

Variational Methods in Collision Problems

TOSIO KATO
Department of Physics, Tokyo University, Tokyo, Japan
June 22, 1950

RECENTLY variational methods have been applied successfully to scattering problems by several authors. However, it appears to be rather strange that so many different methods have been proposed for the one simple problem of scattering by a center of force. In the present note we wish to point out some simple relations existing among these apparently independent procedures.

For simplicity consider the radial wave equation for S -scattering

$$L[u] \equiv d^2u/dr^2 + k^2u + W(r)u = 0. \quad (1)$$

Let us normalize the trial wave function by the conditions

$$u(0) = 0, \quad u(r) \rightarrow \cos(kr + \theta) + \lambda \sin(kr + \theta), \quad r \rightarrow \infty, \quad (2)$$

in which θ is a fixed constant (usually zero or $\pi/2$) and λ is an adjustable parameter. For the correct wave function λ is connected with the phase, η , by the relation $\lambda = \cot(\eta - \theta)$.

It is easily shown that

$$\delta \int_0^\infty u L[u] dr = k \delta \lambda$$

for the correct wave function, $u = u_0$. In other words, the functional

$$F \equiv F[u] = k\lambda - \int_0^\infty u L[u] dr \quad (3)$$

is stationary for $u = u_0$ and is equal to $k \cot(\eta - \theta)$ since $L[u_0] = 0$. If we set $\theta = \pi/2$ (hence $\lambda = -\tan \eta$), we have the variational method originally due to Kohn¹ and equivalent also to Huang's method² if we make a slight modification in the latter.

The methods of Hulthén³ and Schwinger⁴ can also be derived directly from (3) with $\theta = 0$ (hence $\lambda = \cot \eta$). To show this, it is convenient to set

$$u = \cos(kr) - y + \lambda \sin(kr), \quad (4)$$

$$y(0) = 1, \quad y \rightarrow 0 \text{ as } r \rightarrow \infty.$$

Substitution of (4) into (3) and integration by parts yields

$$F = F_H \equiv -J + 2(k - N)\lambda - k\eta B \lambda^2, \quad (5)$$

with

$$J = \int_0^\infty [k^2 y^2 - (dy/dr)^2 + W(\cos(kr) - y)^2] dr, \quad (6)$$

$$N = \int_0^\infty \sin(kr) \cdot [\cos(kr) - y] W dr, \quad k\eta B = \int_0^\infty \sin^2 kr \cdot W dr.$$

Here y contains some adjustable constants c_1, c_2, \dots . To make F_H stationary we set

$$\partial F_H / \partial c_n = 0, \quad \partial F_H / \partial \lambda = 0,$$

or

$$\partial J / \partial c_n + 2\lambda \partial N / \partial c_n = 0, \quad (n = 1, 2, \dots), \quad (7)$$

$$k\eta B \lambda = k - N. \quad (8)$$

These equations are in complete agreement with those of Hulthén's second method.⁵ Furthermore, we have by (5) and (8)

$$F_H = -J + (k - N)\lambda = k\lambda - \Delta, \quad \Delta = J + \lambda N. \quad (9)$$

Since (9) should give $k \cot \eta$ correctly up to the first order, this also coincides with his result:⁶ $\cot \eta = \lambda - k^{-1}\Delta$. Thus Hulthén's second method is equivalent to our (3) with $\theta = 0$, and hence it is based on the correct variation principle, although his original derivation is not very simple. Also it will be noted that his method gives $k \cot \eta$ explicitly as the stationary value⁷ of (3).

Next, consider the functional

$$F_s = F_H + \int_0^\infty (L[u])^2 W^{-1} dr. \quad (10)$$

An application of the variation principle to F_s leads to the same results as those given above, for the second term on the right-hand side of (10) vanishes for the correct solution, together with its variation. On substituting (4) into (10) and integrating by parts, we obtain,

setting $z = \cos(kr) - y$,

$$F_s = \int_0^\infty (d^2z/dr^2 + k^2z)^2 W^{-1} dr + \int_0^\infty z(d^2z/dr^2 + k^2z) dr. \quad (11)$$

Setting $d^2z/dr^2 + k^2z = -Wv$, and noting that $z \rightarrow \cos(kr)$ as $r \rightarrow \infty$, we obtain from Green's theorem

$$z(r) = \int_0^\infty G(r, r') W(r') v(r') dr', \quad (12)$$

where $G(r, r')$ is the Green's function used in Schwinger's method.⁸ In this way we find

$$F_s = \int_0^\infty W v^2 dr - \int_0^\infty W v dr + \int_0^\infty G(r, r') W(r') v(r') dr'. \quad (13)$$

It will be noted that

$$k^{-1} \int_0^\infty W v \sin(kr) dr = 1$$

by virtue of the condition $y(0) = 1$. If we remove this restriction on v and write (13) in a homogeneous form by the well-known method, F_s becomes just the expression for $k \cot \eta$ in Schwinger's method,⁹ which is thus connected with Hulthén's by the simple relation (10). Sometimes it would be convenient to use the former in the form (10) which does not contain a double integral, in contrast to (13). An interesting consequence of (10) is that the Schwinger method always gives a larger (smaller) value of $k \cot \eta$ than does Hulthén's if $W(r) \geq 0$ [$W(r) \leq 0$] everywhere. It can even be shown that it gives an upper (lower) bound for $k \cot \eta$ if W is not too strong (more precisely, if $|\eta| < \pi$).¹⁰

These results can be extended to more general cases (higher angular momentum, inclusion of Coulomb potential).

¹ W. Kohn, Phys. Rev. **74**, 1763 (1948), Eq. (2.14).

² S. Huang, Phys. Rev. **76**, 1878 (1949).

³ L. Hulthén, K. Fysiogr. Sällsk. Lund Föohandl. **14**, No. 21 (1944); Arkiv. Mat. Astr. Fys. **35A**, No. 25 (1948).

⁴ J. Schwinger, Phys. Rev. **72**, 742 (1947); **78**, 135 (1950). J. M. Blatt and J. D. Jackson, Phys. Rev. **76**, 18 (1949).

⁵ See reference 3, second paper, Eqs. (23) and (24).

⁶ See reference 5, Eq. (36).

⁷ His first method (reference 3, first paper) can also be derived easily from our standpoint. We have only to replace (8) by $\int u L[u] dr = 0$; this changes the trial function, u , only by a first-order quantity and hence F is unaffected to the first order. Since F reduces to $k\lambda$ in this case, this is exactly equivalent to the first method of Hulthén.

⁸ J. M. Blatt and J. D. Jackson, reference 4, Eq. (2.7).

⁹ See reference 8, Eq. (2.11). It will be remarked that our function, v , does not necessarily satisfy the boundary condition $v(0) = 0$. But this is not essential, for it follows for the correct solution automatically from the variation principle (natural boundary condition).

¹⁰ The proof will be given elsewhere together with generalizations.

Mass Assignments of Alpha-Active Isotopes in the Rare-Earth Region*

J. O. RASMUSSEN, F. L. REYNOLDS, S. G. THOMPSON, AND
A. GHIORSO

Radiation Laboratory and Department of Chemistry,
University of California, Berkeley, California
September 7, 1950

IN a previous communication from this laboratory, the production of alpha-radioactivity in the rare-earth elements was reported.¹ The suggestion was made that this might be due to the influence of the stable configuration of 82 neutrons on the daughter nuclides and some likely isotopic assignments were proposed on this basis. We have succeeded in testing this suggestion through the use of the mass spectrograph to make an isotopic assignment for one of the major artificial rare-earth alpha-activities with the result that this explanation seems to be confirmed.

The mass assignment of the alpha-emitting terbium isotope of 4.0-hr. half-life and 4.0-Mev alpha-particle energy was made by performing a mass spectrographic separation of terbium activity onto a photographic plate and detecting alpha-activity by a transfer plate technique. The terbium activity (6×10^7 alpha-disintegrations per minute at end of a 5-hr. bombardment) was produced by bombardment of 30 mg of gadolinium oxide with 150-Mev protons in the 184-inch cyclotron, and rapid chemical separation was made by elution from cation exchange columns

with 1/4 μg terbium carrier added before elution. The equipment and method used in the separations were essentially as described previously in the work by Thompson *et al.* on the new element berkelium.² Two column separations were made in order to remove all of the gadolinium, the first column of 1.0 cm diameter, the second of 2 mm diameter. One-fourth μg of samarium nitrate in solution was added to the active terbium fraction before mass spectrographic separation to serve as an internal mass standard. The products of the mass spectrographic separation in the 60° slit-type mass spectrograph, using a thermal ionization source from a tungsten filament, were collected on an Eastman III-0 photographic plate. Before development this plate was left face to face with an Eastman NTA transfer plate for a day. After development the collection plate showed solid lines at the mass numbers corresponding to all the stable samarium isotopes (as both Sm^+ and SmO^+) and to stable terbium (as Tb^+). The transfer plate was searched with a microscope for alpha-tracks. A concentration of alpha-tracks was observed on the transfer plate only in a region corresponding to mass 149. The 4-hr. terbium alpha-activity was the only alpha-activity here present in large enough amount to be detected by this technique. Tb^{149} has 84 neutrons and would thus be expected to have the maximum alpha-decay energy of the terbium isotopes in this mass region.

The suggestion was also made in the previous communication¹ that the long-known natural radioactivity of samarium might be assigned to Sm^{147} or Sm^{148} , rather than to Sm^{149} , since this assignment would be more consistent with decay toward the stable configuration of 82 neutrons (on this basis the most alpha-unstable samarium isotope would be Sm^{146} , and its anomalous absence from nature would thus be explained). This hypothesis has also been tested and it has been found that a major part of this natural radioactivity should indeed be assigned to Sm^{147} . The possibility that there may be also some alpha-radioactivity of nearly the same energy associated with Sm^{148} has not been ruled out.

A sample of isotopically pure Sm^{147} was obtained by ion exchange chemical separation from an 0.8 mg amount of Pm^{147} (a beta-emitter variously reported as 2.26-yr.³ or 3.7-yr.⁴ half-life) which had been allowed to decay for about a year. This samarium sample was analyzed in an optical spark spectrograph to establish its chemical purity, in the mass spectrograph to prove the material was isotopically pure mass 147, and was examined for alpha-activity in an ionization chamber with differential pulse-height analyzer, which affords an alpha-energy determination in addition to detection. Alpha-activity of the same energy as that of the natural samarium alpha-activity was observed. The specific alpha-activity of this small sample of Sm^{147} has not yet been accurately determined, but it is roughly of the order of magnitude to account for the total alpha-activity observed in natural samarium.

Dempster⁵ had previously come to the conclusion that the natural samarium alpha-activity should be assigned to Sm^{147} on the basis of a continuance of his work using isotopic separation with the mass spectrograph together with the photograph technique for detection.

We are grateful for the advice and suggestions of Glenn T. Seaborg. We wish to thank Dr. John Swartout of Oak Ridge National Laboratory for making available to us the Pm^{147} . The help of J. C. Conway and M. F. Moore in the spectrographic analysis is also gratefully acknowledged. We wish also to thank J. T. Vale and the crew of the 184-inch cyclotron for their assistance in this work.

* This work was performed under the auspices of the AEC.

¹ Thompson, Ghiorso, Rasmussen, and Seaborg, *Phys. Rev.* **76**, 1406 (1949).

² Thompson, Cunningham, and Seaborg, *J. Am. Chem. Soc.* **72**, 2798 (1950).

³ Inghram, Hayden, and Hess, *Phys. Rev.* **79**, 271 (1950).

⁴ J. A. Seiler and L. Winsberg, *Radiochemical Studies: The Fission Products* (McGraw-Hill Book Company, Inc., New York), National Nuclear Energy Series, Plutonium Project Record, Vol. 9B (to be published).

⁵ A. J. Dempster, tentative result given in Argonne National Laboratory Report ANL-4355 (October, 1949), unpublished.

Magnetic Shielding Constant of H_2

G. F. NEWELL

Physics Department, University of Illinois, Urbana, Illinois
September 20, 1950

RECENT investigations of the magnetic shielding effects in the H_2 molecule¹⁻³ have shown that, to calculate $-\Delta H/H$, the fractional change of the magnetic field H at a nucleus due to the electrons, it is necessary to know the average value of r^{-1} . Here r is the distance of one of the electrons from the nucleus considered and the average must be taken over the electron distribution of the ground state of H_2 .

The electronic wave function derived previously by the author⁴ is used to determine average r^{-1} as a function of the internuclear distance R . The results are given in Table I.

Averaging these values over the zero-point vibration of the molecule gives average $r^{-1} = 0.904 \pm 0.003$. The error is estimated following the procedure used in reference 4 to determine the error in the electric field gradient. Further assurance of the reliability of the estimated limits of error is obtained by comparison with the known error of the electron energy⁴ calculated from this wave function. Since average r^{-1} is $\frac{1}{4}$ of the potential energy of the molecule excluding the mutual repulsion of the two electrons, it is one of the major contributions to the energy of the molecule. The percentage error given for average r^{-1} is comparable to the percentage error in the energy of the electron distribution, as one would expect it to be.

TABLE I. Average r^{-1} as a function of the internuclear separation R . r^{-1} and R are given in atomic units.

R	Average r^{-1}
1.2	0.982
1.3	0.946
1.4	0.915
1.5	0.886

The formula for the magnetic shielding constant of H_2 as given by Ramsey² is

$$\sigma = -\Delta H/H = \frac{1}{3}\alpha^2(\text{average } r^{-1}) - (\alpha^2 a_0 R^2 / 6\mu_N) [(2Z\mu_N/R^3) - (\mu' H_r / MJ)].$$

The notation is essentially that used by Ramsey (Eq. (24) of reference 2).

A new value $(3.21 \pm 0.01) \times 10^{-5}$ obtained for the first term of σ is to be compared with the value 3.24×10^{-5} given by Anderson¹ using Nordsieck's wave function⁵ and the value 3.16×10^{-5} by Hylleraas and Skavlem.³ The latter two values are those at the equilibrium value of R and are not averages over the molecular vibration. This explains the difference between the present value and Anderson's; the present calculation giving 3.25×10^{-5} at the equilibrium position $R=1.4$. The Hylleraas and Skavlem value was obtained from a much less accurate wave function.

The second term of σ is given by Ramsey as $(0.56 \pm 0.01) \times 10^{-5}$, the error being only that due to the experimental error in H_r . Anderson⁶ has pointed out that the molecular vibration contributes an additional source of error in this term. A correction for this is less easily made here than in the first term because H_r is not known as a function of R . An experimentally measured value of H_r , which itself corresponds to an average over the molecular vibration, is known, however. A theoretical expression² for H_r is composed of integrals containing the factor r^{-3} . For this reason, we assume that $H_r(R)$ varies as R^{-n} , choose $n \sim 3$, and require that the average of $H_r(R)$ be 13.66 as given by Ramsey.

The average value of the second term of σ calculated in this way becomes 0.55×10^{-5} . Because of the uncertainty of the assumptions made above, the error of this is taken to be 5 percent, which would correspond to an error in n of about ± 1.5 .