[6] L. Michel and A. S. Wightman, Phys. Rev. **98**, 1190 (1955); F. W. Lipps and H. A. Tolhoek, Physica **20**, 85 (1954).

[7] M. Yamada and M. Morita, Prog. Theor. Phys. **8**, 431 (1952).

[8] L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 407 (1957), Soviet Phys. JETP **5**, 337 (1957).

[9] T. D. Lee and C. N. Yang, Phys. Rev. **105**, 1671 (1957).

Translated by W. H. Furry
296

SOVIET PHYSICS JETP VOLUME 6 (33), NUMBER 6 JUNE, 1958

CONNECTION BETWEEN THE HULTHÉN AND KOHN METHODS IN COLLISION THEORY

Iu. N. DEMKOV and F. P. SHEPELENKO

Leningrad State University

Submitted to JETP editor May 30, 1957

J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 1483-1487 (December, 1957)

Various possible direct variational methods for the determination of the phase shifts of the radial wave function are considered. It is shown that the most natural criterion of the quality of the trial function is the condition of the consistency of the equations. The comparison of the phase-shift results obtained by the Hulthén and Kohn methods, and the verification of whether the integral identity is satisfied, are not independent criteria and in fact reduce to the consistency condition. It is also shown how the correct value can be chosen from two phase-shift values obtained by the Hulthén method, without resorting to comparison with the results of other methods.

WE consider the equation for the phase shift in collision theory:

$$\psi''(r) + (k^2 - V)\psi(r) = 0; \tag{1}$$

$$\psi(0) = 0, \quad \psi|_{r\to\infty} \sim A\sin(kr + \eta). \tag{2}$$

The variational principle for this problem can be written in the form[1]

$$\delta J = \delta\int_0^\infty \psi(r)\left(\frac{d^2}{dr^2} + k^2 - V\right)\psi(r)\,dr = -A^2k\delta\eta. \tag{3}$$

If we substitute in this functional an approximate function $\tilde{\psi}(r)$ which satisfies the conditions (2) and which depends on the parameters α_i, we can obtain equations for these parameters from the variational principle. It is well known that, in contrast to the problem of the discrete spectrum, the set of equations can be formed in this case, in a non-unique fashion.

We consider the very simple but also very important case in which a linear combination of n functions $\varphi_i(r)$ are substituted in the functional J:

$$\tilde{\psi}(r) = \sum_{i=1}^{n} \alpha_i\varphi_i(r). \tag{4}$$

In this case, let

$$\varphi_i(0) = 0, \quad i = 1, 2, \ldots, n;$$

$$\text{for } r \to \infty \quad \varphi_1 \sim \sin kr, \quad \varphi_2 \sim \cos kr, \quad \varphi_j \to 0, \quad j = 3, 4, \ldots, n. \tag{5}$$

Then the functional J will be quadratic in

$$J(\tilde{\psi}) = \sum_{i,j=1}^{n} \alpha_i \alpha_j J_{ij}, \tag{6}$$

where

$$J_{ij} = \frac{1}{2}\left[\int_0^\infty \varphi_i \left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi_j \, dr + \int_0^\infty \varphi_j \left(\frac{d^2}{dr^2} + k^2 - V\right)\varphi_i \, dr\right]. \tag{7}$$

The amplitude and phase for such a choice of wave function are determined by the coefficients α_1 and α_2. It is evident that $\alpha_1 = A\cos\eta$, $\alpha_2 = A\sin\eta$, and

$$A^2 \delta\eta = \alpha_1 \delta\alpha_2 - \alpha_2 \delta\alpha_1. \tag{8}$$

Thus, the variational principle (3) can be written in the form

$$\delta J = k(\alpha_2 \delta\alpha_1 - \alpha_1 \delta\alpha_2). \tag{9}$$

The equations for the coefficients $\alpha_1, \ldots, \alpha_n$ have in this case the form[2]

$$\sum_{j=1}^{n} J_{1j}\alpha_j = \frac{k\alpha_2}{2}; \quad \sum_{j=1}^{n} J_{2j}\alpha_j = -\frac{k\alpha_1}{2}; \quad \sum_{j=1}^{n} J_{ij}\alpha_j = 0 \quad (i = 3, 4, \ldots, n). \tag{10}$$

The condition for the existence of a non-trivial solution of this system,

$$\begin{vmatrix} J_{11} & J_{12} - k/2 & \ldots & J_{1n} \\ J_{21} + k/2 & J_{22} & \ldots & J_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ J_{n1} & J_{n2} & & J_{nn} \end{vmatrix} = 0, \tag{11}$$

is generally not satisfied. Discarding one of the equations (10), we can make the system solvable and arrive at a different formulation of the variational principle. Thus, for example, by discarding the first of these equations, we obtain Kohn's method.[3] The coefficient α_1 is not varied here and is assumed to be equal to unity. Then $\alpha_2 = \tan\eta$, $\delta\alpha_1 = 0$, and

$$\delta J = -k\delta\alpha_2 = -k\delta(\tan\eta). \tag{12}$$

Hulthén[1] discards the first two equations of the system (10) but adds the equation J = 0, which is obtained if each of Eqs. (10) is multiplied by the corresponding α_i and all are added together. The condition J = 0 holds because the functional is stationary relative to a variation of the normalizing constant A.

In the Kohn method[3] for the determination of the coefficients α, we have the set of equations

$$\begin{aligned} J_{21} + J_{22}\alpha_2 + \ldots + J_{2n}\alpha_n &= -k/2, \\ J_{31} + J_{32}\alpha_2 + \ldots + J_{3n}\alpha_n &= 0, \\ \ldots\ldots\ldots\ldots\ldots\ldots & \\ J_{n1} + J_{n2}\alpha_2 + \ldots + J_{nn}\alpha_n &= 0. \end{aligned} \tag{13}$$

Solving this set, we find the approximate wave function $\tilde{\psi}$. Inasmuch as the coefficient α_1 is fixed, we can no longer vary the normalizing constant A freely; consequently, the value of $J(\tilde{\psi})$ will generally differ from zero. This makes it possible to improve the value for $\tan\eta$ by making use of Eq. (12). Thus,

$$\tan\eta = \alpha_2 + J(\tilde{\psi})/k. \tag{14}$$

This formula can be transformed by using the system (13). Actually,

$$\begin{aligned} J(\tilde{\psi}) = \sum_{i=1}^{n} \alpha_i (J_{i1}\alpha_1 + J_{i2}\alpha_2 + \ldots + J_{in}\alpha_n) = \alpha_1 (J_{11}\alpha_1 + J_{12}\alpha_2 + \ldots + J_{1n}\alpha_n) \\ - k\alpha_2/2 = J_{11} + J_{12}\alpha_2 + J_{13}\alpha_3 + \ldots + J_{1n}\alpha_n - k\alpha_2/2, \end{aligned} \tag{15}$$

and Eq. (14) takes the form

$$k \tan \eta = J_{11} + (J_{12} + k/2)\,\alpha_2 + J_{13}\alpha_3 + \ldots + J_{1n}\alpha_n. \tag{16}$$

In order to establish the connection between the methods of Hulthén and Kohn, we eliminate $\alpha_3, \alpha_4, \ldots \alpha_n$ with the aid of the last (n − 2) equations of (13). This leads to a system of two equations for α_1 and α_2:

$$A_{11}\alpha_1 + A_{12}\alpha_2 = k\alpha_2/2, \quad A_{21}\alpha_1 + A_{22}\alpha_2 = -\,k\alpha_1/2. \tag{17}$$

Multiplying the first equation by α_1 and the second by α_2, and adding them together, we get the Hulthén equation

$$J = A_{11}\alpha_1^2 + 2A_{12}\alpha_1\alpha_2 + A_{22}\alpha_2^2 = 0. \tag{18}$$

Then, for the desired quantity $\alpha_2/\alpha_1 = \tan\eta$ we get, by Hulthén's method,

$$\tan \eta = (-A_{12} \pm \sqrt{A_{12}^2 - A_{11}A_{22}})/A_{22}. \tag{19}$$

Similarly, by Kohn's method,

$$\alpha_2 = -\frac{1}{A_{22}}\left(A_{12} + \frac{k}{2}\right); \quad \tan \eta = -\frac{1}{A_{22}}\left(A_{12} + \frac{k}{2}\right) + \frac{1}{A_{22}k}\left(A_{11}A_{22} - A_{12}^2 + \frac{k^2}{4}\right). \tag{20}$$

The results obtained by both methods will be identical if Eqs. (17) are consistent, i.e., if the condition

$$A_{12}^2 - A_{11}A_{22} = k^2/4. \tag{21}$$

is satisfied. This condition clearly coincides with condition (11).

It is easy to see that if the radical in (19) is taken with the minus sign, then Eqs. (19) and (20) actually coincide when Eq. (21) is satisfied. In this way, in order to select the true root from the two possible roots of the Hulthén equation, there is no necessity (as is pointed out in Ref. 4, for example) of comparing the results obtained here with the results of two approximate calculations. The root with the minus sign in front of the radical has physical meaning. Furthermore, the condition (21) itself gives a sufficiently reliable criterion of the quality of the wave function thus obtained. It is also evident from this why the Hulthén method does not give complex values for $\tan\eta$, provided the function is chosen satisfactorily. In fact, the radicand is close to the value $k^2/4$ in this case, and is thus positive.

To understand the formal nature of the second solution in the Hulthén method, we note that if condition (21) is satisfied, the second root becomes

$$\tan \eta = (-A_{12} + k/2)/A_{22}. \tag{22}$$

We can get the same value for $\tan\eta$ from a formal attempt to satisfy, in the space of the functions (4), the variational equation

$$\delta J = -\,k\,(\alpha_2\,\delta\alpha_1 - \alpha_1\,\delta\alpha_2) = A^2 k\delta\eta, \tag{23}$$

which is obtained from the variational principle (9) by replacement of k by −k on the right hand side.

However, it is evident that Eq. (23) makes no sense. In fact, the wave function is already uniquely determined because the functional J is stationary relative to variations that vanish at infinity. It therefore follows that this result, which is obtained for δJ in the variation of a function of asymptotic form, is unique and cannot be changed at will. Consequently, Eq. (23) in general defines no function at all. If we solve the problem by the Hulthén method, increasing gradually the number n of the functions φ_i, then the second root [the plus sign in Eq. (19)] either will not tend to a definite limit, or this limit will depend essentially on the choice of the sequence of functions φ_i. Actual calculations verify this statement.

Now let us consider in what measure the integral identity, which stems from the variational principle, must be satisfied for the resultant approximate functions. In the given case, this identity has the form

$$\tan \eta = \frac{1}{k}\int_0^\infty \psi(r)\left(\frac{d^2}{dr^2} + k^2 - V\right)\sin kr\,dr = -\frac{1}{k}\int_0^\infty \psi(r)\,V\sin kr\,dr, \quad \psi\,|_{r\to\infty} \sim \sin kr + \tan\eta\cos kr. \tag{24}$$

Let us assume that $\varphi_i(r) = \sin kr$; such a choice is simplest; in practice they all behave in this fashion. We substitute the approximate expression (4) in Eq. (24) in place of the exact wave function. We then get

$$\tan\eta = \frac{1}{k}\sum_{i=1}^{n}\alpha_i\int_0^\infty \varphi_i\left(\frac{d^2}{dr^2}+k^2-V\right)\varphi_1\,dr = \frac{1}{k}\sum\alpha_i J_{i1}+\frac{1}{2}\alpha_2. \tag{25}$$

This equation coincides with (16) and thus the integral identity is automatically satisfied in the calculation of the phase shift by the Kohn method.

Along with this, if on the left side of Eq. (25) we substitute the coefficient α_2 for $\tan\eta$, we obtain the first equation of the set (10). If then follows that if the integral identity is satisfied in the phase calculation by Hulthén's method, then the set of equations (10) is consistent, the determinant (11) vanishes, and both the Hulthén method and the Kohn method give the same results. Hence a test of the fulfillment of the integral identity is equivalent to a direct comparison of the results of the calculation of the phase shift by the methods of Hulthén and Kohn, and therefore is not an independent criterion that confirms the validity of the variational calculation.

As an example, we have carried out a calculation of the phase η for the case of electron scattering by a static field of a hydrogen atom with

$$V = -2(1+1/r)e^{-2r}$$

in atomic units. In this case the following functions were used:

$$\varphi_1 = \sin kr, \quad \varphi_2 = (1-e^{-r})\cos kr, \quad \varphi_3 = e^{-r}(1-e^{-r})\cos kr; \tag{a}$$

$$\varphi_1 = \sin kr, \quad \varphi_2 = \cos kr - e^{-r}, \quad \varphi_3 = re^{-kr}. \tag{b}$$

The function (a) was employed in the work of Massey and Moiseiwitsch and was taken by us for comparison since it gives results close to the data of the numerical integration. The data for $\tan\eta$ computed by both methods, and also the values of $D = A_{12}^2 - A_{11}A_{22}$ in comparison with $k^2/4$ for each function are given in the table.

As is seen from the table, the values of D for the function (a) are close to $k^2/4$ and the values of $\tan\eta$ obtained by the two methods are practically identical. For the function (b), D differs considerably from $k^2/4$, and the value of $\tan\eta$ themselves, according to Hulthén and Kohn, differ significantly from each other and from the results obtained with functions (a), especially for $k < 1$. The function (b) evidently gives worse results for $\tan\eta$. However, at $k = 1.7$, the condition $D = k^2/4$ is approximately satisfied, and the values of $\tan\eta$, according to Kohn and Hulthén, coincide with the data of the numerical integration.

k	function (a)			function (b)			$\frac{k^2}{4}$
	$\tan\eta$		D	$\tan\eta$		D	
	according to Hulthén	according to Kohn		according to Hulthén	according to Kohn		
0.1	0.8783	0.8787	0.0026	0.4156	0.4184	0.0018	0.0025
0.15	1.2173	1.2174	0.0058	0.6138	0.6217	0.0036	0.0056
0.2	1.4248	1.4242	0.0104	0.7848	0.8009	0.0057	0.0100
0.3	1.7181	1.7189	0.0236	1.0373	1.0749	0.0107	0.0225
0.4	1.9076	1.9087	0.0429	1.1837	1.2399	0.0170	0.0400
0.5	1.7202	1.7211	0.0667	1.2564	1.3246	0.0252	0.0625
0.6	1.6285	1.6298	0.0964	1.2830	1.3546	0.0359	0.0900
0.8	1.4332	1.4353	0.1710	1.2630	1.3222	0.0692	0.1600
1.0	1.2722	1.2733	0.2616	1.1978	1.2343	0.1274	0.2500
1.2	1.1411	1.1404	0.3726	1.1192	1.1360	0.2244	0.3600
1.5	1.0031	0.9950	0.5533	0.9962	0.9978	0.4823	0.5625
2.0	0.8327	0.8356	0.9581	0.8266	0.8324	1.3807	1.0000

Thus Eq. (21), i.e., the condition of consistency of the initial system (10), can be regarded as a sufficiently reliable criterion for the validity of the choices of the variable function. If this condition is satisfied, then the integral identity (24) is also satisfied, and the results of the calculation of the phase by the methods of Hulthén and Kohn coincide.

---

[1] L. Hulthén, Kgl. Fys. Sallskap. Forh. 14, No. 2 (1944).

[2] Iu. N. Demkov, Dokl. Akad. Nauk SSSR 89, 249 (1953).

[3] W. Kohn, Phys. Rev. 74, 1763 (1948).

[4] H. S. W. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) 205A, 483 (1951).

Translated by R. T. Beyer