

## Schwinger variational principle for electron-molecule scattering: Application to electron-hydrogen scattering

D. K. Watson, R. R. Lucchese, and V. McKoy

*A. A. Noyes Laboratory of Chemical Physics, \* California Institute of Technology, Pasadena, California 91125*

T. N. Rescigno

*Theoretical Atomic and Molecular Physics Group, Lawrence Livermore Laboratory, University of California, Livermore, California 94550*

(Received 10 August 1979)

The authors report the first application of the Schwinger variational principle to electron-molecule scattering. Results for electron-H<sub>2</sub> scattering in the static-exchange approximation show that the Schwinger method can provide accurate solutions of the scattering problem with small discrete basis sets. The Schwinger variational expression is found to converge far more quickly with respect to the size of the basis than any other algebraic expansion technique considered to date. Results are also presented for hybrid trial scattering wave functions containing both continuum and discrete basis functions.

### I. INTRODUCTION

Of the various formulations of the scattering problem, the Schwinger variational principle offers a number of distinct advantages over other stationary expressions.<sup>1</sup> Most notably, the Schwinger expression for the scattering amplitude is independent of the normalization employed in the trial wave function.<sup>2</sup> This feature is particularly attractive for applications to electron-molecule scattering where discrete basis functions can be used to advantage in the solution of the collision problem. Several  $L^2$  techniques have been introduced, but they all seem to require large numbers of basis functions to achieve adequately converged results.<sup>3,4</sup> Recently we discussed two new techniques which are applicable to atomic and molecular scattering problems.<sup>5</sup> One of these is an analytical approximation to the Schwinger variational principle; the results of its application to  $e$ -He scattering strongly indicate that accurate results can be obtained with limited-basis-set expansions. In a later study we developed numerical integration techniques for the exact evaluation of the Schwinger principle and these results confirmed the original observations.<sup>6</sup>

The Schwinger principle does not suffer from the spurious singularities which arise in algebraic variational methods of the Kohn type.<sup>7</sup> The latter are generally based on finding an approximate solution of the Schrödinger equation with a trial wave function that has the correct asymptotic behavior. For the case of simple potential scattering, this trial function has the form

$$\psi^t(r) = \sum_{i=1}^N c_i \phi_i(r) + S(r) + tC(r). \quad (1)$$

The  $N+1$  unknowns in this trial function—the li-

near coefficients  $c_i$  and the tangent  $t$  of the phase shift—are determined by requiring

$$\langle \phi_i | H - E | \psi^t \rangle = 0, \quad i = 1, \dots, N, \quad (2)$$

along with one other constraint. The fact that the algebraic problem is overdetermined—there are  $N+2$  terms in the trial function but only  $N+1$  unknowns—leads to an arbitrariness in choosing the final algebraic condition. The singularities that arise in variational procedures of this type are symptomatic of this arbitrariness.<sup>8</sup>

In contrast, the Schwinger variational method depends on the fact that the exact wave function satisfies the Lippmann-Schwinger integral equation. Indeed, it can be shown that when a trial function with only linear parameters in the Schwinger variational principle is used,

$$\psi^s(r) = \sum_{i=1}^N c_i \phi_i(r) \quad (3)$$

is equivalent to solving the Lippmann-Schwinger equation for the scattering amplitude exactly for the separable potential of the form<sup>9</sup>

$$V^s(r, r') = \sum_{i,j=1}^N \langle r | V | \phi_i \rangle \langle \phi_j | V | r' \rangle. \quad (4)$$

In Eq. (4)  $V$  is the  $N \times N$  matrix representation of the potential in the basis  $\{\phi_i\}$ . The Schwinger principle thus gives a stationary expression for the scattering amplitude which is the exact solution for a potential of finite rank and hence does not show any singularities at physical energies.

In spite of its attractive features, there have been few applications of the Schwinger variational method to problems in atomic and molecular physics. The principal drawback to its application has been the evaluation of the term of the second-Born type, i.e.,  $\langle \psi^{(-)} | VG_0^{(+)} V | \psi^{(+)} \rangle$ . We have de-

veloped an efficient numerical procedure for evaluating such matrix elements.<sup>10</sup> We will also discuss an analytical technique for approximating these matrix elements. This procedure is efficient and particularly useful in applications to larger molecular systems in which Cartesian Gaussian functions will be used in the expansion of the trial scattering function.

In this paper we present the results of the first application of the Schwinger variational principle to electron-molecule scattering. The results are for  $e$ -H<sub>2</sub> scattering in the static-exchange approximation. The method is found to be quite economical and capable of yielding accurate results with very few basis functions.

In Sec. II we discuss the Schwinger principle, and present the results of the applications to H<sub>2</sub> in Sec. III. In the Appendix we present results using combinations of discrete basis functions and continuum functions as trial functions in the Schwinger principle.

## II. THEORY

The Schwinger variational expression for the  $T$  matrix can be written (atomic units throughout)

$$\langle \vec{k}' | T^s | \vec{k} \rangle = \frac{\langle \vec{k}' | U | \tilde{\psi}_{\vec{k}}^{(+)} \rangle \langle \tilde{\psi}_{\vec{k}}^{(+)} | U | \vec{k} \rangle}{\langle \tilde{\psi}_{\vec{k}}^{(+)} | U - UG_0^{(+)}U | \tilde{\psi}_{\vec{k}}^{(+)} \rangle}, \quad (5)$$

where  $G_0^{(\pm)}$  is the free-particle Green's function for the outgoing (incoming) wave boundary condition,  $\tilde{\psi}_{\vec{k}}^{(\pm)}$  is a corresponding trial scattering wave function, and  $U=2V$ , with  $V$  the effective interaction between the target and the incident electron. If  $\tilde{\psi}_{\vec{k}}^{(\pm)}$  is expanded in an arbitrary set of basis functions as

$$|\tilde{\psi}_{\vec{k}}^{(\pm)}\rangle = \sum_{\alpha} a_{\alpha}(\vec{k}) |\alpha\rangle \quad (6)$$

and Eq. (5) is varied with respect to the coefficients  $a_{\alpha}(\vec{k})$  one obtains the following expression for the  $T$  matrix<sup>9</sup>:

$$\langle \vec{k}' | T^s | \vec{k} \rangle = \sum_{\alpha, \beta} \langle \vec{k}' | U | \alpha \rangle (D^{(+)-1})_{\alpha\beta} \langle \beta | U | \vec{k} \rangle, \quad (7)$$

where

$$D_{\alpha\beta}^{(+)} = \langle \alpha | U - UG_0^{(+)}U | \beta \rangle. \quad (8)$$

This expression is equivalent to using a separable expansion of the form of Eq. (4) in the Lippmann-Schwinger equation for  $T$

$$T = U + UG_0^{(+)}T. \quad (9)$$

The  $T$  matrix of Eq. (7) is the exact solution of the Lippmann-Schwinger equation with the potential of Eq. (4) and is thus unitary.

We expand the trial scattering wave function in a

set of Cartesian Gaussian functions of the form

$$\phi_{\alpha}(\mathbf{r}) = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha(\vec{r} - \vec{A})^2}, \quad (10)$$

where  $\vec{A}$  locates the origin of the basis function and  $N_{lmn}$  is a normalization factor. With such a basis one can evaluate the bound-free integrals  $\langle \vec{k} | U | \alpha \rangle$  in the numerator of Schwinger expression exactly.<sup>5,11</sup> These integrals contain three Gaussian functions and a plane wave. It is the term  $UG_0^{(+)}U$  in the denominator, however, which has always been viewed as extremely difficult to evaluate. One way around this problem is to insert the approximate completeness relation

$$I \cong \sum_{i=1}^N |\alpha\rangle \langle \alpha| \quad (11)$$

between  $G_0^{(\pm)}$  and  $U$  and approximate the matrix element of  $UG_0^{(\pm)}U$  by

$$\langle \alpha | UG_0^{(+)}U | \beta \rangle \cong \sum_{\gamma, \delta} \langle \alpha | U | \gamma \rangle \langle \gamma | G_0^{(+)} | \delta \rangle \langle \delta | U | \beta \rangle. \quad (12)$$

Since matrix elements of  $G_0^{(\pm)}$  in a Cartesian Gaussian basis can be obtained analytically in terms of complex error functions,<sup>11,12</sup> this insertion technique gives a completely analytic approximation to the second-Born-like terms that are required. The set of functions used in this insertion need not be the same as the basis set in which the scattering wave function is expanded and may in general be larger without any significant increase in computational effort. In a recent application of this technique to electron-helium scattering insertion of a small scattering basis set gave accurate results.<sup>5</sup> By observing how the results approach unitarity one can determine when the inserted set is "complete."

To obtain the physical differential cross section by means of the fixed-nuclei amplitude of Eq. (5) requires averaging over all orientations of the molecule with respect to the incident electron beam. This averaging must be carried out numerically and can add considerably to the computational effort. For this reason it is convenient to obtain the partial-wave components of the scattering amplitude directly. We have thus developed efficient numerical schemes for the evaluation of all the matrix elements required in the Schwinger variational expression<sup>10</sup> for the partial-wave components of the  $T$  matrix. In the partial-wave representation we choose to work with the  $K$  matrix, for which the Schwinger expression is (for linear molecules)

$$K_{l_1 l_2 m}^s = -k \sum_{\alpha\beta} \langle j_1(kr) Y_{l_1 m}(\hat{r}) | U | \alpha \rangle (D^{(P)-1})_{\alpha\beta} \times \langle \beta | U | j_2(kr) Y_{l_2 m}(\hat{r}) \rangle, \quad (13)$$

TABLE I. Basis sets for the SCF calculation and for the  ${}^2\Sigma^+$   $K$  matrix in  $H_2$ .

SCF basis <sup>a</sup>	${}^2\Sigma_g^+$ (5 functions)	${}^2\Sigma_g^+$ (12 functions)	${}^2\Sigma_u^+$ (8 functions)
$A = (0, 0, \pm 0.7003)$			
0 0 0	48.447 9	0 0 0 1.918 77	0 0 0 1.018 77
0 0 0	7.283 46	0 0 0 0.290 199	0 0 0 0.290 199
0 0 0	1.651 39	0 0 1 1.0	0 0 1 0.2
0 0 0	0.462 447	0 0 1 0.5	0 0 1 0.1
0 0 0	0.145 885	0 0 1 0.2	0 0 1 0.05
0 0 1	1.5		
0 0 1	0.5		
$A = (0, 0, 0)$			
	0 0 0 0.4	0 0 0 0.8	0 0 1 0.025
	0 0 2 0.1	0 0 0 0.4	0 0 1 0.01
		0 0 0 0.1	0 0 1 0.005
		0 0 2 0.2	
		0 0 2 0.1	
		0 0 2 0.05	
		0 0 2 0.025	

<sup>a</sup>Basis-set-parameter specifications follow the notation of Eq. (10).

where  $D^{(P)}$  is given by Eq. (8) but with the principal-value Green's function. Working with the real  $K$  matrix always yields a unitary result even when the denominator  $D^{(P)-1}$  of Eq. (13) is evaluated approximately through Eqs. (11) and (12)

### III. RESULTS

#### A. Exact evaluation of Schwinger variational expression

In this section, we present the results of a calculation in which we have numerically evaluated the second-Born-like matrix elements in the denominator of the Schwinger variational expression (Eq. 13) as well as the partial-wave bound-free matrix elements in the numerator. This procedure allows us to assess the rate of convergence of the Schwinger expression and provides the partial-wave  $K$ -matrix elements in terms of which all physical cross sections can be expression analytically. In addition, it will provide us with a measure of the utility of the approximate scheme to be presented in Sec. III B.

We have used the Schwinger principle to study electron- $H_2$  scattering in the static-exchange approximation. For the self-consistent-field (SCF) target wave function we used the (5s2z) Gaussian basis shown in Table I. The SCF energy in this basis is  $-1.1330$  a.u., and the quadrupole moment is  $0.452$  a.u. The scattering basis sets for the  ${}^2\Sigma_g^+$  and  ${}^2\Sigma_u^+$  symmetries are given in Table I and those for the  ${}^2\Pi_g$  and  ${}^2\Pi_u$  symmetries are shown in Table II. These basis sets contain Cartesian Gaussian functions centered both on the nuclei and at the center of the molecule. In Tables I and II

we list the basis sets used in the SCF calculation and in the expansion of the scattering wave function. For the  ${}^2\Sigma_g^+$  symmetry we used one basis set with five functions and another with twelve functions. The basis sets contain eight functions for the  ${}^2\Sigma_u^+$  calculations and six functions each for the  ${}^2\Pi_g$  and  ${}^2\Pi_u$  symmetries.

The resulting  $K$ -matrix elements are given in Tables III and IV. We compare the results with those of Robb, Collins, and Morrison,<sup>13</sup> which were obtained by numerical integration of the integro-differential equations obtained by expansion about a single center. The calculations using twelve basis function give  $\Sigma_g^+$   $K$  matrices, i.e.,  $K_{000}$ ,  $K_{020}$ , and  $K_{220}$  of Table III, which agree well with those of Robb *et al.*<sup>13</sup> These results indicate that the Schwinger principle can provide accurate results with relatively small basis sets. Some

TABLE II. Basis sets for the  ${}^2\Pi$   $K$  matrix in  $H_2$ .

${}^2\Pi_u$ (6 functions) <sup>a</sup>	${}^2\Pi_g$ (6 functions)
$A = (0, 0, 0 \pm 0.7003)$	
1 0 0 0.2	1 0 0 0.2
1 0 0 0.1	1 0 0 0.1
1 0 0 0.05	1 0 0 0.05
$A = (0, 0, 0)$	
1 0 0 0.025	1 0 1 0.025
1 0 0 0.1	1 0 1 0.01
1 0 0 0.005	1 0 1 0.005

<sup>a</sup>Basis-set-parameter specifications follow the notation of Eq. (10).

TABLE III.  $K$ -matrix elements for  ${}^2\Sigma^+$  symmetry in  $H_2$ .

$k$	$K_{000}^S$ (5 functions)	$K_{000}^S$ ( ${}^2\Sigma_g^+$ 12 functions)	$K_{000}^R$	$K_{110}^S$ (8 functions)	$K_{110}^R$ ( ${}^2\Sigma_u^+$ )
0.1	-0.220	-0.211	-0.217 <sup>a</sup>	0.108(-1) <sup>b</sup>	0.127(-1) <sup>a</sup>
0.2	-0.457	-0.444	-0.451	0.428(-1)	0.463(-1)
0.3	-0.734	-0.718	-0.722	0.112	0.119
0.4	-1.09	-1.06	-1.07	0.233	0.243
0.5	-1.59	-1.55	-1.55	0.409	0.421
0.6	-2.41	-2.32	-2.32	0.627	0.638
0.7	-4.09	-3.85	-3.88	0.854	0.863
1.0	7.31	8.07	8.05	1.332	1.34
	$K_{020}^S$	$K_{020}^S$	$K_{020}^R$	$K_{130}^S$	$K_{130}^R$
0.1	0.76(-4)	0.88(-3)	0.39(-2)	0.75(-3)	0.15(-2)
0.2	0.61(-3)	0.46(-2)	0.73(-2)	0.27(-2)	0.23(-2)
0.3	0.21(-2)	0.81(-2)	0.11(-1)	0.39(-2)	0.34(-2)
0.4	0.48(-2)	0.10(-1)	0.13(-1)	0.53(-2)	0.49(-2)
0.5	0.94(-2)	0.14(-1)	0.15(-1)	0.79(-2)	0.71(-2)
0.6	0.16(-1)	0.15(-1)	0.15(-1)	0.11(-1)	0.10(-1)
0.7	0.25(-1)	0.75(-2)	0.93(-2)	0.16(-1)	0.14(-1)
1.0	0.39(-1)	0.13	0.11	0.33(-1)	0.29(-1)
	$K_{220}^S$	$K_{220}^S$	$K_{220}^R$	$K_{330}^S$	$K_{330}^R$
0.1	0.68(-5)	0.13(-3)	0.21(-2)	0.11(-3)	0.73(-3)
0.2	0.20(-3)	0.25(-2)	0.45(-2)	0.22(-2)	0.20(-2)
0.3	0.13(-2)	0.86(-2)	0.74(-2)	0.36(-2)	0.31(-2)
0.4	0.46(-2)	0.14(-1)	0.11(-1)	0.53(-2)	0.43(-2)
0.5	0.11(-1)	0.17(-1)	0.18(-1)	0.64(-2)	0.56(-2)
0.6	0.21(-1)	0.25(-1)	0.27(-1)	0.80(-2)	0.72(-2)
0.7	0.33(-1)	0.36(-1)	0.39(-1)	0.95(-2)	0.93(-2)
1.0	0.69(-1)	0.92(-1)	0.93(-1)	0.15(-1)	0.20(-1)

<sup>a</sup>All numbers in this column are from Ref. 13.<sup>b</sup>0.108(-1) = 0.108 × 10<sup>-1</sup>.TABLE IV.  $K$ -matrix elements for  ${}^2\Pi$  symmetry in  $H_2$ .

$k$	$K_{111}^S$	$K_{111}^R$ ( ${}^2\Pi_u$ )	$K_{221}^S$	$K_{221}^R$ ( ${}^2\Pi_g$ )
0.1	-0.243(-2) <sup>b</sup>	-0.306(-2) <sup>a</sup>	0.469(-3)	0.103(-2) <sup>a</sup>
0.2	0.180(-2)	0.200(-2)	0.201(-2)	0.231(-2)
0.3	0.197(-1)	0.218(-1)	0.356(-2)	0.400(-2)
0.4	0.540(-1)	0.581(-1)	0.587(-2)	0.675(-2)
0.5	0.103	0.108	0.102(-1)	0.114(-1)
0.6	0.159	0.164	0.166(-1)	0.185(-1)
0.7	0.216	0.220	0.261(-1)	0.283(-1)
1.0	0.333	0.335	0.685(-1)	0.713(-1)
	$K_{131}^S$	$K_{131}^R$	$K_{241}^S$	$K_{241}^R$
0.1	0.60(-3)	0.12(-2)	0.11(-3)	0.630(-3)
0.2	0.22(-2)	0.19(-2)	0.14(-2)	0.11(-2)
0.3	0.30(-2)	0.28(-2)	0.16(-2)	0.15(-2)
0.4	0.35(-2)	0.38(-2)	0.24(-2)	0.20(-2)
0.5	0.51(-2)	0.50(-2)	0.28(-2)	0.24(-2)
0.6	0.72(-2)	0.65(-2)	0.35(-2)	0.30(-2)
0.7	0.89(-2)	0.82(-2)	0.37(-2)	0.35(-2)
1.0	0.12(-2)	0.14(-1)	0.65(-2)	0.58(-2)

<sup>a</sup>All numbers in this column are from Ref. 13.<sup>b</sup>-0.243(-2) = -0.243 × 10<sup>-2</sup>.

differences between our  $K_{020}$  and  $K_{220}$  elements and those of Robb *et al.* at very low momenta could be due to the different SCF wave functions used in the two calculations. In Table III we also show the results of a  ${}^2\Sigma_g^+$  calculation using a very small basis of five functions. This basis, while evidently not sufficient to provide the higher partial-wave elements of the  $K$  matrix, does give surprisingly accurate  $K_{000}$  elements over a wide range of energies. Table III also shows the partial-wave  $K$ -matrix elements for the  ${}^2\Sigma_u^+$  symmetry. The  $K_{110}$ ,  $K_{130}$ , and  $K_{330}$  elements, which are obtained with eight basis functions, agree well with those of Robb *et al.* and also with those of the variationally corrected  $T$ -matrix calculations of Fliflet and McKoy.<sup>14</sup>

In Table IV we list the  $K_{111}$  and  $K_{131}$  elements for the  ${}^2\Pi_u$  symmetry and the  $K_{221}$  and  $K_{241}$  elements for the  ${}^2\Pi_g$  case, which again agree well with those of Ref. 13 and those of Ref. 14. The basis sets contained six functions. The  $K_{331}$  and  $K_{441}$  elements of the  $K$  matrix would be most effectively described by including the appropriate spherical Bessel functions along with discrete basis functions in the trial scattering wave function. The inclusion of these continuum functions would be more efficient by far than the addition of Cartesian Gaussian functions with very diffuse exponents. The use of spherical Bessel functions alone as trial functions or along with discrete functions in the Schwinger variational principle can be a significant technical asset of the method. We defer a discussion of this aspect of the method to the Appendix.

#### B. Approximate evaluation of Schwinger variational expression

With Cartesian Gaussian functions as trial functions, we can analytically evaluate the approximation of Eq. (12) for the  $\langle\alpha|UG_0^{(+)}U|\beta\rangle$  matrix elements in the denominator of Schwinger variational expression. However, we are at present only able to derive analytic expressions for plane-wave matrix elements of the  $T$  operator as opposed to partial-wave matrix elements, because the required bound-free (Gaussian-Bessel function) matrix elements of the potential cannot be obtained in closed form in the latter case. Consequently, this procedure does require a numerical averaging over molecular orientations to obtain the differential cross section, but it can be useful in applications of the method to larger molecular systems. The key question in the assessment of this procedure is the convergence of the matrix elements  $\langle\alpha|UG_0U|\beta\rangle$  as the inserted basis is increased in Eq. (12). It is important to recognize that the basis used for this insertion around  $G_0$  need not be the same as the scattering basis and should generally be larger.

For this purpose we used this analytical approximation to evaluate the  $\langle\alpha|UG_0^{(P)}U|\beta\rangle$  term of the denominator of the Schwinger expression,  $D^{(P)}$  of Eqs. (8) and (13), along with the partial-wave matrix elements of the numerator which were obtained numerically as in Sec. III A. Table V shows these results for the  $K_{000}$ ,  $K_{020}$ , and  $K_{220}$  elements of the  ${}^2\Sigma_g^+$  case with three different basis sets. In these calculations the scattering basis contains

TABLE V. Convergence of the approximate Schwinger expression as the inserted basis around  $G_0^{(P)}$  is increased. The scattering basis is a set of four functions obtained by deleting the  $zz$  function from the 5-term set of Table I.

$k$	4 functions	9 functions	12 functions	Exact <sup>b</sup> $K^S$
$K_{000}$				
0.1	-0.181	-0.204	-0.223	-0.222
0.3	-0.707	-0.741	-0.737	-0.743
0.5	-1.724	-1.845	-1.585	-1.616
$K_{020}$				
0.1	-0.39(-4) <sup>a</sup>	-0.46(-4)	-0.48(-4)	-0.43(-4)
0.3	-0.12(-2)	-0.12(-2)	-0.12(-2)	-0.12(-2)
0.5	-0.66(-2)	-0.51(-2)	-0.46(-2)	-0.56(-2)
$K_{220}$				
0.1	0.83(-6)	0.82(-6)	0.82(-6)	0.82(-6)
0.3	0.19(-3)	0.19(-3)	0.19(-3)	0.19(-3)
0.5	0.21(-2)	0.21(-2)	0.20(-2)	0.20(-2)

<sup>a</sup> -0.39(-4) =  $-0.39 \times 10^{-4}$ .

<sup>b</sup> These are the numerical results with 4-basis functions.

four functions. The results in Table V correspond to first using the scattering basis in the insertion around  $G_0^{(P)}$  and then augmenting this basis to nine and twelve functions successively. The results show that this insertion technique converges well and can be useful in applications of the Schwinger principle to molecular systems.

#### IV. CONCLUSIONS

We have presented the results of the first application of the Schwinger variational principle to electron-molecule scattering. The results of these applications to electron- $H_2$  scattering in the static-exchange approximation show that the Schwinger principle provides accurate solutions of the scattering problem with small basis sets. In the present calculations the trial scattering wave function was expanded in basis sets containing six to twelve Cartesian Gaussian functions. The use of Cartesian Gaussian functions is shown to lead to some distinct computational advantages in applications of the Schwinger principle to molecular systems. These advantages include an approximate but analytical evaluation of the difficult second-Born-type term which appears in the variational expression. However, we have also developed efficient schemes for the numerical evaluation of all the required matrix elements. The numerical integration techniques allow us to use a hybrid trial scattering wave function containing both continuum and discrete basis functions.

Applications of the Schwinger method to the scattering of electrons by polar and polyatomic molecules are under way.

#### ACKNOWLEDGMENT

The work of one of us (T. N. R.) was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore Laboratory under Contract No. W-7405-Eng-48.

#### APPENDIX

For those higher partial waves which can be described well by the first Born approximation, it would be efficient to include spherical Bessel functions of order  $l$  multiplied by spherical harmonics of the same order along with Cartesian Gaussian functions in the trial scattering functions. For example, in the  ${}^2\Sigma_g^+$  channel the trial scattering function would be

$$\bar{\psi}(r) = \sum_{i=1}^N c_i \phi_i(r) + \alpha j_0(kr) Y_{00} + \beta j_2(kr) Y_{20}(kr), \quad (A1)$$

where the  $\phi_i(r)$  are multicenter Cartesian Gaussian functions,  $\alpha$  and  $\beta$  are variational parameters,

TABLE VI.  $K$ -matrix elements with hybrid trial functions for the  ${}^2\Sigma^+$  symmetry in  $H_2$ .<sup>a</sup>

$k$	${}^2\Sigma_g^+$		${}^2\Sigma_u^+$	
	$K_{000}^S$	$K_{000}^R$	$K_{110}^S$	$K_{110}^R$
0.3	-0.707	-0.722 <sup>b</sup>	0.112	0.119 <sup>b</sup>
1.0	7.86	8.05	1.32	1.34
	$K_{020}^S$	$K_{020}^R$	$K_{130}^S$	$K_{130}^R$
0.3	0.009	0.011	0.0034	0.0034
1.0	0.112	0.11	0.030	0.029
	$K_{220}^S$	$K_{220}^R$	$K_{330}^S$	$K_{330}^R$
0.3	0.0069	0.0074	0.0029	0.0031
1.0	0.093	0.093	0.019	0.020

<sup>a</sup> See text: the basis contains spherical Bessel functions and three  $s$  Gaussian functions with exponents of 1.0, 0.316, and 0.1.

<sup>b</sup> All numbers in this column are from Ref. 13.

ters, and  $j_0 Y_{00}$  and  $j_2(kr) Y_{20}$  are Born scattering wave functions for  $s$  and  $d$  waves. In general, for a given angular momentum eigenfunction, one could include spherical Bessel functions of other orders. However, for the present purpose one need not consider such additional flexibility in the radial trial function. The spherical Bessel functions can be included in a straightforward manner in our calculations since all required matrix elements are evaluated numerically.

First we present some results for the  $\Sigma_g^+$  and  $\Sigma_u^+$  symmetries in which we used three  $s$  Cartesian Gaussian functions on each nucleus and two spherical Bessel functions at the on-shell value of  $k$ . Hence for the  $\Sigma_g^+$  case we include  $j_0(kr)$  and  $j_2(kr)$  and similarly  $j_1(kr)$  and  $j_3(kr)$  for the  $\Sigma_u^+$  symmetry.

TABLE VII.  $K$ -matrix elements with continuum trial functions for the  ${}^2\Pi$  symmetry in  $H_2$ .<sup>a</sup>

$k$	${}^2\Pi_u$		${}^2\Pi_g$	
	$K_{111}^S$	$K_{111}^R$	$K_{221}^S$	$K_{221}^R$
0.3	0.022	0.0218 <sup>b</sup>	0.0037	0.004 <sup>b</sup>
1.0	0.326	0.335	0.0688	0.0713
	$K_{131}^S$	$K_{131}^R$	$K_{241}^S$	$K_{241}^R$
0.3	0.0027	0.0028	0.0015	0.0015
1.0	0.014	0.014	0.0056	0.0058
	$K_{331}^S$	$K_{331}^R$	$K_{441}^S$	$K_{441}^R$
0.3	0.0022	0.0023	0.0014	0.0015
1.0	0.0157	0.017	0.0061	0.0067

<sup>a</sup> See text: trial scattering wave function contains two spherical Bessel functions at the on-shell energy.

<sup>b</sup> All numbers in this column are from Ref. 13.

Table VI shows the partial-wave  $K$  matrices at  $k=0.3$  and  $1.0$ . The results are very encouraging and show that these trial functions are effective.

For the  $\Pi_u$  and  $\Pi_g$  symmetries we used the  $l=1$  and  $3$  and  $l=2$  and  $4$  spherical Bessel functions,

respectively, as trial functions. For the partial waves of these symmetries we expect such trial functions to be effective. Table VII shows the first three partial-wave  $K$ -matrix elements for these two cases. As expected these trial functions are very adequate for these partial waves.

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\*Contribution No. 6086.

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