

## Low-energy $e^-$ - $H_2$ elastic cross sections using discrete basis functions\*

T. N. Rescigno, C. W. McCurdy, Jr., and V. McKoy

Arthur Amos Noyes Laboratory of Chemical Physics,<sup>†</sup> California Institute of Technology, Pasadena, California 91109

(Received 5 August 1974)

Differential elastic cross sections for the scattering of electrons by hydrogen molecules are calculated for incident momenta  $\leq 0.7$  a.u. Calculations are performed using a Gaussian basis-set expansion technique developed previously by the authors for use with nonspherical potentials. With the static-exchange model, cross sections are computed in the body-fixed frame and then averaged over molecular orientations. Our results agree well with those of previous workers. The method is economical and has wide applicability to the electron-molecule scattering problem.

### I. INTRODUCTION

In two earlier papers,<sup>1,2</sup> we outlined a new method for calculating cross sections for scattering involving nonspherical potentials. It was there indicated that this method would find numerous applications in low-energy electron-molecule scattering problems.

Progress in the *ab initio* calculation of such cross sections has been hampered because of the difficulties involved in the calculation of accurate molecular continuum wave functions. When compared to the advances that have been made in the area of electron-atom scattering, the study of electron-molecule collisions is still in a very unsatisfactory stage. Nevertheless, the need for accurate low-energy electron-molecule cross sections is very great. For example, the excitation mechanism for many existing and proposed gas-laser systems is direct excitation by electron impact in a gaseous discharge.<sup>3</sup> Furthermore, there is now considerable experimental low-energy data with which to compare results.

This paper describes the first results of the application of our new method to elastic scattering of low-energy electrons by hydrogen molecules. We have limited ourselves here to a study of the static-exchange approximation. This model has been studied previously by others<sup>4,5</sup> for  $e^-$ - $H_2$  and we compare our results with theirs. Our point here is to show that calculations such as the present are quite feasible and, in fact, require only slightly more effort than a standard bound-state molecular computation.

The plan of this paper is as follows. In Sec. II we give a general outline of the method used to calculate elastic cross sections. Section III contains our results for  $e^-$ - $H_2$  scattering and a comparison with the work of others. Section IV contains a brief discussion.

### II. THEORY

#### A. General formulation

Here we restrict ourselves to scattering in the static-exchange approximation, which can be formulated by writing the wave function for the entire system ( $e^- + H_2$ ) as

$$\psi^+(1, 2, 3) = \alpha[\chi_k^\pm(1)\Phi(2, 3)], \quad (1)$$

where  $\Phi(2, 3)$  is the ground-state wave function of  $H_2$ , which we take to be the Hartree-Fock solution. Substitution of Eq. (1) into the Schrödinger equation yields an equation for the spatial part of  $\chi_k^\pm$  in which the effective potential is simply the Hartree-Fock potential of  $H_2$ ,

$$V = -\frac{1}{r_{N_1}} - \frac{1}{r_{N_2}} + 2\hat{J} - \hat{K}, \quad (2)$$

that is, the sum of the nuclear attraction and the usual Coulomb and exchange operators. For a homonuclear diatomic molecule (e.g.,  $H_2$ ) this potential possesses cylindrical and inversion symmetry.

It should be noted that the method we are employing is by no means restricted to the static-exchange model. A more realistic inclusion of correlation effects could be accomplished either by including excited target states in the trial wave function given by Eq. (1) or, if a single-channel model is desired, by using an optical potential. We have chosen the static-exchange approximation in order to keep the computational details fairly simple and to facilitate comparison with previous work.

We further assume that the molecule remains stationary during the collision, and hence its rotational motion need not be considered in the elastic scattering problem. It is well established that this is an excellent approximation for all but the

lowest incident energies (less than 0.1 eV).<sup>4-6</sup> This allows us to perform the calculation in the frame of the molecule, transform the result to the laboratory frame, and then average the cross section over molecular orientations.<sup>7</sup>

Since the potential does not have spherical symmetry it is convenient to work with the integral equation for the full scattering amplitude subject to the above restrictions. We *do not* employ a single-center expansion of the potential.

The solution of the Lippmann-Schwinger equation using a finite set of square-integrable basis functions has been described in detail elsewhere,<sup>1,2</sup> and thus only a brief outline of the method will be given here. The approximation on which our approach is based is the representation of the potential in a finite, discrete basis. This truncated potential

$$V^t = \sum_{\alpha, \beta} |\alpha\rangle \langle \alpha| V |\beta\rangle \langle \beta| \quad (3)$$

leads to a separable kernel in the Lippmann-Schwinger equation,<sup>8</sup> which becomes a linear equation for the matrix elements of the truncated transition operator  $T^t$ :

$$\langle \alpha | T^t(E) | \beta \rangle = \langle \alpha | U | \beta \rangle + \sum_{\gamma, \delta} \langle \alpha | U | \gamma \rangle \langle \gamma | G_0(E) | \delta \rangle \times \langle \delta | T^t(E) | \beta \rangle, \quad (4)$$

where  $U = 2V$  in atomic units. The exact scattering amplitude for the truncated potential may be obtained from the matrix of  $T^t$  by the transformation to the laboratory frame,

$$\begin{aligned} f(\vec{k}_{\text{out}} - \vec{k}_{\text{in}}) &= -\frac{1}{4\pi} \langle \vec{k}_{\text{out}} | T^t(E) | \vec{k}_{\text{in}} \rangle \\ &= -\frac{1}{4\pi} \sum_{\alpha, \beta} \langle \vec{k}_{\text{out}} | \alpha \rangle \langle \alpha | T^t(E) | \beta \rangle \langle \beta | \vec{k}_{\text{in}} \rangle, \end{aligned} \quad (5)$$

where

$$\langle k | \alpha \rangle = \int e^{-i\vec{k} \cdot \vec{r}} \langle \gamma | \alpha \rangle d^3r. \quad (6)$$

The scattering amplitude  $f(\vec{k}_{\text{out}} - \vec{k}_{\text{in}})$  depends on the orientation of the molecule as well as the scattering angle. Equation (5) renders the calculations of differential cross sections and averages over molecular orientation particularly simple since all angular dependences are contained in the Fourier transforms of Eq. (6).

The solution of Eq. (4) requires only matrix elements of the potential and the free-particle Green's function in a discrete basis. Once these matrix elements are known, the matrix  $\underline{T}^t$  is obtained by a single matrix inversion,

$$\underline{T}^t = [\underline{1} - \underline{U}^t \underline{G}_0(E)]^{-1} \underline{U}^t. \quad (7)$$

It should be noted that the approximation of using a truncated potential is employed universally in bound-state calculations on molecular systems. It arises whenever the Schrödinger equation is solved by diagonalizing the Hamiltonian in a basis set.

For molecular systems a natural approach to the solution of Eq. (4) is to construct the set  $\{|\alpha\rangle\}$  by orthogonalizing a set of the usual Gaussian basis functions of molecular bound-state calculations.<sup>9</sup> Since we are restricting our attention to cylindrically symmetric systems, we first make combinations of the Gaussian functions  $\mathcal{G}_\alpha$ ,

$$\mathcal{G}_\alpha(\vec{r} - \vec{A}) = x^l y^m (z - A)^n e^{-\alpha [x^2 + y^2 + (z - A)^2]}, \quad (8)$$

which have  $g$  or  $u$  inversion symmetry:

$$\varphi_\alpha = \mathcal{G}_\alpha(\vec{r} - \vec{A}) \pm \mathcal{G}_\alpha(\vec{r} + \vec{A}), \quad (9)$$

and also require that the  $\varphi_\alpha$  transform with irreducible representations of the point group  $D_{\infty h}$ . Equation (4) may then be solved separately for each symmetry, e.g.,  $\Sigma_g^+$ ,  $\Sigma_u^+$ ,  $\Pi_g$ ,  $\Pi_u$ , etc. An immediate advantage of using Gaussian basis functions is that the Fourier transforms of Eq. (6) may be done in closed form and are simply Gaussians modulated by Hermite polynomials.<sup>10</sup>

A number of simplifications can be realized in the calculation of the matrix elements of the free-particle Green's function which reduce the computational effort required to solve Eq. (4) to little more than is expended in molecular self-consistent-field calculations on bound states. In computing matrix elements of the Green's function an integration over  $d^3k$  is required. The use of Gaussians allows the two angular integrations to be performed analytically. The remaining integration over  $|k|$  may be handled by a simple numerical quadrature technique; details can be found in Ref. 2. In addition, matrix elements of the Hartree-Fock potential were extracted from existing bound-state molecular programs.

## B. Born correction

The leading term in the scattering amplitude, Eq. (5), is the matrix approximation to the Born contribution. It was found necessary to represent this term exactly. This can be accomplished by subtracting  $\langle \alpha | U | \beta \rangle$  from the computed value of  $\langle \alpha | T^t(E) | \beta \rangle$ , and in Eq. (5) adding the exact Born matrix element  $\langle \vec{k}_{\text{out}} | U | \vec{k}_{\text{in}} \rangle$ . In addition to improving the computed  $T$ -matrix elements, this correction includes Born contributions from all symmetries not explicitly included in the computation of the scattering amplitude. One expects contributions from higher symmetries (analogous to higher partial waves in central-field problems) to

be well represented in the Born approximation.

Computation of  $\langle \vec{k}_{\text{out}} | U | \vec{k}_{\text{in}} \rangle$  requires direct and exchange free-free interaction matrix elements. The direct terms can be reduced to the Fourier transform of a product of two Gaussian basis functions on different centers; these integrals are well known.<sup>11</sup> The exchange matrix elements can be written in terms of error functions of a complex argument. Details are given in the Appendix. All such matrix elements depend on the scattering angle and the molecular orientation.

It should be pointed out that the Born correction discussed here is simply the leading term in a full variational correction of the computed amplitude. The details of such a correction are discussed at length in Ref. 2. In this connection, it is interesting to compare this method with the more-standard variational procedures such as the Kohn method. We would require bound-free and free-free matrix elements only in evaluating the Kato correction, whereas the Kohn method always needs such matrix elements. Furthermore, since we are computing the *exact* amplitude for an approximate potential, we would not expect to find singularities of the type that frequently occur when using the Kohn method.

### C. Cross sections

The physical cross section is obtained by averaging the cross section for a particular molecular orientation over all orientations of the molecule. The cross section  $\sigma(\Omega, \Omega_0)$  depends on the angles  $\Omega_0$  specifying the molecular orientation in the laboratory-fixed frame and on the angles  $\Omega$  specifying the orientations of  $\vec{k}_{\text{in}}$  and  $\vec{k}_{\text{out}}$ . The average over orientations is given by

$$\sigma_{\text{ave}}(\theta) = (1/4\pi) \int \sigma(\Omega, \Omega_0) d\Omega_0. \quad (10)$$

The coordinate system is shown in Fig. 1. The  $z$  axis of this system lies along the momentum-transfer vector  $\vec{Q} = \vec{k}_{\text{in}} - \vec{k}_{\text{out}}$ . This was done in order that the ranges of integration over  $\theta$  and  $\varphi$  (see Fig. 1) could both be reduced to the interval  $[0, \pi/2]$  by using the symmetry of the cross section under inversion of the molecule and under interchange of  $\vec{k}_{\text{in}}$  and  $\vec{k}_{\text{out}}$ . This symmetry obviously applies only to homonuclear molecules.

### III. RESULTS

Elastic scattering calculations were performed for incident momenta 0.3, 0.4, 0.5, 0.6, and 0.7 a.u. A basis of 22  $S$ -type Gaussians on each hydrogen atom was constructed from the Huzinaga<sup>12</sup> expansion of a 1S Slater function (orbital exponent = 1.2) in 10 Gaussians by adding diffuse Gaussians

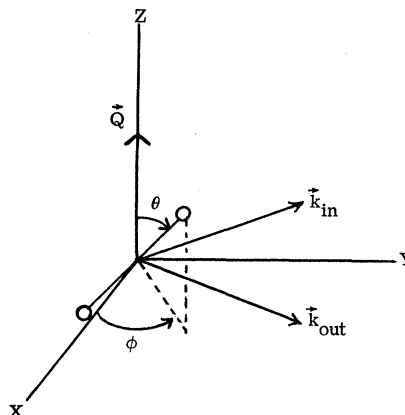


FIG. 1. Coordinate system used for averaging the cross section over molecular orientations.

with exponents chosen in a geometric series with a ratio of 1.6. A similar prescription has been used successfully by Schneider in a calculation on electron-helium scattering.<sup>13</sup> Diffuse basis functions were found to be necessary to properly represent the asymptotic portions of the potential. With this basis set, contributions for  $\Sigma_g^+$  and  $\Sigma_u^+$  symmetries may be computed. An indication of the completeness of the basis for these symmetries may be obtained by comparison of the sum of the  $\Sigma_g^+$  and  $\Sigma_u^+$  Born contributions (i.e.,  $\langle \vec{k}_{\text{out}} | U^t | \vec{k}_{\text{in}} \rangle$ ) with the exact Born amplitude at a molecular orientation at which only these two symmetries contribute. This is the case for forward scattering with the axis of the molecule along  $\vec{k}_{\text{in}}$ . For  $k=0.3$  a.u. at this orientation the exact Born amplitude is 8.51 and the sum of the  $\Sigma_g^+$  and  $\Sigma_u^+$  approximate Born contributions was 8.60.

Our results for the differential cross sections at five energies and five angles are presented in Table I. The angular average for these cross sections was performed using a six-point Gauss-Legendre quadrature in  $\theta$  and  $\varphi$ . We compare our

TABLE I. Differential cross sections for  $e^-$ -H<sub>2</sub> elastic scattering. Cross sections are in units of  $a_0^2$  and  $k$  is in atomic units. Results have been averaged over molecular orientations and Born corrections (see text) included.

$k$	$\theta$				
	0°	45°	90°	135°	180°
0.3	2.29	2.62	3.59	4.78	5.33
0.4	1.94	2.14	3.06	4.49	5.21
0.5	3.43	3.07	3.23	4.57	5.41
0.6	4.14	3.28	2.65	3.47	4.13
0.7	4.97	3.67	2.31	2.56	2.99

results at  $k=0.3, 0.4,$  and  $0.6$  a.u. with the results of Tully and Berry,<sup>4</sup> and at  $k=0.7$  a.u. with the static-exchange results of Hara<sup>5</sup> (case C in his work), in Fig. 2. The calculation of Tully and Berry differs slightly from the present work in that they used the Weinbaum function<sup>14</sup> for the ground state of  $H_2$ ; their cross sections were generated by direct numerical solution of the two-dimensional Schrödinger equation. Hara's results<sup>5</sup> were obtained by numerical solution of the Schrödinger equation in ellipsoidal coordinates. The

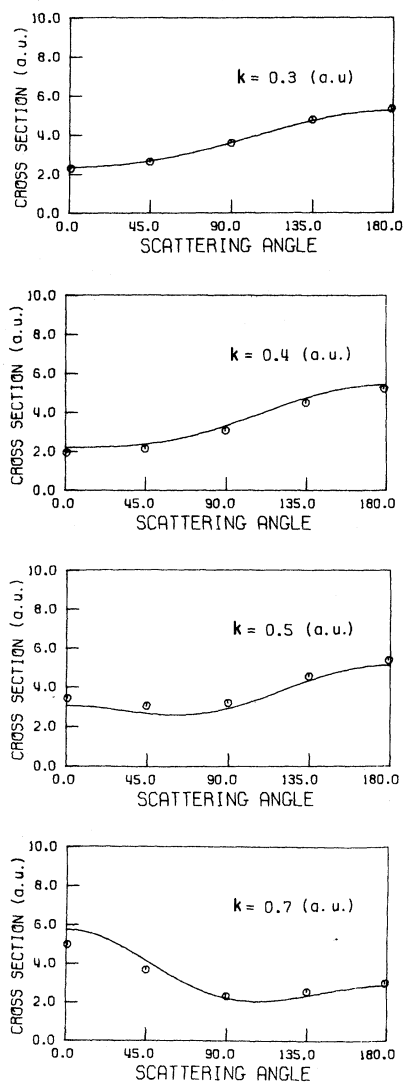


FIG. 2. Differential cross sections for elastic scattering of electrons by  $H_2$ . Cross sections are given in units of  $a_0^2$  and  $k$  is measured in atomic units. Our results are given by open circles; the solid curves are those of Tully and Berry (Ref. 4) and (at  $k=0.7$  a.u.) Hara (Ref. 5).

agreement between our results and those obtained by numerical integration is quite good.

The importance of including the exact Born correction can be assessed by comparison of our corrected and uncorrected cross sections at  $k=0.6$  a.u. with those of Tully and Berry in Fig. 3. Again, there is good agreement with our corrected results, although the uncorrected results (which are particularly easy to generate) are moderately accurate and display the correct shape. This was found to be the case at other energies also.

Our calculations were performed on an IBM 370-158 computer. The self-consistent-field (SCF) calculation and the construction of the Hartree-Fock potential using the 22-S-Gaussian basis on each hydrogen required 16.6 min. The calculation of uncorrected cross sections for all energies and angles reported here required 2.7 min. The calculation of all required Born corrections which were performed with a smaller (12 S on each atom) basis required an additional 13.0 minutes. The 12-S basis gives identical results for  $\langle \vec{k}_{out} | U | \vec{k}_{in} \rangle$  as the 22-S basis.

#### IV. DISCUSSION

These results indicate that the use of Gaussian basis functions provides an efficient method for computing elastic electron-molecule cross sections. In our case, the entire scattering calculation required less time than the SCF calculation for the ground state and the construction of the potential. The bulk of the time expended in the scattering calculation was used in computing the Born corrections.

The calculations reported here were minimal; only  $\Sigma_g^+$  and  $\Sigma_u^+$  symmetries were included and polarization effects were ignored. Correlation effects can easily be included in this computational

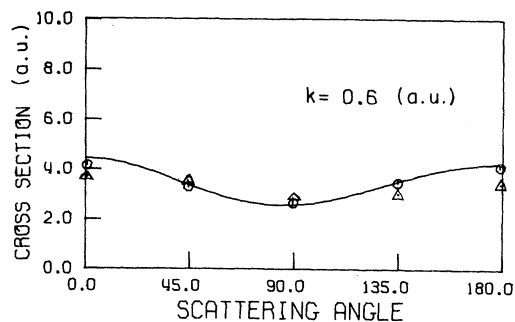


FIG. 3. Differential cross section at  $k=0.6$  a.u. compares our corrected (○) and uncorrected (△) results with those of Tully and Berry (solid curve).

scheme through the use of an approximate optical potential.<sup>15</sup> The efficiency of the method and the accuracy of the results obtained here suggest that the prospects for more detailed calculations as well as application to larger molecules are good.

#### APPENDIX: EVALUATION OF EXCHANGE FREE-FREE MATRIX ELEMENTS

Consider the exchange integral for S-type Gaussians,

$$I \equiv \int d^3r_1 d^3r_2 e^{-i\vec{k}' \cdot \vec{r}_1} e^{-\alpha(\vec{r}_2 - \vec{A})^2} \times \frac{1}{|\vec{r}_1 - \vec{r}_2|} e^{i\vec{k} \cdot \vec{r}_2} e^{-\beta(\vec{r}_1 - \vec{B})^2}. \quad (A1)$$

By completing squares in the exponents of Eq. (A1) we obtain a matrix element involving Gaussians referring to complex centers:

$$I = e^{-k^2/4\alpha} e^{-k'^2/4\beta} e^{+i\vec{k} \cdot \vec{A}} e^{-i\vec{k}' \cdot \vec{B}} \times \int e^{-\alpha[\vec{r}_1 - (\vec{A} + i\vec{k}/2\alpha)]^2} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \times e^{-\beta[\vec{r}_2 - (\vec{B} - i\vec{k}'/2\beta)]^2} d^3r_1 d^3r_2. \quad (A2)$$

Following Shavitt,<sup>9</sup> this integral may be performed by expressing  $1/|\vec{r}_1 - \vec{r}_2|$  as its Gaussian transform,

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{\sqrt{\pi}} \int_0^\infty s^{-1/2} e^{-s|\vec{r}_1 - \vec{r}_2|^2} ds. \quad (A3)$$

With this substitution, the integral of Eq. (A2) may be performed by elementary methods to give

$$I = \frac{2\pi^{5/2}}{\alpha\beta\sqrt{\alpha+\beta}} e^{-k^2/4\alpha} e^{-k'^2/4\beta} e^{i\vec{k} \cdot \vec{A}} e^{-i\vec{k}' \cdot \vec{B}} \times F_0 \left( \left( \frac{\alpha\beta}{\alpha+\beta} \right)^{1/2} \left| (\vec{A} - \vec{B}) - i \left( \frac{\alpha\vec{k}' + \beta\vec{k}}{2\alpha\beta} \right) \right| \right), \quad (A4)$$

where the function  $F_0(X)$  is

$$F_0(X) = (\sqrt{\pi}/2X) \operatorname{erf}(X). \quad (A5)$$

Expressions for integrals involving  $p, d$ , etc., Gaussians may be derived from Eq. (A4) by differentiation with respect to the components of  $\vec{A}$  and  $\vec{B}$ . An efficient algorithm for computing error functions of complex argument given by Gautschi was used in this work.<sup>16</sup>

\*This work was supported by a grant from the NSF.

†Contribution No. 4932.

<sup>1</sup>T. N. Rescigno, C. W. McCurdy, and V. McKoy, *Chem. Phys. Lett.* **27**, 401 (1974).

<sup>2</sup>T. N. Rescigno, C. W. McCurdy, and V. McKoy, *Phys. Rev. A* **10**, 2240 (1974).

<sup>3</sup>C. K. Rhodes and A. Szöke, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-Dubois (North-Holland, Amsterdam, 1972), p. 265.

<sup>4</sup>J. C. Tully and R. S. Berry, *J. Chem. Phys.* **51**, 2056 (1969).

<sup>5</sup>S. Hara, *J. Phys. Soc. Jpn.* **27**, 1009 (1969).

<sup>6</sup>P. G. Burke and A. L. Sinfailam, *J. Phys. B* **3**, 641 (1970).

<sup>7</sup>A. Temkin and K. V. Vasavada, *Phys. Rev.* **160**, 109 (1967).

<sup>8</sup>B. H. Bransden, *Atomic Collision Theory* (Benjamin, New York, 1970), p. 176.

<sup>9</sup>I. Shavitt, *Methods of Computational Physics* (Academic, New York, 1963), Vol. II, p. 30.

<sup>10</sup>A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Tables of Integral Transforms* (McGraw-Hill, New York, 1954), Vol. 1, p. 121.

<sup>11</sup>K. J. Miller and M. Krauss, *J. Chem. Phys.* **47**, 3754 (1967).

<sup>12</sup>S. Huzinaga, *J. Chem. Phys.* **42**, 1293 (1965).

<sup>13</sup>B. Schneider, *Chem. Phys. Lett.* **25**, 140 (1974).

<sup>14</sup>S. Weinbaum, *J. Chem. Phys.* **1**, 593 (1933).

<sup>15</sup>See, for example, B. Schneider, H. S. Taylor, and R. Yaris, *Phys. Rev. A* **1**, 855 (1970).

<sup>16</sup>W. Gautschi, *SIAM J. Num. Anal.* **7**, 187 (1970).