PHYSICAL REVIEW B VOLUME 8, NUMBER 2 15 JULY 1973

Theoretical Evaluation of the g Shift in the Alkali Metals, Li, Na, K, Rb, and Cs

R. A. Moore and C. F. Liu
Department of Physics, University of Waterloo, Waterloo, Ontario, Canada
(Received 12 September 1972)

The spherical-wave-expansion procedure has been used to solve, in the spherical-cell approximation, the one-electron Schrödinger equation containing the spin-orbit interaction, and the results have been used to evaluate the g shift in Li, Na, K, Rb, and Cs. Convergence of the numerical work is clearly demonstrated. The cellular potential seen by the conduction electron has been taken to consist of a local ion-core potential plus the Hartree field of the other conduction electrons, assumed uniformly distributed. This model, with the choice of local potentials made in the text, yields calculated values in good agreement with observed values for Li, Na, and K. However, there is a large discrepancy between the results of this model and observation for Rb and Cs. Possible sources of this discrepancy are discussed.

I. INTRODUCTION

Recent measurements[1,2] of the conduction-electron g shifts in rubidium and cesium indicate that some corrections must be made to the theoretical determination of this quantity. Corrections, of course, can be made either to the theoretical formulation of the problem or to the numerical evaluation of existing theories. It is this latter aspect that is examined herein.

Rather extensive numerical work has been carried out by Bienenstock and Brooks.[3] We comment that an earlier cesium measurement[4] disagrees with all later values. Only two modifications to the numerical work, these being for lithium[5] and sodium,[6] have been made since. We investigate one of the possible sources of the discrepancies suggested in Ref. 3, namely, that the k power-series expansion of the one-electron wave function may be slowly convergent. Slow convergence of this expansion has been noted in the evaluation of other properties.[7,8]

The theoretical formulation of the g shift due to the conduction electrons was initiated by Yafet[9] and gradually developed,[10–12] with the latest work being by de Graaf and Overhauser.[13] We use the equations as written down in Ref. 13.

The first step[3] in the evaluation of the g shift is to solve for the wave function of the one-electron Hamiltonian including the spin-orbit interaction [e.g., see Ref. 13, Eq. (2)],

$$H=\frac{p^2}{2m}+V(\vec{r})+\frac{\hbar}{4m^2c^2}[\vec{\sigma}\times\nabla V]\cdot\vec{p}\,. \tag{1}$$

Since we do not wish to confuse the results of a model and the numerical approximations we use the single model where $V(\vec{r})$ is taken to consist of a local ion-core contribution plus a Hartree-field contribution from the other conduction electrons. This latter field is taken to be that of a uniform charge distribution equal to the conduction-electron charge. Bienenstock and Brooks[3] have considered alternative models in which they allow for the inclusion or omission of a slightly different Hartree field. It has been retained here on the basis that it is physically reasonable to include some such effect as it appears necessary in other calculations.[7] Further, since the Fermi surfaces of the alkali metals are nearly spherical and the net g shift is given by a Fermi-surface average, the spherical-cell approximation is made at the outset. One does not anticipate this approximation introducing a significant error and it is tacitly assumed in all previous calculations. In Sec. II the solution of Eq. (1) is obtained using a modification of the spherical-wave-expansion procedure[8] to include the effect of the spin-orbit interaction. The solution in this form is readily accommodated on a computer and convergence of the results ascertained.

The second step is to use the solutions obtained above to evaluate the g shift [e.g., see Ref. 13, Eq. (30)],

$$\begin{aligned}\delta g(\vec{k})=&\frac{2}{\hbar}\left[\frac{\partial\alpha}{\partial k_x}\pi^y_{0\uparrow0\uparrow}-\frac{\partial\alpha}{\partial k_y}\pi^x_{0\uparrow0\uparrow}\right]+[\delta g(\vec{k})]''+[\delta g(\vec{k})]'''\\&+\frac{2}{i\hbar}\int\left[\left(\frac{\partial u^\dagger_{0\vec{k}\uparrow}}{\partial k_x}\right)\pi^y u_{0\vec{k}\uparrow}-\left(\frac{\partial u^\dagger_{0\vec{k}\uparrow}}{\partial k_y}\right)\pi^x u_{0\vec{k}\uparrow}\right]d^3r\\&+\frac{2}{\hbar}\,[X_{0\uparrow0\uparrow}\pi^y_{0\uparrow0\uparrow}-Y_{0\uparrow0\uparrow}\pi^x_{0\uparrow0\uparrow}]+2[X_{0\uparrow0\uparrow}k_y-Y_{0\uparrow0\uparrow}k_x]\,.\end{aligned} \tag{2}$$

The various terms will be defined in Sec. III where they are reduced to forms that can be evaluated using the results of Sec. II.

The numerical results and analysis are presented in Secs. IV and V. Note that the calculations have been carried out for lattice constants at 20 °C except for cesium which is at − 10 °C. This was simply a matter of convenience in using tabulated values.[14] The volume dependence in going to low temperatures (generally, 5 °K) was checked and found to be insignificant (less than +5% in the g shift). This is consistent with Ref. 3 over the same range.

Good agreement is obtained between the observed and calculated g-shift values for lithium, sodium, and potassium. However, a large discrepancy still exists for rubidium and cesium. This work confirms the general character of the earlier calculation[3] and shows that the discrepancies do not arise from any numerical inaccuracies. Also, the method presented is applicable to a number of alternative models.

II. SOLUTION TO THE SCHRÖDINGER EQUATION CONTAINING THE SPIN-ORBIT INTERACTION IN THE SPHERICAL-CELL APPROXIMATION

As previously pointed out, the first step in evaluating the g shift is to obtain a solution, in one form or another, of sufficient accuracy to the Schrödinger equation, Eq. (1), including the spin-orbit term. Throughout, we shall measure length in atomic units $\rho = r/a_0$, where $a_0 = \hbar^2/me^2$ is the Bohr radius, energies are in rydbergs, $W = E/(me^4/2\hbar^2)$ and $U = V/(me^4/2\hbar^2)$. Also, the complete calculation will be carried out in the spherical-cell approximation of the Wigner–Seitz unit cell. The conversion of Eq. (1) to the prescribed units and the spherical approximation yields

$$H = -\nabla_\rho^2 + U(\rho) + \frac{\alpha^2}{4\rho}\frac{dU(\rho)}{d\rho}\,\vec{\sigma}\cdot\hat{L}, \tag{3}$$

where $\alpha = e^2/\hbar c$ is the usual fine-structure constant and $\hat{L} = \vec{L}/\hbar$, $\vec{L}$ being the usual angular momentum operator. Since the g shift is to be calculated to first order in α^2 we look for a solution using α^2 as the expansion parameter.

The zero-order equation is readily written down,

$$H^0 \phi^0_{\vec{k}s}(\vec{\rho}) = W^0(\mathrm{k})\,\phi^0_{\vec{k}s}(\vec{\rho}), \tag{4}$$

and is the standard one-electron equation; here

$$H^0 = -\nabla_\rho^2 + U(\rho). \tag{5}$$

The solution of this equation in the spherical-cell approximation has been discussed adequately elsewhere[8,15,16] and hence we merely summarize the relevant results in what follows. The solutions are of the form

$$\phi^0_{\vec{k}\uparrow}(\vec{\rho}) = \begin{pmatrix}1\\0\end{pmatrix}\psi^0_{\vec{k}}(\vec{\rho}) \tag{6a}$$

and

$$\phi^0_{\vec{k}\downarrow}(\vec{\rho}) = \begin{pmatrix}0\\1\end{pmatrix}\psi^0_{\vec{k}}(\vec{\rho}), \tag{6b}$$

where in the single cell

$$\psi^0_{\vec{k}}(\vec{\rho}) = \sum_{L=0} i^L C_L(k)\,F^0_L(W^0(k);\rho)\,Y^0_L(\mu), \tag{7}$$

where the Y^0_L's are the usual normalized spherical harmonics and $\mu = \hat{k}\cdot\hat{\rho}$ is the cosine of the angle between the vectors $\vec{k}$ and $\vec{\rho}$. The radial functions are normalized in the Wigner–Seitz sphere and are solutions to the homogeneous radial equations

$$\left[-\frac{d^2}{d\rho^2} + U(\rho) + \frac{L(L+1)}{\rho^2} - W^0(k)\right]\rho F^0_L = 0. \tag{8}$$

The eigenvalue $W^0(k)$ and the coefficients $C_L(k)$ are determined by the normalization condition

$$\sum_{L=0}[C_L(k)]^2 = 1, \tag{9}$$

and the Kohn variational equations.[15] We remark that in the spherical approximation the Kohn variational equations represent an optimization of the spherical-cell boundary-condition equations; that is,

$$[e^{-\vec{k}\cdot\vec{\rho}}\,\phi^0_{\vec{k}s}(\vec{\rho})]_{\vec{\rho}=-\vec{\rho}_0} = [e^{-i\vec{k}\cdot\vec{\rho}}\,\phi^0_{\vec{k}s}(\vec{\rho})]_{\vec{\rho}=\vec{\rho}_0} \tag{10a}$$

and

$$\left[e^{-i\vec{k}\cdot\vec{\rho}}\frac{\partial}{\partial\rho}\,\phi^0_{\vec{k}s}(\vec{\rho})\right]_{\vec{\rho}=-\vec{\rho}_0} = -\left[e^{-i\vec{k}\cdot\vec{\rho}}\frac{\partial}{\partial\rho}\,\phi^0_{\vec{k}s}(\vec{\rho})\right]_{\vec{\rho}=\vec{\rho}_0} \tag{10b}$$

before the series, Eq. (7), is truncated. The solution is tested by the accuracy by which the boundary condition, Eq. (10a), written in the form

$$\frac{\Sigma_{L=0}(-)^L C_{2L+1}F^0_{2L+1}Y^0_{2L+1}(\mu)}{\Sigma_{L=0}(-)^L C_{2L}F^0_{2L}Y^0_{2L}(\mu)}\cot(\vec{k}\cdot\vec{\rho}_0) = 1, \tag{11}$$

is satisfied.

Before discussing the first-order equations, we remark that all matrix elements of the form

$$\left(\phi^0_{\vec{k}s'}\left|\frac{1}{4\rho}\,\frac{dU(\rho)}{d\rho}\,\vec{\sigma}\cdot\hat{L}\right|\phi^0_{\vec{k}s}\right) \equiv 0, \tag{12}$$

where the integration is over the Wigner–Seitz sphere. Hence there is no first-order contribution to the energy and also no mixing of the degenerate levels so that the usual nondegenerate perturbative expansion is valid. Equation (12) follows from the angular integrals

$$\int Y^0_{L'}(\mu)\,\hat{L}_z Y^0_L(\mu)\sin\theta_\rho\,d\theta_\rho\,d\phi_\rho = \left[\frac{4\pi}{2L+1}\right]\delta_{L'L}\sum_M M\,|Y^M_L(\hat{k})|^2 \equiv 0, \tag{13}$$

where the argument $\hat{k}$ denotes both angular factors. The above result is most simply obtained using the spherical-harmonic addition theorem,

$$P_L(\mu) = \left[\frac{4\pi}{2L+1}\right]\sum_M Y^{M*}_L(\hat{k})\,Y^M_L(\hat{\rho}), \tag{14}$$

and the usual orthonormality properties of the spherical harmonics. The same results follow for $\hat{L}_x$ and $\hat{L}_y$ from the rotational properties of these operators and the spherical harmonics.

We are now ready to discuss the first-order equation which will be

$$[H^0 - W^0]\,\phi^1_{\vec{k}s}(\vec{\rho}) + \frac{1}{4\rho}\,\frac{dU(\rho)}{d\rho}\,\vec{\sigma}\cdot\hat{L}\;\phi^0_{\vec{k}s}(\vec{\rho}) = 0. \qquad (15)$$

First, from the above discussion and the fact that ϕ^1 must be orthogonal to ϕ^0 we know that ϕ^1 has no admixture of either spin-up or spin-down zero-order wave function. Second, since the operators L_i ($i = x, y, z, +, -$, whichever is appropriate) all commute with H^0 and the radial function in the interaction, then the components of ϕ^1 can be written in the form $L_i\psi^1_{\vec{k}}(\vec{\rho})$. Finally, on application of the boundary conditions we find that only a single $\psi^1_{\vec{k}}(\vec{\rho})$ occurs for all four components possible in the spin-up and spin-down wave functions. Thus

$$\phi_{\vec{k}\uparrow}(\vec{\rho}) = \begin{pmatrix}1\\0\end{pmatrix}\,\psi^0_{\vec{k}}(\vec{\rho}) + \alpha^2\vec{\sigma}\cdot\hat{L}\begin{pmatrix}1\\0\end{pmatrix}\,\psi^1_{\vec{k}}(\vec{\rho}) + \cdots; \qquad (16)$$

$\phi_{\vec{k}\downarrow}$ is given simply by reversing the spinor throughout.

Substitution of (16) into (15) and removal of the angular momentum operator yields a differential equation for $\psi^1_{\vec{k}}(\vec{\rho})$. The spherical symmetry permits us to write

$$\psi^1_{\vec{k}}(\vec{\rho}) = \sum_{L=1} i^L\,C_L(k)\,F^1_L(W^0(k);\rho)\,Y^0_L(\mu), \qquad (17)$$

where we notice that the $L = 0$ component must be absent. The F^1_L's satisfy the differential equation

$$\left[-\frac{d^2}{d\rho^2} + U(\rho) + \frac{L(L+1)}{\rho^2} - W^0(k)\right]\rho F^1_L + \frac{1}{4}\,\frac{dU}{d\rho}\;F^0_L = 0. \qquad (18)$$

The solutions for F^1_L will be of the form

$$F^1_L = F^P_L + \alpha_L F^0_L, \qquad (19)$$

where F^0_L, the zero-order solution, is the complementary function in this case and F^P_L is the particular solution. The α_L's must be chosen so that the boundary conditions are satisfied. We remark that all the components of the first-order functions satisfy the same differential equations and the boundary conditions give the same equations for the α_L's, and hence we conclude that only the single $\psi^1_{\vec{k}}$ occurs.

Notice that using Eq. (13) one sees that the solution, Eq. (16), defined by Eqs. (7) and (17) satisfies all the orthonormality relations to first order in α^2. Further, the form of the solution obtained here is identical to that presented by Bienenstock and Brooks[3]; however, the authors feel that the present derivation is considerably simpler and more concise than theirs. Also, the above solution is the general solution, reducing to that of Bienenstock and Brooks[3] only when the $C_L(k)$'s and the $F_L(W(k);\rho)$'s are expanded in power series in k. It is on this last point that the major difference occurs between the two works. The solution written in our form is readily solved, at a given energy, for an aribtrary number of terms in the expansions, with the now available present-day computers. Thus convergence of the numerical results can be ensured.

Finally, to complete the analysis, the boundary conditions, Eqs. (10), must be applied to first order in α^2. Note that they are satisfied to zero order in α^2 by the choice of the C_L's. Now, since the operators L_i act only on the angular components, the factors $L_i\mu$, which will appear throughout, can be removed from both sides of the equations. When this is done, Eq. (10) reduces to

$$\mathrm{Im}\left[e^{-i\vec{k}\cdot\vec{\rho}}\,\frac{\partial}{\partial\mu}\,\psi^1_{\vec{k}}\right]_{\vec{\rho}_0} = 0 \qquad (20a)$$

and

$$\mathrm{Re}\left[e^{-i\vec{k}\cdot\vec{\rho}}\,\frac{\partial}{\partial\mu}\,\frac{\partial}{\partial\rho}\,\psi^1_{\vec{k}}\right]_{\vec{\rho}_0} = 0. \qquad (20b)$$

Since these equations are independent of L_i they are identical for all the components of the first-order solutions, thus proving our earlier assertion that only the single function $\psi^1_{\vec{k}}$ occurs. Equations (20) can be reduced to

$$\sum_{l=1} a_{Ll}[F^P_l + \alpha_l F^0_L]_{\rho_0} = 0, \quad L \text{ even} \qquad (21a)$$

and

$$\sum_{l=1} a_{Ll}\left[\frac{\partial}{\partial\rho}\,F^P_l + \alpha_l\,\frac{\partial}{\partial\rho}\,F^0_l\right]_{\rho_0} = 0, \quad L \text{ odd} \qquad (21b)$$

where

$$a_{Ll} = \frac{l(l+1)}{(2l+1)^{1/2}}\,C_l\left[\sum_{l'=|L-l+1|,2}^{L+l-1} i^l(-i)^{l'+L+1}\,\frac{(2l'+1)}{(2L+1)}\right.$$
$$\times\,|(l'l-1\;00|L0)|^2 j_{l'}(k\rho) - \sum_{l'=|L-l-1|,2}^{L+l+1} i^l(-i)^{l'+L+1}$$
$$\left.\times\frac{(2l'+1)}{(2L+1)}\,|(l'l+1\;00|L0)|^2 j_{l'}(k\rho)\right]. \qquad (22)$$

The $j_{l'}$'s are the usual spherical Bessel functions and the $(l'l\;00|L0)$'s are the usual Clebsch–Gordan coefficients. Equation (21) constitutes a set of linear inhomogeneous equations for the α_l's and hence the solution is completely specified.

The solution is obtained by choosing a particular cellular potential and numerically integrating the necessary differential equations and solving for the coefficients. In all instances the cellular potential was taken to consist of an ion-core contribution plus the Hartree field of the conduction electrons, whose charge density was approximated by an equivalent constant-charge density.

III. REDUCTION OF THE g SHIFT EXPRESSION TO TRACTABLE FORM

The next step is to rewrite Eq. (2) in a form appropriate for the solutions of Sec. II. The various terms will be collected in a way to facilitate comparison with previous calculations. Since the calculations are being carried out to first order in α^2 all higher-order contributions will be ngelected. Further, of the first-order terms a number will be such that their Fermi-surface averages are zero and hence can be omitted.

Rewriting Eq. (2) in terms of the ϕ's yields, notice the subscripts can be suppressed,

$$\delta g(\vec{\mathrm{k}}) = [\delta g(\vec{\mathrm{k}})]^{\alpha} + [\delta g(\vec{\mathrm{k}})]'' + [\delta g(\vec{\mathrm{k}})]''' + 2\int \phi^{\dagger}(x\hat{\pi}_y - y\hat{\pi}_x)\,\phi\, d^3r + 2\left[\left\{i\frac{\partial}{\partial k_x}\right\}\{\hat{\pi}_y\} - \left\{i\frac{\partial}{\partial k_y}\right\}\{\hat{\pi}_x\}\right]$$

$$+ 2[\{x\}\{\hat{\pi}_y\} - \{y\}\{\hat{\pi}_x\}] - 2i\int\left[\left(\frac{\partial}{\partial k_x}\phi^{\dagger}\right)\hat{\pi}_y\phi - \left(\frac{\partial}{\partial k_y}\phi^{\dagger}\right)\hat{\pi}_x\phi\right] d^3r, \qquad (23)$$

where $\{O\}$ for an operator O denotes

$$\{O\} = \int \phi^{\dagger} O\, \phi\, d^3r \qquad (24)$$

and the integrations are all over a unit cell. Also

$$\hat{\pi} = (1/\hbar)\,\vec{\pi} = -i\nabla + \tfrac{1}{8}\alpha^2\vec{\sigma}\times\nabla U. \qquad (25)$$

In this form $\delta g(\vec{\mathrm{k}})$ is clearly dimensionless and hence can be evaluated in any system of units.

The first term in Eq. (23) are all those terms containing the phase angle $\alpha(\vec{\mathrm{k}})$ and has a Fermi-surface average of zero.[13]

The second term is given by

$$\begin{aligned}[\delta g(\vec{\mathrm{k}})]'' &= -\frac{1}{m^2c^2}\int \phi^{\dagger}p^2\phi\, d^3r \\ &= \alpha^2\int \phi^{\dagger}\nabla_{\rho}^2\phi\, d^3\rho \\ &= \alpha^2[\{U\} - W^0(k)] + \cdots, \end{aligned} \qquad (26)$$

where

$$\begin{aligned}\{U\} &= \int \phi^{0\dagger}U(\rho)\,\phi^0 d^3\rho \\ &= \int_0^{\rho_0} U(\rho)\sum_{L=0}(C_LF_L^0)^2\rho^2 d\rho. \end{aligned} \qquad (27)$$

The third term is at least second order[13] in α^2.

The fourth term can be reduced to a number of terms, only two of which are first order in α^2. The first one arises from the α^2 component of $\hat{\pi}$ and is

$$\begin{aligned}[\delta g(\vec{\mathrm{k}})]' &= \tfrac{1}{4}\alpha^2\int \phi^{0\dagger}\left[x\frac{\partial U}{\partial x} + y\frac{\partial U}{\partial y}\right]\sigma_z\phi^0 d^3r \\ &= \tfrac{1}{4}\alpha^2\int \psi^{0*}\rho\frac{dU}{d\rho}\psi^0\{\sin^2\theta \\ &\qquad - [(\tfrac{1}{2}\sin^2\theta - \cos^2\theta)(1-\mu^2)]\}\, d^3\rho, \end{aligned}$$

where θ is the angle between $\vec{\mathrm{k}}$ and the z axis and $\mu = \hat{\rho}\cdot\hat{k} = \hat{r}\cdot\hat{k}$. The Fermi-surface average of the factor $\frac{1}{2}\sin^2\theta - \cos^2\theta$ is zero and hence one has only to evaluate

$$[\delta g(\vec{\mathrm{k}})]'_1 = \tfrac{1}{4}\alpha^2\sin^2\theta\int_0^{\rho_0}\rho\frac{dU}{d\rho}\sum_{L=0}(C_LF_L^0)^2\rho^2 d\rho. \qquad (28)$$

The second contribution arises from the mixing of the zero-order and first-order parts of the wave function and is

$$\begin{aligned}[\delta g(\vec{\mathrm{k}})]_V^P &= 2\alpha^2\int[\psi^{0*}\hat{L}_z^2\psi^1 + (\hat{L}_z\psi^1)^*\hat{L}_z\psi^0]\, d^3r \\ &= 4\alpha^2\sin^2\theta\sum_{L=1}\tfrac{1}{2}L(L+1)C_L^2\int_0^{\rho_0}F_L^1F_L^0\rho^2 d\rho. \end{aligned} \qquad (29)$$

The reduction is readily made using the addition theorem, Eq. (14), and the relation

$$\frac{4\pi}{2L+1}\sum_M M^2|Y_L^M(\hat{k})|^2 = \tfrac{1}{2}L(L+1)\sin^2\theta. \qquad (30)$$

The fifth term in Eq. (23) has a linear term in α^2 resulting from the product of a first-order contribution of $\{i\,\partial/\partial k_i\}$ and a zero-order contribution from $\{\hat{\pi}_i\}$. The net result can be written as

$$[\delta g(\vec{\mathrm{k}})]_{S1}^P = -2\alpha^2A_\pi^0A_k^1\sin^2\theta, \qquad (31)$$

where

$$\begin{aligned}A_\pi^0 &= \frac{k}{k_y}\int\phi^{0\dagger}\left(-i\frac{\partial}{\partial y}\right)\phi^0 d^3r \\ &= \rho_0^3\sum_{L=0}\frac{(L+1)C_LC_{L+1}}{(2L+1)^{1/2}(2L+3)^{1/2}} \\ &\qquad \times\left[F_L^0\frac{\partial F_{L+1}^0}{\partial\rho} - F_{L+1}^0\frac{\partial F_L^0}{\partial\rho}\right]_{\rho_0}. \end{aligned} \qquad (32)$$

The reduction to the surface values follows directly from the differential equations satisfied by the

TABLE I. Lithium: boundary-condition check and the Fermi energy in Rydbergs as functions of L(max).

θ (deg) \ L(max)	4	5	6
0	0.691	1.050	1.035
15	0.759	1.075	1.007
30	1.421	1.035	0.925
45	0.837	1.170	0.973
60	1.282	0.992	0.984
75	1.751	0.832	1.045
$W^0(k_F)$	0.2954	0.2989	0.2985

TABLE II. Lithium: convergence of the coefficients $C_L(k)$ as functions of L(max).

L \ L(max)	4	5	6
0	0.38075	0.46205	0.45424
1	0.89435	0.84400	0.85130
2	0.21222	0.27114	0.26040
3	0.08231	0.00644	0.02327
4	−0.05802	−0.00260	−0.02246
5		−0.02464	−0.00770
6			−0.00736

radial functions F_L^0. Next,

$$A_k^1 = -\frac{k}{k_y}\int\left[\phi^{0\dagger}\, i\,\frac{\partial}{\partial k_x}\,\phi^1 + \phi^{1\dagger}\, i\,\frac{\partial}{\partial k_x}\,\phi^0\right] d^3r$$

$$= \sum_{L=1} \frac{L(L+1)}{k}\, C_L^2 \int_0^{\rho_0} F_L^0 F_L^1 \rho^2 d\rho. \qquad (33)$$

Notice that A_k^1 causes $[\delta g(\vec{k})]_{S1}^P$ to be proportional to $[\delta g(\vec{k})]_V^P$, Eq. (29), and that these contributions are of opposite sign and tend to largely cancel.

The last two terms in Eq. (23) can be combined and reduced to a surface integral,[13] namely,

$$-i\int d\vec{S}\cdot[\phi^\dagger\hat{\pi}(\vec{r}\times\nabla_k)_z\phi + (\hat{\pi}\phi)^\dagger(\vec{r}\times\nabla_k)_z\phi].$$

In the spherical approximation the α^2 term in $\hat{\pi}$ gives no first-order contribution. Thus, the first-order contribution is given by the mixing of the zero-order and first-order parts of the wave function. Again this contribution has a part whose Fermi-surface average is zero which is taken out. The remaining contribution can be written in the form

$$[\delta g(\vec{k})]_{S2}^P = \tfrac{1}{2}\alpha^2\sin^2\theta \sum_{L=1} \frac{L(L+1)}{(2L+1)^{1/2}}\left[\frac{LA(L-1,\,L)+B(L-1,\,L)}{(2L-1)^{1/2}} - \frac{(L+1)A(L+1,\,L)-B(L+1,\,L)}{(2L+3)^{1/2}}\right], \qquad (34)$$

where

$$A(L\mp 1, L) = 2\,\frac{\rho_0^3}{k}\, C_{L\mp 1} C_L \left[F_L^1\, \frac{\partial F_{L\mp 1}^0}{\partial\rho} - F_{L\mp 1}^0\, \frac{\partial F_L^1}{\partial\rho}\right]_{\rho_0} \qquad (35)$$

and

$$B(L\mp 1, L) = \frac{\rho_0^3}{k}\left[2k\,\frac{\partial}{\partial\rho}(C_{L\mp 1}F_{L\mp 1}^0)\,\frac{\partial}{\partial k}(C_L F_L^1) + 2k\,\frac{\partial}{\partial k}(C_{L\mp 1}F_{L\mp 1}^0)\,\frac{\partial}{\partial\rho}(C_L F_L^1) - \frac{k}{r}\,\frac{\partial}{\partial k}(C_{L\mp 1}F_{L\mp 1}^0 C_L F_L^1)\right.$$
$$\left. - k\,\frac{\partial}{\partial k}\left(C_{L\mp 1}F_{L\mp 1}^0 C_L \frac{\partial F_L^1}{\partial\rho} + C_L F_L^1 C_{L\mp 1}\frac{\partial F_{L\mp 1}^0}{\partial\rho}\right) - \frac{2}{\rho}\, C_{L\mp 1}F_{L\mp 1}^0 C_L F_L^1\right]_{\rho_0}. \qquad (36)$$

This completes the reduction of the g shift to a suitable form and only the evaluation remains.

IV. DETAILED NUMERICAL ANALYSIS FOR LITHIUM

The general behavior of the numerical results is similar for all of the alkalis, differing only in the rate of convergence with increasing number of terms in Eqs. (7) and (17) and the relative sizes of the various contributions to δg. Hence, the details for only one of them, lithium, is presented herein. The results for the remaining alkalis are presented in Sec. V and an over-all survey is given in Table VII.

For lithium, the lattice parameter[14] at 20 °C yields $r_0 = 3.26a_0$ for the radius of the Wigner-Seitz sphere. The Seitz semiempirical potential[17] has been used for the ion-core contribution to the

TABLE III. Lithium: overlap integrals $\int_0^{\rho_0} F_L^0\, F_L^1\, \rho^2\, d\rho$ as functions of L(max).

L \ L(max)	4	5	6
0	0.0	0.0	0.0
1	−0.25132	−0.25087	−0.25063
2	0.10709	0.06470	0.06883
3	0.16501	2.89813	0.79129
4	−0.24674	−2.80428	−0.35943
5		−0.13947	−0.30633
6			−0.12570

TABLE IV. Lithium: values of the radial functions and their spatial derivatives of ρ_0 and the Fermi energy for $L(\text{max}) = 6$.

L	F_L^0	$\frac{\partial F_L^0}{\partial\rho}$	F_L^1	$\frac{\partial F_L^1}{\partial\rho}$
0	0.26682	−0.07588	...	...
1	0.30341	−0.00616	−0.03145	0.03440
2	0.41650	0.18411	0.03203	0.01788
3	0.48904	0.39036	0.38815	0.31157
4	0.54877	0.62075	−0.19664	−0.22134
5	0.60133	0.87462	−0.18385	−0.26662
6	0.64902	1.15056	−0.08134	−0.14360

TABLE V. Lithium: k derivatives of the end-point values of the radial functions times the coefficients $C_L(k)$ at $L(\mathrm{max}) = 6$.

L	$\frac{\partial}{\partial k} C_L F_L^0$	$\frac{\partial}{\partial k} C_L \frac{\partial}{\partial \rho} F_L^0$	$\frac{\partial}{\partial k} C_L F_L^1$	$\frac{\partial}{\partial k} C_L \frac{\partial}{\partial \rho} F_L^1$
0	−0.629 76	0.043 32	···	···
1	0.152 51	−0.212 72	−0.140 24	0.101 32
2	0.301 49	0.087 61	−0.001 42	−0.000 84
3	0.066 27	0.049 55	0.038 17	0.028 01
4	−0.098 92	−0.109 09	0.028 97	0.031 54
5	−0.021 23	−0.029 96	0.010 94	0.015 62
6	−0.054 69	−0.096 21	0.006 61	0.011 57

TABLE VI. Lithium: contributions to $(\delta g)^P$ and δg as functions of $L(\mathrm{max})$, all $\times 10^4$.

$L(\mathrm{max})$	4	5	6
$(\delta g)'$	0.061	0.064	0.065
$(\delta g)''$	−0.286	−0.307	−0.305
$(\delta g)_V^P$	−0.267	−0.235	−0.238
$(\delta g)_{S1}^P$	0.163	0.163	0.163
$(\delta g)_{S2}^P$	−0.462	−0.236	−0.260
δg	−0.791	−0.550	−0.575

cell potential. There are, of course, other possibilities but this particular function was chosen because it is convenient, it represents a reasonable first approximation, and it has been extensively investigated.

Table I contains the boundary-condition check, Eq. (11), and the Fermi energy $W^0(k_F)$ as functions of the highest L value, $L(\mathrm{max})$, used in the wave-function expansions. Both these quantities have converged well at $L(\mathrm{max}) = 6$. Table II contains a similar set of values for the coefficients C_L. The three dominant coefficients have essentially converged at $L(\mathrm{max}) = 5$. Coupling this result to the energy convergence gives immediately that the conduction-electron density and hence $[\delta g]'$, Eq. (28), and $[\delta g]''$, Eq. (26), converge rapidly. Further, these terms turn out to be relatively small and thus less care needs to be taken in their determination, except in lithium. This is in agreement with Yafet's[9] arguments.

The overlap integrals relevant for $[\delta g]_V^P$, Eq. (29), are given in Table III. Again, the leading terms converge rapidly and the total expression is given predominatly by the first two terms, by virtue of the C_L^2 factor.

The additional quantities needed in evaluating $[\delta g]_{S1}^P$, Eq. (31), and $[\delta g]_{S2}^P$, Eq. (34), are tabulated in Tables IV and V, and the final results (i.e., the Fermi-surface averages) for the g shift in Table VI. Since the F_L^0's are normalized in the unit cell and the energy is rapidly convergent their values are hardly affected by changing $L(\mathrm{max})$. On the other hand the F_L^1's, by virtue of their dependence on the α_L's, that is, the boundary conditions, are much more dependent on $L(\mathrm{max})$. A measure of this dependence is given by the overlap integrals, Table III. Fortunately, for lithium, the leading term dominates and the net convergence is good.

Our calculated result for the Margenau term $\delta g^M = (\delta g)' + (\delta g)''$, is -0.24×10^{-4} and is in fair agreement with the estimate of -0.29×10^{-4} made

TABLE VII. Summary of g-shift values, all $\times 10^4$. Only later more complete theoretical values are included for lattice parameters near room temperature. Reference 3 contains four models, NP-H, NP-NH, P-H, and P-NH, listed in in order below. The first is most comparable to the present calculation.

Metal	Experimental values, reference, and date			Theoretical values, reference, and date	
Lithium	−0.02 ± 0.02	(29)	(1963)	−0.44, −0.25, −0.42, −0.23	(3) (1964)
	−0.61 ± 0.02	(18)	(1968)	−0.54	(5) (1969)
				−0.575	present
Sodium	−10 ± 2	(23)	(1954)	−7.0, −6.0, −5.9, −4.6	(3) (1964)
	−8 ± 2	(21)	(1955)	−5.0	(6) (1970)
	−6 ± 2	(20)	(1960)	−7.84	present
	−8 ± 2	(22)	(1966)		
Potassium	−41 ± 5	(25)	(1964)	−26, −23, −14, −6	(3) (1964)
	−47 ± 26	(30)	(1965)	−31.2	present
	−25 ± 1	(26)	(1966)		
Rubidium	−33 ± 1	(1)	(1966)	−110, −78, −10, +74	(3) (1964)
	−39 ± 1	(2)	(1966)	−150	present
Cesium	−700 ± 200	(4)	(1956)	−260, −110, +580, +770	(3) (1964)
	107 ± 20	(1)	(1966)	−526	present
	32 ± 10	(2)	(1966)		

TABLE VIII. Sodium: contributions to $(\delta g)^P$ and δg as functions of L(max), all × 10^4.

L(max)	3	4	5	6
$(\delta g)'$	0.12	0.11	0.12	0.12
$(\delta g)''$	−0.49	−0.46	−0.47	−0.47
$(\delta g)_V^P$	−4.58	−4.28	−4.48	−4.47
$(\delta g)_{S1}^P$	4.21	4.32	4.45	4.45
$(\delta g)_{S2}^P$	−11.32	−5.88	−7.55	−7.47
δg	−12.06	−6.19	−7.93	−7.84

TABLE X. Rubidium: contributions to $(\delta g)^P$ and δg as functions of L(max), all × 10^4.

L(max)	4	5	6	7	8
$(\delta g)'$	0.2	0.2	0.2	0.2	0.2
$(\delta g)''$	−0.6	−0.6	−0.6	−0.6	−0.6
$(\delta g)_V^P$	−39.7	−58.3	−56.9	−57.1	−57.1
$(\delta g)_{S1}^P$	35.3	55.2	53.4	53.7	53.7
$(\delta g)_{S2}^P$	−26.4	−160.7	−143.2	−146.1	−145.8
δg	−31.2	−164.2	−147.1	−149.9	−149.6

by Overhauser and de Graaf[5] for this term. The sum of the remaining contributions, denoted by δg^P, is -0.34×10^{-4} and is somewhat larger than the value -0.25×10^{-4} obtained by Bienenstock and Brooks.[3] The net value, $\delta g=-0.58\times10^{-4}$, is in very good agreement with the experimental value of -0.61×10^{-4} measured by VanderVen.[18] This result along with other investigations (e.g., Refs. 7 and 8) imply that the above model represents a reasonable first approximation for lithium.

V. NUMERICAL RESULTS FOR SODIUM, POTASSIUM, RUBIDIUM, AND CESIUM

These remaining alkali metals are discussed individually below and a general survey is given in Table VII.

Sodium. At 20 °C the lattice parameter[14] yields a value for the Wigner–Seitz sphere radius $r_0=3.99a_0$. The Prokofjew[19] potential has been used as the ion-core potential. The numerical results are summarized in Table VIII and it is seen that convergence has been achieved by $L(\max)=5$. The analysis of the various terms is the same as that for lithium. The final value of δg is marginally higher than that calculated in Ref. 3 (-7.0×10^{-4}) and is considerably higher than the value in Ref. 6 (-5.0×10^{-4}). First, one can conclude that the arguments[3] made against the use of the Prokofjew potential in this calculation are not valid. Second, one sees that, when the present wave functions, which are anticipated to be reasonably realistic, are used, the surface terms are not negligible and give a net contribution of -3.0×10^{-4} in a total of -7.8×10^{-4}. This total value is in excellent agreement with all the experimental determinations[20–23]: $(-6\pm2)\times10^{-4}$, $(-8\pm2)\times10^{-4}$, $(-10\pm2)\times10^{-4}$.

Potassium. At 20 °C the Wigner–Seitz sphere radius is $4.95a_0$.[14] In this instance the semiempirical Taylor[24] potential has been used as the ion-core potential. The results, listed in Table IX, are similar to the lithium values and convergence is achieved by $L(\max)=6$. The net value of $\delta g=-31\times10^{-4}$ is marginally higher than the corresponding value of -26×10^{-4} of Ref. 3 and lies between the two observed values of $(-41\pm5)\times10^{-4}$,[25] and $(-25\pm1)\times10^{-4}$.[26]

Rubidium. At 20 °C the Wigner–Seitz sphere radius is $r_0=5.30a_0$.[14] Here we have used the potential calculated by Callaway and Morgan[27] as the ion-core potential. The results are summarized in Table X and one sees that the results have converged by $L(\max)=7$. The net value of $\delta g=-150\times10^{-4}$ is somewhat higher than the comparable value of -110×10^{-4} given in Ref. 3. These theoretical values are in marked disagreement with those reported[1,2] recently, that is, $(-33\pm10)\times10^{-4}$ and $(-39\pm1)\times10^{-4}$.

Cesium. The tabulated value[14] at −10 °C was

TABLE IX. Potassium: contributions to $(\delta g)^P$ and δg as functions of L(max), all × 10^4.

L(max)	4	5	6	7
$(\delta g)'$	0.14	0.14	0.14	0.14
$(\delta g)''$	−0.49	−0.50	−0.50	−0.50
$(\delta g)_V^P$	−11.42	−14.57	−14.32	−14.36
$(\delta g)_{S1}^P$	10.67	13.77	13.50	13.55
$(\delta g)_{S2}^P$	−10.81	−32.01	−29.59	−30.00
δg	−11.91	−33.17	−30.77	−31.17

TABLE XI. Cesium: contributions to $(\delta g)^P$ and δg as functions of L(max), all × 10^4.

L(max)	4	5	6	7	8
$(\delta g)'$	0.2	0.2	0.2	0.2	0.2
$(\delta g)''$	−0.7	−0.8	−0.8	−0.8	−0.8
$(\delta g)_V^P$	4.0	−68.9	−66.1	−66.7	−66.7
$(\delta g)_{S1}^P$	−2.7	64.2	59.8	60.8	60.8
$(\delta g)_{S2}^P$	182.2	−638.2	−500.8	−521.5	−520.0
δg	183.0	−643.5	−507.7	−528.0	−526.5

used with $r_0 = 5.72a_0$ and the potential derived by Callaway and Haare[28] as the ion-core potential. The numerical results are displayed in Table XI and one has convergence of δg by $L(\max) = 7$ at the value of -527×10^{-4}. This is considerably higher than the comparable value of -260×10^{-4} from Ref. 3 and is also in marked disagreement with the observed values[1,2] of $(+107 \pm 20) \times 10^{-4}$ and $(+32 \pm 10) \times 10^{-4}$. It is interesting to note that the calculated value is in reasonable agreement with an earlier observed[4] value of $(-700 \pm 200) \times 10^{-4}$.

VI. CONCLUSIONS

We have used the spherical-wave-expansion procedure in the spherical-cell approximation to determine the one-electron wave function and then to evaluate the g shift in the alkali metals. This method is particularly amenable to the use of modern computing facilities and convergence of the numerical work can be determined and is ensured in the above calculations.

In all instances, the model of a single conduction electron moving in a simple local cellular potential consisting of an ion-core potential plus the Hartree field of the other conduction electrons, assumed to be uniformly distributed, is used. Although the calculations have been carried out at or near room temperature, the volume dependence of this calculation in going to near absolute zero has been checked and found to be less than 5%. This is not a significant effect. Our results agree in general behavior and order of magnitude to a previous calculation (Ref. 3, model NP-H), using one model comparable to this model.

In lithium, sodium, and potassium the values obtained herein agree favorably with the observed values and with previous estimates. Coupled with previous calculations[7] the model appears to be a reasonable first approximation for these metals and the method adequate in evaluating a number of their properties.

In rubidium and cesium the calculated results are still in marked disagreement with observation. There is now no doubt that one must look at the physical model to find the answer. Although the exact value of δg will depend on the actual cellular potential used, of which there are a variety, the authors feel that the rapid increase in δg with atomic number is a characteristic of the use of a local potential and that one will not succeed with this model. Whether a model having an angular-momentum-dependent or nonlocal potential will be adequate, or whether one of the corrections, core-polarization effects or further relativistic effects, suggested by Bienenstock and Brooks[3] is necessary can be answered only by further work.

---

[1] S. Schultz and M. R. Shanabarger, Phys. Rev. Letters 16, 178 (1966).

[2] W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, Phys. Rev. Letters 16, 181 (1966).

[3] A. Bienenstock and H. Brooks, Phys. Rev. 136, A784 (1964).

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

[5] A. W. Overhauser and A. M. de Graaf, Phys. Rev. Letters 22, 127 (1969).

[6] A. M. deGraaf and A. W. Overhauser, Phys. Rev. B 2, 1437 (1970).

[7] R. A. Moore and S. H. Vosko, Can. J. Phys. 46, 1425 (1968).

[8] R. Taylor, R. A. Moore, and S. H. Vosko, Can. J. Phys. 44, 1995 (1966).

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

[10] L. M. Roth, J. Phys. Chem. Solids 23, 433 (1962).

[11] E. I. Blount, Phys. Rev. 126, 1636 (1962).

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

[13] A. M. de Graaf and A. W. Overhauser, Phys. Rev. 180, 701 (1969).

[14] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Academic, New York, 1958), Vol. I.

[15] W. Kohn, Phys. Rev. 87, 472 (1952).

[16] W. Kohn, Phys. Rev. 96, 590 (1954).

[17] F. Seitz, Phys. Rev. 47, 400 (1935) [see W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954)].

[18] N. S. VanderVen, Phys. Rev. 168, 787 (1968).

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

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

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

[22] Ch. Ryter, Phys. Letters 4, 69 (1963).

[23] I. H. Solt, Jr. and M. W. P. Strandberg, Phys. Rev. 95, A607 (1954).

[24] Roger Taylor (private communication).

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

[26] W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, Phys. Rev. 142, 414 (1966).

[27] J. Callaway and D. F. Morgan, Jr., Phys. Rev. 112, 334 (1958).

[28] J. Callaway and E. L. Haare, Phys. Rev. 108, 217 (1957).

[29] R. J. Pressley and H. L. Berk, Phys. Rev. 140, 1207 (1963).

[30] J. E. Cousins and R. Dupree, Phys. Let. 14, 177 (1965).