

Numerical Asymptotic Functions in Variational Scattering Theory*

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A procedure for explicitly incorporating the effects of long range potentials in variational trial functions for electron-atom and electron-ion scattering is outlined. The component of the wavefunction that represents the asymptotic solution consists of two parts. Outside a certain boundary radius, the asymptotic solutions are generated numerically. The total trial wavefunction is made everywhere smooth and continuous by matching these asymptotic solutions at the boundary with two fixed analytical linearly independent functions, defined within the radius in each channel. Two choices of the fixed internal functions are considered. The numerical feasibility of this approach is investigated by application to the problem of scattering of electrons from atomic hydrogen in the static exchange approximation and from the positive He ion in the static approximation.

I. INTRODUCTION

Variational methods have been successfully applied to some problems of electron-atom scattering [1, 2]. In the approaches so far considered, the channel wavefunctions have been expanded in terms of Slater orbitals complemented with free solutions which behave asymptotically as Bessel and Neumann functions of appropriate order. Some difficulties have, however, been experienced due to the fact that atomic problems have long range potentials; and therefore Bessel and Neumann functions are not always the best approximations to the asymptotic solutions. Seiler *et al.* [2], in their work on electron-hydrogen scattering, have tried to incorporate the corrections to the free solutions by including in the basis set normalizable trigonometric functions in addition to the usual Slater orbitals. Further, to our knowledge, there has not been any meaningful application of the variational formalism to the problem of electron-ion scattering because of difficulties in evaluating matrix elements involving coulombic functions. The only exception is the calculation of Bransden and Dalgarno [3], who in 1953 computed *s*-wave phase shifts for e^- -He $^+$ scattering using simple trial functions.

In this paper we consider an alternative method which is a natural extension

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of the previous variational approaches. We replace the free asymptotic solutions by those generated by numerical integration in the asymptotic region. The numerically 'exact' solutions in the asymptotic region are integrated inwards to a fixed boundary radius, which may be the distance within which the exchange effects are important. These solutions at the boundary are now arbitrarily extended to the origin by matching at the boundary with two fixed inner functions which are well behaved at the origin. Thus the asymptotic solutions, consisting of the numerical functions outside the boundary and linear combinations of known analytical functions inside it, are everywhere continuous and have continuous first derivatives. The effects of long range potentials, both in electron-atom and electron-ion scattering, are explicitly taken into account by numerical integration in the asymptotic region. The expansion of open channel functions in terms of Slater orbitals is now expected to smooth out the distortions in these functions, occurring due to the presence of fixed inner functions within the boundary radius.

This procedure is closely related to the R -matrix method [4] in the sense that known numerical asymptotic solutions are used outside a boundary radius. In the R matrix method, the wave function within the boundary is expanded in terms of basis functions which have a fixed but arbitrary logarithmic derivative of the boundary. An approximate value of the logarithmic derivative of the true wavefunction at the boundary is obtained by using Green's theorem; and the scattering information is then obtained from the knowledge of known asymptotic solutions. It can be shown that the R -matrix method is equivalent to a variational formalism in which there is a discontinuity in the slope of the wavefunction at the boundary radius [5]. Our approach is motivated by the desire to remove this discontinuity in the slope of the wavefunction which should hopefully improve convergence of the results with respect to the basis functions. Further, in contrast to the R -matrix approach, the basis orbitals in the present method can continue to be Slater orbitals which are defined over the full range of space. Therefore all matrix elements, both for electron-atom and electron-ion scattering, can be evaluated relatively easily.

Details of the proposed method are given in Section II. In Section III, we consider the numerical feasibility of this approach by application to electron-hydrogen atom and electron-helium ion scattering in the static exchange and static approximations respectively. Section IV contains a brief discussion and conclusions.

II. FORMALISM

For simplicity and in order to bring out the salient features of the proposed method, we shall consider only elastic scattering here. Extension to multichannel problems is straightforward. Consider l -wave scattering from a potential $V(r)$,

which may be local or nonlocal. The radial Schrödinger equation in Hartree atomic units is

$$[H - k^2/2] \psi = 0 \quad (1)$$

where

$$H = (1/2)[-(d^2/dr^2) + (l(l+1)/r^2)] + V(r)$$

with

$$\lim[rV(r)] = Z \quad \text{as } r \rightarrow \infty$$

and

$$\lim[r^2V(r)] = 0 \quad \text{as } r \rightarrow 0.$$

The general solution of Eq. (1) can be written as

$$\psi(r) = \psi_0(r) + t\psi_1(r) \quad (2)$$

with the boundary conditions: $\psi_0(0), \psi_1(0) = 0$ and $\psi_0(r) \sim_{r \rightarrow \infty} k^{1/2} \sin \theta$; $\psi_1(r) \sim_{r \rightarrow \infty} k^{-1/2} \cos \theta$, where

$$\theta = kr - (l\pi/2) + (Z/k) \ln(2kr) + \arg \Gamma(l+1 - iZ/k). \quad (3)$$

Here the parameter t is the tangent of the phase shift.

In the variational procedures, the functions ψ_0 and ψ_1 are approximated as

$$\psi_I(r) = \sum_a C_{a,I} \eta_a(r) + F_I(r); \quad I = 0, 1. \quad (4)$$

Here η_a are quadratically integrable functions and the asymptotic forms of functions ψ_0 and ψ_1 are contained in the functions F_0 and F_1 , respectively. Generally the functions $F_I(r)$ are taken to be analytical functions which are regular at the origin and which behave asymptotically as regular and irregular free solutions of Eq. (1).

We propose to use functions F_I which are the 'exact' numerical solutions to Eq. (1) outside a boundary radius r_0 and are defined arbitrarily within this boundary. The radius r_0 may be chosen to be a point beyond which the nonlocal part of the potential $V(r)$ is negligible. Therefore, ignoring the nonlocal part of the potential, two linearly independent solutions, defined as $G_I(r)$, can be generated numerically outside r_0 , starting from an asymptotic value. The asymptotic expansions of Burke and Schey [6] can be used to calculate the solutions at an asymptotic position. Now define two linearly independent functions g_1 and g_2 within the boundary radius such that

$$\begin{aligned} F_I(r) &= a_{1,I} g_1(r) + a_{2,I} g_2(r) & \text{for } r \leq r_0, \\ \text{and } G_I(r) & & \text{for } r \geq r_0. \end{aligned} \quad (5)$$

The coefficients $a_{1,I}$ and $a_{2,I}$ are determined by matching the functions $F_I(r)$ and $G_I(r)$ and their derivatives at r_0 . Notice that by construction

$$[H - k^2/2]F_I(r) = 0 \quad \text{for } r \geq r_0. \tag{6}$$

Now we can use the functions ψ_I of Eq. (4) in the variational formalism to determine the quantity t , the tangent of the phase shift. The functions g_1 and g_2 may be selected to be of forms which are rather elementary. We have considered two choices.

Choice I : $g_1 = r^{l+1}, g_2 = r^{l+2}.$

Choice II: $g_1 = (1 - e^{-r})^{l+1} \sin kr, g_2 = (1 - e^{-r})^{l+1} \cos kr.$

With these choices, the evaluation of the required matrix elements is straightforward. To see this we consider the variational formalism in some detail.

The tangent of the phase shift is given in terms of the matrix m_{IJ} defined as [7]

$$m_{IJ} = M_{IJ} - \sum_{ab} M_{Ia}(M^{-1})_{ab} M_{bJ} \tag{8}$$

where I, J can have values of 0 and 1. The other matrices defined are:

the bound-bound matrix

$$M_{ab} = \langle \eta_a | H - E | \eta_b \rangle; \tag{9}$$

the bound-free matrix

$$M_{aI} = M_{Ia} = (\eta_a | H - E | F_I); \tag{10}$$

and the free-free matrix

$$M_{IJ} = (F_I | H - E | F_J). \tag{11}$$

Here the round brackets denote integration limits from 0 to r_0 . In evaluating Eqs. (10) and (11) we exploit the fact that the functions F_I are exact solutions outside the radius r_0 , as stated in Eq. (5). In actual computations it is convenient to avoid the explicit evaluation of the inverse of the bound-bound matrix. More accurate evaluation of the second term in Eq. (8) can be achieved by triangular factorization of the bound-bound matrix [8]. In terms of the quantities m_{IJ} of Eq. (8), the Kohn variational result for the tangent of the phase shift is

$$t_k = -(m_{10}/m_{11}) - (2/m_{11})[m_{00}m_{11} - m_{01}m_{10}]. \tag{12}$$

An analogous formula for the cotangent of the phase shift is

$$t_k^{-1} = -(m_{01}/m_{00}) + (2/m_{00})[m_{00}m_{11} - m_{01}m_{10}]. \quad (13)$$

A judicious choice between the two alternative formulas (12) and (13) can be made by using the ratio m_{00}/m_{11} as a criterion [7].

III. APPLICATION TO e^- -(H, He⁺) SCATTERING

The formalism is applied to the problem of scattering of electrons from the hydrogen atom in the static exchange approximation and from the helium ion in the static approximation. The potential $V(r)$ in Eq. (1) is given by the expression

$$V(r)\psi(r) = \left[-\frac{(Z-1)}{r} - e^{-2Zr} \left(Z + \frac{1}{r} \right) \right] \psi(r) + (-1)^S \frac{R_0(r)}{2} \quad (14)$$

$$\times \left[-\delta_{l,0}(Z^2 + k^2) \int_0^\infty R_0(x) \psi(x) dx + \frac{2}{(2l+1)} \int_0^\infty R_0(x) \psi(x) \frac{x_{<}^l}{x_{>}^{l+1}} dx \right],$$

where for the partial wave l , S is the total spin, Z is the nuclear charge, $R_0(r)$ is the reduced radial function for the ground state of the target and $x_{<}(x_{>})$ is the smaller (larger) of r and x . A simple choice of the fixed internal functions is: $g_1 = r^{l+1}$, $g_2 = r^{l+2}$. In Table I, we present the computed phase shifts of several partial waves for e^- -H scattering. The expansion functions in Eq. (4) are taken to be of the form

$$\eta_i = r^{i+l} e^{-\alpha r}, \quad i = 1, N. \quad (15)$$

For s - and p -wave scattering, the exponent $\alpha = 2.5$ was used and the boundary radius r_0 was fixed at ten Bohr radii. For numerical integration outside this radius, the exchange terms were ignored since they vanish exponentially. For higher partial waves, the radius can be chosen to be even smaller, since the centrifugal term dominates the exchange effects. This is substantiated by the results for d -waves in Table I, where we choose the radius to be eight Bohr radii. For d -wave scattering, $\alpha = 3.5$ was used for the basis functions of Eq. (15).

For the problem of e^- -He⁺ scattering in the static exchange approximation, there are no satisfactory tabulated results. Sloan [9] has pointed out that the Bransden and Dalgarno [3] phase shifts are not very accurate and he has displayed his results in a graphic form. We have therefore obtained 'exact' results by numerical integration of Eq. (1), but in the "static" approximation, ignoring the exchange terms in Eq. (14). This does not detract from our final conclusion, since we have already shown how exchange terms can be treated within the radius of integration.

TABLE I

Singlet Phase Shifts for Scattering of Electrons from Atomic Hydrogen in the Static Exchange Approximation Using Choice I(II) of Fixed Internal Functions.

The two choices are defined by Eq. (7) in the text. N denotes the expansion length and the 'exact' results are taken from Ref. [10].

	k	8	N 16	24	Exact
$L=0$	0.1	2.377(2.398)	2.398(2.398)	2.398(2.398)	2.396
	0.3	1.441(1.512)	1.511(1.512)	1.512(1.512)	1.508
	0.5	0.955(1.031)	1.031(1.031)	1.031(1.031)	1.031
	0.8	0.127(0.651)	0.641(0.651)	0.650(0.651)	0.651
$L=1$	0.1	-0.001(-0.002)	-0.001(-0.001)	-0.001(-0.001)	-0.001
	0.3	-0.024(-0.025)	-0.024(-0.024)	-0.024(-0.024)	-0.024
	0.5	-0.203(-0.070)	-0.073(-0.078)	-0.072(-0.070)	-0.070
	0.8	-0.188(-0.116)	-0.121(-0.115)	-0.117(-0.115)	-0.116
$L=2$	0.1	$-3 \times 10^{-6}(-2 \times 10^{-4})$	$-3 \times 10^{-6}(-4 \times 10^{-6})$	$-3 \times 10^{-6}(-3 \times 10^{-6})$	0.000
	0.3	$-5 \times 10^{-4}(-0.024)$	$-5 \times 10^{-4}(-6 \times 10^{-4})$	$-5 \times 10^{-4}(-5 \times 10^{-4})$	0.000
	0.5	-0.005(-0.028)	-0.004(-0.004)	-0.004(-0.004)	-0.004
	0.8	-0.322(-0.016)	-0.021(-0.014)	-0.016(-0.014)	-0.014

The numerically 'exact' phase shifts in the static approximation agreed to three significant figures with the variational phase shifts when a radius of two Bohr radii was chosen. In Table II, we present the s -wave phase shifts for e^- -He⁺ scattering in the static approximation for five energies chosen by Bransden and Dalgarno. It is seen from Tables I and II that the present method gives good results with large expansion lengths both for e^- -H and e^- -He⁺ scattering. However for high energies, especially for e^- -He⁺ scattering for $k = 1.353$ and $k = 1.895$, even for an expansion length of 24, the results are not fully converged for choice I of the internal functions. This we ascribe to the fact that at high energies, the channel wave functions are highly oscillatory and therefore a polynomial choice of fixed internal functions is not a good approximation. For the ions, however, since the target states are very localized, even a smaller boundary radius can be chosen and we find that for a radius of five Bohr radii, the phase shifts are obtained within one percent of the 'exact' phase shifts. This leads us to a second choice of the fixed internal functions which are oscillatory by construction. We choose $g_1 = (1 - e^{-r})^{l+1} \sin kr$ and $g_2 = (1 - e^{-r})^{l+1} \cos kr$. As seen from Tables I and II, the latter choice gives excellent results for both e^- -H and e^- -He⁺ scattering.

TABLE II

S-Wave Phase Shifts for Scattering of Electrons from Positive Helium Ion in the Static Approximation.

Row (a) corresponds to a radius of five Bohr radii and (b) corresponds to a radius of ten Bohr radii. Choices I and II have the same meaning as in Table I. 'Exact' results are obtained by numerical integration.

k		N			Exact
		8	16	24	
0.491	(a)	0.571(0.576)	0.576(0.577)	0.576(0.577)	0.577
	(b)	0.398(0.537)	0.566(0.576)	0.577(0.577)	
0.779	(a)	0.542(0.557)	0.557(0.559)	0.558(0.560)	0.560
	(b)	-0.682(0.514)	0.555(0.559)	0.559(0.560)	
1.076	(a)	0.531(0.536)	0.534(0.536)	0.536(0.537)	0.536
	(b)	-0.152(0.483)	0.445(0.534)	0.526(0.537)	
1.353	(a)	0.481(0.513)	0.511(0.513)	0.512(0.513)	0.513
	(b)	1.0783(0.512)	0.507(0.513)	0.504(0.513)	
1.895	(a)	0.315(0.466)	0.446(0.468)	0.462(0.468)	0.468
	(b)	-0.470(0.471)	-0.364(0.461)	0.457(0.469)	

IV. CONCLUSIONS

We have outlined a procedure for incorporating the effects of long range potentials in variational methods for scattering. The proper choice of the boundary radius up to which the numerical solutions are to be integrated is crucial to this approach. It is observed that the smaller this radius, the lower the number of expansion functions needed to approximate an exact wavefunction. However if the radius is too small, the nonlocal potentials cannot be completely ignored in the numerical integration of the differential equations. It is shown by the examples considered here that good results can be obtained with reasonable values of the boundary radius and of the expansion length of the normalizable functions especially if choice II (Eq. 7)) of the fixed internal functions is made. However the computer time required for the calculation of integrals is considerably more as compared to using choice I. If the ultimate goal is to justify use of choice I of fixed internal functions by making the boundary radius small, one would need to consider the small effect of nonlocal potentials outside the boundary radius in some approximate way.

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