(b) Ten percent of the *F* centers formed by x-raying KBr at 300°K can be bleached by *F* light at 5° or at 78°K. Over half of the bleached centers are rebuilt in the dark after several hours. After the dark recovery, one may bleach the *F* band again. If one shines *F′* light on a bleached crystal, it recovers in a few seconds. The changes in the *F′* absorption band were too small to directly establish its presence.

(c) About 20 percent of the *F* centers can be bleached in a crystal x-rayed at 78°K. There is a partial recovery in the dark, the fraction recovered being less than the previous case. After this crystal has been put through the cycle of bleaching and dark recovery several times, it behaves similarly to a crystal x-rayed at 300°K.

It is to be stressed that no qualitative calculations on tunneling have been made as yet. Some idea of the order of magnitude of the distance the electron can tunnel through would be very helpful in interpreting the above data. Photoconductivity measurements at 5°K would undoubtedly throw a great deal of light on the mechanisms of bleaching. Nevertheless, the following interpretation of the above data is offered: These data indicate the tunneling from one imperfection to another occurs if the distance is small. This tunneling can cause significant and readily measurable effects. These experiments suggest that the color centers are not distributed uniformly throughout the crystal but have a relatively high concentration in certain layers. The concentration of imperfections in these layers depends on the temperature at which the crystal is x-rayed. Higher concentrations are obtained at lower temperatures. If the Nabarro-Seitz production hypothesis is correct, the location of high concentrations is determined by the distributions of dislocations.

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An Augmented Plane Wave Method for the Periodic Potential Problem

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A new method is proposed for solving a periodic potential problem in which the potential can be approximated as a constant outside spheres surrounding the atoms, spherically symmetrical within the spheres. We set up unperturbed functions consisting of a plane wave outside the spheres, joined continuously and with continuous derivative to functions derived from the spherical problem within the spheres. These spherical solutions are linear combinations of eigenfunctions of Schrödinger's equation within the spheres, subject to the boundary conditions that the logarithmic derivative of the function of each l value at the surface equals the logarithmic derivative of the corresponding Bessel function in the expansion of the plane wave, thereby insuring continuity of the derivative of the wave function over the sphere if the function itself is continuous. The coefficients in the expansion within the spheres are determined by demanding that the expectation value of the energy of the wave function be stationary when the coefficients are varied. The secular equation connected with this variation problem can be solved exactly, leading to wave functions having the general character of orthogonalized plane waves. A linear combination of such functions is then used to build up an approximate solution of Schrödinger's equation. It is shown that the tightly-bound states are handled quite differently from the conduction band, and that the treatment of the conduction band can well resemble the free-electron approximation, thereby perhaps explaining the empirical success of the free-electron approximation for the conduction electrons in metals. The method can be extended to a case where the potential does not have the simple behavior postulated, by treating the difference between the actual potential and the postulated form as a perturbation.

1. GENERAL FORMULATION OF THE METHOD

THE solution of the wave-mechanical problem of an electron moving in a three-dimensional periodic potential of the type found in a crystal as treated by a self-consistent field method is an important part of the theory of solids. No existing approximate solution is completely satisfactory, and we present in this paper a new method having certain advantages over each of the existing approximations. The method is directly applicable to a problem in which the potential is spherically symmetrical within spheres surrounding the various nuclei, and is constant in the region between the spheres, which are assumed not to overlap, though we shall later show how to extend it to more general potentials.

For such a potential, it has been generally assumed that the wave function in the region between spheres could be well approximated by a superposition of a relatively small number of plane waves. On the other hand, such a wave function behaves very badly in the neighborhood of the atoms. Herring[1] has suggested the method of orthogonalized plane waves, by which one adds to each of these plane waves a set of atomic func-

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

tions corresponding to the tightly bound states of the various atoms, with such coefficients that the resulting function is orthogonal to Bloch sums representing wave functions of all the tightly bound states. Herring and Hill[2] have applied this method with success to beryllium, Herring and Parmenter[3] to lithium, and Herman and Callaway[4] to diamond and germanium. Relatively few such orthogonalized or augmented plane waves suffice to give a rather good approximate wave function. The method has drawbacks, however, as Herman found in treating diamond. An energy band of $2p$-like symmetry in diamond has no lower, tightly-bound state to which it must be orthogonalized, and as a result the method merely uses ordinary plane waves to construct such a wave function, with rather poor convergence. Herman[5] has suggested that in such a case we could augment the plane wave by adding something which would make it behave more nearly like an atomic function near the nucleus, even though this was not required for orthogonalization, but this has not been carried out in an actual case.

The present method may be regarded as a straightforward procedure for augmenting a plane wave by adding to it a contribution near each nucleus such as to make the resulting wave function satisfy Schrödinger's equation as closely as possible. We set it up in a slightly different form, however: we use for an unperturbed wave function a plane wave of given $\mathbf{k}$ value, or propagation constant, in the region between the atomic spheres, but join this smoothly onto a function within each sphere which represents the best possible solution of Schrödinger's equation. We call such a function an augmented plane wave. Then to get the final result, we make a linear combination of a number of such augmented plane waves, with different $\mathbf{k}$ values, being led thereby to a secular equation as in the method of Herring. Since we start with the best approximate functions which we can set up, our method should converge as rapidly as any such augmented plane wave method can.

We set up these augmented plane waves in the following way. Outside an atom located at vector position $\mathbf{R}_i$, the wave function is assumed to be $a_0\exp(i\mathbf{k}\cdot\mathbf{r})$, where a_0 is a constant. Let the atomic sphere have a radius r_i. Then the value of this wave function at points on the surface of the sphere is

$$a_0\exp(i\mathbf{k}\cdot\mathbf{R}_i)\sum(l)\ (2l+1)i^lP_l(\cos\theta)j_l(kr), \tag{1}$$

where r, θ are spherical coordinates with the origin at the nucleus of the atom, and the axis along the direction of the propagation vector $\mathbf{k}$. We now wish to set up a wave function within the sphere which joins continuously and with continuous derivative onto this plane wave. This cannot be a solution of Schrödinger's equation, for we know that a solution of Schrödinger's equation within a spherical atom cannot in general be joined smoothly onto a plane wave; scattering theory shows that it can only be joined to a plane wave plus scattered wavelets. We shall, however, try to make the solution inside as good an approximation to a solution of Schrödinger's equation as we can.

As a first step, we set up Schrödinger's equation within the sphere, separate variables in the usual way, and find that the radial function u associated with a given l value satisfies the equation

$$\left[\frac{-d^2}{dr^2}+V_i(r)+l(l+1)/r^2\right](ru)=Eru, \tag{2}$$

where $V_i(r)$ is the potential within the sphere; we use the Bohr radius as unit of length, the Rydberg as unit of energy. We solve this Schrödinger equation for all energy values E, finding the solution regular at the origin, and find the logarithmic derivative $(1/u)du/dr$ at the surface of the sphere, or at $r=r_i$, as a function of E. We pick out those particular values of E for which this logarithmic derivative equals the logarithmic derivative of $j_l(kr)$ at $r=r_i$. The corresponding wave functions form a complete orthogonal set within the sphere. To prove the orthogonality, we set up Eq. (2) first for one eigenvalue and eigenfunction E_1 and u_1, then for another E_2 and u_2, and proceed by the usual method for showing orthogonality. We find

$$(E_2-E_1)\int_0^{r_i} r^2u_1u_2dr=r_i^2u_1(r_i)u_2(r_i) \\ \times[(1/u_1)du_1/dr-(1/u_2)du_2/dr]|_{r_i}, \tag{3}$$

where the expression on the right is to be computed when $r=r_i$. Since the two logarithmic derivatives are equal, each being equal to the logarithmic derivative of $j_l(kr)$, the orthogonality is proved. We normalize each of the wave functions $u(r)P_l(\cos\theta)$ over the sphere. Each of the wave functions and energy values should really carry three indices: one (i) to indicate which atom we are dealing with, a second (n) to indicate which of the eigenvalues we are dealing with, numbering up from the lowest energy, and finally the l value. Thus we shall call them u_{inl}, E_{inl}.

Now we build up within the sphere a linear combination of these wave functions, of the form

$$\sum(n,l)a_{inl}u_{inl}(r)P_l(\cos\theta). \tag{4}$$

We choose the a's to obtain continuity with the plane wave outside. That is,

$$\sum(n)\ a_{inl}u_{inl}(r_i)=a_0\exp(i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)i^lj_l(kr_i), \tag{5}$$

for each l value. Since each of the u_{inl}'s has the same logarithmic derivative as $j_l(kr)$, this means that if we

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[2] C. Herring and A. G. Hill, Phys. Rev. 58, 132 (1940).

[3] C. Herring, Phys. Rev. 55, 598 (1939); R. H. Parmenter, Phys. Rev. 86, 552 (1952).

[4] F. Herman, Phys. Rev. 88, 1210 (1952); F. Herman and J. Callaway, Phys. Rev. 89, 518 (1953).

[5] F. Herman, Ph.D. Thesis, Columbia University, 1953 (unpublished).

make the wave function continuous, we shall also automatically make its derivative continuous. We must now determine the a's. We do this as follows. We set up the expectation value of the energy of our augmented plane wave, consisting of the function (4) within the ith sphere, and the plane wave outside the spheres. This expectation value is

$$E=\sum(inl)\,a_{inl}^*a_{inl}E_{inl}+a_0^*a_0E_0\Omega, \qquad (6)$$

where E_0 is the kinetic energy of a plane wave of propagation vector k, and Ω is the volume of the space outside the spheres. We may carry our integrations over unit cell, in which case Ω is the volume of unit cell outside the spheres, and the summation over i goes over all atoms in the unit cell; but we may equally well use the whole crystal. We wish to have the wave function normalized over the same volume, and this leads to the condition

$$1=\sum(inl)\,a_{inl}^*a_{inl}+a_0^*a_0\Omega. \qquad (7)$$

Now we demand that the a's be chosen so that the expectation value E of the energy is stationary with respect to variation of these parameters, consistent with always maintaining a normalized wave function, and always satisfying the condition (5) of continuity.

This variation problem can be handled by the method of undetermined multipliers; and by a great piece of good fortune, as shown in the Appendix, the solution of the resulting secular problem can be carried out explicitly. We find in the first place that the eigenvalues E are given by the equation

$$-\Omega^{-1}\sum(il)\,(2l+1)^2j_l^2(kr_i)(E_0-E)^{-1} \times\{\sum(n)\,[u_{inl}^2(r_i)/(E_{inl}-E)]\}^{-1}=1. \qquad (8)$$

This equation can be handled by computing the function of E appearing on the left side of the equation, and finding the values of E for which it equals 1. We can show that there is an eigenvalue closely equal to each of the tightly bound energy levels of each of the atoms, and also an infinite number of higher eigenvalues; in fact, we can set up a one-to-one correspondence between the eigenvalues and the E_{inl}'s, one eigenvalue being found between each pair of E_{inl}'s.

Having found the E's from Eq. (8), we can next determine the a's. We find

$$a_{inl}=a_0\exp(i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)i^lj_l(kr_i)u_{inl}(r_i)(E_{inl}-E)^{-1} \times\{\sum(n')\,[u_{in'l}^2(r_i)/(E_{in'l}-E)]\}^{-1}. \qquad (9)$$

This equation determines the relation between the coefficients of the spherical functions and the coefficient a_0 of the plane wave. In Eq. (9) of course we are to insert one of the E values determined from Eq. (8). To find a_0, we use the normalization relation, which leads to

$$a_0^*a_0\Omega\{\Omega^{-1}\sum(il)\,(2l+1)^2j_l^2(kr_i)\sum(n) \times[u_{inl}^2(r_i)/(E_{inl}-E)^2] \times[\sum(n')\,u_{in'l}^2(r_i)/(E_{in'l}-E)]^{-2}+1\}=1. \qquad (10)$$

We thus have completely determined our augmented plane waves. For tightly bound states, these functions are much like Bloch waves. We find an eigenvalue close to each of the tightly bound atomic levels of each of the atoms, as we have stated, and in such a case the wave function within the atoms of that type is approximately the corresponding atomic function, joined on to a plane wave of very small amplitude outside, and with very small contributions in the other types of atoms which do not have this eigenvalue. For the higher-energy values, however, such as we find in the valence and conduction bands, the eigenvalue E will no longer approach an atomic value, and the wave function will be of significant size in all the types of atoms, and in the region between.

The various wave functions for a given $\mathbf{k}$ value, being solutions of a secular problem, are orthogonal to each other, and have no nondiagonal matrix components of energy between them. These facts, which we expect from general principles, are explicitly proved in the Appendix. They thus form in a very real sense orthogonalized plane waves, but the wave functions of the tightly bound states are set up by the same method used for the higher energy levels, and we have a systematic procedure for finding all such functions. On the other hand, the wave functions for different $\mathbf{k}$ values are not orthogonal to each other, and will have nondiagonal matrix components of energy between them. The required nondiagonal matrix components of energy, and of unity, are easily computed, and are needed in setting up the secular problem involved in making a linear combination of a number of augmented plane waves.

These matrix components come from two contributions: integration over the spheres, and integration over the volumes outside the spheres. Within the ith sphere, the Hamiltonian operating on the wave function will give $\sum(nl)\,a_{inl}E_{inl}u_{inl}P_l(\cos\theta)$. We must now multiply this by another wave function, and integrate over the sphere. We integrate first over the spherical harmonics, getting nothing unless both terms are connected with the same l value; we note that the axes of the spherical harmonics will be different for the two functions. We are then left with the integral over the sphere of a u_{inl} connected with one $\mathbf{k}$ value, and a $u_{in'l}$ connected with another $\mathbf{k}$ value. These two functions have different logarithmic derivatives at r_i, and the integral of their product does not vanish; but by Eq. (3), we can reduce the integral to quantities on the surface of the sphere which are already known. For the integrations over the regions outside the spheres, we must merely integrate E_0 times the product of two plane waves, which itself is a plane wave. The integral of this product over a whole unit cell is zero. Thus the integral over the region outside the spheres is the negative of the integral over the interiors of the spheres. Within each sphere, the plane wave can be expanded in spherical harmonics of angle times spherical Bessel functions; these can be integrated explicitly, so that we have the complete answer.

We thus see that the matrix components of energy are easily determined between two augmented plane waves of different **k**'s. The integral of the product of the wave functions is equally simple, found merely by omitting the E_{inl}'s. We then set up a secular equation between the augmented plane waves which we wish to combine, and solve it in the standard way. We can handle the non-orthogonality of wave functions of different **k**'s either by orthogonalizing them initially, or by carrying the overlap integrals in the secular equation. As in the orthogonalized plane wave method, if we are dealing with a symmetry point in the Brillouin zone, the coefficients of a number of orthogonalized plane waves will automatically be equal, so that the order of the required secular equation may be much less than the number of waves which we are superposing.

2. DISCUSSION AND CONCLUSIONS

For each **k** value, we have found an infinite number of augmented plane waves, corresponding to the various eigenvalues E. These eigenvalues depend on the magnitude of **k**, but not on the direction, and will be continuous functions of $|\mathbf{k}|$. They depend on the number of atoms of each type in the volume, but not on their arrangement. All directional effects, and all effects of crystal structure, appear in the process of combining a number of augmented plane waves to get our final wave function. In this respect our method resembles the free-electron method, as well as Herring's orthogonalized plane wave method.

There is a feature which is present in our method, however, which is different from the other methods so far proposed: there is a great redundancy of wave functions, and we must use our judgment in deciding which ones to use. We can understand this redundancy from a simple case, the tight-binding wave function made up from the $1s$ atomic orbital on one of the atoms. One of the eigenvalues E will lie close to the atomic energy of this state, and the wave functions will be almost like Bloch combinations of the $1s$ atomic orbitals, but joined onto plane waves of very small amplitudes between the atoms. Now let us consider two **k** values, one differing from the other by one of the vectors of the reciprocal lattice. The plane wave of either of these **k** values will have the same phase at each of the atoms, so that the corresponding Bloch sums will be almost precisely the same, and the wave functions corresponding to these two **k**'s will be practically identical within the atoms, where they are large, but will be quite different between the atoms, where they are small, being plane waves of different propagation constants. The integral of the product of the wave functions will mostly come from the interiors of the spheres, and will be practically unity, instead of zero as it would be if they were orthogonal. Clearly in our expansion we do not wish to use both of these wave functions. In fact, by analogy with the tight binding approximation, we know that we can get all the $1s$-like wave functions which we need by taking just those values of **k** in the central Brillouin zone.

We might think that we could get all the wave functions we needed for any case if for each of the eigenvalues of E we chose only those **k**'s in the central Brillouin zone; this would be closely analogous to the tight-binding approximation. Yet it clearly is not sufficient, for in this case we should have no secular problem, and the wave function between the atoms would be represented only by a single plane wave with a **k** vector in the central Brillouin zone. For the tightly bound states, for which the wave function is small between the atoms anyway, this is not a bad approximation, though we find that for p-like states we must have propagation vectors in three central Brillouin zones, for d-like states in five zones, and so on, to get the necessary number of functions. For valence and conduction bands, however, the wave function between the atoms is important, and we must certainly superpose waves with a number of **k** values to get a good approximation. The question remains whether these waves should all correspond to the same eigenvalue of E (that is, to the eigenvalues which join smoothly onto each other as **k** changes), or to different eigenvalues. It seems clear, from our information about wave functions from other sources, that in some cases we wish to use waves with **k**'s in many Brillouin zones, but all corresponding to the same eigenvalue.

The most straightforward case of this would be sodium. There we know, mainly from the cellular method, that for energies in the conduction band, the wave function is well approximated by a single plane wave between the atoms, joining onto solutions of a spherical problem within the atoms. This means that a single augmented plane wave, with a **k** value which can range through many Brillouin zones, may well be a very good approximation to a solution, for this particular case. This would imply that we were working with a single eigenfunction, which would reduce for $\mathbf{k}=0$ essentially to a combination of $3s$-like orbitals obeying the Wigner-Seitz boundary condition of zero slope at the boundary, in each unit cell. As **k** increases, we see from Eq. (9) that we shall also have contributions from p-like, then d-like, orbitals, and so on, coming in with gradually increasing coefficients (on account of the way in which $j_l(kr_i)$ increases with k, more slowly with high l values). We might well expect in this case that the energy of this state would be approximately proportional to k^2, as with a free-electron wave function, and that the wave functions corresponding to **k**'s in different Brillouin zones might approach orthogonality, instead of being almost identical as with the bound states. If we found this type of behavior, as seems plausible, we might get a very good approximation by taking linear combinations of such augmented plane waves. We should find very small nondiagonal matrix components of energy, since the unperturbed functions were so nearly solutions as they stood. Two wave functions connected with **k**'s in different unit cells in **k** space will be degenerate if their **k**'s satisfy the Bragg condition, so that along the planes where the Bragg condition is satisfied we shall have to introduce linear combinations of these plane waves. We shall have, in other words, an almost complete analogy to a free-electron calculation, and this may well prove to be the justification of the well-known fact that free-electron methods for the conduction electrons work much better than we should expect from any of the approximate methods usually in use.

We see, then, that we may have two quite different ways of choosing unperturbed wave functions, out of the great superfluity of functions which our method yields. For tightly bound states, we choose functions whose eigenvalues are close to the energies of the atomic states, and with **k**'s in the central Brillouin zone for *s* states, the central three zones for *p* states, and so on (it will be interesting to make a detailed study of the symmetry relations arising from these tightly bound *p* and *d* states, at some future time). For the conduction band, however, we are much more likely to want to choose functions all corresponding to the same eigenvalue, but to **k**'s in different Brillouin zones. This corresponds to the way we have been in the habit of handling such problems, treating the tightly bound states separately by the Bloch method, and the conduction band as if by the free-electron method, but disregarding the fact that these electrons are in fact far from free. The justification seems to come only from such an augmented plane wave method as described here.

We now note that there can be cases that are ambiguous, and presumably the first one of these which will appear in the periodic table comes with the iron group, where the 3*d* electrons are being incorporated into the interior of the atom. For potassium, calcium, and the elements following immediately after, the atomic 3*d* energy level lies above the 4*s*. We may presume that in these cases we wish to use a single eigenvalue, which reduces to something like the 4*s* atomic level for $\mathbf{k}=0$, and to follow continuously along to higher **k** values, using wave functions in many Brillouin zones. On the other hand, when we have gone through iron, cobalt, and nickel, to copper and zinc, the 3*d* level in the atom has become rather tightly bound. In this case presumably we wish to treat the appropriate wave functions in central Brillouin zones (we remember that we must use five such zones), and to start again with a higher eigenvalue and a continuous set of **k** values, to represent the conduction band of the elements starting with copper. The change in the method of treatment which will arise in this way would be a very interesting thing to study, and may well explain many of the paradoxes associated with the energy bands of the transition elements, and the question as to which electrons are to be treated as free electrons, which as bound or atomic electrons.

We may note two generalizations of the method which follow easily. In the first place, we have noted that the setting up of the augmented plane waves does not demand a regular crystalline arrangement of the atoms. Thus we have an equally valid starting point for a treatment of perturbed or irregular lattices. Secondly, the potential function in a real crystal does not have the properties postulated here, of being spherically symmetrical within each atomic sphere, and constant outside. If we wish to take account of the deviations of the real potential function from such a behavior, we may first set up as good an approximation to the real potential as possible which has the behavior we have postulated, and set up the wave functions using this potential. When we come to compute the diagonal and nondiagonal matrix components of energy, however, and to solve the secular problem, we may include the deviations of the real potential from this simplified value as perturbations, computing their contributions to the matrix components of energy numerically, if no analytic method is available. This possibility of taking into account deviations from this simplified potential is found in the orthogonalized plane wave method, but not in the cellular method, and it results in considerable shortcomings in the applications of the latter method.

We may observe in closing that our method is really a form of cellular method in which we have transferred the problem of satisfying boundary conditions from the surfaces of the polyhedral cells, to the surfaces of the inscribed spheres; we may regard the regions where we expand the wave functions in plane waves as matching regions, extending the wave functions smoothly from one spherical cell to another. The writer[6] attempted in 1937 to avoid the difficulties of the cellular method by a method somewhat like the present one. That suggestion, however, suffered from mathematical complications so severe that it has never proved useful. It is hoped that these mathematical difficulties have been overcome by the present method, sufficiently so that it may be better adapted for application to real crystals than the hitherto available methods.

APPENDIX

To find the required wave functions, we wish to vary the a_{inl}'s and a_0 so as to make the energy in Eq. (6) stationary, while maintaining the conditions (5) and (7). To do this by the method of undetermined multipliers, we may add the derivative of Eq. (6) with respect to one of the a_{inl}^*'s (formally treating this as independent of the corresponding a_{inl}), plus appropriate constants times the derivative of Eq. (7), and of the conjugates of each of Eqs. (5), with respect to the same quantity, and set this equal to zero; we do the same for

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[6] J. C. Slater, Phys. Rev. **51**, 846 (1937).

derivatives with respect to a_0^*. We thus have

$$a_{inl}(E_{inl}-E)-\lambda_{il}u_{inl}(r_i)=0, \tag{11}$$

$$a_0\Omega(E_0-E)+\sum(il)\,\lambda_{il}\times\exp(-i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)(-i)^l j_l(kr_i)=0. \tag{12}$$

Here we have chosen the undetermined multiplier for Eq. (6) to be $-E$ [we shall shortly prove that this E is the same as the expectation value appearing in Eq. (6)], and that connected with Eq. (5) for a particular i and l to be $-\lambda_{il}$. We can now solve Eqs. (11) and (12) very simply. We have at once

$$a_{inl}=\lambda_{il}u_{inl}(r_i)/(E_{inl}-E); \tag{13}$$

$$a_0\Omega=-\sum(il)\,\lambda_{il}\exp(-i\mathbf{k}\cdot\mathbf{R}_i)\times(2l+1)(-i)^l j_l(kr_i)/(E_0-E). \tag{14}$$

We must next determine the multipliers λ_{il} and E. First we eliminate the λ_{il}'s, and get an equation for E. We substitute Eqs. (13) and (14) in Eq. (5), obtaining

$$\begin{aligned}\lambda_{il}\sum(n)\,[u_{inl}^2(r_i)/(E_{inl}-E)]&=-\Omega^{-1}\exp(i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)i^l j_l(kr_i)\\&\quad\times\sum(i'l')\,\lambda_{i'l'}\exp(-i\mathbf{k}\cdot\mathbf{R}_{i'})(2l'+1)(-i)^{l'}\\&\quad\times j_{l'}(kr_{i'})/(E_0-E).\end{aligned} \tag{15}$$

We multiply both sides by

$$\{\sum(n)\,[u_{inl}^2(r_i)/(E_{inl}-E)]\}^{-1}\exp(-i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)(-i)^l j_l(kr_i),$$

and add terms for all i and l values. We then can cancel terms from both sides of the equation, and are led at once to Eq. (8). Now that E has been determined, we see at once from Eq. (15) that

$$\lambda_{il}=b\exp(i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)i^l j_l(kr_i)\times\{\sum(n)\,[u_{inl}^2(r_i)/(E_{inl}-E)]\}^{-1}, \tag{16}$$

where b is a constant. By substituting Eq. (16) in Eq. (12), and using Eq. (8), we find at once that $b=a_0$. Thus we are led to Eq. (9). Substitution in Eq. (7) leads at once to Eq. (10).

We can now prove the three theorems we desire about our wave functions: the quantity introduced as an undetermined multiplier E is the same as the expectation value of energy defined in Eq. (6); and the functions are orthogonal, and have no nondiagonal matrix components of energy between them. To prove the first, we start with Eq. (15), multiply by λ_{il}^*, and sum over i and l. We have

$$\begin{aligned}\sum(inl)\,\lambda_{il}^*\lambda_{il}u_{inl}^2(r_i)/(E_{inl}-E)&=-\Omega^{-1}[\sum(il)\,\lambda_{il}^*\exp(i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)i^l j_l(kr_i)]\\&\quad\times[\sum(i'l')\,\lambda_{i'l'}\exp(-i\mathbf{k}\cdot\mathbf{R}_{i'})(2l'+1)(-i)^{l'}\\&\quad\times j_{l'}(kr_{i'})/(E_0-E)].\end{aligned} \tag{17}$$

We multiply and divide each term on the left by $E_{inl}-E$, and multiply and divide on the right by E_0-E. We may then rewrite the result, using Eqs. (11) and (12), as

$$\sum(inl)\,a_{inl}^*a_{inl}(E_{inl}-E)+a_0^*a_0\Omega(E_0-E)=0,$$

from which it follows at once, from Eqs. (6) and (7), that E is the expectation value of the energy.

To prove the other theorems, we must use two energy values, E_1 and E_2, with corresponding coefficients λ_{il1}, λ_{il2}, a_{01}, a_{02}, etc. We then set up Eq. (15) for the state 2, multiply it by λ_{il1}^*, and by a coefficient A, and sum over i and l; we also set up Eq. (15) for the state 1, take its conjugate, multiply by λ_{il2}, and by a coefficient B, and sum over i and l; and subtract this from the first equation. The result of this is

$$\begin{aligned}\sum(inl)\,\lambda_{il1}^*\lambda_{il2}u_{inl}^2(r_i)[A/(E_{inl}-E_2)-B/(E_{inl}-E_1)]&=-\Omega^{-1}[\sum(il)\,\lambda_{il1}^*\exp(i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)i^l j_l(kr_i)]\\&\quad\times[\sum(i'l')\,\lambda_{i'l'2}\exp(-i\mathbf{k}\cdot\mathbf{R}_{i'})(2l'+1)(-i)^{l'}\\&\quad\times j_{l'}(kr_{i'})]A/(E_0-E_2)+\Omega^{-1}[\sum(il)\,\lambda_{il2}\\&\quad\times\exp(-i\mathbf{k}\cdot\mathbf{R}_i)(2l+1)(-i)^l j_l(kr_i)][\sum(i'l')\,\lambda_{i'l'1}\\&\quad\times\exp(i\mathbf{k}\cdot\mathbf{R}_{i'})(2l'+1)i^{l'}j_{l'}(kr_{i'})]B/(E_0-E_1).\end{aligned} \tag{18}$$

We reduce the fractions on the left to a common denominator, use Eqs. (13) and (14), and have

$$\sum(inl)\,a_{inl1}^*a_{inl2}[(A-B)E_{inl}+(-AE_1+BE_2)]+a_{01}^*a_{02}\Omega[(A-B)E_0+(-AE_1+BE_2)]=0. \tag{19}$$

The two constants A and B are at our disposal. First let us chose them so that $A-B=0$, $-AE_1+BE_2=1$. Then we have

$$\sum(inl)\,a_{inl1}^*a_{inl2}+a_{01}^*a_{02}\Omega=0, \tag{20}$$

which is the expression of the fact that the two wave functions are orthogonal to each other. Next let $A-B=1$, $-AE_1+BE_2=0$. Then

$$\sum(inl)\,a_{inl1}^*a_{inl2}E_{inl}+a_{01}^*a_{02}\Omega E_0=0, \tag{21}$$

showing that the nondiagonal matrix component of energy between the two states is zero.