

## LETTER TO THE EDITOR

# A parameter-free non-adiabatic polarisation potential for low-energy e–H<sub>2</sub> collisions

Thomas L Gibson and Michael A Morrison

Department of Physics and Astronomy, University of Oklahoma, Norman, Oklahoma 73019, USA

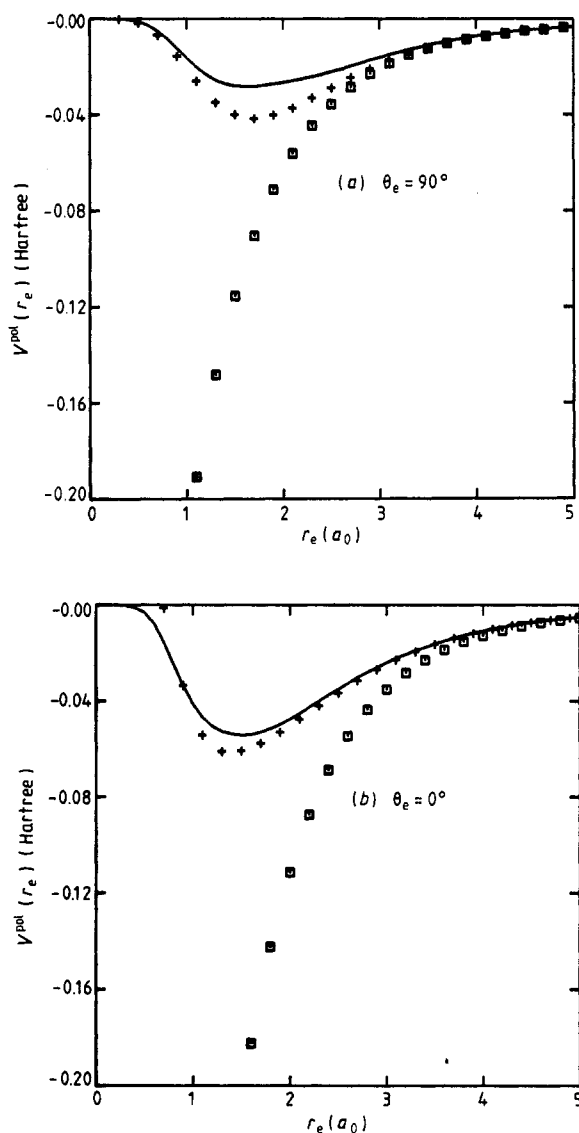
Received 21 December 1981

**Abstract.** We have determined an *ab initio*, approximate, non-adiabatic polarisation potential for the e–H<sub>2</sub> system. The scattering results using this polarisation potential together with an accurate static model exchange potential are found to be in very good agreement with a variety of recent experimental measurements. In addition, an analytic fit of our polarisation potential is presented.

An accurate representation of the electron–molecule interaction potential, which consists of static, exchange and polarisation contributions, is necessary for a detailed study of low-energy collisions (Lane 1980). The dominant, short-range, static potential can be efficiently determined at the near-Hartree–Fock level of accuracy from the electronic wavefunction of the target (Morrison 1980, Collins *et al* 1980). For e–H<sub>2</sub> collisions, the non-local exchange interaction can be accurately included by a local, energy-dependent model exchange potential (Gibson and Morrison 1981, Weitzel *et al* 1981).

The induced polarisation interaction, which is a second-order effect arising from the distortion of the target by the scattering electron, is the most difficult of the three contributions to include properly; the principal difficulty arises from the dynamic (non-adiabatic) nature of this interaction. Polarisation effects have often been represented by a semiempirical approximation based on the known asymptotic form of this potential. In order to simulate non-adiabatic effects, the semiempirical form contains an adjustable cut-off parameter,  $r_c$ , which can be ‘tuned’ (cf Morrison *et al* 1977) to bring the calculated cross sections into agreement with some experimentally determined feature of the scattering (e.g., a shape resonance). Alternatively,  $r_c$  may be chosen to coincide with the approximate radius of the molecular charge cloud. Accurate *ab initio* studies of the polarisation interaction (Morrison and Hay 1979, Truhlar *et al* 1979) have demonstrated some of the inaccuracies associated with the semiempirical approach. However, in these studies, the motion of the scattering electron was assumed to be strictly adiabatic. This assumption leads to unphysically strong potentials near the molecular target, where non-adiabatic corrections are expected to be largest (cf figure 1).

Polarisation potentials including approximate non-adiabatic effects have been generated by Lane and Henry (1968) and Hara (1969b). In order to obtain the proper asymptotic behaviour, both of these potentials had to be scaled, thereby introducing some uncertainty into the short- and intermediate-range regions (Lane 1980). More



**Figure 1.** Polarisation potentials for the following cases: in figure 1(a) the scattering electron approaches along a perpendicular bisector of the internuclear axis  $\theta_e = \pi/2$ ; in figure 1(b) the scattering electron approaches along the internuclear axis  $\theta_e = 0$ . The calculations shown include the present non-penetrating dipole potential (—), the scaled non-penetrating dipole potential of Hara (1969b) (+), and the strictly adiabatic potential of the present work ( $\square$ ).

recently, Schneider (1977), using a pseudostate approach, and Klonover and Kaldor (1978), using a second-order optical potential, have calculated low-energy, static-exchange-polarisation (SEP) scattering results in which non-adiabatic effects were included at various levels of approximation.

In this letter we report a new *ab initio* polarisation potential that contains an approximate treatment of non-adiabatic effects and SEP cross sections for e-H<sub>2</sub>

scattering determined using this potential. For these calculations, the internuclear separation  $R$  was fixed at its equilibrium value,  $1.4 a_0$ ; unless otherwise stated, atomic units<sup>†</sup> are used throughout. Our treatment of polarisation utilises a self-consistent-field (SCF) technique (see Morrison and Hay 1979 and references therein) in which the second-order Hartree–Fock energy of the perturbed molecule is variationally minimised. The molecular target is represented by a near-Hartree–Fock wavefunction for the ground ( $X^1\Sigma_g^+$ ) state that we determined from a (6s3p/4s3p) set of Cartesian–Gaussian basis functions. This wavefunction yields the (unperturbed) ground-state energy  $-1.13295 E_h$  and the polarisabilities  $\alpha_\perp = 4.54 a_0^3$ ,  $\alpha_\parallel = 6.53 a_0^3$ . These values may be compared with the accurate configuration interaction (CI) values of Kolos and Wolniewicz (1965, 1967):  $-1.17447 E_h$ ,  $\alpha_\perp = 4.578 a_0^3$  and  $\alpha_\parallel = 6.381 a_0^3$ .

To calculate a polarisation potential in the *adiabatic approximation*, one fixes the position of the scattering electron relative to the centre of mass of the molecule and then calculates the energy lowering due to this stationary point charge (cf Morrison and Hay 1979). For low-energy collisions, the adiabatic approximation is expected to work well when the scattering electron is far from the target. However, as the scattering electron approaches the molecule it experiences more of the attractive static exchange potential, thereby gaining a ‘local kinetic energy’ comparable with that of the bound electrons. The approximation that the target relaxes adiabatically in the field of a stationary scattering electron becomes less valid as the distance between the molecule and the projectile electron decreases.

In the present calculation, *non-adiabatic effects* are approximated by a ‘cut-off’ (non-penetrating) procedure (Temkin 1957, Lane and Henry 1968) and by the exclusion of one of the multipole contributions from the polarisation potential. The non-penetrating procedure is implemented by truncating certain integrals involved in computing the second-order Hartree–Fock energy of the perturbed molecule. These integrals have the form

$$I = \langle \eta'(r) | -1/|r - r_e| | \eta(r) \rangle dr \quad (1)$$

where  $\eta$  and  $\eta'$  are nucleus-centred Gaussian-type orbitals. In equation (1)  $|r - r_e|$  is the distance from the scattering electron at position  $r_e$  to the bound-electron charge density at  $r$ , both coordinates being measured in a body-fixed reference frame with the origin at the molecular centre of mass. In performing these integrals (within the non-penetrating approximation) we make use of the expansion

$$\frac{1}{|r - r_e|} = \begin{cases} \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \left( \frac{4\pi}{2\lambda+1} \right) \frac{r^\lambda}{r_e^{\lambda+1}} Y_{\lambda}^{\mu*}(\hat{r}) Y_{\lambda}^{\mu}(\hat{r}_e) & r < r_e \\ 0.0 & r > r_e. \end{cases} \quad (2a)$$

$$(2b)$$

The use of this expansion effectively ‘cuts off’ the interaction between the scattering electron and the bound electron whenever the former is inside ( $r_e < r$ ) the bound-electron charge cloud. This modification weakens the polarisation potential at small values of  $r_e$ , as a rigorous non-adiabatic correction would be expected to do (Callaway *et al* 1968, Jean and Schrader 1978).

In using the above procedure to calculate a polarisation potential for electron–atom scattering, one finds that the leading contribution to the potential comes from the

<sup>†</sup> In atomic units  $\hbar = m_e = a_0 = e = 1$ . The unit of energy is  $\hbar^2/m_e a_0^2 = 1$  Hartree = 2 Ryd = 27.212 eV. The unit of distance is the first Bohr radius ( $a_0$ ) = 1 Bohr =  $0.52918 \times 10^{-10}$  m.

dipole ( $\lambda = 1$ ) term in equation (2) (Temkin 1957). However, in the electron-molecule case, the leading contribution for small and intermediate values of  $r_e$  arises from the monopole ( $\lambda = 0$ ) term (Weatherford *et al* 1973). The inclusion of the monopole term leads to a potential which is too attractive, giving unphysical scattering results. Therefore, as an additional correction, we exclude the monopole term from our non-adiabatic polarisation potential. We find that the resulting polarisation potential converges rapidly in  $\lambda$  and (for use in scattering calculations) is well represented by retaining only the dipole contribution (Obedkov 1964, Hara 1969b). Additional details of these calculations will be presented in a future paper.

In figure 1(a) we show polarisation potentials calculated for the case in which the scattering electron makes its approach along a perpendicular bisector of the internuclear axis ( $\theta_e = \pi/2$ ). In figure 1(b) we show the corresponding results obtained for an approach along the internuclear axis ( $\theta_e = 0$ ). Included in these figures are our strictly adiabatic results, the scaled non-penetrating dipole potential of Hara (1969b), and our non-penetrating dipole results. The adiabatic potential calculated by Truhlar *et al* (1979) (not shown) is in excellent agreement with our own adiabatic results. A comparison of Hara's and our non-adiabatic results with those of the strictly adiabatic treatment reveals the importance of the non-adiabatic corrections for  $r_e \leq 5.0 a_0$ . Hara's potential was calculated using a variation-perturbation technique in a two-centre formulation. He obtained the polarisability values  $\alpha_{\perp} = 4.359 a_0^3$  and  $\alpha_{\parallel} = 4.851 a_0^3$ , and found, therefore, that an overall scaling was required to ensure agreement with the correct asymptotic form.

To determine cross sections for e-H<sub>2</sub> scattering, we calculated an *ab initio* static potential (Morrison 1980, Collins *et al* 1980) using the near-Hartree-Fock H<sub>2</sub> X <sup>1</sup>Σ<sub>g</sub><sup>+</sup> wavefunction of Feldt and Morrison (1982). This same H<sub>2</sub> wavefunction was used to incorporate exchange effects via the tuned free-electron-gas model exchange potential, which is known (Gibson and Morrison 1981, Morrison and Collins 1978) to reproduce accurately the exact static-exchange total cross sections (Collins *et al* 1980) for e-H<sub>2</sub> scattering at energies  $\leq 1.0$  Ryd.

The static and exchange potentials are expanded in a Legendre polynomial series viz,

$$V^{\text{st(ex)}}(r_e) = \sum_{\lambda=0}^{\lambda_{\text{max}}} v_{\lambda}^{\text{st(ex)}}(r_e) P_{\lambda}(\cos \theta_e) \quad (3)$$

with  $\lambda_{\text{max}} = 8$ . We find that the polarisation potential is well represented by the two term expansion

$$V^{\text{pol}}(r_e) = v_0^{\text{pol}}(r_e) + v_2^{\text{pol}}(r_e) P_2(\cos \theta_e) \quad (4)$$

with  $v_0^{\text{pol}}$  and  $v_2^{\text{pol}}$  given by

$$v_0^{\text{pol}}(r_e) = \frac{1}{3} (V_{\parallel}^{\text{pol}}(r_e) + 2V_{\perp}^{\text{pol}}(r_e)) \quad (5a)$$

$$v_2^{\text{pol}}(r_e) = \frac{2}{3} (V_{\parallel}^{\text{pol}}(r_e) - V_{\perp}^{\text{pol}}(r_e)). \quad (5b)$$

For use in other scattering calculations, we have determined an analytic fit<sup>†</sup> to our

<sup>†</sup> The use of this analytic fit in SEP scattering calculations results in less than a 3% difference for the integrated rotational-excitation cross sections and a difference of less than 1% for total integrated cross sections.

(numerical) polarisation potential, viz,

$$v_0^{\text{pol}}(r_e) = \begin{cases} \frac{-4.0}{2(r_e^2 + b_0 r_e + r_0^2)^2} \{1 - \exp[-(r_e/1.1)^{2.6}]\} & r_e < 10 a_0 \\ -\alpha_0/2r_e^4 & r_e \geq 10 a_0 \end{cases} \quad (6a)$$

$$r_e \geq 10 a_0 \quad (6b)$$

where  $b_0 = -2.036 a_0$ ,  $r_0 = 2.79 a_0$ , and the spherical polarisability  $\alpha_0 = 5.2 a_0^3$ ;

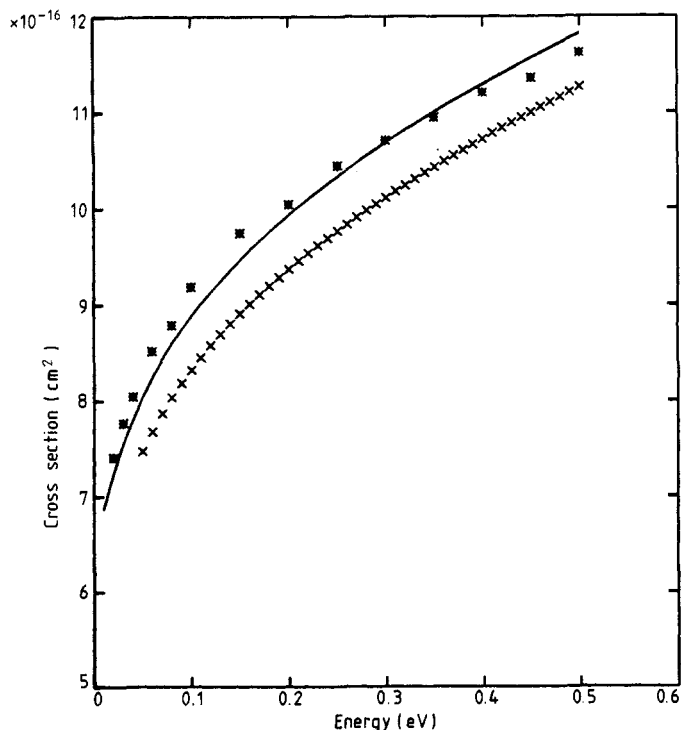
$$v_2^{\text{pol}}(r_e) = \begin{cases} \frac{-1}{2(r_e^2 + b_1 r_e + r_1^2)^2} \{1 - \exp[-(r_e/0.9)^{5.8}]\} & r_e < 4 a_0 \\ \frac{-1.32}{2(r_e^2 + b_2 r_e + r_2^2)^2} & 4 a_0 \leq r_e < 10 a_0 \\ \frac{-\alpha_2}{2(r_e^2 + 1)^2} & r_e \geq 10 a_0 \end{cases} \quad (7a)$$

$$r_e \geq 10 a_0 \quad (7b)$$

$$r_e \geq 10 a_0 \quad (7c)$$

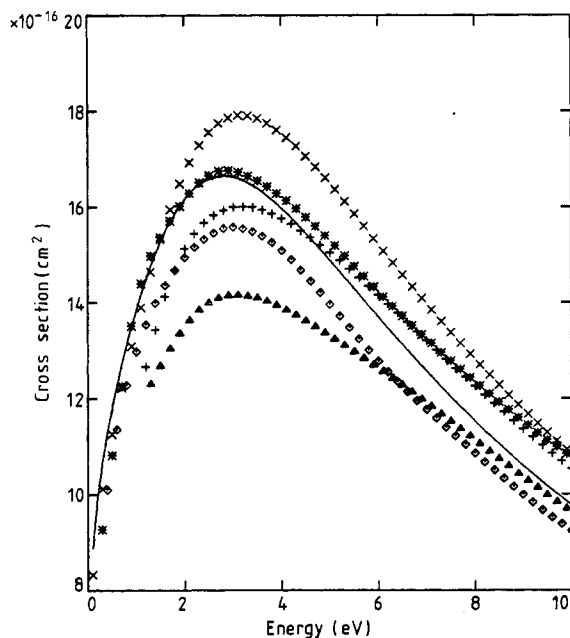
with  $b_1 = -1.82 a_0$ ,  $r_1 = 2.42 a_0$ ,  $b_2 = 0.03365 a_0$ ,  $r_2 = 0.767 a_0$ , and the non-spherical polarisability  $\alpha_2 = 1.32 a_0^3$ .

Using this SEP e-H<sub>2</sub> interaction potential, we have calculated the integrated elastic and rotational-excitation cross sections in a laboratory frame close-coupling formulation (Arthurs and Dalgarno 1960, Lane and Geltman 1967). A numerical procedure based on an integral equations algorithm (Sams and Kouri 1969, Morrison 1979) was used to solve the scattering equations.



**Figure 2.** Total integrated cross sections for very-low-energy e-H<sub>2</sub> scattering: —, this work; \*, measured values of Ferch *et al* (1980); x, theoretical result of Henry and Lane (1969).

In figure 2 we compare our integrated total (elastic plus rotational excitation) cross sections with the measured values of Ferch *et al* (1980) and with the close-coupling results of Henry and Lane (1969) for scattering energies from 20.0 to 500.0 meV. A modified effective-range-theory (O'Malley *et al* 1962) fit to our cross sections (which are globally converged to better than 1%) produces a scattering length  $A = 1.26 a_0$ . This value is in excellent agreement with that reported by Chang (1981), who obtained  $A = 1.27 \pm 0.01 a_0$  by fitting the experimentally determined results of Crompton *et al* (1969) and those of Ferch *et al* (1980). Cross sections for higher energies are presented in figure 3, where we show the theoretical curves of Henry and Lane (1969), Hara (1969a), and Klonover and Kaldor (1978) as well as the measured values of Golden *et al* (1966) and Dalba *et al* (1980). All of the theoretical results presented in figure 3 were calculated with a fixed internuclear separation; Klonover and Kaldor (1979) have shown that explicit integration over  $R$  can lead to a small increase in the integrated cross section.



**Figure 3.** Total integrated cross sections for e-H<sub>2</sub> scattering. All of the theoretical results in this figure were calculated with the internuclear separation fixed at its equilibrium value. Theoretical curves presented: —, this work; ×, Henry and Lane (1969); +, Hara (1969a); △, Klonover and Kaldor (1978). Experimental curves shown: \*, Dalba *et al* (1980); ◇, Golden *et al* (1966).

In table 1 we compare our rotational-excitation cross sections for  $j = 0 \rightarrow j' = 2$  with those of Henry and Lane (1969) and with the swarm measurements of Crompton *et al* (1969). Additional rotational-excitation cross sections for  $j = 1 \rightarrow j' = 3$  are shown in figure 4, where our results are compared with those of Henry and Lane (1969), Hara (1969c), and the experimentally determined values of Linder and Schmidt (1971).

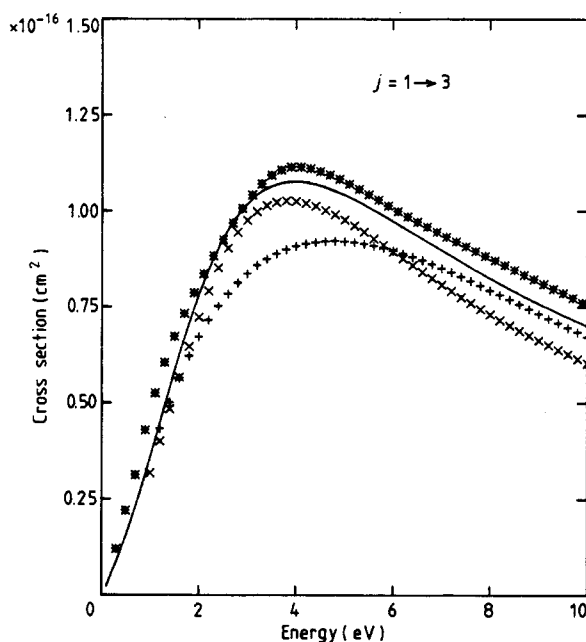
The *ab initio* polarisation potential presented in this letter has been used to produce SEP scattering results that are in excellent agreement with a variety of existing experimental cross sections. Although non-adiabatic effects are included in an approxi-

**Table 1.** Integrated cross sections (in  $10^{-16} \text{ cm}^2$ ) for the  $j = 0$  to  $j' = 2$  transition in e- $\text{H}_2$  scattering.

Energy (eV)	CGM <sup>a</sup>	HL <sup>b</sup>	Present results
0.05	0.027	0.024	0.023
0.07	0.053	0.052	0.048
0.10	0.074	0.074	0.069
0.15	0.099	—	0.096
0.20	0.120	0.119	0.120
0.30	0.160	0.161	0.169
0.40	0.210	—	0.222
0.50	0.263	0.254	0.280

<sup>a</sup> Crompton *et al* (1969).<sup>b</sup> Henry and Lane (1969).

mate way, this treatment of polarisation requires no scaling, contains no adjustable parameters, and has the advantage that the same near-Hartree-Fock wavefunction can be used to calculate all the components of the e- $\text{H}_2$  interaction potential, thereby assuring internal consistency.

**Figure 4.** Integrated cross sections for the  $j = 1$  to  $j' = 3$  transition in e- $\text{H}_2$  scattering: —, this work; \*, the measurements of Linder and Schmidt (1971); x, Henry and Lane (1969); +, Hara (1969c).

We are currently extending our study of the polarisation interaction to include non-equilibrium values of the internuclear separation  $R$ . A potential containing this explicit  $R$  dependence will then be used to perform both vibrationally-elastic and -inelastic calculations. In addition, work is under way to extend this method of calculating the polarisation potential to other electron scattering systems.

The authors gratefully acknowledge the invaluable assistance of Dr Andrew Feldt in performing the analytic fit of our polarisation potential. We would like to thank Dr J Ferch and Dr U Kaldor for providing us with tables of their results. In addition, we would like to thank Drs N F Lane and R J W Henry for timely and useful discussions regarding this work and Rick Weitzel for reading and commenting on a preliminary form of this manuscript. This work was supported by the Office of Basic Energy Science, US Department of Energy. One of us (MAM) also acknowledges support by the Research Corporation.

## References

- Arthurs A M and Dalgarno A 1960 *Proc. R. Soc. A* **256** 540–51  
 Callaway J, LaBahn R W, Pu R T and Duxler W M 1968 *Phys. Rev.* **168** 12–21  
 Chang E S 1981 *J. Phys. B: At. Mol. Phys.* **14** 893–901  
 Collins L A, Norcross D W and Schmid G B 1980 *Comput. Phys. Commun.* **21** 79–90  
 Crompton R W, Gibson D K and McIntosh A I 1969 *Aust. J. Phys.* **22** 715–31  
 Dalba G, Fornasini P, Lazzizzera I, Ranieri G and Zecca A 1980 *J. Phys. B: At. Mol. Phys.* **13** 2839–48  
 Feldt A N and Morrison M A 1982 *J. Phys. B: At. Mol. Phys.* **15** 301–8  
 Ferch J, Raith W and Schröder K 1980 *J. Phys. B: At. Mol. Phys.* **13** 1481–90  
 Gibson T L and Morrison M A 1981 *J. Phys. B: At. Mol. Phys.* **14** 727–39  
 Golden D E, Bandel H W and Salerno J A 1966 *Phys. Rev.* **146** 40–2  
 Hara S 1969a *J. Phys. Soc. Japan* **27** 1009–19  
 — 1969b *J. Phys. Soc. Japan* **27** 1262–7  
 — 1969c *J. Phys. Soc. Japan* **27** 1592–7  
 Henry R J W and Lane N F 1969 *Phys. Rev.* **183** 221–31  
 Jean Y C and Schrader D W 1978 *Phys. Rev. A* **18** 2030–41  
 Klonover A and Kaldor U 1978 *J. Phys. B: At. Mol. Phys.* **11** 1623–32  
 — 1979 *J. Phys. B: At. Mol. Phys.* **12** L61–65  
 Kolos W and Wolniewicz L 1965 *J. Chem. Phys.* **43** 2429–41  
 — 1967 *J. Chem. Phys.* **46** 1426–32  
 Lane N F 1980 *Rev. Mod. Phys.* **52** 29–119  
 Lane N F and Geltman S 1967 *Phys. Rev.* **160** 52–67  
 Lane N F and Henry R J W 1968 *Phys. Rev.* **173** 183–90  
 Linder F and Schmidt H 1971 *Z. Naturf.* **26a** 1603–17  
 Morrison M A 1979 *Electron-Molecule and Photon-Molecule Collisions* ed T N Rescigno, V McKoy and B I Schneider (New York: Plenum) pp 15–50  
 — 1980 *Comput. Phys. Commun.* **21** 63–77  
 Morrison M A and Collins L A 1978 *Phys. Rev. A* **17** 918–38  
 Morrison M A and Hay P J 1979 *Phys. Rev. A* **20** 740–8  
 Morrison M A, Lane N F and Collins L A 1977 *Phys. Rev. A* **15** 2186–201  
 Obedkov V D 1964 *Opt. Spectrosc.* **17** 101–4  
 O'Malley T F, Rosenberg L and Spruch L 1962 *Phys. Rev.* **125** 1300–10  
 Sams W N and Kouri D J 1969 *J. Chem. Phys.* **51** 4809–14  
 Schneider B I 1977 *Chem. Phys. Lett.* **51** 578–81  
 Temkin A 1957 *Phys. Rev.* **107** 1004–12  
 Truhlar D G, Dixon D A and Eades R A 1979 *J. Phys. B: At. Mol. Phys.* **12** 1913–25  
 Weatherford C A, Henry R J W and Bruels M C 1973 *Proc. Ind. Natl. Sci. Acad. A* **39** 432–7  
 Weitzel W F, Gibson T L and Morrison M A 1981 *Comput. Phys. Commun.* submitted