drop off rather rapidly. Moreover, since the repulsive term $l(l+1)/r^2$ tends to screen out the core potential fairly strongly for high l value, these functions are rather well represented by the plane wave terms in the expansion.

¹³ In an earlier paper, E. Brown and J. A. Krumhansl, *Phys. Rev.* **109**, 30 (1958), such an expansion was tested by an application to lithium. Unfortunately, some doubt was cast upon the inherent accuracy of the method because of a further approximation which was made for nonzero \mathbf{k} . Instead of taking a Bloch sum of atomic orbitals of appropriate \mathbf{k} , the simpler approximation was made that $\psi_{\mathbf{k}}(\mathbf{r}) = \psi_0(\mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}}$. In comparing results with the more accurate ones of W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954), a compensating error was made in converting units, yielding an unwarranted good agreement. The present author would like to thank Dr. J. Callaway for pointing out our error in reporting the results of Kohn and Rostoker.

¹² J. Callaway, *Phys. Rev.* **97**, 933 (1955).

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APPENDIX

Consider a Hamiltonian operator \mathbf{H} , and let

$$\mathbf{H}_t^N = \mathbf{P}_N \mathbf{H} \mathbf{P}_N, \quad (\text{A1})$$

where \mathbf{P}_N is the operator¹⁴ which projects an arbitrary vector into the N -dimensional space defined by the independent vectors $|\alpha_1\rangle, |\alpha_2\rangle, \dots, |\alpha_N\rangle$.

Let

$$\mathbf{H}_t^N |\psi_i^N\rangle = E_i^N |\psi_i^N\rangle, \quad i=1, 2, \dots, N \quad (\text{A2})$$

where the eigenvalues are arranged such that

$$E_1^N \leq E_2^N \leq E_3^N \leq \dots \leq E_N^N. \quad (\text{A3})$$

In addition to the above, consider an augmented space consisting of the original N vectors plus one other. In this latter space similar definitions are used in which the symbol N is replaced by $N+1$.

¹⁴ If $|\beta_1\rangle, |\beta_2\rangle, \dots, |\beta_N\rangle$ are N orthonormal vectors in the given space, then

$$\mathbf{P}_N = \sum_{i=1}^N |\beta_i\rangle \langle \beta_i|.$$

Define $|\phi_0\rangle$ by the following:

$$|\phi_0\rangle = \sum_{i=1}^M a_i |\psi_i^N\rangle \quad (\text{A4})$$

$$\langle \psi_i^{N+1} | \phi_0 \rangle = 0, \quad i=1, 2, \dots, M-1, \quad (\text{A5})$$

where $\langle \phi_0 | \phi_0 \rangle \neq 0$.

These equations determine $M-1$ of the coefficients a_i in terms of one other. Thus $|\phi_0\rangle$ is determined except for amplitude. From the orthogonality expressed in Eq. (A5) it follows that

$$|\phi_0\rangle = \sum_{i=M}^{N+1} b_i |\psi_i^{N+1}\rangle. \quad (\text{A6})$$

Thus $|\phi_0\rangle$ is a vector in the subspace defined by $|\psi_1^N\rangle, |\psi_2^N\rangle, \dots, |\psi_M^N\rangle$ and also in the subspace defined by $|\psi_M^{N+1}\rangle, |\psi_{M+1}^{N+1}\rangle, \dots, |\psi_{N+1}^{N+1}\rangle$.

Let $|\alpha\rangle$ be an arbitrary vector in the former subspace, and let $|\beta\rangle$ be one in the latter. Then

$$E_M^N = \max(\langle \alpha | \mathbf{H} | \alpha \rangle / \langle \alpha | \alpha \rangle) \geq \langle \phi_0 | \mathbf{H} | \phi_0 \rangle / \langle \phi_0 | \phi_0 \rangle, \quad (\text{A7})$$

$$E_M^{N+1} = \min(\langle \beta | \mathbf{H} | \beta \rangle / \langle \beta | \beta \rangle) \leq \langle \phi_0 | \mathbf{H} | \phi_0 \rangle / \langle \phi_0 | \phi_0 \rangle. \quad (\text{A8})$$

Thus

$$E_M^{N+1} \leq E_M^N. \quad (\text{A9})$$

From this it follows that the M th eigenvalue forms a monotonically nonincreasing sequence. Thus the approximate eigenvalues approach the correct eigenvalues from above.