Perturbation Treatment of the Variable-Phase Method*

Uzi Landman[†]

Department of Chemistry, University of California, Santa Barbara, California 93106
and Department of Physics, University of Illinois, Urbana, Illinois 61801

A perturbation treatment of the variable-phase method for scattering is presented. The zeroth-order phase shift is given by the solution of a first-order nonlinear differential equation. The perturbation corrections are given as the solutions of first-order nonhomogeneous *but linear* differential equations. A variational procedure for the optimization of the zeroth-order approximation is formulated. The results of a test calculation for the s-wave scattering from an attractive exponential potential are included.

PERTURBATION TREATMENT

In the theory of scattering, the scattering phase shifts provide us with the complete information which is needed in order to solve for the cross sections.[1,2] Recently, new variation[3-6] and variation-perturbation[7] methods for the calculation of the phase shifts have been proposed and applied to potential- and low-energy electron–hydrogen-atom scattering problems. In this note we apply the variation-perturbation theory to the variable-phase method[1,8] and indicate the applicability of the method by performing a test calculation for a simple potential-scattering problem. The scattering by a central potential $V(r)$ is described by the Schrödinger equation

$$[\nabla^2 + k^2 - U(r)] \psi(\vec{r}) = 0, \quad U(r) = (2m/\hbar^2)V(r) , \tag{1}$$

with the finiteness at the origin and the asymptotic boundary conditions imposed on the solutions.

In the theory of the variable-phase method one introduces two auxiliary functions defined by

$$s_l(r) = - k^{-1} \int_0^r dr' \, U(r')\hat{j}_l(kr')u_l(r') , \tag{2}$$

$$c_l(r) = 1 - k^{-1} \int_0^r dr' \, U(r')\hat{n}_l(kr')u_l(r') , \tag{3}$$

where $U(r)$ is the potential, $\hat{j}_l(x)$ and $\hat{n}_l(x)$ are the Ricatti-Bessel functions,[1] and $u_l(r)$ is the radial lth partial-wave amplitude. Using the well-known asymptotic behavior of these functions, the phase shift of the lth partial wave is defined as

$$\tan\delta_l = s_l/c_l , \tag{4}$$

where

$$c_l \equiv c_l(\infty) \quad \text{and} \quad s_l \equiv s_l(\infty) . \tag{5}$$

Introducing the "tangent function" $t_l(r)$ which is defined as

$$t_l(r) = s_l(r)/c_l(r) = \tan\delta_l(r) , \tag{6}$$

it is easily inferred from (4) that

$$\lim_{r \to \infty} t_l(r) \equiv t_l = \tan\delta_l . \tag{7}$$

Let us partition the potential $U(r)$ into a zeroth-order term and a perturbation part:

$$U(r) = V_0(r) + \lambda V_1(r) . \tag{8}$$

The partitioning is dictated by the condition that $U(r) - V_0(r)$ has to be small enough; otherwise the convergence of the perturbation series is doubtful. In other words, $V_0(r)$ has to be a sufficiently accurate description of the true potential $U(r)$.

Under these conditions let us expand the radial function in a power series of the perturbation parameter λ,

$$u_l(r) = u_l^{(0)}(r) + \lambda u_l^{(1)}(r) + \lambda^2 u_l^{(2)}(r) + \cdots . \tag{9}$$

Substitution in the equations defining $s_l(r)$ and $c_l(r)$, (2) and (3), yields

$$s_l(r) = s_l^{(0)}(r) + \lambda s_l^{(1)}(r) + \lambda^2 s_l^{(2)}(r) + \cdots , \tag{10}$$

where

$$s_l^{(0)}(r) = - k^{-1} \int_0^r dr' \, V_0(r')\hat{j}_l(kr')u_l^{(0)}(r') ,$$

$$s_l^{(1)}(r) = -k^{-1}\int_0^r dr'\, V_0(r')\hat{j}_l(kr')u_l^{(1)}(r')$$

$$-k^{-1}\int_0^r dr'\, V_1(r')\hat{j}_l(kr')u_l^{(0)}(r')\ ,$$

etc., and

$$c_l(r) = c_l^{(0)}(r) + \lambda c_l^{(1)}(r) + \lambda^2 c_l^{(2)}(r) + \cdots, \tag{11}$$

where

$$c_l^{(0)}(r) = 1 - k^{-1}\int_0^r dr'\, V_0(r')\hat{n}_l(kr')u_l^{(0)}(r')\ ,$$

$$c_l^{(1)}(r) = -k^{-1}\int_0^r dr'\, V_0(r')\hat{n}_l(kr')u_l^{(1)}(r')$$

$$-k^{-1}\int_0^r dr'\, V_1(r')\hat{n}_l(kr')u_l^{(0)}(r'),$$

etc.

Substituting the series for $s_l(r)$ and $c_l(r)$, (10) and (11), into the definition of $t_l(r)$ and identifying terms in the resulting expression with the corresponding terms in the expansion of $t_l(r)$

$$t_l(r) = t_l^{(0)}(r) + \lambda t_l^{(1)}(r) + \lambda^2 t_l^{(2)}(r) + \cdots, \tag{12}$$

we get

$$t_l^{(0)}(r) = s_l^{(0)}(r)/c_l^{(0)}(r)\ , \tag{13}$$

$$t_l^{(1)}(r) = \frac{s_l^{(1)}(r)}{c_l^{(0)}(r)} - \frac{c_l^{(1)}(r)}{c_l^{(0)}(r)}t_l^{(0)}(r)\ , \tag{14}$$

$$t_l^{(2)}(r) = \frac{s_l^{(2)}(r)}{c_l^{(0)}(r)} - \frac{c_l^{(1)}(r)}{c_l^{(0)}(r)}t_l^{(1)}(r) - \frac{c_l^{(2)}(r)}{c_l^{(0)}(r)}t_l^{(0)}(r)\ . \tag{15}$$

In order to get the equation for $t_l^{(0)}(r)$ we follow Calogero.[1] Taking the first derivative of $s_l^{(0)}(r)$ and $c_l^{(0)}(r)$ and making use of the expression for $u_l^{(0)}(r)$, we obtain

$$s_l'^{(0)}(r) = -k^{-1}V_0(r)\hat{j}_l(kr)[c_l^{(0)}(r)\hat{j}_l(kr) - s_l^{(0)}(r)\hat{n}_l(kr)], \tag{16}$$

$$c_l'^{(0)}(r) = -k^{-1}V_0(r)\hat{n}_l(kr)[c_l^{(0)}(r)\hat{j}_l(kr) - s_l^{(0)}(r)\hat{n}_l(kr)]\ . \tag{17}$$

Multiplying Eq. (16) by $c_l^{(0)}(r)$ and Eq. (17) by $s_l^{(0)}(r)$, subtracting the second from the first and dividing by $[c_l^{(0)}(r)]^2$, and comparing with the derivative of Eq. (13), we obtain the following first-order nonlinear equation for $t_l^{(0)}(r)$:

$$t_l'^{(0)}(r) = -k^{-1}V_0(r)[\hat{j}_l(kr) - t_l^{(0)}(r)\hat{n}_l(kr)]^2\ . \tag{18}$$

Performing similar manipulations and comparing with the first derivatives of Eqs. (14) and (15) yields the following first-order nonhomogeneous *but linear* equations for $t_l^{(1)}(r)$ and $t_l^{(2)}(r)$, respectively:

$$t_l'^{(1)}(r) = -2k^{-1}\hat{n}_l(kr)V_0(r)[\hat{n}_l(kr)t_l^{(0)}(r) - \hat{j}_l(kr)]t_l^{(1)}(r)$$

$$-k^{-1}V_1(r)[\hat{j}_l(kr) - \hat{n}_l(kr)t_l^{(0)}(r)]^2\ , \tag{19}$$

$$t_l'^{(2)}(r) = -2k^{-1}\hat{n}_l(kr)V_0(r)[\hat{n}_l(kr)t_l^{(0)}(r) - \hat{j}_l(kr)]t_l^{(2)}(r)$$

$$-k^{-1}\hat{n}_l^{(2)}(kr)V_0(r)[t_l^{(1)}(r)]^2 - 2k^{-1}\hat{n}_l(kr)V_1(r)$$

$$\times[\hat{n}_l(kr)t_l^{(0)}(kr) - \hat{j}_l(kr)]t_l^{(1)}(r)\ . \tag{20}$$

By substituting Eq. (12) in Eq. (6), writing in the right-hand side the expansion for $\delta_l(r)$ in powers of λ, and expanding the trigonometric function, we get for the zeroth-order phase shift

$$t_l^{(0)}(r) = \tan\delta_l^{(0)}(r) \tag{21}$$

and the following expressions for the corrections:

$$t_l^{(1)}(r) = \delta_l^{(1)}(r)[\cos\delta_l^{(0)}(r)]^{-2}\ , \tag{22}$$

$$t_l^{(2)}(r) = \{\delta_l^{(2)}(r) + [\delta_l^{(1)}(r)]^2 t_l^{(0)}(r)\}[\cos\delta_l^{(0)}(r)]^{-2}\ , \tag{23}$$

etc.

In the limit of $r \to \infty$, we get the corresponding phase shifts (7). The same equations can be derived starting with Calogero's first-order nonhomogeneous equation for the exact $t_l(r)$[1], by substituting the partitioned potential U and the series expansion for $t_l(r)$ and then equating terms in orders of λ.

Following Calogero we define the S-matrix function $S_l(r)$ in the following way:

$$S_l(r) = \frac{c_l(r) + is_l(r)}{c_l(r) - is_l(r)}\ , \quad S_l(0) = 1. \tag{24}$$

The scattering-matrix function can be written in the following equivalent form:

$$S_l(r) = e^{2i\delta_l(r)} = 1 + 2i\delta_l(r) - 2\delta_l^2(r) + \cdots\ . \tag{25}$$

The solution of Calogero's differential equation for $S_l(r)$,

$$\frac{dS_l(r)}{dr} = (2ik)^{-1}U(r)\{[\hat{j}_l(kr) + i\hat{n}_l(kr)]S_l(r)$$

$$+ \hat{j}_l(kr) - i\hat{n}_l(kr)\}^2\ , \tag{26}$$

with the boundary condition $S_l(0) = 1$, yields in the asymptotic limit the scattering matrix S_l:

$$\lim_{r\to\infty} S_l(r) = S_l(\infty) \equiv S_l\ . \tag{27}$$

The perturbation treatment can be applied to the equations determining $S_l(r)$ in close analogy to the way we have done it for $t_l(r)$. The corresponding equations for the zeroth-order approximation $S_l^{(0)}(r)$ and for its perturbation corrections have the same general form and behavior as Eqs. (18)–(20).

It is obvious that the $t_l^{(i)}(r)$ ($i = 0, 1, 2, \ldots$) functions have a pole whenever $\delta_l^{(0)}(r)$ takes a value equal to an odd multiple of $\frac{1}{2}\pi$. As was pointed out by Calogero, we may resolve this difficulty by introducing the "cotangent function" $ct_l(r)$ defined in the following way:

$$ct_l(r) = 1/t_l(r) = \cot\delta_l(r) \ . \qquad (28)$$

The corresponding equations for $ct_l^{(0)}(r)$ and the corrections to it can be easily derived by applying the same procedure that was used in deriving Eqs. (18)–(20). When integrating Eqs. (21)–(23) from the origin to a point $r = R_1$ where a value larger in modulus than unity is obtained for $t_l^{(0)}(r)$, we convert to the corresponding "cotangent equations," with R_1 as the lower limit and integrate them until a point $r = R_2$ is reached, for which $ct_l^{(0)}(r)$ goes through a value larger in modulus than unity, and we switch back to the "tangent equations." We proceed in this way until the functions become asymptotically constant. The number of times and the location of the points where one has to switch from one set of equations to the other (corresponding) one, depends on the range and on the strength of the potential relative to the initial energy of the incident particle.

METHOD OF SOLUTION AND APPLICATION TO s-WAVE SCATTERING FROM AN EXPONENTIAL POTENTIAL

The intricacy of the problem lies in the solution of the equation for $t_l^{(0)}(r)$ [or $s_l^{(0)}(r)$] because of its nonlinearity. Many authors addressed themselves to this problem, and various methods of solution have been proposed.[9] The existing approximation methods can be divided into three main classes: (i) First are iteration schemes, which try to linearize or quasilinearize the equations; these methods end up with Born or modified Born-type approximations. (ii) Second are variational and extremum principles. (iii) Third are numerical methods; the applicability of these methods may be greatly enhanced by a convenient choice of the form of V_0 (subjected to the conditions which we have stated in the introduction).

If the zeroth-order potential is written in the form $V_0(r; c_1, c_2, \ldots)$, where the c_1, c_2, ... are a set of parameters, we may optimize the zeroth-order approximation with respect to these parameters,[7] by using the variational condition for the tangent of the phase shift. The resulting optimized values of the parameters in V_0 are then used in the equations for the corrections to $t_l^{(0)}(r)$ [or $s_l^{(0)}(r)$].

The variational optimization procedure consists of the following steps: (i) Solve the Schrödinger equation for $u_l^{(0)}$,

$$\frac{d^2}{dr^2} u_l^{(0)}(r; \vec{c}) + \left(k^2 - \frac{l(l+1)}{r^2} - V_0(r; \vec{c})\right) u_l^{(0)}(r; \vec{c}) = 0 \ ,$$

$$(29)$$

where $\vec{c}$ is the parameter vector. (ii) Construct the trial function $\tilde{t}_l(r)$,

$$\tilde{t}_l(r; \vec{c}) = \frac{-k^{-1}\int_0^r dr' \ V_0(r'; \vec{c})\hat{j}_l(kr')u_l^{(0)}(r'; \vec{c})}{1 - k^{-1}\int_0^r dr' \ V_0(r'; \vec{c})\hat{n}_l(kr')u_l^{(0)}(r'; \vec{c})} \ .$$

$$(30)$$

(iii) Apply the variational principle for the solution of first-order differential equations[10] to Calogero's equation for $t_l(r)$ [corresponding to $U(r)$], with $\tilde{t}_l(r)$, Eq. (30), as a trial function. The variations are taken with respect to the set of parameters $\vec{c}$. The variational principle reads here as follows:

$$\delta\{- k^{-1}\int_0^r dr' \ U(r')[\ \hat{j}_l^2(kr') - \tilde{t}_l(r'; \vec{c})\hat{n}_l^2(kr')]$$

$$\times \exp[2k^{-1}\int_{r'}^r ds \ U(s)\hat{n}_l(ks)(\hat{j}_l(ks)$$

$$- \tilde{t}_l(s; \vec{c})\hat{n}_l(ks))]\} = 0 \ . \qquad (31)$$

This results in a set of equations for the set of parameters $\vec{c}$. The solution of this equation will be denoted by $\vec{c}_{opt}$. Substituting $\vec{c}_{opt}$ in (30), we get an optimized value for the zeroth-order function $\tilde{t}_l^{(0)}(r; \vec{c}_{opt})$; in the limit of $r \to \infty$, we get

$$\lim_{r \to \infty} \tilde{t}_l^{(0)}(r; \vec{c}_{opt}) = \tan\bar{\delta}_l^{(0)} \ ,$$

where $\bar{\delta}_l^{(0)}$ is the optimized zeroth-order phase shift. As we noted before, the integration of Eqs. (19), (20), etc., for the perturbation corrections is carried out with the functions $\tilde{t}_l^{(0)}(r; \vec{c}_{opt})$ and $V_0(r; \vec{c}_{opt})$ substituted for $t_l^{(0)}(r)$ and $V_0(r)$.

In order to test the applicability of the method we have applied the above procedure to s-wave scattering from an attractive exponential potential

$$V(r) = - e^{-r} \ . \qquad (32)$$

Following Knudson and Kirtman[7] the zeroth-order approximation was taken as the spherical well:

$$V_0 = -D, \quad r \le r_0$$
$$V_0 = 0, \qquad r > r_0 \ . \qquad (33)$$

The parameter vector $\vec{c}$ consists of two components (r_0, D).

The Schrödinger equation (29) can be solved exactly for this potential, and by substituting the solutions in (30) we evaluate an expression for $\tilde{t}_l(r; r_0, D)$. By substitution of the expression for $\tilde{t}_l$ in the variational (31) and by taking the variations with respect to r_0 and D, we get two simultaneous equations for the nonlinear parameters r_0 and D, which were solved numerically by the Newton-Raphson method. The optimized parameters were used in (30), and after taking the limit we got the optimized zeroth-order phase shifts $\bar{\delta}_0^{(0)}$. In order to find the perturbation corrections we solved the first-order nonhomogeneous equations (19) and (20). The results are summarized in Table I. It is of

UZI LANDMAN

TABLE I. s-wave phase shifts for the scattering of an electron by the potential $V(r) = -e^{-r}$.

D (a.u.)	r_0 (a.u.)	E_0 (a.u.)	$\bar{\delta}_0^{(0)}$ (rad)	$\delta_0^{(1)}$	$\delta_0^{(2)}$	δ	$\delta_{K-K}^{(0)}$ (Ref. 5)	δ_{K-K} (Ref. 5)	δ_{exact}
0.3126	2.195	0.01	2.0988	0.0299	0.0051	2.1338	2.0826	2.1348	2.1334
0.3542	1.913	0.10	1.2694	0.0148	0.0018	1.2860	1.2632	1.2860	1.2857
0.3125	2.940	0.5	0.7673	0.0121	0.0009	0.7803	0.7579	0.7806	0.7801
0.2517	2.293	0.8	0.6501	0.0069	0.0005	0.6575	0.6663	0.6580	0.6574
0.5752	2.041	2.0	0.4513	0.0035	0.0001	0.4549	0.4492	0.4549	0.4549

interest to note that in the example studied here the values which we get for the optimized zeroth-order phase shifts $(\bar{\delta}_0^{(0)})$ are better than the zeroth-order phase shifts which were computed by the variation-perturbation method with the Hulthen variational principle.[7] Moreover, carrying the calculation through first-order, we get already good results which are improved by the second-order correction. Comparing our results with the exact results, we see that in the present method there is no need for third-order calculations which are essential in the variation-perturbation method suggested by Knudson and Kirtman. This, and the relative simplicity of the correction equations (19) and (20) are the main encouraging conclusions that we draw from the above example. The observation that $\bar{\delta}_0^{(0)}$ is a lower bound to the exact result and that the total phase shift (δ) is an upper bound calls also for further study of the present method.

Finally, let us remark about an obvious generalization of the method. Let us denote the sum of the centrifugal term and the potential $U(r)$ by $W_l(r)$,

$$W_l(r) = l(l+1)/r^2 + U(r) .$$ (34)

$W_l(r)$ can always be written as a sum of two terms $W^{(1)}(r)$ and $W^{(2)}(r)$. The first is the one that we include in the differential equation

$$\frac{d^2 y_l(r)}{dr^2} + [k^2 - W^{(1)}(r)] y_l(r) = 0 .$$ (35)

$W^{(2)}(r)$ is the interaction potential. In our preceding discussion we used $W^{(1)}(r) = l(l+1)/r^2$ and $-W^{(2)}(r) = U(r) = V_0 + \lambda V_1$, and thus we identified (35) as the Ricatti-Bessel differential equation. Other choices of $W^{(1)}(r)$ are possible (the convenient ones are those which yield an equation which is solvable in closed form). In such cases the solutions of (35) will replace $\hat{j}_l$ and $\hat{n}_l$ (the regular and irregular solutions, respectively) in the above formulation.

ACKNOWLEDGMENT

[1] F. Calogero, Variable Phase Approach to Potential Scattering (Academic, New York, 1967).

[2] T. Y. Wu and T. Ohmura, Quantum Theory of Scattering (Prentice-Hall, Englewood Cliffs, N. J., 1962).

[3] (a) F. E. Harris, Phys. Rev. Letters 19, 173 (1967);

(b) H. H. Michels and F. E. Harris, ibid. 19, 885 (1967).

[4] R. K. Nesbet, Phys. Rev. 175, 134 (1968).

[5] H. J. Kolker, J. Chem. Phys. 53, 4637 (1970).

[6] K. J. Miller, Phys. Rev. A 3, 607 (1971).

[7] S. K. Knudson and B. Kirtman, Phys. Rev. A 3, 972 (1971).

[8] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933).

[9] See Ref. 1 and references and bibliography listed therein.

[10] Reference 1, Appendix II.