An *ab initio*, momentum-space optical potential for electron–molecule scattering

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Abstract. The polarization potential describing the effect of higher reaction channels on electron–molecule elastic scattering is approximated by an *ab initio* equivalent-local potential. It is added to the exact static-exchange potential for a momentum-space calculation of $e^- - H_2$ scattering. The static-exchange-optical (SEO) model which results is implemented for the selected incident energies 5, 10, 30 and 80 eV for the hydrogen molecule. Differential and integrated elastic cross sections are compared with available experimental data.

1. Introduction

The static-exchange model is incomplete in that it does not include the second-order effect arising from real and virtual excitation of target states. The polarization potential so induced is important in that it contributes significantly to the scattering problem, particularly at low energies and for forward scattering at intermediate energies. It is also the potential most difficult to include properly due to the dynamic (non-adiabatic) nature of the interaction it represents. A variety of methods have been employed in trying to define an accurate polarization potential (Lane 1980), including simple semi-empirical analytic formulae, elaborate close-coupling techniques, cut-off asymptotic forms and the optical potential method (Burke *et al* 1983, Schneider and Collins 1983, Gibson and Morrison 1982).

Here we derive a complex, local and *ab initio* optical potential for use within the coupled channels formalism.

2. Formal theory

A complete theory of scattering within the coupled channels formalism requires the solution of a set of coupled integral equations where coupling occurs between all channels, open and closed. The fact that all channels are coupled suggests that unobserved channels have an effect on observed channels. Real excitation of unobserved channels is known as absorption. It removes flux from observed channels. Virtual excitation of unobserved channels is referred to as polarization of the target. The optical potential is used to take both into account.

The problem is formulated in terms of a finite set of Lippmann–Schwinger integral equations for transitions between a finite discrete set of channels (in the present derivation

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only the elastic channel is incorporated) projected from the whole space by an operator P, which acts on the target, ψ_0.

Target states are expressed in the independent-particle model using SCF orbitals that are linear combinations of primitive Gaussians centred at the atomic sites. We use closure over the vibrational and rotational states. The nuclei are assumed to be fixed at their equilibrium sites. Electron correlation in the target may be ignored to a very good degree of accuracy as validated by several (e, 2e) reactions on molecules (see Weigold *et al* 1977a, b, Brion *et al* 1984).

The remaining channels including the continuum are projected by the complementary operator, Q:

$$P + Q = 1. \tag{1}$$

P-space always includes the entrance channel, and may include other channels strongly coupled to it. Here only the former is taken into account:

$$P = |\psi_0\rangle\langle\psi_0|. \tag{2}$$

The Schrödinger equation may be written with the definitions $V = V_N + V_{ee}$ and $K = K_0 + H_T$, where: K_0 is the kinetic energy operator; V_{ee} is the electron–electron potential; V_N is the potential due to the nuclei, and H_T is the target Hamiltonian, for the total scattering wavefunction $\Psi^{(+)}$,

$$(E - K)|\Psi^{(+)}\rangle = V|\Psi^{(+)}\rangle. \tag{3}$$

We introduce the unit operator (1) and operate on the left with P:

$$P(E - K)(P + Q)|\Psi^{(+)}\rangle = PV(P + Q)|\Psi^{(+)}\rangle. \tag{4}$$

We rearrange this expression using

$$P(E - K)Q|\Psi^{(+)}\rangle = 0. \tag{5}$$

This equation follows from the fact that P commutes with $E - K$ since they operate on different parts of the channel space and

$$PQ = 0 \tag{6}$$

since Q-space does not include any of the states in P-space. The rearranged form of (4) is

$$P(E - K - V)P|\Psi^{(+)}\rangle = PVQ|\Psi^{(+)}\rangle. \tag{7}$$

Similarly

$$Q(E - K - V)Q|\Psi^{(+)}\rangle = QVP|\Psi^{(+)}\rangle. \tag{8}$$

Using the projection operator identity

$$Q^2 = Q \tag{9}$$

and defining the appropriate inverse operator we formally solve (8) for $Q|\Psi^{(+)}\rangle$:

$$Q|\Psi^{(+)}\rangle = Q\frac{1}{Q(E^{(+)} - K - V)Q}QVP|\Psi^{(+)}\rangle. \tag{10}$$

We now define the polarization potential W by substituting $Q|\Psi^{(+)}\rangle$ from (10) into the P-projected set of equations (7). Then

$$P(E - K - V)P|\Psi^{(+)}\rangle = PWP|\Psi^{(+)}\rangle \tag{11}$$

where W is defined by

$$PWP|\Psi^{(+)}\rangle = P\left[VQ\frac{1}{Q(E^{(+)} - K - V)Q}QV\right]P|\Psi^{(+)}\rangle. \tag{12}$$

The new set of integral equations for the scattering wavefunction $\Psi^{(+)}$ may now be derived:

$$\langle k'0|T|0k\rangle = \langle k'0|V + W|0k\rangle + \int d^3q \sum_j \langle k'0|V + W|jq\rangle \frac{1}{E^{(+)} - \frac{1}{2}q^2 - \varepsilon_j} \langle qj|T|0k\rangle .$$

(13)

To implement the calculation of the polarization matrix elements $\langle k'0|W|0k\rangle$ we first make the approximation of weak coupling of channels for which the target state is in Q-space. The time-reversed state vector for scattering with entrance channel n is denoted $|\Psi_n^{(-)}\rangle$. Here n is a discrete notation for a one- or two-body continuum. The projection operator Q in this notation is

$$Q = \sum_n |\Psi_n^{(-)}\rangle\langle\Psi_n^{(-)}|$$

(14)

and the approximation gives

$$\langle k'0|W|0k\rangle = \sum_{n\in Q} \langle k'0|V|\Psi_n^{(-)}\rangle \frac{1}{E^{(+)} - E_n} \langle\Psi_n^{(-)}|V|0k\rangle .$$

(15)

Note that (14) contains exact amplitudes for the excitation of channel n from the entrance channel. We proceed by making the Born approximation for these amplitudes. This high-energy approximation has proved excellent for optical-potential matrix elements in electron–atom scattering (McCarthy *et al* 1981)

$$\langle\Psi_n^{(-)}(q)|V|0k\rangle = \langle qn|V|0k\rangle .$$

(16)

Substituting (16) in (15) we obtain for the present case where P-space consists only of the ground state 0,

$$\langle k'0|W|0k\rangle = \int d^3q \left(\sum_n \langle k'0|V|nq\rangle \frac{1}{E^{(+)} - \varepsilon_n - \frac{1}{2}q^2} \langle qn|V|0k\rangle \right.$$
$$\left. - \langle k'0|V|0q\rangle \frac{1}{E^{(+)} - \varepsilon_0 - \frac{1}{2}q^2} \langle q0|V|0k\rangle \right) .$$

(17)

We treat the first term of (17) by the closure approximation, which replaces ε_n by a state-independent parameter ε, thereby eliminating the target states n by the closure theorem

$$\sum_n |n\rangle\langle n| = 1 .$$

(18)

The parameter ε represents the average energy of the effectively excited target states.

We make one further extension to the high energy approximation by replacing ε_0 with ε in (17). This significantly simplifies the numerical analysis. It is expected to hold well in the scattering domain we are considering.

The total optical potential matrix element for elastic channel scattering with incident and outgoing momenta, k and k', respectively, is then

$$\langle k'0|W|0k\rangle = \langle k'0|W_C|0k\rangle - \langle k'0|W_0|0k\rangle$$

(19)

or in function notation

$$W(k', k) = W_C(k', k) - W_0(k', k) .$$

(20)

3. The equivalent local-central polarization potential

In the Green function closure approximation the higher state energy eigenvalues ε_i are replaced by an 'average' value ε. In practice the optical potential is insensitive to values of ε in a realistic range and we set $\varepsilon = 0$, thereby stating that the average energy lies at the ionization threshold:

$$\langle k'0|W_C|0k\rangle = \int d^3q \int d^3r \langle k'0|V|rq\rangle \frac{1}{E^{(+)} - \varepsilon - \frac{1}{2}q^2} \langle qr|V|0k\rangle. \quad (21)$$

The closure approximation is expected to be valid at incident energies several times the ionization threshold. At such energies exchange amplitudes are relatively unimportant in (21) and are omitted.

$$\langle k'0|W_C|0k\rangle = \left(\int d^3q \frac{1}{2\pi^2|k - q|^2} \frac{1}{2\pi^2|k' - q|^2} G_\varepsilon^{(+)}(q) \right)$$
$$\times \left(\int d^3r |\psi_0(r)|^2 e^{-i(k'-k)\cdot r} \right). \quad (22)$$

The Green function notation is defined by

$$G_\varepsilon^{(+)}(q) = \frac{1}{E^{(+)} - \varepsilon - \frac{1}{2}q^2} \quad (23)$$

where E is the total energy of the projectile–target system, and ε is the closure energy parameter:

$$\langle k'0|W_0|0k\rangle = \left(\int d^3q \frac{1}{2\pi^2|k - q|^2} \frac{1}{2\pi^2|k' - q|^2} G_\varepsilon^{(+)}(q) \right)$$
$$\times \left(\int d^3r \, e^{-i(k'-q)\cdot r} |\psi_0(r)|^2 \right) \left(\int d^3r \, e^{i(k-q)\cdot r} |\psi_0(r)|^2 \right). \quad (24)$$

In both expressions (22) and (24) a form factor must be evaluated. We label this integral $\Xi(K)$ and define it with

$$\Xi(K) = \int d^3r \, e^{-iK\cdot r} |\psi_0(r)|^2. \quad (25)$$

Making the definition

$$P = k' - k \quad (26)$$

for the momentum transfer,

$$W_C(k, P) = \Xi(P) \int d^3q \frac{1}{2\pi^2|k - q|^2} \frac{1}{2\pi^2|k + P - q|^2} G_\varepsilon^{(+)}(q)$$
$$\equiv \Xi(P) \int d^3q \, \Lambda(k, P, q) \quad (27)$$

making a notational definition for Λ.

In the same notation, the ground-state optical matrix element becomes

$$W_0(k, P) = \int d^3q \, \Lambda(k, P, q) \Xi(k + P - q) \Xi(q - k). \quad (28)$$

Combining the two expressions above gives

$$W(k, P) = \int d^3q \, \Lambda(k, P, q)(\Xi(P) - \Xi(k' - q)\Xi(q - k)). \quad (29)$$

The Green function may be re-expressed in terms of a principal value and a delta function,

$$\frac{1}{E^{(+)} - \varepsilon - \frac{1}{2}q^2} = \frac{1}{E_C^{(+)} - \frac{1}{2}q^2}$$

$$= \mathcal{P}\frac{1}{\frac{1}{2}(k_C^2 - q^2)} - \frac{i\pi}{k_C}\delta(k_C - q) \tag{30}$$

where

$$E_c = E_0 + \varepsilon_0 - \varepsilon \equiv \frac{1}{2}k_C^2. \tag{31}$$

For scattering below the threshold energy, i.e. for $E_c \leqslant 0$ the imaginary term vanishes as does the singularity at $k_C = q$. Then the Green function is real and given by

$$\frac{1}{E^{(+)} - \varepsilon - \frac{1}{2}q^2} = -\frac{1}{\frac{1}{2}(k_C^2 + q^2)}. \tag{32}$$

At this point we make a local, central approximation to the form factor in an attempt to make the calculation tractable. In the special atomic case of spherically symmetric potentials it is exact.

It follows from (25) and the expansion of the plane wave in terms of spherical Bessel functions that averaging over all solid angles in momentum space gives

$$\overline{\Xi}(P) = (4\pi)^{-1} \int d\hat{P}\, \Xi(P)$$

$$= \int_0^{\infty} dr\, r^2 j_0(Pr) \int d\hat{r}\, |\psi_0(r)|^2. \tag{33}$$

Here j_0 is the spherical Bessel function of order zero. For future reference we name this approximation the spherical form factor approximation (SFFA). Using the expansions outlined in McCarthy and Rossi (1994) we arrive at the following:

$$\overline{\Xi}(P) = 16\pi^2 \sum_{\substack{ijk \\ lml'm' \\ \sigma\xi\rho\zeta}} c_{kj}c_{ij}\gamma_{kl'm'}\gamma_{ilm}(-)^{\rho+\sigma}Y_{\rho\zeta}^*(\hat{R}_i)Y_{\sigma\xi}^*(\hat{R}_k)A_{mm'\xi\zeta}^{ll'\sigma\rho}$$

$$\times \int_0^{\infty} dr\, \frac{r^{l+l'+1}\sin(Pr)}{P}e^{-\alpha_k(r^2+R_k^2)}e^{-\alpha_i(r^2+R_i^2)}i_\sigma(2\alpha_k r R_k)i_\rho(2\alpha_i r R_i) \tag{34}$$

where

$$A_{mm'\xi\zeta}^{ll'\sigma\rho} = \sum_{st}\frac{\sqrt{(2l'+1)(2\rho+1)(2\sigma+1)(2l+1)}}{4\pi(2s+1)}C_{\rho l's}^{\zeta m't}C_{\rho l's}^{000}C_{\sigma ls}^{\xi mt}C_{\sigma ls}^{000}. \tag{35}$$

Note here that the summation over i and k in (34) effectively removes dependence on the atomic site coordinates as it must if $\overline{\Xi}(P)$ is to be independent of the nuclear orientation and thus spherically symmetric in momentum space.

The optical potential of (29) is now averaged over the angles of $\hat{P}$. This makes it local and central in coordinate space. Experience with phenomenological polarization potentials shows that anisotropic second-order terms in the optical potential play a relatively minor role with very little effect on cross sections. Then, one further approximation is made in order to separate the Λ function from the remaining factors of $\overline{\Xi}$. In the event that either of these

functions is sufficiently isotropic in angular distribution the following general expression holds, for some arbitrary functions A and B:

$$(4\pi)^{-1} \int d\hat{P} \, A(P)B(P) \approx (4\pi)^{-2} \left(\int d\hat{P}' A(P') \right) \left(\int d\hat{P} \, B(P) \right) \quad (36)$$

noting that $|P'| = P$. This is exact once again when either A or B is isotropic in angular distribution. This is equivalent to saying that the potential is radial in coordinate space as either A or B is its Fourier transform. We call this the spherically separable approximation (SSA).

Then, implementing the SSA and SFFA gives

$$W_C(k, P) \approx (4\pi)^{-1} \overline{\Xi}(P) \int d^3q \left(\int d\hat{P} \, \Lambda(k, P, q) \right)$$

$$W_0(k, P) \approx (4\pi)^{-2} \int d^3q \left(\int d\hat{P} \, \Lambda(k, P, q) \right) \left(\int d\hat{P} \, \overline{\Xi}(|k + P - q|) \overline{\Xi}(|q - k|) \right) .$$

$$(37)$$

4. The spherical averaging of $\Lambda(k, P, q)$

$$\Lambda(k, P, q) = \int d\hat{P} \, \Lambda(k, P, q)$$

$$= \frac{1}{2\pi^2 |k - q|^2} G_\varepsilon^{(+)}(q) \int d\hat{P} \, \frac{1}{2\pi^2 |k + P - q|^2} . \quad (38)$$

We make a spherical harmonic expansion,

$$\frac{1}{|k + P - q|^2} = (2\pi) \sum_{lm} \Upsilon_l(|k - q|, P) \widehat{\langle k - q|lm \rangle} \langle lm|\hat{P} \rangle \quad (39)$$

where

$$\Upsilon_l(k, q) = \int_{-1}^{1} dx \, \frac{P_l(x)}{k^2 - 2kqx + q^2} . \quad (40)$$

Integrating over the angles of P and evaluating Υ_0 analytically gives

$$\int d\hat{P} \, \frac{1}{|k + P - q|^2} = (2\pi) \Upsilon_0(|k - q|, P)$$

$$= \frac{\pi}{KP} \left[\ln(K^2 + P^2 + 2KP) - \ln(K^2 + P^2 - 2KP) \right] \quad (41)$$

where $K = |k - q|$. This leads to our final expression for the optical potential,

$$W(k, P) = \int d^3q \, \Gamma(k, P, q) G_\varepsilon^{(+)}(q) \quad (42)$$

where we have defined

$$\Gamma(k, P, q) = \frac{\ln(K^2 + P^2 + 2KP) - \ln(K^2 + P^2 - 2KP)}{16\pi^4 K^3 P}$$

$$\times \left[\overline{\Xi}(P) - (4\pi)^{-1} \overline{\Xi}(K) \int d\hat{P} \, \overline{\Xi}(|K + P|) \right] . \quad (43)$$

Removing the singularity via on-shell subtraction (see McCarthy and Stelbovics 1983) and expanding the Green function using (30) produces the final complex form,

$$W(k, P) = \left[\int d^3q \, \frac{\Gamma(k, P, q) - \Gamma(k, P, k_C)}{\frac{1}{2}(k_C^2 - q^2)} \right] - i\pi k_C \int d\hat{q} \, \Gamma(k, P, k_C) . \tag{44}$$

where $\hat{k}_C = \hat{q}$. k defines the incident direction and is fixed in the laboratory frame to lie along the $\hat{z}$-axis.

5. The optical potential reduced matrix elements

The reduced matrix elements can now be found directly from the multipole component of $W(P)$. We fix the incident wavevector k to lie along the z-axis so it has been removed from the argument list, being a constant of the scattering problem:

$$\langle k'LM \| W \| kLM \rangle = (2\pi) \int_{-1}^{1} dx \, W(P) P_L(x) \tag{45}$$

where $P^2 = k'^2 + k^2 - 2kk'x$ and $P_L(x)$ are the Legendre polynomials. The total reduced V-matrix element for the static-exchange plus optical potential (SEO) calculation is

$$\langle k'L'M' \| V \| kLM \rangle = \langle k'L'M' \| V_D \| kLM \rangle - \frac{1}{2} \langle k'L'M' \| V_E \| kLM \rangle$$
$$+ \langle k'L'M' \| W \| kLM \rangle \delta_{MM'} \delta_{LL'} . \tag{46}$$

6. Results and discussion

Figure 1 shows the DCS for elastic scattering from H_2 at 5, 10, 30 and 80 eV. Due to the fact that the high energy approximations made for the optical potential are not strictly valid for scattering energies below several times threshold, only the real part was kept in the calculation at 30 eV. For $\varepsilon = 0$ the threshold lies at 16.11 eV. Below threshold the imaginary part disappears and the real part was found to display the correct asymptotic behaviour typical of an induced dipole potential, namely

$$V(r) = -\frac{\alpha_0}{2r^4} \tag{47}$$

where $\alpha_0 = 5.2$ au is the dipole polarizability for the hydrogen molecule.

At 5 eV agreement within experimental error is comprehensive over the full angular range. For small angle scattering the present curve agrees with all but the data of Srivastava *et al* (1975). At backward scattering agreement with the points of Shyn and Sharp (1981) is excellent whilst disagreement with the group of Brunger *et al* (1991) appears to increase with angle.

At 10 eV our curve disagrees at extreme backward scattering with the only available data of Shyn and Sharp (1981). At intermediate angles there exists a discrepancy between the points of Furst *et al* (1984) and Shyn and Sharp (1981) with our curve favouring the former, hence disagreeing with the latter for all but a small angular range. The curve overestimates by at most 30% all the experimental data for angles $\leqslant 60°$. No agreement exists with the results of Linder and Schmidt (1971) although they report the smallest error in their measurements of 5%; too small to appear on the plot.

At 30 eV the DCS lies within experimental error for all angles $\leqslant 100°$. A dipping of the curve below experiment occurs for backward scattering angles centred at about 130°.
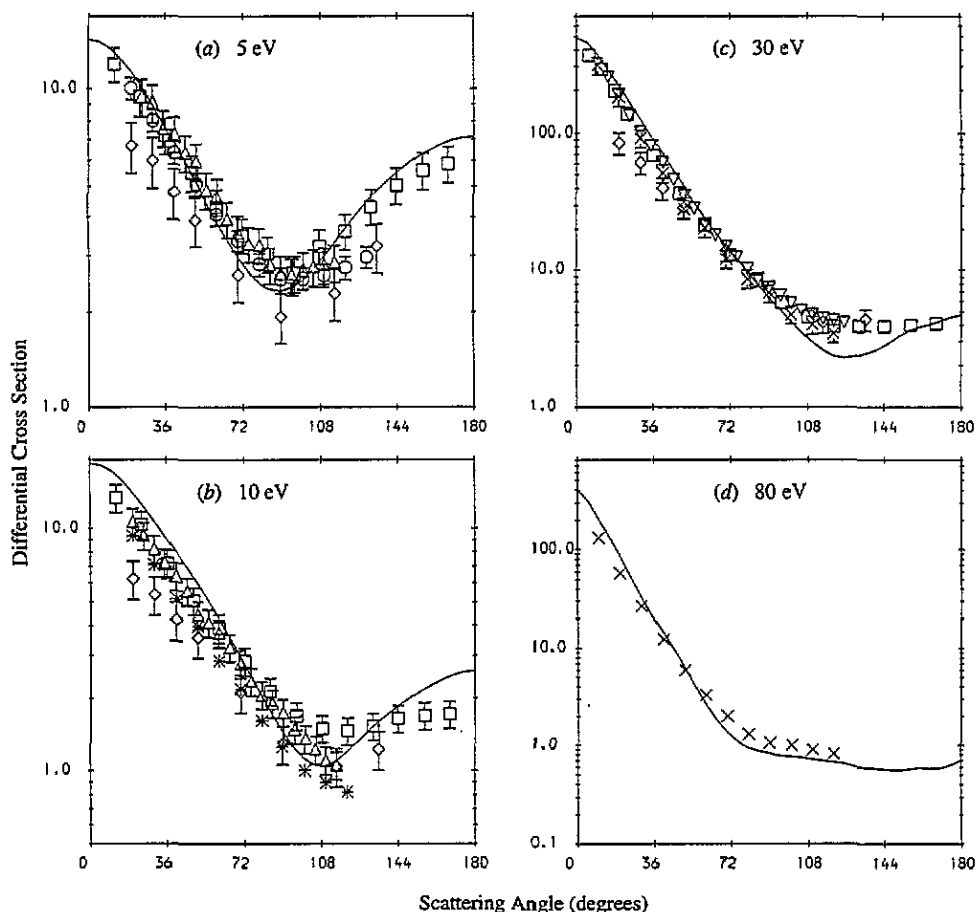
Figure 1. H_2 elastic differential cross section at incident energies: (a) 5 eV (a_0^2 sr^{-1}) (b) 10 eV (a_0^2 sr^{-1}) (c) 30 eV (10^{-18} cm^2 sr^{-1}) (d) 80 eV (10^{-18} cm^2 sr^{-1}). Present work: full curve, SEO. Experimental: ◯, Brunger *et al* (1991); △, Furst *et al* (1984); □, Shyn and Sharp (1981); ▽, Khakoo and Trajmar (1986); ∗, Linder and Schmidt (1971); ◊, Srivastava *et al* (1975); ×, Nishimura *et al* (1985).

The data of Srivastava *et al* (1975) disagrees significantly with all other experimental data at low angles and so is not taken into account.

At 80 eV the DCS has the correct form but disagrees at very small angles by as much as 30% and at intermediate angles by no more than 10%.

Table 1 shows integrated elastic cross sections comparing the results with experiment and the theoretical model of Gibson and Morrison (1984). The present SEO data lie within experimental error except at an incident scattering energy of 80 eV where it overestimates the error bar of Nishimura *et al* (1985) by 2%. The static-exchange-polarization (SEP) calculation of Gibson and Morrison (1984) incorporates an *ab initio*, parameter-free polarization potential based on the variational method with an approximate treatment of non-adiabatic effects. It is applied to low energy scattering from H_2. Interpolation of the data was required for comparison with the present values for the integrated cross sections at 5 and 10 eV. Multipoles up to $\lambda = 24$ were retained in the non-adiabatic polarization potential expansion to achieve the best comparison with our calculations. Agreement

between these two very different methods can be seen to be good at this level and very good with experiment.

Table 1. Integrated cross sections for elastic electron scattering on H_2 (10^{-18} cm^2) in the SE and SEO approximations. Numbers in parentheses refer to the percentage error.

Energy (eV)	SE	SEO	Theory[a]	Expt 1[b]	Expt 2[c]
5.0	1137.6	1593.7	1502.2		1390.0(8)
10.0	733.8	1246.8	1009.8		
30.0	246.8	379.9		363(16)	
80.0	78.09	106.3			

Energy (eV)	Expt 3[d]	Expt 4[e]	Expt 5[f]	Expt 6[g]
5.0	1520.0(10)	1110.0(18)	1590.0(13)	
10.0	1020.0(8)	768.0(18)	1129.0(13)	1010.0(15)
30.0		224.0(18)	336.0(13)	325.0(20)
80.0				86.6(20)

[a] Gibson and Morrison (1984).
[b] Khakoo and Trajmar (1986).
[c] Brunger *et al* (1991).
[d] Furst *et al* (1984).
[e] Srivastava *et al* (1975).
[f] Shyn and Sharp (1981).
[g] Nishimura *et al* (1985).

7. Conclusions

The static-exchange-optical model has been shown to be very good at describing scattering from the hydrogen molecule over a wide range of incident electron energies. Some discrepancies still exist and this may be linked to error introduced by the local, high energy approximations made in the optical potential. There is hope that improvements here will remove any remaining disagreements.

Acknowledgments

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