PHYSICAL REVIEW VOLUME 136, NUMBER 3A 2 NOVEMBER 1964

g Value in Alkali-Metal Conduction-Electron Spin Resonance*

ARTHUR BIENENSTOCK AND HARVEY BROOKS
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts

(Received 10 June 1964)

A method for examining the convergence of expansions of wave functions for nearly free electrons is presented. It is shown that Bardeen-type expansions of alkali-metal conduction-electron wave functions converge sufficiently slowly so that it is necessary, when calculating the value of a physical quantity to any given power of $\mathbf{k}$, to include all terms of all orders in $u(\mathbf{k}, \mathbf{r})$ which contribute to that power. Consequently, wave-function expansions to third order in $\mathbf{k}$ which include the effects of spin-orbit interaction to first order are derived, in the spherical approximation, for these metals. Using these wave functions in Yafet's equation, the g shift, to second order in $|\mathbf{k}|$, is expressed in terms of radial wave functions. The radial functions are evaluated numerically using the quantum defect nethod under four different approximations: (i) With and without the so-called "polarization correction" and (ii) with and without a term in the potential corresponding to an approximate self-consistent Hartree field due to the presence of other conduction electrons within the Wigner-Seitz sphere. The best agreement with experiment is obtained when the "polarization correction" is neglected and the Hartree term included. In this approximation the effective mass ratio, m/m,* is considerably closer to unity in the heavier alkali metals than was predicted by earlier calculations. The "polarization correction" is examined in detail in an unsuccessful effort to determine why it leads to a considerable decrease in the agreement with experiment.

I. INTRODUCTION

THE quantum defect method (QDM)[1–3] has been used, with considerable success, to develop wave functions for the alkali-metal conduction electrons near the surface of the Wigner-Seitz polyhedron or sphere. The wave functions have been used to calculate a number of measurable properties of the metals. In most cases the agreement with experiment has been quite satisfactory, within the somewhat wide limits of uncertainty in the theory. These properties are the cohesive energy,[4,5] the compressibility,[4,5] and the Knight shift[6] as a function of temperature. A common characteristic of the properties is that they depend mainly on the "s" portion of the wave functions. In addition, calculations of the effective mass[5,7] and the shape of the Fermi surface[8] have been made. Both quantities depend on higher-order terms in the spherical harmonic expansion of the wave function and are a partial check on these terms. Measurements[9] which depend on the shape of the Fermi surface indicate that the calculations have overestimated the distortion from sphericity of this surface. It is suggested in the present work and confirmed by other calculations[10] that these results are due to the approximations used in earlier versions of the QDM of replacing the true crystal potential by that of the bare ion cores, neglecting screening by the charge of the valence electrons. Direct measurements[11] of the effective mass at the Fermi surface yield values which are about 30% high in comparison with the present calculations. The interpretation of this discrepancy is complicated by many-body and phonon interactions which still cannot be predicted accurately from first principles.

The shift of the alkali metal conduction electron g from the free-electron value depends directly on spin-orbit interaction. For this reason, the calculation depends primarily on the quality of the $l>0$ terms in the expansion of the wave function. The $l=0$ terms influence the calculation primarily through normalization.

Three other numerical calculations of the g shift are reported in the literature. Two, by Brooks[12] and by Yafet,[12] were based on an incomplete theory of Yafet[12] and yielded values which were approximately one-half the observed values. The third, by Bienenstock and Brooks,[13] used the more complete theory of Yafet,[14] but a wave function which had been expanded to only second order in the Bloch vector. The shifts obtained were consistently and significantly larger in magnitude than the observed values.

In the work reported here, it is shown that it is possible to obtain improved agreement with experiment. Such agreement, however, depends sensitively on the choice of approximations made in deriving the wave functions. In particular, it was necessary to (i) use the expansion of the wave function to third order in the

---

* Portions of this work were submitted by one of us (AB) in partial fulfillment of the requirements for the Ph.D., Harvard University, 1962. The work was supported by National Science Pre- and Post-Doctoral Fellowships, the U. S. Office of Naval Research and the Advanced Research Projects Agency.

[1] H. Brooks, Nuovo Cimento Suppl. **7**, 165 (1958).

[2] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950), and F. S. Ham, Solid State Phys. **1**, 27 (1955).

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

[4] H. Brooks, Phys. Rev. **91**, 1027 (1953).

[5] H. Brooks, Trans. Am. Inst. Mining, Met. Petrol. Engrs. **227**, 546 (1963).

[6] H. Brooks (unpublished work). See G. Benedek and T. Kushida, Phys. Chem. Solids **5**, 241 (1958).

[7] H. Brooks (unpublished work).

[8] F. S. Ham, Phys. Rev. **128**, 82, 2524 (1962).

[9] K. Okumura and I. M. Templeton, Phil. Mag. **7**, 1239 (1962); **8**, 889 (1963); and D. Schoenberg and P. J. Stiles (unpublished work).

[10] V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

[11] C. C. Grimes and A. F. Kip, Phys. Rev. **132**, 1991 (1963).

[12] H. Brooks, Phys. Rev. **94**, 1411(A) (1954); Y. Yafet, *ibid.* **85**, 478 (1952).

[13] A. Bienenstock and H. Brooks, Bull. Am. Phys. Soc. **5**, 253 (1960).

[14] Y. Yafet, Phys. Rev. **106**, 679 (1957).

wave vector; (ii) include, in the potential, a Hartree term, due to the presence of the other conduction electrons in the Wigner-Seitz cell; and (iii) neglect the "so-called polarization correction."[3] Since (i) was not in keeping with earlier analyses of the convergence properties of the Bardeen expansion, these properties have been re-examined. In addition, some of the parameters which enter into the expansion of the energy in powers of the magnitude of the Bloch vector, around the bottom of the band, have been recalculated. It is found that, in all cases, the deviation from free-electron values is smaller than those values previously obtained using the bare ion core potential rather than an approximately self-consistent one.

II. CONVERGENCE OF THE WAVE FUNCTIONS

The formulation of Yafet[14] for the g shift yields an expression which is valid to second order in the wave vector. This expression requires a knowledge of the expansion of the wave functions to third order. In the initial calculation of Bienenstock and Brooks,[13] it was assumed that the expansion of the periodic part, $u(\mathbf{k},\mathbf{r})$, of the wave functions is rapidly convergent, so that the third-order terms could be neglected. We have since found that this is not the case. In this section, the rate of convergence is discussed in terms of the $\mathbf{k}\cdot\mathbf{p}$ expansion. For simplicity, spin-orbit interaction is at first neglected.

We are concerned with finding alkali-metal conduction-band solutions of the Schrödinger equation

$$\frac{p^2}{2m}\psi(\mathbf{r})+\int V(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}'=E\psi(\mathbf{r}'),\qquad(2.1)$$

where $V(\mathbf{r},\mathbf{r}')$ is a nonlocal potential which includes the effects of exchange and, to some extent, valence-core correlation. Using the Bardeen method, the periodic part of the wave function at a point $\mathbf{k}$ may be expanded in terms of the complete set of functions associated with the points $k=0$. The analyses of convergence presented previously have been based on the assumption that the effective one-electron potential is weak and local. We now proceed to show that even in this case the convergence of the $\mathbf{k}\cdot\mathbf{p}$ expansion is slow when $|k|$ is not a small parameter forcing convergence.

With $V(\mathbf{r},\mathbf{r}')=V(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ the Bardeen expansion is, to second order,

$$u_0(\mathbf{k},\mathbf{r})=|0\rangle+2i\sum_l{}'\frac{|l\rangle\langle l|\mathbf{k}\cdot\boldsymbol{\nabla}|0\rangle}{(E_0-E_l)}-4\sum_l{}'\left\{\sum_n{}'\frac{|l\rangle\langle l|\mathbf{k}\cdot\boldsymbol{\nabla}|n\rangle\langle n|\mathbf{k}\cdot\boldsymbol{\nabla}|0\rangle}{(E_0-E_l)(E_0-E_n)}-\frac{|l\rangle\langle l|\mathbf{k}\cdot\boldsymbol{\nabla}|0\rangle\langle 0|\mathbf{k}\cdot\boldsymbol{\nabla}|0\rangle}{(E_0-E_l)^2}-\frac{1}{2}\frac{|0\rangle\langle 0|\mathbf{k}\cdot\boldsymbol{\nabla}|l\rangle\langle l|\mathbf{k}\cdot\boldsymbol{\nabla}|0\rangle}{(E_0-E_l)^2}\right\}.\qquad(2.2)$$

Here $|l\rangle$ denotes $u_l(0,\mathbf{r})$ with $l=0$ indicating the conduction band.

For metals in which the electrons are nearly free there are three types of matrix elements which enter into Eq. (2.2). The simplest are those which are zero from symmetry considerations. These may be found using group theory. The second class of matrix elements are those which are not zero from symmetry considerations, but are zero for free electrons. These will be considered as small parameters. The third class includes all other matrix elements. For the purpose of discussing convergence of wave functions, we shall consider the deviations of these matrix elements from their free-electron values as small parameters compared to the matrix elements themselves. Thus, to determine their values we may use as basis functions at $\mathbf{k}=0$ the eigenfunctions of the irreducible representations of the symmetry group of the crystal constructed from plane waves whose wave vectors are the reciprocal lattice vectors—the so-called "symmetrized combinations of plane waves" (SCPW).

The second class of matrix elements contains then those which are nonzero by symmetry considerations, but involve bands constructed from different sets of degenerate reciprocal lattice points, while the third class contains those taken between different states constructed from the same set of degenerate reciprocal lattice points.

In the alkali metals the bottom of the conduction band corresponds to the reciprocal lattice point $\mathbf{K}=0$. This point is nondegenerate (ignoring spin degeneracy) and the wave functions have the symmetry Γ_1. It is easily shown that the $\mathbf{k}\cdot\mathbf{p}$ perturbation mixes only Γ_1 and Γ_{15}. The first set of reciprocal lattice points (using the body-centered rather than the primitive cell to define the reciprocal lattice indices) are of the form (110) and there is a twelvefold degeneracy. From the plane waves of the form $\exp i\alpha(x+y)$, where $\alpha=2\pi/a$, and a is the lattice constant, we can construct SCPW which transform according to the irreducible representations Γ_1, Γ_{15}, Γ_{12}, Γ_{25}, and Γ_{25}'. The term of first order in $\mathbf{k}$ mixes in the three eigenfunctions of Γ_{15}, which we denote as $|x\rangle$, $|y\rangle$, and $|z\rangle$. The matrix elements are

$$\frac{\langle x|\mathbf{k}\cdot\mathbf{p}|0\rangle}{k_x}=\frac{\langle y|\mathbf{k}\cdot\mathbf{p}|0\rangle}{k_y}=\frac{\langle z|\mathbf{k}\cdot\mathbf{p}|0\rangle}{k_z}=\beta\alpha,\qquad(2.3)$$

where β is a small parameter, as it is zero for free electrons. Thus we find, as has been demonstrated by a number of authors, that the terms of order higher than zero in $u_0(\mathbf{k},\mathbf{r})$ are very small compared to $u_0(0,\mathbf{r})$, at least outside the atomic cores. This is a necessary consequence of the free-electron nature, as, for free electrons, $u(\mathbf{k},\mathbf{r})=u(0,r)=1$.

The analysis becomes more interesting when we consider terms of higher order. $\mathbf{k}\cdot\mathbf{p}$ mixes Γ_{15} with Γ_1, Γ_{12}, Γ_{15}', and Γ_{25}'. Of these, the representations of Γ_1, Γ_{12}, and Γ_{25}' are contained in the (110) combinations and may lead to appreciable matrix elements. Those matrix elements of the second class, involving points other than (110) may be neglected as they lead to terms which are of second order in small parameters. To determine the significant matrix elements we need an explicit form for the basis functions. Examples are shown below. They are constructed in the manner discussed by Jones[15] and normalized so that their quadratic integral over the full cubic unit cell is unity.

$$\begin{aligned}
&\Gamma_1\\
&\quad |1\rangle = (2/3a^3)^{1/2}(\cos\alpha x\,\cos\alpha y+\cos\alpha y\,\cos\alpha z\\
&\qquad\qquad +\cos\alpha z\,\cos\alpha x)\\
&\Gamma_{15}\\
&\quad |x\rangle = (2/a^3)^{1/2}\sin\alpha x(\cos\alpha y+\cos\alpha z)\\
&\Gamma_{12}\\
&\quad |A\rangle = (2/a^3)^{1/2}[\cos\alpha z(\cos\alpha x+\cos\alpha y)\\
&\qquad\qquad -2\cos\alpha x\,\cos\alpha y]\\
&\quad |B\rangle = (2/a^3)^{1/2}\cos\alpha z(\cos\alpha x-\cos\alpha y)\\
&\Gamma_{25}'\\
&\quad |xy\rangle = (4/a^3)^{1/2}\sin\alpha x\,\sin\alpha y.
\end{aligned}\tag{2.4}$$

Using these functions in Eq. (2.2) we find that, to second order in $\mathbf{k}$ and first order in small parameters,

$$\begin{aligned}
u_0(\mathbf{k},\mathbf{r}) = {} & |0\rangle - i\beta/\alpha(k_x|x\rangle+k_y|y\rangle+k_z|z\rangle)\\
& -\beta(2k_z^2-k_x^2-k_y^2)|A\rangle/\sqrt{3}\alpha^2\\
& -\beta(k_x^2-k_y^2)|B\rangle/4\alpha^2\\
& +\beta(k_xk_y|xy\rangle+k_yk_{-}|yz\rangle+k_zk_x|zx\rangle)/\sqrt{2}\alpha^2\\
& -\beta(2)^{1/2}k^2|1\rangle/12\alpha^2+\text{terms from}\\
& \qquad\text{other reciprocal lattice sets.}
\end{aligned}\tag{2.5}$$

Equation (2.5) reveals the most important lesson to be gained from this analysis. That is, in all orders of perturbation it is possible to construct terms which are linear in the small parameter β. Thus, there is no reason to expect $u_0(\mathbf{k},\mathbf{r})$ to converge as quickly, in general, as the ratio of the first- to zero-order terms. Indeed, the contribution from this set of reciprocal lattice points indicates that the convergence factors are of the order of $\frac{1}{2}(k/\alpha)$, which is equal to 0.31 at the Fermi surface (spherical approximation).

This method of analysis has been chosen because the free electron functions show the symmetry of the actual wave functions. It is predicated, however, on the assumption that all sets in reciprocal space contribute terms to the expansion which converge at approximately the same rate. This is not the case. In order to examine the contribution of all sets it has been found necessary to consider functions which do not display the symmetry.

The easiest manner of determining the contribution of all reciprocal lattice points to the convergence is to obtain first-order weak-binding solutions to the Schrödinger equation and expand these as a power series in the wave vector. The solutions under consideration are for the wave function outside the core, which are considered equivalent to the orthogonalized wave functions in a weak, nonlocal pseudopotential.[16]

Following Mott and Jones,[17] we write

$$\psi(\mathbf{k},\mathbf{r}) = \sum_{\mathbf{K}_n} A(\mathbf{K}_n)\exp[i(\mathbf{k}-\mathbf{K}_n)\cdot\mathbf{r}]. \tag{2.6}$$

The nonlocal pseudopotential can be expressed as

$$\begin{aligned}
V(\mathbf{r},\mathbf{r}') = \sum_{\mathbf{K}_n}\int V(\mathbf{K}_n-\boldsymbol{\kappa},\boldsymbol{\kappa})\exp(-i\mathbf{K}_n\cdot\mathbf{r})\\
\times\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{r}'-\mathbf{r})]d\boldsymbol{\kappa}
\end{aligned}\tag{2.7}$$

since $V(\mathbf{r}+\mathbf{R},\,\mathbf{r}'+\mathbf{R}) = V(\mathbf{r},\mathbf{r}')$ when $\mathbf{R}$ is a repeat vector of the lattice.

In keeping with the previous analysis, the $V(\mathbf{K}_n-\boldsymbol{\kappa},\boldsymbol{\kappa})$ are assumed to be sufficiently small so that terms which are quadratic or higher in them may be neglected.

Substitution of Eq. (2.6) and (2.7) into (2.1) yields

$$\begin{aligned}
&\sum_{\mathbf{K}_n} A(\mathbf{K}_n)[(\hbar^2k^2/2m)(\mathbf{k}-\mathbf{K}_n)^2-E]\\
&\quad\times\exp[i(\mathbf{k}-\mathbf{K}_n)\cdot\mathbf{r}]+\int\sum_{\mathbf{K}_n,\mathbf{K}_n'}\\
&\quad\times\int\{V(\mathbf{K}_n-\boldsymbol{\kappa},\,\boldsymbol{\kappa})A(\mathbf{K}_n')\exp[i(\mathbf{k}-\mathbf{K}_n'-\boldsymbol{\kappa})\cdot\mathbf{r}']\\
&\qquad\qquad\times\exp[i(\boldsymbol{\kappa}-\mathbf{K}_n)\cdot\mathbf{r}]\}d\boldsymbol{\kappa}d\mathbf{r}'=0.
\end{aligned}\tag{2.8}$$

The integrals over $\mathbf{r}'$ and $\boldsymbol{\kappa}$ can be performed, yielding

$$\begin{aligned}
&\sum_{\mathbf{K}_n} A(\mathbf{K}_n)[(\hbar^2/2m)(\mathbf{k}-\mathbf{K}_n)^2-E]\exp[i(\mathbf{k}-\mathbf{K}_n)\cdot\mathbf{r}]\\
&\quad+\sum_{K_n,K_n'} V(\mathbf{K}_n-\mathbf{K}_n'-\mathbf{k},\mathbf{k})A(\mathbf{K}_n')\\
&\qquad\qquad\times\exp[i(\mathbf{k}-\mathbf{K}_n-\mathbf{K}_n')\cdot\mathbf{r}]=0.
\end{aligned}$$

Since all the $V(\mathbf{K}_n)$ are considered small, those terms involving $A(\mathbf{K}_n')$, in which $\mathbf{K}_n'\neq 0$, may be neglected. In addition, to first order in the $V(\mathbf{K}_n)$, $E=(\hbar^2k^2/2m)$. Thus,

$$\begin{aligned}
&\sum_{K_n}\{A(\mathbf{K}_n)[(\mathbf{k}-\mathbf{K}_n)^2-\mathbf{k}^2]\\
&\quad+(2m/\hbar^2)A(0)V(\mathbf{K}_n-\mathbf{k},\mathbf{k})\}\exp(i\mathbf{K}_n\cdot\mathbf{r})=0
\end{aligned}$$

or

$$A(\mathbf{K}_n) = \left(\frac{-2m}{\hbar^2}\right)\frac{V(\mathbf{K}_n-\mathbf{k},\,\mathbf{k})}{\mathbf{K}_n^2-\mathbf{k}\cdot\mathbf{K}_n}. \tag{2.9}$$

To first order in the potential

$$\begin{aligned}
\psi(\mathbf{k},\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}A(0)\Bigg[1-\frac{2m}{\hbar^2}\sum_{K_n\neq 0}\frac{V(\mathbf{K}_n-\mathbf{k},\,\mathbf{k})}{K_n^2-\mathbf{k}\cdot\mathbf{K}_n}\\
\times\exp(i\mathbf{K}_n\cdot\mathbf{r})\Bigg].
\end{aligned}\tag{2.10}$$

---

[15] H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960), Sec. 30.

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

[17] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

To obtain correspondence with the $\mathbf{k}\cdot\mathbf{p}$ expansion each term in the sum is expanded as a power series in $\mathbf{k}$ to yield

$$\psi(\mathbf{k},\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}A(0)\biggl\{1-\frac{2m}{\hbar^2}\sum_{K_n\neq 0}\sum_s\sum_p\frac{1}{(s-p)!}\times[(\mathbf{k}\cdot\nabla_{\mathbf{k}'})^{s-p}V(\mathbf{K}_n-\mathbf{k}',\mathbf{k}')]_{k'=0}\times\frac{1}{K_n^2}\left(\frac{\mathbf{k}\cdot\mathbf{K}_n}{K_n^2}\right)^p\exp(i\mathbf{K}_n\cdot\mathbf{r})\biggr\}. \quad (2.11)$$

This expression, unfortunately, does not lend itself to a simple qualitative analysis. Some idea of the convergence properties may be obtained by considering the local potential $V(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$. In this case $V(\mathbf{K}_n-\mathbf{k},\mathbf{k})=V(\mathbf{K}_n)$ for all k. All the gradients with respect to $\mathbf{k}'$ vanish in (2.11) yielding

$$\psi(\mathbf{k},\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}A(0)\biggl[1-\frac{2m}{\hbar^2}\sum_p\sum_{K_n\neq 0}V(\mathbf{K}_n)\times\left(\frac{\mathbf{k}\cdot\mathbf{K}_n}{\mathbf{K}_n^2}\right)^p\frac{\exp(i\mathbf{K}_n\cdot\mathbf{r})}{\mathbf{K}_n^2}\biggr]. \quad (2.12)$$

The contributions of the nth reciprocal lattice point to the pth-order term goes as $(1/\mathbf{K}_n^2)(\mathbf{k}\cdot\mathbf{K}_n/\mathbf{K}_n^2)^p$. This factor produces a convergence which is increasingly rapid with increasing $|\mathbf{K}_n|$. Thus, the argument based on the (110) set of reciprocal lattice points underestimates the rate of convergence if points of large $|\mathbf{K}_n|$ contribute an appreciable portion of the first-order term. Since the number of points with fixed $|\mathbf{K}_n|$ goes as $|\mathbf{K}_n|^2$, the contribution to the first-order term of regions of $\mathbf{K}$ space with fixed $|\mathbf{K}_n|$ goes as $V(\mathbf{K}_n)(\mathbf{k}\cdot\mathbf{K}_n)/|\mathbf{K}_n|^2$. Thus, if the potential is restricted to a small portion of the unit cell near the nucleus, so that $V(\mathbf{K})$ is a slowly varying function of $|\mathbf{K}_n|$, the convergence will be considerably more rapid than that indicated by the (110) analysis, but will probably be less rapid than that indicated by the ratio of first- to zero-order terms. On the other hand, if the potential is slowly varying, so that terms with large $|\mathbf{K}_n|$ make little contribution to the first order term, the (110) analysis is more nearly correct.

No calculations of pseudopotentials have been made for the alkali metals. Some idea of the form of the $V(\mathbf{K}_n)$ for local pseudopotentials can, however, be obtained from the work of Phillips and Kleinman[18] on silicon. In this case, the repulsive terms associated with orthogonalization effectively cancel all but the first shell components of the potential. Thus, the $\mathbf{k}\cdot\mathbf{p}$ expansions of the alkali-metal wave functions outside the core probably converge as slowly as is indicated in the (110) analysis. It thus becomes necessary, when calculating the value of a physical quantity to any given power of $\mathbf{k}$, to include all terms of $u(\mathbf{k},\mathbf{r})$ which contribute to that power. This is the reason why the wave function is carried to third order in the following section. A complete analysis of the convergence is not possible as the nonlocal nature of the potential has not been investigated in sufficient detail to allow a complete analysis of Eq. (2.11). Finally, it should be pointed out that this argument does not necessarily apply to the convergence of a calculation of any physical quantity in a power series in $\mathbf{k}$. Each such quantity must be examined individually. This model may often be used, however.

We may now ask how the spin-orbit terms will converge. When we include this interaction in the $\mathbf{k}\cdot\mathbf{p}$ scheme, we get an additional term of the form $\omega\nabla V\times\mathbf{p}\cdot\mathbf{s}$, where ω is a small parameter. This interaction differs essentially from the $\mathbf{k}\cdot\mathbf{p}$ interaction in that it mixes nondegenerate free electron states. ω is the small parameter which gives us the rapid first-order convergence. The terms in the $\mathbf{k}\cdot\mathbf{p}$ expansion which will dominate are those in which the mixing of nondegenerate reciprocal lattice states is done with the spin-orbit term. All other terms will be quadratic in small parameters. Hence, the rate of convergence is close to the rate of convergence of the $\mathbf{k}\cdot\mathbf{p}$ terms.

III. DERIVATION OF THE WAVE FUNCTIONS

The wave functions desired are solutions of the Schrödinger equation which correspond to electrons in the conduction band of the alkali metals, and which include the effects of spin-orbit interaction. We simplify the problem immediately by demanding solutions within a spherical atomic cell. In this case, it is assumed that the Schrödinger equation can be written in the form

$$\{-\nabla^2+\epsilon\}\psi(\mathbf{r})-\int V(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}'-\tfrac{1}{2}\alpha^2\int W(\mathbf{r},\mathbf{r}')\mathbf{L}'\cdot\mathbf{S}'\psi(\mathbf{r}')d\mathbf{r}'=0. \quad (3.1)$$

The wave function, $\psi(\mathbf{r})$, is a two-component spinor, and the integrals include spin summations. Terms of higher order in $(1/mc^2)$ which come from a further decoupling of the Dirac equation have been neglected. ϵ is minus the energy in rydberg units, $(-me^4/2\hbar^2)$. The first Bohr radius, $(\hbar^2/me^2)$, is the unit of length, and α is the fine structure constant, $(e^2/\hbar c\cong 1/137)$. The nonlocal $V(\mathbf{r},\mathbf{r}')$ should include spin-independent relativistic terms to this order. $W(\mathbf{r},\mathbf{r}')$ is an attempt to simulate these, and spin-other orbit interactions, in the spin-orbit term. This form remains as an unproved assumption, but seems consistent with the work of Blume and Watson.[19] It is sufficient in this analysis, to have a nonlocal interaction such that J^2, L^2, and m_J (the magni-

---

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

[19] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **270**, 127 (1962).

tudes of the total angular momentum and the orbital angular momentum, and the third component of the total angular momentum) are good quantum numbers, and which falls off sufficiently quickly so that $W(\mathbf{r},\mathbf{r}')$ is negligible when $\mathbf{r}$ or $\mathbf{r}'$ is in the region outside the ionic cores.

The wave function may be written in the Bloch form

$$\psi_n(\mathbf{k},\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_n(\mathbf{k},\mathbf{r}). \tag{3.2}$$

This is a consequence of the periodicities

$$V(\mathbf{r}+\mathbf{R},\,\mathbf{r}'+\mathbf{R})=V(\mathbf{r},\mathbf{r}')$$

and

$$W(\mathbf{r}+\mathbf{R},\,\mathbf{r}'+\mathbf{R})=W(\mathbf{r},\mathbf{r}'), \tag{3.3}$$

where $\mathbf{R}$ is any repeat vector of the lattice.

In the spherical approximation, it is assumed that within the spherical cell $V(\mathbf{r},\mathbf{r}')$ and $W(\mathbf{r},\mathbf{r}')$ are invariant under simultaneous rotations or reflections of both coordinates.

For each value of the energy parameter ϵ there exists a set of solutions of this partial differential equation which correspond to eigenfunctions of the operators $|\mathbf{J}|$, $|\mathbf{L}|$, and m_J. These functions are complete for describing an arbitrary solution of Eq. (3.1) with fixed energy ϵ. They are of the form

$$\begin{aligned}F_{J,L}(r)|J,L,m_J\rangle&=\frac{F_{L+\frac{1}{2},L}(r)}{(2L+1)^{1/2}}\begin{pmatrix}(L+m+1)^{1/2}Y_{L,m}(\hat{r})\\(L-m)^{1/2}Y_{L,m+1}(\hat{r})\end{pmatrix},\quad J=L+\tfrac{1}{2}\\&=F_{L-\frac{1}{2},L}(r)\begin{pmatrix}(L-m)^{1/2}Y_{L,m}(\hat{r})\\(L+m+1)^{1/2}Y_{L,m+1}(\hat{r})\end{pmatrix},\quad J=L-\tfrac{1}{2}\end{aligned} \tag{3.4}$$

where $m=m_J-\frac{1}{2}$; with respect to an arbitrary axis usually determined by an external magnetic field.

The spherical harmonics are normalized on a unit sphere, and their arguments are the orientation angles of the vector r. The F's obey the differential equation

$$\begin{aligned}-(\nabla_r^2+\epsilon)F_{J,L}(r)-\int V_L(r,r')F_{J,L}(r')dr'&\\-(\alpha^2/4)[J(J+1)-L(L+1)-3/4]&\\\times\int W_L(r,r')F_{J,L}(r')dr'&=0,\end{aligned} \tag{3.5}$$

where

$$\nabla_r^2=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{L(L+1)}{r^2}. \tag{3.6}$$

The $V_L(r,r')$ and $W_L(r,r')$ are defined in the Appendix.

The procedure used for the determination of the form of the wave function is an analog of that described by Brooks.[1] ψ is expanded in a power series in $\mathbf{k}$, with terms retained to third order. Corresponding to the alkali metal conduction electrons, ψ is required to be s like at the bottom of the band ($k=0$), where S_z is a good quantum number, and to obey the Wigner-Seitz boundary conditions

$$\begin{aligned}\exp(-i\mathbf{k}\cdot\mathbf{r}_s)\psi(\mathbf{k},\mathbf{r}_s)&=\exp(i\mathbf{k}\cdot\mathbf{r}_s)\psi(\mathbf{k},\,-\mathbf{r}_s),\\\exp(-i\mathbf{k}\cdot\mathbf{r}_s)\partial\psi(\mathbf{k},\mathbf{r}_s)/\partial r&\\=-\exp(i\mathbf{k}\cdot\mathbf{r}_s)&\partial\psi(\mathbf{k}-,\mathbf{r}_s)/\partial r,\end{aligned} \tag{3.7}$$

where $\mathbf{r}_s$ is an arbitrarily oriented vector to the surface of the Wigner-Seitz sphere. Using the completeness of the functions of Eq. (3.4), we may write, to third order,

$$\psi=\sum_{q=0}^{3}\sum_{L=0}^{\infty}\sum_{J=L-\frac{1}{2}}^{L+\frac{1}{2}}\sum_{m_J}k^qA_{q,J,L,m_J}(\hat{k})F_{J,L}(\epsilon,r)\times|J,L,m_J\rangle. \tag{3.8}$$

This is not yet a true expansion in k, as ϵ is also a function of k. To third order,

$$\epsilon=\epsilon_0-E_2k^2 \tag{3.9}$$

and

$$F_{J,L}(\epsilon,r)=F_{J,L}(\epsilon_0,r)-E_2k^2\partial F_{J,L}(\epsilon_0,r)/\partial\epsilon. \tag{3.10}$$

Then

$$\begin{aligned}\psi=\sum_{q=0}^{3}\sum_{L,J,m_J}k^q\Big[&A_{q,J,L,m_J}(\hat{k})F_{J,L}(\epsilon_0,r)|J,L,m_J\rangle\\&-A_{q-2,J,L,m_J}(\hat{k})E_2\frac{\partial F_{J,L}(\epsilon_0,r)}{\partial\epsilon}|J,L,m_J\rangle\Big].\end{aligned} \tag{3.11}$$

Henceforth, the label ϵ_0 is dropped from the notation. For simplicity, the $F_{J,L}$'s are normalized in the following manner:

$$\begin{aligned}F_{J,0}(\epsilon,r_s)=F_{J,1}(\epsilon,r_s)=F_{J,3}(\epsilon,r_s)&=1,\\r_s\partial F_{J,2}(\epsilon,r_s)/\partial r&=1,\end{aligned} \tag{3.12}$$

for all ϵ. In addition, we write

$$\begin{aligned}F_L(\epsilon,r)&=\frac{L+1}{2L+1}F_{J+\frac{1}{2},L}(\epsilon,r)+\frac{L}{2L+1}F_{L-\frac{1}{2},L}(\epsilon,r),\\\Delta F_L(\epsilon,r)&=F_{L+\frac{1}{2},L}(\epsilon,r)-F_{L-\frac{1}{2},L}(\epsilon,r).\end{aligned} \tag{3.13}$$

The functions $F_L(\epsilon,r)$ are good approximations to the radial functions which are obtained when spin-orbit interaction is neglected. They differ by terms which are second order in the spin-orbit parameter. The $\Delta F_L(\epsilon,r)$ are first order in the spin-orbit parameter.

The wave function of Eq. (3.11) is capable of satisfying the boundary equations (3.7) to third order in $\mathbf{k}$. As discussed by Brooks,[1] for each value of q, one of these equations forces L to be even or odd as q is even or odd. The other equation, since $\mathbf{r}_s$ is arbitrarily oriented, must be obeyed by the coefficient of each $Y_{L,m}$. This fixes all but two of the coefficients in Eq. (3.11). One result is that the value of L within a "q" term cannot exceed q itself. This result follows, as well, from the $\mathbf{k}\cdot\mathbf{p}$ analysis of the last section. The remaining two coefficients are fixed by the requirement that the wave functions be normalized in the Wigner-Seitz sphere. That is

$$\int |\psi|^2 d\mathbf{r}=1. \tag{3.14}$$

To evaluate Eq. (3.14), Eq. (A1.1) is used.

Finally, the following abbreviations are introduced:

$$\begin{aligned} r_s\partial F_L(r_s)/\partial r&=\phi_L, \quad L=0,\,1,\,3\\ 1/F_2(r_s)&=\phi_2, \\ r_s\partial\Delta F_L(r_s)/dr&=\Delta\phi_L. \end{aligned} \tag{3.15}$$

Derivatives of the ϕ_L and $\Delta\phi_L$ with respect to ϵ are denoted by primes.

Two types of angular variation appear in the wave function. The first, that which is present in wave function expansions which neglect spin-orbit interaction, has terms proportional to

$$\frac{4\pi}{2L+1}\sum_m \begin{pmatrix} Y_{L,m}^*(\hat{k})Y_{L,m}(\hat{r}) \\ 0 \end{pmatrix} = P_L(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}. \tag{3.16}$$

To first order in spin-orbit interaction, the coefficients of these factors are equal to the coefficients in Brooks's expansion.[1] The spin-orbit interaction introduces angular variations of the form

$$\frac{4\pi}{2L+1}\sum_m \begin{pmatrix} (mY_{L,m}^*(\hat{k})Y_{L,m}(\hat{r}) \\ ((L+m+1)(L-m))^{1/2}Y_{L,m}^*(\hat{k})Y_{L,m+1}(\hat{r}) \end{pmatrix} = (\mathbf{L}\cdot\boldsymbol{\sigma})P_L(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix} = (-i/kr)(\mathbf{r}\times\mathbf{k}\cdot\boldsymbol{\sigma})P_L(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}, \tag{3.17}$$

where

$$\boldsymbol{\sigma}=\begin{pmatrix}0&1\\1&0\end{pmatrix}\hat{x}+\begin{pmatrix}0&-i\\i&0\end{pmatrix}\hat{y}+\begin{pmatrix}1&0\\0&-1\end{pmatrix}\hat{z}. \tag{3.18}$$

The coefficients of these terms are proportional, to first order in spin-orbit interaction, to the $\Delta F_L(r_s)$ or some derivative of them. These terms indicate the admixture of a small negative spin component into a primarily positive spin wave function.

The wave function which includes the effects of spin-orbit interaction to first order in that interaction and which satisfies the Wigner-Seitz boundary conditions to third order in the Bloch vector is

$$\begin{aligned} \frac{\psi(k,r)}{N}=&\left\{F_0(r)-\frac{(kr_s)^2}{3}\left(\frac{\phi_1}{\phi_0'}\right)^{1/2}\frac{\partial}{\partial\epsilon}\left[\left(\frac{\phi_1}{\phi_0'}\right)^{1/2}F_0(r)\right]\right\}P_0(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}+ikr_s\left\{F_1(r)\left[1+(kr_s)^2\left(\frac{1}{5}-\frac{4\phi_1}{15\phi_2}\right)\right]\right.\\ &\left.-\frac{(kr_s)^2}{3}\left(\frac{\phi_1}{\phi_0'}\right)^{1/2}\frac{\partial}{\partial\epsilon}\left[\left(\frac{\phi_1}{\phi_0'}\right)^{1/2}F_1(r)\right]\right\}P_1(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}+\frac{ikr_s}{3}\left\{\Delta F_1(r)\left[1+(kr_s)^2\left(\frac{1}{5}-\frac{4\phi_1}{15\phi_2}\right)\right]\right.\\ &\left.-\left(\frac{\Delta\phi_1}{5\phi_2}+\frac{6\phi_1\Delta F_2(r_s)}{25}\right)(kr_s)^2F_1(r)-\frac{(kr_s)^2}{3}\left(\frac{\phi_1}{\phi_0'}\right)^{1/2}\frac{\partial}{\partial\epsilon}\left[\left(\frac{\phi_1}{\phi_0'}\right)^{1/2}\Delta F_1(r)\right]\right\}(\mathbf{L}\cdot\boldsymbol{\sigma})P_1(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}\\ &-[2(kr_s)^2/3]\phi_1F_2(r)P_2(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}-[2(kr_s)^2/15][\phi_1\Delta F_2(r)+(5/6)\Delta\phi_1F_2(r)](\mathbf{L}\cdot\boldsymbol{\sigma})P_2(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}\\ &-i(kr_s)^3(2/5)\left[\left(\frac{\phi_1}{\phi_2}\right)-\frac{1}{3}\right]F_3(r)P_3(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}-i(kr_s)^3(2/35)\left\{\left[\left(\frac{\phi_1}{\phi_2}\right)-\frac{1}{3}\right]\Delta F_3(r)+[7\Delta\phi_1F_3(r)/(9\phi_2)]\right.\\ &\left.+[14\Delta F_2(r_s)F_3(r)/15]\right\}(\mathbf{L}\cdot\boldsymbol{\sigma})P_3(\hat{k}\cdot\hat{r})\begin{pmatrix}1\\0\end{pmatrix}. \end{aligned} \tag{3.19}$$

The normalizing factor is

$$N=(4\pi r_s\phi_0')^{-1/2}. \tag{3.20}$$

When the F's and ΔF's are obtained from the solutions of the Schrödinger equation (A1.11) with nonlocal J- and L-dependent potentials, the wave equation (3.19) is formally equivalent to a third-order $\mathbf{k}\cdot\mathbf{p}$ expansion of the wave function which includes the effects of the nonlocal potential and which is first order in spin-orbit interaction.

In the calculations which are described below, all terms which are proportional to $\Delta F_2(r)$, $\Delta F_3(r)$ or their derivatives have been neglected. These terms are significantly smaller than terms proportional to ΔF_1. This is because the radial functions for $L>1$ are smaller than $F_1(r)$ in the vicinity of the nucleus, where the spin-orbit interaction is significant, owing to the centrifugal potential in the radial wave equation. The neglect of these terms has been justified by numerical calculations.

IV. EVALUATION OF THE g SHIFT

Using the techniques of Luttinger and Kohn,[20] as extended by Kjeldaas and Kohn,[21] Yafet[14,22] has shown that the g shift is given by the average over the Fermi surface of

$$2[(\mathbf{X}\pi_y-\mathbf{Y}\pi_x)_{nn}+\mathbf{X}_{nn}(\pi_y)_{nn}-\mathbf{Y}_{nn}(\pi_x)_{nn}], \tag{4.1}$$

where the subscripts nn indicate that these are expectation values for conduction band states. π is the velocity operator, $\mathbf{p}+(1/2c^2)\mathbf{S}\times\nabla V$, and the matrix elements of $\mathbf{X}$ are defined by

$$\mathbf{X}_{nm}=\int_{\text{unit cell}} u_n^*(\mathbf{k},\mathbf{r})i\frac{\partial u_m(\mathbf{k},\mathbf{r})}{\partial \mathbf{k}_x}d\mathbf{r}. \tag{4.2}$$

The z axis is the direction of the applied dc magnetic field.

This expression was obtained under the approximation that the one-electron potential is local. The effects of a nonlocal potential are now being studied.

To second order in the Bloch vector, this expression may be rewritten as

$$\begin{aligned}\Delta g=&\frac{2}{i}\int\psi^*(\mathbf{r}\times\nabla)_z\psi d\mathbf{r}\\&+(1/mc^2)\int\psi^*[x\partial V/\partial x+y\partial V/\partial y]\psi d\mathbf{r}\\&-\int_s\Big[u^*(\mathbf{r}\times\nabla_k)_z\partial u/\partial\nu+2ik_\nu u^*(\mathbf{r}\times\nabla_k)_z u\\&-\left\{\frac{\partial u}{\partial k_y}\frac{\partial}{\partial\nu}(xu^*)-\frac{\partial u}{\partial k_x}\frac{\partial}{\partial\nu}(yu^*)\right\}\Big]d\mathbf{S}\\&-\operatorname{Im}\int\left[\frac{k_y}{k_x}\frac{\partial\psi^*}{\partial k_x}\frac{\partial}{\partial\nu}\frac{\partial\psi}{\partial k_x}-\frac{k_x}{k_y}\frac{\partial\psi^*}{\partial k_y}\frac{\partial}{\partial\nu}\frac{\partial\psi}{\partial k_y}\right]d\mathbf{S},\end{aligned} \tag{4.3}$$

where the integrals are over the atomic polyhedron, and ν indicates the direction of the normal to the surface of this polyhedron. In the spherical approximation, ν is the parameter r. V is the local potential used in the $\mathbf{k}\cdot\mathbf{p}$ analysis.

The first term is twice the expectation value of the z component of the orbital angular momentum, which was first calculated by Brooks.[12] It is recalculated here to take advantage of further refinements of the QDM. The additional terms have been discussed by Yafet.[22]

Substituting the wave function of Eq. (3.19), with neglect of terms proportional to $\Delta F_2(r)$ and $\Delta F_3(r)$ and terms which are quadratic in $\Delta\phi_1$, using Eq. (A1.1), performing the required surface integral, and averaging over all directions of $\mathbf{k}$, the following expression is obtained for the g shift:

$$\begin{aligned}\Delta g=&-\Delta\phi_1\left\{\frac{2r_s^2}{9\phi_0'}+\frac{2k^2r_s^4}{27\phi_0'}\left[2-\frac{4\phi_1}{\phi_2}\frac{\partial}{\partial\epsilon}\left(\frac{\phi_1}{\phi_0'}\right)\right]\right\}\\&+\Delta\phi_1'\left\{\frac{6(kr_s)^2}{81\phi_0'}\left[2+\frac{r_s^2\phi_1}{\phi_0'}\right]\right\}\\&+\frac{1}{mc^2}\int\psi^*\left[x\frac{\partial V}{\partial x}+y\frac{\partial V}{\partial y}\right]\psi d\mathbf{r}.\end{aligned} \tag{4.4}$$

The authors have been unable to convert the last term into an expression in terms of the values of the radial functions at the surface of the atomic polyhedron. This prevents use of the QDM for its evaluation. This term yields a nonvanishing addition to the g shift in the absence of spin-orbit components in the wave function. Since the term is multiplied by the small parameter $1/mc^2$, the dominant portion of the integral can be obtained by writing $u(\mathbf{k},\mathbf{r})=u(0,\mathbf{r})$. In this case the integral reduces to

$$\frac{8\pi\alpha^2}{3}\int|\psi(0,r)|^2r^3\frac{\partial V}{\partial r}dr, \tag{4.5}$$

where $\alpha(=1/137)$ is the fine structure constant.

For Li and Na, local, $\mathbf{k}$-independent potentials have been constructed, and can be used to evaluate this expression numerically. For Li, the corrected potential of Seitz[23] and the wave functions of Silverman[24] have been used at $r_s=3.2$, $\epsilon_0=0.683$. The value obtained was 2.3×10^{-5}, as compared to a contribution of -2 to -5×10^{-5} from all other terms. For Na, using the Prokofjew[25] potential with the Wigner-Seitz[26] wave functions, a contribution of 1.2×10^{-5} is obtained, as compared to $5-10\times10^{-4}$ from all other terms. For reasons which are discussed below, little confidence can be placed in numerical results which depend on values of derivatives of Prokofjew-like potentials sampled

---

[20] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[21] T. Kjeldaas, Jr., and W. Kohn, Phys. Rev. **105**, 806 (1957).

[22] Y. Yafet, Solid State Phys. **14**, 1 (1963).

[23] F. Seitz, Phys. Rev. **47**, 400 (1935).

[24] R. A. Silverman, Ph.D. thesis, Harvard University, 1951 (unpublished).

[25] W. Prokofjew, Z. Physik **58**, 255 (1929).

[26] E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).

near the origin. The orders of magnitude, however, are reliable. We expect this term to diminish in importance with increasing atomic number. The spin-orbit interaction goes as $(1/r)dV/dr$. For a spread-out dV/dr, as in lithium, the r weighting factor enhances the effect of this term, relative to the others. When dV/dr is only appreciable near the nucleus, the r weighting factor reduces the effect. Knowing that this term is insignificant for sodium, we can safely neglect it for potassium, rubidium, and cesium.

It is of some value to examine expression (4.4) for free electrons. The vanishing of Δg comes directly from the vanishing of $\Delta\phi_1$ and $\Delta\phi_1'$. In addition, it can easily be shown, using the values of the ϕ_L and their derivatives given by Brooks,[1] that the term proportional to $\Delta\phi_1$ reduces to

$$-\left(\frac{2k^2r_s^4\Delta\phi_1}{27\phi_0'}\right)\left(\frac{3}{k^2r_s^2}-1\right). \tag{4.6}$$

Taking the Fermi surface value of k in the spherical approximation, $(kr_s)^2=3.68$. The second factor is approximately 0.185. The individual terms which enter into this factor are of the order of 1 or 2. Thus we expect, if the p and d functions are correct and close to free-electron-like, to have an approximate cancellation in the second factor. The contribution of this term, however, is extremely sensitive to the quality of the wave functions because it involves the cancellation of large terms.

With the neglect of the last integral in Eq. (4.4), the g shift is determined entirely by the values of the radial functions and their derivatives at the surface of the Wigner-Seitz sphere. The methods of obtaining these values are discussed below.

V. THE RADIAL FUNCTIONS

The radial functions are solutions of Eq. (3.7) which are regular at the origin. The difficulty of constructing such solutions comes primarily from the lack of knowledge of the $V_L(r,r')$. The $V_L(r,r')$ are one-electron potentials which include not only the Coulomb interaction with the nucleus and core electrons, but certain many-body effects such as exchange and core polarization.

In the usual Wigner-Seitz type calculation it is assumed that the potential, within the sphere, is the same as that seen by an atomic valence electron. Before considering the validity of this procedure, we examine its implication with respect to a calculation of the parameters $\Delta\phi_L$ and their derivatives. The obvious procedure, which has been used in many calculations of the properties of lithium and sodium, is to construct Prokofjew-like potentials which match the atomic spectra. The shortcomings and difficulties in using such a procedure to calculate other properties of the alkali metals heavier than sodium have been discussed in detail in earlier papers on the QDM.[1–3]

These difficulties are demonstrated explicitly in the analysis of the sphericalized nonlocal potential. That is, the effective potentials in the wave equations determining the radial functions are J and L dependent. In studies of the spin-orbit interactions, another weakness of the Prokofjew method becomes apparent. It is least likely to be an accurate representation of the potential in the region of small r. This inaccuracy leads to an even greater uncertainty in the value of its derivative near the origin whence comes the greatest contribution to the spin-orbit splitting. Thus, its use in a g-shift calculation is unlikely to give good agreement with experiment.

To see the increase in error of the Prokofjew potential with decreasing r, it is necessary to examine the manner in which this potential is obtained. Prokofjew[25] used the expression

$$(n-L-\tfrac{1}{2})=(\sqrt{2}/\pi)\int\{Q(r)-\tfrac{1}{2}\times[\epsilon r^2+(L+\tfrac{1}{2})^2]\}^{1/2}dr/r, \tag{5.1}$$

where $n=\epsilon^{-1/2}$ and $Q(r)=r^2V(r)$ to derive $V(r)$. The limits of the integral bound the region in which the integrand is real. It is assumed, for sodium, that the potential is Coulombic, i.e., $Q(r)=2r$, for $r>6.74$. For $r<6.74$ it is assumed that in given regions $Q(r)=\alpha r^2+\beta r+\delta$. Examination of the integrand shows that as ϵ and L vary, the limits of integration vary. Here, starting with $Q(r)=2r$ for $r>6.74$, the choices of atomic eigenvalue ϵ's and L's can be such that regions of decreasing r are brought into the integration. For each new region of r a new set of α, β and γ are defined. Three equations determine these parameters. Two of these are chosen to match $Q(r)$ and its first derivative at the boundary of the region. The third is chosen so that Eq. (5.1) is satisfied. Because the functional form used is probably not that of the "best" effective potential, errors are introduced. It is clear that these errors will tend to pile up for small r. The Prokofjew potential tends to give good results when it is integrated over a large region with a smoothly varying function, such as the absolute square of a wave function. The values of the potential in the region near the nucleus are less reliable. Finally, the derivative of the potential near the origin can be seriously in error.

In addition to this source of error, there is another problem associated with using the Prokofjew potential to calculate the spin-orbit splittings. The work of Blume and Watson[17] shows that, due to the different manner in which exchange enters into the two terms, the potential appearing in the spin orbit term is not the same as the effective potential which is derived from the atomic spectra.

These shortcomings of the Prokofjew potential in treating spin-orbit interaction are shown numerically below. They demonstrate the potential virtues of the QDM, which avoids the explicit construction of a potential in the region close to the nucleus, and automatically gives a correct treatment of the spin-orbit term. It is this method which has been used to calculate the radial functions. Since the method has been described in detail by Brooks and Ham,[1–3] it will be discussed in only the degree of detail necessary to justify the adaptation used in this paper.

In its simplest form, the method assumes that the potential seen by an atomic alkali metal valence electron is Coulombic in the region outside the ion core. In this case, the radial solution for a state with fixed total orbital angular momentum and energy $E=-\epsilon=-1/n^2$ can be written as $(1/r)U^L(\epsilon,r)$, where $U^L(\epsilon,r)$ satisfies the differential equation

$$\frac{d^2U^L}{dr^2}+\left[\epsilon+\frac{2}{r}-\frac{L(L+1)}{r^2}\right]U^L=0. \tag{5.2}$$

This equation has two linearly independent solutions. Brooks and Ham have chosen to work with the pair

$$\begin{aligned} {}^0U^{L,n}(r)&=(z/2)J_{2L+1}{}^n(z)\,,\\ {}^2U^{L,n}(r)&=(z/2)N_{2L+1}{}^n(z)\,, \end{aligned} \tag{5.3}$$

where $z=(8r)^{1/2}$. These functions have been discussed in detail by Kuhn and Ham,[27] and tabulated by Blume, Briggs, and Brooks.[28] As ϵ goes to zero they approach the Bessel and Neumann functions, respectively. Then

$$U^L(\epsilon,r)=\alpha(n)\ {}^0U^{L,n}(r)+\beta(n)\ {}^2U^{L,n}(r)\,. \tag{5.4}$$

For an atomic eigenstate, the ratio $\alpha(n)/\beta(n)$ is fixed entirely by the condition that $U^L(r)$ vanish as r goes to infinity.

This ratio is

$$\frac{\alpha(n)}{\beta(n)}=\frac{\Gamma(n+L+1)}{n^{2L+1}\Gamma(n-L)\ \tan\pi\delta_m}, \tag{5.5}$$

where δ_m is the quantum defect, in terms of which the eigenvalue is expressed as

$$\epsilon=(m-\delta_m)^{-2}. \tag{5.6}$$

Here m is an integer that increases by unity between successive terms of a given series.

If it is assumed that the potential seen by an alkali metal conduction electron, when it is within the ionic core, is the same as that seen by the atomic valence electron, and that the potential in the region outside the core and enclosed by the Wigner-Seitz sphere is pure Coulombic, then the radial wave function outside the core can be obtained quite simply. In this case, the solutions will again be linear combinations of Coulomb solutions of the form of Eq. (5.4), with n corresponding to the solid-state energies. The problem is to find the correct ratio $\alpha(n)/\beta(n)$. Brooks and Ham have shown that if the quantity η is defined by the expression

$$\tan\pi\eta=-n^{2L+1}\Gamma(n-L)\ \tan\pi\delta_m/\Gamma(n+L+1) \tag{5.7}$$

at the atomic eigenvalues, the ratio of $\alpha(n)$ to $\beta(n)$ is given by

$$\beta(n)/\alpha(n)=-\tan\pi\eta(n) \tag{5.8}$$

at the solid-state energies. Here, $\eta(n)$ is the value obtained by extrapolation of the function $\eta(n)$ obtained from the atomic eigenvalues down to the solid-state energies. With a knowledge of η it is possible to obtain the radial functions. Before doing this, however, we list the two major assumptions which must be made.

(1) The atomic potential is Coulombic beyond the core.

(2) The potential in the solid is the same, within the core, as the atomic potential, and is Coulombic from the core surface to the Wigner-Seitz sphere radius.

Corrections will have to be made for deviations from these assumptions. Before dealing with these corrections, we proceed to evaluate the alkali-metal parameters that are needed.

It is evident that the η function is, like the quantum defect, an indication of the deviation of the core potential from pure local Coulombic. It follows from the analysis of Appendix I that there must exist a different η function for each J and L value, corresponding to the different $V_L(r,r')$'s and $W_L(r,r')$'s as well as the different coefficients associated with the spin-orbit interaction.

For each J, L function with $\epsilon=\epsilon_0$, we can write for $r_0<r<r_s$, where r_0 is the ion core radius,

$$F_{J,L}(r)\propto[{}^0U^{L,n}(r)-\tan\pi\eta_{J,L}(n)\ {}^2U^{L,n}(r)]/r.$$

Since n always corresponds to the energy at the bottom of the band, this index is dropped, henceforth. The condition that $F_{J,L}(r_s)=1$, $L=0, 1, 3$, implies that

$$F_{J,L}(r)=\frac{r_s[{}^0U^L(r)-\tan\pi\eta_{J,L}{}^2U^L(r)]}{r[{}^0U^L(r_s)-\tan\pi\eta_{J,L}{}^2U^L(r_s)]}. \tag{5.9}$$

In analogy with Eq. (3.15) we write

$$\begin{aligned} \eta_L&=[(L+1)\eta_{L+\frac{1}{2},L}+L\eta_{L-\frac{1}{2},L}]/(2L+1)\\ \Delta\eta_L&=\eta_{L-\frac{1}{2},L}-\eta_{L+\frac{1}{2},L}\,. \end{aligned} \tag{5.10}$$

$\Delta\eta_L$ represents the effects of spin-orbit interaction and is a small parameter for all the alkali metals. Expanding $\tan\pi\eta_{J,L}$ about $\tan\pi\eta_L$, we get

$$F_L(r)=\frac{r_s[{}^0U^L(r)-\tan\pi\eta_L{}^2U^L(r)]}{r[{}^0U^L(r_s)-\tan\pi\eta_L{}^2U^L(r_s)]}+O[(\Delta\eta_L)^2] \tag{5.11}$$

and

$$\begin{aligned} \Delta F_L(r)=\pi r_s\Delta\eta_L\sec^2\pi\eta_L[{}^0U^L(r_s)-\tan\pi\eta_L{}^2U^L(r_s)]^{-2}\\ \times\{{}^2U^L(r)[{}^0U^L(r_s)-\tan\pi\eta_L{}^2U^L(r_s)]\\ -{}^2U^L(r_s)[{}^0U^L(r)-\tan\pi\eta_L{}^2U^L(r)]\}\,. \end{aligned} \tag{5.12}$$

---

[27] T. S. Kuhn, Quart. Appl. Math. **9**, 1 (1951), and F. Ham, *ibid.* **15**, 31 (1957).

[28] M. Blume, N. Briggs, and H. Brooks, Technical Report No. 260, Cruft Laboratory, Cambridge, Massachusetts, 1959 (unpublished).

From the usual Wronskian relation, Brooks and Ham[3] have shown that

$$ {}^0U^L(r)\frac{\partial^2U^L(r)}{\partial r} - {}^2U^L(r)\frac{\partial^0U^L(r)}{\partial r} = \frac{2}{\pi}. \qquad (5.13) $$

Differentiating Eq. (5.12) with respect to r, evaluating it at $r=r_s$, and using Eq. (5.13) we get

$$ \Delta\phi_L = 2r_s\Delta\eta_L \sec^2\pi\eta_L \times[{}^0U^L(r_s) - \tan\pi\eta_L {}^2U^L(r_s)]^{-2}. \qquad (5.14) $$

Similar relations are obtained for the $L=2$ functions, which are normalized differently.

In Table I, the extrapolation formulas used to calculate the η_L and $\Delta\eta_L$ are listed. For $L=0$, these are identical to those obtained by Brooks and Ham[3] for all the metals but cesium. It was noticed that the atomic spectra of cesium used by those authors, as obtained from Bacher and Goudsmit,[29] are different from the more recently observed values which are listed in Moore.[30] Extrapolation formulas for the $\eta_{J,1}$ were developed using the three lowest conduction-free atom eigenstates, plus the ionization potential for the singly-ionized atom, as discussed by Ham.[2] These were then used to calculate η_1 and $\Delta\eta_1$. $\Delta\eta_2$ was calculated in the same manner as $\Delta\eta_1$, while the "best" extrapolation formulas of Brooks and Ham[3] were used for η_2. The reasons for this are discussed below.

Thus far, it has been assumed that the two conditions, mentioned above, for the validity of the QDM are satisfied. Unfortunately, this is not the case. In the following subsections, the effects of various deviations from these assumptions are discussed.

TABLE I. Extrapolation formulas for the η and $\Delta\eta$.[a]

	a	b	c	d
Lithium				
η_0	0.399501	0.029405	0.00238	···
η_{0p}	0.399106	0.027458	0.00238	···
η_1	0.047368	0.020899	0.02888	···
η_{ip}	0.046997	0.013018	0.02888	···
$\Delta\eta_1$	0.000004	−0.000097	0.00055	···
η_2	0.00086	0.00032	···	···
$\Delta\eta_2$	0.000004	0.000086	0.000298	···
Sodium				
η_0	1.34797	0.06197	0.01071	···
η_{0p}	1.34673	0.05606	0.01071	···
η_1	0.855176	−0.01876	0.05212	−0.01977
η_{1p}	0.853052	−0.04462	0.05212	−0.01977
$\Delta\eta_1$	0.000858	−0.00036	0.00167	−0.00040
η_2	0.01041	−0.0072	···	···
$\Delta\eta_2$	−0.000023	0.00019	−0.00085	···
Potassium				
η_0	2.180059	0.13915	0.0502	···
η_{0p}	2.176388	0.12243	0.0502	···
η_1	1.711980	0.07427	0.0988	−0.0574
η_{1p}	1.706392	0.01709	0.0988	−0.0574
$\Delta\eta_1$	0.003031	−0.00170	0.0019	−0.0002
η_2	0.2672	−0.2969	0.2289	···
$\Delta\eta_2$	−0.000158	−0.00269	0.0100	···
Rubidium				
η_0	3.13119	0.18164	0.0879	···
η_{0p}	3.12560	0.16017	0.0879	···
η_1	2.646294	0.16186	0.08573	−0.07367
η_{1p}	2.637512	0.08976	0.08573	−0.07367
$\Delta\eta_1$	0.013216	−0.01333	0.01787	−0.00404
η_2	1.3371	0.0385	−0.5256	···
$\Delta\eta_2$	0.001646	−0.01659	0.0284	···
Cesium				
η_0	4.04967	0.23156	0.27776	−0.033852
η_{0p}	4.04161	0.19545	0.27776	−0.033852
η_1	3.56983	0.30396	0.02483	−0.07774
η_{1p}	3.55598	0.20848	0.02483	−0.07774
[$\Delta\eta_1$	0.03256	−0.04274	0.05396	−0.01338
η_2	2.4642	0.1687	0.9023	···
$\Delta\eta_2$	0.0091	−0.04884	0.04470	···

[a] The extrapolation formulas are of the form $\eta = a + b\epsilon + c\epsilon^2 + d\epsilon^3$.

A. The Polarization Correction—Brooks and Ham

Due to the fact that the valence electron tends to polarize the ionic core, the potential seen by the valence electron is never pure Coulombic. Treating the ion core as a dipole, Brooks and Ham have found correction terms for the η extrapolation formulas. The g-shift calculations have been performed with and without the corrections applied for $L=0$ and 1. For the $L=2$ states, as discussed by Brooks,[1] it is impossible to obtain consistent extrapolation formulas for Rb and Cs without the polarization correction. Thus, these have been used throughout.

B. Spin-Orbit Interaction Outside the Core

In principle, the spin-orbit interaction outside the core could influence the $\Delta\eta_L$ values. For most of the alkali-metal atoms, however, the major portion of the interaction takes place near the nucleus; it can easily be shown, using first-order perturbation theory, that a small deviation of potential δV from Coulombic in the region outside the core, will lead to a change in the η calculated from an atomic eigenvalue given by

$$ \delta\eta = -\int_{r_0}^{\infty} [U^L(r)]^2 \delta V dr / \sec^2\pi\eta. \qquad (5.15) $$

Then, to lowest order in $\Delta\eta$, the contribution to $\Delta\eta$ from spin-orbit interaction outside the core is given by

$$ \delta\Delta\eta_L = \frac{-(2L+1)\alpha^2}{4\sec^2\pi\eta_L} \int_{r_0}^{\infty} [U^L(r)]^2 \frac{dr}{r^3}, \qquad (5.16) $$

where r_0 is the cutoff radius used by Brooks and Ham in the polarization correction.

To obtain the order of magnitude of this integral, the asymptotic expansion of the Whittaker function has been used. Brooks and Ham show that for an atomic

---

[29] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

[30] C. E. Moore, Natl Bur. Std. (U. S.) Circ. 467, Vols. I, II, and III (1949, 1952, 1958).

eigenstate

$$U^{L,n}(r)=n^{L+1}\frac{\sec[\pi(n-L-1)]}{\Gamma(n+L+1)}W_{n,L+\frac{1}{2}}(2r/n). \quad (5.17)$$

Using the first term of the asymptotic expansion of $W_{n,L+\frac{1}{2}}(2r/n)$,

$$W_{n,L+\frac{1}{2}}(2r/n)=2e^{-r/n}r^{n}(2/n)^{n}, \quad (5.18)$$

in Eqs. (5.17) and (5.16) and performing the required integration, one finds

$$\delta\Delta\eta=\frac{-(2L+1)\alpha^2n^{2L}\cos^2\pi\eta\Gamma(2n-2)\{1-I[2r_0/n(2n-2)^{1/2},\,2n-3]\}}{\cos^2[\pi(n-L-1)]\Gamma^2(n+L+1)}, \quad (5.19)$$

where I is the incomplete gamma function,

$$I(x,p)\equiv\int_0^{x(p+1)^{1/2}}e^{-x}x^{p}dx\bigg/\int_0^{\infty}e^{-x}x^{p}dx. \quad (5.20)$$

The values obtained for the $\delta\Delta\eta$'s are listed in Table II. The numerical values of $\Delta\eta$ at these values of n, computed from the extrapolation formulas of Table I, are also listed. Only for lithium is $\delta\Delta\eta$ an appreciable fraction of $\Delta\eta$. For the Li $2p$ state, the $\delta\Delta\eta$ is approximately 24% of $\Delta\eta$. For the $3p$ and $4p$ states the observed value of $\Delta\eta$ is zero, while a finite and measurable value is calculated for $\delta\Delta\eta$. This is due to the inadequacy of the calculation. Since the potential is monotonically decreasing for all r, the contribution to the diagonal elements of the spin-orbit interaction must always have the same sign. The contribution from the surface of the core outward cannot exceed the total contribution. The error probably comes from the use of only the first term of the asymptotic expansion of the Whittaker function. Most of the contribution to the integral comes from the region near the surface of the core, because of the fast drop off of both the radial function and $1/r^3$. In this region the first term approximation is least valid, and becomes less valid with increasing n. In view of this error it is reasonable to ignore this calculation for the lithium $3p$ and $4p$ states and to do a more accurate calculation for the lithium $2p$ state.

The calculation does place an upper bound on $\delta\Delta\eta$. Thus, the $\delta\Delta\eta$'s for the remaining elements can be treated as negligible.

TABLE II. $\delta\Delta\eta$ for p states of the alkali-metal atoms.

State	$-\delta\Delta\eta\times10^4$	$\Delta\eta\times10^4$
Li–$2p$	0.0376	0.1567
$3p$	0.126	0
$4p$	0.207	0
Na–$3p$	0.0299	8.564
$4p$	0.129	8.438
$5p$	0.222	8.424
K–$4p$	0.0208	27.64
$5p$	0.116	29.42
$6p$	0.189	29.43
Rb–$5p$	0.0173	112.9
$6p$	0.110	121.5
$7p$	0.196	125.6
Cs–$6p$	0.0165	265.1
$7p$	0.100	292.5
$8p$	0.204	305.0

For the lithium $2p$ state the integral

$$\int_{2.8}^{10.0}[U^1(r)]^2dr/r^3$$

was carried out using quantum defect wave functions (i.e., using the tabulated Coulomb radial functions with a ratio determined from the quantum defects). The value of the integral was 0.1076. A calculation of the remainder of the integral, from 10.0 to infinity, using the first term of the asymptotic expansion, yielded the negligible value of 1.955×10^{-4}. The corresponding $\delta\Delta\eta$ is -0.417×10^{-5}. The resulting extrapolation formula is listed in Table I.

For sodium a more complete discussion of atomic spin-orbit splitting is possible, because of the existence of the effective one-electron potential of Prokofjew[25] and the radial functions, $(1/r)P_3(r)$, of Biermann and Leubeck.[31] These wave functions are solutions of the Hartree radial equation with core polarization included in the potential.

A numerical integration of $\{[P_3(r)]^2(1/r)(dV/dr)dr\}$ yields the result that over half the total value of the integral comes from the region $r<0.20$, while almost the total value of the integral is reached before $P_3(r)$ has its first maximum at $r=0.45$. This localization of the interaction becomes much greater with increasing atomic number.

This calculation shows two things. First, spin-orbit interaction outside the core is negligible for all the alkali metal atoms but lithium. Second, the interaction is confined to that region in which the Prokofjew potential is least accurate.

The total value of the integral yields a splitting, $\Delta E=1.942\times10^{-4}$, while the observed value is 1.567 $\times10^{-4}$. The discrepancy cannot be reduced by second-order perturbation. The error is either due to an error in the radial functions (which would have to be over 10%) or the failure of the derivative of the Prokofjew potential to represent the spin-orbit interaction. For the reasons presented at the beginning of this section, it is felt that the latter is the more likely cause.

---

[31] L. Biermann and K. Lubeck, Z. Astrophys. 25, 325 (1948).

C. Influence of the Interaction Between Conduction Electrons on the One-Electron Potential

The assumption that within the Wigner-Seitz sphere the potential is Coulombic outside the core is based on the Wigner-Seitz approximate treatment of the interaction between conduction electrons. They assume that both exchange and correlation tend to keep all other conduction electrons out of the sphere under consideration. The other conduction electrons contribute no electric field in the sphere and may be ignored in the one-electron potential.

Phillips[32] has derived an effective one-electron Hamiltonian which includes conduction electron interactions within the random phase approximation. This Hamiltonian includes, in addition to the Wigner-Seitz potential, a Hartree term due to the k-space average of the conduction electron density, a screened exchange term, and a term due to part of the second-order screened Coulomb interactions. In a subsequent paper, Phillips and Kleinman[33] showed that the Slater[34] generalization of the free-electron exchange potential is a good approximation to these exchange and correlation terms in silicon. The Slater potential should be a still better approximation in the region outside the alkali metal cores, as the electron density is a considerably more slowly varying function of position than it is for silicon.

The Slater potential, however, depends only on the electron density. Throughout most of the region outside the alkali metal cores the electron density is essentially constant. The Slater exchange potential is just a constant which changes absolute energy values, but not the wave functions. For this region an approximately self-consistent Hartree term has been added to the potential outside the core. A method of obtaining such a potential which is consistent with the QDM is described below.

The restriction on the form of potentials in the solid can be relaxed in the following manner. The potential within the core must be the same as the atomic potential. Let the potential outside the core reduce to the atomic potential for $r<r_i$, where $r_0\leq r_i\leq r_s$. Solutions of the resulting differential equation can be adjusted so that they reduce to the solutions of the radial equation at $r=r_i$. In that case, their ratio at $r=r_i$, and, hence, for $r>r_i$, is determined by Eq. (5.8). Thus, the QDM can be extended to treat any potential which reduces to Coulombic at and below some acceptable r_i. We choose, therefore, for the construction of the appropriate Hartree potential, a spherical shell of constant electron density extending from the core surface to the surface of the Wigner-Seitz sphere. The electron density in this shell is equal to the density at the surface of the sphere, $|\psi(r_s)|^2$. The contributions of all but the $k=0$ part of the $u(\mathbf{k},\mathbf{r}_s)$ are neglected. The other terms are small but may not be negligible.

Then

$$|\psi(\mathbf{r}_s)|^2=(4\pi r_s\phi_0')^{-1}. \tag{5.21}$$

The resulting potential, whose constant part is chosen so that $V(r_0)=0$, is

$$V(r)=-(3r_s\phi_0')^{-1}[(r^2-r_0^2)+2r_i^3(r^{-1}-r_0^{-1})]. \tag{5.22}$$

The resulting radial differential equation is

$$\frac{d^2U}{dr^2}+\left[\epsilon'+\frac{2}{r}-\frac{L(L+1)}{r^2}+(3r_s\phi_0')^{-1}\times[(r^2-r_0^2)+2r_0^3(r^{-1}-r_0^{-1})]\right]U=0. \tag{5.23}$$

Here ϵ' is an energy parameter equal to ϵ plus a term resulting from the choice of boundary conditions. This will be treated in more detail by one of us (H.B.) in a discussion of the cohesive energy. It is of no interest in the determination of the radial functions.

In order to take advantage of previously tabulated functions, equation (5.23) has been simplified further. Blume, Briggs, and Brooks[35] have obtained numerical values for the solutions of

$$\frac{d^2U}{dr^2}+\left[\epsilon'+\frac{2}{r}-\frac{L(L+1)}{r^2}+\beta(r^2-4)\right]U=0 \tag{5.24}$$

with β and ϵ' in the desired range. This corresponds to neglect of the r_0^3/r term, and fixing of r_0 equal to 2. Since, in terms of the electric field intensity, the r_0^3/r term tends to provide a partial cancellation of the r^2 term, this approximation probably leads to an overestimation of the effects of the Hartree term. As will be shown, however, the results obtained are not without interest.

Self-consistent solutions of Eq. (5.24) have been found iteratively. It was required that solutions of Eq. (5.24) simultaneously satisfy the conditions

$$\phi_{0c}(\epsilon_0')=0 \tag{5.25}$$

and

$$\beta_u=(3r_s\phi_0')^{-1}. \tag{5.26}$$

ϕ_{0c}' is the calculated value of ϕ_0'. Equation (5.27) comes from the Wigner-Seitz boundary conditions. β_u is the value of β used in the differential equation for the solution ϕ_0'.

VI. NUMERICAL RESULTS

In Table III the results obtained in four different calculations of the g shift, minus the contribution of the term of expression (4.5), are listed. The different calculations are the combinations of inclusion and exclusion of the polarization corrections (N and NP, respectively) and the Hartree term (H and NH, re-

---

[32] J. C. Phillips, Phys. Rev. **123**, 420 (1961).

[33] J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).

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

[35] M. Blume, N. Briggs, and H. Brooks (unpublished work).

Table III. Alkali-metal energy parameters and g shifts.

r_s	ϵ_0 or ϵ_0'	E_2	$-E_4$	$-\Delta g$
Li–2.8				
NP–NH	0.7002	0.6123	0.0204	1.645×10^{-5}
P–NH	0.6975	0.6124	0.0180	1.234
NP–H	0.7798	0.6240	0.0020	5.512
P–H	0.7768	0.6237	0.0101	5.667
Li–3.2				
NP–NH	0.6878	0.7318	0.0316	2.502
P–NH	0.6860	0.7320	0.0293	2.299
NP–H	0.7844	0.7473	0.1232	4.401
P–H	0.7826	0.7467	0.1190	4.236
Li–3.6				
NP–NH	0.6568	0.8035	0.0298	2.403
P–NH	0.6557	0.8037	0.0273	2.298
NP–H	0.7560	0.8152	0.0348	4.521
P–H	0.7549	0.8153	0.0320	4.429
Na–3.6				
NP–NH	0.6369	1.0192	0.0115	7.425×10^{-4}
P–NH	0.6330	1.0443	0.0544	4.442
NP–H	0.7467	1.0091	0.0327	8.729
P–H	0.7429	1.0361	0.0681	5.938
Na–4.0				
NP–NH	0.6056	1.0159	0.0088	5.980
P–NH	0.6028	1.0334	0.0036	4.596
NP–H	0.7099	1.0082	0.0107	7.024
P–H	0.7074	1.0273	0.0135	5.852
Na–4.4				
NP–NH	0.5739	1.0137	0.0331	4.626
P–NH	0.5717	1.0264	0.0492	3.918
NP–H	0.6699	1.0087	0.0400	5.520
P–H	0.6681	1.0226	0.0230	4.994
K–4.4				
NP–NH	0.5139	1.1230	0.4353	2.611×10^{-3}
P–NH	0.5064	1.2178	0.8226	−1.614
NP–H	0.6442	1.0843	0.4385	3.080
P–H	0.6375	1.1892	0.7804	−3.098
K–4.8				
NP–NH	0.4939	1.0987	0.3445	2.389
P–NH	0.4882	1.1669	0.6069	0.317
K–4.8				
NP–H	0.6097	1.0682	0.2581	2.766
P–H	0.6051	1.1440	0.5880	1.186
K–5.2				
NP–NH	0.4731	1.0825	0.2888	2.004
P–NH	0.4686	1.1333	0.4707	0.891
NP–H	0.5754	1.0565	0.2007	2.326
P–H	0.5721	1.1134	0.3526	1.625
Rb–4.8				
NP–NH	0.4846	1.1999	0.5645	0.853×10^{-2}
P–NH	0.4764	1.3518	1.3678	−2.562
NP–H	0.6121	1.1432	0.2564	1.554
P–H	0.6059	1.3131	0.7375	−0.781
Rb–5.2				
NP–NH	0.4648	1.1631	0.4941	0.788
P–NH	0.4584	1.2731	1.0538	−0.980
NP–H	0.5764	1.1174	0.2411	1.202
P–H	0.5718	1.2420	0.6301	−0.064
Rb–5.6				
NP–NH	0.4455	1.1372	0.4789	0.659
P–NH	0.4402	1.2194	0.8767	−0.333
NP–H	0.5410	1.0909	0.1991	0.992
P–H	0.5377	1.1859	0.5263	0.263
Cs–5.4				
NP–NH	0.4350	1.1895	0.9228	0.742×10^{-2}
P–NH	0.4252	1.4110	2.7528	−13.975
NP–H	0.5472	1.0828	0.4022	2.878
P–H	0.5401	1.3345	1.6452	−9.904
Cs–5.8				
NP–NH	0.4189	1.1644	0.7277	1.153
P–NH	0.4110	1.3304	2.0014	−6.623
NP–H	0.5148	1.0641	0.3858	2.587
P–H	0.5098	1.2586	1.4025	−4.545
Cs–6.2				
NP–NH	0.4033	1.1449	0.7385	1.083
P–NH	0.3966	1.2711	1.6536	−3.382
NP–H	0.4607	0.7036	−0.9616	8.734
P–H	0.4620	1.0361	−0.5865	3.926

spectively). In addition, the results of calculations of ϵ_0, E_2, and E_4 are tabulated. These energy parameters are determined by the equations[1]

$$\phi_0(\epsilon_0)=0\,, \tag{6.1}$$

$$E_2\equiv(m/m^*)=[r_s^2\phi_1/(3\phi_0')]\,, \tag{6.2}$$

and

$$E_4=\frac{2r_s^4\phi_1}{15\phi_0'}\left[1-\frac{2\phi_1}{3\phi_2}-\frac{5\phi_1'}{6\phi_0'}+\frac{5\phi_0''\phi_1}{12(\phi_0')^2}\right]. \tag{6.3}$$

We now proceed to examine the results for each of the alkali metals.

Lithium. The results for lithium are particularly uncertain because of the large spin-orbit interaction outside the core and the magnitude of expression (4.5). The numerical calculation of expression (4.5) using Silverman's wave functions corresponds to a *NH–NP* calculation. If the results, at $r_s=3.26$, are added to the results of the *NH–NP* calculation, the g shift obtained is -2×10^{-6}, compared to the experimental value of $(-2\pm2)\times10^{-6}$ obtained by Pressley and Berk.[36] It is clear that no significance can be attached to the calculated number, as it is the result of the subtraction of two numbers that are not accurate to the order of magnitude of the result.

Sodium. The results for sodium are particularly interesting. In this case, there are experimental determinations of the g shift by Feher and Kip[37] as well as King, Miller, Carlson, and McMillan.[38] The two measurements yield $\Delta g=(-8\pm2)\times10^{-4}$ and $(-6\pm2)\times10^{-4}$,

---

[36] R. J. Pressley and H. L. Berk, Bull. Am. Phys. Soc. **8**, 345 (1963).

[37] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

[38] G. J. King, B. S. Miller, F. F. Carlson, and R. C. McMillan, J. Chem. Phys. **32**, 940 (1960).

respectively. The shape of the Fermi surface is very close to spherical, and the wave functions outside the core are very close to free-electron wave functions. All the approximations made in the theory, as well as the analysis of convergence, should be valid.

The primary result of the calculation is the good agreement with the experimental values. As shown in Fig. 1, the result of the *NP-H* calculation at $r_s=3.92$ is -7×10^{-4}. The *NP-NH* also lies within the region of agreement of the two measurements. Those calculations which include the polarization correction lie somewhat outside the area of overlap of the two measurements.

Potassium. The following four results were obtained for potassium at $r_s=4.85$: *NP-NH*, -2.2×10^{-3}; *P-NH*, -0.6×10^{-3}; *NP-H*, -2.5×10^{-3}; *P-H*, -1.4×10^{-3}. The value measured by McMillan[39] was $(-4.1\pm0.5)\times10^{-3}$. None of the calculations are in good agreement with the experimental results.

There is a clear separation between the results of calculations in which the polarization correction is included, and those in which it is neglected. The latter are in significantly better agreement with experiment.

Rubidium. No measurements of the g shift of rubidium have been reported. We note that of the four calculations, those in which the polarization correction is included have extremely small negative or positive g values at physically realizable values of r_s.

Cesium. The values calculated for Δg are shown in Fig. 2, along with the result of the measurement of Levy.[40] This figure shows quite clearly the trends associated with increasing atomic number, from Na on. First, $|\Delta g|_{\text{calc}}$ becomes too small for all types of calculations.

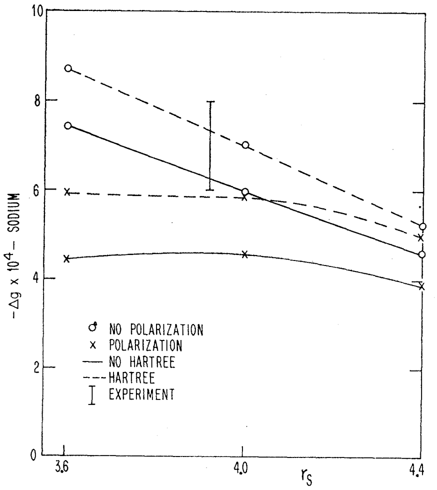

FIG. 1. Calculated values of the sodium g shift, including (P) and not including (NP) the polarization correction, and including (H) and not including (NH) the approximate Hartree term in the potential.

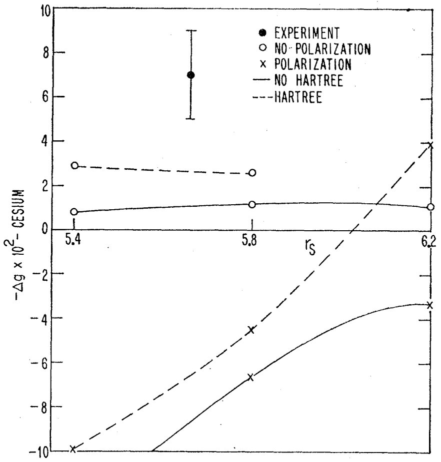

FIG. 2. Calculated values of the cesium g shift.

The best agreement is obtained when the polarization correction is neglected, and the Hartree term is included. The neglect of the Hartree leads to poorer agreement with experiment, while the inclusion of the polarization correction considerably decreases the agreement.

The relative contributions of the Hartree term to sodium and cesium are as expected. Whereas, for sodium the *NH-NP* and *H-NP* results are quite similar, the *NH-NP* calculated cesium g shift is only approximately one third that predicted by the *H-NP* calculation. It has been shown,[1] using a perturbation theory argument, that the effect of the Hartree term increases with increasing deviation from free-electron character. The relative importance of the Hartree term in the sodium and cesium calculations illustrates this quite clearly.

A detailed analysis of various terms in the *H-NP* calculated cesium shift shows that the value fails to agree with experiment because of an unexpectedly large positive value for the terms proportional to $\Delta\phi_1$. This term causes all the polarization corrected values to be too positive. It was shown, in the discussion of (4.6), that these terms are expected, for nearly free electrons, to yield a small positive contribution due to cancellations. Since cesium wave functions show considerable deviation from free-electron functions, less cancellation was expected. It can be shown, however, that if expression (4.6) is used to calculate this term, there is some, but insufficient, improvement in the agreement with experiment. The failure to obtain agreement with experiment is due to the large value of $\Delta\phi_1$. Equation (5.14) was used to calculate this parameter. It has been shown, in addition, that no reasonable extrapolation of $\Delta\eta_1$ will yield a calculated shift in cesium which is in agreement with experiment. Finally, it has been shown that η_1 is sufficiently close to a half-integer at the energies involved so that small errors can make a considerable difference in the factor $\sec^2\pi\eta_1[{}^0U^1(r_s)$

---

[39] R. C. McMillan, Phys. Chem. Solids **25**, 773 (1964).

[40] R. A. Levy, Phys. Rev. **102**, 31 (1956).

$-\tan\pi\eta_1{}^2U^1(r_s)]^{-2}$. In fact, it is these differences in η_1, both in the factor just quoted and in the partial cancellations, which account for almost all the difference in the P and NP calculations.

Since the k-series expansion of the energies converges rather slowly, it is not unreasonable to question the validity of using only the first two terms of the expansion of the g shift. It turns out that the contribution of the second-order term is approximately one-quarter of that of the zero-order terms in the NP–H calculations for r_s equal 5.4 and 5.8. It is probable that the fourth-order term is no larger than the second. Since it would be necessary to double the calculated shift to obtain agreement with experiment, it is highly unlikely that poor convergence is the major cause of the discrepancy.

Thus, it appears as if agreement with experiment can be obtained for sodium using wave functions which include a Hartree term, but which neglect the polarizations correction to η_0 and η_1, while including them in η_2. The same procedure leads to the "best" calculations for the remainder of the alkali metals. For these, the inclusion of the $L=0$ and 1 polarization corrections lead to physically unreasonable results, while the inclusion of the Hartree term makes the results more reasonable.

VII. THE POLARIZATION CORRECTION

The consistent failure of the polarization corrected results, which becomes more drastic with increasing Z, casts considerable doubt on the validity of the correction. In this section, we present a detailed study of the correction, in an effort to understand its failure.

A. The Polarization Perturbation

In making the polarization correction, a $\delta\eta_L$ has been subtracted from the uncorrected η_L. This $\delta\eta_L$ is computed, as discussed in Secs. VA and VB, using first-order perturbation theory to find the expectation value of the polarization potential, $2\alpha'/r^4$, from a radius r_0, outside the core and inside r_s, outward. r_0 is chosen to be approximately equal to the sum of the core and conduction electron screening radii. This choice was made for the following reason. Within the solid, when the electron is within the screening radius from the core, the interaction between it and the core tends to approximate that interaction in the free atom. When the electron is beyond the screening radius, the interaction tends to be screened. Three possible sources of error in this approach may be mentioned.

It is assumed that the core (nucleus plus electron core) distorts as a dipole, i.e., that the effect of the conduction electron on the core can be treated as if the electron core acts as a rigid body. Thus, a dipole is created at the nucleus. In reality, of course, the conduction electron distorts the electron cloud near the surface of the core. This surface distortion partially shields the inner electrons from the Coulomb field of the conduction electron. However, since the electron-electron interaction, when the conduction electron is outside the core, is Coulombic, the effective interaction can be treated as a sum of multipoles at the nucleus. The dominance of the dipole interaction is shown by a simple calculation. The expectation value of finding the "f" electrons of the lighter alkali-metal free atoms within the core is exceedingly small. Their quantum defects, and the corresponding η's should be due, almost entirely, to the polarization interaction. We have calculated $\delta\eta$ for these electrons, using the Brooks and Ham dipole correction.[3] In all cases calculated, the results are in sufficient agreement with the η calculated from the observed quantum defects to justify the dipole approximation.

It should be noted that in choosing the Brooks and Ham polarization correction the Pauling[41] free-ion polarizabilities are used, rather than those of Tessman, Kohn, and Shockley[42] (TKS). This choice was originally[3] dictated by the fact that the latter give quantum defects for $L=3$ which are larger than those observed experimentally. It has since become apparent, due to the work of Dick and Overhauser,[43] that the (TKS) polarizabilities, which are derived from alkali-halide dielectric constants, are not to be equated with free-ion polarizabilities. This is because the relative displacements of alkali halide ions lead to distortions of the ion cores. These distortions contribute to the dielectric constant. Since, however, an appreciable portion of the forces causing the displacement are not electrostatic in nature, they should not be included in the free-ion polarizabilities. The reader is referred to the paper of Dick and Overhauser for an extremely lucid discussion of the details.

Another approximation is made in the derivation of Eq. (5.15). It is assumed that $\sec^2\pi\eta d\eta/d\epsilon$ is small compared to $(2/\pi)dk/d\epsilon$. Here $d\eta/d\epsilon$ is the derivative of the η extrapolation formula at the atomic eigenvalue, while $dk/d\epsilon$ is the change of the k of Eq. (5.5) with a change in the atomic eigenvalue. This approximation was checked for the $5p$ state of cesium, for which the polarization correction is large, and was found to be valid.

Thus, it seems highly unlikely that an approximation in the perturbation calculation of $\delta\eta_{PL}$ for the free atom is responsible for the poor results obtained.

B. Polarization Effects in the Solid

The conduction electron in the solid also polarizes the core. This fact is only partially taken into account in the simple QDM. For $r<r_0$ it is assumed that the

---

[41] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

[42] J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[43] B. G. Dick, Jr., and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

polarization potential energy is the same as that in the free atom. For $r>r_0$ the core polarization potential energy is not included. As discussed in an earlier paper,[1] there are two basic problems in the solid which do not appear in the free atom. The first is that in the solid there are other conduction electrons which tend to shield the interaction between the core and the electron under consideration. The second is that the electron considered may polarize several cores. We now consider both effects, starting with the shielding.

In Ref. 1 the polarization interaction is worked out under the assumption that it can be treated as follows. The conduction electron creates a dipole at the origin. The field creating the dipole is a screened Coulomb field, with a screening radius, $k_c=1.3r_s^{1/2}$, determined by Pines.[44] The potential, due to the dipole, acting on the electron, is also screened with the same screening radius. The resulting potential energy is given by

$$V(r)=-\int_r^\infty \frac{8\alpha'}{r^5}\exp\left(\frac{-r}{0.65r_s^{1/2}}\right)dr. \qquad (7.1)$$

The magnitude of this potential energy, relative to the free-atom polarization, is readily seen when an expression of the form $V(r)=2\alpha'(A/r_s^4-b/r^4)$ is made to agree with Eq. (7.1) at the cutoff and Wigner-Seitz sphere radii. For cesium, $r_s=5.4$, the result is

$$V(r)=2\alpha'(0.0138r_s^{-4}-0.0285r^{-4}). \qquad (7.2)$$

Both the potential and the field magnitude $-dV/dr$ are significantly smaller than the corresponding free-atom values. If this model is correct, the interaction between the electron and cores in neighboring atomic polyhedra is negligible. In this context, it is probably more valid to use the Thomas-Fermi screening radius. Such a procedure yields even smaller values for the potential and its derivative, so that we have not felt it necessary to perform the numerical calculation.

This model, however, has a serious shortcoming. The success of the Dick-Overhauser[43] shell model of the core indicates that an appreciable portion of the free-ion polarizability is due to distortion of the outer portion of the core. This is particularly true for those heavy alkali atoms in which the polarizability is appreciable. In the atom the distortion can be treated as a dipole at the origin because the interaction between the conduction and core electrons is strictly Coulombic.

The applicability of this model to the solid becomes questionable when it is considered that the screening radius is comparable with the radius of the core. Thus, in the solid, as opposed to the free atom, the valence electron sees the nearer side of the core with much greater effectiveness than the further side and, in consequence, the dipole model may considerably underestimate the core polarization effects in the solid.

There is another way of looking at this problem which tends to confirm this argument. Let us suppose that, for all values of r, the interaction between the conduction electron and the core can be treated by an effective electric field. The field in the solid is different from that for the free electron. Within the core, however, they should be quite similar. In the free atom this field is continuous and should approach $-(8\alpha'/r^5+2/r^2)$ as r approaches the cutoff radius from within. Since, in the QDM, the field within the cutoff radius is assumed to be identical to the free atom field, there is an inconsistency. That is, if the shielded interaction is used outside the cutoff radius, there is a discontinuity in the field at this radius.

Note that all the polarization-corrected QDM results presented here and elsewhere in the literature have this discontinuity built into them, since the solid-state polarization correction is neglected. To use the QDM then, it appears as if a term which yields a field of $-8\alpha'/r^5$ at the cutoff radius is approached from without should be included in the solid-state potential.

This argument leads directly to the second question; when the electron is within one Wigner-Seitz sphere, does it experience an appreciable polarization interaction with the other spheres? A partial answer to this question can be obtained by considering the shielded interaction potential of Eq. (7.1). Cores in neighboring polyhedra will be shielded in approximately the manner described by this equation and this interaction should be negligible.

It is important to note that since the valence electron frequencies are smaller than plasma frequencies, valence electron screening will be significant. In fact, the field of the valence electron will be screened by the static dielectric constant, as discussed, e.g., by Pines.[44] The opposite is the case for the van der Waals interactions between cores, since the frequencies involved are greater than the plasma frequency.

We are led to demand, then, a potential which gives the $-8\alpha'/r^5$ field at the core surface, and a vanishing field at and beyond r_s. A reasonable approximation to this was proposed previously[1]:

$$V(r)=\begin{cases}2\alpha'(r_s^{-4}-r^{-4}), & r_0\leq r\leq r_s\\ 0, & r_s\leq r.\end{cases} \qquad (7.3)$$

This expression probably overestimates the field for $r\doteq r_s$.

The effects of this potential on the parameters used in calculating the g shift have been calculated. In all cases, the resulting changes were insignificant. This is not unexpected, as the potential is small.

It should be noted that the argument given above, resulting in Eq. (7.3), leads to another disturbing conclusion. The polarization correction was calculated on the assumption that the potential within the core in the metal is the same as that in the free atom. This leads to the discontinuity in potential. The use of Eq.

---

[44] D. Pines, Solid State Phys. 1, 367 (1955).

(7.3) outside the core in the metal corrects the discontinuity in the field, but not in the potential.

To remove this discontinuity it is necessary to subtract, from the free-atom eigenergies, an additional term equal to the expectation value of $-2\alpha'/r_0^4$ within the core. Then it will be necessary to add, to the solid-state potential, a perturbation term which is constant within the core, zero outside the core, and which makes $V(r)$ continuous at the core surface. This term is

$$V_{cc}(r)=2\alpha'(r_s^{-4}-r_0^{-4}). \tag{7.4}$$

We may add this correction throughout the cell, where it only changes the definition of ϵ_0 or ϵ_0'. Then it must be subtracted outside the core. This perturbation also has a negligible effect on the parameters of importance.

The effect of the term $-2\alpha'/r_0^4$ can be calculated using Eq. (5.15) and the relation[3]

$$\int_0^{r_0}[U^L(r)]^2dr=\left[U^L\frac{\partial^2U^L}{\partial r\partial\epsilon}-\frac{\partial U^L}{\partial r}\frac{\partial U^L}{\partial\epsilon}\right]_{r=r_0}. \tag{7.5}$$

The resulting change in η for the cesium $6p$ and $7p$ states are 0.0183 and 0.1099, respectively. This leads to an extrapolation equation correction

$$\delta\eta_c(\epsilon)=0.0209-0.0142\epsilon. \tag{7.6}$$

For a core radius of 4.961 the original polarization correction is

$$\delta\eta(\epsilon)=0.0138+0.095\epsilon. \tag{7.7}$$

At solid-state energies the two corrections tend to add. This additional correction makes the polarization corrected values even worse.

In view of this it is justifiable to ask what would happen if the analysis of shielding in the solid is completely wrong. The extreme case would occur if the polarization interaction were completely unscreened. The conduction electron would interact with all the cores in the solid. Some idea of the order of magnitude of the changes can be obtained by calculating the effect on ϕ_1, and $\Delta\phi_1$, due to a completely unscreened interaction with the central core. For cesium, $r_s=5.4$, the largest parameter change is of the order of 2% of the parameter itself. It seems likely that the contribution from other cells can be neglected.

We are then led to a striking paradox. The total polarization interaction leads to small changes in the free-atom eigenenergies. The corresponding change in η, at the atomic eigenenergies, is very small. When the most extreme polarization interaction in the solid is used it changes the solid-state parameters by only a few percent. Yet the Brooks-Ham correction can change ϕ_1 by 20% and can double $\Delta\phi_1$. These results suggest that the η and/or polarization $\delta\eta$ extrapolations are in error.

C. The Polarization Correction Extrapolation

It will now be shown that there is good reason to believe that the $\delta\eta$ extrapolations are incorrect, but it will also be shown that this error is insufficient to account for the poor results obtained.

A cubic η extrapolation formula which has not been corrected for polarization is determined by the condition that it yields the observed η's of three atomic conduction electron states and one core state. The Brooks-Ham linear polarization correction formula describes the correction to the conduction electron states quite accurately. The probability of finding the core electrons outside the core is negligible. Thus, we can approximate the core state corrections by zero. The same is true of any state with energy close to the core energies. Thus, it is expected that the polarization correction, and its derivative with respect to energy, will vanish at core energies. Examination of the extrapolation formula shows that $\delta\eta$ and $d\delta\eta/d\epsilon$ are relatively large at these energies, indicating that the extrapolation formula is in error. This difficulty can be overcome by requiring that the extrapolation formula give the correct values for the two lowest valence electron states and have the desired properties at the core state energy. Such a formula, for cesium, is

$$\delta\eta_p=0.0113+0.1381\epsilon-0.1707\epsilon^2+0.0504\epsilon^3. \tag{7.8}$$

The formula for $\delta\eta_c$ must also give correct results at core energies. In this case, since the electron is almost entirely within the core, $\delta\epsilon\doteq 2\alpha'/r_0^4$. However, at core energies, the changes of a calculated value of η with a change in ϵ is small. The resulting $\delta\eta_c$ is negligible so that we demand that $\delta\eta_c$ vanish at the core energy. The resulting extrapolation formula is

$$\delta\eta_c=0.0209-0.0146\epsilon+0.0014\epsilon^2.$$

At $\epsilon_0=0.54$, corresponding to cesium, $r_s=5.4$, the $(B\text{–}H)$ polarization correction is 0.0651, $\delta\eta_p=0.0440$, $\delta\eta_c=0.0134$, and $\delta\eta_p+\delta\eta_c=0.0574$. Thus, there is a reduction in $\delta\eta$, but only by about 12%. This change is not even sufficient, taken alone, to reduce the $\Delta\phi_1$ of the polarization correction value to a point where the calculated g shift is negative.

Thus we find that although the situation is improved by a more careful extrapolation of $\delta\eta$, most of the improvement is canceled by the additional correction.

D. The η Extrapolation

There is still another possible cause of the difficulty encountered with the polarization correction. It may be that the extrapolation of the η functions, in the absence of the polarization corrections, are in error. If this is the case, the additional error contributions to the η's must be of the same sign as the polarization corrections.

This sort of error would consistently explain a large number of QDM calculations. There is one calculation which tends to decrease our belief in its significance. Ham[45] has calculated $E(k)$ relations for the alkali metals using the QDM, but expanding in the region of the Fermi surface. Here the determination of the η's involves an interpolation, rather than extrapolation, from free-atom energies. Brooks[46] has compared the parameters ϵ_0 and E_2 of the $NH-P$ calculation with the equivalent parameters obtained by extrapolating Ham's $E(k)$ results to the bottom of the band. In all cases, the agreement is good.

It is highly likely that the parameters obtained by extrapolating η are much more sensitive to extrapolation errors than are the extrapolations of the energy parameters themselves. Thus, the agreement between the two methods indicates that it is not too probable that the η extrapolation is the cause of the errors.

VIII. CONCLUSIONS

The results obtained in this paper may be summarized as follows:

(1) Using wave functions which involve the third-order $\mathbf{k}\cdot\mathbf{p}$ expansion of their periodic part, which include a Hartree term in the potential, and which ignore the polarization corrections to the observed quantum defects, it is possible to calculate g shifts which agree with experimental values for sodium.

(2) In the expansion of a physical quantity to a given power of $\mathbf{k}$, it is necessary to retain all orders of $\mathbf{k}\cdot\mathbf{p}$ in $u_n(\mathbf{k},\mathbf{r})$ which contribute to that power. That is, beyond the first order the convergence of the $\mathbf{k}\cdot\mathbf{p}$ expansion is slow.

(3) For those alkali metals in which m^*/m deviates from unity, neglect of the Hartree term leads to considerable error in the calculated g shift.

(4) None of the values calculated for potassium and cesium are in good agreement with experiment.

(5) The polarization correction invariably removes the agreement with experiment. Although the polarization correction has been studied in detail and improvements made, no source of error in them has been found sufficient to explain the discrepancy.

The failure of these calculations for the heavier alkali metals remains unexplained and disturbing. There are a number of possible explanations.

The first is that the choice of a local potential in the derivation of Yafet has led to the neglect of important terms in the g shift. It is known, from the work of Kane,[47] that the inclusion of a nonlocal potential leads to additional terms in the $\mathbf{k}\cdot\mathbf{p}$ expression for the effective mass. While it seems clear that the expression for E_2 used here takes account of them, there is no indication that the g-shift expression also does.

The second possibility is that the g-shift expression does not converge sufficiently rapidly to allow the neglect of higher order terms. It has been shown that the wave function outside the core converges in the following manner. The ratio of the first- to zero-order term is small because the pseudopotential is weak. The convergence rate beyond first order is fairly rapid, because the pseudopotential is localized. Spin-orbit interaction, however, depends on the properties of the wave function in the region near the nucleus. The wave function in this region is determined by the properties of the true potential. This potential is not nearly as localized as the pseudopotential. Thus, if the potential was sufficiently weak so that it could be treated by nearly free electron theory, the core function expansion would be expected to converge at a much slower rate than the function outside the core. This implies that the higher-order terms of the g shift may be significant. The disturbing aspect of this analysis is that by analyzing their effects at the Wigner-Seitz sphere radius, we would probably meet small wave function differences magnified by large coefficients. Such an analysis points to the need for a calculation of the g shift directly at the Fermi surface.

Another factor which has been neglected is the true shape of the Wigner-Seitz polyhedron and, correspondingly, the Fermi surface. No efforts to evaluate the accuracy of the spherical approximation have been made. However, the now-recognized small distortion of the Fermi surfaces from spherical shape suggests that this effect could not account for the errors.

We note that the Hartree terms tend to bring the values of E_2 closer to unity. The parameter (E_2-1) is reduced by ten to thirty percent for the heavier alkali metals. Since (E_2-1) can be related[48] to the distortion of the Fermi surface, it is highly likely that it is the neglect of the Hartree term which led to the disagreement between Ham's[49] calculation and recent experimental values.[50]

ACKNOWLEDGMENTS

The authors would like to acknowledge helpful discussions with Yako Yafet on the meaning of the terms in the g shift and their calculation. Discussions with Frank Ham helped the authors to clarify their ideas on errors in the QDM.

In addition, discussions with David Adler, Gerald Peterson, and Shan-Chun Yu on a variety of topics have been of considerable aid.

APPENDIX 1. A GENERALIZATION OF BOWERS' THEOREM

In the course of the analysis described in Secs. III and IV, it was necessary to integrate quadratic func-

---

[45] F. S. Ham, Phys. Rev. **128**, 82 (1962).

[46] H. Brooks, Trans. Met. Soc. AIME, **227**, 546 (1963).

[47] E. O. Kane, Phys. Chem. Solids **8**, 38 (1959).

[48] M. H. Cohen and V. Heine, Advan. Phys. **7**, 395 (1958).

[49] F. S. Ham, Phys. Rev. **128**, 2524 (1962).

[50] K. Okumura and I. M. Templeton, Phil. Mag. **7**, 1239 (1962); **8**, 889 (1963).

tions of the radial solutions. In this Appendix the generalization of Bowers[51] theorem,

$$\int_0^{r_p} F_{J,L}^2(r)r^2dr = F_{J,L}(r_p)\frac{\partial^2 F_{J,L}(r_p)}{\partial r\partial\epsilon} - \frac{\partial F_{J,L}(r_p)}{\partial r}\frac{\partial F_{J,L}(r_p)}{\partial\epsilon}, \qquad \text{(A1.1)}$$

appropriate to nonlocal potentials is derived. The derivation is presented because one important approximation is made within it which limits the general applicability of this theorem.

For each ϵ there exists a set of solutions of the Schrödinger Eq. (3.1) which can be labeled as

$$\psi_{J,L,m_J}(\mathbf{r}) = F_{J,L}(r)\phi_{J,L,m_J}(\hat{r})\,. \qquad \text{(A1.2)}$$

The ϕ's are two-component spinors whose arguments are the orientation angles of the vector $\hat{r}$. They are normalized on the unit sphere with spin summation included.

Similarly, since V and W of Eq. (3.1) must be invariant under the transformation $\mathbf{r}$ and $\mathbf{r}'$ going into $\mathbf{S}\mathbf{r}$ and $\mathbf{S}\mathbf{r}'$, respectively, where S is a member of the rotation group, they can be written in the general form

$$V(\mathbf{r},\mathbf{r}') = \sum\nolimits_L V_L(r,r')P_L(\hat{r}\cdot\hat{r}')\,. \qquad \text{(A1.3)}$$

Differentiating Eq. (3.1) by ϵ, and multiplying on the left be ψ^*, we obtain

$$\psi^*(\mathbf{r})\{-\nabla^2+\epsilon\}\frac{\partial\psi(\mathbf{r})}{\partial\epsilon} - \psi^*(\mathbf{r})\int V(\mathbf{r},\mathbf{r}')\frac{\partial\psi(\mathbf{r}')}{\partial\epsilon}d\mathbf{r}' - \tfrac{1}{2}\alpha^2\psi^*(\mathbf{r})\int W(\mathbf{r},\mathbf{r}')\mathbf{L}'\cdot\mathbf{S}'\frac{\partial\psi(\mathbf{r}')}{\partial\epsilon}d\mathbf{r}' = -\psi^*(\mathbf{r})\psi(\mathbf{r})\,. \qquad \text{(A1.4)}$$

Similarly, multiplying the Schrödinger equation for ψ^* by $\partial\psi(\mathbf{r})/\partial\epsilon$, on the right we obtain

$$\{(-\nabla^2+\epsilon)\psi^*(\mathbf{r})\}\frac{\partial\psi(\mathbf{r})}{\partial\epsilon} - \int\psi^*(\mathbf{r}')V^*(\mathbf{r},\mathbf{r}')d\mathbf{r}'\frac{\partial\psi(\mathbf{r})}{\partial\epsilon} - \tfrac{1}{2}\alpha^2\int\psi^*(\mathbf{r}')(\mathbf{L}'\cdot\mathbf{S}')W^*(\mathbf{r},\mathbf{r}')\frac{\partial\psi(\mathbf{r})}{\partial\epsilon}d\mathbf{r}' = 0\,. \qquad \text{(A1.5)}$$

Subtracting the first equation from the second, using the forms of Eq. (A1.2) for $\psi(r)$ and (A1.3) for V and W, and integrating the result over a sphere of radius r_p, we obtain the result

$$\begin{aligned}\int_0^{r_p} F_{J,L}^2(r)r^2dr &= F_{J,L}(r_p)\frac{\partial^2 F_{J,L}(r_p)}{\partial r\partial\epsilon} - \frac{\partial F_{J,L}(r_p)}{\partial r}\frac{\partial F_{J,L}(r_p)}{\partial\epsilon}\\ &+\int_0^{r_p}\int_0^{\infty}\left[F_{J,L}(r)V_L(r,r')\frac{\partial F_{J,L}(r')}{\partial\epsilon} - F_{J,L}(r')V_L^*(r,r')\frac{\partial F_{J,L}(r)}{\partial\epsilon}\right]r'^2dr'r^2dr\\ &+(\alpha^2/4)[J(J+1)-L(L+1)-3/4]\\ &\times\int_0^{r_p}\int_0^{\infty}\left[F_{J,L}(r)W(r,r')\frac{\partial F_{J,L}(r')}{\partial\epsilon} - F_{J,L}(r')W_L^*(r,r')\frac{\partial F_{J,L}(r)}{\partial\epsilon}\right]r'^2dr'r^2dr\,. \end{aligned} \qquad \text{(A1.6)}$$

The two integrals make this expression particularly inconvenient to use. In the QDM, as used here, the potentials $V_L(r,r')$ and $W_L(r,r')$ are assumed to be local for r greater than some radius r_p which is greater than the core radius and less than the Wigner-Seitz sphere radius. The condition that the Hamiltonian be Hermitian leads to the requirement

$$V_L(r,r') = V_L^*(r',r)$$

and

$$W_L(r,r') = W_L^*(r',r)\,. \qquad \text{(A1.7)}$$

This requirement implies that $V_L(r,r')$ and $W_L(r,r')$ are local for $r'>r_p$. Thus, the integrals can be written as

$$\begin{aligned}&\int_0^{r_p}\int_0^{r_p}\left[F_{J,L}(r)V_L(r,r')\frac{\partial F_{J,L}(r')}{\partial\epsilon} - F_{J,L}(r')V_L^*(r,r')\frac{\partial F_{J,L}(r)}{\partial\epsilon}\right]r'^2dr'r^2dr\\ &+\int_0^{r_p}\int_{r_p}^{\infty}\left[F_{J,L}(r)V_L(r)\delta(r-r')\frac{\partial F_{J,L}(r')}{\partial\epsilon} - F_{J,L}(r')V_L^*(r)\delta(r-r')\frac{\partial F_{J,L}(r)}{\partial\epsilon}\right]r'^2dr'r^2dr\,. \end{aligned} \qquad \text{(A1.8)}$$

The first integral vanishes because of Eq. (A1.7). The second integral vanishes because the ranges of r and r' do not overlap. Any ambiguity about the method of treating the integral at r_p is eliminated by Eq. (A1.7). The terms of Eq. (A1.6) involving W are treated in the same manner. With the vanishing of the two integrals Eq. (A1.6) reduces to the desired expression, Eq. (A1.1).

---

[51] W. A. Bowers, Ph.D. thesis Cornell University, Ithaca, New York, 1943 (unpublished).