PHYSICAL REVIEW A VOLUME 49, NUMBER 6 JUNE 1994

Momentum-space calculation of electron-molecule scattering

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(Received 27 August 1993; revised manuscript received 22 February 1994)

The momentum-space calculation of electron-molecule elastic scattering is described and illustrated as the first step in a program of electron-molecule scattering that takes all reaction channels into account. The method is the analog for molecules of the integral-equation methods that have had essentially complete success for structurally simple atoms. Although scattering is a single-center problem in momentum space its multicentered nature in coordinate space results in the integral equations for different orbital angular momenta being coupled. There are no restrictions in principle on the nature of the target molecule. For illustrative purposes the static exchange calculation is supplemented by a phenomenological polarization potential that will be replaced by an *ab initio* optical potential and coupled electronic channels in the planned development of a general scattering method.

PACS number(s): 34.80.Bm

I. INTRODUCTION

Momentum-space methods in electron-molecule scattering theory are attractive from two points of view. First, differential cross sections are expressed in terms of initial and final electron momenta so that the amplitudes involved in the calculation are directly related to experiment. Second, the electron-molecule system has a single center in momentum space, whereas a tractable coordinate-space representation is multicentered. The price paid for this is that in an orbital-angular-momentum expansion, equations for different angular momenta are coupled.

The momentum-space formulation of electron-atom scattering [1] has led to fully converged numerical solutions of the whole problem [2] in the case of one-electron targets [the convergent-close-coupling (CCC) method]. It is used in the coupled-channels-optical (CCO) method [3], whose results are very close to CCC, and which gives excellent agreement with very detailed experiments [4] in a variety of cases, many involving electron spin analysis.

The application of the theory to molecules follows naturally on this success. The framework remaining essentially the same, the theory is nevertheless significantly complicated in the case of molecules by the multicenter nature of the potentials. In addition, processes nonexistent in atoms, such as rotational and vibrational excitations, appear. On a more practical level, molecules are often composed of many more electrons and nuclei, dictating a larger number of computations and use of a greater slice of available computer resources.

Many and various attempts at coming to terms with these difficulties have been made, the solutions coming generally through the use of approximations and simplifications. A comprehensive review of the methods available up to the year 1980 can be found in the article by Lane [5]. In particular, two *ab initio* methods are described which have subsequently been developed further. The *R*-matrix method has been developed by workers such as Schneider *et al.* [6–8] and Burke *et al.* [9]. The *T*-matrix expansion method of Rescigno *et al.* [10–12] approximates the two-center molecular potential by its projection onto a subspace of discrete Gaussian basis functions. The Lippmann-Schwinger equation for the *T* matrix is then solved using standard matrix techniques. Within this framework direct, exchange, and polarization terms were used and the theory finally applied to vibrational and vibrational-rotational excitation of H_2 [13–15]. More recently, several collaborators [16–18] have introduced the Schwinger multichannel theory (SMC) for use in electron-molecule scattering. Here the Schwinger variational principle is extended to include multichannel scattering along with polarization effects.

These various theoretical treatments are currently being applied to rotational and vibrational excitation, resonance processes, and to molecules much larger than the hydrogen molecule, such as CH_4, SF_6, and H_2O. The review article of Gianturco and Jain [19] reports the state of the field as of 1986.

We have started on a program of calculations whose final objective is to couple two electronic channels (the elastic channel and one other observed channel) and to treat remaining channels, including the ionization continuum, by adding an *ab initio* polarization potential to the coupling potential. The present work describes the elastic calculation for a general molecule and illustrates it with a one-channel (static-exchange) calculation for the hydrogen molecule, H_2. For comparison with experiment we have included a real phenomenological polarization potential, which is to be eventually replaced by the complex, nonlocal *ab initio* polarization potential.

Electron-molecule scattering is reduced to an electronic problem by the Born-Oppenheimer approximation, using closure over the vibrational and rotational states. The nuclei are assumed fixed at their equilibrium sites.

The formulation of the two-channel scattering problem in momentum space is in terms of two coupled Lippmann-

Schwinger integral equations in the three-dimensional momentum variables. They are reduced to coupled equations in radial momentum variables by partial-wave expansions. Because the coupling potentials are not spherical, equations for different partial waves are coupled. For larger values of orbital angular momentum the nonspherical aspect of the potential is obscured by the centrifugal barrier, matrix elements that are off diagonal in orbital angular momenta become negligible, and the partial-wave equations become uncoupled. As the number of coupled partial-wave equations is increased the solution converges.

The quantities involved in the coupled integral equations are the potential matrix elements of the Born approximation, on and off shell. Target states are expressed in terms of the independent-particle model using self-consistent-field (SCF) orbitals that are linear combinations of primitive Gaussians centered at the atomic sites. Direct and exchange matrix elements are calculated by analytic angular and numerical radial integrations.

II. THE LIPPMANN-SCHWINGER EQUATION

The electronic T-matrix element for scattering from the molecular ground state $|0\rangle$ to a state $|i\rangle$ is given [1] in atomic units by the integral equation

$$\langle \mathbf{k}'i|T|0\mathbf{k}\rangle = \langle \mathbf{k}'i|V|0\mathbf{k}\rangle + \sum_j \int d^3q \langle \mathbf{k}'i|V|j\mathbf{q}\rangle \times \frac{1}{E^{(+)} - \varepsilon_j - \frac{1}{2}q^2} \langle \mathbf{q}j|T|0\mathbf{k}\rangle. \qquad (1)$$

Momenta are expressed in a body-fixed frame of reference. The electronic states of the molecule are given in terms of the electronic Hamiltonian H_T,

$$(\varepsilon_i - H_T)|i\rangle = 0. \qquad (2)$$

The electron-molecule potential is V. The total energy of the electron-molecule system is E.

We treat the molecular states in the Hartree-Fock approximation. In the present work $|i\rangle$ and $|j\rangle$ are restricted to the ground state. This is the static-exchange approximation. We consider only closed-shell molecules. The potential matrix elements consist of direct V_D and exchange V_E terms. The coordinate-space representations of the potentials [1] are

$$V_D(\mathbf{r}_0) = \sum_{j=1}^{N} \int d^3r_1 \langle \phi_j|\mathbf{r}_1\rangle \frac{1}{|\mathbf{r}_0 - \mathbf{r}_1|} \langle \mathbf{r}_1|\phi_j\rangle - \sum_{n=1}^{M} \frac{Z_n}{|\mathbf{r}_0 - \mathbf{R}_n|}, \qquad (3)$$

$$V_E(\mathbf{r}_0, \mathbf{r}_1) = -\sum_{j=1}^{\frac{N}{2}} \langle \phi_j|\mathbf{r}_1\rangle \left[E_0 - \varepsilon_j - \frac{1}{|\mathbf{r}_0 - \mathbf{r}_1|}\right] \langle \mathbf{r}_0|\phi_j\rangle. \qquad (4)$$

Here E_0 is the energy of the incident electron. The Hartree-Fock orbitals and corresponding energies are ϕ_j and ε_j respectively. The coordinate of the ith of N electrons is $\mathbf{r}_i$. The coordinate of the nth of M nuclei is $\mathbf{R}_n$ and the corresponding charge is Z_n. The sum in Eq. (4) is taken over the $N/2$ electrons with the same spin projection.

III. THE PHENOMENOLOGICAL POLARIZATION POTENTIAL

The static-exchange approximation omits the effect on elastic scattering of real and virtual excitation of target states. In order to compare our illustrative calculation with experiment we represent the effect by a phenomenological polarization potential

$$V_{\mathrm{pol}}(\mathbf{r}) = v_0(r) + v_2(r)P_2(\cos\theta). \qquad (5)$$

In future work the polarization potential will be calculated *ab initio*. The forms used are

$$v_0(r) = -\frac{\alpha_0}{2r^4}\left\{1 - \exp\left[-\left(\frac{r}{a}\right)^b\right]\right\},$$
$$v_2(r) = -\frac{\alpha_2}{2r^4}\left\{1 - \exp\left[-\left(\frac{r}{a}\right)^b\right]\right\}, \qquad (6)$$

where the spherical and nonspherical polarizabilities are taken to be respectively $\alpha_0 = 5.2$ and $\alpha_2 = 1.32$. The effect on the differential cross section of changing a and b and omitting v_2 has been tested.

IV. SOLUTION OF THE INTEGRAL EQUATIONS

We make the following partial-wave expansion of the potential matrix elements.

$$\langle \mathbf{k}'0|V|0\mathbf{k}\rangle = \sum_{LML'M'} \langle \hat{\mathbf{k}}'|L'M'\rangle \langle k'L'M'||V||kLM\rangle \langle LM|\hat{\mathbf{k}}\rangle. \qquad (7)$$

The reduced potential matrix element is given by inverting Eq. (7).

$$\langle k'L'M'||V||kLM\rangle = \int d\hat{\mathbf{k}} \int d\hat{\mathbf{k}}' \langle L'M'|\hat{\mathbf{k}}'\rangle \langle \mathbf{k}'0|V|0\mathbf{k}\rangle \langle \hat{\mathbf{k}}|LM\rangle. \qquad (8)$$

The reduced T-matrix elements are defined similarly.

The reduced Lippmann-Schwinger equation is

$$\langle k'L'M'||T||kLM\rangle = \langle k'L'M'||V||kLM\rangle + \sum_{L''M''} \int dq q^2 \langle k'L'M'||V||qL''M''\rangle \times \frac{1}{E_0^{(+)} - \frac{1}{2}q^2} \langle qL''M''||T||kLM\rangle. \tag{9}$$

It is a set of coupled integral equations, which is solved by matrix inversion after representing the q integration by a quadrature rule. The solution is described in Ref. [1].

In practice as L increases the off-diagonal potential matrix elements decrease and become negligible after a value L_0. For $L \leq L_0$ the corresponding set of coupled equations is solved fully. For $L > L_0$ the potential is essentially spherical and uncoupled integral equations are solved for each L.

V. COMPUTATION OF REDUCED POTENTIAL MATRIX ELEMENTS

The molecular orbital ϕ_j is represented by a linear combination of "atomic" orbitals (LCAO) centered at the nuclear sites $\mathbf{R}_n$. In the present calculation we use s and p orbitals, expressing the p orbitals in the Cartesian representation (see, for example, Snyder and Basch [20]). The principles involved in refining the representation by including d or f orbitals are sufficiently illustrated by our formalism.

$$\langle \mathbf{r}|\phi_j\rangle = \sum_{gnpk} c_{gnpkj}\, \mathrm{e}^{-\alpha_{gnpk}|\mathbf{r}+\mathbf{R}_n|^2} \sum_{lm} \gamma_{pnlm} r^l Y_{lm}(\hat{\mathbf{r}}), \tag{10}$$

where p labels the symmetry of the "atomic" orbital (e.g., S, P_x, P_y, P_z), k labels the atomic orbital, which is a linear combination of primitive Gaussians, and g labels the primitive Gaussian.
The coefficients γ_{pnlm} transform the Cartesian representation in terms of the components x, y, z of $\mathbf{r}$ and x_n, y_n, z_n of $\mathbf{R}_n$ into the spherical representation, where $Y_{lm}(\hat{\mathbf{r}})$ is a spherical harmonic. They are given by Table I.

In detailing the computational form of the potential matrix elements we abbreviate the set of indices $gnpk$ by a superindex i. Quantities labeled with i may depend only on a subset of $gnpk$. Primed indices are used for the complex conjugate orbital $\langle\phi_j|\mathbf{r}\rangle$.

The Gaussians in Eq. (10) are expanded in spherical Bessel functions of imaginary argument $i_\sigma(x)$;

$$\mathrm{e}^{-\alpha_i|\mathbf{r}+\mathbf{R}_i|^2} = \mathrm{e}^{-\alpha_i(r^2+R_i^2)} \sum_{\sigma\chi} (-1)^\sigma (4\pi) i_\sigma(2\alpha_i r R_i) \times Y^*_{\sigma\chi}(\hat{\mathbf{r}}) Y_{\sigma\chi}(\hat{\mathbf{R}}_i). \tag{11}$$

We make use of the multipole expansion of the Coulomb potential,

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{\lambda\mu} \frac{4\pi}{2\lambda+1} Y^*_{\lambda\mu}(\hat{\mathbf{r}}) Y_{\lambda\mu}(\hat{\mathbf{r}}') \frac{r_<^\lambda}{r_>^{\lambda+1}}. \tag{12}$$

The reduced potential matrix elements of Eq. (8) are evaluated by using the expansions (10)–(12) and performing the angular integrations. The reduced matrix element of the direct potential is given by

$$\langle k'L'M'||V_D||kLM\rangle = i^{L-L'}\sqrt{\frac{2L'+1}{2L+1}} \times \int_0^\infty dr r^2 j_L(kr) j_{L'}(k'r) \times \sum_{\lambda\mu} C^{M'\mu M}_{L'\lambda L} C^{000}_{L'\lambda L} F_{\lambda\mu}(r), \tag{13}$$

where the coefficients C are Clebsch-Gordan coefficients and the functions $F_{\lambda\mu}(r)$ are defined by

$$\begin{aligned} F_{\lambda\mu}(r) = 16 \sum_{j=1}^{N/2} \int_0^\infty dr' r'^2 \left(\frac{r_<^\lambda}{r_>^{\lambda+1}}\right) & \sum_{\substack{lml'm' \\ \sigma\chi\rho\zeta \\ pqstii'}} c_{ij} c_{i'j} (-1)^{\sigma+\rho} i_\sigma(2\alpha_i r' R_i) i_\rho(2\alpha_{i'} r' R_{i'}) \\ & \times \gamma_{ilm}\, \gamma^*_{i'l'm'}\, r'^{l+l'}\, \mathrm{e}^{-\alpha_i(r'^2+R_i^2)}\, \mathrm{e}^{-\alpha_{i'}(r'^2+R_{i'}^2)} Y^*_{\sigma\chi}(\hat{\mathbf{R}}_i)\, Y_{\rho\zeta}(\hat{\mathbf{R}}_{i'}) \\ & \times \frac{\sqrt{(2l+1)(2\sigma+1)(2l'+1)(2\rho+1)}}{(2p+1)} C^{\chi mq}_{\sigma lp} C^{000}_{\sigma lp} C^{\zeta\mu t}_{\rho\lambda s} C^{000}_{\rho\lambda s} C^{m'tq}_{l'sp} C^{000}_{l'sp} \\ & -\frac{2}{\pi} \sum_n Z_n \int_0^\infty dr' r'^2 \frac{\delta(r'-R_n)}{R_n^2\, r_>}. \end{aligned} \tag{14}$$

The quantities k (projectile momentum) and LM (projectile angular momentum quantum numbers) and the corresponding primed quantities have the meaning assigned to them in (8).

The exchange potential (4) has separable and nonseparable terms. We treat the matrix elements of the corresponding operators V_{SE} and V_{NE} individually.

$$\langle k'L'M'||V_{\rm NE}||kLM\rangle = 8i^{L-L'}\sum_{j=1}^{N}\sum_{\substack{\lambda\mu ilm\\ \rho\zeta st}}(-1)^{\rho}\left[\int_0^{\infty}dr'\,r'^{2+l}\,H_{\lambda\mu}^{LM}(r')\,j_{L'}(k'r')\,{\rm e}^{-\alpha_i(r'^2+R_i^2)}i_{\rho}(2\alpha_i r'R_i)\right]$$
$$\times Y^*_{\rho\zeta}(\hat{\mathbf{R}}_i)\gamma_{ilm}\sqrt{\frac{(2l+1)(2\rho+1)}{(2L'+1)}}C^{\zeta\mu t}_{\rho\lambda s}C^{000}_{\rho\lambda s}C^{mtM'}_{lsL'}C^{000}_{lsL}, \tag{15}$$

where

$$H^{LM}_{\lambda\mu}(r') = \sum_{\substack{i'l'm'\\ \sigma\chi pq}}(-1)^{\sigma}\left[\int_0^{\infty}dr\,r^{2+l'}\left(\frac{r_<^{\lambda}}{r_>^{\lambda+1}}\right)j_L(kr)\,{\rm e}^{-\alpha_{i'}(r^2+R_{i'}^2)}\,i_{\sigma}(2\alpha_{i'}rR_{i'})\right]$$
$$\times Y_{\sigma\chi}(\hat{\mathbf{R}}_{i'})\gamma^*_{i'l'm'}\sqrt{\frac{(2l'+1)(2\sigma+1)}{(2L+1)}}C^{\chi\mu q}_{\sigma\lambda p}C^{000}_{\sigma\lambda p}C^{m'qM}_{l'pL}C^{000}_{l'pL}. \tag{16}$$

The reduced matrix element of the separable exchange potential is

$$\langle k'L'M'||V_{\rm SE}||kLM\rangle = -\sum_{j=1}^{N}(E_0-\varepsilon_j)\langle\phi_j||kLM\rangle\langle k'L'M'||\phi_j\rangle, \tag{17}$$

where

$$\langle\phi_j||kLM\rangle = \int d\hat{\mathbf{k}}Y_{LM}(\hat{\mathbf{k}})\langle\phi_j|\mathbf{k}\rangle, \tag{18}$$
$$= 2^{\frac{3}{2}}i^L\sum_{i'l'm'\sigma\chi}(-1)^{\sigma}Y_{\sigma\chi}(\hat{\mathbf{R}}_{i'})\gamma^*_{i'l'm'}\int_0^{\infty}dr\,r^{2+l'}j_L(kr)\,{\rm e}^{-\alpha_{i'}(r^2+R_{i'}^2)}$$
$$\times i_{\sigma}(2\alpha_{i'}rR_{i'})\sqrt{\frac{(2\sigma+1)(2l'+1)}{(2L+1)}}C^{\chi m'M}_{\sigma l'L}C^{000}_{\sigma l'L}. \tag{19}$$

Similarly for $\langle k'L'M'||\phi_j\rangle$.

The reduced matrix elements of the polarization potential are

$$\langle k'L'M'||v_0||kLM\rangle$$
$$= \frac{2}{\pi}i^{L-L'}\int_0^{\infty}drr^2j_L(kr)j_{L'}(k'r)v_0(r), \tag{20}$$

$$\langle k'L'M'||v_2||kLM\rangle$$
$$= \frac{2}{\pi}i^{L-L'}\sqrt{\frac{2L+1}{2L'+1}}C^{0MM'}_{2LL'}C^{000}_{2LL'}$$
$$\times\int_0^{\infty}drr^2j_L(kr)j_{L'}(k'r)v_2(r). \tag{21}$$

TABLE I. The Cartesian-spherical transformation coefficients γ_{pnlm}.

p	l	m	γ_{pnlm}
1	0	0	$\sqrt{4\pi}$
2	0	0	$-\sqrt{4\pi}x_n$
	1	-1	$\sqrt{2\pi/3}$
	1	1	$-\sqrt{2\pi/3}$
3	0	0	$-\sqrt{4\pi}y_n$
	1	-1	$i\sqrt{2\pi/3}$
	1	1	$i\sqrt{2\pi/3}$
4	0	0	$-\sqrt{4\pi}z_n$
	1	0	$\sqrt{4\pi/3}$

VI. COMPUTATION OF CROSS SECTIONS

The differential cross section for exit channel i is

$$\left(\frac{d\sigma_{i0}}{d\Omega}\right) = (2\pi)^4\frac{k_i}{k_0}|\langle\mathbf{k}_i i|T|0\mathbf{k}_0\rangle|^2, \tag{22}$$

where $\mathbf{k}_0$ and $\mathbf{k}_i$ are the respective channel momenta. We use an abbreviated notation for the reduced T-matrix element, defined in analogy with (8):

$$T_{L'M'LM} \equiv \langle k_iL'M'||T||k_0LM\rangle. \tag{23}$$

For target molecules in the gas phase we assume random initial orientations and treat rotational excitation as an adiabatic process. This is equivalent to averaging the differential cross section over molecular orientations.

Following the work of Gallup [21] we transform our entrance and exit channel momenta $\mathbf{k}_0$ and $\mathbf{k}_i$, which are expressed in the body-fixed frame, into momenta $\mathbf{p}_0$ and $\mathbf{p}_i$ in the space-fixed (laboratory) frame. The transformation is effected by the rotation matrices.

$$\langle\mathbf{p}_i i|T|0\mathbf{p}_0\rangle = \sum_{LML'M'\mu\mu'}T_{L'M'LM}D^L_{M\mu}D^{L'\,*}_{M'\mu'}$$
$$\times Y_{L\mu}(\hat{\mathbf{p}}_0)Y^*_{L'\mu'}(\hat{\mathbf{p}}_i). \tag{24}$$

We choose the positive $\hat{\mathbf{z}}$ axis to be $\hat{\mathbf{p}}_0$.

The differential cross section is

$$\left(\frac{d\sigma_{i0}}{d\Omega}\right) = 4\pi^3 \sum_{L_1 M_1 L_1' M_1' \mu_1'} \sum_{L_2 M_2 L_2' M_2' \mu_2'} \left\{ \sqrt{(2L_1+1)(2L_2+1)} T_{L_1 M_1 L_1' M_1'} T^*_{L_2 M_2 L_2' M_2'} \right.$$
$$\times \delta_{\mu_1' \mu_2'} \delta_{M_1+M_2'\; M_1'+M_2} \sum_J \frac{1}{2J+1} C^{M_1\; M_2'\; M_1+M_2'}_{L_1\; L_2'\; J} C^{M_1'\; M_2\; M_1'+M_2}_{L_1'\; L_2\; J}$$
$$\left. \times C^{0\; \mu_2'\; \mu_2'}_{L_1\; L_2'\; J} C^{\mu_1'\; 0\; \mu_1'}_{L_1'\; L_2\; J} Y^*_{L_1' \mu_1'}(\hat{\mathbf{p}}_i) Y_{L_2' \mu_2'}(\hat{\mathbf{p}}_i) \right\}. \tag{25}$$

The integrated cross section for exit channel i is obtained by integrating the expression (25) over $\hat{\mathbf{p}}_i$.

$$\sigma_{i0} = 4\pi^3 \sum_{L_1 M_1 L_2 M_2 M_1' M_2' L} \left\{ T_{L_1 M_1 L M_1'} T^*_{L_2 M_2 L M_2'} \sum_{\mu J} \frac{1}{2J+1} C^{M_1\; M_2'\; M_1+M_2'}_{L_1\; L\; J} C^{M_1'\; M_2\; M_1+M_2'}_{L\; L_2\; J} C^{0\; \mu\; \mu}_{L\; L_2\; J} C^{\mu\; 0\; \mu}_{L\; L_2\; J} \right\}. \tag{26}$$

TABLE II. Differential cross sections for elastic scattering of electrons on H_2 (units are 10^{-18}cm^2/sr).

Scattering Angle (deg)	1 eV		15 eV		100 eV	
	SE	SEP	SE	SEP	SE	SEP
0	86.4	27.5	147.8	336.7	74.7	391.3
5	86.5	27.0	146.7	312.7	72.1	280.1
10	86.6	26.4	143.4	263.0	64.7	164.4
15	87.0	26.2	138.3	218.3	54.1	96.1
20	87.5	26.5	131.6	185.4	42.4	56.5
25	88.3	27.4	123.7	158.4	31.3	33.1
30	89.4	29.0	114.7	135.0	21.9	20.1
35	90.7	31.2	105.1	116.1	14.6	12.4
40	92.1	34.0	95.0	100.6	9.45	7.92
45	93.7	37.4	84.8	86.8	5.96	5.11
50	95.5	41.3	74.9	74.9	3.69	3.32
55	97.5	45.9	65.4	64.9	2.26	2.14
60	99.6	51.1	56.7	55.9	1.36	1.33
65	101.9	56.8	48.7	48.0	0.789	0.800
70	104.3	63.1	41.6	41.2	0.440	0.443
75	106.9	69.9	35.4	35.3	0.236	0.237
80	109.6	77.1	30.1	30.2	0.125	0.121
85	112.4	84.7	25.8	25.9	0.0682	0.0650
90	115.2	92.6	22.2	22.4	0.0397	0.0377
95	118.1	100.8	19.5	19.5	0.0256	0.0259
100	121.0	109.1	17.4	17.3	0.0201	0.0199
105	123.9	117.5	15.9	15.7	0.0203	0.0218
110	126.8	125.9	14.8	14.6	0.0244	0.0247
115	129.6	134.2	14.2	13.9	0.0310	0.0316
120	132.3	142.4	13.9	13.6	0.0394	0.0397
125	135.0	150.3	13.8	13.5	0.0481	0.0471
130	137.6	157.9	13.9	13.7	0.0546	0.0545
135	140.0	165.1	14.2	14.1	0.0580	0.0559
140	142.2	171.8	14.4	14.6	0.0598	0.0590
145	144.3	177.8	14.7	15.1	0.0626	0.0603
150	146.1	183.3	15.1	15.7	0.0676	0.0658
155	147.7	188.0	15.3	16.2	0.0737	0.0717
160	149.0	192.0	15.6	16.6	0.0796	0.0766
165	150.0	195.0	15.8	17.0	0.0850	0.0833
170	150.8	197.3	16.0	17.4	0.0904	0.0859
175	151.2	198.6	16.1	17.5	0.0950	0.0943
180	151.4	199.0	16.1	17.4	0.0968	0.0882

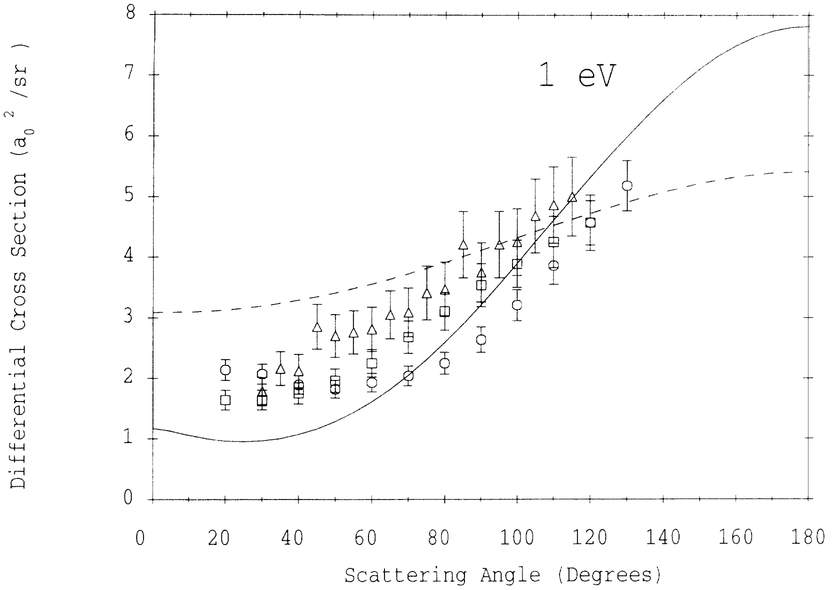

FIG. 1. H_2 elastic differential cross section for scattering at E_0= 1 eV. Theoretical: solid curve, SEP; dashed curve, static exchange. Experimental: ○, Ref. [23]; △, Ref. [24]; □, Ref. [25].

VII. DISCUSSION

A. On method

$(e,2e)$ studies [22] have shown that, to a very good approximation, molecular wave functions require only S, P, and D atomic orbitals in the LCAO description of the molecular SCF orbitals of the target. We use this description without further approximation. The method's applicability is, in theory at least, independent of molecular orbital shape or size so it can be applied to nonlinear, multiatomic molecules of any size. In practice, the computation required is large and increases with molecular size. There are ways around this problem. For large molecules, it is only necessary to accurately represent the valence orbitals, as the remaining orbitals, defining an inert core, do not critically affect the scattering, provided they are normalized and orthogonal. This removes the numerical problems which arise in the process of expressing the inner molecular orbitals in an accurate linear combination of basis Gaussians, by keeping otherwise large primitive Gaussian exponents small. Large exponents produce functions too peaked for accurate numerical integration and numbers too large for the computer to manage. In the case of hydrogen, no approximation of this type was necessary as exponents were small enough in any case.

It would be computationally advantageous if the calculation could be segmented into a product of a reaction-dependent expression, made up of functions of the incident and outgoing projectile momenta, and a static factor containing complete structural information on the molecule. This would allow a one-time calculation for

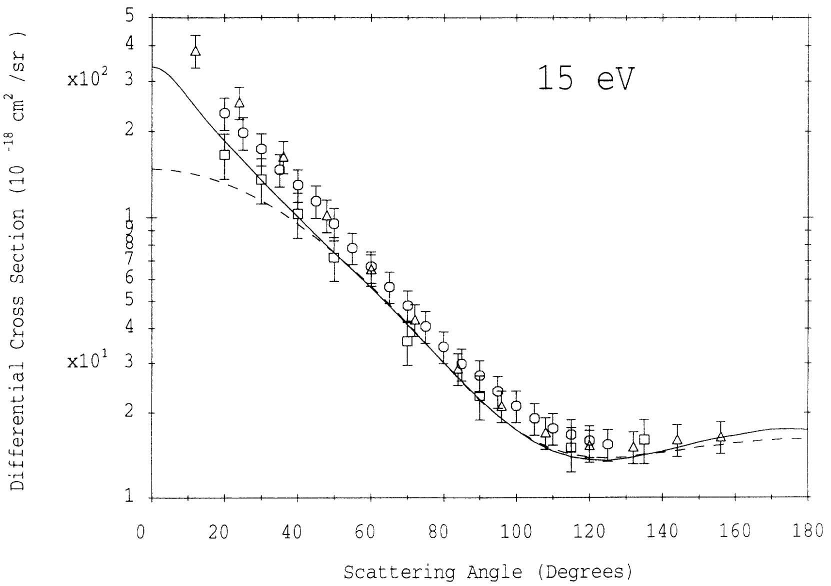

FIG. 2. H_2 elastic differential cross section for scattering at E_0= 15 eV. Theoretical: solid curve, SEP; dashed curve, static exchange. Experimental: ○, Ref. [26]; □, Ref. [27]; △, Ref. [28].

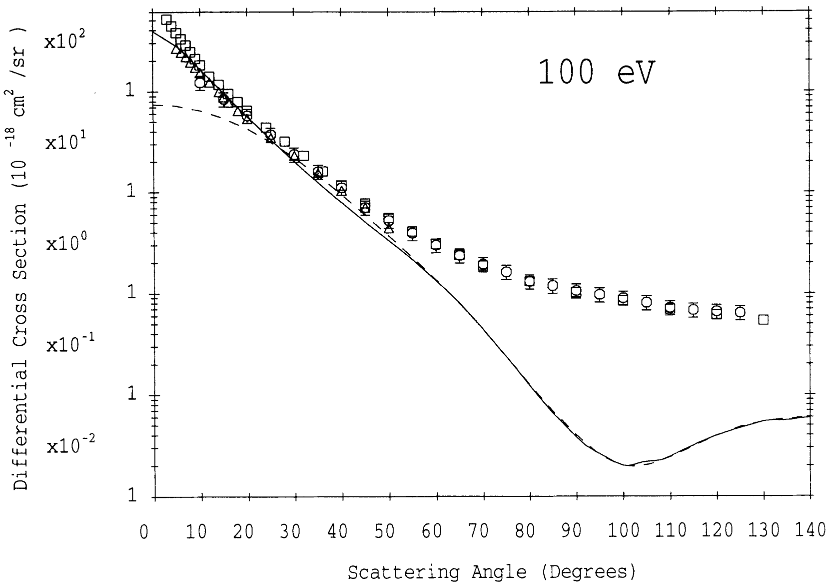

FIG. 3. H_2 elastic differential cross section for scattering at E_0= 100 eV. Theoretical: solid curve, SEP; dashed curve, static exchange. Experimental: ○, Ref. [26]; □, Ref. [29]; △, Ref. [30].

the static functions which would be stored permanently and then recalled repeatedly for the complete calculation at different electron impact energies. This is in fact the case for the evaluation of the direct V-matrix elements in Eqs. (13) and (14). The $F_{\lambda\mu}$ functions possess all the structural detail of the molecule and do not depend on reaction conditions. The greater part of the total computation time would be due to these functions if repeated evaluation was required. This leads to a significant saving in computer time. Unfortunately, the nonseparable exchange matrix elements cannot be dealt with so easily and repeated calculation of the full expression given by Eqs. (15) and (16) is necessary.

The summation over σ, χ or ρ, ζ in Eqs. (14), (19), (15), and (16) is pivotal to the convergence of the total calculation for the direct and exchange matrix elements. The sum is terminated when the Gaussian-Bessel function product

$$e^{-\alpha r^2} i_\sigma(2\alpha r R_i) \qquad (27)$$

is negligibly small for all r. A cutoff value of $\sigma = 6$ was found to be sufficient in all cases.

Little variation was found in the differential cross sections as a result of the implementation of the different forms for the polarization potential outlined in Sec. II. The results were in general, and to a good approximation, insensitive to the differing parameter values and radial structure of the models tested. Where a difference existed, better results were obtained through the exclusion of the nonspherical term in the truncated Legendre expansion of Eq. (5).

B. On numerical analysis

Coupling between partial waves was observed to become negligible beyond $L = 6$ to better than 1% accuracy for the hydrogen molecule. Selection rules were responsible for the fact that off-diagonal V-matrix elements with odd partial-wave quantum number L or L' and M or $M' \neq 0$ were zero. All numerical integrations were performed to an accuracy of at least 1%, usually significantly better. The quadrature meshes used at each incident energy to solve the Lippmann-Schwinger equation were checked for stability against number of points and range of integration. A range of 10 a.u. was found to be universally adequate. 20, 13, and 10 quadrature points were used at 1 eV, 15 eV, and 100 eV, respectively. The $H^{LM}_{\lambda\mu}$ functions of Eq. (16) were interpolated using cubic splines before substitution into Eq. (15). Once again the error introduced was less than 1%.

TABLE III. Integrated cross sections for elastic electron scattering on H_2 (10^{-18} cm^2). Numbers in parentheses refer to the percentage error.

Energy (eV)	Present results	Expt. 1[a]	Expt. 2[b]	Expt. 3[c]	Expt. 4[d]	Expt. 5[e]	Expt. 6[f]	Expt. 7[g]
1	1258.2			1459.0(8)	1420(13)			
15	572.7	704.0(16)				554.0(18)	561.0(13)	717.0(20)
100	80.8	83.4(19)	88.8(10)				77.0(13)	64.8(15)

[a] Reference [26].
[b] Reference [29].
[c] Reference [23].
[d] Reference [24].
[e] Reference [27].
[f] Reference [28].
[g] Reference [31].

VIII. RESULTS AND EXPERIMENTAL COMPARISON

Table II gives the theoretical differential cross sections for electron scattering from the hydrogen molecule at incident energies of 1 eV, 15 eV, and 100 eV with (SEP) and without (SE) polarization supplementing the static-exchange model. Figures 1–3 show the curves at these energies. Experimental results are indicated. The dashed line is for the static-exchange calculation and the solid curve includes polarization. Integrated elastic cross sections at these energies are given in Table III.

It is clear that, even though approximate, the polarization potential, at all incident energies, has a profound effect on the cross section especially at forward scattering angles. We conclude that virtual excitation is important in electron-molecule scattering and must be described accurately. Our intention is to further develop this method with the inclusion of an *ab initio* complex, nonlocal polarization potential. We expect that this will lead to better agreement with experiment. Agreement at intermediate to high energies and at backward scattering angles should improve with the development of a complete theory taking all channels into account.

ACKNOWLEDGMENTS

We would like to acknowledge support from the Australian Research Council. We thank G. A. Gallup for use of his program and his time in helping us with the spherical averaging of the differential cross section, and Igor Bray for his many helpful suggestions and constant assistance with programming and numerical analysis.

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