

provided $(k_0/4\pi i) \int g(\mathbf{k}, \mathbf{k}') d\Omega' > 0$. Putting the value of $C(\mathbf{k}, \mathbf{k}_0)$ in (2), we get

$$f^{(n+1)}(\mathbf{k}, \mathbf{k}_0) = \frac{\left[g(\mathbf{k}, \mathbf{k}_0) + \frac{k_0}{4\pi i} f^{(n)}(\mathbf{k}, \mathbf{k}_0) \int g(\mathbf{k}, \mathbf{k}') d\Omega' - \frac{k_0}{4\pi i} \int g(\mathbf{k}, \mathbf{k}') f^{(n)}(\mathbf{k}', \mathbf{k}_0) d\Omega' \right]}{1 + \frac{k_0}{4\pi i} \int g(\mathbf{k}, \mathbf{k}') d\Omega'} \quad (7)$$

Assuming $f^{(n)}(k, k_0)$ not dependent on angles, Eq. (7) gives, as first iteration:

$$C^{(n+1)}(\mathbf{k}, \mathbf{k}_0) = g(\mathbf{k}, \mathbf{k}_0) \left/ \left[1 + \frac{k_0}{4\pi i} \int g(\mathbf{k}, \mathbf{k}') d\Omega' \right] \right. \quad (8)$$

The criterion of convergence² may be very easily deduced. We simply state that the absolute value of the correction amplitude does not exceed the maximum amount of deviation of the foregoing approximate amplitude from the exact amplitude; i.e.,

$$|K^{(n+1)}(\mathbf{k}, \mathbf{k}_0)| \leq \epsilon^{(n)}_{\max} \text{ if } g(\mathbf{k}, \mathbf{k}') > 0 \text{ and } |\mathbf{k}_0| > 0,$$

where $\epsilon^{(n)}_{\max}$ is the maximum of all deviations of the approximate solutions from the true solution.

Further, the average amounts of the deviations $\epsilon^{(n)}(\mathbf{k}, \mathbf{k}_0)$, $\epsilon^{(n+1)}(\mathbf{k}, \mathbf{k}_0), \dots$, of the approximate amplitudes from the true amplitudes converge towards zero if

$$1 + |C(\mathbf{k}, \mathbf{k}_0)| + \frac{k_0}{4\pi i} \int |C(\mathbf{k}, \mathbf{k}')| |g(\mathbf{k}, \mathbf{k}')| d\Omega' \leq \theta,$$

where $0 < \theta \leq 1$.

The general reliability of this method may be shown by considering the scattering of positive mesons by neutrons. It will be shown that the solution (8) gives the exact result as obtained by Ma³ and Goldberger⁴ using variational methods.

The relevant matrix element for this process may be written as

$$\langle \mathbf{p}, \mathbf{k} | \mathcal{G} | \mathbf{p}_0, \mathbf{k}_0 \rangle = \bar{u}(a_1 + a_2 \gamma_4) u_0 / 2\epsilon_0 (W_0^2 - M^2),$$

where \bar{u} and u_0 are the usual Dirac spinors corresponding to four-momenta \mathbf{p} and \mathbf{p}_0 , respectively. \mathbf{k} and \mathbf{k}_0 are the final and initial four-momenta of the meson, and $\epsilon_0 = (\mu^2 + q^2)^{1/2}$, where q is the magnitude of the momentum of either particle and μ the meson mass. W_0 is the total energy. $a_1 = f^2 M$ and $a_2 = f^2 W_0$ in the case of pseudoscalar coupling.

Writing $\langle \mathbf{p}, \mathbf{k} | \mathcal{G} | \mathbf{p}_0, \mathbf{k}_0 \rangle = (\frac{1}{2}\epsilon_0) (\bar{u}g(\mathbf{p}, \mathbf{p}_0)u)$, the Heitler equation reduces to

$$f(\mathbf{p}, \mathbf{p}_0) = g(\mathbf{p}, \mathbf{p}_0) + \frac{iq}{32\pi^2 W_0} \int d\Omega' g(\mathbf{p}, \mathbf{p}') (-i\gamma \cdot \mathbf{p}' + M) f(\mathbf{p}', \mathbf{p}_0).$$

Using the solution (7), we have

$$f(\mathbf{p}, \mathbf{p}_0) = g(\mathbf{p}, \mathbf{p}_0) \left/ \left[1 - \frac{iq}{32\pi^2 W} \int d\Omega' g(\mathbf{p}, \mathbf{p}') (-i\gamma \cdot \mathbf{p}' + M) \right] \right. \\ = g(\mathbf{p}, \mathbf{p}_0) / (1 - i\lambda), \quad (9)$$

where

$$\lambda = (q/8\pi W_0) g(\mathbf{p}, \mathbf{p}_0) (E_0 \gamma_4 + M),$$

M being the nucleon mass and E_0 the nucleon energy.

The same result has been obtained by Goldberger⁴ and Ma.³

That (9) is the exact solution may be verified by iterating this result by means of (7). The second iteration will give the same result (9).

The author wishes to thank Dr. D. Basu for suggesting the problem and for helpful guidance. Detailed calculations and various applications to meson-nucleon and nucleon-nucleon scattering are in progress and will be published elsewhere.

¹ W. Heitler, Proc. Cambridge Phil. Soc. **37**, 291 (1941).

² C. Wagner, J. Math. and Phys. **30**, 23 (1951).

³ S. T. Ma, Proc. Cambridge Phil. Soc. **39**, 168 (1943).

⁴ M. L. Goldberger, Phys. Rev. **84**, 929 (1952).

Gamma Radiation Following Decay of $I^{131}\dagger$

HARRY C. HOYT* AND JESSE W. M. DUMOND
California Institute of Technology, Pasadena, California
(Received June 29, 1953)

IN view of the long time which elapsed between the first measurements of I^{131} gamma radiation with the curved crystal gamma-ray spectrometer¹ and the most recent calibration of the instrument,² these radiations have been remeasured. Three gamma-ray lines, of approximately 364, 284, and 80 keV, were detected and measured at this time. The wavelengths, in both x units (Siegbahn scale) and milliangstroms, and the energies of these lines are given in Table I. The stated uncertainties are

TABLE I. Wavelengths and energies of radiation following decay of I^{131} .

Wavelength in x units (Siegbahn scale)	Wavelength in milliangstroms	Energy in keV
33.946 ± 0.0045	34.016 ± 0.0047	364.467 ± 0.050
43.517 ± 0.0073	43.607 ± 0.0075	284.307 ± 0.049
154.336 ± 0.0161	154.656 ± 0.0170	80.164 ± 0.0088

standard deviations. As reported in reference 1, these three gamma-ray lines form a Ritz combination. Equation (1) shows the excellent agreement of the present results when expressed in such a form:

$$(284.307 \pm 0.049) + (80.164 \pm 0.0088) - (364.467 \pm 0.050) \\ = 0.004 \pm 0.071. \quad (1)$$

We wish to thank Mr. Floyd Humphrey for his assistance in preparing the gamma-ray source and Dr. James R. Wilts for his assistance in evaluating the data.

[†] Work supported in part by the U. S. Atomic Energy Commission.

* Now at Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

¹ Lind, Brown, Klein, Muller, and DuMond, Phys. Rev. **75**, 1544 (1949).

² Muller, Hoyt, Klein, and DuMond, Phys. Rev. **88**, 775 (1952).

Cohesive Energy of Alkali Metals

HARVEY BROOKS

Division of Applied Science, Harvard University, Cambridge, Massachusetts
(Received June 9, 1953)

RECENTLY Kuhn and Van Vleck¹ have given a method for calculating the ground-state energy ϵ_0 and the Fermi energy ϵ_F of an alkali metal in the Wigner-Seitz sphere approximation² without explicit knowledge of the ion-core potential or numerical integration of the radial wave equation. The spectroscopic term values of the free atom were the only empirical data used in the calculation. The Kuhn-Van Vleck method appeared to give reliable results for the ground state energy, but the values for the Fermi energy deviated so drastically from the free electron values, at least for potassium and rubidium, that doubt was thrown on the validity of the method.

It is the purpose of the present note to point out a number of simplifications of the Kuhn-Van Vleck method, which, when applied, not only greatly reduce the numerical labor of a calculation, but also give more reasonable values of the Fermi energy, and permit, for the first time, reasonable theoretical predictions of the cohesive energy of all the alkali metals using only the properties of the free-atom spectra. The chief remaining uncertainties in the calculation are in the exchange and correlation energies.

Kuhn and Van Vleck make use of the fact that in the alkali metals the potential is Coulombic at the surface of the unit cell and that therefore the wave functions in this region may be expressed as linear combinations of confluent hypergeometric functions. The improvement in the present work is that we have found an explicit analytical form of the wave function in terms

of the extrapolated quantum defect. This is, in terms of the conventional Whittaker³ functions:

$$\Psi_l(r) = \sin(\pi\delta_l)W_{n, l+\frac{1}{2}}(2r/n) + (-1)^l [(n+l)!/(2l+1)!] \sin(\pi(n+\delta_l))M_{n, l+\frac{1}{2}}(2r/n), \quad (1)$$

where $n=1/\sqrt{\epsilon}$, ϵ in Rydbergs, and δ_l is the quantum defect which can be found as a smooth function of the energy parameter ϵ by straightforward extrapolation using the free atom term values for each l . The ground state energy ϵ_0 depends on the s -functions, while the Fermi energy depends on the p -functions. The latter also depends on a quantity γ , first introduced by Bardeen,⁴ which is related to the normalized value of the s -function at the surface of the Wigner-Seitz sphere. Recently Kohn⁵ has shown that γ is given by

$$\gamma = \frac{1}{3}r_s^2(\partial\phi_0/\partial\epsilon_0)^{-1}, \quad (2)$$

where ϕ_0 is the logarithmic derivative defined in reference 1. This expression is rigorous, involves only the surface values of the wave functions, and so can be computed from Eq. (1), using the functions tabulated by Kuhn.⁶ This makes a substantial change from the values of γ calculated by Kuhn and Van Vleck, as shown in Table I. The new values of α (defined in references 1 and 4)

TABLE I. Values of γ (the effective mass constant) and α for the alkali metals.

Element	Kuhn and Van Vleck			Present method	
	$z_s = (8r_s)^{\frac{1}{2}}$	γ	α	γ	α
Li	4.5			1.197	0.471
	5.0			1.052	0.674
	5.5			0.993	0.819
Na	5.0	1.120	0.962	1.206	1.001
	5.5	1.020	0.980	1.046	0.984
	6.0	0.930	1.013	0.935	0.999
K	5.5	0.835	0.745	1.272	1.114
	6.0	0.930	0.909	1.108	1.074
	6.5	1.043	1.122	0.986	1.057
Rb	6.0	1.011	0.132	1.182	1.129
	6.5	0.964	0.427	1.036	1.099
	7.0	1.153	0.781	0.901	1.073
Cs	6.0			1.372	1.223
	6.5			1.156	1.189
	7.0			1.027	1.173

show that the "plane wave" approximation for the Fermi energy is a moderately good one as anticipated by Kuhn and Van Vleck.

The resulting theoretical values of cohesive energy and lattice constant (at 0°K) are shown for all the alkali metals in Table II,

TABLE II. Comparison of theoretical and experimental cohesive energies and lattice constants (at 0°K).

Element	Cohesive energy (kcal/mole)	Lattice constant (Å)
Li	theory	38.7
	experiment	36.5
Na	theory	26.5
	experiment	26.0
K	theory	22.2
	experiment	22.6
Rb	theory	20.8
	experiment	18.9
Cs	theory	19.7
	experiment	18.8

with the experimental results for comparison. The experimental lattice constants are those for liquid air temperature. In the case of Rb and Cs the experimental 0°K values may be slightly smaller because of the high compressibility and low Debye tem-

perature. The theoretical results were obtained by using the new values of α from Table I. The ϵ_0 values were taken from Kuhn and Van Vleck after a check calculation with the new method on Na showed that ϵ_0 was not altered significantly. The Li and Cs values were calculated by the new method, since these elements had not previously been treated by Kuhn and Van Vleck. The Li results showed good agreement with the recent calculation of Silverman and Kohn,⁷ thus providing an additional check of the method. Plane wave values of Coulomb, correlation, and exchange energies were used (Table II).

The calculated total energies at three lattice constants were fitted to an expression:

$$E_{\text{coh}} = Ar_s^{-1} + Br_s^{-2} + Cr_s^{-3}. \quad (3)$$

The equilibrium lattice constant was determined by minimizing with respect to r_s . In order to compare results with compressibility data, the relation between p and r_s was determined by differentiation of (3). The theoretical pressure corresponding to observed values of r_s was determined and compared with the pressure at which this value was actually observed. The result is shown in Table III. The pressures were calculated for room tem-

TABLE III. Test of theoretical pressure-volume relation for the alkali metals. The pressures at which r_s was actually observed are given in parentheses.

Element	Theoretical pressure $\times 10^{-3}$ (kg/cm ²)	
Li	40.0	89.4
Na	40.1	83.8
K	38.6	82.8
Rb	22.3	50.2
Cs	24.2 (40)	50.2 (100)

perature and include an approximate correction for the thermal pressure as determined by the Mie-Grüneisen equation of state.⁴ The agreement is fairly good for Li, Na, and K, but Rb and Cs are theoretically too soft. A rough calculation indicates that the discrepancy may possibly be explained by ion-core repulsion.

The present method is more general than the conventional cellular method in that the ion core need not be represented by the same potential for s , p , and d functions. This is probably rather important in practice since Gorin⁸ found it was impossible to devise a unique Prokofiev potential for potassium and the situation is probably worse for rubidium and cesium.

The proof of Eq. (1), which is the heart of the present method, can be carried out with the aid of the WKB asymptotic representation developed by Kuhn.⁹ Kuhn's equation contains an error which does not affect his conclusions. His equation (6) should be:

$$P^{-\frac{1}{2}} \cos(z + \eta - \frac{1}{4}\pi) \rightarrow |P|^{-\frac{1}{2}} \times [\sin\eta \exp|z| + \frac{1}{2} \exp(-i\eta) \exp(-|z|)], \quad (4)$$

as follows directly from his Eq. (2). Expressing η in terms of the quantum defect in accordance with Kuhn's procedure, and comparing Eq. (4) with the known asymptotic forms of the confluent hypergeometric functions, Eq. (1) finally results.

Further details and applications of this calculation will be published at a later date.

The author is indebted to Dr. Kuhn for access to his original calculation sheets and for many stimulating and fruitful discussions.

¹ T. S. Kuhn and J. H. Van Vleck, Phys. Rev. **79**, 382 (1950).

² E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

³ E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1935), pp. 337-339.

⁴ J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

⁵ R. A. Silverman, Phys. Rev. **85**, 227 (1952); W. Kohn, Phys. Rev. **87**, 472 (1952).

⁶ T. S. Kuhn, Quart. Appl. Math. **9**, 1 (1951).

⁷ R. Silverman and W. Kohn, Phys. Rev. **80**, 912 (1950).

⁸ K. E. Gorin, Physik. Z. Sowjetunion **9**, 328 (1936).

⁹ T. S. Kuhn, Phys. Rev. **79**, 515 (1950).