

THE SCHWINGER AND RELATED VARIATIONAL PRINCIPLES
IN ELECTRON-MOLECULE COLLISION PROCESSES

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1. INTRODUCTION

In this contribution we want to discuss several features and applications of the Schwinger and related variational principles to the study of collisions of low energy electrons with molecules and molecular ions. The Schwinger variational principle has long been known to be a potentially useful formulation of the collision problem which has certain features that can be of considerable practical importance.⁽¹⁾ For example, the trial scattering wave function need not satisfy any specific asymptotic boundary conditions. This feature implies that the trial function could be expanded exclusively in terms of discrete basis functions, if such expansions were particularly advantageous. Another useful feature is that spurious singularities do not arise in this variational principle. On the other hand, the occurrence of matrix elements arising from VG_0V term in the variational functional has generally been regarded as a drawback to its applications to realistic systems.

Our main objective will be to outline the principle features of an iterative approach to the solution of the Lippmann-Schwinger integral equation for electron-molecule scattering which is based on the use of the Schwinger variational principle. This form of the theory is quite suitable for applications to electron-molecule collisions at the static-exchange level or for use with optical potentials. For the collisions of electrons with strong polar molecules we will discuss a new variational principle which is related to the Schwinger variational principle but is based on a slightly different form of the integral equation for the wave function. We will then discuss the results of some applications of these methods to a few systems which illustrate some important features. We will also present some results of applications of this method to molecular photoionization.

Finally, we will comment briefly on multichannel extensions of the Schwinger variational principle. We will then present some results of the applications of these extensions of the Schwinger variational principle to a simple and exactly soluble two-channel model problem. We will end our discussion by summarizing some recent developments in our multichannel formulation of these variational principles.

2. THEORY

In the fixed-nuclei approximation the Schrodinger equation for the scattered electron is of the form

$$\left(-\frac{1}{2}\nabla^2 + V(\mathbf{R}, \vec{r}) - \frac{1}{2}k^2\right)\Psi_{\vec{k}}^{(+)}(\mathbf{R}, \vec{r}) = 0. \quad (1)$$

The partial wave expansion of $\Psi_{\vec{k}}^{(+)}$ can be written as

$$\Psi_{\vec{k}}^{(+)} = \left(\frac{2}{\pi}\right)^{1/2} \sum_{\ell m} i^{\ell} \psi_{k\ell m}^{(+)}(\vec{r}) Y_{\ell m}^*(\hat{k}) \quad (2)$$

where $\psi_{k\ell m}^{(+)}$ satisfies the Lippmann-Schwinger equation

$$\psi_{k\ell m}^{(+)} = \phi_{k\ell m} + G_0 U \psi_{k\ell m} \quad (3)$$

with $U = 2V$. The Schwinger variational principle is applied directly to the $\psi_{k\ell m}$ of eqn.(3) to obtain

$$\tilde{T}_{\ell\ell'm} = \frac{\langle \phi_{k\ell m} | U | \tilde{\psi}_{k\ell'm}^{(+)} \rangle \langle \tilde{\psi}_{k\ell m}^{(-)} | U | \phi_{k\ell'm} \rangle}{\langle \tilde{\psi}_{k\ell m}^{(-)} | U - UG_0U | \tilde{\psi}_{k\ell'm}^{(+)} \rangle} \quad (4)$$

where we have assumed the molecule to be linear. In eqn. (3) $\phi_{k\ell m}$ is the regular free-particle solution. We now expand the trial function $\tilde{\psi}_{k\ell m}^{(\pm)}$ in a basis $\{\eta_{\pm}\}$ and insert this expansion into eqn(4). Variation of the coefficients of this expansion leads to

$$\begin{aligned} \tilde{T}_{\ell\ell'm} &= \sum_{i,j} \langle \phi_{k\ell m} | U | \eta_i \rangle [(D^{(+)})^{-1}]_{ij} \\ &\times \langle \eta_j | U | \phi_{k\ell'm} \rangle \end{aligned} \quad (5)$$

where

$$D_{ij}^{(+)} = \langle \eta_i | U - UG_0^{(+)} U | \eta_j \rangle \quad (6)$$

The initial step in our Schwinger variational procedure is to evaluate eqn.(5) with a set of discrete basis functions. (2) In applications one can actually vary the size and composition of such basis sets in calculations at one energy, select the optimum basis, and then use this basis set in calculations at several other energies. This procedure does not necessarily provide converged solutions. To improve the solutions and to obtain converged solutions, if required, we have developed an iterative procedure. This procedure begins by observing that the result of eqn.(5) is equivalent to using a separable potential of the form

$$U^{S_0} = \sum_{\alpha_i, \alpha_j} U | \alpha_i \rangle [U^{-1}]_{ij} \langle \alpha_j | U \quad (7)$$

in the Lippmann-Schwinger equation. The solutions for this potential, U^{S_0} , are

$$\psi_{k\ell m}^{S_0} = \phi_{k\ell m} + \sum_{i,j} G_0 U | \alpha_i \rangle [(D^{(+)})^{-1}]_{ij} \langle \alpha_j | U | \phi_{k\ell m} \rangle \quad (8)$$

The functions $\psi_{k\ell m}^{S_0}$ are obtained by solving a set of uncoupled equations for $\psi_{\ell\ell'm}$ where

$$\psi_{k\ell m}^{S_0} = \sum_{\ell'} \psi_{\ell\ell'm}^{S_0} Y_{\ell'm}(\hat{x}) \quad (9)$$

We next add these approximate continuum solutions

$\{\psi_{k\ell_1 m}^{S_0}, \psi_{k\ell_2 m}^{S_0}, \dots, \psi_{k\ell_p m}^{S_0}\}$ to the original set of functions in eqn(6) to obtain

$$T^{S_1} = \sum_{\chi_i, \chi_j} U | \chi_i \rangle [(D^{(+)})^{-1}]_{ij} \langle \chi_j | U \quad (10)$$

The solutions of eqn.(10) now yield a new set of solutions $\{\psi_{k\ell_1 m}^{S_1}, \psi_{k\ell_2 m}^{S_1}, \dots, \psi_{k\ell_p m}^{S_1}\}$. We augment this basis with the initial set of discrete basis functions and repeat the procedure. Simple criteria for the convergence of this procedure have been discussed.

We now want to discuss some aspects of a related variational principle which we have found to be useful in describing the collisions of electrons with strongly polar molecules. The Schwinger variational principle is based on the use of the integral equation for the total wave function which we now write as

$$\psi_i = S_i + G_0 V \psi_i \quad (11)$$

From eqn.(11) we readily obtain an integral equation for $C_i = \psi_i - S_i$ in the form

$$C_i = G_0 V S_i + G_0 V C_i \quad (12)$$

The variational functional associated with this equation is (3)

$$[X_{ij}] = \frac{\langle \tilde{C}_i | V G_0 V | S_j \rangle \langle S_i | V G_0 V | \tilde{C}_j \rangle}{\langle \tilde{C}_i | V - V G_0 V | \tilde{C}_j \rangle} \quad (13)$$

We shall refer to this functional as the \tilde{C} functional. This functional is stationary around the exact function C_i with a stationary value given by

$$X_{ij} = \sum_{\alpha, \beta} \langle S_i | V G_0 V | \alpha \rangle (D^{-1})_{\alpha\beta} \langle \beta | V G_0 V | S_j \rangle \quad (14)$$

with the matrix D defined as in eqn.(6). The K matrix is then given in terms of the first and second Born terms and X_{ij}

$$- \frac{1}{2} K_{ij} = \langle S_i | V | S_j \rangle + \langle S_i | V G_0 V | S_j \rangle + X_{ij} \quad (15)$$

This \tilde{C} functional has some interesting features. First, the computational effort required to evaluate eqn.(13) is essentially the same as that of the Schwinger principle in eqn.(5). The numerator of X_{ij} and the second Born term in eqn.(15) can be evaluated by the same procedure used for the $V G_0 V$ term in D_{ij} of eqn.(6) since these integrations are done numerically. Secondly, the free wave components S_i are completely factored out from the basis set used in $[X_{ij}]$ and included exactly in the first and second Born terms. Accordingly one can expect that the requirements of the basis functions will be simpler for the expansion of \tilde{C}_i than ψ_i . It can also be shown that the K matrix obtained from the \tilde{C} functional is one rank higher than the K matrix of

the Schwinger variational principle. Furthermore, the K matrix obtained from the \tilde{C} functional should be roughly comparable to the K matrix obtained after one iteration of the iterative Schwinger method. Finally an iterative method can also be developed based on the \tilde{C} functional.

3. SOME APPLICATIONS

The variational procedures based on the Schwinger and \tilde{C} functionals have been used to study the scattering of low-energy electrons by several molecular systems such as N_2 , $N_2^+(4)$, CO^+ , $CO_2^{(5)}$, $CO_2^+(6)$, $LiH^{(7)}$, and $C_2H_2^+$ at the static-exchange level. Here we will discuss the results of three applications of these procedures which we believe illustrate some important features.

Table 1 gives the K matrix for a Schwinger variational calculation starting from a one-term separable approximation to the static-exchange potential⁽²⁾. This potential is constructed using a single S Cartesian Gaussian of exponent 0.5 centered on the nuclei. This example illustrates that the iterative procedure converges quite rapidly starting from a very small basis. We have found this to be very characteristic for the scattering of electrons by non-polar systems.

Table 1

Convergence of the Schwinger variational K matrix starting from an expansion of one basis function for $e-H_2(^2\Sigma_g)$ at $k = 0.5$.

(ℓ, ℓ')	S_n $K_{\ell\ell'}$		
	$n=0$	1	2
(0,0)	-2.045	-1.552	-1.548
(0,2)	-0.276(-1) ^(a)	0.133(-1)	0.134(-1)
(2,2)	-0.372(-3)	0.163(-1)	0.163(-1)

^(a) Values in parentheses indicate powers of ten.

As a second example we compare some results for the scattering of electrons by LiH obtained from the Schwinger and \tilde{C} functionals.⁽³⁾ In these studies we used scattering basis sets of thirteen and seven Cartesian Gaussian functions for the $^2\Sigma$ and $^2\Pi$ symmetries, respectively. The basis set used in these

calculations was not optimized for the \tilde{C} functional method but was simply chosen to be the same as the basis used previously in the iterative Schwinger method⁽²⁾. We note that the uniterated results obtained with the \tilde{C} functional are considerably better than those of the Schwinger method. These initial basis sets were specifically chosen to be small and optimization of this basis or choosing a larger basis would give more accurate results at this level, i.e., $n = 0$. The results of the \tilde{C} functional are very encouraging and suggest that a larger basis set could give even more accurate results without the need for any iterations. This feature can be important in applications to polar polyatomic systems and multichannel extensions of this method. Finally we note the very different behavior of the K matrix elements and the eigenphase sums in successive steps of the iterative procedure.

Finally we present some results of the application of this procedure to the study of molecular photoionization⁽⁸⁾. Figure 1 shows the branching ratios for the production of $v' = 1$ and $v' = 0$ levels of the $X^2\Sigma_g^+$ state in the photoionization of N_2 . These significant non-Franck-Condon effects in the final vibrational state distributions are produced by a shape resonance in the $e-N_2^+$ system and have been studied previously^(9,10). In the Franck-Condon approximation this branching ratio would be independent of photon energy and in this case equal to 7.86%⁽⁸⁾. These results show that the electron-molecular ion scattering solutions at the static exchange level can provide accurate estimates of these effects. These applications can be extremely useful in view of the increasing number of such experimental studies which probe the dynamical aspects of molecular photoionization.

4. MULTICHANNEL APPLICATIONS

We have formulated a multichannel extension of the variational principles based on both the Schwinger and \tilde{C} functional. Before discussing some aspects of these multichannel extensions we will present some results of the application of the Schwinger principle to the two-channel model problem of Huck⁽¹¹⁾ so as to make some very preliminary assessment of the effectiveness of the method for multichannel cases⁽¹²⁾. This model problem is defined by the Hamiltonian $H = H_0 + V$ with

Table 2
K-matrix elements and eigenphase sums for e-LiH

Iteration	Schwinger method			\tilde{C} -functional	
	0	1	2	0	1
$k = 0.5(^2\Sigma)^a$					
K_{00}	0.268	0.916	0.921	0.904	0.922
K_{01}	-1.475	-0.304	-0.233	-0.346	-0.215
K_{12}	-1.185	-2.392	-2.614	-2.036	-2.526
K_{23}	-0.028	-0.177	-0.211	-0.094	-0.202
δ^b	2.558	2.698	2.751	2.733	2.769
SUM					
$k = 0.1(^2\Pi)^a$					
K_{11}	0.009	0.419	0.750	0.493	0.788
K_{12}	-0.001	-0.449	-0.544	-0.504	-0.500
K_{13}	$\sim 0.1 \times 10^{-4}$	0.012	0.071	0.017	0.030
δ	0.009	0.269	0.454	0.304	0.493
SUM					

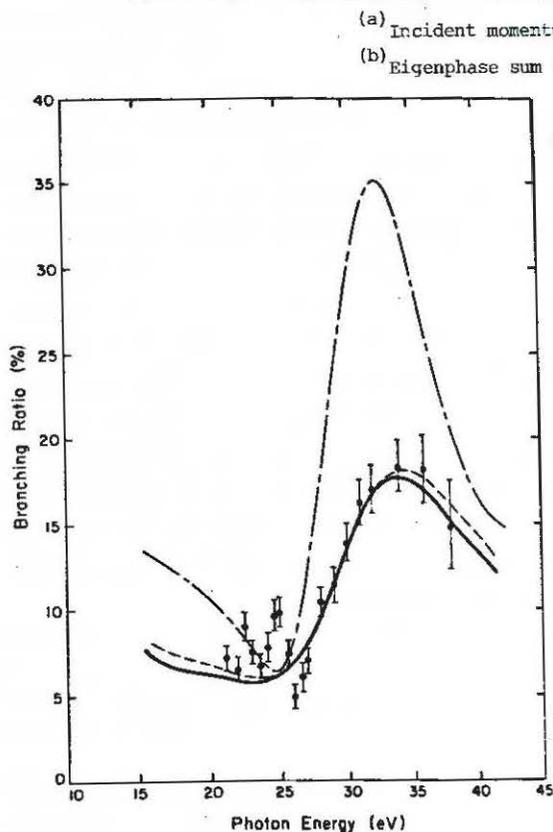


Fig. 1 Vibrational branching ratios for the $v' = 1$ and $v' = 0$ levels in the photoionization of N_2 to the $^2\Sigma^+$ state: — results using the static-exchange scattering wave functions and the dipole-length approximation; --- same but with dipole-velocity form; -·- CMSM results.

$$H_0 = \langle \chi_0 | \left(-\frac{1}{2} \frac{d^2}{dr^2} \right) | \chi_1 \rangle + | \chi_2 \rangle \left(-\frac{1}{2} \frac{d^2}{dr^2} + \Delta E \right) \times \langle \chi_2 | \quad (16)$$

and

$$V = \sum_{m \neq n} \chi_m \langle \chi_m | V | \chi_n \rangle \quad (17)$$

where

$$V_{12} = V_{21} = \begin{cases} \frac{1}{2} C & (r < a) \\ 0 & (r > a) \end{cases}$$

we choose $a = 1.0$, $C^2 = 10$, $E = 0.5$, and $\Delta E = 0.375$ and the trial function is expanded in the discrete basis

$$\eta_i^m = | \chi_{im} \rangle = r^i e^{-\alpha r} \quad (i = 1, 2, \dots, N) \quad (18)$$

with $\alpha = 0.9$.

Table 3 compares the results obtained from the Schwinger variational principle with the exact values⁽¹³⁾, with those of the RIAF variant of the Kohn method⁽¹⁴⁾, and with the more recent results of a variational K-matrix method⁽¹⁵⁾. Our results for this model problem are very encouraging. The rate of convergence of the method with respect to the number of basis functions is rapid. For example, all

Table 3
Results for a model two-channel problem

Deviation of K-matrices from the exact values ^(b)			
	Schwinger ^(c)	RIAF ^(d)	RMAT(w ₀ , w ₁) ^(d)
ΔK ₁₁ N = 2	2	-1.53971	0.73103
	4	-0.00004	0.03725
	6	0.0	-3.00448
ΔK ₁₂ N = 2	2	0.96567	0.49875
	4	0.00002	0.02561
	6	0.0	1.91839
ΔK ₂₂ N = 2	2	-0.60478	0.34029
	4	-0.00002	0.01762
	6	0.0	-1.22670

(a) See reference 11.

(b) The exact values are K₁₁ = 21.76525, K₁₂ = -14.12742, and K₂₂ = 8.73385.

(c) Discrete basis functions only.

(d) Reference 15.

results are fully converged with six basis functions. No continuum trial functions are included in our basis.

We have formulated multichannel extensions of the Schwinger and \tilde{C} functionals in forms suitable for describing the collisions of low-energy electrons with both linear and nonlinear molecules^(16,17). We will discuss some features of this extension for the Schwinger principle since we have already obtained some results for e-H collisions below the inelastic threshold with this method.⁽¹⁶⁾ Computer codes for application of the \tilde{C} functional have been developed.

The essential features of this formulation can be readily seen as follows. The Schrodinger equation for the (N+1) particle system is

$$(E-H) \psi_m^{(+)} = 0 \quad (19)$$

The total Hamiltonian H is given by

$$H = H_N + T_{N+1} + \sum_{i=1}^N \frac{1}{r_{i,N+1}} - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha,N+1}} \quad (20)$$

where H_N is the total Hamiltonian of the target, T_{N+1} is the kinetic energy operator of the (N+1)th particle, and the third and fourth terms the electron-electron and electron-nucleus interactions respectively. Identifying H_N + T_{N+1} as the zeroth-

order Hamiltonian we can write

$$\psi_m^{(+)} = S_m + G_0^{(+)} V \psi_m^{(+)} \quad (21)$$

where G₀ is the Green's function associated with E-H₀ and S_m the regular solution of E-H₀.

Next we define the projection operator which projects onto the space of open channels, i.e.,

$$P = \sum_m |\phi_m\rangle \langle \phi_m| \quad (22)$$

where

$$H_N \phi_m = E_m \phi_m, \quad E - E_m > 0 \quad (23)$$

We apply P to eqn. (21) to obtain the projected equation

$$P \psi_m^{(+)} = S_m + G_P^{(+)} V \psi_m^{(+)} \quad (24)$$

and G_P⁽⁺⁾ is the projected Green's function

$$G_P^{(+)} = \sum_m |\phi_m\rangle \langle \phi_m| g_m^{(+)}(\vec{r}_{N+1}, \vec{r}_{N+1}') \langle \phi_m| \quad (25)$$

where g_m⁽⁺⁾($\vec{r}_{N+1}, \vec{r}_{N+1}'$) is the Green's function associated with the operator E-E_m-T_{N+1}. From eqn. (24) we obtain

$$(V P - V G_P^{(+)} V) \psi_m^{(+)} = V S_m \quad (26)$$

To recover the unprojected component of G_P⁽⁺⁾, i.e., G₀⁽⁺⁾ - G_P⁽⁺⁾ we can derive⁽¹⁶⁾ the additional equation

$$[\hat{H} - a(P \hat{H} + \hat{H} P)] \psi_m^{(+)} = a(V P - P V) \psi_m^{(+)} \quad (27)$$

where $\hat{H} = E-H$ and a is equal to (N+1)/2. From eqns. (24) and (27) we finally obtain the equation

$$\left[\frac{1}{2} (P V + V P) - V G_P^{(+)} V \right] \psi_m^{(+)} = \frac{1}{2a} [H - a(P H + H P)] \psi_m^{(+)} = V S_m \quad (28)$$

Based on this inhomogeneous equation we can construct a variational functional of the form

$$= \frac{1}{2} K_{mn} = \frac{\langle \psi_m | V | S_n \rangle \langle S_m | V | \psi_n \rangle}{\langle \psi_m | A | \psi_n \rangle} \quad (29)$$

where

$$A = \frac{1}{2} (P V + V P) - V G_P^{(+)} V + \frac{1}{(N+1)} \left\{ H - \frac{(N+1)}{2} (P \hat{H} + \hat{H} P) \right\} \quad (29a)$$

Table 4
Phase shifts for a $1s-2s-\overline{2p}_{DK}$ calculation for the e-H system.

(a) Singlet phase shifts by various methods						
Method	$k^2 =$	0.01	0.09	0.25	0.49	0.64
Static-exchange, CC ^(a, b)		2.396	1.508	1.031	0.744	0.651
$12-2s-\overline{2p}$, CC		2.529	1.657	1.155	0.875	0.823
$1s-2s-2p-\overline{2p}$, CC		2.532	1.663	1.162	0.881	0.832
$1s-2s-\overline{2p}$ (this work)		2.550	1.684	1.179	0.895	0.818
$12-2s-2p-\overline{3s-3p-3d}$ ^(c)		2.545	1.683	1.187	0.917	0.873
$1s-\overline{2s-2p}$ (this work)		2.565	1.715	1.217	0.945	0.878
exact ^(d)		2.556	1.696	1.201	0.930	0.887

(b) Triplet phase shifts						
Static-exchange, CC		2.908	2.461	2.070	1.749	1.614
$1s-2s-\overline{2p}$, CC		2.937	2.498	2.102	1.777	1.641
$1s-2s-2p-\overline{2p}$, CC		2.937	2.498	2.102	1.777	1.642
$1s-2s-\overline{2p}$ (this work)		2.930	2.496	2.111	1.783	1.644
$1s-2s-2p-\overline{3s-3p-3d}$		2.937	2.498	2.102	1.777	1.641
$1s-\overline{2s-2p}$ (this work)		2.926	2.503	2.113	1.777	1.648
exact ^(d)		2.939	2.500	2.105	1.780	1.644

(a) CC denotes close coupling.

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for the K matrix. The trial functions Ψ_m and Ψ_n are expanded in basis functions and eqn. (29) varied to obtain the stationary expansion. A \tilde{C} functional of similar form can also be derived. ⁽¹⁷⁾ Computer codes for the application of these functionals to a range of problems in electron-molecule collisions are being developed.

We now compare the results of application of this Schwinger formulation with those of the close-coupling approach for the e-H system below the inelastic threshold. For convenience we choose our trial functions to be of the same form as in the close coupling approach, although this is not necessarily required. Table 4 shows the results of these studies. The notation is obvious. The $2p$ pseudostate, which is denoted as $2p_{DK}$, has a radial part of $r^2(1 + \frac{r}{2})e^{-r}$. Further details are given in ref. 16. In these calculations three basis functions were used in the expansion of the open and closed s channels and four for the closed p channel.

These basis functions were Slater functions. The results are encouraging and show that the convergence of the formulation is good with respect to the size of the basis for both open- and closed-channel orbitals.

5. CONCLUSIONS

We have discussed several features of the Schwinger and related variational methods. The results of the application of these methods to several problems in electron-molecule collisions are encouraging and show that these methods provide viable and effective approaches to such collision problems. Applications of the multichannel extensions of the methods are underway.

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