Energy Bands in Solids—The Quantum Defect Method

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This paper describes a procedure for the calculation of electron energy bands in certain solids from spectroscopic data for the corresponding free atom. This method is an improved version of one used by Kuhn and Van Vleck to calculate the energy bands of sodium, potassium, and rubidium. It avoids explicit construction of a one-electron potential to represent the interaction between the valence and core electrons.

We assume that the interaction between a valence electron and an ion in the crystal is approximately the same as in the isolated atom. If the interaction is accurately represented by a Coulomb potential outside the ion core, we may express solutions of the radial differential equation in this region as linear combinations of standard Coulomb functions. The combination corresponding to the solution which is well-behaved at the nucleus involves a coupling constant which depends upon the ion potential through a parameter that is a slowly varying function of the energy. At an eigenvalue this parameter can be evaluated from the quantum defect. Hence if the eigenvalue spectrum is known, we may obtain this parameter by extrapolation for arbitrary nearby energies, and the regular solution of the radial equation is consequently determined explicitly, outside the core. This is sufficient information for the calculation of energy bands with available techniques.

We establish an approximate formula for the ratio of the amplitude of the wave function near the nucleus to its value at a point outside the core. For an *s* function this relation involves only the nuclear charge, standard Coulomb functions, and the aforementioned parameter derived from spectroscopic data. It therefore provides a convenient means of calculating P_F and P_A, the squared amplitudes at the nucleus appropriate to the Knight shift and the atomic hyperfine splitting, respectively. In the latter case our result is identical with a formula given by Fermi and Segrè, which gives reasonable agreement with experiment.

Arguments are presented in support of the thesis that the quantum defect method takes very general account of exchange and correlation interactions between the valence electron and core electrons. Relativistic effects, including spin-orbit coupling, are also included naturally. We also discuss modifications in the method to take into account deviations of the ion or crystal potential outside the core from Coulomb form. Tables of the essential data, including improved polarization corrections, are given for the alkali metals.

1. INTRODUCTION

THE quantum defect method described in this paper is an improvement and extension of a procedure used by Kuhn and Van Vleck[1-3] in calculating the ground state energy and effective mass for metallic sodium, potassium, and rubidium from the experimental spectroscopic term values of the corresponding free atom. This approach to energy band calculations has the advantage of avoiding both explicit construction of a crystal potential for the valence electron in the solid and numerical integration of the usual Hartree or Hartree-Fock equation. However, it is applicable only when one can assume that to a good approximation the interaction between the valence electron and the ion core is the same in the solid as in the free atom and that the mutual interaction of the valence electrons can be taken into account by a free electron approximation and a suitable modification of the crystal potential in the volume outside of the ion cores. These assumptions are best suited to the alkali metals and somewhat less well suited to the monovalent noble metals. Application of the quantum defect method has so far been confined to these solids[4-7] although other applications of the method to divalent and trivalent metals have been started.[7]

The quantum defect method has several advantages over the procedure of Kuhn and Van Vleck. Like Kuhn's WKB method,[3] it depends upon the extrapolation of a parameter which is obtained directly from the experimental spectroscopic term values and which varies less rapidly as a function of energy than does the logarithmic derivative used by Kuhn and Van Vleck in their extrapolation. However, the quantum defect method makes direct use of Coulomb wave functions, tables of which are now available,[8] instead of approximate WKB-type functions. Consequently it does not encounter the difficulties met in Kuhn's method when the WKB turning points in the Coulomb potential are close together or off the real *r* axis.[2] This situation occurs at energies of interest in band calculations for values of the angular momentum *L* greater than zero. The quantum defect method is simpler in application than Kuhn's method once the Coulomb functions have been tabulated, and the theoretical arguments for its justification are more satisfying than those advanced by Kuhn and Van Vleck for their method.

In an article elsewhere,[9] one of us has discussed the quantum defect method[10] primarily from the point of view of the Hartree-Fock approximation. In the present

[1] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950).
[2] J. H. Van Vleck, *Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, 1953* (Science Council of Japan, Tokyo, 1954), p. 640.
[3] T. S. Kuhn, Phys. Rev. **79**, 515 (1950).
[4] H. Brooks, Phys. Rev. **91**, 1027 (1953).
[5] K. Kambe, Phys. Rev. **99**, 419 (1955).
[6] F. S. Ham, Ph.D. Thesis, Harvard University, Cambridge, Massachusetts, 1954 (unpublished).
[7] H. Brooks, in *Theory of Alloy Phases* (American Society for Metals, Cleveland, 1956), p. 199.

[8] F. S. Ham, Technical Report No. 204, Cruft Laboratory, Harvard University, Cambridge, Massachusetts, 1955 (unpublished).
[9] F. S. Ham, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 27.
[10] We shall henceforth refer to the quantum defect method by the abbreviation QDM.

paper we shall first present the complete WKB derivation that provides the principal justification of QDM, in order to develop an important formula for the amplitude of the valence wave function at the nucleus. We shall then give arguments to support our view that QDM takes account of correlation and exchange effects in the interaction between a valence electron and the ion cores. We shall also show that the method seems to include relativistic effects, including spin-orbit coupling, so that QDM offers a valuable tool in calculations involving the heavy elements. In our initial presentation in Secs. 2 and 3 we shall neglect such complicated effects for the sake of clarity and shall assume that the valence-core interaction can be represented by a simple one-electron potential. In the course of this discussion we shall occasionally refer to the previously mentioned article,[9] where some arguments are given in greater detail.

2. DEVELOPMENT OF THE QUANTUM DEFECT METHOD

We consider a monovalent atom and assume that the interaction between the valence electron and the ion can be represented by a spherically symmetric one-electron potential $V(r)$ which is equal to the Coulomb potential $-2/r$ (in atomic units[11]) outside a "core radius" r_0. Such potentials have been constructed by Prokofjew[12] for sodium and Seitz[13] for lithium, the former reproducing the experimental term values to within 1%, the latter to an even better accuracy. Furthermore, we assume that the crystal potential for a valence electron in the solid may be approximated within each atomic cell by this same $V(r)$ associated with the ion in the cell. This assumption is probably not too well justified, but it forms a convenient starting point for the calculation. Later, we shall see that it can be improved upon by first order perturbation calculations. The "core radius" r_0 shall be less than or equal to the radius of the sphere inscribed in the cell.

Expanding a Bloch function in the solid in spherical harmonics about the position of one of the ions,

$$\psi(\mathbf{r}) = \sum_{L,M} A_{LM} Y^{LM}(\theta,\varphi)(1/r)U^L(r), \quad (2.1)$$

we find that within the smallest sphere in which the crystal potential is equal to $V(r)$ the Schrodinger equation for $\psi(r)$ separates in spherical coordinates, yielding

$$\frac{d^2 U^L}{dr^2} + \left[-\frac{1}{n^2} - V(r) - \frac{L(L+1)}{r^2} \right] U^L = 0. \quad (2.2)$$

Our problem is to determine explicitly for $r > r_0$ the solutions $U^L(r)$ which satisfy the boundary condition $U^L(0) = 0$, for arbitrary values of the energy $\epsilon = -1/n^2$. Once these are known we may calculate the eigenvalues at various points in the Brillouin Zone by finding the energy for which (2.1) satisfies the appropriate boundary conditions on the surface of the atomic cell or of the equivalent sphere. Such calculations may be done using the spherical approximation of Wigner and Seitz,[14,15] together with Bardeen's treatment of the effective mass,[16] or more recent methods of Howarth and Jones,[17] Kohn and Rostoker,[18] Slater and Saffren,[19,20] and Leigh.[21] These methods all require knowledge of $U^L(r)$ on the surface of either the atomic cell or a sphere of radius comparable with that of the inscribed or equivalent spheres.[22]

Since for $r > r_0$ we have assumed $V(r) = -2/r$, we can express $U^L(r)$ in this region as a linear combination of any two independent solutions of the Coulomb radial differential equation. It is shown in a paper[23] by one of us and in earlier work by Wannier[24] and Kuhn[25] that two such independent functions are

$$^0U_c{}^{L,n}(r) = (z/2)J_{2L+1}{}^n(z)$$
$$= [n^{L+1}/\Gamma(2L+2)]M_{n,L+\frac{1}{2}}(2r/n), \quad (2.3a)$$

$$^2U_c{}^{L,n}(r) = (z/2)N_{2L+1}{}^n(z), \quad (2.3b)$$

where $z = (8r)^{\frac{1}{2}}$ and the notation is that of Wannier. The first of these functions vanishes at the origin, whereas the second is singular there and consequently cannot contribute to $U^L(r)$ in the special case of a pure Coulomb potential. If $V(r)$ has a non-Coulomb core region, however, we have, for $r > r_0$,

$$U^L(r) = \alpha(n) \, {}^0U_c{}^{L,n}(r) + \gamma(n) \, {}^2U_c{}^{L,n}(r). \quad (2.4)$$

We shall now show that $\alpha(n)/\gamma(n)$ may be determined for all energies from the spectroscopic data.

This ratio is known at any eigenvalue of the free atom, for at such an energy $U^L(r)$ satisfies the additional boundary condition of vanishing at infinity and must therefore agree in the Coulomb region with the only solution of the Coulomb differential equation that has this property. This function, $W_{n,L+\frac{1}{2}}(2r/n)$, can be expressed in the form (2.4).[26] We find that, at an

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[11] The unit of energy (1 Rydberg unit) is the ionization energy of the hydrogen atom with infinite nuclear mass $(me^4/2\hbar^2)$; the unit of length is the radius of the smallest Bohr orbit $(\hbar^2/me^2)$.

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

[13] F. Seitz, Phys. Rev. 47, 400 (1935). This potential was published incorrectly in Seitz's paper, although Seitz used the correct potential in his calculations. The correct potential has been published by W. Kohn and N. Rostoker [Phys. Rev. 94, 1111 (1954)].

[14] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).

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

[16] J. Bardeen, J. Chem. Phys. 6, 367, 372 (1938).

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

[18] W. Kohn and N. Rostaker, Phys. Rev. 94, 1111 (1954).

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

[20] J. C. Slater and M. M. Saffren, Phys. Rev. 92, 1126 (1953).

[21] R. S. Leigh, Proc. Phys. Soc. (London) A69, 388 (1956).

[22] See reference 9 for a discussion of the use of QDM with these procedures.

[23] F. S. Ham, Quart. Appl. Math. 15, 31 (1957).

[24] G. H. Wannier, Phys. Rev. 64, 358 (1943).

[25] T. S. Kuhn, Quart. Appl. Math. 9, 1 (1951).

[26] E. T. Whittaker and G. N. Watson, A Course in Modern Analysis, (Cambridge University Press, Cambridge, 1952), fourth edition, Chap. 16.

eigenvalue,

$$\frac{\alpha(n)}{\gamma(n)} = -\frac{\Gamma(n+L+1)}{n^{2L+1}\Gamma(n-L)\tan(\pi\delta_m)}, \quad (2.5)$$

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

$$\epsilon = -(m-\delta_m)^{-2}. \quad (2.6)$$

Here m is an integer that increases by unity between successive terms of a given series. Furthermore, we can prove that if δ_m is known at the eigenvalues corresponding to a given L, the ratio $\alpha(n)/\gamma(n)$ is determined for all energies. This follows from the assumed form of $V(r)$ because it can be shown[9] that this ratio equals a known function plus a meromorphic function of the complex variable ϵ. The latter is therefore determined in principle from (2.5) for all energies if δ_m is known at the eigenvalues of this L, since there are an infinite number of eigenvalues with $\epsilon=0$ as a limit point. Hence $\alpha(n)/\gamma(n)$ is determined in principle for all ϵ by the spectrum. In practice, of course, we know only approximate values of δ_m at a finite number of eigenvalues, so that $\alpha(n)/\gamma(n)$ is not completely determined at all energies. We shall show below that we can express this ratio in terms of a parameter which is a slowly varying function of energy throughout the range of energies near the valence eigenvalues, and which therefore can be determined in this range if a few eigenvalues are known.

Kuhn and Van Vleck[1] determined $\alpha(n)/\gamma(n)$ by arguing that for reasonably small values of r, the logarithmic derivative $[U^L(r)]^{-1}[dU^L(r)/dr]$ is a slowly varying function of energy which can be determined at the eigenvalues and interpolated between these values. The resulting curve and the values of the Coulomb functions and their derivatives can then be used to obtain $\alpha(n)/\gamma(n)$ at an arbitrary energy. However, the analytical argument given by Kuhn and Van Vleck for the slow variation of the logarithmic derivative as a function of energy is valid only for r smaller than the radius of the innermost node of the wave function, and consequently it can give no information concerning the behavior of, say, a $2s$ or $3p$ function outside the core. Hence it is little more than an empirical observation that for the larger radius the logarithmic derivative is sufficiently smooth to be of any use. Moreover, at a radius clearly outside the core this function does vary sufficiently, especially near a zero of $U^L(r)$, to make the necessary extrapolation rather uncertain.

Kuhn[3] has suggested an alternate means of approximating $U^L(r)$ outside the core by replacing the Coulomb functions in (2.4) by approximate solutions of the Coulomb radial equation obtained from Imai's revision of the WKB procedure.[27] He shows that the ratio of the coefficients corresponding to $\alpha(n)$ and $\gamma(n)$

[27] I. Imai, Phys. Rev. 74, 113 (1948).

can be expressed as a function of a parameter obtained by plotting a smooth curve through the experimental values of the quantum defect. This procedure is unsatisfactory at energies so low (below -0.4 ry for $L=1$) that the WKB turning points are close together or at complex values of r, for the approximate Imai functions are inaccurate or ambiguously defined at such energies.[2] Kuhn's method shares with the quantum defect method the use of an extrapolated parameter closely related to the experimental quantum defect, but, even for $L=0$, it necessitates more laborious computations.

We shall now express $\alpha(n)/\gamma(n)$ in (2.4) in the form

$$\frac{\alpha(n)}{\gamma(n)} = -\frac{\Gamma(n+L+1)}{n^{2L+1}\Gamma(n-L)\tan\pi\nu(n)}. \quad (2.7)$$

This is valid for *all* energies, whereas Eq. (2.5) is valid only at eigenvalues of the free atom. This relation *defines* a parameter $\nu(n)$ which at an eigenvalue differs from the experimental quantum defect δ_m by at most an integer. We assert that $\nu(n)$ is equal to δ_m at the eigenvalues and is obtained at other energies from a smooth curve drawn through these given points. The only uncertainty occurs at energies below roughly the lowest eigenvalue of the Coulomb potential for the value of L under consideration or the energy at which the outer WKB turning point penetrates the core region, whichever is the higher. There is unfortunately no rigorous proof that this procedure is correct, and indeed below this limiting energy the extrapolation of the quantum defect can be shown to be inaccurate. However, we shall give a derivation based on the WKB approximation which shows quite clearly that between the higher eigenvalues $\nu(n)$ is slowly varying, so that our procedure is an excellent approximation in this range. We shall then discuss the appropriate modifications necessary in the lower energy range. We should remark at this point that although we use the WKB approximation to provide some of the evidence that the quantum defect method is correct, the latter is evidently more accurate than the WKB method because it is based directly upon the experimental eigenvalues. This view is supported by the results of an exact calculation on a convenient potential model.

Following Kuhn,[3] we introduce into the radial differential equation (2.2) the change of variable $x=\ln(-\epsilon r)$ $=\ln(r/n^2)$, $u(x)=\exp(-x/2)U$, and obtain

$$(d^2u/dx^2)+P(x)u=0, \quad (2.8)$$

where

$$P(x)=[-n^2e^{2x}-n^4e^{2x}V(n^2e^x)-(L+\tfrac{1}{2})^2]. \quad (2.9)$$

The vicinity of the real axis in the x plane is shown schematically in Fig. 1. Points x_1 and x_2 are the turning points, where $P(x)=0$. On T_1, the part of the real axis between x_1 and x_2, $P(x)$ is real and positive. The limit as x approaches $-\infty$ along S_2' corresponds to the approach of r to zero along the positive real r axis.

The WKB approximation tells us that far from x_2 (and far from other turning points as well), u is given accurately by

$$u \sim [P(x)]^{-\frac{1}{4}}[Ae^{iz}+Be^{-iz}] \qquad (2.10)$$

if the constants A and B are appropriately chosen and if

$$z = \int_x^{x_2} [P(x)]^{\frac{1}{2}}dx. \qquad (2.11)$$

However, as we follow a path encircling x_2, we must choose different values of A and B in different regions bounded by the Stokes lines S_1, S_2, and S_3, on which z is pure imaginary, in order to represent a given single valued function.[28,29] Assuming that x_1 and x_2 are sufficiently well separated to allow us to consider asymptotic expansions about either point, and choosing the phase of the square root in (2.11) so that $[P(x)]^{\frac{1}{2}}$ is positive real on T_1, we may use Furry's result[30] that a single-valued function given on T_1 by (2.10) with A_1 and B_1 has a similar expansion with

$$\begin{aligned} A_2 &= A_1 + iB_1, \\ B_2 &= B_1, \end{aligned} \qquad (2.12)$$

on T_2. Similarly upon expanding about x_1, we have

$$u \sim [P(x)]^{-\frac{1}{4}}[A'e^{iz'}+B'e^{-iz'}], \qquad (2.13)$$

$$z' = \int_{x_1}^x [P(x)]^{\frac{1}{2}}dx, \qquad (2.14)$$

and

$$\begin{aligned} A_2' &= A_1' + iB_1', \\ B_2' &= B_1', \end{aligned} \qquad (2.15)$$

on T_2' if A_1' and B_1' are appropriate to T_1.

The function u vanishes at $r=0$, so that the coefficient A_2' of the increasing exponential in (2.13) is identically zero in the vicinity of S_2'. From (2.15) we have therefore $A_1' = -iB_1'$, so that if on S_2'

$$u \sim [P(x)]^{-\frac{1}{4}}B_1'e^{-iz'}, \qquad (2.16)$$

we have on T_1

$$u \sim [P(x)]^{-\frac{1}{4}}B_1'[-ie^{iz'}+e^{-iz'}]. \qquad (2.17)$$

On T_1 we can also make use of the asymptotic expansion about x_2,

$$u \sim [P(x)]^{-\frac{1}{4}}C\cos(z+\mu-\pi/4), \qquad (2.18)$$

which leads via (2.12) to

$$u \sim \tfrac{1}{2}C[P(x)]^{-\frac{1}{4}}\exp(i\pi/4)[2\sin\mu e^{iz}+e^{-iz-i\mu}], \qquad (2.19)$$

[28] E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), Sec. 21.

[29] G. N. Watson, *A Treatise on the Theory of Bessel Functions*, (Cambridge University Press, Cambridge, 1948), second edition, p. 201.
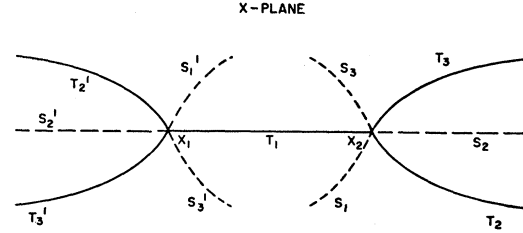
[30] W. H. Furry, Phys. Rev. **71**, 360 (1947).

FIG. 1. The complex x plane near the WKB turning points x_1 and x_2. The curves S are the Stokes lines on which z or z' is imaginary. On the curves T, z or z' is real. All three of the quantities z, z', and $[P(x)]^{\frac{1}{2}}$ are real and positive on T_1, which represents the real x axis between the turning points.

on T_2. Requiring that (2.18) be identical with (2.17) on T_1, we find that

$$\mu = (p+\tfrac{1}{2})\pi - \int_{x_1}^{x_2} [P(x)]^{\frac{1}{2}}dx, \qquad (2.20)$$

and

$$B_1' = (\tfrac{1}{2})C(-)^p e^{i\pi/4}, \qquad (2.21)$$

where p is some integer which is chosen once and for all in defining μ. These relations provide the link between the asymptotic expansions (2.16) and (2.19) valid on S_2' and T_2, respectively.

We now define[3]

$$\pi\delta_w = \int_{x_1}^{x_2} [P(x)]^{\frac{1}{2}}dx - \int_{x_1'}^{x_2'} [P_h(x)]^{\frac{1}{2}}dx, \qquad (2.22)$$

where $P_h(x)$ is obtained from (2.9) with $V(r)=-2/r$ for all r. The second integration can be done exactly, and we obtain

$$\mu = \pi(p+L+1-n-\delta_w). \qquad (2.23)$$

At an eigenvalue, u must approach zero as r or $x \to +\infty$ along the real axis (S_2 in Fig. 1), and from (2.19) and the chosen phase of the square root in z this shows that $\sin\mu=0$. Hence at an eigenvalue μ is an integral multiple of π, and

$$\epsilon = -n^{-2} = -(m-\delta_w)^{-2}. \qquad (2.24)$$

From the definition of μ we see that m is an integer which increases by unity in going from one eigenvalue to the next. Thus, as Kuhn has shown,[3] δ_w is the WKB approximation to the experimental quantum defect at the eigenvalues and is, moreover, a slowly varying function of the energy provided that the outer turning point is in the Coulomb region. We shall now show that δ_w is to be identified with the parameter $v(n)$ defined by (2.7) and used in representing the exact solution (2.4) as a linear combination of the two Coulomb functions.

To do this we shall compare the asymptotic form of the WKB solution with that of the exact solution in Coulomb functions in the vicinity of the line T_2 of Fig. 1, where $\exp(iz)$ is oscillatory. We assume that the outer turning point x_2 is in the Coulomb region, in which $V(r)=-2/r$. We could then evaluate $\exp(iz)$

by carrying out the integral (2.11) from x_2 to some x far out along T_2. If we do this for a pure Coulomb potential, for which $U^L(r)={}^0U_c{}^{L,n}(r)$ is the exact solution satisfying $U^L(0)=0$, we find that the asymptotic form of the WKB solution is correct in the limit $n\to\infty$ and that otherwise the error is $O(1/|n|)$. Such an error is of course characteristic of the WKB approximation, and this method usually gives a worse approximation to the wave function than to the eigenvalues.[30] However, if x_2 for a potential with a non-Coulomb core region lies in the Coulomb region, the integral (2.11) defining z is exactly the same as that for the pure Coulomb potential. Hence, we may "evaluate" it by replacing $\exp(iz)$ by the "correct" value obtained from the asymptotic form of the exact solution for the pure Coulomb potential when $-\pi<\arg(2r/n)<0$,[23]

$${}^0U_c{}^{L,n}(r)\sim[n^{+L+1}/\Gamma(L+1-n)](2r/n)^{-n}\exp(r/n)$$
$$+[n^{L+1}\exp\{\pi i(n-L-1)\}/\Gamma(n+L+1)]$$
$$\times(2r/n)^n\exp(-r/n). \quad (2.25)$$

We find in this manner

$$\exp(2iz)=\exp(2r/n)(2r/n)^{-2n}(2\pi)^{-1}$$
$$\times\Gamma(n+L+1)\Gamma(n-L). \quad (2.26)$$

For a potential with a non-Coulomb core region, we must compare the asymptotic expansion of (2.4) along T_2 with (2.19), into which (2.26) and (2.23) are inserted on the assumption that x_2 is in the Coulomb region. From (2.25) and the expansion

$${}^2U_c{}^{L,n}(r)\sim[n^{-L}\pi^{-1}\exp(in\pi)]$$
$$\times\{\exp[-i\pi(L-\tfrac12)]\sin[\pi(n-L)]$$
$$\times\Gamma(L+1-n)\exp(-r/n)(2r/n)^n$$
$$-\Gamma(L+1+n)\cos[\pi(n-L)]$$
$$\times\exp(r/n)\exp(-i\pi n)(2r/n)^{-n}\}, \quad (2.27)$$

for $-\pi<\arg(2r/n)<0$, we obtain in this way the connection relations

$$\frac{\alpha(n)}{\gamma(n)}=-\frac{\Gamma(n+L+1)}{n^{2L+1}\Gamma(n-L)\tan\pi\delta_w} \quad (2.28)$$

and

$$C=\gamma(n)\frac{n^{-L+\frac12}(-)^{p+1}}{\sin\pi\delta_w}\left[\frac{2\Gamma(n+L+1)}{\pi\Gamma(n-L)}\right]^{\frac12}. \quad (2.29)$$

We have used (2.28) in establishing (2.29). From (2.28) and (2.7), we see that $\nu(n)$ in (2.7) is to be identified with a slowly varying function coinciding with the experimental quantum defect δ_m at the eigenvalues, at least to the accuracy of the WKB approximation. We have already seen that $\nu(n)$ must differ from δ_m at the eigenvalues by at most an integer, so that the WKB argument confirms our assertion that $\nu(n)$ is to be interpolated smoothly between the experimental values of δ_m. The WKB derivation can be extended to positive energies and leads again to (2.28) with δ_w defined by (2.22) as before, provided that the energy is not so high

that the inequality $\exp(-2\pi|n|)\ll1$ is violated.[9] However, at negative energies at which x_2 is in the non-Coulomb core region, it can be shown[9] that the WKB result (2.28) is not accurate. Consequently we cannot justify with the WKB procedure the use of (2.7) with an extrapolated $\nu(n)$ below about -0.9 Rydberg unit for Li and Na for $L=0$ and -0.7 Rydberg unit for K, Rb, and Cs for $L=0$. For $L=1$ this minimum energy is about -0.4 Rydberg unit for all the alkalies.

At negative energies there is the further complication that the factor

$$\frac{\Gamma(n+L+1)}{n^{2L+1}\Gamma(n-L)}=\frac{(n^2-L^2)[n^2-(L-1)^2]\cdots(n^2-1)}{n^{2L}} \quad (2.30)$$

vanishes if $1/n^2$ equals the reciprocal of the square of any integer less than or equal to L. Since from (2.4) it is clear that $\alpha(n)/\gamma(n)$ cannot vanish for all potentials at such energies, we see from (2.7) that $\tan\pi\nu(n)$ must vanish and that $\nu(n)$ must equal an integer at such points. These "forced zeros" of $\tan\pi\nu(n)$ were not suggested by the WKB analysis and lead to an inconvenient oscillation of $\nu(n)$ as a function of energy between these points. Consequently extrapolation of $\nu(n)$ into this region (below -0.25 for $L=2$) is quite unreliable.

In view of these uncertainties concerning the extrapolation of $\nu(n)$ towards large negative energies, we may seek another parameter that can be extrapolated more safely. Several considerations lead us to expect that upon setting

$$\alpha(n)/\gamma(n)=-1/\tan\pi\eta(n), \quad (2.31)$$

we shall find that $\eta(n)$ is more suitable for extrapolation than $\nu(n)$. Of greatest importance, $\tan\pi\eta(n)$ has no forced zeros, and (2.30) increases monotonically to unity as $\epsilon\to0$ for energies above the highest forced zero of $\tan\pi\nu(n)$. Consequently we should expect $\eta(n)$ to be as well behaved as $\nu(n)$ in the range of energies corresponding to the valence eigenvalues and better behaved at lower energies. These expectations are completely borne out by the values of $\eta(n)$ and $\nu(n)$ for the alkali metals as derived from the eigenvalue spectra. They are also supported by calculations on a model potential

$$V(r)=-2Z/r \quad \text{for} \quad r<r_0$$
$$=-2/r \quad \text{for} \quad r>r_0, \quad (2.32)$$

results for which were given elsewhere.[9] This potential is not a realistic model for an ionic potential because of the discontinuity at r_0, but it should serve to illustrate the behavior of $\nu(n)$ and $\eta(n)$ for a potential with a nonhydrogenic core.

If it is necessary to extrapolate η far from the energy range of the valence eigenvalues, there are some general rules which can be helpful.[31] Most of these are of little consequence in calculations of energy band structure

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[31] Reference 9, pp. 164–5.

for the alkali metals, for which a simple quadratic extrapolation of η from the valence eigenvalues usually suffices (Appendix C). However, for the noble metals Kambe[5] has found it essential to recognize that additional points on the $\eta(n)$ *vs* energy curve may be obtained from the energy parameters appearing in the Hartree-Fock equations for the *ionized* core (*not* the neutral atom).[9] Furthermore, for the alkali metals K, Rb, and Cs, we have been able to eliminate some uncertainty in the extrapolation of η for $L=2$ to the ground state energy of the solid by expressing the necessarily positive integral $\int_0^a [U^L(r)]^2 dr$ in terms of η, the derivative of η with respect to energy, and standard Coulomb functions (Appendix B). The resulting expression is not inherently positive for all values of η, so that this requirement places bounds on the extrapolation. Details are given in Appendix C. Needless to say, energy band results depending sensitively on uncertain extrapolations are not reliable.

3. CORRECTIONS FOR DEVIATIONS FROM A COULOMB POTENTIAL OUTSIDE THE CORE

In speaking above of obtaining $\eta(n)$ from the experimentally determined eigenvalues, we have been assuming that the ion potential $V(r)$ equals $-2/r$ outside a core radius r_0 which is no larger than the radius of the sphere inscribed in the atomic cell. We have also assumed that in the solid the best one-electron potential within each cell is the $V(r)$ of the free ion. We shall now relax these assumptions.

For a monovalent atom the potential outside the conventional core radius differs from pure Coulomb form not only because of the small but finite probability that a core electron will be found at such a distance from the nucleus but also because of the polarization of the core by the valence electron. The latter effect introduces into the one-electron potential a term

$$-2\alpha'/r^4, \qquad (3.1)$$

in which α' is a constant determined by the polarizability of the ion core.[32] Let us suppose that we wish to determine the value of the logarithmic derivative of a radial function $U^L(r)$ at a radius r_0 at which (3.1) and other non-Coulomb terms are not insignificant. We introduce a new fictitious potential $V^1(r)$ which equals $V(r)$ for $r < r_0$ and $-2/r$ for $r > r_0$. Since $U^L(0) = 0$, the function $U^L(r)$ satisfying (2.2) is the same function of r for $r < r_0$ for both $V(r)$ and $V^1(r)$, except perhaps for an arbitrary multiplicative constant. We can therefore apply the analysis of Sec. 2 to $V^1(r)$ and can determine $U^L(r)$ at $r = r_0$ from (B.3) (Appendix B) if we determine $\eta(n)$ from the eigenvalues of $V^1(r)$ rather than from those of $V(r)$. Similarly, we can use this $\eta(n)$ in (B.5) to evaluate $\int_0^{r_0} [U^L(r)]^2 dr$.

Finding the eigenvalues of $V^1(r)$ from those of $V(r)$

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[32] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932), Chap. 8.

is relatively simple if $V(r)$ is known accurately for $r > r_0$ and if $|-(2/r) - V(r)|$ is small enough for $r > r_0$ to allow the use of perturbation theory. This situation holds for the alkali metals, and the details of the application of this procedure to the alkalies are given in Appendix C. We should remark here that this procedure leads to results significantly different from those obtained elsewhere[9] with the WKB approximation. We believe the difference is due to the inaccuracy of the WKB method in calculating the difference in η for two potentials differing by a rapidly varying discontinuous function $(2\alpha'/r^4, r > r_0)$.

In applying QDM to a solid, we may wish to let the one-electron potential in the cell differ, for $r > R$, from that of the free ion. Such deviations arise if we try to include interactions with other conduction electrons and nearby ions. We may apply the above procedure to obtain $U^L(r)$ and its derivatives at $r = R$, and we can integrate (2.2) explicitly to larger r with the chosen potential (assuming spherical symmetry) using boundary conditions of continuity at R. A similar procedure should be useful with divalent and trivalent metals, for which we can obtain a smoothly varying η from the spectrum of the suitably ionized alkali-like atom. Neglecting the contribution to the potential of the other valence electrons within the core, we can use this procedure to include the effect of their interaction (which we must estimate) outside the core. Further deviations within the core can be taken roughly into account by a perturbation procedure (assuming we can estimate the form of the wave functions over the desired region). Deviations from spherical symmetry could be corrected for by similar perturbation methods after an approximate set of wave functions has been determined for the solid.

4. CALCULATION OF WAVE FUNCTION AT THE NUCLEUS

The arguments of Sec. 2 may be extended to a calculation of the wave function in the vicinity of the nucleus. We assume that near the nucleus

$$V(r) = -(2Z/r) + V_0 \qquad (4.1)$$

in (2.2) and that the inner turning point x_1 of (2.9) lies in this inner Coulomb region where (4.1) is valid. Here Z is the nuclear charge and V_0 the potential at the nucleus due to the core electrons. Introducing the variables

$$\frac{1}{n^{*2}} = \frac{1}{Z^2}\left[\frac{1}{n^2} + V_0\right], \qquad (4.2)$$

$$r^* = Zr,$$

we find from (2.2) that in this region $U^L(r)$ satisfies the equation

$$\frac{d^2U^L}{dr^{*2}} + \left[-\frac{1}{n^{*2}} + \frac{2}{r^*} - \frac{L(L+1)}{r^{*2}}\right]U^L = 0, \qquad (4.3)$$

which has the form of the standard Coulomb differential equation in the starred variables. Since $U^L(0)=0$, we must have in the inner Coulomb region

$$U^L(r)=A\ {}^0U_c{}^{L,}(r^{n**})\qquad(4.4)$$

in the notation of (2.3a). Equating the lowest term in the power series expansion of (4.4) in r with (2.16), upon recalling that $u(x)=\exp(-x/2)U^L$, we find on S_2' the connecting formula

$$u\sim B_1'(L+\tfrac{1}{2})^{-\frac{1}{2}}e^{-iz'-i\pi/4}=A\left(\frac{r}{n^2}\right)^{-\frac{1}{2}}\frac{(2r^*)^{L+1}}{\Gamma(2L+2)},\qquad(4.5)$$

where we have used

$$\lim_{x\to\infty,\ \text{on}\ S_2'}[P(x)]^{-\frac{1}{4}}=e^{-i\pi/4}(L+\tfrac{1}{2})^{-\frac{1}{2}}.\qquad(4.6)$$

This does not yet suffice to relate B_1' to A insofar as $e^{-iz'}$ has not been determined accurately. Instead of carrying out the integral (2.14), we proceed as in Sec. 2 to "evaluate" $e^{-iz'}$ by comparing the WKB solution with the asymptotic expansion of an exact solution. This time we use the assumption that x_1 is in the inner Coulomb region, so that $e^{-iz'}$ on S_2' is defined just as it would be if the potential were equal to (4.1) everywhere. For such a potential (4.3) and (4.4) hold everywhere, and we can introduce the WKB approximation to relate the asymptotic expansion on S_2' with that on T_2 and thereby to evaluate $e^{-iz'}$ in (4.5). Thus, introducing

$$\begin{aligned}x^*&=\ln(r^*/n^{*2}),\\u^*&=\exp(-x^*/2)U,\end{aligned}\qquad(4.7)$$

in (4.3) and using Eqs. (2.10) through (2.21) in terms of the starred variables, we find from (2.19), (2.25), (2.26), and (4.4) that

$$C^*=A(-)^p n^{*(L+\frac{3}{2})}\left[\frac{2}{\pi}\frac{\Gamma(n^*-L)}{\Gamma(n^*+L+1)}\right]^{\frac{1}{2}}.\qquad(4.8)$$

Then from (2.21) we obtain

$$B_1'^*=Ae^{i\pi/4}n^{*(L+\frac{3}{2})}\left[\frac{\Gamma(n^*-L)}{2\pi\Gamma(n^*+L+1)}\right]^{\frac{1}{2}}.\qquad(4.9)$$

Substituting this into (4.5) [first placing an asterisk on all the parameters in (4.5)], we obtain

$$\exp(-iz'^*)=\frac{2(2r^*/n^*)^{L+\frac{1}{2}}}{\Gamma(2L+2)}$$
$$\times\left[\frac{\pi\Gamma(n^*+L+1)(L+\tfrac{1}{2})}{\Gamma(n^*-L)}\right]^{\frac{1}{2}}.\qquad(4.10)$$

Here

$$z'^*(r^*)=\int_{x_1^*}^{\ln(r^*/n^{*2})}[P^*(x^*)]^{\frac{1}{2}}dx^*,\qquad(4.11)$$

and

$$P^*(x^*)=[-n^{*2}e^{2x^*}+2n^{*2}e^{x^*}-(L+\tfrac{1}{2})^2]$$
$$=\frac{n^{*4}e^{2x^*}}{Z^2}\left[-\frac{1}{n^2}+\frac{2Z}{r}-V_0-\frac{(L+\tfrac{1}{2})^2}{r^2}\right]\qquad(4.12)$$
$$=P(x),$$

where we have used (4.2) and (2.9). Since $dx^*=dr^*/r^*$ $=dr/r$, we obtain from (2.14) and (4.11) with the use of (4.12)

$$z'^*(rZ)=z'(r),\qquad(4.13)$$

which gives us immediately from (4.10)

$$\exp[-iz'(r)]=\frac{2(2Zr/n^*)^{L+\frac{1}{2}}}{\Gamma(2L+2)}$$
$$\times\left[\frac{\pi\Gamma(n^*+L+1)(L+\tfrac{1}{2})}{\Gamma(n^*-L)}\right]^{\frac{1}{2}}.\qquad(4.14)$$

We may now use this expression in (4.5), which connects the WKB and exact solutions in the inner Coulomb region of the *ion* potential (which equals $-2/r$ outside the core). We find

$$B_1'=Ann^{*(L+\frac{1}{2})}Z^{\frac{1}{2}}e^{i\pi/4}\left[\frac{\Gamma(n^*-L)}{2\pi\Gamma(n^*+L+1)}\right]^{\frac{1}{2}}.\qquad(4.15)$$

Combining this result with the WKB formula (2.21) to link the inner and outer Coulomb regions, we obtain from (2.29)

$$\gamma(n)=-AZ^{\frac{1}{2}}\sin\pi\nu(n)$$
$$\times\left[\frac{\Gamma(n^*-L)n^{*(2L+1)}}{\Gamma(n^*+L+1)}\frac{\Gamma(n-L)n^{2L+1}}{\Gamma(n+L+1)}\right]^{\frac{1}{2}},\qquad(4.16)$$

where we have replaced δ_w in (2.29) by $\nu(n)$, which is to be obtained from the experimental spectrum by interpolation. Finally, upon combining (4.16), (2.4), (2.7), and (4.4), we obtain for the ratio of the amplitudes of $U^L(r)$ at points r_a and r_s in the inner and outer Coulomb regions, respectively,

$$\frac{U^L(r_a)}{U^L(r_s)}=\left\{\frac{{}^0U_c{}^{L,n^*}(r_aZ)}{Z^{\frac{1}{2}}\cos\pi\nu(n)\left[\frac{\Gamma(n^*-L)n^{*(2L+1)}}{\Gamma(n^*+L+1)}\frac{\Gamma(n+L+1)}{n^{2L+1}\Gamma(n-L)}\right]^{\frac{1}{2}}}\right\}$$
$$\times\left\{\left[{}^0U_c{}^{L,n}(r_s)-\frac{n^{2L+1}\Gamma(n-L)\tan\pi\nu(n)}{\Gamma(n+L+1)}{}^2U_c{}^{L,n}(r_s)\right]^{-1}\right\}.\qquad(4.17)$$

In the interesting case of an s function $(L=0)$, the expression (2.30) is identically equal to unity, and we obtain from (4.17) the ratio of the amplitude of the wave function $\psi_0(r) = r^{-1}U^0(r)$ at the nucleus to its value at r_s,

$$\frac{\psi_0(0)}{\psi_0(r_s)} = \frac{2Z^{\frac{1}{2}}r_s}{\cos\pi\nu(n)[{}^0U_c{}^{0,n}(r_s) - \tan\pi\nu(n)\,{}^2U_c{}^{0,n}(r_s)]}.$$

(4.18)

This is the principal result of the derivation of this section. It is noteworthy that n^* has vanished from this equation, so that the result is formally independent of the inner potential V_0 and depends on $V(r)$ only through the quantum defect $\nu(n)$ and the nuclear charge Z. Hence the ratio (4.18) can be determined uniquely for $L=0$ from spectroscopic data.

The derivation of (4.18) depends essentially upon the use of the WKB approximation to connect the asymptotic expansions of $U^L(r)$ in the inner and outer Coulomb regions. Moreover, whereas only the phases of the WKB functions need be joined in approximating the eigenvalues, the derivation of (4.18) requires matching the amplitude as well. It is known that WKB amplitudes are rather less accurate than are the phases.[30] Hence even though we have used comparison methods between the WKB and exact solutions to improve the accuracy of our connection formulas and have replaced the WKB δ_w by $\nu(n)$ as derived from experiment, we cannot claim that (4.18) is based solely upon experimental data and therefore very much more accurate than the WKB approximation used to establish it. We do make this claim for (2.7) and (2.31). However, because of our use of the experimental $\nu(n)$ and of comparison methods to correct the WKB formulas in the region near the nucleus where the potential varies most rapidly, we can expect that (4.18) is somewhat more accurate than a straight-forward WKB result. In Appendix A we shall show for an eigenfunction of the free atom that (4.18) is equivalent to a formula derived by Fermi and Segrè.[33,34] This leads to calculated values for the atomic hyperfine splitting of the ground state of the alkali metals which are about five to ten percent too large, once relativistic corrections are introduced, in conformity with our view that (4.18) is only approximate but nevertheless reasonably accurate. In particular, the results for sodium and lithium differ from the experimental values by about the same amount (though in the opposite direction) as do those obtained from wave functions calculated by numerical integration of the Prokofjew or Seitz potentials.[35,36] As discussed in Appendix A, the calculated ratio of the amplitude of an s-function at the nucleus at the Fermi level

in the solid to that in the free atom should be more accurate than either amplitude alone.

The validity of (4.17) and (4.18) depends further upon the assumption that the radial differential equation is strictly Coulombic both inside the inner turning point and outside the outer turning point. For any energies that occur in practice for either solid state or free atom calculations for the alkali metals, this condition appears to be satisfactorily fulfilled only for $L=0$. To show this for the inner turning point, we note that the deviation from constancy of the inner potential arises almost entirely from the innermost K electrons. The total potential is then approximately

$$V(r) = -2Z/r + V_0 - \tfrac{4}{3}Z^3r^2.$$

(4.19)

It is readily shown that an approximate expression for the relative shift in the inner turning point resulting from the last term is

$$\delta r/r = (Z/12)(L+\tfrac{1}{2})^6 = (Z/768)$$

(4.20)

for $L=0$. This relative shift is small only for $L=0$, and is relatively larger for the heavy elements. This criterion for the validity of (4.18) is probably well enough fulfilled for all the alkali metals.

Further error in using (4.18) to obtain results for comparison with experimental data on hyperfine splitting and Knight shift of course arises from our assumption that the valence-core interaction can be represented by a simple one-electron potential and that relativistic effects can be neglected. We have not been able to generalize (4.18) to a more complicated interaction while retaining the framework of the quantum defect method. However, in deriving (4.18) we need not require that the one-electron core potential be the same for different L, so that to this extent we can argue that the result includes exchange effects if not correlation interactions. In view of the evident inaccuracy due to the WKB connection through the core, it does not seem worthwhile to attempt to justify (4.18) more carefully in the presence of more complicated interactions. Relativistic corrections to the hyperfine interaction, especially important for Rb and Cs, may be made using the procedure of Breit and Racah (Appendix A). We should remark that since we have assumed the existence of an outer Coulomb region, in which r_s and the outer turning point are to lie, in the presence of core polarization one should use the quantum defect appropriate to the modified potential $V^1(r)$ of Sec. 3 which is exactly Coulombic beyond an appropriate r_0. This modification is unnecessary in calculating atomic hyperfine splitting using the Fermi-Segrè formula (Appendix A).

5. EXCHANGE AND CORRELATION IN THE ELECTRON-ION INTERACTION

We have assumed heretofore that the interaction between a valence electron and the ion could be represented by a potential. This assumption is satisfactory

[33] E. Fermi and E. Segrè, Z. Physik 82, 729 (1933).
[34] E. Fermi and E. Segrè, Mem. reale accad. Italia Classe sci. fis. mat. e nat. 4, 131 (1933).
[35] W. Kohn, Phys. Rev. 96, 590 (1954).
[36] T. Kjeldaas and W. Kohn, Phys. Rev. 101, 66 (1956).

for lithium and sodium, as Prokofjew[12] and Seitz[13] have shown, but not for the heavy elements. Gorin[37] was able to construct a potential which reproduced the s terms of potassium within several percent and a second potential that reproduced the p terms, but he could not find a single potential that gave both. This difficulty arises because exchange, correlation, and relativistic effects are of greater importance for the heavy elements, and it is impossible to represent these effects accurately with a one electron potential valid for states of different angular momenta.[38] Callaway[39,40] has recently calculated the band structure of solid potassium using different potentials for s, p, d, and f states which take approximate account of exchange. His result for the cohesive energy is much closer to the experimental value than was Gorin's. We shall now give a derivation indicating that QDM takes account of such complications. The method should be particularly useful, therefore, in band calculations for the heavier elements.

Our procedure will be to generalize the Hartree-Fock approximation to include strong mutual correlations between core electrons and weak correlations between the core and valence electrons as well as exchange.[41] We shall then show that the part of the wave function describing a valence electron satisfies an equation which is identical outside the ion core with the Schrödinger equation for an electron in the potential field of a polarizable ion. This part of the wave function can therefore be expressed in terms of Coulomb functions outside the core if account is taken of polarization as in Sec. 3. Moreover, we can show in the spirit of the Wigner-Seitz approximation that this equation is the same near an ion in the solid as in the corresponding free atom. It should therefore be possible to obtain the proper combination of Coulomb functions outside the core for any L and arbitrary energy from spectroscopic data for the free atom. In particular, we should expect to find that the parameter η varies slowly from one experimental eigenvalue to the next. If this indeed is found to be true from the data, we assume we can interpolate η as with a simple potential and thus construct the combination of Coulomb functions which appear in the solutions of the equation in the solid. These can then be combined for different L to satisfy the proper periodic boundary conditions and to determine the energy levels of the solid. The complicated effects of exchange and correlation between the valence electrons and the core will then be found to be contained in η as it is obtained from the experimental data.

Our detailed arguments below cannot be entirely rigorous because of the complicated nature of the

problem of constructing a many-electron wave function for a solid. They are intended to be consistent with the spirit of the Wigner-Seitz approximation and are therefore particularly appropriate to a monovalent solid. However, these generalizations in no way improve upon the rather crude treatment of correlation and exchange between *different valence electrons* in the Wigner-Seitz approach, so that a calculation using QDM must be corrected for these important effects. We shall defer mention of relativistic effects until Sec. 6.

Instead of assuming a many-electron wave function n the Slater determinant form,[42] we approximate the wave function of an atom with p valence electrons and q core electrons by

$$\Psi = C \sum^{P} (-)^{P} P \psi_1(\mathbf{r}_1) \cdots \psi_p(\mathbf{r}_p)$$
$$\times \phi(\mathbf{r}_{p+1}, \cdots \mathbf{r}_{p+q}; \mathbf{r}_1 \cdots \mathbf{r}_p). \quad (5.1)$$

Here $\psi_i(\mathbf{r})$ is a one-electron function representing a valence electron, and $\phi(\mathbf{r}_{p+1}, \cdots \mathbf{r}_{p+q}; \mathbf{r}_1 \cdots \mathbf{r}_p)$ represents the core, being an antisymmetrical function of the q coordinates $\mathbf{r}_{p+1}, \cdots \mathbf{r}_{p+q}$ (which include spin) which depends parametrically[43] on $\mathbf{r}_1, \cdots \mathbf{r}_p$. The operator $\sum_{P} (-)^{P} P$ antisymmetrizes the entire function by permuting the $p+q$ coordinates and multiplying resulting terms by $+1$ or -1 according as to whether the permutation is even or odd, and C is a constant which normalizes the entire function to unity under integration over all coordinates. Such a function permits us to take account of correlations among the core electrons, since $\phi(\mathbf{r}_{p+1}, \cdots \mathbf{r}_{p+q}; \mathbf{r}_1, \cdots \mathbf{r}_p)$ can be any function of $\mathbf{r}_{p+1}, \cdots \mathbf{r}_{p+q}$. Through the parametric dependence of ϕ on $\mathbf{r}_1, \cdots \mathbf{r}_p$, we can include approximately correlations between the core and valence electrons. This comes about only through the dependence of the core function on the instantaneous valence coordinates since we use one-electron functions $\psi_i(\mathbf{r})$ for the valence states. As we shall see, that part of the apparent potential determining $\psi_i(\mathbf{r})$ which arises from the core electrons is produced by the average charge distribution of the core, polarized by the instantaneous valence electron positions. We are assuming, thus, that the core electron orbits are influenced by the instantaneous valence electron positions but that the reverse effect is negligible. This is reasonable in view of the higher frequencies of the core electrons.[44] With such a wave function we cannot, of course, include correlations between valence electrons.

[37] E. Gorin, Physik Z. Sowjetunion **9**, 328 (1936).
[38] Herman, Callaway, and Acton, Phys. Rev. **95**, 371 (1954).
[39] J. Callaway, Phys. Rev. **103**, 1219 (1956).
[40] Berman, Callaway, and Woods, Phys. Rev. **101**, 1467 (1956).
[41] See reference 9 for a discussion of the justification of QDM from the more restricted point of view of the Hartree-Fock equations.

[42] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 237.
[43] By a parametric dependence we mean that ϕ depends on $\mathbf{r}_1$, say, sufficiently slightly so that we can neglect terms like $\nabla_1^2 \phi$ or $\nabla_1 \phi$.
[44] A simple classical calculation of the motions of two weakly coupled harmonic oscillators of very different frequencies shows that the oscillator of higher frequency is polarized by the instantaneous position of the second oscillator approximately as if the latter were fixed, whereas the oscillator of lower frequency is very much less polarized than if the other were fixed. It is also out of phase with the faster oscillator. The frequency shift of the oscillator of lower frequency is the greater.

We now restrict attention to a monovalent atom, for which (5.1) can be written as

$$\Psi = C\left[\psi(\mathbf{r}_1)\phi(\mathbf{r}_2,\cdots\mathbf{r}_{q+1};\mathbf{r}_1) - \sum_{i=2}^{q+1} \psi(\mathbf{r}_i)\phi(\mathbf{r}_2,\cdots\mathbf{r}_{i-1},\mathbf{r}_1,\mathbf{r}_{i+1}\cdots\mathbf{r}_{q+1};\mathbf{r}_i)\right]. \tag{5.2}$$

We then form

$$\int \Psi^*\mathfrak{IC}\Psi d\tau_1\cdots d\tau_{q+1}\Big/ \int \Psi^*\Psi d\tau_1\cdots d\tau_{q+1}, \tag{5.3}$$

in which $\mathfrak{IC}$ is the nonrelativistic Hamiltonian of the system

$$\mathfrak{IC} = \sum_{i=1}^{q+1}\left[-\nabla_i^2 + V_0(\mathbf{r}_i)\right] + \sum_{ij \text{ pairs}} V_1(|\mathbf{r}_i - \mathbf{r}_j|), \tag{5.4}$$

with $V_0(\mathbf{r}_i)$ the potential of the ith electron in the field of the nucleus and $V_1(|\mathbf{r}_i - \mathbf{r}_j|)$ the interaction potential between electrons. Minimizing (5.3) with respect to arbitrary variations in $\psi^*(\mathbf{r})$, we find that the optimal ψ for a fixed ϕ should satisfy the following equation:

$$[-\nabla_x^2 + V_0(\mathbf{x})]\psi(\mathbf{x}) + \psi(\mathbf{x})\frac{\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\{\mathfrak{IC}' + \sum_{j=2}^{q+1} V_1(|\mathbf{r}_j - \mathbf{x}|)\}\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}{\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}$$

$$-\frac{\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\mathfrak{IC}\sum_{i=2}^{q+1}\psi(\mathbf{r}_i)\phi(\mathbf{r}_2\cdots\mathbf{r}_{i-1},\mathbf{x},\mathbf{r}_{i+1}\cdots\mathbf{r}_{q+1};\mathbf{r}_i)d\tau_2\cdots d\tau_{q+1}}{\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}$$

$$-E\left\{\psi(\mathbf{x}) - \frac{\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\sum_{i=2}^{q+1}\psi(\mathbf{r}_i)\phi(\mathbf{r}_2\cdots\mathbf{r}_{i-1},\mathbf{x},\mathbf{r}_{i+1}\cdots\mathbf{r}_{q+1};\mathbf{r}_i)d\tau_2\cdots d\tau_{q+1}}{\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}\right\} = 0. \tag{5.5}$$

Here $\mathfrak{IC}'$ is the Hamiltonian of the singly ionized atom, in terms of $\mathbf{r}_2\cdots\mathbf{r}_{q+1}$. We have defined E to be the minimum of (5.3) and thus our approximation to the total energy of the system once ϕ has been chosen optimally. We have also neglected all derivatives of ϕ with respect to its parametric dependence.

Now if $\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})$ differs only slightly from the wave function of the singly ionized atom, then E_I, the energy of the latter, is given approximately by

$$E_I \cong \int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\mathfrak{IC}'\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}\Big/ \int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}, \tag{5.6}$$

since this expression is a minimum for the exact ϕ of the ionized atom. With this assumption that the core function in the neutral atom is not greatly different from that of the ion,[45] we can therefore replace the expectation value of $\mathfrak{IC}'$ in (5.5) by E_I with an error of only the second order in the change in ϕ. We furthermore examine (5.5) when $\mathbf{x}$ lies outside the core (the core radius r_c being defined such that if any $|r_i| > r_c$, $\phi(\mathbf{r}_1\cdots\mathbf{r}_{q+1};\mathbf{x})$ has negligible amplitude). The exchange terms containing $\phi(\mathbf{r}_2\cdots\mathbf{r}_{i-1},\mathbf{x},\mathbf{r}_{i+1}\cdots\mathbf{r}_{q+1};\mathbf{r}_i)$ are then negligible, and (5.5) reduces to the

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[45] This assumption should be very satisfactory for the alkalies. D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A193**, 299 (1948), Proc. Cambridge Phil. Soc. **34**, 550 (1938).

form of a simple one-electron Schrödinger equation for an electron in the field of a polarized core:

$$[-\nabla_x^2 + V_0(\mathbf{x})]\psi(\mathbf{x}) + \psi(\mathbf{x})\frac{\displaystyle\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\sum_{j=2}^{q+1}V_1(|\mathbf{r}_j-\mathbf{x}|)\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}{\displaystyle\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}$$

$$= (E-E_I)\psi(\mathbf{x}) = \epsilon\psi(\mathbf{x}). \quad (5.7)$$

Inside the core, however, $\psi(\mathbf{x})$ must satisfy a more complicated integro-differential equation because of the exchange terms. We note that we have nowhere assumed that $\psi(\mathbf{x})$ and ϕ are normalized or orthogonal.

To complete the analysis of the atom, we now minimize (5.3) with respect to arbitrary variations of $\phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{r}_1)$. Eliminating $[-\nabla^2+V_0(\mathbf{r})]\psi(\mathbf{r})$ from the resulting equation by substituting from (5.5) [with (5.6)], we obtain a complicated equation for ϕ which simplifies when one $\mathbf{r}_i(=\mathbf{x})$ is outside the core to [assuming still that $\phi(\mathbf{r}_2,\cdots\mathbf{x},\cdots\mathbf{r}_{q+1};\mathbf{r}_i)\sim 0$ if $|\mathbf{x}|>r_c$]

$$\mathcal{3C}'\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x}) + \phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})$$

$$\times\left\{\sum_{j=2}^{q+1}V(|\mathbf{r}_j-\mathbf{x}|) - \sum_{j=2}^{q+1}\frac{\displaystyle\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})V(|\mathbf{r}_j-\mathbf{x}|)\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}{\displaystyle\int \phi^*(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})d\tau_2\cdots d\tau_{q+1}}\right\} = E_I\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x}). \quad (5.8)$$

We see that for such a value of $\mathbf{x}$ (5.8) is just the Schrödinger equation for the ionized atom with two additional perturbing terms. One is the polarizing potential of a fixed electron charge at $\mathbf{x}$ [we note that this potential is independent of $\psi(\mathbf{x})$], and the other is a constant term (depending only on $\mathbf{x}$) which cancels the expectation value of the first term when (5.8) is multiplied by $\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{x})$ and integrated over $\mathbf{r}_2\cdots\mathbf{r}_{q+1}$, so that (5.6) re-emerges. Thus we seem to be justified, at least when $\mathbf{x}$ is outside the core, in regarding ϕ as a polarized core function. When $\mathbf{x}$ is inside the core the analysis is complicated by exchange, but the general character of ϕ should be the same.

We have shown so far that, in the approximation of (5.2) for the isolated atom, the form of $\psi(\mathbf{r})$ outside the core is determined by the simple Schrödinger-type equation (5.7) in which the potential is that of the polarized core. At the free atom eigenvalues, then, we can obtain explicit expressions for $\psi(\mathbf{r})$ outside the core by integrating this equation in from infinity, where the boundary condition $\lim\psi(\mathbf{r})=0$ as $|\mathbf{r}|\to\infty$ applies. We need know only the ion core potential, which equals the usual Coulomb term plus a polarization potential which we know approximately and which is small but by no means negligible. Hence, despite the complicated Eq. (5.5) satisfied by $\psi(\mathbf{r})$ within the core, we can obtain $\psi(\mathbf{r})$ explicitly outside the core at the eigenvalues, and this has the same form as found for a simple potential as in Secs. 2 and 3.

We shall show below that in the spirit of the Wigner-Seitz approximation essentially the same Eq. (5.5) is satisfied by a valence Bloch function $\psi(\mathbf{r})$ within the atomic cell of the solid and that (5.7) holds in the cell outside the core. With the assumption

that $\phi(\mathbf{r}_2\cdots\mathbf{r}_{q+1};\mathbf{r}_1)$ is approximately independent of the form of $\psi(\mathbf{r}_1)$ (which we have shown to be true for the atom at least for $|\mathbf{r}_1|>r_c$ and which we shall assume in general henceforth), (5.5) is linear in ψ. Hence a Bloch function can be separated into terms each satisfying (5.5) and reducing outside the core to the product of a spherical harmonic and associated radial function satisfying (5.7). From our work in Secs. 2 and 3, we then expect that despite the more complicated interactions indicated by (5.5), the radial functions outside the core will depend upon the core interaction only through a slowly varying quantum defect (or the corresponding η). We do indeed find that the experimental atomic spectrum gives us such a parameter. Hence we believe that we may obtain radial functions outside the core by the QDM interpolation procedures using the experimental eigenvalues (or more properly those of the modified potential of Sec. 3, which we can obtain approximately by perturbation methods), and that these functions, when used in constructing Bloch functions, take approximate account of complicated interactions with the core.

To show that (5.5) also is true for a monovalent solid, we approximate the wave function of the solid by

$$\Psi = C\sum_P (-)^P P\prod_{i=1}^N \psi_i(\mathbf{r}_i)$$

$$\times\prod_{j=1}^N \phi_{\mathbf{R}_j}(\mathbf{r}_{1j},\mathbf{r}_{2j},\cdots\mathbf{r}_{qj};\{\mathbf{r}_i\}) \quad (5.9)$$

in analogy to (5.1). Here $\phi_{\mathbf{R}_j}$ represents the core function at the lattice site $\mathbf{R}_j$, and it depends parametrically on all valence coordinates $\mathbf{r}_1\cdots\mathbf{r}_N$. It will be shown that

the N valence functions $\psi_i(\mathbf{r}_i)$ may be assumed to have the Bloch form. We substitute this into (5.3), where now $\mathcal{3C}$ is the Hamiltonian of the entire crystal:

$$\mathcal{3C}=\sum_{i=1}^{NZ}\left[-\nabla_i^2+V_0(\mathbf{r}_i)\right]+\sum_{ij\text{ pairs}}V_1(|\mathbf{r}_i-\mathbf{r}_j|)$$

$$+\sum_{ij\text{ pairs}}\frac{2Z^2}{|\mathbf{R}_i-\mathbf{R}_j|}, \quad (5.10)$$

where $V_0(\mathbf{r})=-\sum_{i=1}^{N}(2Z/|\mathbf{r}-\mathbf{R}_i|)$, and the last term arises from the nuclear interaction, which we introduce to make (5.3) represent the energy of the crystal as a whole.

The resulting expression is a complicated one involving integrals over products of the ψ's and ϕ's with all possible permutations of the coordinates. Terms containing factors of the form $\phi_{\mathbf{R}_i}(\mathbf{r}_1,\mathbf{r}_2\cdots\mathbf{r}_n)\times\phi_{\mathbf{R}_j}(\mathbf{r}_1,\mathbf{r}_{n+1},\cdots\mathbf{r}_{2n-1})$ vanish if $i\neq j$ since we assume that the ϕ's are localized and nonoverlapping, but many other terms do not. Hence, whereas in deriving (5.5) we did not assume orthonormality of the wave functions, it appears here that we must.

We can readily require

$$\int\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\tau=\delta_{ij}, \quad (5.11)$$

but orthogonality between the valence and core functions is more troublesome. We shall assume that

$$\int\psi_i^*(\mathbf{r}_1)\phi_{\mathbf{R}_j}(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_n)d\tau_1\cong0, \quad (5.12)$$

[recalling that ϕ is antisymmetric so that (5.12) holds regardless of the order of $(\mathbf{r}_1,\mathbf{r}_2,\cdots\mathbf{r}_n)$], and we shall not treat the parameters in $\phi_{\mathbf{R}_j}$ as variables in using (5.12). This approximation permits the simplification of (5.3). It is hard to estimate the extent of the associated error except to observe that we needed no orthonormality restrictions in deriving (5.5) and that one consequently suspects that the error here is small. We further require

$$\int\phi_{\mathbf{R}_i}^*(\mathbf{r}_1\cdots\mathbf{r}_n)\phi_{\mathbf{R}_i}(\mathbf{r}_1\cdots\mathbf{r}_n)d\tau_1\cdots d\tau_n\cong1, \quad (5.13)$$

with no regard for difficulties concerning the parameters.

We now minimize (5.3) for variations in one of the ψ^*'s, say $\psi_k^*(\mathbf{r})$, which are arbitrary except for the restrictions (5.11) and (5.12), to be introduced by Lagrange multipliers. We obtain an equation for $\psi_k(\mathbf{x})$:

$$0=\left[-\nabla_x^2+V_0(\mathbf{x})+\sum_{ij\text{ pairs}}\frac{2Z^2}{|\mathbf{R}_i-\mathbf{R}_j|}\right]\psi_k(\mathbf{x})$$

$$+\psi_k(\mathbf{x})\sum_{i=1}^N\int\psi_i^*(\mathbf{r})V_1(|\mathbf{r}-\mathbf{x}|)\psi_i(\mathbf{r})d\tau-\sum_{i=1}^N\psi_i(\mathbf{x})\int\psi_i^*(\mathbf{r})V_1(|\mathbf{r}-\mathbf{x}|)\psi_k(\mathbf{r})d\tau$$

$$+\psi_k(\mathbf{x})\sum_{i=1}^N\sum_{j=1}^n\int\phi_{\mathbf{R}_i}^*(\mathbf{r}_1,\cdots\mathbf{r}_n;\mathbf{x})V_1(|\mathbf{r}_j-\mathbf{x}|)\phi_{\mathbf{R}_i}(\mathbf{r}_1\cdots\mathbf{r}_n;\mathbf{x})d\tau_1\cdots d\tau_n$$

$$-\sum_{i=1}^N\int\phi_{\mathbf{R}_i}^*(\mathbf{r}_1\cdots\mathbf{r}_n;\mathbf{x})\mathcal{3C}^{n+1}(\mathbf{r}_1,\cdots\mathbf{r}_n,\mathbf{x})\sum_{j=1}^n\psi_k(\mathbf{r}_j)\phi_{\mathbf{R}_i}(\mathbf{r}_1\cdots\mathbf{r}_{j-1},\mathbf{x},\mathbf{r}_{j+1},\cdots\mathbf{r}_n;\mathbf{r}_j)d\tau_1\cdots d\tau_n$$

$$-\lambda_k\psi_k(\mathbf{x})-\sum_i{}'\mu_{ik}\psi_i(\mathbf{x})-\sum_{i=1}^n\int W_k(\mathbf{r}_2,\cdots\mathbf{r}_n)\phi_{\mathbf{R}_i}(\mathbf{x},\mathbf{r}_2,\cdots\mathbf{r}_n)d\tau_2\cdots d\tau_n, \quad (5.14)$$

where λ_k, μ_{ik}, and $W_k(\mathbf{r}_2,\cdots\mathbf{r}_n)$ are Lagrange multipliers arising from (5.11) and (5.12), and $\mathcal{3C}^{n+1}(\mathbf{r}_1,\cdots\mathbf{r}_n,\mathbf{x})$ is the Hamiltonian for $n+1$ electrons in the potential V_0. If all the ψ_i are assumed to have the Bloch form, and if $W_k(\mathbf{r}_2+\mathbf{R}_j,\cdots\mathbf{r}_n+\mathbf{R}_j)=\exp(i\mathbf{k}\cdot\mathbf{R}_j)W_k(\mathbf{r}_2,\cdots\mathbf{r}_n)$, an assumption that is consistent with the rest of the analysis, all terms in (5.14) represent periodic linear operators on ψ_k if all the μ_{ik} are set equal to zero. Hence these assumptions are consistent with $\mu_{ik}=0$ and insure the validity of (5.11) for states of parallel spin (assuming a single band); for opposite spin (5.11) and $\mu_{ik}=0$ are automatically consistent since we have not included spin-dependent terms in $\mathcal{3C}$. Also, since $W_k(\mathbf{r}_2,\cdots\mathbf{r}_n)$ arises from (5.12) and would appear similarly if we required (5.12) in the atomic case, for an atom at $\mathbf{R}_i$, we shall identify each such term in (5.14) with the second term in the bracket multiplied by E in (5.5) for the corresponding $\phi_{\mathbf{R}_i}$, with $\psi(\mathbf{r}_i)$ replaced by $\psi_k(\mathbf{r}_i)$. This identification cannot be rigorously correct, but it seems reasonable in conjunction with the Wigner-Seitz assumptions introduced below.

Finally, to identify λ_k we use (5.14) to evaluate (5.3), the approximate total energy of the crystal, in terms of λ_k and other quantities. Using (5.10), (5.6) and the assumption of nonoverlapping cores, we obtain

$$E_{\text{tot}}=\sum_{i=1}^N E_{Ii}+\sum_{ij\text{ pairs}}\frac{2}{|\mathbf{R}_i-\mathbf{R}_j|}+\sum_{k,k'\text{ pair}}\int\psi_k^*(\mathbf{r})\psi_{k'}^*(\mathbf{r}')V_1(|\mathbf{r}-\mathbf{r}'|)\psi_k(\mathbf{r}')\psi_{k'}(\mathbf{r})d\tau d\tau'$$

$$-\sum_{kk'\text{ pairs}}\int\psi_k^*(\mathbf{r})\psi_{k'}^*(\mathbf{r}')V(|\mathbf{r}-\mathbf{r}'|)\psi_k(\mathbf{r})\psi_{k'}(\mathbf{r}')d\tau d\tau'+\sum_k\left(\lambda_k-\sum_{ij\text{ pairs}}\frac{2Z^2}{|\mathbf{R}_i-\mathbf{R}_j|}\right). \quad (5.15)$$

Hence $\{\lambda_k - \sum_{ij\text{ pairs}}[2Z^2/|\mathbf{R}_i - \mathbf{R}_j|]\} = \epsilon_k$ is the one-electron energy parameter which equals (as in Koopman's theorem)[46] the energy necessary to remove the kth electron from the crystal (neglecting correlation between valence electrons, of course).

To compare (5.14) with (5.5) we now take $\mathbf{x}$ to lie within the cell at $\mathbf{R}_i$. In (5.14) all exchange terms between ψ_k and $\phi_{\mathbf{R}_j}$ are zero except for the one with $\mathbf{R}_j = \mathbf{R}_i$, which is identical with the exchange term in (5.5). We now make use of the Wigner-Seitz assumption[14,15] that we can neglect terms in (5.14) arising from Coulomb interactions with charge distributions outside the cell at $\mathbf{R}_i$, because each cell is neutral and approximately spherical in shape. We also introduce their further assumption that within the cell at $\mathbf{R}_i$ we may eliminate from (5.14) the direct Coulomb and exchange terms arising from the interaction between the valence electrons, on the understanding that the expression (5.15) for the total energy must now be modified to improve upon this over-simplified treatment of correlation and exchange. With W_k and μ_{ik} identified as above and all terms except $-[2Z/|\mathbf{x} - \mathbf{R}_i|]$ cancelled from $V_0(\mathbf{x})$ the equation resulting from (5.14) is identical with (5.5) and simplifies to (5.7) outside the core.

We therefore find that with the approximations mentioned, the $\psi_k(\mathbf{r})$ may be chosen to have the Bloch form (and therefore must satisfy the usual periodicity boundary conditions on the surface of the cell), and that they satisfy the same equation within the cell as that appropriate to the valence electron in the free atom. We can therefore use the experimental spectrum (modified if necessary as in Sec. 3) to obtain by QDM radial functions at arbitrary energies which can be used in the construction of Bloch functions, and we see that we can expect such a procedure to take approximate account of correlation and exchange effects with the ion core.

6. RELATIVISTIC EFFECTS, INCLUDING SPIN-ORBIT COUPLING

There has been recent interest in relativistic corrections to electronic wave functions in solids and to their energy band structure. This has arisen primarily because such corrections lift certain degeneracies at symmetry points and thereby significantly alter the qualitative shapes of the bands. This effect is now known to be important for the valence bands of semiconductors such as Ge, Si, and InSb. Moreover, Callaway[47] has suggested that relativistic contributions to the band shapes and cohesive energies of the heavier alkali metals might be appreciable.

Most estimates of relativistic effects have used perturbation theory with nonrelativistic wave functions calculated from approximate atomic potentials ordinarily corrected for exchange. However, it is quite

simple to reformulate the band calculations such that relativistic contributions can be included from the start. We shall not do this in detail here, but we shall make a few observations to support our contention that the corrections suggested by Callaway are already included in QDM and that relativistic splittings of degenerate levels in solids can be obtained with QDM from the appropriate spectroscopic data. Callaway, Woods, and Sirounian have recently come to essentially the same conclusion.[48] However, our use of QDM to obtain the amplitude of the wave function at the origin does not include relativistic effects because we have assumed $V = -2Z/r + V_0$ near the nucleus. The appropriate relativistic corrections to hyperfine interaction are discussed in Appendix A. It appears that these are very important for the interpretation of the Knight shift in the heavier metals.

In our conventional band calculations we expand a nonrelativistic wave function in spherical harmonics about an ion and determine the corresponding radial wave function for each value of orbital angular momentum L within the region in which the potential is spherically symmetric. In a relativistic theory, using an independent-electron approximation, we should have to introduce 4-component wave functions and make a corresponding expansion in eigenfunctions of the total angular momentum J and of the operator K.[49,50] However, as Condon and Shortley[50] show, the small components ψ_+ of positive-energy functions can be evaluated from the large components by means of the relation

$$\psi_+ = \frac{-c}{E + 2mc^2 - V(r)} \mathbf{p} \cdot \boldsymbol{\sigma} \psi_-, \qquad (6.1)$$

where $\mathbf{p}$ is the momentum operation and $\boldsymbol{\sigma}$ a vector whose components are the Pauli spin matrices. The large components satisfy an equation

$$\frac{1}{2m}\{p^2 + (\mathbf{p} \cdot \boldsymbol{\sigma})q(r)(\mathbf{p} \cdot \boldsymbol{\sigma})\}\psi_- + V(r)\psi_- = E\psi_-, \qquad (6.2)$$

where

$$q(r) = \left[1 + \frac{E - V(r)}{2mc^2}\right]^{-1} - 1 \qquad (6.3)$$

is appreciably different from zero only near the nucleus. Outside the core, therefore, (6.2) reduces to a simple Schrödinger equation for each component of ψ_-. In a spherically symmetric potential $V(r)$, both components of ψ_- for an eigenfunction of K and J are eigenfunctions of the orbital angular momentum L with the same eigenvalue $L = J \pm \frac{1}{2}$. Hence if $V(r)$ is Coulombic out-

[46] Reference 42, p. 313.
[47] J. Callaway, Phys. Rev. 102, 919 (1956).

[48] Callaway, Woods, and Sirounian, Phys. Rev. 107, 934 (1957).
[49] We use the notation of Condon and Shortley (reference 50, Chap. 5, Sec. 5) where a review of the relativistic theory can be found.
[50] E. V. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, 1953).

side the core, the radial parts of both components of ψ_- satisfy the Coulomb radial equation for $L=J\pm\frac{1}{2}$. From spectroscopic data we can obtain the quantum defect for atomic eigenstates of K and J. The radial function of ψ_- outside the core can then be obtained for the same eigenvalues of K and J and intermediate energies by interpolating the quantum defect and using standard Coulomb functions for the corresponding value of $L=J\pm\frac{1}{2}$. We can thus obtain explicit expressions on the atomic cell for all terms in the expansion of each component of a ψ_- appropriate to a periodic $V(r)$. The coefficients of these terms and the energy eigenvalue can be determined from the usual periodicity boundary conditions imposed on ψ_-, since the Dirac equation has the periodicity of $V(r)$. Then ψ_+ can be evaluated from (6.1).

We see, thus, that if we expand our relativistic Bloch functions in eigenfunctions of K and J, we can determine the corresponding radial functions outside the core from the atomic spectroscopic data. As before, we do not need an explicit expression for the Dirac equation within the core. Hence once again the experimental data give us the correct linear combination of Coulomb functions outside the core which connect correctly to functions within the core which are complicated by relativistic effects. It is for this reason that we assert that QDM includes the relativistic effects emphasized by Callaway and makes possible calculations of relativistic splittings once band theory is carried through in terms of expansions in eigenfunctions of K and J. In most of our work, heretofore, we have not done this, and our quantum defects for the alkali metals have been determined from weighted averages of the energies of spectral doublets. However, one of us has used the more accurate theory in calculating the g factors for the alkalis, and we shall examine the corrections introduced by this theory in our continuing calculations on the alkali band structures. The extensions of the usual theory are quite simple; for example, Callaway, Woods, and Sirounian[48] have shown that Bardeen's formula for the reciprocal effective mass becomes (in the notation of Brooks[4])

$$\alpha=\gamma\left\{\frac{2}{3}\frac{r_s}{U_{\frac{1}{2}}^1}\frac{dU_{\frac{1}{2}}^1}{dr}+\frac{1}{3}\frac{r_s}{U_{\frac{3}{2}}^1}\frac{dU_{\frac{3}{2}}^1}{dr}-1\right\},\qquad(6.4)$$

where $U_{\frac{1}{2}}^1$ and $U_{\frac{3}{2}}^1$ are the radial functions (times r) at the ground state energy and equivalent sphere radius for $J=\frac{1}{2}$, $\frac{3}{2}$ and $L=1$, and γ has its usual significance. Callaway et al.[48] have found very little difference in the effective mass for Cs between the result from (6.4) and the "nonrelativistic" (weighted average of doublet) value.

APPENDIX A. ATOMIC HYPERFINE SPLITTING— THE FERMI-SEGRÈ FORMULA

The hyperfine splitting of a $^2S_{\frac{1}{2}}$ term in an alkali-like atom with one valence electron is, in cm^{-1} [51];

$$\Delta\nu=h^{-1}c^{-1}(8\pi/3)\mu_I\mu_B[(2I+1)/I]$$
$$\times P_A F_r(j,Z)(1-\delta)(1-\epsilon).\quad(A.1)$$

Here h is Planck's constant, c the velocity of light, μ_I the nuclear magnetic moment, μ_B the Bohr magneton, I the nuclear spin quantum number, and $P_A=|\psi(0)|^2$ the squared amplitude at the nucleus of the nonrelativistic approximation to the valence wave function. The factor

$$F_r(j,Z)=\frac{4j(j+\frac{1}{2})(j+1)}{\rho(4\rho^2-1)^{\frac{1}{2}}},\qquad(A.2)$$

with $\rho=[(j+\frac{1}{2})^2-\alpha^2Z^2]^{\frac{1}{2}}$, is an approximate relativistic correction due to Racah and Breit for a point nucleus.[52,53] Z is the nuclear charge in units of the charge of the electron, α is the fine structure constant $e^2/\hbar c$, and j is the total angular momentum quantum number of the valence electron ($j=\frac{1}{2}$ for a $^2S_{\frac{1}{2}}$ state). The Breit-Crawford-Schawlow correction $(1-\delta)$ arises from the change in the Dirac wave function due to the finite dimension of the nucleus.[54,55] Finally, the distribution of magnetic dipole-moment over the nucleus leads to the further correction $(1-\epsilon)$.[56] These corrections are tabulated in Table I for the alkalies, together with the values of $\Delta\nu$ obtained from atomic beam experiments. The "experimental" values for P_A listed in Table I were calculated from (A.1) using these values for $\Delta\nu$ and known values of μ_I and I, which are also listed.

To obtain a theoretical value for $|\psi(0)|^2$ for the valence electron in an isolated atom, we make use of our expression for $\psi(0)/\psi(r_s)$ in (4.18). Setting $\psi(r)=Ar^{-1}U^0(r)$, with $U^0(r)$ given by (B.3) in the Coulomb region outside the core ($\eta=\nu$ for $L=0$), we obtain from (4.18) and (B.3)

$$|\psi(0)|^2=4ZA^2/\cos^2\pi\nu.\qquad(A.3)$$

Normalizing $\psi(r)$ to unity in cgs units, and using (B.7) and (B.9) for $L=0$ and the fact that at an eigenvalue $\sec^2\pi n=\sec^2\pi\nu$, we find

$$(P_A)_{\text{theor}}=(Z/\pi a_0^3)(n^3-2d\nu/d\epsilon')^{-1}.\qquad(A.4)$$

Here $\epsilon'=1/n^2$ is the negative of the energy of the valence electron, and a_0 is the Bohr radius $\hbar^2/me^2$.

This theoretical expression for P_A turns out to be identical with one given long ago by Fermi and Segrè[33,34] namely

$$(P_A)_{\text{theor}}=(Z/2\pi)(a_0^3Rhc)^{-1}(dE/dm),\qquad(A.5)$$

[51] H. Kopfermann, *Kernmomente* (Akademische Verlagsgesellschaft, Frankfurt-am-Main, 1956), second edition, p. 111.
[52] G. Breit, Phys. Rev. **35**, 1447 (1930).
[53] G. Racah, Z. Physik **76**, 431 (1931).
[54] J. Rosenthal and G. Breit, Phys. Rev. **41**, 459 (1932).
[55] M. Crawford and A. Schawlow, Phys. Rev. **76**, 1310 (1949).
[56] A. Bohr and V. Weisskopf, Phys. Rev. **77**, 94 (1950).

TABLE I. Atomic hyperfine interaction for alkali metals.

Atom	Z	A	$F_r(j,z)^a$	δ^b	ϵ^c	$\Delta\nu$ (cm⁻¹)	$\dfrac{\mu_I^d}{(e\hbar/2M_pc)}$	I^d	$\dfrac{(P_A)_{expt}^e}{(a_0^{-3})}$	$\dfrac{(P_A)_{theor}^f}{(a_0^{-3})}$	$\dfrac{(P_A)_{theor}^g}{(a_0^{-3})}$
Li	3	6				0.007613[h]	0.82189	1	0.2314	0.2420	0.223
Li	3	7	1.0009	...	...	0.026805[h]	3.2559	$\frac{3}{2}$	0.2314	0.2420	0.223
Na	11	23	1.0119	...	...	0.059103[i]	2.2171	$\frac{3}{2}$	0.7411	0.8402	0.685
K	19	39				0.015403[h]	0.391	$\frac{3}{2}$	1.074	1.162	
K	19	41	1.0363	~0.005	...	0.008474[h]	0.215	$\frac{3}{2}$	1.075	1.162	
Rb	37	85				0.10127[i]	1.353	$\frac{5}{2}$	2.062	2.178	
Rb	37	87	1.1504	~0.01	~0.004	0.22797[j]	2.750	$\frac{3}{2}$	2.056	2.178	
Cs	55	133	1.3904	~0.03	~0.01	0.30663[i]	2.577	$\frac{7}{2}$	2.925	2.970	

a Reference 51, Table 8, p. 431.
b Reference 51, p. 117.
c Reference 51, p. 118, and reference 56.
d J. E. Mack, Revs. Modern Phys. **22**, 64 (1950): M_P is the proton mass.
e Obtained from Eq. (A.1).
f Obtained from the Fermi-Segrè formula (A.4) or (A.5).
g Obtained by integrating the Seitz (Li) and Prokofjew (Na) potentials: references 35 and 36.
h Millman, Kusch, and Rabi, Phys. Rev. **57**, 765 (1940).
i S. Millman and P. Kusch, Phys. Rev. **60**, 91 (1941).
j S. Millman and P. Kusch, Phys. Rev. **58**, 438 (1940).

where

$$E = -Rhc/(m-\nu)^2, \qquad (A.6)$$

and R is the Rydberg constant. To show this, we differentiate (A.6) with respect to m, which we treat as a continuous variable:

$$\frac{dE}{dm} = \frac{2Rhc}{(m-\nu)^3}\left(1 - \frac{d\nu}{dE}\frac{dE}{dm}\right). \qquad (A.7)$$

Solving for dE/dm, and setting $E = -Rhc\epsilon' = -Rhc/n^2$, we obtain (A.4) upon substitution in (A.5). Hence our expression (4.18) for $\psi(0)/\psi(r_s)$ is a generalization of the Fermi-Segrè formula, the latter being valid only for atomic states. However, whereas our derivation of (4.18) required that the outer WKB turning point lie in the outer Coulomb region, no such requirement is needed in Fermi and Segrè's derivation[34] (which is also a nonrelativistic WKB-based procedure). Hence (A.4) [but not necessarily (4.18)] is more general than the assumptions used in deriving it, and in particular we can use in (A.4) the interpolated expression for ν as obtained directly from the spectroscopic data without having to worry about polarization corrections and the like. Such corrections should, of course, be used in applying (4.18) to solid state problems.

We have tabulated $(P_A)_{theor}$ for the alkali metals in Table I. The agreement with $(P_A)_{expt}$ is within about 10% and only slightly worse for Li and Na than theoretical values obtained by Kohn[35] and Kohn and Kjeldaas[36] by integrating the Seitz and Prokofjew potentials. These two values, which are also listed, are too small, whereas our values are too large.

The accuracy of (4.18) for calculations of the Knight shift is presumably similar to that of (A.4). However, particularly since the Fermi energy in the alkali metals is not very different from the energy of the normal state of the atom, the accuracy of the ratio $|\psi_s(0)|^2/P_A$, where $\psi_s(0)$ is the amplitude at the nucleus of a nonrelativistic s function evaluated at the Fermi energy and normalized in the atomic cell, should be consider-

ably better if $\psi_s(0)$ and P_A are calculated from (4.18) [using (B.5) for normalization] and (A.4), respectively. The further evaluation of $P_F = |\psi(0)|^2$ for an electron at the Fermi surface then requires that we determine the radio of $s, p, d, \cdots$ functions that make up the wave function. Calculations of this sort have been carried out by one of us (HB).

APPENDIX B. NORMALIZATION INTEGRALS

Differentiating (2.2) with respect to the parameter $\epsilon' = 1/n^2$ and integrating with respect to r, we obtain

$$\int_0^a [U^L(r)]^2 dr = \left[U^L, \frac{d}{d\epsilon'}U^L\right]_{r=a}, \qquad (B.1)$$

where we use the notation

$$[V,W] = V(r)\frac{dW(r)}{dr} - W(r)\frac{dV(r)}{dr}. \qquad (B.2)$$

Assuming that a is in the Coulomb region, $a > r_0$, we can substitute into the right-hand side of (B.1) from a renormalized form of (2.4), using (2.31),

$$U^L(r) = {}^0U_c^{L,n}(r) - \tan\pi\eta\,{}^2U_c^{L,n}(r) \quad \text{for} \quad r > r_0. \qquad (B.3)$$

We obtain, with use of the Wronskian relation

$$[{}^0U_c^{L,n}, {}^2U_c^{L,n}] = 2/\pi, \qquad (B.4)$$

the result

$$\int_0^a [U^L(r)]^2 dr = -2\frac{d\eta}{d\epsilon'}\sec^2\pi\eta$$

$$+\left[{}^0U_c^{L,n}, \frac{d}{d\epsilon'}({}^0U_c^{L,n})\right]_{r=a}$$

$$-2\tan\pi\eta\left[{}^0U_c^{L,n}, \frac{d}{d\epsilon'}({}^2U_c^{L,n})\right]_{r=a}$$

$$+\tan^2\pi\eta\left[{}^2U_c^{L,n}, \frac{d}{d\epsilon'}({}^2U_c^{L,n})\right]_{r=a}. \qquad (B.5)$$

This relation enables us to evaluate normalization integrals over the core region in terms of known functions at $r=a$ if η is known as a function of ϵ' for the potential under consideration.

In a similar manner, we may integrate the square of the Whittaker function[57] which vanishes at infinity,

$$W_{n,\,L+\frac{1}{2}}(2r/n)$$

$$=\Gamma(n+L+1)n^{-L-1}\cos[\pi(n-L-1)]$$
$$\times\{{}^{0}U_{c}{}^{L,n}(r)+K_{L}(n)\,{}^{2}U_{c}{}^{L,n}(r)\}, \quad (B.6)$$

where

$$K^{L}(n)=\frac{\Gamma(n-L)n^{2L+1}}{\Gamma(n+L+1)}\tan[\pi(n-L-1)], \quad (B.7)$$

and $n=+(\epsilon')^{-\frac{1}{2}}$. We obtain

$$\int_{a}^{\infty}[W_{n,\,L+\frac{1}{2}}(2r/n)]^{2}dr$$

$$=-[\Gamma(n+L+1)n^{-L-1}\cos\pi(n-L-1)]^{2}$$

$$\times\left\{\left[{}^{0}U_{c}{}^{L,n},\frac{d}{d\epsilon'}({}^{0}U_{c}{}^{L,n})\right]_{r=a}\right.$$

$$+2K^{L}(n)\left[{}^{0}U_{c}{}^{L,n},\frac{d}{d\epsilon'}({}^{2}U_{c}{}^{L,n})\right]_{r=a}+[K_{L}(n)]^{2}$$

$$\times\left[{}^{2}U_{c}{}^{L,n},\frac{d}{d\epsilon'}({}^{2}U_{c}{}^{L,n})\right]+\frac{2}{\pi}\frac{d}{d\epsilon'}K_{L}(n)\right\}. \quad (B.8)$$

At an eigenvalue we have $1/n^{2}=1/(m-\delta)^{2}$, where m is an integer, and from this we may show that $\tan\pi\eta = -K_{L}(n)$, as is also evident from (B.6) and (B.3). Hence at an eigenvalue we can combine (B.5) and (B.8) to give us

$$\int_{0}^{\infty}[U^{L}(r)]^{2}dr=\left\{-2\frac{d\eta}{d\epsilon'}\sec^{2}\pi\eta-\frac{2}{\pi}\frac{d}{d\epsilon'}K_{L}(n)\right\}, \quad (B.9)$$

where we normalize U according to (B.3).

APPENDIX C. QUANTUM DEFECT DATA FOR THE ALKALI METALS

In Table II we list formulas quadratic in $\epsilon'=1/n^{2}$ (the negative of the energy in Rydberg units) which reproduce the values of η obtained from the *experimental* term values of the alkali metals for $L=0$, 1. These expressions fit exactly the values of η for the lowest three valence eigenvalues and are very little in error for the higher eigenvalues.[58]

In Table III we list coefficients for expressions of the form

$$\Delta\eta=\left(\frac{a_{1}}{r_{0}{}^{3}}+\frac{a_{2}}{r_{0}{}^{2}}\right)+\left(\frac{b_{1}}{r_{0}{}^{3}}+\frac{b_{2}}{r_{0}{}^{2}}\right)\epsilon', \quad (C.1)$$

[57] Reference 26, p. 339.
[58] See reference 9, Sec. X.

TABLE II. Interpolation expressions[a,b] for experimental η for alkali metals for $L=0$, 1.

Li:	$L=0$,	$\eta=+(0.399501)+(0.029405)\epsilon'+(0.00238)\epsilon'^{2}$
	$L=1$,	$\eta=+(0.047366)+(0.02092)\epsilon'+(0.02886)\epsilon'^{2}$
Na:	$L=0$,	$\eta=+(1.347970)+(0.06197)\epsilon'+(0.01071)\epsilon'^{2}$
	$L=1$,	$\eta=+(0.855151)-(0.01791)\epsilon'+(0.04443)\epsilon'^{2}$
K:	$L=0$,	$\eta=+(2.180059)+(0.13915)\epsilon'+(0.0502)\epsilon'^{2}$
	$L=1$,	$\eta=+(1.711928)+(0.07617)\epsilon'+(0.0801)\epsilon'^{2}$
Rb:	$L=0$,	$\eta=+(3.13119)+(0.18164)\epsilon'+(0.08790)\epsilon'^{2}$
	$L=1$,	$\eta=+(2.646250)+(0.163965)\epsilon'+(0.06192)\epsilon'^{2}$
Cs:	$L=0$,	$\eta=+(4.04808)+(0.2586)\epsilon'+(0.1054)\epsilon'^{2}$
	$L=1$,	$\eta=+(3.5696)+(0.3019)\epsilon'+(0.0479)\epsilon'^{2}$

[a] These expressions reproduce experimental values of η obtained from the three lowest valence eigenvalues for each L. (See Table II of reference 9.) For $L=1$, spin-orbit splitting has been neglected, and the eigenvalue taken as the center of gravity of the doublet. Eigenvalues were converted from wave number (cm^{-1}) to Rydberg units using a finite mass Rydberg constant appropriate to each element.
[b] Here $\epsilon'=1/n^{2}$ is the negative of the energy in Rydberg units.

which may be *subtracted* from the corresponding formulas of Table II in order to obtain approximate expressions for η appropriate to the fictitious potential $V^{1}(r)$ of Sec. 3 which is exactly equal to $-2/r$ for $r>r_{0}$. The free ion potential has been assumed to differ from this for $r>r_{0}$ by a polarization term of the form (3.1). That we can neglect contributions to $V(r)$ from the small probability of finding a core electron at values of r_{0} of interest is evident from Table IV. Values of α' for use in (3.1) are listed in Table IV and have been taken from work of Pauling.[59] These may not be too accurate and indeed differ appreciably from those computed recently by Tessman, Kahn, and Shockley.[60] The latter values give quantum defects for $L=3$ which are larger than those observed experimentally, so that we have preferred Pauling's smaller values. This polarization correction is not accurate to better than perhaps 30%.

The coefficients in Table III were obtained by evaluating by perturbation methods the change in η, at the three lowest valence eigenvalues for each L, due to replacing the ion potential $(-2/r-2\alpha'/r^{4})$ by the Coulomb potential $(-2/r)$ for $r>r_{0}$. One can show from the

TABLE III. Polarization corrections[a,b] to η for alkali metals for $L=0$, 1.

Metal	L	a_1	a_2	b_1	b_2
Li	0	+0.0217	−0.00426	+0.0805	−0.0118
	1	+0.0463	−0.0130	+0.0918	+0.0335
Na	0	−0.0628	+0.0332	+1.172	−0.261
	1	+0.4044	−0.0890	−0.176	+0.369
K	0	−0.620	+0.212	+8.317	−1.595
	1	+1.870	−0.324	−0.529	+1.204
Rb	0	−1.698	+0.486	+17.02	−3.195
	1	+3.316	−0.523	−2.620	+2.123
Cs	0	−3.114	+0.826	+33.40	−5.844
	1	+5.447	−0.757	−3.855	+3.127

[a] See Eq. (C.1). Note that the value of $\Delta\eta$ obtained from (C.1) and this table is to be *subtracted* from the experimental η of Table II. The values of r_0 appropriate to (C.1) are in units of the Bohr radius of hydrogen.
[b] Calculated from (C.2).

[59] See reference 32, Chap. 8.
[60] Tessman, Kahn, and Shockley, Phys. Rev. 92, 890 (1953).

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Table IV. Deviations from Coulomb potential for alkali ions.[a]

Element	r_s	r_i	$Z(0.7r_i)$	$2[Z_p(0.7r_i)-1]$	$Z(r_i)$	$2[Z_p(r_i)-1]$	$2[Z_p(r_i)-1]/r_i$	α'	$2\alpha'/r_i^4$
Li	3.19[b]	2.81[b]						0.099	
Na	3.92[b]	3.45[b]						0.611	
K	4.84[b]	4.26[b]	0.22[c,d]	0.055[c,d]	0.018[c,d]	0.003[c,d]	0.0007[c]	2.83	0.017
			0.12[e,f]	0.025[e,f]	0.005[e,f]	<0.001[e,f]	<0.0002[e]		
Rb	5.17[b]	4.55[b]	0.36[c,g]	0.094[c,g]	0.03[c,g]	0.006[c,g]	0.0013[c]	4.77	0.022
Cs	5.51[b]	4.85[b]	0.57[c,d]	0.15[c,d]	0.05[c,d]	0.008[c,d]	0.0016[c]	8.22	0.027

[a] r_s =equilibrium equivalent sphere radius at 4.2°K in atomic units [Bohr radius =1 atomic unit of length =0.529 A; ionization energy of hydrogen (infinite nuclear mass) =1 unit of energy =1 Rydberg =13.60 ev]; r_i =equilibrium inscribed sphere radius at 4.2°K in atomic units; $Z(r)$ =total charge situated beyond radius r in the singly ionized atom, in units of charge of the electron; $Z_p(r)$: potential= $-2Z_p(r)/r$ in the singly ionized atom (neglecting polarization); α': polarization correction to potential for the valence electron in the neutral atom is $-2\alpha'/r^4$.
[b] C. A. Swenson, Phys. Rev. 99, 423 (1955).
[c] Calculated without exchange.
[d] D. R. Hartree, Proc. Roy. Soc. (London) A143, 506 (1934).
[e] Calculated with exchange.
[f] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A166, 450 (1938).
[g] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A151, 96 (1935).

differential equation (2.2) that, to first order in α',

$$\Delta\eta = \left(\alpha'\int_{r_0}^{\infty}[r^{-4}(U^L)^2]dr\right)\Big/\sec^2\pi\eta, \qquad (C.2)$$

where U^L and η are evaluated at the eigenvalue of $V^1(r)$ (and U^L is therefore a multiple of the Whittaker function which approaches zero at infinity). U^L is normalized as in (B.3). In practice these integrals were evaluated numerically for two values of r_0 (near r_i and r_s of Table IV) at the experimental eigenvalues using the asymptotic expansion of the Whittaker function.[61] These computed values of $\Delta\eta$ for a given r_0 vary less smoothly as functions of energy than the original experimental η. We attribute this to the fact that $-2/r-V(r)$ approaches zero asymptotically for the true ion potential, whereas $-2/r-V^1(r)$ drops abruptly to zero at a finite r. We have chosen to approximate these computed

Table V. Polarization corrections[a,b] to η for the alkali metals for $L=2$.

Metal	L	$1/n^2$	η_{exp}[c]	a_1	a_2
Li	2	0.1112205	0.00300	−0.0649	+0.0400
		0.0625524	0.00239	−0.0357	+0.0250
		0.0400282	0.00218	−0.0270	+0.0202
Na	2	0.1118769	0.02095	−0.4044	+0.2551
		0.0628869	0.01756	−0.0990	+0.1216
		0.0402139	0.01654	−0.0395	+0.0904
K	2	0.1227898	0.26634	+1.649	+0.2292
		0.0693696	0.26568	+2.631	−0.2553
		0.0439638	0.26857	+2.646	−0.3358
Rb	2	0.1306385	1.36247	+3.570	−0.1352
		0.0727987	1.35303	+3.941	−0.4931
		0.0455865	1.35044	+3.485	−0.4756
Cs	2	0.153516	2.4828	+3.795	−0.4216
		0.080100	2.4791	+1.629	−0.1064
		0.048698	2.4758	+0.400	+0.1275

[a] See Eq. (C.3). Note that the value of $\Delta\eta$ obtained from (C.3) and this table is to be subtracted from η_{exp} at the eigenvalues. The values of r_0 appropriate to (C.3) are in units of the Bohr radius of hydrogen.
[b] Calculated from (C.2).
[c] Table II of reference 9.

[61] Reference 26, p. 343.

values of $\Delta\eta$ by an expression linear in ϵ' and have found that their variation with r_0 is fairly well given by (C.1). The expressions obtained from Table III agree with all of our computed values within 10%.

Values of $\Delta\eta$ obtained from (C.2) differ significantly from those obtained[62] from the WKB approximation. We attribute this to the inaccuracy of the WKB method in calculating the difference in η for two potentials differing by a rapidly varying discontinuous function $(2\alpha'/r^4, r>r_0)$.

For $L=2$ the experimental values of η vary less smoothly with energy than do those for $L=0$, 1, and the valence eigenvalues span a smaller range of energy. Consequently extrapolation of η to energies perhaps half a Rydberg unit below the lowest valence eigenvalue is much less reliable than for $L=0$, 1. Furthermore, values of the polarization correction $\Delta\eta$ are larger than for $L=0$, 1. We have evaluated $\Delta\eta$ at three eigenvalues using (C.2), and we list in Table V the experimental value of η and coefficients for the evaluation of $\Delta\eta$ from the formula

$$\Delta\eta = \left(\frac{a_1}{r_0^3}+\frac{a_2}{r_0^2}\right), \qquad (C.3)$$

both for each experimental eigenvalue. In Table VI we list for K, Rb, and Cs an expression for what we consider the most reasonable extrapolation of $(\eta_{exp}-\Delta\eta)$ (for a single value of r_0, as given in the table) in the energy range of principal interest. We list in addition two expressions labeled "upper bound" and "lower bound" which represent approximate bounds on possible alternative extrapolations. Curves appreciably above the "upper bound" lead with (B.5) to a negative value in some range of energy for the normalization integral $\int_0^a [U^L(r)]^2dr$ with a between r_i and r_s of Table IV, an obviously absurd result. Curves below the "lower bound" do not seem consistent with smooth extrapolation from the values of $(\eta_{exp}-\Delta\eta)$ at the eigenvalues. The general shape of the curve was checked by com-

[62] Table III of reference 9.

TABLE VI. Values of η for alkali metals,[a] $L=2$, with polarization correction.[b]

Metal	r_0	A	B	C	Range	Comments
Li	2.880	+0.00086	+0.00032	0	all	
Na	3.511	+0.01041	−0.0072	0	all	
K	4.351	+0.2674	−0.3177	+0.3863	$1/n^2 < 0.14$	
	4.351	+0.2672	−0.2969	+0.2289	$1/n^2 > 0.14$	Reasonable
	4.351	+0.2568	−0.1825	+0.1438	$1/n^2 > 0.14$	Upper bound
	4.351	+0.2643	−0.2750	+0.0167	$1/n^2 > 0.14$	Lower bound
Rb	4.651	+1.3390	−0.0168	−0.2094	$1/n^2 < 0.15$	
	4.651	+1.3371	+0.0385	−0.5256	$1/n^2 > 0.15$	Reasonable
	4.651	+1.3425	−0.0700	−0.0500	$1/n^2 > 0.15$	Upper bound
	4.651	+1.3336	+0.1435	−1.1214	$1/n^2 > 0.15$	Lower bound
Cs	4.961	+2.4592	+0.2151	−0.9923	$1/n^2 < 0.17$	
	4.961	+2.4642	+0.1687	−0.9023	$1/n^2 > 0.17$	Reasonable
	4.961	+2.4611	+0.1622	−0.7289	$1/n^2 > 0.17$	Upper bound
	4.961	+2.454	+0.3000	−1.3750	$1/n^2 > 0.17$	Lower bound

[a] The coefficients given are appropriate to an expression of the form $\eta = A + B(1/n^2) + C(1/n^2)^2$ for the range of $1/n^2$ indicated and for the listed value of r_0. See text following Eq. (C.3) for significance of the notations "reasonable," "upper bound," and "lower bound."
[b] Polarization corrections were evaluated at the eigenvalues from the data of Table V for the value of r_0 listed above.

puting η exactly for a potential which is constant in the core region and equal to $-2/r$ outside the core, the value of the constant potential being such as to give the same value of η at $E=0$ as found for the alkali atom. For another choice of r_0, one may evaluate $(\eta_{exp} - \Delta\eta)$ at the eigenvalues from Table V and (C.3) and determine the most reasonable extrapolation, using approximately the same "upper bound" curve used here. There is evidently a large discrepancy between the "lower bound" and "upper bound" curves at an energy of $\epsilon' = 0.5$ and consequently a large uncertainty in the extrapolated value of η. Results of calculations on the band structure of the alkalis undertaken to date have not been very sensitive to this uncertainty, so that they

appear reliable despite this difficulty. Any result that is sensitive to this uncertainty of course is not reliable.

For $L=2$ for Li and Na, $(\eta_{exp} - \Delta\eta)$ is so small that we have chosen to approximate it by an expression linear in ϵ' over the range for which $(\eta_{exp} - \Delta\eta)$ is positive. Expressions for appropriate values of r_0 are given in Table VI.

As a general criterion of the reliability of any extrapolation formula, we suggest comparing the value obtained from the formula at some energy of interest with that obtained by extrapolating $(\eta_{exp} - \Delta\eta)$ graphically from the values at the valence eigenvalues. Reliable theoretical results of band calculations must not depend sensitively on such differences.