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# New Method for Calculating Wave Functions in Crystals and Molecules*

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For metals and semiconductors the calculation of crystal wave functions is simplest in a plane wave representation. However, in order to obtain rapid convergence it is necessary that the valence electron wave functions be made orthogonal to the core wave functions. Herring satisfied this requirement by choosing as basis functions "orthogonalized plane waves." It is here shown that advantage can be taken of crystal symmetry to construct wave functions $\varphi_\alpha$ which are best described as the smooth part of symmetrized Bloch functions. The wave equation satisfied by $\varphi_\alpha$ contains an additional term of simple character which corresponds to the usual complicated orthogonalization terms and has a simple physical interpretation as an effective repulsive potential. Qualitative estimates of this potential in analytic form are presented. Several examples are worked out which display the cancellation between attractive and repulsive potentials in the core region which is responsible for rapid convergence of orthogonalized plane wave calculations for $s$ states; the slower convergence of $p$ states is also explained. The formalism developed here can also be regarded as a rigorous formulation of the "empirical potential" approach within the one-electron framework; the present results are compared with previous approaches. The method can be applied equally well to the calculation of wave functions in molecules.

## 1. INTRODUCTION

IN 1940 Herring[1] proposed the method of orthogonalized plane waves which has since proved to be the most flexible and powerful means for calculating the electronic wave functions of metals[2] and semiconductors.[3] He observed that if the crystal wave functions are expanded in plane waves the boundary conditions at the surface of the unit cell are automatically satisfied so that if enough plane waves are used very good crystal wave functions can be obtained. In order to include the radial nodes of the valence wave functions in the core region, however, so many plane waves are required as to make the method impracticable. For this reason Herring suggested orthogonalizing each plane wave to all core wave functions, which has the effect of augmenting each plane wave by adding to it a suitable linear combination of core orbitals. The resulting wave function includes radial nodes and Herring showed that rapid convergence would result.

The principal disadvantage of Herring's procedure was that in orthogonalizing a single plane wave to the core functions the spherical symmetry of the core was lost. As a consequence the orthogonalization terms that appear in the secular equation have a complicated form which makes their physical interpretation difficult and calculations involving them laborious. Slater[4] has preferred to take advantage of the atomic spherical symmetry by using augmented plane waves. His procedure in practice has proved to be at least as laborious as the OPW method even when the necessary condition that the potential be approximately constant outside the atomic region has been well satisfied.

Calculations using the OPW method have used group theory[3] to reduce the secular equation at symmetry points of the Brillouin Zone. The resulting basis functions are combinations of plane waves transforming according to irreducible representations of the group of the wave vector. The most important simplifications introduced by our method are a consequence of our choosing as basis functions terms *resembling* such symmetrized combinations of plane waves instead of single plane waves; these are *then* orthogonalized to the core wave functions. It will be seen that this sequence enables us to take maximum advantage of atomic symmetry. For this reason in Sec. 2 we restrict our discussion to $s$ and $p$ bands of cubic crystals at $\mathbf{k}=0$. From the fact that core wave functions and energy levels are nearly independent of the position of $\mathbf{k}$ in the reduced Brillouin Zone it is evident that these restrictions can easily be removed; the procedure for doing this is discussed in Sec. 4.

The derivation presented in Sec. 2 introduces basis functions $\varphi_\alpha$ which are best described as the smooth part of symmetrized combinations of Bloch functions. The wave equation satisfied by $\varphi_\alpha$ contains an additional term which corresponds to the orthogonalization terms in the OPW formalism. This term has the form of a repulsive potential and depends on the core wave functions and the valence wave function in the core region. In principle the core wave functions are best computed from Hartree-Fock wave functions for free atoms but in practice the valence functions, which vary slowly in the core region, are quite insensitive to the detailed nature of the core potential, so that the core functions can be replaced by analytic functions. This circumstance can be used as the basis of a qualitative investigation of the nature of the effective potential (attractive plus repulsive). The method we have used

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

[2] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).

[3] F. Herman, Phys. Rev. **88**, 1210 (1952); **93**, 1214 (1954).

[4] J. C. Slater, Phys. Rev. **92**, 603 (1953).

for doing this and the results that were obtained are presented in Sec. 3 as a guide to the qualitative nature of the effective potential. We also discuss in Sec. 3 the possibility of modifying the repulsive potential slightly in such a way as to reproduce the free-atom term values; this might be especially useful for heavy atoms. In this respect the results represent a generalization of the quantum-defect method of Kuhn and Van Vleck[5] and Brooks and Ham,[6] which has yielded very good results for alkali metals.

The form of the repulsive potential developed in Sec. 2 is actually quite general and should be useful in calculating wave functions in crystals other than metals or semiconductors and in molecules as well. In Sec. 5 we discuss briefly one of the many possible other applications of the formalism, namely the calculation of wave functions of color centers in alkali halides.

## 2. THEORY AT $k=0$

We shall assume to simplify the derivation that all electrons move in the same potential. If necessary the derivation could easily be extended to include $l$-dependent terms, which might arise if an "averaged" exchange potential were used for different values of $l$ in the core region. Further we consider at first only valence and conduction band wave functions having $s$ or $p$ atomic character in cubic crystals at $\mathbf{k}=0$. These latter restrictions will be removed in Sec. 4. We begin by imagining that we *know* the exact crystal wave function $\psi_\alpha$ which transforms according to an irreducible representation of the cubic point group $\Gamma_\alpha$ which has $s$ or $p$ atomic symmetry.[7] Since $\psi_\alpha$ must be orthogonal to the core states of similar symmetry, we have

$$\psi_\alpha=\varphi_\alpha+\sum_n a_n{}^\alpha\varphi_\alpha{}^n, \qquad (2.1)$$

$$a_n{}^\alpha=-(\varphi_\alpha,\varphi_\alpha{}^n). \qquad (2.2)$$

If we had chosen $\varphi$ to be a single plane wave Herring's[1] results would follow. Our results already show a trivial, but important, simplification, which is that valence wave functions of, say, $s$ character need be orthogonalized only to $s$ core functions.[8] We now seek the wave equation satisfied by $\varphi_\alpha$, the "smooth" part of $\psi_\alpha$. We have

$$H\psi_\alpha=E\psi_\alpha, \qquad (2.3)$$

and substituting (2.1) in (2.3) we find

$$H\varphi_\alpha+\sum_n a_n{}^\alpha(E^n-E)\varphi_\alpha{}^n=E\varphi_\alpha, \qquad (2.4)$$

where $H\varphi_\alpha{}^n=E^n\varphi_\alpha{}^n$. We now introduce

$$V_r{}^\alpha=\sum_n a_n{}^\alpha(E^n-E)\varphi_\alpha{}^n/\varphi_\alpha, \qquad (2.5)$$

and Eq. (2.4) assumes the desired form:

$$(H+V_r{}^\alpha)\varphi_\alpha=E\varphi_\alpha. \qquad (2.6)$$

So far our discussion has applied equally well to molecules or crystals, as our only assumption has been that the atomic character of $\psi_\alpha$ is known. We now specialize to the case of crystals, and in particular metals or semiconductors. Then we can solve Eq. (2.6) by expanding $\varphi_\alpha$ in symmetrized combinations of plane waves.

$$\varphi_\alpha=\sum_n b_\alpha{}^n|\kappa_n\rangle_\alpha, \qquad (2.7)$$

where $|\kappa_n\rangle_\alpha$ denotes a sum of plane waves having equivalent reciprocal lattice wave vectors and transforming according to the irreducible representation $\alpha$. Since $\varphi_\alpha$ represents the "smooth" part of $\psi_\alpha$ we may expect to obtain a convergence about as rapid as that of the orthogonalized plane wave method. Furthermore, from the form of (2.6) it is clear that substitution of Eq. (2.7) leads to a secular equation of the same form as those obtained in OPW calculations after the secular determinant has been factored (reduced by group theory), but with the important difference that the unwieldy orthogonalization terms have disappeared completely.

The great utility of the arrangement of terms given in Eqs. (2.5) and (2.6) can be seen from a closer investigation of Eq. (2.5) which we write more explicitly by introducing $a_n{}^\alpha$ from (2.2). Then

$$V_r{}^\alpha=\sum_n(E-E^n)(\varphi_\alpha,\varphi_\alpha{}^n)\varphi_\alpha{}^n/\varphi_\alpha, \qquad (2.8)$$

and it can be seen that this term has an especially simple form because of the atomic character of $\varphi_\alpha{}^n(\mathbf{r})$. In the region where $\varphi_\alpha{}^n(\mathbf{r})$ is appreciable $\varphi_\alpha$ may be written as the product of a single spherical harmonic and a radial function of $r$. The orthogonality relations for spherical harmonics then cause the complete cancellation of all angle-dependent terms from (2.8) so that the orthogonality terms have a much simpler form here than in the OPW formalism. In addition if $\varphi_\alpha$ varies sufficiently slowly in the core region compared to $\varphi_\alpha{}^n$ (which will generally be the case) that it can be approximated by a constant in this region, then from Eq. (2.8) we see that $V_r{}^\alpha$ is independent of $\varphi_\alpha$. In general it will be found that the repulsive potential is quite insensitive to $\varphi_\alpha$.[9,10]

We can now be more explicit in our definition of the repulsive potential. At the outset we assumed $\varphi_\alpha$ was known. From Eq. (2.8) it is clear that it is sufficient to know $\varphi_\alpha$ in the region where $\varphi_\alpha{}^n$ is large, i.e., in the core region. In metals and semiconductors for valence and conduction band wave functions usually only $b_1$ and $b_2$ will be large in (2.7). Then in (2.8) the radial part of $\varphi_\alpha$ may be assumed to vary as $j_l(\kappa_1 r)$. Corrections to this

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[5] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950).

[6] H. Brooks and F. S. Ham, Phys. Rev. **112**, 344 (1958).

[7] H. Bethe, Ann. Physik **3**, 133 (1929).

[8] Here and elsewhere we shall neglect overlap of core orbitals on different atoms. If necessary the $\varphi_\alpha{}^n$ may be chosen orthogonal to core orbitals on other atoms.

[9] The form of the repulsive potential displayed in Eq. (2.7) is very similar to that of the exchange potential which, when written in this form, is known[10] to be less sensitive to $\varphi$ than the exchange terms themselves. The situation here is even more favorable since $\varphi$ may be chosen to have no nodes.

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

approximation are of order $(b_2/b_1)^2(\kappa_2^2-\kappa_1^2)a^2$, where $a$ is a typical core dimension; this is ordinarily quite small. For rough calculations $j_l(\kappa_1 r)$ may be replaced by $r^l$; the resulting correction is then of order $\kappa_1^2a^2$.

The repulsive potential given in Eq. (2.8) is also energy-dependent. In practice one can often guess $E$ for a given state to better than 0.1 ry, and in this case choosing this value for $E$ in (2.8) will leave $E$ only on the diagonal of the secular equation obtained by substituting (2.7) in (2.6). In practice $(E^n-E)$ is of the order of 10 ry, so that the error resulting from this approximation is also quite small.

It is easy to show that Eq. (2.6) is exactly equivalent to the OPW equations if the exact form of $\varphi_\alpha$ is used in $V_r$:

$$E=(\varphi_\alpha,\mathcal{H}\varphi_\alpha)+\sum\nolimits_n(E-E_\alpha{}^n)(a_n{}^\alpha)^2, \tag{2.9}$$

$$(\varphi_\alpha,\varphi_\alpha)=1. \tag{2.10}$$

Now substitute the expression for $\varphi_\alpha$ given by Eq. (2.7). The resulting bilinear form in the $b_m$'s is exactly the same as the one that is obtained in the OPW formalism after the forms have been factored into different irreducible representations. By approximating $\varphi_\alpha$ and $E$ in $V_r$ as described above we obtain a considerable simplification of the wave equation with an error that is small.

It is interesting to note at this point that if a variational function is used for the radial part of $\varphi_\alpha$ then Eq. (2.9) represents a convenient starting point for calculation of free-atom wave functions and term values.

Finally from Eq. (2.8) it is clear that the repulsive potential is $l$-dependent. Some care must therefore be exercised in extending the results of this section to $\mathbf{k}\neq 0$ and in the calculation of effective masses. We postpone a discussion of this matter to Sec. 4, and now turn our attention to the problem of obtaining qualitative estimates of the repulsive potential $V_r$.

## 3. ANALYTIC AND EMPIRICAL APPROXIMATIONS TO $V_r$

The relative magnitude of the various terms in the repulsive potential as well as the convergence properties of the method can be investigated by introducing analytic expressions for the wave functions in the core region. The earliest such analytic expressions were developed by Slater.[11,12] More accurate expressions for some atoms have since been developed by Löwdin.[13–15] For the present we are interested only in obtaining qualitative estimates of the repulsive and attractive potentials. Thus we shall use Slater's simplified analytic expressions with the radial part of $\varphi_\alpha$ given by

$$\varphi_\alpha \sim r^n e^{-\lambda r}, \tag{3.1}$$

where $n$ and $\lambda$ are variational parameters. However it is important for our purposes that each $\psi_\alpha$ be an eigenfunction of our potential. Thus we shall assume a potential of the form (in atomic units)

$$V_c(r)=-\frac{2Z}{r}-\frac{2(A-Z)}{r}e^{-\lambda r}, \tag{3.2}$$

where $A$ is the atomic number of the atom in question and $Z$ and $\lambda$ are varied to give the correct core and valence levels as determined from Hartree calculations or x-ray and spectroscopic term values. We have carried out calculations for Si with two choices of $Z$ and $\lambda$ to study the qualitative behavior of the repulsive potential when the attractive potential is changed.

It may be felt that the Slater form of $\varphi_\alpha$ is not sufficiently general to yield accurate wave functions and hence accurate repulsive potentials. To check this point we have calculated wave functions and energy levels in hydrogen using the Slater form (3.1). For the $1s$ and $2p$ wave functions this is of course exact, but it should be noted that for higher states this is one of the worst cases that could have been chosen. [The reason is that hydrogenic wave functions for higher states of principal quantum number $n$ have the form $\exp(-r/n)g(r)$ where $g$ is a polynomial in $r$. Our wave function has the form $\sum_n b_n r^n \exp(-r/n)$ so that the inner oscillations have the wrong wavelength. In a screened Coulomb potential such as (3.2) the inner oscillations will have more nearly the correct wavelength.] In spite of this we find that $E_{2s}$ is correct to within 0.01% (correct repulsive potential) and $E_{3s}$ to within 1% (incorrect repulsive potential). The details of the calculation, including a comparison of $\psi_{3s}$ in the Slater form with the hydrogen wave function, are given in the Appendix.

*Note added in proof.*—Further calculations show that although the Slater-Löwdin expressions yield good results for atoms, they have only qualitative significance for band splittings. The reason is that analytic expressions fit the tails of the core orbitals poorly, while these tails make an important contribution to the low Fourier coefficients of the effective potential. A more detailed discussion is given in reference 23(a).

Our first calculation used $A=14$, $Z=2.9$, and $\lambda=3.2$ in Eq. (3.2). The resulting eigenvalues are listed in

Table I. Core and valence eigenvalues for Si in Rydbergs. The values listed under Cases I and II were derived as described in the text, while the core values derived by Woodruff[16] are listed in the third column. Experimental valence values, as defined in the text, are also listed in the third column.

| Level | Case I | Case II | Woodruff |
|---|---|---|---|
| $1s$ | −135.6 | −119.2 | −134.6 |
| $2s$ | −11.64 | −10.93 | −11.12 |
| $3s$ | −2.34 | −2.43 | −2.14 |
| $2p$ | −7.99 | −7.69 | −8.18 |
| $3p$ | −1.78 | −1.90 | −1.65 |

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[11] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[12] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[13] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).

[14] P. O. Löwdin, Phys. Rev. **94**, 1600 (1954).

[15] P. O. Löwdin and K. Appel, Phys. Rev. **103**, 1746 (1956).

TABLE II. Values of the parameters appearing in Eq. (3.4) for the potentials described in Sec. 3.

| | | | | | |
|---|---|---|---|---|---|
| | | | Case I | | |
| | $1s$ | $2s$ | $2s$ | $2p$ | |
| $j$ | 1 | 1 | 2 | 1 | |
| $C_j$ | 101.0 | −29.0 | 81.5 | 36.1 | |
| $m_j$ | 1.0 | 1.0 | 2.2 | 1.7 | |
| $b_j$ | 13.66 | 13.66 | 5.08 | 4.30 | |
| | $3s$ | $3s$ | $3s$ | $3p$ | $3p$ |
| $j$ | 1 | 2 | 3 | 1 | 2 |
| $m_j$ | 1.0 | 2.2 | 2.5 | 1.7 | 2.0 |
| $b_j$ | 13.66 | 5.08 | 1.63 | 4.30 | 1.20 |
| | | | Case II | | |
| | $1s$ | $2s$ | $2s$ | $2p$ | |
| $j$ | 1 | 1 | 2 | 1 | |
| $C_j$ | 91.3 | −22.3 | 69.1 | 31.2 | |
| $m_j$ | 1.0 | 1.0 | 2.2 | 1.7 | |
| $b_j$ | 12.77 | 12.77 | 4.78 | 4.03 | |
| | $3s$ | $3s$ | $3s$ | $3p$ | $3p$ |
| $j$ | 1 | 2 | 3 | 1 | 2 |
| $m_j$ | 1.0 | 2.2 | 2.5 | 1.7 | 2.0 |
| $b_j$ | 12.77 | 4.78 | 1.58 | 4.03 | 1.18 |

Table I under case I. Core eigenvalues due to Woodruff[16] are also listed for comparison.

It is also possible to calculate valence eigenvalues in this potential. For monovalent atoms this yields an especially straightforward test of the correctness of the potential for valence electrons, since these eigenvalues can be compared directly with spectroscopic term values. If a potential can be found which reproduces the latter values sufficiently well, this approach would represent a generalization of the quantum-defect method of Kuhn and Van Vleck[5] and Brooks and Ham.[6]

For polyvalent atoms a direct comparison with spectroscopic term values is not so easily obtained, since each valence electron partially shields the other valence electrons from the core. A rough measure of the degree of this shielding can be obtained as follows. Each valence electron is treated on an equal footing. Then $n\epsilon_s+m\epsilon_p$ is set equal to the energy required to remove all the valence electrons from the atom. Here $n$ and $m$ are the numbers of $s$ and $p$ valence electrons and $\epsilon_s$ and $\epsilon_p$ the lowest $s$ and $p$ term values in the effective potential. The required second equation for $\epsilon_s$ and $\epsilon_p$ is obtained setting $\epsilon_p-\epsilon_s$ equal to the average $s$-$p$ term difference of the successively ionized atom. The values of $\epsilon_s$ and $\epsilon_p$ derived in this way from the spectroscopic values are also listed in Table I. It can be seen that our potential does indeed have about the right shielding.

The complete core wave functions can be written

$$\psi_{nl}=Y_{lm}(\theta,\varphi)P_{nl}(r)/r, \tag{3.3}$$

$$P_{nl}(r)=\sum_j C_j r^{m_j}e^{-b_j r}. \tag{3.4}$$

The constants occurring in Eqs. (3.3) and (3.4) are listed in Table II. The corresponding constants for valence wave functions in the free atom are also listed. The repulsive potentials listed under cases I and II in Table III used the free-atom valence wave functions listed in Table II. Thus with these constants our atomic effective potential for valence electrons in the crystal is completely determined. We choose to display its Fourier transform,

$$V^k=\frac{2}{\Omega_0}\int V(r)e^{i\mathbf{k}\cdot\mathbf{r}}d^3r, \tag{3.5}$$

where the integral is extended over all space, and $V$ denotes either $V_c$ or $V_r$. Here $\Omega_0=a^3/4$ is the volume of the unit cell in a silicon crystal, the factor of 2 represents the number of atoms per cell, and $a$ is the lattice constant. If $V^k$ is multiplied by the form factor $\cos(\mathbf{k}\cdot\boldsymbol{\tau})$ with $\boldsymbol{\tau}=\frac{1}{8}a(1,1,1)$, then we have essentially the potential which determines the energy bands of silicon. (The potential for the crystal is then taken as a superposition of the spherically symmetric atomic potentials with a neutralizing uniform negative charge $2Z$ per atom.)

TABLE III. Fourier transforms of electrostatic and repulsive potentials. Here $k$ is measured in units of $2\pi a^{-1}$ and $V^k$ in Rydbergs. The repulsive potentials listed under cases I and II were calculated assuming that the radial parts of $\varphi_l$ were described by the functions listed in Table II. The repulsive potentials in the last two columns were obtained from Woodruff's wave functions assuming $\varphi_l\sim r^l$.

| | Case I | | | Case II | | | Woodruff[a] | | |
|---|---|---|---|---|---|---|---|---|---|
| $k^2$ | $V_c^k$ | $V_r^s$ | $V_r^p$ | $V_c^k$ | $V_r^s$ | $V_r^p$ | $V_c^k$ | $V_r^s$ | $V_r^p$ |
| 3 | −0.662 | 0.463 | 0.240 | −0.686 | 0.542 | 0.271 | −0.718 | 0.560 | 0.407 |
| 8 | −0.336 | 0.375 | 0.183 | −0.340 | 0.438 | 0.199 | −0.372 | 0.424 | 0.347 |
| 11 | −0.275 | 0.334 | 0.159 | −0.275 | 0.392 | 0.170 | −0.301 | 0.363 | 0.317 |
| 16 | −0.217 | 0.281 | 0.129 | −0.215 | 0.333 | 0.134 | −0.234 | 0.289 | 0.277 |
| 64 | −0.083 | 0.113 | 0.036 | −0.079 | 0.144 | 0.035 | −0.083 | 0.077 | 0.113 |
| 0 | | 0.528 | 0.288 | | 0.580 | 0.319 | | 0.650 | 0.457 |

[a] See reference 16.

The values of $V_c^k$ and $V_r^k$ for values of $\mathbf{k}$ corresponding to some of the reciprocal lattice vectors for the silicon crystal are listed in Table III. For $s$ states we have taken $E=-1.1$ ry and for $p$ states $E=-1.5$ ry. The resulting potentials are also shown in Fig. 1 for $s$ states and in Fig. 2 for $p$ states.

From these results several interesting conclusions can be drawn. First we notice that for large $k$ (which corresponds to the core region) the repulsive $s$ potential very nearly cancels the attractive potential. Thus high Fourier coefficients of the effective potential in $s$ states are quite small; in particular only $V_{111}$ is large. In the expansion (2.7) usually only $b_\alpha^1$ and perhaps $b_\alpha^2$ will be large; a convergent eigenvalue is obtained when $n$ is large enough to include all symmetrized combinations of plane waves $|\kappa_n\rangle$ such that $\langle\kappa_1|V|\kappa_n\rangle$ or $\langle\kappa_2|V|\kappa_n\rangle$ contains $V_{111}$.

We see from Fig. 2 that such excellent cancellation does not obtain for $p$ states. This is not surprising, for the orthogonalization procedure can be regarded as another way of including the radial kinetic energy in the core region in the calculation. Nothing can be done

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[16] T. O. Woodruff, Phys. Rev. **103**, 1159 (1956).

about the angular kinetic energy, however, and it is not surprising that if we add the usual centrifugal term representing the angular kinetic energy to the $p$ repulsive potential the resulting potential, which is shown in Fig. 2, resembles the $s$ repulsive potential quite closely. The slow convergence of $p$ states in the orthogonalized plane wave method, which has been discussed quite extensively in the literature (e.g., Woodruff[16]), is therefore intrinsic to the method.

We have checked these general conclusions by varying our parameters in Eq. (3.2) and recalculating new wave functions. The results for $Z=3.1$, $A=13.1$, and $\lambda=3.1$ are listed in Tables I, II, and III as case II. Finally we also list in Table III the results previously obtained by Woodruff using trial wave functions of the Löwdin[13] form but a starting potential derived from core wave functions having the form (3.1) with the parameters determined by rules due to Slater.[11,12] It can be seen that the effective potentials in the three cases are qualitatively similar.

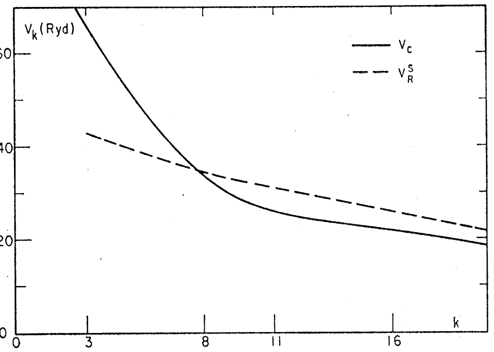

FIG. 1. Fourier transforms of attractive and repulsive $s$ potentials in Si as derived in Sec. 3.

*Note added in proof.*—Using our formalism, a more complete discussion of cancellation effects has been given by M. H. Cohen and V. Heine (to be published).

We now compare our results with the empirical potentials that have been proposed from time to time to represent the repulsive effect of the core. One of the earliest was that used by Hellmann[17] for alkali metals. Hellmann's attractive potential had the form (3.2) while his repulsive potential was proportional to the last term of (3.2). For alkali metals $Z$ was set equal to 1 and $\lambda$ and the coefficient of the screened Coulomb term were determined by fitting the lower spectroscopic term values of the free atom. Hellmann's repulsive potential thus had the correct form (similar to the core part of the attractive potential) but it was $l$-independent. Callaway[18] has shown that a careful radial integration of the Hellmann potential leads to values of the parameters which correspond to a very strong and short range repulsive potential. This unphysical result is a consequence of the $l$-independence of the potential; in order to weaken the repulsive potential seen by $p$ states compared to $s$ states it is necessary to make the potential very strong and short range. The resulting wave function (which is analogous to our $\varphi_\alpha$) will consequently no longer be smooth and a plane-wave expansion, for example, will converge more slowly. Incidentally it should be noticed that the discrepancy discussed by Callaway accounts for the consistently poor results obtained by Antončík[19] in similar calculations for alkali metals.

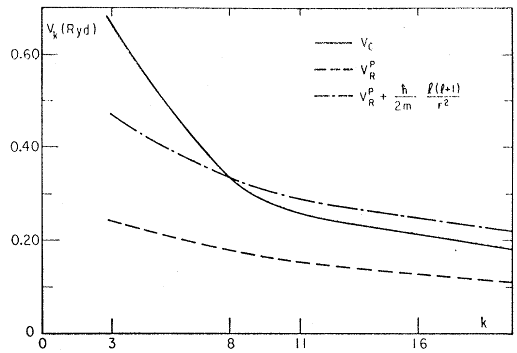

FIG. 2. Fourier transforms of attractive and repulsive $p$ potentials in Si as derived in Sec. 3.

Although the empirical potentials used by Hellmann are poor they are demonstrably superior to the ones proposed by Gombás[20] based on the Thomas-Fermi method. The best expression for the repulsive potential given by Gombás is

$$V_r=(\pi^2/4)\rho_l^2+1/2r^2, \tag{3.6}$$

where the last term represents a spurious angular momentum contribution arising from the statistical approximations of the theory. In Eq. (3.6) $\rho_l=\int d\Omega\, 4\pi r^2 \sum_n \psi_{nl}^*\psi_{nl}$ and the potential is of fourth degree in core orbitals, whereas expression (2.8) shows it should be of second degree. This has the effect of overemphasizing the shell structure and in turn this has a simple intuitive interpretation (see Fig. 3). Here we show 1$s$ and 2$s$ wave functions. The requirement that the 2$s$ wave function be orthogonal to the 1$s$ function forces the 2$s$ function to have a node near the maximum of the 1$s$ function, and Eq. (3.6) has the same effect by

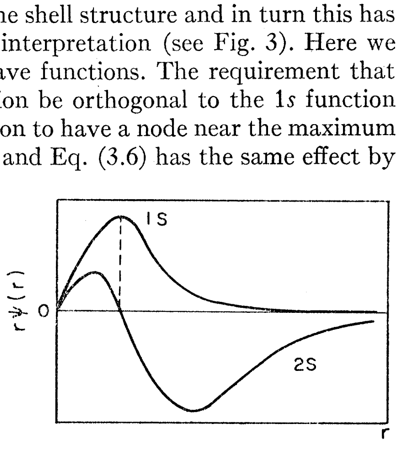

FIG. 3. A sketch of the effect of orthogonality on the radial parts of atomic wave functions. The node in the 2$s$ wave function must occur at about the same position as the antinode of the 1$s$ function.

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[17] H. Hellmann and W. Kassatotschkin, Acta Physicochim. U. R. S. S. **5**, 23 (1936).

[18] J. Callaway, Phys. Rev. **112**, 322 (1958).

[19] E. Antončík, Czechoslov J. Phys. **4**, 439 (1954).

[20] P. Gombás, Acta Physiol. Acad. Sci. Hung. **3**, 127 (1953).

sharpening the shell structure. Thus it might be thought that Eq. (3.6) would produce a wave function resembling our $\varphi_\alpha$ as defined by (2.1). This appears to be the case for some monovalent atoms, but for polyvalent atoms the surprising result is obtained that the outer wave function is forced *inside* the inner one. In any event there is no point in using (3.6) when the rigorous and actually simpler result (2.8) is available.

## 4. CALCULATIONS FOR $k\neq 0$; EFFECTIVE MASS FORMALISM

The expression for the repulsive potential at $\mathbf{k}=0$ given in Eq. (2.7) apparently depends on the irreducible representation $\alpha$. Actually to a very good approximation it depends only on $l(\alpha)$, the value of $l$ associated with core orbitals transforming according to $\alpha$. For cubic groups at $\mathbf{k}=0$ these have been determined by group theory by Bethe.[7] Similar techniques can be used at other points of the Brillouin zone possessing sufficiently high symmetry; the results for bcc lattices have been listed by Howarth and Jones.[21]

These results are actually only approximately correct even at $\mathbf{k}=0$. Thus at $\mathbf{k}=0$ the cubic field actually introduces an admixture of $g$ functions into $s$ functions, for example. This admixture is certainly negligible at $\mathbf{k}=0$, but at points of somewhat lower symmetry such as $\mathbf{k}=\pi a^{-1}(1,1,1)$ in fcc and diamond lattices one finds $d$ functions admixed into $s$ functions. We must therefore investigate now the form of the repulsive potential when $\varphi_\alpha$ is a combination of several different $l$ values in the core region. Our aim is to show that a corresponding mixture of the $l$-dependent repulsive potentials will lead to a correct secular equation.

We assume that within a region of radius $R$ about each nucleus the potential is spherically symmetric and that $\varphi_\alpha$ is known in this region. (This can be done by iteration.) To simplify the notation we assume that $\varphi_\alpha$ contains only $s$ and $p$ components and that the coordinate axes can be chosen so that only $m=0$ spherical harmonics occur. We add a superscript $R$ to remind ourselves that we are in the core region; then

$$\begin{aligned}\psi^R &= \varphi_\alpha{}^R(\mathbf{r})+\sum_n a_n{}^\alpha\psi_\alpha{}^n(\mathbf{r})\\ &= \sum_{l=0}^{1} b_l P_l(\theta)\left[\varphi_{\alpha l}{}^R(r)+\sum_n a_n{}^l\psi_l{}^n(r)\right], \end{aligned}\tag{4.1}$$

$$a_n{}^l = -\left(\varphi_{\alpha l}{}^R(r),\psi_l{}^n(r)\right). \tag{4.2}$$

By a process similar to that of Sec. 2 we obtain for the repulsive potential

$$V_r=\sum_n\sum_{l=0}^{1} b_l(E_l{}^n-E)a_n{}^l P_l(\theta)\psi_l{}^n(r)\Big/\sum_{l=0}^{1} b_l P_l(\theta)\varphi_{\alpha l}{}^R(r). \tag{4.3}$$

If we now take matrix elements of $V_r$ we obtain

$$(\varphi_\alpha{}^R,V_r\varphi_\alpha{}^R)=\sum_n\sum_{l=0}^{1} b_l{}^2(E_l{}^n-E)(a_n{}^l)^2, \tag{4.4}$$

$$=\sum_{l=0}^{1} b_l{}^2(\varphi_{\alpha l}{}^R,V_r{}^l\varphi_{\alpha l}{}^R), \tag{4.5}$$

where $V_r{}^l$ denotes the $l$-dependent repulsive potential appropriate to a single value of $l$.

We now wish to find a function of $r$ only, $V(r)$, such that

$$(\varphi_\alpha,V_r\varphi_\alpha)=(\varphi_\alpha,V(r)\varphi_\alpha). \tag{4.6}$$

From Eqs. (4.1) and (4.5) this means

$$\sum_{l=0}^{1} b_l{}^2(\varphi_{\alpha l}{}^R,V(r)\varphi_{\alpha l}{}^R)=\sum_{l=0}^{1} b_l{}^2(\varphi_{\alpha l}{}^R,V_r{}^l\varphi_{\alpha l}{}^R). \tag{4.7}$$

It is natural to try to satisfy Eq. (4.7) with

$$V(r)=\sum_{l=0}^{1}\omega_l V_r{}^l(r). \tag{4.8}$$

Now Eq. (4.7) provides one condition on $V(r)$, while (4.8) contains two constants which are under-determined. If we demand further that (4.7) hold for arbitrary $b_l$ we find that (4.8) in general will not yield a solution. The best choice here appears to be obtained if we notice that for $r$ in the region of the last shell of the core $V_r{}^0(r)\sim V_r{}^1(r)$. [The wave functions $\psi_l{}^n$ are similar but the energies $(E_l{}^n-E)$ differ. See Sec. 3.] Then (4.7) and (4.8) require that

$$\sum_{l=0}^{1}\omega_l=1, \tag{4.9}$$

a plausible result which we can use to determine $\omega_l$ in general. Combining (4.7), (4.8), and (4.9) we find

$$\omega_0=\frac{c_0{}^2}{c_0{}^2+c_1{}^2},\quad \omega_1=\frac{c_1{}^2}{c_0{}^2+c_1{}^2}, \tag{4.10}$$

$$c_l{}^2=b_l{}^2(\varphi_{\alpha l},\,(V_r{}^0-V_r{}^1)\varphi_{\alpha l}). \tag{4.11}$$

Thus only $b_l\varphi_{\alpha l}(r)$ enters in the definition of $\omega_l$ so that $\omega_l$ is independent of the normalization used in (4.1). In actual calculations $b_l$ can be determined by expanding the plane waves in Eq. (2.7) in spherical harmonics. The weighting factors calculated from Eq. (4.11) will involve essentially the orthogonality coefficients $A_{nl}$ of the orthogonalized plane wave formalism.[22]

In practice calculations have been carried out only at points of high symmetry; at these points the operations described above are particularly easy to carry out.

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[21] D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

[22] By a similar argument it is easy to show that if the expansion of $\varphi_\alpha$ contains $m\neq 0$ spherical harmonics, i.e.,

$$\varphi_{\alpha l}=\Sigma_{m=-l}{}^l\,\beta_{lm}P_l{}^m(\theta)e^{im\varphi}\varphi_{\alpha lm}{}^R(r),$$

then $b_l{}^2$ in (4.11) should be replaced by $\Sigma_{m=-l}{}^l\,\beta_{lm}{}^2$.

Perturbation theory can be used to compute bands and wave functions at neighboring points in **k**-space; the resulting curvatures at band edges are the effective masses. The formal details of such calculations have been discussed by many workers, for example, Dresselhaus, Kip, and Kittel.[23] Since our potentials are *l*-dependent it might appear that a basic modification of this formalism would be necessary. However, accurate calculations can be carried out quite simply by returning to Eq. (2.1) and using for $\phi_\alpha^n$ the analytic expressions discussed in Sec. 3. Details of the method with application to Si will be published elsewhere.[23a]

## 5. OTHER APPLICATIONS

Applications of the formalism described in Sec. 2 can be made to a variety of problems in molecular and solid state physics. In this section we will discuss briefly several interesting possibilities.

In simplified calculations of the properties of polyvalent metals plane-wave and point-ion approximations are often made. The above results suggest that this is a fairly good approximation which can be improved by including the *l*-dependence of the effective potential.

Similar simplifications have been made by Gourary and co-workers[24–26] in the calculation of color centers in alkali halides. Again the calculations should be improved by including the *l*-dependence of the effective potential.

## 6. CONCLUDING REMARKS

The earliest methods of calculating wave functions in crystals were the tight-binding and plane-wave formalisms. The former represents core functions accurately, and the latter represents valence functions accurately in metals and semiconductors except in the neighborhood of the core. Both the orthogonalized plane wave and augmented plane wave formalisms can be regarded as attempts to patch together wave functions having the correct form both inside and outside the core. Unfortunately both formalisms lead to rather complicated calculations, the former because it fails to take maximum advantage of atomic symmetry and the latter because it fails to utilize the fact that the form of the valence wave function in the core is determined almost entirely by the requirement that it be orthogonal to the core orbitals. We have investigated here the physical effect of the core region by expressing the orthogonalization terms as an effective repulsive potential. This leads to some loss in accuracy but as compensation we maintain the great simplicity of the tight-binding treatment of the core regions and the plane-wave treatments of the rest of the crystal. This was easily demonstrated in Sec. 2 for cubic crystals at $\mathbf{k}=0$. The convergence features of the formalism were then investigated qualitatively in Sec. 3 and the physical significance of the repulsive potential was discussed. In particular it was noticed that the simple form of the repulsive potential made possible direct comparison with free-atom term values, thus offering the possibility of generalizing the quantum-defect method to crystals where the potential is not spherically symmetric and Coulombic outside each core. Finally in Sec. 4 it was noticed that for most problems of interest the restriction to $\mathbf{k}=0$ could be removed. This was physically obvious since the interaction of valence wave functions with the core could only be expected to change for reasons of symmetry, as valence-electron wavelengths are long compared to the size of the core.

## ACKNOWLEDGMENTS

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## APPENDIX

We list here the wave functions and energies obtained for hydrogen according to the methods of Sec. 3. The

TABLE IV. Values of parameters appearing in Eq. (3.4) and energies for hydrogen.

| | 1*s* | 2*s* | 2*s* | 2*p* |
|---|---|---|---|---|
| $E$ | 1.000 | 0.2499 | | 0.2500 |
| $j$ | 1 | 1 | 2 | 1 |
| $C_j$ | 2.000 | 0.688 | 0.085 | 0.204 |
| $m_j$ | 1.00 | 1.00 | 2.75 | 2.00 |
| $b_j$ | 1.000 | 1.000 | 0.557 | 0.500 |

| | 3*s* | 3*s* | 3*s* | 3*p* | 3*p* |
|---|---|---|---|---|---|
| $E$ | 0.1117 | | | 0.1111 | |
| $j$ | 1 | 2 | 3 | 1 | 2 |
| $C_j$ | 0.279 | 0.0428 | 0.00052 | 0.0976 | 0.00142 |
| $m_j$ | 1.00 | 2.75 | 4.50 | 2.00 | 3.90 |
| $b_j$ | 1.000 | 0.557 | 0.387 | 0.500 | 0.364 |

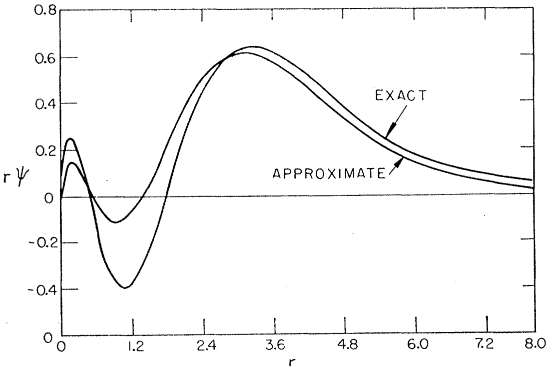

FIG. 4. A comparison of the 3*s* wave function for atomic hydrogen, as calculated by the methods of Sec. 3, with the exact wave function.

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[23] Dresselhaus, Kip, and Kittel, Phys. Rev. **98**, 368 (1955).

[23a] L. Kleinman and J. C. Phillips (to be published).

[24] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[25] B. S. Gourary and P. J. Luke, Phys. Rev. **107**, 960 (1957).

[26] B. S. Gourary, Phys. Rev. **112**, 337 (1958).

energy obtained for the 2s state is 0.2499 ry and for the 3p state 0.11110, as one would expect from the variational principle and the fact that (3.1) is exact for the 1s and 2p states. The 2s wave function cannot be exact if (3.1) is used for each shell, however, and the 3s energy can therefore be lower than the exact value; we find the value 0.1117 ry.

The wave functions are described by the parameters of Eq. (3.4), and these are listed in Table IV. The 3s wave function constructed in this way is compared with the corresponding hydrogen wave function in Fig. 4.

Similar results for hydrogen have been derived by Antončík[27] using the Thomas-Fermi expression (3.6) derived by Gombás.[20]

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[27] E. Antončík, Czechoslov J. Phys. 7, 118 (1957).

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# Magnetic Properties of the Manganese Chromite-Aluminates*

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The mixed-crystal spinel series $MnCr_{2-t}Al_tO_4$ has been synthesized and found to form a single cubic phase with a cell edge that is a linear function of the aluminum content. An x-ray study indicates that the series is an almost-normal spinel series with the $A$ sites occupied by divalent manganese ions and about 5% of the trivalent aluminum ions.

The magnetization-temperature curves have approximately zero slope at absolute zero and exhibit no peaks or compensation points. The saturation moment is $1.16\mu_B$ for $t=0.0$, increasing to $1.37\mu_B$ at $t=0.8$, and dropping to $1.25\mu_B$ at $t=1.0$. The reciprocal-susceptibility *vs* temperature curves have the hyperbolic shape characteristic of ferrimagnets. The observed magnetic properties cannot be explained by the Néel theory but can be accounted for, at least qualitatively, by the five-parameter Yafet and Kittel theory.

## INTRODUCTION

In 1948 Néel showed that the magnetic moments of a number of magnetic oxides having the spinel structure and the chemical formula $MN_2O_4$ (where $M$ is a divalent and $N$ is a trivalent ion) can be explained in terms of two crystallographically unique sublattices $A$ and $B$.[1] For the materials he considered, and many more studied since then, the interactions of the sublattices are such as to orient them antiparallel to each other, and the observed magnetic moment is the moment of one sublattice minus the moment of the other.

Although the Néel theory was very successful in many cases, there are theoretical objections to parts of the theory. For certain values of the interaction parameters, one of the two sublattices would be unsaturated, resulting in a nonzero slope of the magnetization *vs* temperature curve at absolute zero, which is in conflict with the third law of thermodynamics. Another objection is that for certain other values, which may be quite large, of the interaction parameters the material remains paramagnetic at all temperatures. This does not seem reasonable, since for strong interactions one would expect some kind of ordering at low temperatures.

Yafet and Kittel in 1952 published a modification of the Néel theory in which the two sublattices were again divided, giving four sublattices, $A_1$, $A_2$, $B_1$, and $B_2$, and which overcame the above difficulties.[2] Those cases explainable by the Néel theory are also explainable by this theory, and in a similar fashion. One feature of this theory is that for those cases in the Néel theory requiring an unsaturated $A$ sublattice, for example, the Yafet and Kittel theory requires nonparallel alignment of saturated $A_1$ and $A_2$ sublattices. The Yafet and Kittel theory also introduced the interesting possibility that magnetic ordering transitions may occur at temperatures other than that at which the spontaneous moment appears.

The Yafet and Kittel theory has been used by several authors to explain observed magnetic effects that are not in agreement with the Néel model. Gorter has suggested that the saturation magnetization of the $MnCr_2O_4$-$MnFe_2O_4$ series might be explained in terms of angles on the $B$ sublattice.[3] Lotgering has used the theory to explain the magnetization of $MnCr_2O_4$ and $FeCr_2O_4$ and has given approximate values of the interaction parameters.[4] The measurements of McGuire, Howard, and Smart[5] show a kink in the susceptibility curve of $NiCr_2O_4$ near 300°K, and later work by Volger[4] shows a specific heat anomaly and that by

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[1] L. Néel, Ann. phys. 3, 137 (1948).

[2] Y. Yafet and C. Kittel, Phys. Rev. 87, 290 (1952).

[3] E. W. Gorter, Philips Research Repts. 9, 295, 321, 403 (1954).

[4] F. K. Lotgering, Philips Research Repts. 11, 337 (1956).

[5] McGuire, Howard, and Smart, Ceram. Age 60, 22 (1952).