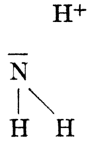
require the σ-bond wave function of multiple bonded N to be $(1/\sqrt{2})\psi_s+(1/\sqrt{2})\psi_p$ rather than[10] $\frac{1}{2}\psi_s+(\sqrt{3}/2)\psi_p$, and would favor structures of the type



for ammonia rather than that written $N\equiv H_3$ by Townes and Dailey.

TABLE IV. Nuclear constants of N^{14}.

Nucleus	Spin	Coupling in NF_3 $eQ(\partial^2V/\partial z^2)$	Quadrupole moment
N^{14}	1	-7.07 ± 0.10 Mc/sec.	0.01×10^{-24} cm^2

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An Application of the W.K.B. Method to the Cohesive Energy of Monovalent Metals

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A new method is developed which, within the limits of the spherical cell approximation first presented by Wigner and Seitz, will permit 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. Analytic formulas for approximate solid state wave functions are produced in the region outside the atomic core by utilizing Imai's form of the W.K.B. method with the phase constant determined explicitly in terms of the known quantum defect of the free atom. These wave functions are applied to the determination of the minimum ground state energy in the alkali metals and of the sphere radius at which this occurs as functions of the quantum defects of the free atoms. These functions, when applied to Fröhlich's semi-empirical formula, yield a rapid and accurate method for the computation of the ground-state energy as a function of sphere radius.

I. Introduction: A previous paper[1] has developed the "function matching method" which permits computation of solid state wave functions to be undertaken without a knowledge of the potential function of the atomic core. Before the discovery of that technique an attempt had been made to achieve the same result with wave functions of the W.K.B. type. This proved to be feasible only in theory, for the region in which the wave functions are of physical interest lies near the outer turning point of the wave equation where the W.K.B. approximation tends to break down. Even Langer's[2] W.K.B. formalism yielded significant errors in this region, so the attempt was abandoned in favor of the function matching technique.

Recently Imai[3] has suggested a revision of the W.K.B. method which materially improves the approximation near the turning point. His formalism is applied in the present paper to the computation of wave functions for the solid state and, in a sample specialization, yields numerical results almost identical with those computed by more exact methods. Because the computations involved are less arduous and because this revised W.K.B. technique proves less critically sensitive to small changes in the experimental data, it is presented here as an improvement on our earlier method. No attempt has been made, however, to duplicate the computations made in the earlier paper (**A**), for there is every evidence that the two formalisms will yield almost identical results.

The objectives and the physical presuppositions of this paper are identical with those discussed in (**A**). Readers acquainted with (**A**) will note that the general solution of the radial wave equation, there produced as an arbitrary linear combination of Whittaker's two solutions of the confluent hypergeometric equation, is here replaced by Imai's W.K.B. solution with an undetermined phase constant. The condition that the wave function be zero at the origin is then seen to determine explicitly the phase constant used in the W.K.B. expansion about the inner turning point, so that the phase constant to be used about the outer turning point can be determined as a function of the quantum defect of the atom by an obvious modification of the usual phase-integral quantum condition. This procedure serves to determine the wave functions for the solid without the computation of the logarithmic derivative function required by the earlier, function matching procedure.

II. The Imai Procedure for the Solid State: Imai has shown that a differential equation,

$$d^2U/(dx^2)+k^2P(x)U=0, \tag{1}$$

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* Junior Fellow, Society of Fellows.

[1] T. S. Kuhn and J. H. Van Vleck, Phys. Rev., **79**, 382 (1950). This paper will be referred to as (**A**).

[2] R. E. Langer, Phys. Rev. **51**, 669 (1937).

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

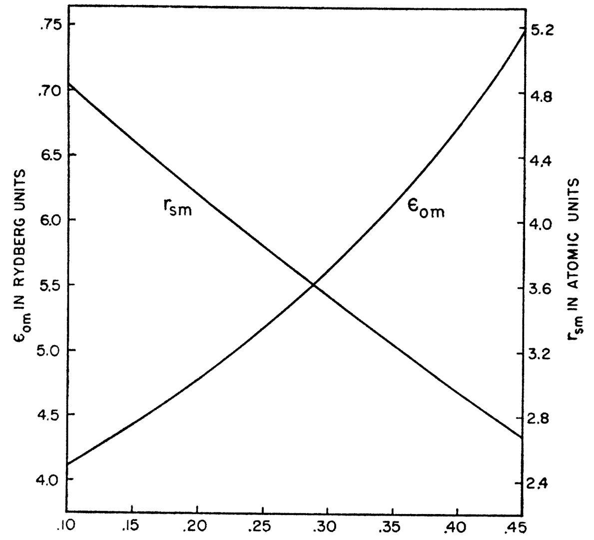

FIG. 1. Curves of ϵ_{om} and r_{sm} as functions of δ.

possesses, in the vicinity of its ith turning point x_i, an approximate general solution of the form

$$U = z^{1/6}\xi^{\frac{1}{2}}P^{-\frac{1}{4}}[\cos(\tfrac{1}{3}\pi+\eta_i)J_{1/3}(\tfrac{1}{3}\kappa\xi^{\frac{3}{2}}) + \cos(\tfrac{1}{3}\pi-\eta_i)J_{-1/3}(\tfrac{1}{3}\kappa\xi^{\frac{3}{2}})], \quad (2)$$

in which an arbitrary amplitude factor has been omitted, η_i is an arbitrary constant, and

$$z = \int_{x_i}^{x} [P(x)]^{\frac{1}{2}}dx, \quad \xi = (3z)^{\frac{2}{3}} + \lambda\kappa^{-2}. \quad (3)$$

Here it has been supposed that in the vicinity of the turning point, x_1, $P(x)$ can be expressed in the form

$$P(x) = \sum_{m=1}^{\infty} a_m(x-x_i)^m, \quad (4)$$

so that the constants κ and λ are then defined in terms of the first four coefficients, a_m, of (4) by

$$\begin{aligned}\kappa^2 &= k^2 - (4/75)(14a_2^3 - 35a_1a_2a_3 + 25a_1^2a_4)a_1^{-4},\\ \lambda &= (12/35)(3a_2^2 - 5a_1a_3)(2a_1^2)^{-4/3}.\end{aligned} \quad (5)$$

The family of functions (2) are shown by Imai to be exact solutions of that differential equation which is gained by dropping all but the first four terms of the expansion of $P(x)$ in (1). They are therefore excellent approximate solutions at and near the turning point.

The particular utility of the form (2) is, however, a consequence of its asymptotic behavior, for if k is large enough so that $k^2 \sim \kappa^2$ in (5), the functions (2), at large distances from the turning point, reduce to

$$U \sim P^{-\frac{1}{4}} \cos(kz - \tfrac{1}{4}\pi + \eta_i) \quad \text{for} \quad P > 0, \quad (6a)$$

$$U \sim P^{-\frac{1}{4}}[2 \sin\eta_i e^{|kz|} + \cos\eta_i e^{-|kz|}] \quad \text{for} \quad P < 0, \quad (6b)$$

and, since large k corresponds to large absolute values of the energy in the wave equation, these formulas are seen to be precisely the normal W.K.B. expansions. It follows that the functions (2) are good approximate solutions at distances between but not too near the turning points. Since (6a) and (6b) join smoothly to (2) at opposite sides of the turning point x_i, they are seen to contain the usual connection formulas.

This is the formalism to be applied to the wave equation (A-1) of concern in the theory of solids. By means of the substitutions

$$\theta = -\epsilon r, \quad \gamma = (-\epsilon)^{\frac{1}{2}}, \quad (7)$$

this normal radial wave equation can be written in the more manageable form

$$\frac{d^2U^{(l)}}{d\theta^2} + \frac{1}{\gamma^2}\left[-1 - V(\theta) - \frac{l(l+1)}{\theta^2}\right]U^{(l)} = 0, \quad (8)$$

which will be termed "the standard equation" in this development. Now Langer has pointed out that the standard equation (8) is not suitable for application of the W.K.B. method, because with any physical potential function, $V(\theta)$, its inner turning point, θ_1, will be too near the origin ($\theta = 0$) to permit application of the asymptotic form (6b) anywhere in the region $0 \leq \theta \leq \theta_1$. This deficiency he remedies by introducing the further substitutions

$$\theta = e^x, \quad U^{(l)}(x) = e^{\frac{1}{2}x}u(x), \quad (9)$$

and so transforming (8) to the more suitable form

$$\frac{d^2u}{dx^2} + \frac{1}{\gamma^2}[-e^{2x} - e^{2x}V(e^x) - (l+\tfrac{1}{2})^2\gamma^2]u = 0, \quad (10)$$

which will be called the "transformed" wave equation.

Approximate solutions of (10) in the form (2) or (6) cannot normally be produced without an explicit knowledge of the potential function $V(e^x)$, and this information is not generally available except in the region well outside the atomic core (say for all $x \geq X$) where the potential function is known to be hydrogenic, i.e., where $V(e^x) = -2e^{-x}$. The quantity X, which marks the effective boundary of the hydrogenic region, may be expected to lie between the two turning points of (8) or (10), for physically (see the discussion in (**A**)) the valence electron wave function takes its maximum values in the hydrogenic region, and mathematically these maxima are first attained in the region between the turning points, where the wave functions exhibit sinusoidal behavior.

It follows that for all $x \geq X$ the W.K.B. wave functions are completely defined, except for the phase constant η_2, by an expansion of the form (2) or (6) about the outer turning point, x_2, of the wave equation (10). In this expansion $k^2P(x)$ is given by

$$k^2P_h(x) = \gamma^{-2}[-e^{2x} + 2e^x - (l+\tfrac{1}{2})^2\gamma^2], \quad (11)$$

where the subscript h denotes the hydrogenic form of $P(x)$, and the outer turning point, x_2, to be substituted for x_i in (3), is given by

$$x_2=\ln\{1+[1-(l+\tfrac{1}{2})^2\gamma^2]^{\frac{1}{2}}\}. \tag{12}$$

These formulas permit explicit analytic definitions of z, ξ, λ, and κ, so that the production of explicit approximate wave functions in the hydrogenic region is limited only by our ability to determine the phase constant η_2.

Now for any value of the energy parameter γ the phase constant η_2 is completely determined by the condition that the wave function $e^{\frac{1}{2}x}u(x)$ be zero at the origin. This is equivalent to the condition that the phase constant η_1, used in the expansion (6) about the inner turning point, be zero. For as $x\rightarrow-\infty$, the potential function $V(e^x)$ must behave as $-2Ze^{-x}$, so it follows from (3) and (10) that the term $e^{|kz|}$ in (6*b*) must carry the wave function to infinity at the origin unless $\eta_1=\sin\eta_1=0$.

Between the two turning points the wave function can be expressed as an expansion about either turning point, and since η_1 is now known, the value of η_2 is completely determined by the condition that the two expansions yield identical results in the region where Eq. (6a) is valid. This leads, in the usual fashion, to an explicit definition of η_2 by the formula

$$\eta_2=(m+\tfrac{1}{2})\pi-k\int_{x_1}^{x_2}[P(x)]^{\frac{1}{2}}dx, \tag{13}$$

where m is any integer or zero, and $P(x)$ is γ^{-2} times the square bracket in (10).

Equation (13) cannot, of course, be integrated explicitly unless $V(e^x)$ is known, for it is only near the outer turning point, x_2, that $P(x)$ reduces to the hydrogenic form $P_h(x)$ defined by (11). But a slight modification of a device utilized by Bohr[4] in deriving the Rydberg law makes it possible, from (13), to give values of η_2 in terms of the measured values of the quantum defect. For define δ by the equation

$$\pi\delta=k\int_{x_1}^{x_2}[P(x)]^{\frac{1}{2}}dx-k\int_{x_1'}^{x_2}[P_h(x)]^{\frac{1}{2}}dx, \tag{14}$$

where x_1' is the inner turning point of the hydrogenic form of (10), and the other quantities are those previously defined. Then, as discussed by Kemble,[4] the quantity δ must be virtually independent of the energy parameter γ. For examine the integrands in (14): the quantity $k[P(x)]^{\frac{1}{2}}dx$ may be rewritten

$$k[P(x)]^{\frac{1}{2}}dx=[\epsilon-V(r)+(l+\tfrac{1}{2})^2r^{-2}]dr, \tag{15}$$

and $k[P_h(x)]^{\frac{1}{2}}dx$ has the same form with $V(r)=-2/r$. Now at the upper limit of integration $P(x)=P_h(x)$, for x_2 is in the hydrogenic region; throughout most of the region in which $P(x)\neq P_h(x)$, $|V|\gg|\epsilon|$, so that changes in ϵ do not appreciably influence the integrand; and, finally, the position of the lower limits, x_1 and x_1', are almost independent of ϵ. From all of which it follows that the difference between the integrals can show little dependence on the energy.

The second integration in (14) can now be carried through explicitly, so that (13) and (14) combine to yield

$$\eta_2=n\pi-\delta\pi-\gamma^{-1}\pi, \tag{16}$$

in which n $(=m+l+1)$ is an arbitrary integer greater than l. Equation (16) permits δ to be identified physically, for the atomic wave functions $U^{(l)}$ are just those functions (2) which go to zero both at the origin and at infinity, and the functions which go to zero at infinity are those for which $\eta_2=0$. But if $\eta_2=0$, (16) can be rewritten as

$$\epsilon=-(n-\delta)^{-2}, \tag{17}$$

which is just Rydberg's Law, so that δ is the quantum defect of the atom.

Conversely, if δ is known from spectroscopic data, η_2 can be computed from (16), and the wave functions (2) and (6b) can be produced explicitly, for any value of energy, everywhere in the hydrogenic region. These wave functions may be used, precisely as in (**A**), to compute the three solid state parameters normally treated by the Wigner-Seitz method.

III. An Application to the Ground-State Energy of Monovalent Metals: The accuracy of these W.K.B. wave functions can be tested by a sample application to the computation of the minimum ground state energy, ϵ_{om}, of monovalent metals, and this application will incidentally provide an extremely rapid and compara-

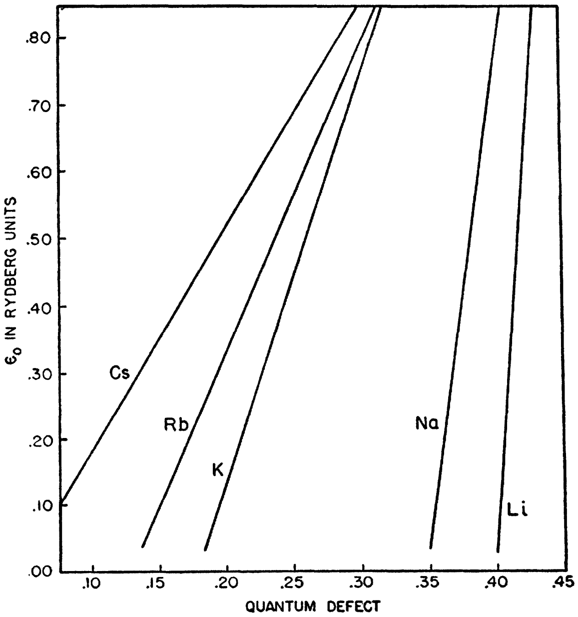

FIG. 2. Quantum defects for the *s*-wave functions of the alkali metals as a function of energy. From the experimental values in Bacher and Goudsmit.

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[4] N. Bohr, Proc. London Phil. Soc. **35**, 296 (1923). See also E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1937), p. 478 ff.

tively accurate means of computing the curve $\epsilon_o(r_s)$ for any monovalent metal for which the quantum defect is known.

For the ground state wave function $U^{(0)}(\theta)$ of the valence electron of a monovalent metallic solid is just that solution of the standard equation (8) which satisfies the Wigner-Seitz boundary condition (A-2) at $\theta=\theta_s$. In terms of the function u and the variable x of of the "transformed equation," this boundary condition may be rewritten as

$$u'(x_s)-\tfrac{1}{2}u(x_s)=0, \tag{18}$$

and this condition, in conjunction with the explicit wave functions given by (2) and (16), must, for a given δ, define the energy parameter γ as a function of the sphere radius variable x_s.

By defining two new functions

$$\begin{aligned} g_\gamma(x)&=z^{1/6}\xi^{\frac{1}{2}}P_h^{-\frac{1}{4}}J_{1/3}(\tfrac{1}{3}\kappa\xi^{\frac{3}{2}})\\ h_\gamma(x)&=z^{1/6}\xi^{\frac{1}{2}}P_h^{-\frac{1}{4}}J_{-1/3}(\tfrac{1}{3}\kappa\xi^{\frac{3}{2}}), \end{aligned} \tag{19}$$

the approximate solution (2) of the "transformed equation" (10) can, with the aid of (16), be written as

$$\begin{aligned} u(x)=\cos(\tfrac{1}{3}-\delta-\gamma^{-1})\pi g_\gamma(x)&\\ +\cos(\tfrac{1}{3}+\delta+\gamma^{-1})\pi h_\gamma(x),& \end{aligned} \tag{20}$$

so that the boundary condition (18) becomes

$$\delta=\frac{1}{\pi}\tan^{-1}\left[(3)^{-\frac{1}{2}}\frac{F_\gamma(x_s)+1}{F_\gamma(x_s)-1}\right]-\frac{1}{\gamma}, \tag{21}$$

with the new function $F_\gamma(x)$ defined by

$$F_\gamma(x)=-\frac{h'_\gamma(x)-\frac{1}{2}h_\gamma(x)}{g'_\gamma(x)-\frac{1}{2}g_\gamma(x)}. \tag{22}$$

With δ determined experimentally (21) can be solved for γ as a function of x_s, and this relationship, with (7) and (9), yields the desired curve for $\epsilon_o(r_s)$.

Such a computation may be usefully and conveniently illustrated at the outer turning point, θ_2, of the "standard equation" (8), for as Fröhlich[5] has shown, at this point the ground-state energy ϵ_o must take its minimum value, ϵ_{om}. With $l=0$ and $V(\theta)=-2/\theta$ in Eq. (8), Fröhlich's theorem states that the minimum sphere ground-state energy, ϵ_{om}, always occurs at a sphere radius r_{sm} to which it is related by the equation

$$\epsilon_{om}=-2/r_{sm} \quad\text{or}\quad \theta_{sm}=2. \tag{23}$$

In terms of the new variable x_s of the transformed equation, (23) states that the minimum ground-state energy must occur at a point x_{sm} given by

$$x_{sm}=\ln 2, \tag{24}$$

a point which lies near but not at the outer turning point $x_2(=\ln[1+(1-\frac{1}{4}\gamma^2)^{\frac{1}{2}}])$ of the "transformed equation."

At distances near the outer turning point x_2, the functions $f_\gamma(x)$, $g_\gamma(x)$, and $F_\gamma(x)$ are conveniently expanded in terms of the variable $x-x_2$, and at the point $x=x_{sm}(x_{sm}(\gamma))$ these expansions yield $F_\gamma(x_{sm})$ as a function of the energy parameter alone. This procedure has been carried through, and a long and extremely arduous manipulation yields the series

$$\begin{aligned} F_{\epsilon_{om}}(x_{sm})=(\tfrac{3}{2})^{\frac{2}{3}}\frac{\Gamma(\frac{4}{3})}{\Gamma(\frac{2}{3})}(-\epsilon_{om})^{\frac{1}{3}}\Bigg[\frac{4}{5}-\frac{5{,}583}{98{,}000}\epsilon_{om}&\\ +\frac{21{,}918{,}107}{6{,}585{,}600{,}000}\epsilon_{om}^2+\cdots\Bigg],& \end{aligned} \tag{25}$$

in which ϵ_{om} has been inserted for $-\gamma^2$.

Equation (25) in conjunction with (21) determines the minimum ground-state energy as a function of the observed quantum defect; the radius r_{sm} at which this minimum occurs can also be found as a function of δ by use of (23). These functions, $\epsilon_{om}(\delta)$ and $r_{sm}(\delta)$, are displayed graphically in Fig. 1. The values of δ are there restricted to the interval $0\leq\delta\leq 1$, since integral changes in δ do not affect the solution of (21). These curves are conveniently utilized in conjunction with experimentally derived curves of $\delta(\epsilon_o)$, and such curves for the five alkali metals are shown in Fig. 2.

From these curves values of ϵ_{om} and r_{sm} can be computed, for if one starts with a trial value of ϵ_{om}, a value of δ can be found from Fig. 2, and this value can be used to find a more accurate ϵ_{om} from Fig. 1. Two or three applications of the procedure suffice to determine ϵ_{om} to three-figure accuracy. Final values of ϵ_{om} and r_{sm} gained by this procedure are compared with the results of other computations in Table I. It will be observed that the agreement is, throughout, well within the limits of computational accuracy.

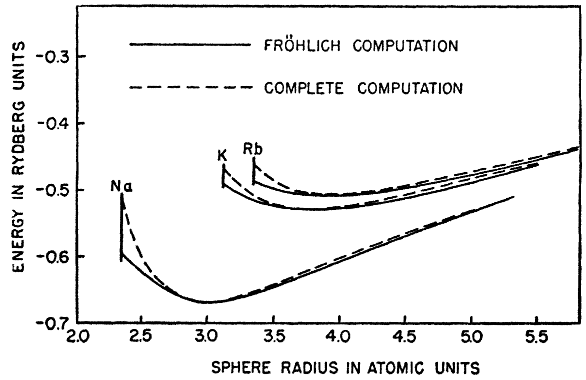

FIG. 3. Ground-state energy as a function of sphere radius for Na, K, and Rb: comparison of Fröhlich's formula with the complete computations of (A).

IV. Application to Fröhlich's Formula: Equation (21) can be used to compute values of ϵ_0 for values of $x_s\neq x_{sm}$, but this computation would be laborious and

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[5] H. Fröhlich, Proc. Roy. Soc. A158, 97 (1937).

seems unnecessary in view of the accuracy of the approximate procedure which follows.

Fröhlich[6] has shown that, to a good approximation, the ground-state energy, ϵ_0, may be represented by

$$\epsilon_o=(a/r_s^3)-(3/r_s), \tag{26}$$

a formula which takes as its minimum value, $\epsilon_o=-2/r_{sm}$, with $r_{sm}=(a)^{\frac{1}{2}}$. Equation (26) may therefore be rewritten in terms of the results of Section II in the form

$$\epsilon_o=\frac{[r_{sm}(\delta)]^2}{r_s^3}-\frac{3}{r_s}. \tag{27}$$

This equation can be used with the values of r_{sm} listed in Table I, and curves of $\epsilon_o(r_s)$ derived from (27) are compared with those derived by the complete computations of (**A**) in Fig. 3. It is immediately indicated that the results of this abridged computation are sufficiently accurate to render the lengthy computation superfluous. Equation (27) can also be used in conjunction with the usual approximate formula for the Fermi energy, $\epsilon_F=2.21/r_s^2$, in an approximate computation of binding energy as a function of sphere radius. This computation should yield results substantially identical with those of the "plane wave" ($\alpha=1$) computation in (**A**), so they have not been carried out here.

V. Comments: The W.K.B. wave functions developed in Section II permit a direct computation of approximate wave functions for the solid state. The application provided in Section III indicates that these wave functions compare favorably with those produced by exact solutions of the wave equation, so we conclude that these functions could be employed for the "complete computation" carried through in (**A**) by the function matching method.

TABLE I. Theoretical values of ϵ_{om} and r_{sm}.

Element	ϵ_{om}(Ry.)		r_{sm}(a.u.)	
	W.K.B.	Other[a]	W.K.B.	Other[a]
Li	0.706	0.700	2.84	2.87
Na	0.667	0.668	3.00	2.97
K	0.530	0.530	3.78	3.75
Rb	0.508	0.506	3.92	3.87
Cs	0.468		4.28	

[a] The values for Li are taken from F. Seitz, Phys. Rev. **47**, 400 (1935). The values for the other elements are taken from (**A**).

This method of producing wave functions shares with the function matching method the advantage that no explicit formula for $V(r)$ is required. It surpasses the function matching method by its less critical dependence upon experimental data, for although no adequate theoretical explanation of the fact has been found, the extrapolations of Fig. 2 turn out to be "safer" than those of $\phi_R^{(l)}(\epsilon_0)$ in (**A**). Also, except in those ranges of the parameter l, and r for which the coefficients $\bar{W}_k^{(l)}(r)$ and $\tilde{W}_k^{(l)}(r)$ of (**A**-12) have been *previously* computed, the computations involved in the W.K.B. approach are simpler than those required for function matching. In any case, for the computation of the ground-state energy, the accuracy of Fröhlich's formula taken in conjunction with the curves of Fig. 1 and Fig. 2 seems to obviate the necessity of any more complete computation procedure.

It should, however, be noted explicitly that the practicability of W.K.B. wave functions in this application is completely dependent upon the revision of the method provided by Imai, for the previous W.K.B. formalisms are too inaccurate near the point r_{sm}. In particular, an attempt to apply Langer's formulas to the computations carried out in Section III, above, produced values of ϵ_{om} and r_{sm} which differed by ten to twenty percent from those listed in Table I.

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[6] H. Fröhlich, reference 5. A better derivation is given by J. Bardeen, J. Chem. Phys. **6**, 372 (1938). Bardeen's treatment does not, however, develop the exact relationship (23).