sign of this coefficient for LiF and NaCl, as calculated from the theory of Mott and Littleton. In all the other cases its sign is well established as negative, and the calculations indicate that the contribution to the decrease of the low frequency dielectric constant from the decrease of the inner field is large. This is shown by the values of $\Delta\epsilon\gamma/\Delta\epsilon$ listed in the third and sixth columns of Table IV.

V. CONCLUSION

The low frequency dielectric constant of ionic crystals was measured at high pressures and found to decrease with increasing pressure. The existing lattice theories explain this decrease as arising not only from the decrease in the lattice polarizability produced by the increase of the repulsive forces but also because the increasing overlap of adjacent ions at high pressures reduces the internal field.

In contradistinction to liquids and gases, the change in density of ionic crystals plays a minor role compared to the change in overlap in affecting the low frequency dielectric constant.

The author wishes to thank his sponsor, Professor A. W. Lawson, for his interest and helpful suggestions throughout the course of the work; Dr. J. B. Garrison for many interesting discussions; Mr. K. Lindholm and Mr. N. D. Nachtrieb for construction of the high pressure apparatus; Mr. J. Getsholtz for optical polishing; Mr. F. Bruce and Mr. T. Y. Tang for assistance in taking data, and the staff of the Institute for the Study of Metals, where this research was carried out, for their generous cooperation at all times. In addition, the author wishes to thank Mr. W. H. Henson of the Norton Company for the gift of the MgO crystals, and Miss Flora E. Riddle of the Pipestone Indian School, Pipestone, Minnesota, for the gift of some pipestone which is used as a high pressure packing.

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A Simplified Method of Computing the Cohesive Energies of Monovalent Metals

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A method is developed which, within the limits of the spherical cell approximation first presented by Wigner and Seitz, permits the evaluation of the cohesive energy, lattice constant, and compressibility of a monovalent metallic solid without the explicit computation of a central field for the atom. It is shown that empirical values of the first few s and p levels of the free atom can supply the relevant information usually obtained through the computation of a central field, so that a considerable simplification is possible. The method is applied to the calculation of the usual solid state parameters for the alkali metals, Na, K, and Rb. The results for Na compare very favorably with experiment as well as with those gained by previous workers. The K and Rb computations agree decidedly less well with experiment, but the values for K are appreciably better than those previously computed utilizing an explicit central field. The errors shown by the K and Rb computations are believed to be the inevitable consequence of any theory derived by replacing the effect of the core electrons by an equivalent central field rather than a result of any peculiarities inherent in the present approach.

I. Introduction: In the well-known s-sphere approximation developed by Wigner and Seitz[1] for the computation of the physical parameters of metallic lattices the ground-state energy of the solid is the lowest eigen-energy, ϵ_0, of the equation

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

solved with $l=0$ subject to the boundary conditions that $U^{(0)}$ be zero at the origin and that

$$\left[r\frac{dU^{(0)}}{dr}\right]_{r=r_s}=U^{(0)}(r_s). \tag{2}$$

In these equations the radius, r, is measured in Bohr units and the energy, ϵ_0, in Rydberg units. The quantity r_s is the radius of the s-sphere and is related to the lattice parameter, d, of a body-centered cubic lattice like that of the alkali metals by the equation

$$d=(8\pi/3)^{\frac{1}{3}}r_s. \tag{3}$$

The potential $V(r)$ is taken to be identical with that of the free atom, so that (1) is just the radial wave equation of the free atom.

In addition to its ground-state energy the solid possesses a mean Fermi energy which, at absolute zero, is given by

$$\epsilon_F=\frac{9\pi}{10}\left(\frac{3}{2\pi}\right)^{\frac{1}{3}}\frac{\alpha}{r_s^2}=\frac{2.21\alpha}{r_s^2}, \tag{4}$$

where α is a constant which Bardeen[1] has shown is

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* Junior Fellow, Society of Fellows.

[1] E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934); F. Seitz, Phys. Rev. 47, 400 (1935). This outline of the method follows the development presented by J. Bardeen, J. Chem. Phys. 6, 367 (1938).

given by

$$\alpha=\frac{r_s[U^{(0)}(r_s)]^2}{3\int_0^{r_s}[U^{(0)}]^2dr}\left[\frac{r}{U^{(1)}}\frac{dU^{(1)}}{dr}-1\right]_{r=r_s}. \tag{5}$$

Here $U^{(1)}(r)$ is that solution of (1) with $l=1$ which goes to zero at the origin.

The total binding energy of the solid is given by

$$\epsilon_B=\epsilon_0+\epsilon_F+\epsilon_C, \tag{6}$$

where ϵ_C is a small correction[2] term introduced to allow for effects of electronic interactions and of deviations of the solid state potential function from that of the free atom. This correction energy may be approximated by

$$\epsilon_C=\frac{0.284}{r_s}-\frac{0.576}{r_s+5.1}. \tag{7}$$

The value of r_s for which ϵ_B takes its minimum value is related to the lattice constant of the metal at absolute zero by (3). The value of this minimum binding energy less the first ionization potential of the free atom is the cohesive energy of the metal at absolute zero. The compressibility of the metal can be computed from the formula

$$\frac{1}{\kappa}=\frac{3.87\cdot 10^{12}}{r_s}\frac{d^2\epsilon_B}{dr_s^2}\ \mathrm{cm^2/dyne}. \tag{8}$$

These three parameters exhaust the important physical information to be gained without more knowledge of the zone structure of the metal than is available in the *s*-sphere approximation.

The problem of computing the above parameters is now reduced to that of integrating Eq. (1) for $l=0$ and $l=1$. The solutions produced must all be zero at the origin and in the case $l=0$ must satisfy the additional condition (2) at the cell boundary. For $l=1$ the desired solutions are completely determined (except in amplitude) by the boundary condition at the origin and the condition that the energy appearing in the wave equation be ϵ_0, the eigen-energy of the solution $U^{(0)}$. Such solutions have been carried out by Wigner and Seitz[1] for Na, by Seitz[1] for Li, by Bardeen[1] for Na and Li, and by Gorin[3] for K. All of these authors utilized central fields of the Prokofjew or of the Hartree type and carried through graphical or numerical integrations of (1). All but Gorin obtained reasonably good agreement with experiment.

Such numerical solutions of the wave equation are entirely practicable, but the required integrations are lengthy and are completely dependent upon the even more tedious computation of a potential function. The function matching method developed here succeeds in avoiding many of these complexities. For it is noted that values of the physical parameters of metallic solids depend primarily upon the behavior of the solid state wave functions outside the atomic core, and that in this region the family of wave functions which are zero at the origin is completely determined by the value of its logarithmic derivative. This logarithmic derivative is, in turn, a single-valued function of the energy parameter in the wave equation and can, with the aid of laboratory values of the first few energy levels of the free atom, be approximated without an explicit knowledge of $V(r)$. The procedure, of course, assumes the existence of some such "best central field" for the atom, but it avoids the difficulties inherent in the calculations of and with such a field.

II. Outline of the Function Matching Method: The functions $U^{(l)}(r)$ may be considered to form a one-parameter family (parameter ϵ_0) of those solutions of (1) which are zero at the origin. In terms of these a new function $\phi_R^{(l)}(\epsilon_0)$ may be defined as the logarithmic derivative of $U^{(l)}(r)$ at $r=R$, i.e., by

$$\phi_R^{(l)}(\epsilon_0)=\left[\frac{1}{U^{(l)}}\frac{dU^{(l)}}{dr}\right]_{r=R}. \tag{9}$$

It can now be shown quite generally that, for sufficiently small values of R, $\phi_R^{(l)}(\epsilon_0)$ is a smooth, non-oscillating function of ϵ_0. For since the function $V(r)$ must be expressible in Rydberg units in the form $-2Z/r+g(r)$, where $g(r)$ is an analytic function with a zero at the origin, it follows straightforwardly that the logarithmic derivative can always be expressed in the form

$$\phi_R^{(l)}(\epsilon_0)=\frac{1}{R}+\sum_{k=0}^{\infty}a_k^{(l)}(\epsilon_0)R^k, \tag{10}$$

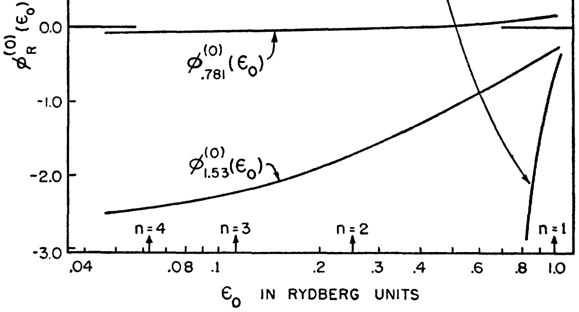

FIG. 1. Logarithmic derivative of hydrogenic wave functions as a function of energy for various sphere radii.

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[2] These corrections are discussed completely in the references above and in E. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. 34, 678 (1938).

[3] E. Gorin, Physik. Zeits. Sowjetunion 9, 328 (1936).

TABLE I. Matching radius and hydrogenic deviations for computations on Na, K, and Rb.

	Na(*s* and *p*)	K(*s*)	K(*p*)	Rb(*s* and *p*)
R	2.00	2.53	3.12	3.12
$Z_{\text{eff}}-1$	0.11[a]	0.08[b]	0.02[b]	0.05[c]

[a] W. Prokofjew, Zeits. f. Physik **58**, 255 (1929).
[b] D. R. Hartree, Proc. Roy. Soc. **A143**, 506 (1934).
[c] D. R. Hartree, Proc. Roy. Soc. **A151**, 96 (1935).

in which the coefficients $a_k^{(l)}$ are polynomial functions of the energy parameter ϵ_0. Further, the degree of these polynomial functions increases quite slowly with k; $a_0^{(l)}$ is independent of ϵ_0, $a_1^{(l)}$ and $a_2^{(l)}$ are linear functions of ϵ_0, and, generally, $a_{2k-1}^{(l)}$ and $a_{2k}^{(l)}$ are polynomials of degree k in ϵ_0. Thus, for all physically significant values of ϵ_0 and for sufficiently small values of R, $\phi_R^{(l)}(\epsilon_0)$ will be constant since terms beyond $a_0^{(l)}$ may be discarded. With R somewhat larger, so that the coefficients through $a_3^{(l)}$ must be kept, $\phi_R^{(l)}(\epsilon_0)$ will show a linear dependence on ϵ_0, etc. The increase of the complexity of the behavior of $\phi_R^{(l)}(\epsilon_0)$ is slow, and the function will be seen to be essentially simple for reasonably large values of R.

An example of this behavior is shown in Fig. 1, where $\phi_R^{(0)}(\epsilon_0)$ is plotted as a function of energy for values of $|\epsilon_0|\leq 1$ *Ry.* and for $R=0.781$, 1.53, and 2.53 a.u. These curves are derived by integrating (1) with a hydrogenic potential, $V=-2/r$, in which case exact solutions, with zeros at the origin, are given by Whittaker's[4] function $M_{n,\frac{1}{2}}(2r/n)$ with $n=1/(-\epsilon_0)^{\frac{1}{2}}$. It will be noted that on a scale which places the radius of the first Bohr orbit at unity, the logarithmic derivative is almost constant for $R=0.753$, well behaved for $R=1.53$, and shows an infinite discontinuity for $R=2.53$. It is believed that curves computed with other atomic potential functions will show qualitatively similar behavior.

This behavior is made physically reasonable by remembering that for small R, $|V(R)|\gg|\epsilon_0|$ so that changes in ϵ_0 have little effect on the solutions of the wave equation, or on the logarithmic derivatives of these solutions. This is confirmed quantitatively in Fig. 1, for if $\epsilon_0=-1$ is the minimum energy of physical interest, then $\epsilon_0=V(R)=-1$ for $R=2$, which is precisely the range in which $\phi_R^{(0)}(\epsilon_0)$ ceases to behave in an essentially simple manner. When heavier atoms are considered, the same reasoning justifies our expecting essentially smooth behavior of $\phi_R^{(l)}(\epsilon_0)$ for all values of R within or immediately outside of the atomic core. This is illustrated by the Na *s*-state wave functions, computed with a non-hydrogenic Prokofjew potential, by Wigner and Seitz[1] which show no appreciable dependence on ϵ_0 for values of the radius $r\leq 2.3$ atomic units.

At large distances from the core of the atom (say for all $r\geq R'$), the potential function, $V(r)$, must exhibit an essentially hydrogenic behavior. In this hydrogenic region the general solution of (1) is given by an arbitrary linear combination of Whittaker's[5] two well-known solutions of the confluent hypergeometric equation, $W_{n,l+\frac{1}{2}}(2r/n)$ and $W_{-n,l+\frac{1}{2}}(-2r/n)$, where again $n=1/(-\epsilon_0)^{\frac{1}{2}}$. The first of these solutions, $W_{n,l+\frac{1}{2}}(2r/n)$ is known to go to zero as $r\rightarrow\infty$, so that if the atomic term levels of the free atom are given by the set $\epsilon_k(k=1,2,3,\ldots)$, then throughout the region $r\geq R'$ the functions $W_{n_k,l+\frac{1}{2}}(2r/n)$ computed with $n_k=1/(-\epsilon_k)^{\frac{1}{2}}$ are the radial wave functions of the valence electron of the free atom. It follows that whenever $\epsilon_0=\epsilon_k$, the function $U^{(l)}(r)$ must be identical (except in amplitude) with the function $W_{n_k,l+\frac{1}{2}}(2r/n)$ throughout the region $r\geq R$, for whenever $\epsilon_0=\epsilon_k$ the functions $U^{(l)}(r)$ are the exact radial wave functions of the free atom. This leads immediately to the conclusion that whenever $\epsilon_0=\epsilon_k$, the logarithmic derivative of the functions $W_{n_k,l+\frac{1}{2}}(2r/n)$, evaluated at $R\,(\geq R')$, must be exactly equal to $\phi_R^{(l)}(\epsilon_k)$.

To this point the development is exact. The next step, however, requires a crucial assumption whose justification will be postponed to the next section. Assume that there is some radius R which is small enough so that $\phi_R^{(l)}(\epsilon_0)$ is an essentially well-behaved function of ϵ_0 and large enough so that $V(r)$ is essentially hydrogenic for all $r\geq R$. Then values of the logarithmic derivative of the well-known functions $W_{n_k,l+\frac{1}{2}}(2r/n)$ computed at $r=R$ and for $n_k=1/(-\epsilon_k)^{\frac{1}{2}}$ will yield a discrete set of points lying on the smooth curve $\phi_R^{(l)}(\epsilon_0)$, and a simple polynomial function passing through these points will serve to represent $\phi_R^{(l)}(\epsilon_0)$ throughout the range of ϵ_0 of physical interest. For any atom satisfying the above assumption, it is thus possible, knowing the values of ϵ_k, to produce a close approximation to $\phi_R^{(l)}(\epsilon_0)$ without a knowledge of the central field of the atom. Further, once this function is given it is possible, for all $r\geq R$ and for any ϵ_0, to compute the solutions, $U^{(l)}(r)$, which satisfy (1) and are zero at the origin. This follows since, in the hydrogenic region, $U^{(l)}(r)$ must be some linear combination of the two known functions $W_{n,l+\frac{1}{2}}(2r/n)$ and $W_{-n,l+\frac{1}{2}}(-2r/n)$, and this linear combination is completely determined (except in amplitude) by its logarithmic derivative $\phi_R^{(l)}(\epsilon_0)$, which is now known.

Finally, if $R\leq r_s$ all the solid state parameters discussed in Section I may be computed utilizing the wave function derived by the procedure above. The only exception is presented by the quantity α, whose definition includes the term

$$\int_0^{r_s}[U^{(0)}(r)]^2dr.$$

However, since the integrand is negligible for values of r inside the core, reasonably accurate values of α are computed by extrapolating values of the integrand into

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[4] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London), fourth edition, §16.1.

[5] Reference 4, §16.12.

TABLE II. The functions $\phi_R^{(0)}$ and $\phi_R^{(1)}$ for Na, K, and Rb: data and results.

Element	ms	$-\epsilon_k$	Source	R	$\phi_R^{(0)}(\epsilon_0)$	mp	$-\epsilon_k$	Source	R	$\phi_R^{(1)}(\epsilon_0)$
Na	3 4 5 6	0.3778 0.1432 0.07518 0.04628	a	2.000	$-0.1820\epsilon_0^2$ $+0.9252\epsilon_0$ $+0.8704$	3 4 5 6	0.22232 0.10197 0.05844 0.03786	b	2.000	$-0.6088\epsilon_0^2$ $+0.8568\epsilon_0$ $+1.7348$
K	4 5 6	0.3191 0.1274 0.06886	a	2.531	$0.8313\epsilon_0$ $+1.0687$	4 5 6 7	0.200522 0.093884 0.054741 0.035893	c	3.125	$-1.0092\epsilon_0^2$ $+1.7112\epsilon_0$ $+1.3340$
Rb	5 6 7	0.3071 0.1236 0.06725	a	3.125	$1.7706\epsilon_0$ $+0.2943$	5 6 7	0.191121 0.090511 0.053187	d	3.125	$0.7342\epsilon_0^2$ $-0.3658\epsilon_0$ $+0.5078$

[a] R. F. Bacher and S. Goudsmit, *Atomic Energy Levels* (McGraw Hill Book Company, New York, 1932).

[b] C. E. Moore, *A Multiplet Table of Astrophysical Interest* (Princeton, New Jersey, 1945, published by the observatory). Corrections for vacuum wavelengths were taken from the *International Critical Tables*.

[c] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Circular 467, Washington, D. C., 1949), Vol. I.

[d] H. R. Kratz, Phys. Rev. **75**, 1846 (1949).

the core from the hydrogenic region in which it is accurately known.

The argument above may be conveniently summarized as follows. For a given value of ϵ_0, the solutions $U^{(l)}(r)$ of the wave equation which is zero at the origin must be identical (in the hydrogenic region $r \geq R$) with some linear combination of Whittaker's two well-known functions. The particular linear combination desired is completely determined by the function $\phi_R^{(l)}(\epsilon_0)$, which is just the logarithmic derivative of the correct solution, $U^{(l)}(r)$, computed at R. If the hydrogenic region extends near enough the core so that $\phi_R^{(l)}(\epsilon_0)$ is a well-behaved function of ϵ_0, then the behavior of $\phi_R^{(l)}(\epsilon_0)$ (and hence of the wave functions in the hydrogenic region) is completely determined by the first few values of $\phi_R^{(l)}(\epsilon_k)$, where the ϵ_k are the atomic term levels. Finally, with the term levels given, these values of $\phi_R^{(l)}(\epsilon_k)$can be computed from the first of Whittaker's functions, $W_{n_k, l+\frac{1}{2}}(2r/n)$.

III. The Choice of a Matching Radius R: There is of course no single radius R beyond which the potential function of a complex atom is rigorously hydrogenic. In practice therefore it is necessary to choose the largest matching radius R such that the points $\phi_R^{(l)}(\epsilon_k)$ lie on a curve which may be described by a simple polynomial. If the field is nearly enough hydrogenic at the largest R, the function matching approach may always be applied, for examination of Fig. 1 clearly disposes of the danger that it should be possible to pass a smooth curve through the points $\phi_R^{(l)}(\epsilon_k)$ under circumstances in which the function $\phi_R^{(l)}(\epsilon_0)$ was itself oscillatory or otherwise irregular.

The computations discussed in the next section show clearly that the points $\phi_R^{(l)}(\epsilon_k)$ can be accurately fitted by a simple curve at distances, R, well outside the atomic core. It will now be indicated that the deviations of the potential from hydrogenic behavior at these distances may be expected to have negligible effect upon the results of computation, for the deviations themselves are small, and the errors they introduce are, to a first approximation, mutually compensating.

TABLE III. Ground state energy and α as a function of sphere radius for Na, K, and Rb.

	Na		K		Rb	
z_s	$-\epsilon_0$	α	$-\epsilon_0$	α	$-\epsilon_0$	α
4.0	0.1440					
4.5	0.6150		−0.0826			
5.0	0.6644	0.962	0.4686		0.3986	
5.5	0.6235	0.980	0.5281	0.745	0.5040	
6.0	0.5666	1.013	0.5070	0.909	0.4933	0.132
6.5	0.5125		0.4679	1.122	0.4584	0.427
7.0			0.4280		0.4202	0.781
7.5			0.3942		0.3866	

If the actual potential function of the atom is written in the standard form $V(r) = -2Z_{\text{eff}}/r$, then the value of $Z_{\text{eff}}-1$ at R is just the fractional deviation of the potential from hydrogenic behavior at the matching radius. Table I lists the matching radii used for the s and p computations for Na, K, and Rb and the corresponding values of $Z_{\text{eff}}-1$ derived from standard Hartree and Prokofjew fields for these atoms. It is observed that the deviations from hydrogenic behavior are comparatively small and that the worst deviation is found to occur for† Na, the only one of the elements for which the over-all computation yields excellent results.

It is not at once apparent that the "small" deviations listed in Table I will have a negligible effect on the computation of the solid-state parameters, but both theory and practice show this to be the case. For example, a repetition of the Na ground-state computation at $R = 2.53$ (an increase of 25 percent in matching radius which reduced $Z_{\text{eff}}-1$ from 0.11 to 0.03) changed the value of the ground-state energy by less than 1.5 percent throughout its range. This behavior, which was duplicated again and again during the computations, indicates both that the procedure is insensitive to changes in R, as it should be, and that a ten percent deviation from hydrogenic behavior at the matching

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† The Prokofjew field for Na would be expected to yield a larger value of $Z_{\text{eff}}-1$ than a Hartree field for the same element, since the former allows for the polarization of the core by the valence electron and the latter does not. However, an estimate of the polarization effect indicates that the Hartree deviation would be at least 0.05, so that the deviation for Na is at least as great as that for the other elements.

radius does not produce errors of equivalent magnitude in the end products of computation.

TABLE IV. Lattice constant, cohesive energy, and compressibility for Na.

	Experiment[a]	Wigner-Seitz[b]	Bardeen[b]	Kuhn and VV
d(A°)	4.25	4.74	4.53	4.14
Cohesive energy (K cal./mole)	26	23.2	23	25.9
$\kappa\cdot 10^{12}$ (cm^2/dyne)	12.3		12.0	13

[a] Except where otherwise noted experimental values are taken from J. Bardeen, J. Chem. Phys. **6**, 372 (1938).
[b] See reference 1.

That the error in the final product of the computation must be smaller than the deviations from hydrogenic behavior can also be discovered by a rigorous quantitative investigation of a closely analogous problem. Consider the potential $V(r)$ to be strictly hydrogenic $(V(r)=-2/r)$ for all $r\geq R'$ and to be given in the region $r\leq R'$ by $-2/r+g(r)$. Then for continuity of potential and field it is necessary that $g(R')=g'(R')=0$. Further, let the functions $U^{(l)}(r)$ be the exact solutions of (1) which are zero at the origin, and define an additional set of functions $W^{(l)}(r)$ which are exact solutions of the hydrogenic form of (1) and which are identical with the functions $U^{(l)}(r)$ for all $r\geq R'$. With these assumptions and definitions the errors due to matching in the non-hydrogenic region may be made explicit.

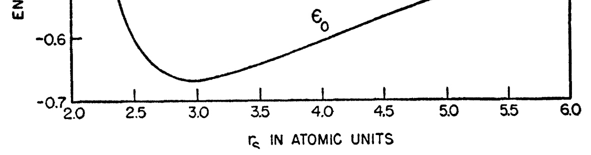

FIG. 2. Ground state and total energy *vs.* sphere radius for sodium.

For suppose that the matching process is carried out at a radius R $(<R')$ and that ξ $(\equiv R'-R)$ is a small quantity. The deviation from hydrogenic behavior of the potential function at the matching radius is then $0(\xi^2)$ and straightforward comparison of the two series expansions about R' shows that the difference between the correct wave functions $U^{(l)}$ and the hydrogenic wave functions $W^{(l)}$ used in computation is only $0(\xi^4)$. The difference between the correct logarithmic derivative $U^{(l)\prime}/U^{(l)}$ and the logarithmic derivative $\phi_R{}^{(l)}$ $(=W^{(l)\prime}/W^{(l)})$ computed with the hydrogenic wave functions is larger, being $0(\xi^3)$. But it can again be shown by the comparison of the appropriate series that when this "wrong" $\phi_R{}^{(l)}$ is used to select an appropriate "wrong" wave function $W^{(l)}$, the two errors are compensatory so that the net error is again $0(\xi^4)$. It follows that if the potential function $V(r)$ shows a small fractional deviation, δ, from hydrogenic behavior at the matching radius, then the total error in the final computation may be expected to be of order δ^2, which will normally be negligible.

IV. Computations and Results: Practical application of the method described in Section II requires an accurate knowledge of the values of the functions $W_{\pm n,\, l+\frac{1}{2}}(2r/n)$ over a wide variety of values of r and n. Since interest is not restricted to integral and half-integral values of n, the existing computations of the confluent hypergeometric function prove inadequate, and it is necessary either to compute Whittaker's functions over the range of r and n of physical interest or to develop a new form for the general solution of the hydrogenic wave equation.

The second alternative has proved the more practical, for it was possible, following a lead provided by Wannier and Jastrow,[6] to produce two independent solutions of the wave equation, $\overline{W}^{(l,\,n)}(r)$ and $\tilde{W}^{(l,\,n)}(r)$, which are related to the standard forms by the formulas

$$M_{n,\,l+\frac{1}{2}}(2r/n)=\Gamma(2l+2)n^{-l-1}\overline{W}^{(l,\,n)}(r) \tag{11a}$$

$$\begin{aligned} W_{n,\,l+\frac{1}{2}}(2r/n)=\Gamma(n+l+1)n^{-l-1}&\\ \times\{\cos(n-l-1)\pi\overline{W}^{(l,\,n)}(r)&\\ +\sin(n-l-1)\pi\tilde{W}^{(l,\,n)}(r)\}.& \end{aligned} \tag{11b}$$

The particular advantage of this choice of solutions is that both $\overline{W}^{(l,\,n)}(r)$ and $\tilde{W}^{(l,\,n)}(r)$ may be computed from the series form

$$\begin{aligned} \overline{W}^{(l,\,n)}(r)&=\sum_{k=0}^{\infty} n^{-2k}\overline{W}^{(l)}(r);\\ \tilde{W}^{(l,\,n)}(r)&=\sum_{k=0}^{\infty} n^{-2k}\tilde{W}^{(l)}(r); \end{aligned} \tag{12}$$

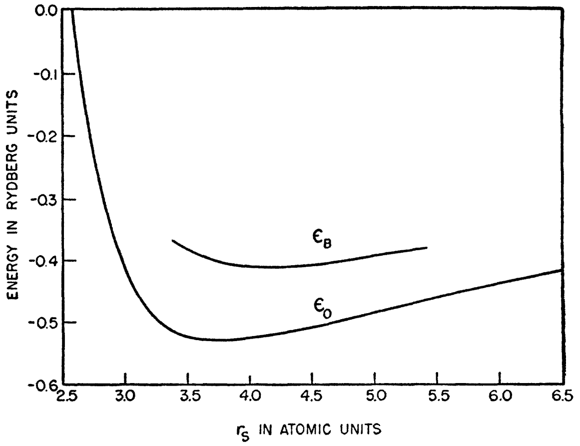

FIG. 3. Ground state and total energy *vs.* sphere radius for potassium (complete computation).

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[6] G. H. Wannier, Phys. Rev. **64**, 358 (1943). R. Jastrow, Phys. Rev. **73**, 60 (1948).

Table V. Lattice constant, cohesive energy, and compressibility for K.

	Experiment[a]	Gorin[b]		Kuhn and VV	
		Uncorrected	Corrected	Complete	Plane wave
d(A°)	5.27	5.8	5.8	4.51	5.01
Cohesive energy (K cal./mole)	22.6[c]	6	14.5	27.9	24.2
$\kappa\cdot 10^{12}$ (cm^2/dyne)	23.9			27	30

[a] See reference a, Table IV.
[b] See reference 3.
[c] F. Seitz, *The Modern Theory of Solids* (McGraw Hill Book Company, New York, 1940), p. 356. Bardeen quotes an earlier measurement in reference a, Table IV.

in which the coefficients $\bar{W}_k^{(l)}$ and $\tilde{W}_k^{(l)}$ are expressible in terms of Bessel functions of the first and second kind. The series (12) shows quite rapid convergence, so that if the coefficients are computed as functions of r, the complete wave functions can be rapidly determined for any value of n by a simple summation. It is really the versatility and manipulability of this form of the general solution of the hydrogenic wave equation which gives the present method its speed and simplicity. In fact, once the values of the coefficients have been tabulated, the computation of a set of curves like those in any one of the figures which follow is little more than a day's work. A complete analytic and numerical account of these solutions is presented elsewhere.[7]

One further remark may be of interest before the presentation of the results of the computations. It has been previously noted that for a suitably chosen value of R the points $\phi_R^{(l)}(\epsilon_k)$ must lie on a smooth curve, and it actually turns out during computation that the possibility of finding such a smooth curve is a very sensitive check on the consistency of a set of experimentally determined energy levels, ϵ_k. This was particularly true of the p-level computation, during which an error of a few tenths of an inverse centimeter in any one of the first four term levels made it impossible to fit a smooth curve to the computed points $\phi_R^{(1)}(\epsilon_k)$.

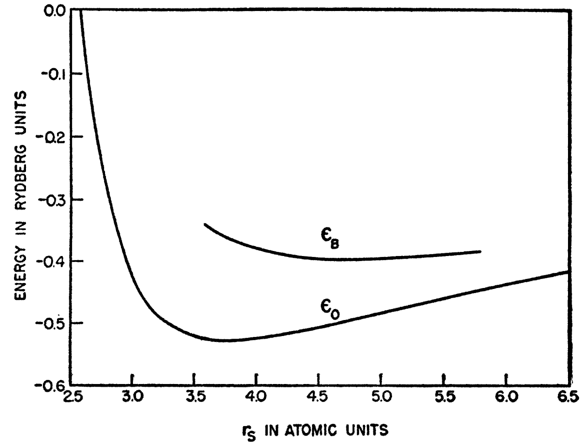

Fig. 4. Ground state and total energy *vs.* sphere radius for potassium (plane wave computation).

Table VI. Lattice constant, cohesive energy, and compressibility for Rb.

	Experiment[a]	Kuhn and VV Plane wave
d(A°)	5.60	5.20
Cohesive energy (K cal./mole)	18.9	24.2
$\kappa\cdot 10^{12}$ (cm^2/dyne)	31.9	26

[a] See reference a, Table IV.

This critical dependence of the products of computation on the precise values of the energy levels employed necessitated a thorough review of the data available on the p-levels of the alkali metals, and the authors are greatly indebted to Dr. Charlotte E. Moore of the Bureau of Standards for her invaluable assistance in locating the most accurate sources of this experimental information.

Table II below lists, for the elements Na, K, and Rb, the experimental energy levels used in the computations as well as the polynomial forms, $\phi_R^{(l)}(\epsilon_0)$, derived from these. In each case one more energy level of the atom is tabulated than was required to determine completely the corresponding polynomial. The extra energy level (normally the algebraically highest) was used to check the polynomial form and agreement was in all cases better than 0.1 percent. Table III gives the values, computed by the function matching method outlined above, of ϵ_0 and of α for various values of a new variable, $z_s=(8r_s)^{\frac{1}{2}}$.

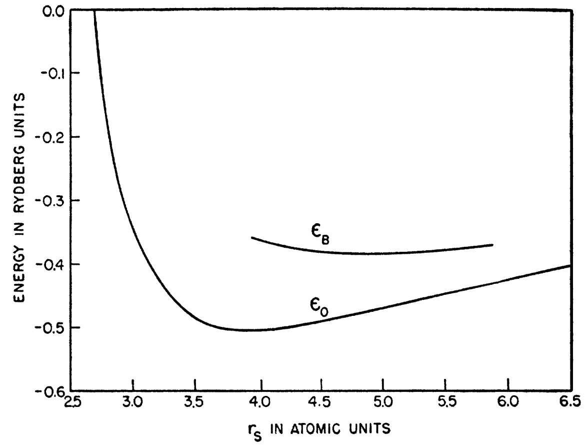

Fig. 5. Ground state and total energy *vs.* sphere radius for rubidium (plane wave computation).

In the range of values of r_s which are of greatest physical interest the functions $\epsilon_0(r_s)$ and $\alpha(r_s)$ are almost linear, so that it proved possible, by graphical interpolation, to compute values of these functions for intermediate values of r_s with an accuracy of better than 0.1 percent. Values computed in this manner were used with Eqs. (3), (4), (6)–(8) in the preparation of Figs. 2–5 and of Tables IV–VI. These tables present together the computed and experimental values of the three solid

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[7] T. S. Kuhn, Quarterly of Applied Math. (to be published).

TABLE VII. Estimate of fractional error due to dipole effects at the matching radius

	Na(s and p)	K(s)	K(p)	Rb(s and p)
$\eta/2R^3$	0.080	0.163	0.086	<0.264

TABLE VIII. Estimate of fractional error due to dipole effects at the sphere radius.

	Na	K complete	K plane wave	Rb
$\eta/2r_s^3$	0.011	0.037	0.026	<0.070

state parameters described in Section I. The results of previous computation are also tabulated for comparison.

Tables V and VI require further explanation. In the first of these Gorin's "uncorrected" results are the end products of a straightforward numerical integration of the wave equation utilizing a Hartree field; his improved or "corrected" results were gained from these by an essentially heuristic device, with little quantitative basis, designed to allow for increased "correlation effects" in the solid. Kuhn and Van Vleck's "complete" computation is the one described above. Because it appeared that much of the error in this result entered during the computation of α from Eq. (5), a second, approximate, computation of the binding energy was undertaken with $\alpha=1$, the value which would obtain in the plane wave case. These results are tabulated in the column headed "Kuhn and VV: plane wave." The values of α obtained in the "complete" rubidium computation were so anomalous that in this case only the "plane wave" computation is tabulated.

V. Conclusions: It will be noted immediately that, in the case of Na, the function matching method yields appreciably better results than those gained with the introduction of an explicit central field. It is not immediately clear that the extent of this improvement is more than fortuitous, since the agreement of these computations with experiment is probably better than ought to be expected from any theory which starts by assuming a spherical cell. But the improvement does confirm our earlier expectation that, in the spherical cell approximation, any results gained with the introduction of an explicit central field may be improved by the function matching method, since the latter bypasses the theoretical and practical difficulties inherent in explicit computation of a central field.

This conclusion is also supported in a general way by the computations for K and Rb. Both of these display marked deviations from experiment, but both are, almost uniformly, in better agreement with experiment than Gorin's computation with a Hartree potential. It is probable that the function matching method shares in the difficulties noted by those previous workers who have attempted a Wigner-Seitz computation for the heavier elements, but within the limits imposed by the uniform assumption that there is *some* best central field for atomic and solid state problems, the method developed above exhibits marked theoretical and practical advantages.

In an attempt to isolate the source of the error in our K and Rb computations, inconclusive attempts have been made to discover some approximation within the procedure which can be shown to break down more and more as the atomic number increases. Table I above, which lists the fractional deviation of the explicit fields from hydrogenic behavior at the matching radius, represents one such attempt. A similar estimate of this deviation at the sphere radius, r_s, (where the error introduced would not be self-compensating) gave even more negative results, for (except in the case of Na) the deviations were less than 0.2 percent, and neither at the matching radius nor at the sphere radius did the discrepancies show any marked increase with atomic number. The possibility that the error enters in fitting a smooth curve to the points $\phi_R^{(l)}(\epsilon_k)$ also seems barred, for again little increase in the difficulty of finding a fit was observed as the mass number increased.

It seems more probable that the existing errors are due to a distortion of the core by the valence electrons. To a first approximation such distortions may be treated as a simple polarization of the core, and this polarization effect does not appear in self-consistent fields like those used (except in the case of Na) for the computation of Table I. The contribution of this polarization to the potential function can, however, be estimated, for it may be expressed as a series whose leading (dipole) term is just η/r^4 Rydbergs, where η is the polarizability of the atom.

The constant η has been estimated by one of us[8] from the known quantum defects of non-penetrating orbits. With these values the fractional deviation due to polarization ($\eta/2r^3$) can be computed at the matching radius, R, and at the sphere radius, r_s. The results of such a computation are given in Tables VII and VIII below.

The estimates in Tables VII and VIII indicate clearly that the polarization effects do increase with atomic number, but there is question as to whether they are large enough to account for the observed discrepancies. The dipole effects represent a serious overestimate of the total polarization at radii so close to the core as those utilized above. The deviations at R are partially self-compensating, and those at r_s seem too small to account for the error. On balance, it is improbable that polarization effects are responsible for the whole of the gross error observed.

A more accurate account of the effects of core distortion would require the evaluation of Fock correlation and exchange integrals between valence and core electron wave functions. Such an analysis would probably do much to eliminate the errors, but it cannot be undertaken with the function matching method, since these correction terms demand a knowledge of the behavior of the wave functions within the atomic core.

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[8] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), p. 215 ff.