

# Theory of electronically inelastic scattering of electrons by molecules

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We discuss a multichannel formulation of the Schwinger and a related variational principle (of one order higher than the Schwinger principle) in a form suitable for application to the scattering of low-energy electrons by both linear and nonlinear molecules. The theory includes the effects of polarization straightforwardly and should be particularly useful for obtaining electronically inelastic cross sections. An expansion of the trial scattering wave function in a discrete basis is possible. With certain choices for these basis functions this feature can be particularly advantageous.

## I. INTRODUCTION

In recent years several approaches have been developed for studying the collisions of low-energy electrons with molecules at an *ab initio* level and within the framework of the fixed-nuclei approximation.<sup>1-10</sup> Many of these methods have been applied to the scattering of electrons by diatomic and linear polyatomic molecules<sup>1-6,11,12</sup> at the static-plus-exchange level, while some of these studies have included the effects of polarization on the cross sections through the use of an effective optical potential.<sup>7-10</sup> Collins and Schneider<sup>13</sup> have also extended and applied their approach to electronic excitation of hydrogenic and atomic ions and of  $H_2^+$ .

Although the methods discussed above can in principle be extended to nonlinear molecules, most such studies to date have been restricted to small linear systems due to the substantial reduction in the numerical complexities which are brought about by the cylindrical symmetry of these systems. There is clearly a present need for a theory of low-energy electron-molecule collisions which can be applied with some flexibility to both linear and nonlinear systems. A suitable theory should be capable of dealing with several important aspects of the problem such as polarization effects, Feshbach resonances, electronically inelastic scattering with several open and closed channels, and, very importantly, nonlinear targets. Single-center expansion techniques would appear to be potentially inefficient for accomplishing these objectives in general.

In this paper we will discuss two variational methods which we believe can provide a practical approach to addressing such problems in electron-molecule collisions for general targets. These two methods are based on the Schwinger variational principle and a related variational functional,<sup>6,14</sup> respectively. Some important features of the methods are as follows. As in the original Schwinger principle,<sup>15</sup> the trial scattering functions need not satisfy any specific boundary conditions and hence can be expanded in an  $L^2$  basis. The method avoids the explicit construction of the closed-channel Green's function and is also free of any spurious singularities. A very practical feature of the formulation is that, with the use of an insertionlike quadrature to evaluate the second-Born-approximation-like terms and with an expansion of the

trial function in a Gaussian basis, all matrix elements in the variational expression can be evaluated analytically. Moreover, this feature is retained even when plane-wave functions are added to the trial scattering basis.<sup>16</sup>

To put the present contribution in a useful perspective, we now summarize some previous developments. Several applications of an iterative version of the Schwinger variational principle<sup>3</sup> have shown that the method is a useful approach to the solution of the collision equations for linear molecules at the static-plus-exchange level.<sup>3,12,17,18</sup> These applications were implemented with a single-center expansion technique. We also extended the Schwinger variational principle to include multichannel scattering along with polarization effects. In this formulation<sup>19</sup> all configurations [in a basis of  $(N+1)$ -electron Slater determinants] representing both open and closed channels are treated equivalently. Any ambiguity in defining the  $P_0$  (open-channel) and  $Q_0$  (closed-channel) spaces is avoided<sup>20</sup> and the method is free of the divergences which can arise in optical-potential methods. Applications of this multichannel extension to  $e$ -H atom collisions below the inelastic threshold showed encouraging convergence characteristics.<sup>19</sup> Although the single-center expansion technique and iterative procedures<sup>3</sup> could be applied to this multichannel extension of the Schwinger principle, the numerical effort required can be substantial. Hence, in developing a method which would be applicable to molecules of varying geometries, it should be advantageous to calculate the body-frame scattering amplitude in the plane-wave representation. Moreover, most nonlinear molecules have dipole moments and the range of such potentials can make it difficult to adequately represent the trial function in an  $L^2$  basis only. Inclusion of oscillatory functions such as plane waves and Bessel functions in the trial function would adequately represent the intermediate and long-range regions of the open-channel scattering orbitals.<sup>21</sup> However, certain difficulties can arise from the presence of these long-range functions in the variational basis. First, in variational methods, including the Kohn principle, one must solve the linear equation

$$A\vec{x} = \vec{b}, \quad (1.1)$$

where  $\vec{x}$  and  $\vec{b}$  are unknown and known vectors, respec-

tively, and  $\underline{A}$  is a matrix representation of the Hamiltonian or other operators. The use of plane waves in the representation of  $\underline{A}$  leads to a directional dependence in  $\underline{A}$  and, moreover, a new matrix must be generated at each energy. Secondly, interference between the short-range  $L^2$  functions and the long-range functions in the trial scattering function can lead to a deterioration of the method.<sup>22</sup> This deterioration results from the interference of these two types of functions in the short-range region. This can be a serious difficulty and must be common to other variational methods.

To improve upon the Schwinger variational principle, without resorting to any numerical iterative procedure and employing only discrete basis functions in the trial function, we proposed the  $\tilde{C}$  functional.<sup>6,14</sup> The  $\tilde{C}$  functional is a straightforward extension of the Schwinger functional which, however, provides a result which is equivalent to that obtained after one iteration in the iterative Schwinger method.<sup>3,6</sup> This improvement is particularly important since the effect of one iteration in the Schwinger procedure is substantial, especially when small basis sets are used.<sup>3,23</sup> Moreover, the matrix  $\underline{A}$  of Eq. (1.1) has no directional dependence.

In this paper we present both a multichannel extension of the  $\tilde{C}$ -functional method and a unifying discussion of several important features of the multichannel forms of the Schwinger and  $\tilde{C}$  functionals. Several aspects of these formulations, which from our experience seem to be in need of clarification, are discussed in some detail.

## II. REVIEW OF VARIATIONAL FUNCTIONALS

We will briefly discuss our formerly proposed variational functionals since these results are needed in the development of the present multichannel theory.

### A. Beyond the static-plus-exchange approximation

Our formulation<sup>19</sup> for collision problems beyond the static-plus-exchange approximation begins with a projected Lippmann-Schwinger equation

$$P\Psi_m^{(+)} = tS_m + G_P^{(+)}V\Psi_m^{(+)}, \quad (2.1)$$

where  $\Psi_m^{(+)}$  is the total scattering wave function of the  $m$ th channel with plane-wave plus outgoing-wave boundary condition.  $P$  defines the open-channel space in terms of the eigenfunctions of the target Hamiltonian  $H_N$ ,

$$P = \sum_{m=1}^{N_0} |\Phi_m(1,2,\dots,N)\rangle \langle \Phi_m(1,2,\dots,N)| \quad (2.2)$$

and

$$H_N |\Phi_m\rangle = E_m |\Phi_m\rangle, \quad E - E_m > 0. \quad (2.3)$$

The free-particle solution  $S_m$  of the unperturbed Hamiltonian  $H_0 = H_N + T_{N+1}$  is

$$S_m = \Phi_m e^{i\vec{k}_m \cdot \vec{r}_{N+1}}. \quad (2.4)$$

The coefficient  $t$  associated with  $S_m$  is explicitly included to remind us that the antisymmetrizer for  $\Psi_m^{(+)}$  is

$$\mathcal{A}_{N+1} = \frac{1}{\sqrt{(N+1)!}} \sum \epsilon_q Q \quad (2.5a)$$

but for  $\Phi_m$  it is

$$\mathcal{A}_N = \frac{1}{\sqrt{N!}} \sum \epsilon_q Q, \quad (2.5b)$$

and hence

$$t = \frac{1}{\sqrt{N+1}}. \quad (2.6)$$

The interaction potential  $V$  is

$$V = H_{N+1} - H_0 \quad (2.7)$$

$$= \sum_{i=1}^N \frac{1}{r_{i,N+1}} - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha,N+1}},$$

where the first term on the right-hand side (rhs) represents the electron repulsion and the second term represents the electron-nuclear attraction. The outgoing-wave Green's function  $G_P^{(+)}$ , which is defined only in the open-channel space ( $P$ ), is

$$G_P^{(+)} = \sum_{m=1}^{N_0} |\Phi_m\rangle g_m^{(+)}(\vec{r}_{N+1}, \vec{r}'_{N+1}) \langle \Phi_m| \quad (2.8)$$

with

$$g_m^{(+)}(\vec{r}, \vec{r}') = -\frac{1}{2\pi} \frac{e^{ik_m|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}. \quad (2.9)$$

We need a projected Schrödinger equation by which the unprojected part of Eq. (2.1) is recovered, viz.,

$$[\hat{H} - a(P\hat{H} + \hat{H}P)]\Psi_m^{(+)} = a(VP - PV)\Psi_m^{(+)}, \quad (2.10)$$

where  $\hat{H} = E - H_{N+1}$  and  $a$  is an arbitrary parameter. The equation contains information about the closed channels without defining the closed-channel Green's function which would in turn include the continuum states of the target.<sup>24</sup>

A very simple combination of Eq. (2.1) and Eq. (2.10) together with  $a = (N+1)/2$  defines a complete equation for  $\Psi_m^{(+)}$ , i.e.,

$$\left[ \frac{1}{2}(PV + VP) - VG_P^{(+)}V \right. \\ \left. + \frac{1}{N+1} \left[ \hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P) \right] \right] \Psi_m^{(+)} = tVS_m. \quad (2.11)$$

Based on this inhomogeneous equation one can construct a variational functional for the scattering amplitude

$$f(\vec{k}_m, \vec{k}_n) = -\frac{1}{2\pi} \frac{\langle S_m | V | \Psi_n^{(+)} \rangle \langle \Psi_m^{(-)} | V | S_n \rangle}{\left\langle \Psi_m^{(-)} \left| \left[ \frac{1}{2}(PV + VP) - VG_P^{(+)}V + \frac{1}{N+1} \left[ \hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P) \right] \right] \right| \Psi_n^{(+)} \right\rangle}. \quad (2.12)$$

We note that the operator

$$\hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P) \quad (2.13)$$

is Hermitian<sup>10</sup> because of the choice of  $a = (N+1)/2$ . In the expansion technique in a variational calculation,  $\Psi_m^{(+)}$  is expanded in a basis of Slater determinants. Unlike the partitioning technique, we do not make any distinction among the configurations such as is made in defining

$$f(\vec{k}, \vec{k}') = -\frac{1}{2\pi} \sum_{i,j} \langle \vec{k} | v_{SE} | \lambda_i \rangle [\langle \lambda_i | (v_{SE} - v_{SEG}^{(+)} v_{SE}) | \lambda_j \rangle]^{-1} \langle \lambda_j | v_{SE} | \vec{k}' \rangle \quad (2.15)$$

which is exactly the Schwinger variational expression in the static-plus-exchange approximation (SE).<sup>3</sup> In Eq. (2.15),  $v_{SE}$  indicates the static-plus-exchange potential formed by the orbitals  $[\phi_r]$ .

### B. $\tilde{C}$ functional

We first consider potential scattering with a well-defined Lippman-Schwinger equation for the scattering orbital, i.e.,

$$\psi_i = s_i + g_0 v \psi_i, \quad (2.16)$$

where  $s_i$  is the regular solution of the unperturbed scattering Hamiltonian, and  $g_0$  is its associated Green's function with standing wave boundary conditions. The subscript  $i$  indicates any possible channels such as angular momentum components of a single-center expansion and  $v$  is an effective potential such as the static-plus-exchange one. The Schwinger variational principle gives the functional for the  $\underline{K}$  matrix

$$K_{ij} = -2 \frac{\langle s_i | v | \psi_j \rangle \langle \psi_i | v | s_j \rangle}{\langle \psi_i | (v - v g_0 v) | \psi_j \rangle}. \quad (2.17)$$

This variational principle works very well if the simple potential  $v$  is of short range. When  $v$  is a long-range potential, such as for a polar molecule, long-range basis functions should be introduced in the expansion of  $\psi_i$ . As stated earlier this can lead to certain difficulties.

As an alternative and to avoid these difficulties we consider another form of the Lippmann-Schwinger equation<sup>14</sup>

$$\tilde{c}_i = g_0 v s_i + g_0 v \tilde{c}_i \quad (2.18)$$

with

$$\tilde{c}_i = \psi_i - s_i. \quad (2.19)$$

The associated variational functional ( $\tilde{C}$  functional) is

$$X_{ij} = \frac{\langle s_i | v g_0 v | \tilde{c}_j \rangle \langle \tilde{c}_i | v g_0 v | s_j \rangle}{\langle \tilde{c}_i | (v - v g_0 v) | \tilde{c}_j \rangle}. \quad (2.20)$$

Feshbach's projection operators.<sup>20</sup>

Finally, we consider the static-plus-exchange approximation for elastic scattering of electrons by a closed-shell molecule as an example of Eq. (2.12). The basis functions for  $\Psi_i^{(+)}$  are

$$u_i = \mathcal{A}_{N+1}(\phi_1 \bar{\phi}_1 \cdots \phi_{N/2} \bar{\phi}_{N/2}) \lambda_i, \quad (2.14)$$

where  $\phi_r$ 's are the Hartree-Fock orbitals and  $\lambda_i$  is a scattering function which is orthogonal to all the  $\phi_r$ 's. After some simple manipulation we find

The  $\underline{K}$  matrix is written as

$$-\frac{1}{2} K_{ij} = \langle s_i | v | s_j \rangle + \langle s_i | v g_0 v | s_j \rangle + X_{ij}. \quad (2.21)$$

We have shown that  $L^2$  functions are generally sufficient to expand  $\tilde{c}_i$  even when  $v$  is a long-range potential.<sup>6</sup> Since in this variational calculation the  $L^2$  functions are completely factored out from the regular long-range functions and treated exactly in the first- and second-Born terms, the interference between the long-range and short-range basis functions is considerably reduced. In fact, the convergence of  $X_{ij}$  of Eq. (2.21) is almost equivalent to that given after one iteration of the iterative Schwinger method.<sup>6</sup> The effect of this one iteration can be quite large, especially when the basis set is not large.<sup>3,23</sup>

## III. UNIFIED VARIATIONAL FUNCTIONAL

We have presented two variational principles with different purposes: one is for multichannel scattering with polarization effects and another is the  $\tilde{C}$  functional designed to deal with long-range potentials. Both functionals have already been numerically<sup>14,19</sup> examined and found to work quite well. Our next step is to unify these functionals, i.e., to construct a  $\tilde{C}$  functional suitable for multichannel scattering theory.

### A. Variational functional

We start our discussion with the Lippmann-Schwinger-Schrödinger equation, Eq. (2.11), written as

$$A^{(+)} \psi_m^{(+)} = t V S_m \quad (3.1)$$

with

$$A^{(+)} = \frac{1}{2}(PV + VP) - VG_P^{(+)}V + \frac{1}{N+1} \left[ \hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P) \right]. \quad (3.2)$$

We define  $S_m^0$  by

$$S_m^0 = \frac{1}{\sqrt{N!}} \mathcal{A}_{N+1} \{ \Phi_m(1, 2, \dots, N) s_m^0(N+1) \}, \quad (3.3)$$

where  $s_m^0$  is a plane wave orthogonalized to all molecular orbitals occurring in the projection operator  $P$ . This orthogonalization can be easily performed by the Schmidt procedure

$$s_m^0 = e^{i\vec{k}_m \cdot \vec{r}} - \sum_r \phi_r \langle \phi_r | e^{i\vec{k}_m \cdot \vec{r}} \rangle, \quad (3.4)$$

where  $\{\phi_r | r=1, 2, \dots, M\}$  is the set of molecular orbitals (both occupied and unoccupied) making up  $P$ . Asymptotically ( $r_{N+1} \rightarrow \infty$ )  $S_m^0$  behaves the same way as  $tS_m$ , i.e.,

$$S_m^0 \sim \frac{1}{\sqrt{N+1}} \Phi_m e^{i\vec{k}_m \cdot \vec{r}_{N+1}} \text{ as } r_{N+1} \rightarrow \infty. \quad (3.5)$$

Next we define  $\tilde{C}_m^{(+)}$  as

$$\tilde{C}_m^{(+)} = \Psi_m^{(+)} - S_m^0. \quad (3.6)$$

Insertion of these equations into Eq. (3.1) gives

$$A^{(+)} | \tilde{C}_m^{(+)} \rangle = tV | S_m \rangle - A^{(+)} | S_m^0 \rangle = | B_m^{(+)} \rangle. \quad (3.7)$$

This is our fundamental equation for the construction of the new  $\tilde{C}$  functional.

The incoming-wave equation associated with Eq. (3.7) is

$$A^{(-)} | \tilde{C}_m^{(-)} \rangle = | B_m^{(-)} \rangle \quad (3.8)$$

in which  $G_p^{(-)}$  replaces  $G_p^{(+)}$  in Eq. (3.7). Owing to the hermiticity of the operator in Eq. (2.13) the conjugate equation of Eq. (3.8) can be written as

$$\langle \tilde{C}_m^{(-)} | A^{(+)} \rangle = \langle B_m^{(-)} |. \quad (3.9)$$

From Eqs. (3.7) and (3.9) we obtain the functional

$$I_{mn} = \langle B_m^{(-)} | \tilde{C}_n^{(+)} \rangle + \langle \tilde{C}_m^{(-)} | B_n^{(+)} \rangle - \langle \tilde{C}_m^{(-)} | A^{(+)} | \tilde{C}_n^{(+)} \rangle \quad (3.10)$$

in a bilinear form or equivalently

$$I_{mn} = \frac{\langle \tilde{C}_m^{(-)} | B_n^{(+)} \rangle \langle B_m^{(-)} | \tilde{C}_n^{(+)} \rangle}{\langle \tilde{C}_m^{(-)} | A^{(+)} | \tilde{C}_n^{(+)} \rangle} \quad (3.11)$$

in a fractional form. These functionals are stationary around the exact functions  $\tilde{C}_m^{(-)}$  and  $\tilde{C}_n^{(+)}$  due to Eq. (3.9), i.e.,

$$\delta[I_{mn}] = \langle \delta \tilde{C}_m^{(-)} | -A^{(+)} \tilde{C}_n^{(+)} + B_m^{(+)} \rangle + \langle -A^{(-)} \tilde{C}_m^{(-)} + B_m^{(-)} | \delta \tilde{C}_n^{(+)} \rangle = 0. \quad (3.12)$$

Thus we have shown that  $I_{mn}$  is a variational functional.

### B. Scattering amplitude

Before deriving the explicit expression for the scattering amplitude, we will discuss some properties of  $A^{(+)}$ , especially the portion defined in Eq. (2.13). We first note the identity (the proof is in the Appendix),

$$\mathcal{A}_{N+1} [1 - (N+1)P] | \mathcal{A}_{N+1} \Phi_m \mu(N+1) \rangle = 0, \quad (3.13)$$

where  $\mu$  is an arbitrary function orthogonal to  $\{\phi_r | r=1, 2, \dots, M\}$ . This identity together with the fact that  $\mathcal{A}_{N+1}$  commutes with  $H_{N+1}$  has two convenient consequences. First, the matrix element of the operator  $\hat{H} - \frac{1}{2}(N+1)(P\hat{H} + \hat{H}P)$  between  $\mathcal{A}_{N+1} \Phi_m \mu$  and any antisymmetrized function  $\chi$  is

$$\begin{aligned} \langle \chi | [\hat{H} - \frac{1}{2}(N+1)(P\hat{H} + \hat{H}P)] | \mathcal{A}_{N+1} \Phi_m \mu \rangle \\ = -\frac{1}{2}(N+1) \langle \chi | (VP - PV) | \mathcal{A}_{N+1} \Phi_m \mu \rangle. \end{aligned} \quad (3.14)$$

Further, if  $\chi$  is also of the form

$$\chi = \mathcal{A}_{N+1} \Phi_n \mu',$$

where  $\mu'$  is again orthogonal to  $\{\phi_r | r=1, 2, \dots, M\}$ ,

$$\langle \mathcal{A}_{N+1} \Phi_n \mu' | [\hat{H} - \frac{1}{2}(N+1)(P\hat{H} + \hat{H}P)] | \mathcal{A}_{N+1} \Phi_m \mu \rangle = 0. \quad (3.15)$$

This latter equation was used in a previous paper<sup>19</sup> to prove the hermiticity of this operator.

Now we will examine  $I_{mn}$ ,

$$I_{mn} = \langle \Psi_m^{(-)} - S_m^0 | A^{(+)} | \Psi_n^{(+)} - S_n^0 \rangle. \quad (3.16)$$

In this expression we insert

$$\begin{aligned} \langle \Psi_m^{(-)} | A^{(+)} | \Psi_n^{(+)} \rangle &= t \langle \Psi_m^{(-)} | V | S_n \rangle \\ &= -2\pi t^2 f_{mn}, \end{aligned} \quad (3.17a)$$

$$\langle \Psi_m^{(-)} | A^{(+)} | S_n^0 \rangle = t \langle S_m | V | S_n^0 \rangle, \quad (3.17b)$$

$$\langle S_m^0 | A^{(+)} | S_n^0 \rangle = \langle S_m^0 | [\frac{1}{2}(PV + VP) - VG_p^{(+)}V] | S_n^0 \rangle \quad (3.17c)$$

resulting in

$$\begin{aligned} -2\pi t^2 f_{mn} &= t \langle S_m | V | S_n^0 \rangle + t \langle S_m^0 | V | S_n \rangle \\ &\quad - \frac{1}{2} \langle S_m^0 | (PV + VP) | S_n^0 \rangle \\ &\quad + \langle S_m^0 | VG_p^{(+)}V | S_n^0 \rangle + I_{mn}. \end{aligned} \quad (3.18)$$

Equation (3.15) is used in obtaining Eq. (3.17). The first three terms in Eq. (3.18) correspond to the first Born term and the fourth term to the second term. Although the Born term in this expression seems somewhat more complicated than the usual one, some cancellation takes place leading to simplifications in actual calculations.

### C. Expansion techniques

As usual the  $\tilde{C}_m$  functions are expanded in basis functions. In our case, the basis functions are Slater determinants ( $u_i$ ) composed of molecular orbitals (occupied or unoccupied) and, if necessary, additional functions. With  $\tilde{C}_m^{(+)}$  expanded as

$$\tilde{C}_m^{(+)} = \sum_i u_i a_{im}, \quad (3.19)$$

the variational expression for  $I_{mn}$  becomes

$$\begin{aligned} I_{mn} &= \sum_{i,j} \langle tVS_m + (VG_p^{(-)}V - PV)S_m^0 | V | u_i \rangle \Delta_{ij} \\ &\quad \times \langle u_j | tVS_n + (VG_p^{(+)}V - PV)S_n^0 \rangle \end{aligned} \quad (3.20)$$

with

$$(\Delta^{-1})_{ij} = \left\langle u_i \left| \left[ \frac{1}{2}(PV + VP) - VG_p^{(+)}V + \frac{1}{N+1} \left[ \hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P) \right] \right] \right| u_j \right\rangle. \quad (3.21)$$

In Eq. (3.20), Eq. (3.14) is used.

In the static-plus-exchange approximation  $u_i$  has the following form:

$$u_i^m = \frac{1}{\sqrt{N!}} \mathcal{A}_{N+1} \Phi_m \lambda_i, \quad (3.22)$$

where  $\lambda_i$  is an arbitrary function which is orthogonal to  $\{\phi_r | r=1, 2, \dots, M\}$ . To represent the closed channels one can replace  $\Phi_m$  with other configurations of energy higher than  $E$ . These configurations contribute to the polarization of the target by the incident electron. The effectiveness of this configuration depends on the choice of the unoccupied molecular orbitals.

A very important feature of Eq. (3.20) is that the long-range functions, e.g.,  $S_m$ ,  $S_m^0$ , are always associated with the potential  $V$  directly. This is still true even when long-range basis functions are included in  $u_i$ . This is a direct consequence of the identity in Eq. (3.13) and does not depend on any properties of the Hamiltonian except that it commutes with  $\mathcal{A}_{N+1}$ . This suggests that the functional in Eq. (3.20) can be used at off-shell values of the energy.

#### IV. UNIQUENESS OF THE SCATTERING AMPLITUDE

We consider the general inhomogeneous equations of the type

$$\Omega^{(+)} | X_m^{(+)} \rangle = | Y_m^{(+)} \rangle \quad (4.1a)$$

and

$$\Omega^{(-)} | X_m^{(-)} \rangle = | Y_m^{(-)} \rangle, \quad (4.1b)$$

where  $\Omega^{(\pm)}$  are the operators describing the scattering process. Examples of  $\Omega^{(\pm)}$  are the following:  $E$ - $H$  in the Kohn principle,  $v - vg^{(\pm)}v$  in the Schwinger principle, and  $A^{(\pm)}$  of Eq. (3.2) in our variational functionals. The question of the uniqueness of the scattering amplitude associated with these solutions now arises: can the solution of the homogeneous counterpart of Eq. (4.1), if any, contaminate the solution  $X_m^{(+)}$  and/or  $X_m^{(-)}$ , leaving the amplitude  $f_{mn}$  nonunique? In this section we discuss some relevant details of the uniqueness of the scattering amplitude associated with inhomogeneous equations.

The motivation for the present discussion can best be seen through the following conjecture. Imagine a solution, say  $F_m^{(+)}$ , which simultaneously satisfies the following two equations:

$$-\frac{N+1}{2} \hat{H} F_m^{(+)} = \beta \quad (4.2a)$$

and

$$\left[ \frac{1}{2}(PV + VP) - VG_p^{(+)}V - \frac{1}{2}(P\hat{H} + \hat{H}P) \right] F_m^{(+)} - tVS_m = \beta, \quad (4.2b)$$

where  $\beta$  is a number or a function. Then the family of the solutions of Eq. (2.11) must include  $F_m^{(+)}$  since by substituting Eq. (4.2a) into Eq. (4.2b), we recover Eq. (2.11). However, it is obvious that the true solutions in the above family are only those which satisfy Eq. (4.2) for  $\beta=0$ . In other words, the solution of Eq. (2.11) is not always the solution to the Schrödinger equation. Hence the scattering amplitudes of Eqs. (2.13) and (3.18) are not uniquely determined.

As we shall see below, the above conjecture is closely related to the nonuniqueness problem, which could arise from the solution of the homogeneous equations. To see this, we note that if we write

$$F_m^{(+)} = \bar{\Psi}_m^{(+)} + \gamma_m^{(+)}, \quad (4.3)$$

where  $\bar{\Psi}_m^{(+)}$  is the exact solution of the Schrödinger equation with the appropriate boundary condition, insertion of Eq. (4.3) into Eq. (2.11) gives

$$\left[ \frac{1}{2}(PV + VP) - VG_p^{(+)}V + \frac{1}{N+1} \left[ \hat{H} - \frac{N+1}{2}(P\hat{H} + \hat{H}P) \right] \right] \gamma_m^{(+)} = 0. \quad (4.4)$$

Therefore  $\gamma_m^{(+)}$  must at most be a solution of the homogeneous equation. Thus the above conjecture is a special case of our general problem.

Now we return to the more general equation (4.1). We shall show that if the following condition is fulfilled:

$$\langle X^{(-)} | \Omega^{(+)} = \langle \Omega^{(-)} X^{(-)} | = \langle Y^{(-)} |, \quad (4.5)$$

the the variational value from the fractional functional

$$J_{mn} = \frac{\langle X_m^{(-)} | Y_m^{(+)} \rangle \langle Y_m^{(-)} | X_n^{(+)} \rangle}{\langle X_m^{(-)} | \Omega^{(+)} | X_n^{(+)} \rangle} \quad (4.6)$$

is necessarily unique even if  $\Omega^{(+)}$  has a nonzero homogeneous solution. Consider the homogeneous equations

$$\Omega^{(+)} | Z^{(+)} \rangle = 0 \quad (4.7a)$$

and

$$\Omega^{(-)} | Z^{(-)} \rangle = 0. \quad (4.7b)$$

Then  $Y_m^{(\pm)} + \omega_m^{(\pm)} Z_m^{(\pm)}$  is also the solution of Eq. (4.1) for any value of  $\omega_m^{(\pm)}$ . We consider simply

$$\langle X_m^{(-)} + \omega_m^{(-)} Z_m^{(-)} | \Omega^{(+)} | X_n^{(+)} + \omega_n^{(+)} Z_n^{(+)} \rangle = \langle X_m^{(-)} | \Omega^{(+)} | X_n^{(+)} \rangle. \quad (4.8a)$$

$$= \langle X_m^{(-)} | Y_n^{(+)} \rangle + (\omega_m^{(-)})^* \langle Z_m^{(-)} | Y_n^{(+)} \rangle \quad (4.8b)$$

$$= \langle Y_m^{(-)} | X_n^{(+)} \rangle + \omega_n^{(+)} \langle Y_m^{(-)} | Z_n^{(+)} \rangle, \quad (4.8c)$$

where the property of Eq. (4.5) was used. Since  $\omega_m^{(\pm)}$  is arbitrary we can conclude

$$\langle Z_m^{(-)} | Y_n^{(+)} \rangle = 0 \quad (4.9a)$$

and

$$\langle Y_m^{(-)} | Z_n^{(+)} \rangle = 0. \quad (4.9b)$$

Therefore  $Z$ 's are either null functions or orthogonal to  $Y$  functions in the above sense. The orthogonality between the solution of such homogeneous and inhomogeneous equations is well known in the elementary theory of linear operators.<sup>25</sup> As a corollary of this orthogonality we observe that even if  $Y_m^{(\pm)}$  is replaced by  $Y_m^{(\pm)} + \omega_m^{(\pm)} Z_m^{(\pm)}$  in the variational expression, the value of  $J_{mn}$  remains unaltered because all the integrals containing  $Z_m^{(\pm)}$  vanish.

In actual calculations where the number of the basis functions is limited, the situation is more complicated. In this case, both  $X_m^{(\pm)}$  and  $Z_m^{(1)}$  only approximately satisfy Eq. (4.1) and Eq. (4.7), respectively, and hence the orthogonality of Eq. (4.9) is not complete. In addition, the coefficient  $\omega_m^{(+)}$  can become extremely large, depending on the basis set chosen. In this case, some singularities may arise in the value of  $J$ , because the contribution to the denominator of  $J$  is dominated by the  $Z$  functions.

An example for which  $\Omega^{(\pm)}$  does not have the property of Eq. (4.5), and  $\Omega^{(+)}$  has a homogeneous solution, is

$$(\epsilon - h)\tilde{c}_i = v s_i, \quad (4.10)$$

which is the differential equation form of Eq. (2.18).  $h$  is the scattering Hamiltonian with the effective potential  $v$  and  $\epsilon$  is the incident energy of the incoming electron. Unless the boundary condition is imposed on  $\tilde{c}_i$  so that  $\epsilon - h$  is Hermitian, the unknown contribution of the homogeneous solution, i.e.,  $(\epsilon - h)\psi_i = 0$ , with  $\tilde{c}_i$ , leads to an incorrect  $K$  matrix. We have discussed the boundary condition which must be imposed on  $\tilde{c}$  elsewhere.<sup>26</sup>

We now consider our specific variational functions, Eqs. (2.13) and (3.11). The general conclusion stated above holds true for our functionals: The operator  $A^{(\pm)}$  in the functionals, Eq. (3.2), satisfies Eq. (4.5), since  $\hat{H} - \frac{1}{2}(N+1)(P\hat{H} + \hat{H}P)$  is Hermitian. Therefore the scattering amplitudes are given uniquely, even if the nonzero solution  $Y_m^{(+)}$  of the homogeneous equation, Eq. (4.4), exists.

Furthermore, we can see that the nonzero solution  $\gamma_m^{(+)}$  itself does not exist. Let us assume that the homogeneous equation [Eq. (4.4)] is meaningful. We apply the following operator:

$$\sum_n u_n V | S_n \rangle \langle \Psi_n^{(-)} | \quad (4.11)$$

onto Eq. (4.4), where  $\Psi_n^{(-)}$  is the exact wave function for in-states, and  $u_n$ 's are positive real (but otherwise arbitrary) numbers,

$$\begin{aligned} & \sum_n u_n V | S_n \rangle \langle \Psi_n^{(-)} | A^{(+)} | \gamma_m^{(+)} \rangle \\ &= \sum_n u_n V | S_n \rangle \langle A^{(-)} \Psi_n^{(-)} | \gamma_m^{(+)} \rangle \\ &= \sum_n u_n V | S_n \rangle \langle S_n | V | \gamma_m^{(+)} \rangle \\ &= 0. \end{aligned} \quad (4.12)$$

Unless one of the eigenvalues of the operator

$$\sum_n u_n V | S_n \rangle \langle S_n | V \quad (4.13)$$

happens to be zero (of course, all the other eigenvalues are positive) the inverse of this operator exists. Then, Eq. (4.12) implies that  $\gamma_m^{(+)}$  must be the null function,

$$\gamma_m^{(+)} = 0. \quad (4.14)$$

Generally speaking, the operator of Eq. (4.13) must be positive when the energy for  $S_n$ 's is real and positive. Thus we can expect generally that the nonzero solutions of  $\gamma_m^{(+)}$  do not exist in our scattering formalism.

This conclusion is not surprising and is consistent with the following physical consideration. The left-hand side of Eq. (2.13) originates from the equation of motion for the target and the scattered particle on which the outgoing boundary condition is imposed through  $G_p^{(+)}$ , while the right-hand side represents the incoming source. Therefore, a nonzero  $\gamma_m^{(+)}$ , if it exists, would be forced to have outgoing wave propagation asymptotically without any incoming source. Thus the nonzero  $\gamma_m^{(+)}$  cannot exist on the positive real axis of the  $E$  plane. A more rigorous statement requires a study of the spectrum of  $A^{(\pm)}$ , but this is beyond the scope of this paper. Numerically we have already observed the uniqueness of our scattering amplitudes in actual calculations. (See Ref. 19 and the accompanying paper.)

Incidentally, the above statement that a nonzero  $\gamma_m^{(+)}$  cannot exist on the positive real axis of the  $E$  plane, or in other words that  $A^{(\pm)}$  does not have eigenvalue at zero, is also relevant to the singularity-free property of the variational functionals. In the Kohn variational principle or with optical potentials, e.g.,  $Q_0 \hat{H} (Q_0 \hat{H} Q_0)^{-1} \hat{H} Q_0$  for inelastic scattering, with  $Q_0$  being a projection operator to define closed channels, well-known singularities can occur. The number of such singularities increases as the basis functions increase,<sup>27</sup> although the widths due to the singularities become narrower. On the other hand, since  $A^{(\pm)}$ , as well as  $v - v g v$  in the Schwinger functional, does not have an eigenvalue at zero, the singularity due to  $(A^{(\pm)})^{-1}$  is expected not to occur on the positive real axis of the  $E$  plane, at least when the basis set is sufficiently large. This characteristic of the theory is very important and requires more detailed study.

In concluding this section, we emphasize that the property of Eq. (4.5) is very important not only because it assures variational stability, but moreover because it guarantees the uniqueness of the associated amplitude or the  $K$  matrix.

## V. CONCLUDING REMARKS

We have proposed a variational principle which can be applied to electronically inelastic scattering of electrons by arbitrary molecules which usually have long-range dipole potentials. The theory also includes polarization effects in a straightforward way. Since our formalism is defined on the total wave function, configuration interaction techniques can be used naturally. All the configurations used here contain short-range functions (molecular orbitals

and/or additional Gaussian functions). Nonetheless this  $\tilde{C}$  functional is anticipated to give accurate scattering amplitudes. When a molecule does not have a long-range potential, as in homopolar diatomic molecules, the  $L^2$  version of the variational principle of Eq. (2.12) should work well.

In the accompanying paper we present the first results of the application of these multichannel formulations of electron-molecule collisions to the  $e$ -H<sub>2</sub> system. Several important aspects of the theory are illustrated in these applications. Applications of this formulation to other systems including N<sub>2</sub> and CH<sub>4</sub> are under way.

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#### APPENDIX

Here we prove the result

$$\mathcal{A}_{N+1}[1-(N+1)P]|\mathcal{A}_{N+1}\Phi_m\mu\rangle=0. \quad (\text{A1})$$

First we note

$$\mathcal{A}_{N+1}=\frac{1}{\sqrt{N+1}}\mathcal{A}_N+\tilde{R}, \quad (\text{A2})$$

where  $\tilde{R}$  includes all possible permutations which act on the  $(N+1)$ th coordinate. Then we have

$$\begin{aligned} P|\mathcal{A}_{N+1}\Phi_m\mu\rangle &= \sum_{n=1}^{N_0} |\Phi_n\rangle \langle \Phi_n | \mathcal{A}_N | \Phi_m \rangle \frac{1}{\sqrt{N+1}} |\mu\rangle \\ &= \frac{\sqrt{N!}}{\sqrt{N+1}} |\Phi_m\rangle |\mu\rangle, \end{aligned} \quad (\text{A3})$$

where the orthogonality of  $\mu$  to  $P$  is used. So,

$$\begin{aligned} \mathcal{A}_{N+1}|\mathcal{A}_{N+1}\Phi_m\mu\rangle - (N+1)\mathcal{A}_{N+1}P|\mathcal{A}_{N+1}\Phi_m\mu\rangle \\ = \left[ \sqrt{(N+1)!} - (N+1)\frac{\sqrt{N!}}{\sqrt{N+1}} \right] |\mathcal{A}_{N+1}\Phi_m\mu\rangle = 0, \end{aligned} \quad (\text{A4})$$

which completes the proof.

Now let us examine some consequences of this result. Let  $\chi$  be an arbitrary antisymmetrized function. We consider the following integral

$$I = \langle \chi | [\hat{H} - \frac{1}{2}(N+1)(P\hat{H} + \hat{H}P)] | \mathcal{A}_{N+1}\Phi_m\mu \rangle. \quad (\text{A5})$$

After a simple rearrangement of the equation, we see

$$\begin{aligned} I &= \langle \chi | \hat{H}[1-(N+1)P] | \mathcal{A}_{N+1}\Phi_m\mu \rangle \\ &\quad - \frac{1}{2}(N+1)\langle \chi | (VP - PV) | \mathcal{A}_{N+1}\Phi_m\mu \rangle. \end{aligned} \quad (\text{A6})$$

The first term on the rhs is zero because of (A4), leaving

$$I = -\frac{1}{2}(N+1)\langle \chi | (VP - PV) | \mathcal{A}_{N+1}\Phi_m\mu \rangle, \quad (\text{A7})$$

which proves Eq. (3.14). The proof of Eq. (3.15) is straightforward.

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<sup>1</sup>See, for example, *Electron-Molecule and Photon-Molecule Collisions*, edited by T. N. Rescigno, V. McKoy, and B. Schneider (Plenum, New York, 1979); N. F. Lane, *Rev. Mod. Phys.* **52**, 29 (1980); P. G. Burke, *Adv. At. Mol. Phys.* **15**, 471 (1979).

<sup>2</sup>L. A. Collins, W. D. Robb, and M. A. Morrison, *Phys. Rev. A* **21**, 488 (1980).

<sup>3</sup>R. R. Lucchese, D. K. Watson, and V. McKoy, *Phys. Rev. A* **22**, 421 (1980).

<sup>4</sup>B. I. Schneider and L. A. Collins, *Phys. Rev. A* **24**, 1264 (1981).

<sup>5</sup>T. N. Rescigno and A. E. Orel, *Phys. Rev. A* **24**, 1267 (1981).

<sup>6</sup>M.-T. Lee, K. Takatsuka, and V. McKoy, *J. Phys. B* **14**, 4115 (1981).

<sup>7</sup>B. I. Schneider, *Chem. Phys. Lett.* **51**, 578 (1977).

<sup>8</sup>A. Klonover and U. Kaldor, *J. Phys. B* **12**, L61 (1979).

<sup>9</sup>B. I. Schneider and L. A. Collins, *Phys. Rev. A* **27**, 2847 (1983).

<sup>10</sup>M. Berman, O. Walter, and L. S. Cederbaum, *Phys. Rev. Lett.* **50**, 1979 (1983).

<sup>11</sup>B. I. Schneider and L. A. Collins, *J. Phys. B* **14**, L101 (1981).

<sup>12</sup>R. R. Lucchese and V. McKoy, *Phys. Rev. A* **25**, 1963 (1982).

<sup>13</sup>L. A. Collins and B. I. Schneider, *Phys. Rev. A* **27**, 101 (1983).

<sup>14</sup>K. Takatsuka and V. McKoy, *Phys. Rev. A* **23**, 2352 (1981).

See also M. Kolsrud, *Phys. Rev.* **112**, 1436 (1958).

<sup>15</sup>See, for example, D. K. Watson, R. R. Lucchese, V. McKoy, and T. N. Rescigno, *Phys. Rev. A* **21**, 738 (1980), and references therein.

<sup>16</sup>V. B. Belyaev, E. Wrzcionko, and B. F. Irigoiziev, *Yad. Fiz.* **20**, 1267 (1974) [*Sov. J. Nucl. Phys.* **20**, 664 (1975)].

<sup>17</sup>R. R. Lucchese, G. Raseev, and V. McKoy, *Phys. Rev. A* **25**, 2572 (1982).

<sup>18</sup>R. R. Lucchese and V. McKoy, *Phys. Rev. A* **26**, 1406 (1982).

<sup>19</sup>K. Takatsuka and V. McKoy, *Phys. Rev. A* **24**, 2473 (1981).

<sup>20</sup>See, for example, H. Feshbach, *Ann. Phys.* **5**, 357 (1958); **19**, 287 (1962); **43**, 410 (1967).

<sup>21</sup>K. Takatsuka, R. R. Lucchese, and V. McKoy, *Phys. Rev. A* **24**, 1812 (1981).

<sup>22</sup>M.-T. Lee, R. R. Lucchese, K. Takatsuka, and V. McKoy (unpublished).

<sup>23</sup>D. K. Watson, T. N. Rescigno, and V. McKoy, *J. Phys. B* **14**, 1875 (1980).

<sup>24</sup>S. Geltman, *Topics in Atomic Collision Theory* (Academic, New York, 1969), p. 99.

<sup>25</sup>B. Friedman, *Principles and Techniques of Applied Mathematics* (Wiley, New York, 1960), p. 45.

<sup>26</sup>K. Takatsuka and V. McKoy, *Phys. Rev. A* **23**, 2359 (1981).

<sup>27</sup>K. R. Brownstein and W. A. McKinley, *Phys. Rev.* **170**, A1255 (1968).