

LETTER TO THE EDITOR

## Application of the Schwinger variational principle to electron scattering

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**Abstract.** We present the results of the first rigorous application of the Schwinger variational principle to electron scattering with the inclusion of exchange. The results of this application to e-He scattering in the static-exchange approximation show that the Schwinger method provides accurate solutions of the scattering problem with small basis set expansions.

The Schwinger variational principle is clearly a powerful formulation of the scattering problem and has several distinct advantages over other variational methods (Taylor 1972). For example, in the Schwinger method the trial scattering wavefunction need not satisfy any specific asymptotic boundary conditions. This feature makes the method particularly attractive for molecular applications since discrete basis functions, which do not satisfy the scattering boundary conditions, can be used in the solution of molecular collision problems. The Schwinger method is also not troubled by the spurious singularities that can arise in the Kohn variational method.

The main drawback to the application of the Schwinger variational principle is the occurrence of the term  $\langle \Psi_k^{(-)} | V G_0 V | \Psi_k^{(+)} \rangle$  in the expression. Recently Watson and McKoy (1979) proposed an approximate, but analytical, procedure for applying the Schwinger principle to electron-molecule collisions. This scheme depends on the use of Cartesian Gaussian basis functions in both the expansion of the scattering function and the insertion of a completeness relationship in the evaluation of the matrix elements of  $V G_0 V$ . We have now developed an efficient numerical procedure for the correct evaluation of the Schwinger variational expression (Lucchese and McKoy 1979).

In this letter we present static-exchange  $K$  matrices for e-He scattering, obtained from the Schwinger variational expression. To our knowledge, these results represent the first exact use of the Schwinger variational principle in electron scattering with inclusion of the exchange potential. For the expansion functions we choose Cartesian Gaussian functions. The results are very encouraging and indicate that the Schwinger variational method provides accurate solutions of the scattering problem and does not require expansions in large basis sets.

The Schwinger variational principle for the  $K$  matrix can be written as

$$\langle \mathbf{k} | K | \mathbf{k}' \rangle = -\frac{1}{2}\pi \frac{\langle \mathbf{k} | U | \Psi_{\mathbf{k}}^{(P)} \rangle \langle \Psi_{\mathbf{k}}^{(P)} | U | \mathbf{k}' \rangle}{\langle \Psi_{\mathbf{k}}^{(P)} | U - U G_0^{(P)} U | \Psi_{\mathbf{k}}^{(P)} \rangle} \quad (1)$$

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where  $\Psi_{\mathbf{k}}^{(P)}$  is the scattering wavefunction with the standing-wave boundary condition,  $G_0^{(P)}$  the corresponding free-particle Green's function, and  $U = 2V$  where  $V$  is the scattering potential. This expression for the  $K$  matrix is stationary with respect to small variations of the exact state vector  $\Psi_{\mathbf{k}}^{(P)}$  about its correct value. Expanding  $\Psi_{\mathbf{k}}^{(P)}$  in the set of basis functions  $|\alpha\rangle$

$$|\Psi_{\mathbf{k}}^{(P)}\rangle = \sum_{\alpha} a_{\alpha}(\mathbf{k}) |\alpha\rangle \quad (2)$$

and requiring that equation (1) be stationary with respect to variation of the coefficients,  $a_{\alpha}(\mathbf{k})$ , leads to the Schwinger variational expression for the  $K$  matrix

$$\tilde{K} = -\frac{1}{2}\pi \sum_{\alpha, \beta} U |\alpha\rangle [D^{-1}]_{\alpha\beta} \langle \beta | U \quad (3)$$

with

$$D_{\alpha\beta} = \langle \alpha | U - U G_0^{(P)} U | \beta \rangle. \quad (4)$$

This expression can also be obtained by assuming a separable expansion of the potential of the form

$$\tilde{U}(\mathbf{r}, \mathbf{r}') = \sum_{\alpha, \beta} \langle \mathbf{r} | U | \alpha \rangle [d^{-1}]_{\alpha\beta} \langle \beta | U | \mathbf{r}' \rangle \quad (5)$$

where

$$d_{\alpha\beta} = \langle \alpha | U | \beta \rangle. \quad (6)$$

Inserting this separable approximation to  $U$  into the Lippmann–Schwinger equation for  $K$

$$K = -\frac{1}{2}\pi U + U G_0^{(P)} K \quad (7)$$

yields equation (3) for  $\tilde{K}$ .

For the expansion functions we choose Cartesian Gaussian functions of the form

$$\langle \mathbf{r} | \alpha \rangle = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha |\mathbf{r} - \mathbf{A}|^2} \quad (8)$$

where  $N_{lmn}$  is a normalisation constant. Also, in actual calculations we use the partial-wave  $K$  matrix elements which are given by

$$\tilde{K}_{ll'm} = -k \sum_{\alpha, \beta} \langle j_l(kr) Y_{lm}(\hat{\mathbf{r}}) | U | \alpha \rangle [D^{-1}]_{\alpha\beta} \langle \beta | U | j_{l'}(kr) Y_{l'm}(\hat{\mathbf{r}}) \rangle \quad (9)$$

for linear molecules. For electron–molecule scattering, the matrix elements  $\langle j_l(kr) Y_{lm}(\hat{\mathbf{r}}) | U | \alpha \rangle$  and  $\langle \alpha | U G_0^{(P)} U | \beta \rangle$  are evaluated numerically. These numerical integration schemes are efficient and rapid. A more detailed explanation of these procedures is given elsewhere (Lucchese and McKoy 1979, Fliflet and McKoy 1978).

We have thus used the Schwinger variational principle to obtain s- and p-wave  $K$  matrices for e–He scattering in the static-exchange approximation. The SCF wavefunction was obtained with Huzinaga's 10s basis set for helium (Huzinaga 1965). With this basis the SCF energy is  $-2.8617$  au. In table 1 we list the exponents of the Cartesian Gaussian functions in which the scattering function is expanded. The same sets of exponents are used in both the s- and p-wave calculations.

**Table 1.** Exponents of the Cartesian Gaussian functions used in the Schwinger variational calculations.

3s and 3p set	5s and 5p set
20.0	20.0
1.41	4.47
0.1	1.0
	0.224
	0.05

The s- and p-wave  $K$  matrices of this Schwinger variational calculation are shown in tables 2 and 3 respectively. The  $K$  matrix elements agree very well with those of the Kohn variational calculations of Sinfailam and Nesbet (1972). Even the results with the 3s scattering basis are close to those of Sinfailam and Nesbet (1972), indicating that the Schwinger variational principle can provide accurate results with small discrete basis sets.

**Table 2.** The s-wave  $K$  matrix elements for e-He scattering.

Momentum $k$	$\hat{K}(3s)$	$\hat{K}(5s)$	$K(SN)^a$
0.01	-0.0151	-0.0148	—
0.1	-0.152	-0.149	-0.149
0.2	-0.309	-0.303	-0.303
0.3	-0.476	-0.467	-0.468
0.4	-0.660	-0.647	-0.647
0.5	-0.870	-0.853	-0.858
1.0	-3.081	-3.031	-3.026
2.0	3.103	3.321	—

<sup>a</sup> Sinfailam and Nesbet (1972).

**Table 3.** The p-wave  $K$  matrix elements for e-He scattering.

Momentum $k$	$\hat{K}(3p)$	$\hat{K}(5p)$	$K(SN)^a$
0.01	0.407(-6) <sup>b</sup>	0.422(-6)	—
0.1	0.404(-3)	0.419(-3)	0.6(-3) <sup>c</sup>
0.2	0.316(-2)	0.326(-2)	0.35(-2)
0.3	0.0103	0.0106	0.0108
0.4	0.0231	0.0236	0.0239
0.5	0.0420	0.0425	0.0426
1.0	0.184	0.185	0.187
2.0	0.320	0.337	—

<sup>a</sup> Sinfailam and Nesbet (1972).

<sup>b</sup>  $0.407(-6) = 0.407 \times 10^{-6}$ .

<sup>c</sup> Private communication, R K Nesbet.

We have presented the results of the first rigorous application of the Schwinger variational principle to electron scattering with the inclusion of exchange (Altshuler 1953—these results are with the static potential of the H atom). These results of this application to e-He scattering show that the Schwinger variational principle is a powerful method for the accurate solution of the scattering problem with small discrete basis sets. This feature makes the Schwinger method particularly attractive for applications to electron-molecule collisions. Applications of the Schwinger method to electron-molecule scattering, including its multichannel extensions, are under way.

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