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Variational Technique for Scattering Theory

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A stationary variational functional for the T matrix that uses trial T matrices rather than trial wave functions is discussed. Taking a trial T matrix expressed as a general linear combination of matrices leads to a Fredholm integral equation of the first kind for the coefficient vector. The special case of a trial function having the same form as the Born series, except with variable coefficients, is treated in detail. Requiring the functional to be stationary with this trial form leads to the previously established result of Padé approximants to the scattering amplitude. Approximate techniques are used to evaluate the high-order Born integrals, and the behavior of the Padé approximants and the Born series is investigated for a Yukawa potential. An upper bound on the series is used to estimate its radius of convergence as a function of energy and potential strength. The variational calculations converge rapidly even for cases where the Born series diverges.

I. INTRODUCTION

The use of variational methods for obtaining scattering amplitudes has always been an attractive procedure.[1] For a particular trial function with variable coefficients, it is possible to obtain a "best" amplitude by varying the coefficients in an appropriate variational principle. Two well-known stationary variational functionals for the T matrix[1] are those of Kohn[2] and Schwinger.[3] Saraph and Seaton[4,5] have developed an iteration-variation method which employs the Kohn principle. Burke and Seaton[6] and Harris and Michels[7] have recently reviewed the use of these and related procedures for electron-atom scattering. Such procedures, as with most that have been used previously, employ variational functionals that require trial wave functions. Since we ultimately want the T matrix from a collision calculation, it can be advantageous to have procedures that deal directly with T and bypass the use of wave functions. Approximate solutions to the Lippmann–Schwinger equation for T [Eqs. (2) and (3) below] can be constructed by a variety of methods,[1,8,9] and these solutions can be further improved by treating them as trial variational functions. In this paper we shall explore the use of a functional presented by Newton that uses trial T matrices.[10] In Sec. II the general approach to obtaining the scattering amplitude from trial functions with linear variational coefficients is reviewed with particular emphasis on the functional using trial T matrices. In Sec. III trial T matrices first suggested by Cini and Fubini[11] are used to illustrate the formalism. In the particular case of

potential scattering we show that some recently developed approximate methods for evaluating high-order Born integrals can be applied to variational calculations. As a special case, scattering from a Yukawa potential is examined in Sec. IV. The behavior of the Born series, the optimized trial T matrices, and the variational estimate of the scattering amplitude are examined.

II. VARIATIONAL METHOD

Consider two colliding bodies (atoms and molecules) described by the Hamiltonian $H = H_0 + V$, where H_0 is the Hamiltonian for the free unperturbed motion of the bodies in the center-of-mass system with eigenfunctions φ and V is the potential of interaction between the bodies. In this section we shall not restrict ourselves to potential scattering (i.e., H_0 and V could depend on internal degrees of freedom so that inelastic events are possible). Schwinger[3] has derived the following bilinear stationary functional for the T matrix:

$$I_{ba} = \langle \varphi_b | V | \psi_a^+ \rangle + \langle \psi_b^- | V | \varphi_a \rangle - \langle \psi_b^- | V | \psi_a^+ \rangle + \langle \psi_b^- | V G_0 V | \psi_a^+ \rangle , \quad (1)$$

where $\psi^\pm = \varphi^\pm + G_0^\pm V \psi^\pm$ is the Lippmann–Schwinger (LS) equation[1] for ψ and

$$G_0^\pm = (E - H_0 \pm i\epsilon)^{-1} ;$$

E is the total energy and a, b label eigenstates of H_0. If ψ_a and ψ_b are exact (i.e., satisfy the LS equation), then Eq. (1) is an identity; $I_{ba} = T_{ba}$. This functional is also stationary about T_{ba} so that if ψ_a and ψ_b differ by $\delta\psi$ from their exact values, then $I_{ba} = T_{ba} + O(\delta\psi)^2$. The error in I_{ba} is second order when the error in ψ is first order.

As we have indicated, it is sometimes more convenient to work with functionals that employ trial T matrices rather than wave functions. The T matrix is closely related to the observed cross section, while the wave function is essentially one step removed from such observables.[1,10] Following the derivation by Newton,[1] consider the two equivalent LS equations for the T operator[12]:

$$T = V + V G_0 T , \quad (2)$$

$$T = V + T G_0 V . \quad (3)$$

Equation (2) can be written as $V = T - V G_0 T$ and substituted into Eq. (3) to obtain

$$T = V + T G_0 T - T G_0 V G_0 T . \quad (4)$$

Now add Eqs. (2) and (3) and subtract Eq. (4):

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \langle \varphi_b | V G_0 T | \varphi_a \rangle + \langle \varphi_a | T G_0 V | \varphi_a \rangle - \langle \varphi_b | T G_0 T | \varphi_a \rangle + \langle \varphi_b | T G_0 V G_0 T | \varphi_a \rangle , \quad (5)$$

where we have taken matrix elements with respect to the unperturbed states φ_b and φ_a. It is easy to show that the Euler equation for I_{ba} is the LS equation. Therefore, if T satisfies the LS equation, then Eq. (5) is an identity; $I_{ba} = T_{ba}$. This *bilinear* functional in T in Eq. (5) is stationary about T_{ba}: If $T_{\text{trial}} = T + \delta T$ is inserted in the right-hand side of Eq. (5), then it is easy to show that $I_{ba} = T_{ba} + O(\delta T)^2$. A companion *fractional* stationary principle can be found by choosing a trial function in Eq. (5) of the form $T_{\text{trial}} = xT$, where x is a variable parameter. Requiring I_{ba} to be stationary with respect to variations of x (i.e., $\delta I_{ba}/\delta x = 0$) leads to

$$x = \frac{\langle \varphi_b | V G_0 T | \varphi_a \rangle}{\langle \varphi_b | T G_0 T - T G_0 V G_0 T | \varphi_a \rangle} = \frac{\langle \varphi_b | T G_0 V | \varphi_a \rangle}{\langle \varphi_b | T G_0 T - T G_0 V G_0 T | \varphi_a \rangle} . \quad (6)$$

Using this value of x in T_{trial} gives

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \frac{\langle \varphi_b | V G_0 T | \varphi_a \rangle \langle \varphi_b | T G_0 V | \varphi_a \rangle}{\langle \varphi_b | T G_0 T - T G_0 V G_0 T | \varphi_a \rangle} . \quad (7)$$

This functional is also stationary about T_{ba}.[13] Equation (7) is independent of the normalization of of T, and it can sometimes be more useful than Eq. (5) owing to its rational function form (see Sec. IV).

Variational functionals,[14] such as those in Eqs. (5) and (7), can in general be used in two different ways: (i) If a *reasonably accurate* T_{trial} is available, then we can obtain an improved T matrix by direct substitution of T_{trial} on the right-hand side of Eq. (5) or (7); (ii) T_{trial} may be chosen with variable parameters, and these parameters varied to make I_{ba} stationary in Eq. (5). There are numerous techniques available for obtaining trial T matrices,[15] and (i) could be a useful adjunct to these methods. Approach (ii) is particularly attractive if T_{trial} has linear parameters to vary, since the quadratic form of Eq. (5) in T_{trial} will yield a set of linear equations for these parameters. We now specialize this general technique to trial T matrices.

Consider the trial form:

$$\langle \varphi_b | T_{\text{trial}} | \varphi_a \rangle = \int dy\, x(y) \langle \varphi_b | \chi(y) | \varphi_a \rangle , \quad (8)$$

where $\chi(y)$ is a family of operators parametrically defined as a function of y, and $x(y)$ is a function to be determined variationally. The path of the integral in Eq. (8) will depend on the nature of $\chi(y)$, and it can be left as arbitrary at this point. It is convenient to view the matrix $\langle \varphi_b | \chi(y) | \varphi_a \rangle$ as a function of the quantum numbers a and b. Equation (8) can therefore be considered as a linear expansion of the T matrix in a basis set $\eta_y(b, a) \equiv \langle \varphi_b | \chi(y) | \varphi_a \rangle$. Trial functions of this general form

have been used to obtain direct approximate solutions to the LS equations in Eq. (2) or (3).[8,9] The functions $\eta_y(b, a)$ should be linearly independent and hopefully complete in the space relevant to T. We note, however, that since Eq. (8) is a trial function, the requirement of completeness will in general be relaxed in favor of choosing a relatively few functions $\eta_y(b, a)$ that can describe $\langle \varphi_b | T | \varphi_a \rangle$ better than, for example, a complete set that may be slowly convergent.

Substituting Eq. (8) into Eq. (5), we find

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \int dy\, x(y)\, m(y) - \tfrac{1}{2} \int\int dy\, dy'\, x(y)\, M(y, y')\, x(y') , \quad (9)$$

where

$$m(y) = \langle \varphi_b | \chi(y)\, G_0 V + V G_0 \chi(y) | \varphi_a \rangle , \quad (10)$$

$$M(y, y') = \langle \varphi_b | \chi(y)\, G_0 \chi(y') + \chi(y')\, G_0 \chi(y) - \chi(y)\, G_0 V G_0 \chi(y') - \chi(y')\, G_0 V G_0 \chi(y) | \varphi_a \rangle . \quad (11)$$

It is understood that the unperturbed states φ_i form a complete set, and the appropriate unit operators $\sum_i |\varphi_i\rangle\langle\varphi_i|$ or $\int_i |\varphi_i\rangle\langle\varphi_i|$ would be inserted into the expressions in Eqs. (10) and (11) where needed. Therefore, here and elsewhere in this paper it is only necessary in practice to deal with the functions $\eta_y(b, a)$ rather than the operators $\chi(y)$. Making I_{ba} stationary with respect to variations in x yields

$$m(y') = \int dy\, x(y)\, M(y, y') . \quad (12)$$

With this result Eq. (9) can now be written as

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \tfrac{1}{2} \int dy\, x(y)\, m(y) . \quad (13)$$

Equation (12) is a Fredholm integral equation of the first kind[16] on a domain defined by the range of y. The kernal $M(y, y')$ is symmetric from Eq. (11), and also complex in general. It is not clear under what conditions M is $\mathfrak{L}_2$,[1] but this will surely depend on the nature of η_y. However, if η_y are linearly independent and if a solution exists, we should be able to at least numerically solve Eq. (12) (a specific example will be given in Sec. IV). Formally we have the solution

$$x(y) = \int dy'\, m(y')\, M^{-1}(y', y) . \quad (14)$$

Finally, we combine Eqs. (13) and (14) to obtain

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \tfrac{1}{2} \int\int dy\, dy'\, m(y)\, M^{-1}(y, y')\, m(y') . \quad (15)$$

This is a very convenient compact expression for the variationally determined T matrix with a given choice of χ. Note that $x(y)$ does not explicitly enter into Eq. (15), but M^{-1} is still required.

Finally this result can be related to the fractional form in Eq. (7). We define

$$m_1(y) = \langle \varphi_b | \chi(y)\, G_0 V | \varphi_a \rangle , \quad (16a)$$

$$m_2(y) = \langle \varphi_b | V G_0 \chi(y) | \varphi_a \rangle , \quad (16b)$$

then $m(y) = m_1(y) + m_2(y)$ and the functional Eq. (7) becomes

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \int dy\, x(y)\, m_1(y) \int dy'\, x(y')\, m_2(y') \Big/ \tfrac{1}{2} \int dy\, x(y)\, m(y) , \quad (17)$$

where we have used the relation in Eq. (12), which was determined from the *bilinear* form of I_{ba}. Now if $\chi(y)$ has the same symmetry property that T exhibited in Eqs. (2) and (3), then $m_1 = m_2 = \frac{1}{2} m$, and the fractional expression in Eq. (17) becomes identical with Eq. (15). The example in Sec. III does have this property.

III. TRIAL T MATRICES AND BORN SERIES

Our main interest is in applying the functionals discussed above to inelastic scattering. In this section we shall discuss one possible choice of basis functions closely related to the Born series. In general, one would probably choose simpler trial functions than those in Eq. (19) below. However, this choice of functions allows us to directly compare the behavior of the variational method and the Born series since the same integrals occur in both cases.

The well-known Born-series solution to Eq. (2) or (3) is[1]

$$\langle \varphi_b | T | \varphi_a \rangle = \sum_{n=1}^{\infty} \langle \varphi_b | T_n | \varphi_a \rangle , \quad (18a)$$

$$T_n = V (G_0 V)^{n-1} . \quad (18b)$$

The series will in general diverge at sufficiently low energy if the potential V is strong enough.[1] Cini and Fubini[11] have suggested the following expansion for the T matrix:

$$\langle \varphi_b | T_{\text{trial}} | \varphi_a \rangle = \sum_{n=1}^{N} x_n \langle \varphi_b | T_n | \varphi_a \rangle , \quad (19)$$

where the x_n are variable coefficients, and we have truncated to N terms. This is a special case of Eq. (8) if we let

$$x(y) = \sum_{n=1}^{N} x_n\, \delta(y - n)$$

and

$$\langle \varphi_b | \chi(n) | \varphi_a \rangle = \langle \varphi_b | (V G_0)^{n-1} V | \varphi_a \rangle .$$

Equations (15), (11), and (10) now become

$$I_{ba} = \langle \varphi_b | V | \varphi_a \rangle + \vec{\mathrm{m}}^T \cdot \vec{\vec{\mathrm{M}}}^{-1} \cdot \vec{\mathrm{m}} , \quad (20a)$$

where

$$m(n)=\langle\varphi_b|\,V(G_0V)^n\,|\varphi_a\rangle\,, \tag{20b}$$

$$M(n,n')=\langle\varphi_b|\,V(G_0V)^{n+n'-1}-V(G_0V)^{n+n'}\,|\varphi_a\rangle \tag{20c}$$

for $n, n' = 1, 2, \ldots, N$. Using Baker's generalization of "Nuttall's compact formula" (see the Appendix), [17] it is easy to show that Eq. (20) reduces to

$$I_{ba}=[N, N+1]\,, \tag{21}$$

where $[N, N+1]$ is a Padé approximant to the Born series in Eq. (18). The Born series can be viewed as a power series in V_0, the strength of the potential. The general $[N, M]$ Padé approximant[17] to the Born series is a rational function:

$$[N, M]=P_M(V_0)/Q_N(V_0)\,,$$

where P and Q are polynomials in V_0 obtained from the first $N+M+1$ terms of the Born series. Nuttall[17] has shown that a treatment similar to ours using the Schwinger functional in Eq. (1) yields the $[N, N-1]$ Padé approximant, and other approximants $[N, M]$ can be obtained by setting some of the $x(n)$'s equal to one and varying the others.

As a specific example, consider scattering by the class of spherically symmetric potentials of the form[18]

$$V(r)=V_0\int_0^\infty dt\,a(t)\,e^{-tr^2}\,, \tag{22}$$

where $a(t)$ can be expressed as the inverse Laplace transform[16] of V. For this case the quantum numbers $a, b \to \vec{k}, \vec{k}'$ and the scattering amplitude becomes[1]

$$f(\theta)=(-4\pi^2m/\hbar^2)\langle\vec{k}'|\,T\,|\vec{k}\rangle \tag{23}$$

with $|\vec{k}| = |\vec{k}'| = K$ and $E=\hbar^2K^2/2m$. The matrix element is over plane-wave states. The difficulty in calculating $I_{\vec{k}'\vec{k}}$ in Eq. (20) stems from the need to evaluate the high-order Born integrals. Recently approximate methods were developed for evaluating such integrals for potentials expressed as in Eq. (22)[18]; we shall only present the results here. The following expression was derived[19] using a small-wavelength approximation on a slowly varying part of the integrands, while still retaining the dominant wavelength dependence:

$$\langle\vec{k}'|\,V(G_0V)^{n-1}\,|\vec{k}\rangle = \frac{V_0}{4\pi^{3/2}}\int_0^\infty db\,bJ_0(|\vec{k}-\vec{k}'|\,b)\,h(b)\,g(b)^{n-1}\,, \tag{24}$$

where

$$h(b)=\int_0^\infty dt\,\frac{a(t)}{t^{1/2}}\,e^{-tb^2}\,, \tag{25a}$$

$$g(b)=\frac{mi\,\pi^{1/2}\,V_0}{2\hbar^2K}\int_0^\infty dt\,\frac{a(t)}{t^{1/2}}\,e^{-tb^2}\,[W(K/t^{1/2})-1]\,, \tag{25b}$$

$$W(x)=e^{-x^2}\,\mathrm{erfc}(-ix)\,. \tag{25c}$$

J_0 is a Bessel function and erfc is the complementary error function.[20] Although Eq. (24) is expected to be most accurate at small wavelengths, previous implementation[18] of these integrals indicated that they give a reasonable approximation even at low energies in many cases. The numerical results in Sec. IV also show this general behavior.

An interesting property of the Born series is its radius of convergence as a function of V_0 and E (or K). We shall always be dealing with the approximate series whose terms are given by Eq. (24); in Sec. IV we shall show that when the approximate series converges, it yields reasonably accurate cross sections. Within this framework we have from Eqs. (18) and (23)

$$f(\theta)=\sum_{n=1}^\infty f_n(\theta)\,, \tag{26a}$$

$$f_n(\theta)=(-4\pi^2m/\hbar^2)\langle\vec{k}'|\,V(G_0V)^{n-1}\,|\vec{k}\rangle\,. \tag{26b}$$

A useful estimate of the radius of convergence of this series can be obtained by bounding it from above;

$$|f(\theta)|\leq\sum_{n=1}^\infty|f_n(\theta)|\,. \tag{27}$$

Now combine Eqs. (24)–(26) to obtain

$$f_n(\theta)=\frac{V_0}{4\pi^{3/2}}\int_0^\infty dt\,\frac{a(t)}{t^{1/2}}\int_0^\infty\cdots\int_0^\infty dt_1\cdots dt_{n-1} \times\prod_{j=1}^{n-1}\left(\frac{mi\pi^{1/2}V_0}{2\hbar^2K}\,\frac{a(t_j)}{t_j^{1/2}}\,[W(K/t_j^{1/2})-1]\right) \times\frac{\exp[-|\vec{k}-\vec{k}'|^2/4(t+t_1+t_2+\cdots+t_{n-1})]}{2(t+t_1+t_2+\cdots+t_{n-1})}\,,$$

where the following identity[20] has been used:

$$\int_0^\infty db\,J_0(bx)\,e^{-yb^2}=(1/2y)\,e^{-x^2/4y}\,.$$

The magnitude of the nth term, $|f_n(\theta)|$, can be bounded by noting that $t_j \geq 0$ and therefore

$$\frac{\exp[-|\vec{k}-\vec{k}'|^2/4(t+t_1+\cdots+t_{n-1})]}{t+t_1+\cdots+t_{n-1}}\leq\frac{1}{t}\,,$$

so that

$$|f_n(\theta)|\leq\frac{|V_0|}{8\pi^{3/2}}\,X^{n-1}\int_0^\infty dt\,\frac{|a(t)|}{t^{3/2}}\,,$$

where

$$X=\frac{m\pi^{1/2}|V_0|}{2\hbar^2K}\int_0^\infty dt'\,\frac{|a(t')[W(K/t'^{1/2})-1]|}{t'^{1/2}}\,.$$

This finally leads to an upper bound on the series:

$$|f(\theta)|\leq\frac{|V_0|}{8\pi^{3/2}}\int_0^\infty dt\,\frac{|a(t)|}{t^{3/2}}\sum_{n=1}^\infty X^{n-1}\,. \tag{28}$$

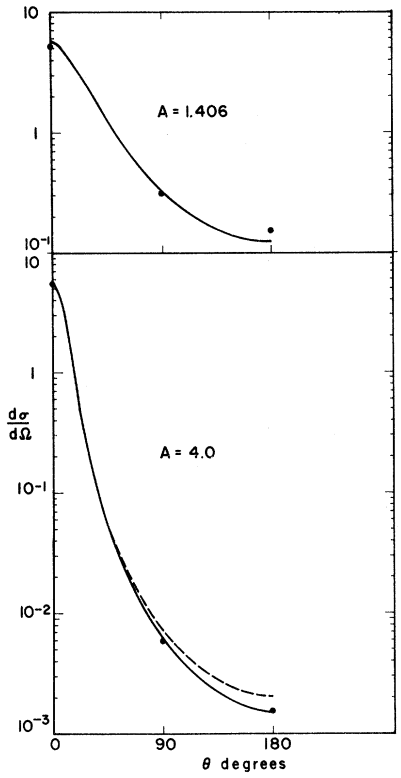

FIG. 1. Differential cross section in units of a_0^2 for the Yukawa potential at two values of A. $B=-2.365$ in this and the remaining figures. The solid lines were computed variationally, the dots are exact results (Ref. 21), and the dashed line for $A=4.0$ is from an impact-parameter formulation of the scattering amplitude (Ref. 18). The dashed and solid curves practically coincide for $A=1.406$.

The series on the right-hand side of Eq. (28) converges to $(1-X)^{-1}$ provided $X<1$. This convergence criterion will in general depend on $|V_0|$ and K as well as the form of $a(t)$. In the case of $K\to 0$ the convergence criterion reduces to a simple relationship if we use the property[20]

$$\lim W(x)\approx 1+2ix/\pi^{1/2} \quad \text{as} \quad x\ll 1 .$$

It is easy to show that $X<1$ becomes

$$|B|<\left(\frac{1}{2a_0^2}\int_0^\infty dt'\,\frac{|a(t')|}{t'}\right)^{-1}, \tag{29}$$

where

$$B=2mV_0a_0^2/\hbar^2$$

and a_0 is the characteristic length associated with the potential. Equation (28) is useful since if the right-hand side converges, then the Born series also converges; a specific application of this is made in Sec. IV.

IV. NUMERICAL CALCULATIONS WITH YUKAWA POTENTIAL

In this section a numerical example using the Yukawa (or screened-Coulomb) potential

$$V(r)=(V_0a_0/r)e^{-r/a_0}$$

is presented based on the use of Cini–Fubini basis functions,[11] as discussed above. For this potential the coefficient $a(t)$ in Eq. (22) becomes[20]

$$a(t)=[a_0/(\pi t^{1/2})]e^{-1/(4ta_0^2)}. \tag{30}$$

Equations (24), (25), and (26b) reduce to

$$f_n(\theta)=-B\int_0^\infty dx\,xJ_0(2xA\sin\tfrac{1}{2}\theta)K_0(x)g(x)^{n-1}, \tag{31}$$

where

$$g(x)=(iB/4A)\int_0^\infty dy\,y\,e^{-1/4y-yx^2}[W(A/y^{1/2})-1]; \tag{32}$$

$f_n(\theta)$ is in units of a_0, $K_0(x)$ is a modified Bessel function[20] arising from the integral in Eq. (25a), $A=Ka_0$, and $B=2mV_0a_0^2/\hbar^2$. Multiplying Eq. (20) by $-4\pi^2m/\hbar^2$ leads to a variational expression for the scattering amplitude:

$$f(\theta)=f_1(\theta)+\vec{m}^T\cdot\vec{\vec{M}}^{-1}\cdot\vec{m}=[N,N+1],$$

$$m(n)=f_{n+1}(\theta),$$

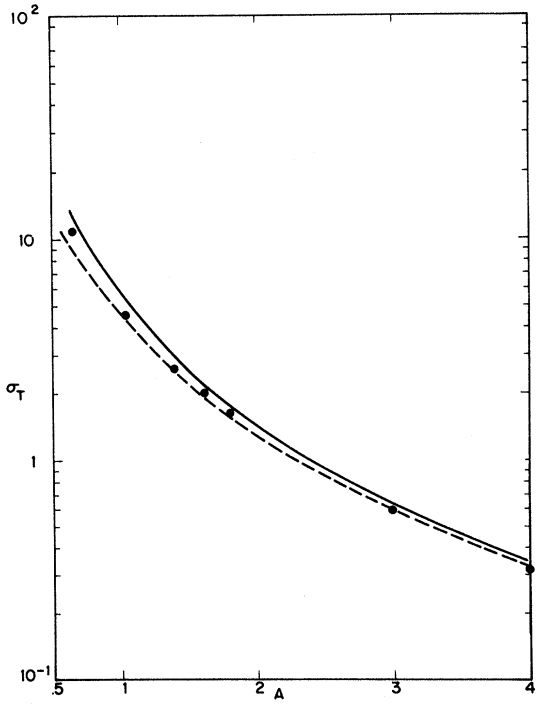

FIG. 2. Total cross sections in units of πa_0^2 from integration of the differential cross section (solid line), and from the optical theorem (dashed line). The dots are exact results.

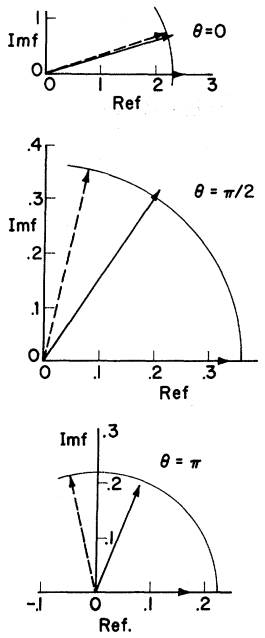

FIG. 3. Argand diagram of the complex scattering amplitude in units of a_0 at $\theta=0$, $\frac{1}{2}\pi$, and π for $A=1.816$. The solid lines are variational, the dashed lines are exact, and the arrows on the real axes are the first Born approximation.

$$M(n,n')=f_{n+n'}(\theta)-f_{n+n'+1}(\theta)\,,$$

$$n,n'=1,2,\ldots,N\,. \qquad (33)$$

The two integrals in Eqs. (31) and (32) were evaluated by quadrature as discussed elsewhere,[18] and the $[N,N+1]$ Padé's in Eq. (33) were constructed. The number of terms, N, was increased until convergence occurred; convergence behavior will be discussed below. Figure 1 shows computed differential cross sections in units of a_0^2 (Figs. 4–6 are also in these units) for $B=-2.365$ at $A=1.406$ and 4.0. The exact results (solid dot) are those of Walters.[21] The accuracy of the variational results (solid curve) improves with increasing A. In a previous paper[18] the summation over n in Eq. (26) and the integration over b in Eq. (24) were interchanged, and the resulting sum performed analytically. This led to a modification of the impact-parameter expression by Blankenbeckler–Goldberger[22] for the scattering amplitude. The dashed curve for $A=4.0$ is from this latter work,[18] and the solid and dashed curves practically coincide for $A=1.406$.

The optical theorem[1] relates the total cross section σ_T to the scattering amplitude:

$$\sigma_T=(4\pi/K)\,\mathrm{Im}f(0)\,.$$

The total cross section is plotted in Fig. 2 computed by the optical theorem and by integrating the differential cross section over all angles. The accuracy is quite reasonable. The optical-theorem results are a measure of the phase dependence of the scattering amplitude. In general the phase is most accurate in the forward direction as indicated in Fig. 3. This is probably associated with the approximate nature of the Born integrals in Eq. (24).

The convergence behavior of the Born series and the variational Padé's is very interesting. We shall focus on the behavior of the differential cross section at $\theta=0$; the convergence behavior at other angles is very similar. First consider the Born series. In Fig. 4 are plotted differential cross sections from a partial summation of the Born series,

$$\frac{d\sigma}{d\Omega}=\left|\sum_{n=1}^{N} f_n(\theta)\right|^2\,,$$

as a function of N, the number of terms included. The different cases correspond to increasing values of A. It is clear that for small values of A the series diverges, while near $A=2.2$ it apparently converges. The behavior of the series for the

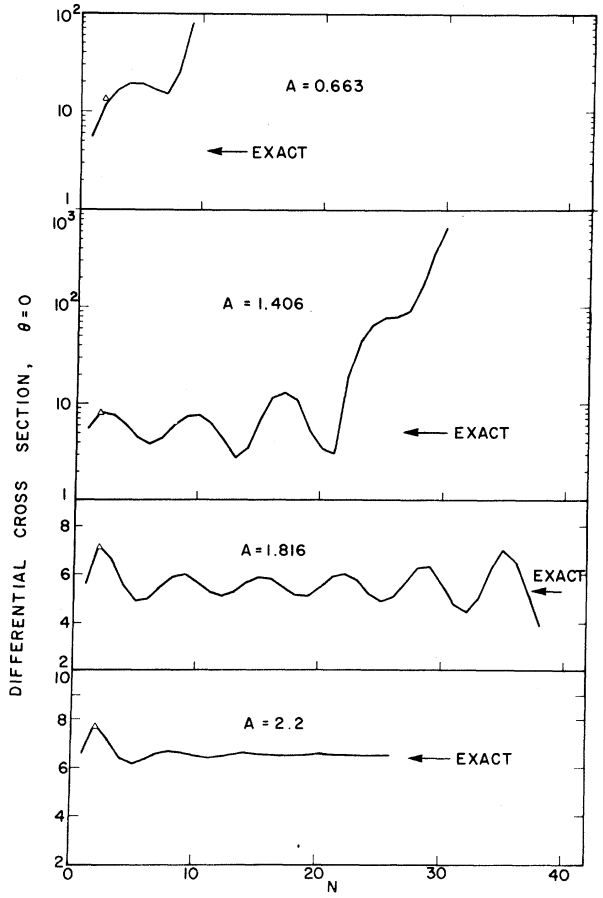

FIG. 4. Convergence behavior of the differential cross section at $\theta=0$ from a partial summation of the Born series to N terms. Each plot corresponds to a different value of A, and the points $\triangle$ at $N=2$ are exact second-order results. Note the change in scale on the ordinate axis.

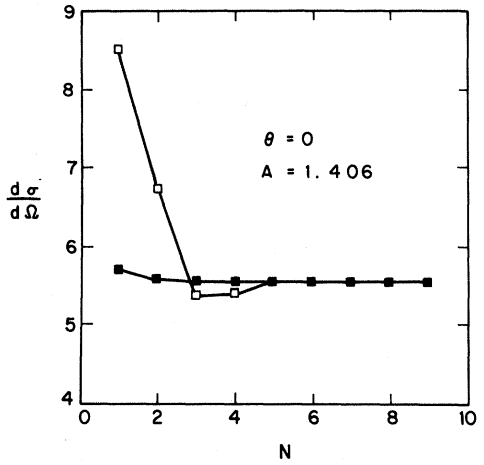

FIG. 5. Convergence plot of the differential cross section at $\theta = 0$ for $A = 1.406$; open square from the optimized trial function in Eq. (35b); closed square, variational. The exact value is 5.1. Note that at this value of A, the Born series diverges (see Fig. 4), but the optimized series does not.

divergent cases (notably $A = 1.81$) is strongly suggestive of an asymptotic expansion,[23] particularly if the envelope of the oscillations is observed. Also note that the differential cross sections oscillate about the exact results. It is possible to obtain a bound on the radius of convergence by considering X in Eq. (28) along with $a(t)$ in Eq. (30):

$$X = \frac{|B|}{4A}\int_0^\infty \frac{dt}{t}\, e^{-1/4t}\,|W(A/t^{1/2}) - 1|$$

$$= \frac{|B|}{2A}\int_0^\infty \frac{ds}{s}\, e^{-s^2/4A^2}\,|W(s) - 1|\ ,$$

where we have changed variables $s = A/t^{1/2}$ in the last step. We now apply the triangle inequality

$$|W(s) - 1| = |(e^{-s^2} - 1) - e^{-s^2}\operatorname{erf}(-is)|$$

$$\leq (1 - e^{-s^2}) + e^{-s^2}|\operatorname{erf}(-is)|\ ,$$

to obtain

$$X \leq \frac{|B|}{2A}\int_0^\infty \frac{ds}{s}\, e^{-s^2/4A^2}[(1 - e^{-s^2}) + e^{-s^2}|\operatorname{erf}(-is)|\,];$$

the remaining integral can be worked out to arrive at

$$X \leq \frac{|B|}{4A}\left(\ln(1 + 4A^2) + 2\sin^{-1}\frac{2A}{(1 + 4A^2)^{1/2}}\right)\ . \qquad (34)$$

If $X < 1$, then the Born series will converge since it will be bounded from above by a convergent series in Eq. (28). For $B = -2.365$, $X < 1$ when $A > A^* = 4.1$. This is an *upper* bound on the radius of convergence since the actual series in Eq. (26) may still converge for A somewhat smaller than A^*. Indeed, the numerical results indicate the radius of convergence is $A \approx 2.5$. Note that $X = |B|$ at $A = 0$, and this gives a *lower* bound of $B^* = 1$ for the radius of convergence since the series in Eq. (26) may still converge for somewhat larger values of B. The exact radius of convergence of the true Born series[24] [not the approximate one in Eq. (26)] is $B^* = 1.68$. In general, Eq. (34) will give an upper bound to A^* for a given fixed B, and a lower bound to B^* for a given fixed A. These can be used as useful estimates of the convergence behavior of the series.

It is actually not necessary to compute the vector $x(n)$ in Eq. (14) in order to obtain the variational scattering amplitude in Eq. (15) or (33). However, it is useful to look at

$$\langle \vec{k}' | T_{\text{trial}} | \vec{k} \rangle = \sum_{n=1}^{N} x(n) \langle \vec{k}' | V(G_0 V)^{n-1} | \vec{k} \rangle \qquad (35a)$$

or

$$\frac{d\sigma}{d\Omega} = \left| \sum_{n=1}^{N} x(n) \langle \vec{k}' | V(G_0 V)^{n-1} | \vec{k} \rangle \right|^2 . \qquad (35b)$$

The vector $x(n)$ was computed by solving the linear equation $\vec{m} = \vec{\vec{M}} \cdot \vec{x}$. The trial function in Eq. (35a) inserted into the variational functional will yield the $[N, N+1]$ Padé in Eq. (33) [after using the relation in Eq. (23)]. Typical convergence behavior of the differential cross section at $\theta = 0$ obtained from Eq. (35b) and from the $[N, N+1]$ Padé's is plotted in Fig. 5 as a function of N. It is clear that the convergence is very rapid; the case here where $A = 1.41$ corresponds to a divergent Born series in Fig. 4. Thus the optimization procedure converts the divergent Born series to a rapidly convergent series and the substitution of this optimized trial function in the variational principle yields further improvement. The same general behavior was obtained for the lowest-energy case, $A = 0.663$, where the series is rapidly divergent in Fig. 4. For $A = 1.406$ in Fig. 5, the converged value is ~9% in error owing to the approximate nature of the Born integrals in Eq. (24); the error is reduced at larger values of A. For $A \leq 1$ and $B = -2.365$, convergence was poor, and this again is due to the approximations in Eq. (24). For $A \gtrsim 1$, convergence

TABLE I. Padé-approximant table for the differential cross section in units of a_0^2 at $\theta = 0$ for $A = 1.816$.

N \ M	0	1	2	3	4	5
0		5.592	7.262	6.637	5.545	4.917
1		6.507	5.632	5.416	5.484	5.549
2		5.854	5.450	5.525	5.545	5.538
3		5.424	5.516	5.543	5.536	5.534
4		5.297	5.547	5.536	5.534	5.535
5		5.387	5.546	5.533	5.535	5.535

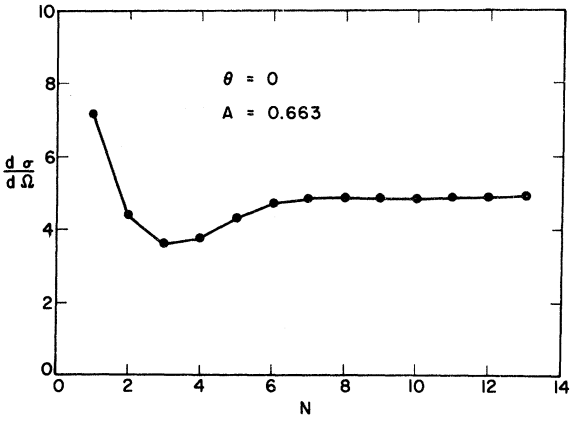

FIG. 6, Convergence behavior of the differential cross section at $\theta = 0$ for $A = 0.663$ determined by taking the trial function as the first N terms in the Born series and directly substituting this into the fractional form in Eq. (7). No optimization was done. Note that the trial function is divergent here, as indicated in Fig. 4.

occurred for $N \leq 5$, and more rapidly for larger A. In addition, the variational and Born-series results agree when the series converges, as they should. It is important to observe that the behavior in Fig. 5 for $N \gtrsim 5$ results from the optimized function $\langle \vec{k}' | T_{\text{trial}} | \vec{k} \rangle$ in Eq. (35a) being just as accurate as $\langle \vec{k}' | T | \vec{k} \rangle$ obtained by further substitution of Eq. (35a) into the right-hand side of Eq. (5). Extrapolating this behavior to other trial functions would indicate that without loss of accuracy considerable labor can be saved by not performing the last substitution.

We have also computed Padé tables (see the Appendix) $[N, M]$ for N, $M = 1, 2, 3, \ldots$, for the differential cross section $d\sigma/d\Omega = |[N, M]|^2$. Table I gives the results for $A = 1.816$. The upper row $|[0, M]|^2$ is the cross section determined from the Born series itself, and the $[N, 0]$ Padé's are zero since the lowest-order term in the Born series is linear in V_0. It is apparent that the sequence of Padé approximants parallel to the diagonal is converging to the same value 5.535 (this is ~4% off the exact value).[21]

We can consider the variational results to have converged when the cross sections from Eq. (35b) and from the Padé's agree (see Fig. 5). For small N it is interesting to note the dramatic improvement that the variational functional gives [recall that the variationally determined Padé can be obtained by directly substituting T_{trial} from Eq. (35a) into the functional]. One must be a little cautious here since if $T_{\text{trial}} = T + \delta T$ and δT is large, then substitution of T_{trial} into the functional could give a worse answer with error $O(\delta T)^2$. A specific case of this would occur if T_{trial} were taken as a partial summation of the Born series

$$\langle \varphi_b | T_{\text{trial}} | \varphi_a \rangle = \sum_{n=1}^{N} \langle \varphi_b | T_n | \varphi_a \rangle$$

when the series is divergent. Substitution of this into the *bilinear* functional in Eq. (5) will yield the Born series to order $2N+1$. Clearly if the series is divergent, the latter result could be worse than the trial function. However, substitution of T_{trial} into the *fractional* form in Eq. (7) may show improved results as indicated in Fig. 6 for $A = 0.663$, which corresponded to a rapidly divergent Born series in Fig. 4. This improvement is probably associated with the rational-function form of Eq. (7).[25]

V. DISCUSSION

The material outlined in Secs. II and III is a general formulation based on a variational functional presented by Newton[1] which employs trial T matrices rather than trial wave functions. The approach is applicable to both elastic and inelastic collisions. Again the main difficulties are choosing appropriate basis functions in which to expand T, and performing the necessary integrals. There are certainly many other physically reasonable and simpler trial functions than those in Eq. (19). However, with the choice in Eq. (19) we were able to simultaneously investigate the corresponding Born series. In Sec. II no assumption was made on the separable or nonseparable character of the basis functions $\eta_\nu(b, a)$. Under certain conditions separable functions $\eta_\nu(b, a) = \psi_\nu(b)\varphi_\nu(a)$ may be appropriate, but the use of nonseparable functions allows the widest flexibility.

We have not used partial-wave analysis in our approach; however, the functional in Eq. (5) could be expanded in partial waves. If only a few partial waves are needed, this would be an advantage. Then it would only be necessary to solve the problem for each partial wave rather than each scattering angle [as we did in Eq. (33)]. However, most chemically interesting problems require many partial waves, and the use of plane waves becomes advantageous.

Note added in proof. Sloan and Brady have recently published a paper[26] utilizing separable basis functions with the functional in Eq. (5). D. Kouri has also kindly provided us with a preprint on the application of this functional to reactive scattering.[27]

APPENDIX

The Born series for the T matrix in Eq. (18) (where the matrix indices a, b have been suppressed for simplification) can be written as

$$T = \sum_{n=0}^{N} T_n \lambda^n , \qquad (36)$$

where $T_0 = 0$ and the ordering parameter λ has been

introduced for convenience. Baker has presented the following generalization of "Nuttall's compact formula"[17] for the $[N, M]$ Padé approximant to Eq. (36):

$$[N, M] = \sum_{l=0}^{M-N} T_l \lambda^l + (\vec{r}^{\,T} \cdot \overleftrightarrow{R}^{-1} \cdot \vec{r}) \lambda^{M-N+1} , \qquad (37)$$

where

$$r_i = T_{M-N+i} , \qquad R_{ij} = T_{M-N+i+j-1} - \lambda T_{M-N+i+j} .$$

The vector $\vec{r}$ and matrix $\overleftrightarrow{R}$ are of dimension N with $i, j = 1, 2, \ldots, N$. The sum in Eq. (37) is replaced by zero if $N > M$ and $T_k = 0$ if $k \leq 0$. As a specific case it is easy to show that replacing T_k by f_k, setting $\lambda = 1$, and taking $M = N+1$ in Eq. (37) will yield the $[N, N+1]$ Padé in Eq. (33).

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[19]Details on the evaluation of $\langle \vec{k}' | T_n | \vec{k} \rangle$ in Eq. (24) can be found in Ref. 18. Note that $W(K/t^{1/2})$ differs by $\sqrt{2}$ in its argument from the approximation $W[K(2/t)^{1/2}]$ presented in Ref. 18. The latter was chosen so that agreement through second order for a single Gaussian potential was maintained. It was found that using Eq. (25b), which is the asymptotic form for $n \gg 1$, gave slightly better results than using $W[K(2/t)^{1/2}]$.

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