

Thomas-Fermi treatment. To a first approximation we find

$$S_\epsilon = \xi_\epsilon \times 8\pi e^2 a_0 (Z_1 Z_2 / Z) (v/v_0), \quad (6)$$

with $Z = (Z_1^{\frac{2}{3}} + Z_2^{\frac{2}{3}})^{\frac{3}{2}}$, and where ξ_ϵ is of order of 1-2, but may vary with Z_1 approximately as $\xi_\epsilon \approx Z_1^{\frac{1}{3}}$. The dependence of S_ϵ on Z_1 and Z_2 in (6) is an expedient to get simple estimates. Empirically, the formula (6) is not far in error. Of course, for $v \gtrsim v'$ the formula (6) no longer holds, and the stopping cross section will reach a maximum and decrease at higher velocities.

We observe that (6) and (3) become equal at some energy E_c . If we put $Z_1 = Z_2$ we find $E_c = Z_2^{\frac{2}{3}} A_2 (\xi_\nu / \xi_\epsilon)^2 \times 750 \text{ ev} \approx Z_2 A_2 \times 500 \text{ ev}$, i.e., $\epsilon_c \approx 6 A_2 Z_2^{-\frac{2}{3}}$, but already somewhat below this energy S_ν has fallen below (3) and $d\sigma_\nu$ approached the Rutherford scattering cross section. In many measurements, then, one observes a nearly constant S at energies about E_c . However, it is composed of a decreasing S_ν and an increasing S_ϵ . This effect will show up, e.g., as a reduction of relative straggling in range, since the straggling from collisions with electrons is negligible.

An instructive application of the above scattering formulas for power potentials is the hydrogen-deuterium isotope effect. In fact, when a heavy ion moves through a light substance ($M_1 \gg M_2$), S_ν varies with M_2 as

$M_2^{1-2/n}$. To S_ν should be added S_ϵ which is independent of M_2 ; accordingly, for $n=2$ the stopping is independent of M_2 . For $n-2$ positive, the heavier isotope will give the larger stopping, and vice versa. This result leads to an interpretation of range differences observed in hydrogen and deuterium. For large ϵ the value of n is between 1 and 2, and therefore $R_D > R_H$.^{4,9} For small ϵ we expect n to increase beyond 2, so that $R_D < R_H$.⁵

Another interesting isotope effect is observed when M_1 is varied for fixed Z_1 . Davies⁶ has measured the shift in projected range between Na^{22} and Na^{24} of energy 24 keV in Al. Here, we expect a small energy loss to electrons, so that Eqs. (1), (3), and (5) are approximately valid. The results of Davies are in fair accord with Eq. (5).

More extensive publications are forthcoming on these and related subjects. Several of the above results were obtained five years ago, following discussions with Dr. R. B. Leachman on his observations of range distributions.² We are much indebted to Dr. Leachman for these discussions. We are grateful to Dr. J. M. Alexander, Dr. B. G. Harvey, and Dr. N. O. Lassen for communication of experimental observations prior to publication.

⁹ J. K. Bøggild, O. H. Arrøe, and T. Sigurgeirsson, *Phys. Rev.* **71**, 281 (1947).

Variational Method for Scattering Length

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The properties of the scattering length obtained by Kohn's method, which is one of Hulthén's variational methods, are studied by assuming a linear trial function with n adjustable parameters. The scattering length $A^{(n)}$ decreases monotonically as the number of adjustable parameters n increases, if there is no bound state in the system. This conclusion essentially comes from the upper bound theorem of Spruch and Rosenberg. When the system has m bound states, the scattering length increases in value only m times, and otherwise decreases monotonically. Therefore, after one verifies the presence of m increases, the calculated value is certain to give an upper bound on the scattering length. The connection between the result above and the condition of Rosenberg, Spruch, and O'Malley is considered. In the Appendix comparison is made of the scattering length $A^{(n)}$ obtained by Hulthén's original method and Kohn's method when m bound states exist in general.

I. INTRODUCTION AND SUMMARY

SPRUCH and Rosenberg¹ have recently proved that the Kohn method, which is one of the Hulthén variational methods, gives an upper bound on the scattering length if there is no bound state in the system. Rosenberg, Spruch, and O'Malley² have extended the

theorem to the case where m bound states exist and showed that the calculated scattering length also gives an upper bound if the trial function is chosen so flexible that m approximate orthogonal-wave functions for the bound states with negative-energy expectation values can be formed by a linear combination of the terms involved in the trial function. The upper-bound theorem is useful because we can judge which is the better calculation and how the result is improved.

The purpose of the present note is to study the nature of convergence in the variational calculation with a

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¹ L. Spruch and L. Rosenberg, *Phys. Rev.* **116**, 1034 (1959).

² L. Rosenberg, L. Spruch, and T. F. O'Malley, *Phys. Rev.* **118**, 184 (1960); **119**, 164 (1960).

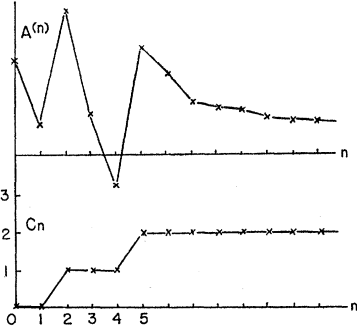


FIG. 1. The behavior of $A^{(n)}$ is schematically shown as a function of n when two bound states exist in the system. C_n is the maximum number of orthogonal states with negative energy expectation value which can be constructed by linear combination of $u_1 e^{-\lambda r}, \dots, u_n e^{-\lambda r}$ ($\lambda > 0, \lambda \rightarrow 0$). $A^{(n)}$ increases in its value only when C_n increases. After two increases, $A^{(n)}$ converges from above to the true value of scattering length. In general $C_n = m$ is the necessary and sufficient condition required for $A^{(n)}$ to give an upper bound. This is true even if some of the adjustable parameters are included nonlinearly in the trial function.

requirement that in Eq. (8) $A^{(n)}$ be stationary, we have

$$\partial A^{(n)} / \partial a_i = 2(H_{i0} + H_{i1}a_1 + \dots + H_{in}a_n) = 0, \quad (i=1, \dots, n). \quad (9)$$

It is assumed that (9) has a meaningful solution. (If not the variational procedure breaks down.) Equations (9) determine a_i ; substituting the solution, a_i , into (8) gives the final result for A in the n th approximation:

$$A^{(n)} = H_{00} + \sum_{i=1}^n H_{10}a_i, \quad A^{(0)} = H_{00}. \quad (10)$$

It will be proved in the last section that

$$A^{(n+1)} - A^{(n)} = -(D_n^2 / B_n B_{n+1}), \quad (11)$$

where

$$B_0 = 1, \quad D_0 = H_{10},$$

$$B_n = \begin{vmatrix} H_{11} & \dots & H_{1n} \\ \vdots & & \vdots \\ H_{n1} & \dots & H_{nn} \end{vmatrix},$$

$$D_n = \begin{vmatrix} H_{11} & \dots & H_{1n} & H_{10} \\ \vdots & & \vdots & \vdots \\ H_{n1} & \dots & H_{nn} & H_{n0} \\ H_{n+1,1} & \dots & H_{n+1,n} & H_{n+1,0} \end{vmatrix}.$$

The nonvanishing of B_n comes from the existence of the solution (9). The sign of $A^{(n+1)} - A^{(n)}$ thus entirely depends on the sign of $B_n B_{n+1}$. Let us consider the behavior of B_n . In order to see the physical meaning of B_n we shall define $H_{ij}(\lambda)$ and $B_n(\lambda)$ by introducing the factor $e^{-\lambda r}$ ($\lambda > 0$) into all $u_i(r)$:

$$H_{ij}(\lambda) = \int_0^\infty u_i e^{-\lambda r} H u_j e^{-\lambda r} dr = H_{ji}(\lambda), \quad (i \geq j \geq 1),$$

$$B_n(\lambda) = \begin{vmatrix} H_{11}(\lambda) & \dots & H_{1n}(\lambda) \\ \vdots & & \vdots \\ H_{n1}(\lambda) & \dots & H_{nn}(\lambda) \end{vmatrix}.$$

Notice that the elements H_{i0} or H_{0i} do not appear in B_n . $H_{ij}(\lambda)$ and $B_n(\lambda)$ are continuous¹ at $\lambda=0$ as functions of λ . After diagonalizing $H_{ij}(\lambda)$ we have the eigenvalues $H_i^{(n)}$. The energy expectation values $E_i^{(n)}$ of these eigenvectors are proportional to $H_i^{(n)}$. $B_n(\lambda)$ is expressed in terms of $E_i^{(n)}$,

$$B_n(\lambda) = H_1^{(n)} H_2^{(n)} \dots H_n^{(n)} = \left(\frac{2m}{\hbar^2} \right)^n N E_1^{(n)} \dots E_n^{(n)},$$

where N is a positive constant determined by the normalization of $u_i e^{-\lambda r}$. The sign of $B_n(\lambda)$ is thus $(-)^{C_n}$, where C_n is the number of negative energy eigenvalues ($C_0=0$). We shall now make use of the following inequalities on the energy eigenvalues³:

$$E_1^{(n+1)} \leq E_1^{(n)} \leq E_2^{(n+1)} \leq E_2^{(n)} \leq \dots \leq E_n^{(n)} \leq E_{n+1}^{(n+1)}. \quad (12)$$

From (12) we see that the number of negative eigenvalues C_{n+1} in the $(n+1)$ th approximation is either

$$C_{n+1} = C_n + 1, \quad (13a)$$

or

$$C_{n+1} = C_n. \quad (13b)$$

The sign of $B_n(\lambda) B_{n+1}(\lambda)$ is negative for (13a) and positive for (13b). Since C_n cannot be larger than the number of actually existing bound states m , the number of places where $A^{(n+1)} - A^{(n)}$ in Eq. (11) has a positive sign does not exceed m .

If the trial-function series is properly chosen so that it can converge to the true solution, the number of negative energy eigenvalues should become m when $n \rightarrow \infty$. Thus it has been shown (for $\lambda > 0$) that $A^{(n)}$ makes m positive jumps⁵ while n increases from zero to infinity (see Fig. 1). The result is also valid for $\lambda=0$ by virtue of the continuity at $\lambda=0$. After m positive jumps, $A^{(n)}$ decreases monotonically, therefore it always gives an upper bound.

It should be noted that $C_n = m$ is equivalent to the condition of Rosenberg, Spruch, and O'Malley² (the improved version obtained in the second paper of reference 2) and is the necessary and sufficient condition required for $A^{(n)}$ to give an upper bound.

When there is no bound state, $A^{(n)}$ decreases monotonically. This is quite natural in view of the upper bound theorem of Spruch and Rosenberg. If one bound state exists (for example, the singlet system of the electron-hydrogen atom scattering), and if $H_{11} < 0$, $A^{(n)}$ ($n \geq 1$) gives an upper bound, because $B_1 = H_{11}$. Another criterion⁶ on the upper boundedness will be furnished if one calculates initially several $A^{(n)}$ and verifies the m positive jumps. These conclusions may

⁵ We assume that $D_n^2 > 0$ for n which satisfies (13a).

⁶ This criterion is also applicable to the variational method proposed by Rosenberg and Spruch for positive (nonzero) energy scattering; namely, a bound on some function of the phase shift is obtained if we verify M positive jumps. See Phys. Rev. **120**, 476 (1960).

TABLE I. The scattering length obtained by the variational method.

λ	-1	-1.69	-7.84
$A^{(0)}$	-2.00*	-3.38	-15.68
$A^{(1)}$	-5.37*	21.99*	0.68
$A^{(2)}$	-5.98 ₃ *	17.311*	-3.36
$A^{(3)}$	-6.00 ₃ *	17.310*	54.28*
Exact	-6.007	17.300	42.29

be important from a practical point of view. So far we have dealt with the simplest scattering problem (1)~(3), but extensions to more general cases are clearly possible and the same conclusions are all valid.

III. ILLUSTRATIVE EXAMPLES

First example. Let us take the case of an exponential potential well,

$$H = -\left(\frac{d^2}{dr^2}\right) + \lambda e^{-r},$$

and choose the trial function,

$$u_0 = r, \quad u_n = e^{-(n-1)r} - e^{-nr}, \quad n \geq 1.$$

The values of scattering length calculated by (9) and (10) are shown in Table I. The number of bound states m is zero for $-1.446 < \lambda < +\infty$, one for $-7.618 < \lambda < -1.446$, two for $-18.72 < \lambda < -7.618$, etc. One jump of $A^{(n)}$ occurs at $A^{(1)}$ for $\lambda = -1.69$, and two jumps occur at $A^{(1)}$ and $A^{(3)}$ for $\lambda = -7.84$. Since $H_{11} < 0$ for both cases, $A^{(1)} > A^{(0)}$. The values with asterisks are certain to give upper bounds on the scattering length.

The second example is given by Hara *et al.*⁷ The scattering length of the electron-hydrogen atom scattering is calculated there by assuming a linear trial function. The scattering length in the triplet state (where bound states do not exist) decreases monotonically starting from $A_t^{(0)} = 5.00 a_B$, $A_t^{(1)} = 2.35 a_B$, to $A^{(6)} = 2.27 a_B$. (a_B = the Bohr radius). There is one increase from $A_s^{(0)} = -7.00 a_B$ to $A_s^{(1)} = 10.90 a_B$ in the singlet state, where one bound state (namely, the H⁻ ion ground state) exists. $A_s^{(n)}$ decreases monotonically from $A_s^{(1)}$ to the best value of $A_s^{(9)} = 6.22 a_B$ in their paper.

IV. PROOF OF EQ. (11)

The difference between $A^{(n+1)}$ and $A^{(n)}$ can be evaluated in a straightforward manner, but it is not very simple. We shall first make a linear transformation of the basis vectors and diagonalize the $n \times n$ matrix (H_{ij}). $A^{(n)}$ in Eq. (8) now takes the form

$$A^{(n)} = H_{00} + H_{11}c_1^2 + \cdots + H_{nn}c_n^2, \quad (14)$$

where the same notation H is used as in (8), but this should not cause confusion. Similar procedures for (9)

and (10) give us the result

$$A^{(n)} = H_{00}, \quad c_1 = c_2 = \cdots = c_n = 0. \quad (15)$$

In this new system $A^{(n+1)}$ has the form,

$$A^{(n+1)} = H_{00} + H_{11}c_1^2 + \cdots + H_{nn}c_n^2 + H_{n+1, n+1}c_{n+1}^2 + 2(H_{0, n+1}c_{n+1} + H_{1, n+1}c_1c_{n+1} + \cdots + H_{n, n+1}c_nc_{n+1}). \quad (16)$$

The procedure corresponding to (9) is

$$\partial A^{(n+1)} / \partial c_i = 2(H_{ii}c_i + H_{i, n+1}c_{n+1}) = 0, \quad (i = 1, \cdots, n) \quad (17a)$$

$$\partial A^{(n+1)} / \partial c_{n+1} = 2(H_{0, n+1} + \sum_{i=1}^n H_{i, n+1}c_i + H_{n+1, n+1}c_{n+1}) = 0. \quad (17b)$$

From (16), (17a), and (17b), we have

$$A^{(n+1)} = H_{00} - H_{0, n+1}^2 \left(H_{n+1, n+1} - \sum_{i=1}^n \frac{H_{i, n+1}^2}{H_{ii}} \right)^{-1}. \quad (18)$$

B_n and B_{n+1} defined in (11) are now, respectively,

$$B_n = H_{11}H_{22} \cdots H_{nn},$$

$$B_{n+1} = \begin{vmatrix} H_{11} & & & & H_{1, n+1} \\ & H_{22} & & 0 & H_{2, n+1} \\ & & \cdots & & \vdots \\ & & & H_{nn} & H_{n, n+1} \\ H_{n+1, 1} & H_{n+1, 2} & \cdots & H_{n+1, n} & H_{n+1, n+1} \end{vmatrix} \quad (19)$$

$$= B_n \left(H_{n+1, n+1} - \sum_{i=1}^n \frac{H_{i, n+1}^2}{H_{ii}} \right).$$

By combining (18) and (19), we have

$$A^{(n+1)} = A^{(n)} - \frac{H_{n+1, 0}^2 B_n}{B_{n+1}}. \quad (20)$$

If we notice that D_n/B_n is reduced to $H_{n+1, 0}$ in this system, we finally get from (20)

$$A^{(n+1)} = A^{(n)} - (D_n^2 / B_n B_{n+1}).$$

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APPENDIX. ORIGINAL HULTHÉN METHOD

It will be shown here that Hulthén's original variational method gives a larger⁸ value for the scattering

⁷ Y. Hara, T. Ohmura, and T. Yamanouchi, Progr. Theoret. Phys. (Kyoto) **25**, 467 (1961).

⁸ Strictly speaking, a not smaller value.

length than Kohn's method does, if the same trial function is used and if the Rosenberg, Spruch, and O'Malley condition (in the first paper of reference 2) is satisfied. This is, however, a sufficient (not necessary) condition. The necessary, and at the same time sufficient, condition is expressed by saying that, for the trial function (6) with n parameters, B_n and F_n (see below) have the same sign. The meaning of this statement will also be given.

To simplify the calculation we shall again transform the basic vectors. The linear transform will be done among (u_0, u_2, \dots, u_n) only, and u_1 remains unchanged. $A^{(n)}$ now takes the form

$$A^{(n)} = H_{00} + H_{11} + \dots + H_{nn} + 2(H_{01}a_1 + H_{21}a_2a_1 + \dots + H_{n1}a_na_1). \quad (\text{A1})$$

The original Hulthén method consists of the following equations:

$$\partial A^{(n)} / \partial a_i = 2H_{ii}a_i + 2H_{i1}a_1 = 0, \quad (i = 2, \dots, n) \quad (\text{A2})$$

$$A^{(n)} = a_1. \quad (\text{A3})$$

From (A2) and (A1) we have

$$A^{(n)} = H_{00} + H_{11}a_1^2 + 2H_{10}a_1 - \sum_{i=2}^n \frac{H_{ii}^2 a_1^2}{H_{ii}}. \quad (\text{A4})$$

On comparing (A3) and (A4) we obtain the value of scattering length $A_H^{(n)}$ in Hulthén's original method from the equation

$$A_H^{(n)} = H_{00} + H_{11}A_H^{(n)2} + 2H_{10}A_H^{(n)} - \sum_{i=2}^n \frac{H_{ii}^2 A_H^{(n)2}}{H_{ii}}. \quad (\text{A5})$$

In the Kohn approximation, from the equation $\partial A^{(n)} / \partial a_i = 0$, ($i = 1, \dots, n$), we have

$$a_i = -(H_{i1}/H_{ii})a_1, \quad i \geq 2 \quad (\text{A6})$$

$$a_1 = - \left(1 - \sum_{i=2}^n \frac{H_{ii}^2}{H_{11}H_{ii}} \right)^{-1} \frac{H_{01}}{H_{11}}. \quad (\text{A7})$$

The scattering length $A_K^{(n)}$ in Kohn's method is given by [see (10)]

$$\begin{aligned} A_K^{(n)} &= H_{00} + H_{10}a_1 \\ &= H_{00} - H_{01}^2 \left(H_{11} - \sum_{i=2}^n \frac{H_{ii}^2}{H_{ii}} \right)^{-1}. \end{aligned} \quad (\text{A8})$$

If we take the difference of (A5) and (A8), we obtain

$$\begin{aligned} A_H^{(n)} - A_K^{(n)} &= \left(H_{11} - \sum_{i=2}^n \frac{H_{ii}^2}{H_{ii}} \right) \\ &\times \left[A_H^{(n)} + H_{10} \left(H_{11} - \sum_{i=2}^n \frac{H_{ii}^2}{H_{ii}} \right)^{-1} \right]^2. \end{aligned} \quad (\text{A9})$$

Since the second factor is always positive, the sign of $(A_H^{(n)} - A_K^{(n)})$ is determined by the first factor which is written B_n/F_n in the original system, where B_n is given by (11) and

$$F_n = \begin{vmatrix} H_{22} & \dots & H_{2n} \\ \vdots & & \vdots \\ H_{n2} & \dots & H_{nn} \end{vmatrix}.$$

Therefore we come to the conclusion that $A_H^{(n)}$ is larger than $A_K^{(n)}$ if B_n and F_n have the same sign. The sign of both B_n and F_n is $(-)^m$ (m is the number of bound states in the system), if the condition of Rosenberg, Spruch, and O'Malley is satisfied. Their condition is that m orthogonal states with negative energy expectation value can be formed by taking linear combinations⁹ of (u_2, \dots, u_n) . The sign of F_n or B_n is $(-)^p$ or $(-)^q$, respectively, where p or q is the maximum number of orthogonal states with negative energy value formed by $(u_2 e^{-\lambda r}, \dots, u_n e^{-\lambda r})$ or $(u_1 e^{-\lambda r}, \dots, u_n e^{-\lambda r})$, respectively. ($\lambda \rightarrow 0$, $\lambda > 0$.)

⁹ They assume square integrability. If u_2, \dots, u_n are assumed to satisfy the weaker condition (7c), these should be multiplied by $e^{-\lambda r}$.