

Aspects of the Schwinger multichannel variational formulation

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We present a discussion which should be helpful in clarifying some key steps in the formulation of a multichannel extension of Schwinger's variational principle for electron-molecule collisions [K. Takatsuka and V. McKoy, *Phys. Rev. A* **30**, 1734 (1984)].

I. INTRODUCTION

We have previously discussed a multichannel collision theory which was specifically formulated for applications to low-energy electron-molecule scattering.^{1,2} Two important features of this method were (i) closed-channel effects were included through a projected Schrödinger equation and not via the closed-channel Green's function, which would in turn require the continuum states of the target, and (ii) although the resulting variational expression required matrix elements of the Hamiltonian, a consequence of the use of the projected Schrödinger equation, the trial scattering wave function need not satisfy any specific boundary conditions and hence could be expanded in an L^2 basis. This second feature has some practical consequences in applications of this approach to nonlinear polyatomic targets.^{3,4} These features make both the theory and steps in its development quite different from what is generally seen in the formulation of other approaches to this collision problem.⁵⁻⁷ Although the derivation of this multichannel theory as presented previously^{1,2} is correct, we believe that it would be useful to further clarify some key steps in the formulation, and in addition, to present alternative arguments for some of these steps. In so doing, we hope to more clearly identify the important underlying assumptions of our multichannel extension of Schwinger's variational method.

II. THEORETICAL DEVELOPMENTS

A. Multichannel equations

The Hamiltonian for the collision system can be written as

$$H = (H_N + T_{N+1}) + V = H_0 + V, \quad (1)$$

where H_N is the target Hamiltonian, T_{N+1} is the kinetic energy operator for the incident electron, and V is the interaction between the incident electron and the nuclei and electrons of the target. The corresponding Lippmann-Schwinger equation is

$$\Psi_m^{(\mp)} = S_m + G_0^{(\mp)} V \Psi_m^{(\mp)}. \quad (2)$$

In this equation $G_0^{(\mp)}$ is the Green's function associated with $E - H_0$ and S_m is an eigenfunction of H_0 , i.e.,

$$\Phi_m \exp(i\mathbf{k}_m \cdot \mathbf{r}_{N+1}).$$

Here Φ_m is a target eigenfunction of H_N with energy E_m and E is the total collision energy. Based on Eq. (2) it is straightforward to construct a Schwinger functional for the scattering amplitude,

$$f_{m,n} = -\frac{1}{2\pi} (\langle S_m | V | \Psi_n^{(+)} \rangle + \langle \Psi_m^{(-)} | V | S_n \rangle - \langle \Psi_m^{(-)} | A^{(+)} | \Psi_n^{(+)} \rangle), \quad (3)$$

where

$$A^{(\mp)} = V - V G_0^{(\mp)} V. \quad (4)$$

Note that the Lippmann-Schwinger equation, multiplied by V , can be written as

$$A^{(\mp)} \Psi_m^{(\mp)} = V S_m, \quad (5)$$

and that, furthermore, the variational stability of this functional requires that

$$A^{(+)\dagger} = A^{(-)}. \quad (6)$$

This requirement could be seen more explicitly by variation of the functional $f_{m,n}$ of Eq. (3) with respect to $\Psi_n^{(+)}$ and $\Psi_m^{(-)}$. Variational stability leads to the following conditions:

$$A^{(+)\dagger} | \Psi_m^{(-)} \rangle = V | S_m \rangle, \quad (7a)$$

$$A^{(+)} | \Psi_n^{(+)} \rangle = V | S_n \rangle. \quad (7b)$$

Equation (7a) is not equivalent to Eq. (5) unless Eq. (6) is satisfied.

Formally, the Schwinger variational principle of Eq. (3) is complete and has no major drawbacks, at least for collisions of nonidentical particles. However, as pointed out by Geltman,⁸ the continuum states of the target must be included in the Green's function in Eq. (2) in order to make the wave function on the left-hand side of this equation antisymmetric. This requirement becomes a major complexity in any application of the Schwinger

variational principle of Eq. (3) to collisions of identical particles as in electron-molecule scattering.

To develop a multichannel scattering theory which avoids this complexity but retains the very important feature of the Schwinger variational principle of not requiring trial wave functions with scattering boundary conditions, we proceeded as follows.¹ We introduced a projection operator P , which is defined by the target states Φ_I , which are open in the collision

$$P = \sum_I^{\text{open}} |\Phi_I(1,2,\dots,N)\rangle \langle \Phi_I(1,2,\dots,N)|. \quad (8)$$

To remove the continuum component from the Green's function we applied P to Eq. (2) to obtain the projected Lippmann-Schwinger equation

$$P\Psi^{(+)} = S_m + G_p^{(+)}V\Psi_m^{(+)}, \quad (9)$$

where the projected outgoing-wave Green's function $G_p^{(+)}$ is given by

$$G_p^{(+)} = \sum_I^{\text{open}} |\Phi_I\rangle g_I^{(+)}(\mathbf{r}_{N+1}, \mathbf{r}_{N+1}) \langle \Phi_I| \quad (10)$$

and $g_I^{(+)}(\mathbf{r}_{N+1}, \mathbf{r}_{N+1})$ denotes the Green's function for T_{N+1} at energy $E - E_I$. Multiplication of Eq. (9) by V leads to

$$(VP - VG_p^{(+)}V)\Psi_m^{(+)} = VS_m. \quad (11)$$

Equation (11) is an open-channel projected equation and does not contain closed-channel information. Furthermore, the operator VP in Eq. (11) is not Hermitian and hence Eq. (6) is not satisfied. To recover the closed-channel component and to obtain a multichannel equation for the total wave function, we projected the Schrödinger equation

$$\hat{H}\Psi_m^{(+)} = (E - H)\Psi_m^{(+)} = 0 \quad (12)$$

with the "closed-channel complement" of aP , $1 - aP$, where a is an arbitrary parameter, i.e.,

$$(1 - aP)\hat{H}\Psi_m^{(+)} = 0, \quad (13)$$

multiplied Eq. (13) by $1/a$, and added the resulting equation to the "open-channel" equation (11),

$$\left[\frac{1}{2}(PV + VP) - VG_p^{(+)}V - \frac{1}{a} \left[\hat{H} - \frac{a}{2}(\hat{H}P + P\hat{H}) \right] \right] \Psi_m^{(+)} = VS_m. \quad (14)$$

This equation defines the full multichannel scattering wave function. Although the parameter a in this equation is arbitrary, we have shown,^{1,2} and will discuss further in the following, that a specific choice of a is necessary to obtain a variational functional for the scattering amplitude from this equation.

That Eq. (14) *does determine* the complete wave function can be seen more directly as follows. We can write the wave function as a sum of the two projected components $aP\Psi_m^{(+)}$ and $(1 - aP)\Psi_m^{(+)}$, i.e.,

$$\Psi_m^{(+)} = aP\Psi_m^{(+)} + (1 - aP)\Psi_m^{(+)}, \quad (15)$$

and require that this $\Psi_m^{(+)}$ satisfies the Schrödinger equation

$$\hat{H}\Psi_m^{(+)} = \hat{H}[aP\Psi_m^{(+)} + (1 - aP)\Psi_m^{(+)}] = 0. \quad (16)$$

Using Eq. (9) for $P\Psi_m^{(+)}$ we get

$$\hat{H}[a(S_m + G_p^{(+)}V\Psi_m^{(+)} + (1 - aP)\Psi_m^{(+)}] = 0. \quad (17)$$

Straightforward manipulation of this equation gives

$$A^{(+)}\Psi_m^{(+)} = VS_m, \quad (18)$$

where $A^{(+)}$ is the operator on the left-hand side of Eq. (14), thus making (18) identical to Eq. (14). In obtaining Eq. (18) we used the relationships

$$[H_0, P] = 0 \quad (19a)$$

and

$$\begin{aligned} \hat{H}P\Psi_m^{(+)} &= \hat{H}_0P\Psi_m^{(+)} - VP\Psi_m^{(+)} \\ &= \frac{1}{2}[\hat{H}_0P + P\hat{H}_0]\Psi_m^{(+)} - VP\Psi_m^{(+)}. \end{aligned} \quad (19b)$$

Here \hat{H}_0 is defined as $E - H_0$.

The steps in Eqs. (15)–(17) can be viewed as first removing the open-channel component from $\Psi_m^{(+)}$ via projection with $1 - aP$, i.e., $(1 - aP)\Psi_m^{(+)}$, and leaving its complement in Schrödinger form, $\hat{H}(1 - aP)\Psi_m^{(+)}$. The open-channel contributions are then added back in via $aP\Psi_m^{(+)}$ and determined by the Lippmann-Schwinger equation, which enforces the appropriate boundary conditions, i.e., $\hat{H}[a(S_m + G_p^{(+)}V\Psi_m^{(+)})]$. Because $aP\Psi_m^{(+)}$ is treated via the integral equation at one point in $A^{(+)}$, i.e., $\hat{H}[a(S_m + G_p^{(+)}V\Psi_m^{(+)})]$, and left in Schrödinger form in the next term, i.e., $\hat{H}(1 - aP)\Psi_m^{(+)}$, unphysical restrictive conditions in the expansion of the scattering wave function could lead to an imbalance in the role of these terms in the action of $A^{(+)}$ on such a trial function.

It is important to note that the P operator of this formulation is defined on the N -particle space of the target and hence $P\Psi_n^{(+)}(1, 2, \dots, N + 1)$ yields the scattering wave function asymptotically only for r_{N+1} and vanishes asymptotically for r_1, \dots, r_N . This property of P is fundamentally different from that of the P operator of Feshbach theory, for which $P_F\Psi_n^{(+)}$ yields the scattering wave function asymptotically for all r_1, \dots, r_{N+1} .

B. Multichannel variational functional

Based on the inhomogeneous equation (18), a fractional expression could be written for the scattering amplitude,^{1,2}

$$f_{m,n} = -\frac{1}{2\pi} \frac{\langle S_m | V | \Psi_n^{(+)} \rangle \langle \Psi_m^{(-)} | V | S_n \rangle}{\langle \Psi_m^{(-)} | A^{(+)} | \Psi_n^{(+)} \rangle}, \quad (20)$$

where $A^{(\mp)}$ is explicitly given as

$$A^{(+)} = \frac{1}{2}(PV + VP) - VG_p^{(\mp)}V + \frac{1}{a} \left[\hat{H} - \frac{a}{2}(\hat{H}P + P\hat{H}) \right]. \quad (21)$$

For this functional to be variationally stable we must re-

quire that $A^{(+)\dagger} = A^{(-)}$. This condition is obviously satisfied for any matrix element of $A^{(+)}$ involving a L^2 component of the scattering wave function. This is true for any value of the parameter a in Eq. (21). However, an important conclusion of our earlier work^{1,2} was that this is not true for matrix elements of $A^{(+)}$ involving only continuum components of the trial scattering wave function unless the parameter a is chosen to be $N + 1$. This is true because, with this choice, the matrix elements of $\hat{H} - \frac{1}{2}a(\hat{H}P + P\hat{H})$ vanish. This property provides variational stability to the functional of Eq. (20) and makes an entirely L^2 expansion of the scattering wave function possible.

It is interesting to note that for the scattering of nonidentical particles such as in positron-molecule col-

lisions the parameter a assumes the value of 1. Applications of the theory to positron-molecule scattering are under way.

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