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Low-energy e–H_2^+ collisions using the *R*-matrix method

J Tennyson†, C J Noble† and S Salvini‡

† SERC Daresbury Laboratory, Warrington WA4 4AD, England
‡ Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland

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Abstract. The R-matrix method is applied to the electronic excitation of the hydrogenic molecular ion by low-energy electron impact using a two-state coupled-channel formalism. Polarisation effects are accounted for by means of an optical potential which involves no arbitrary parameters. These are the first calculations of this type in which both channel coupling and correlation effects are explicitly included. Good agreement is obtained with other computational techniques. New estimates are made of the positions and widths of the two lowest resonances in each of the Σ and Π symmetry states. Excitation cross sections $Q(1\sigma_g, 1\sigma_u)$ are also presented.

1. Introduction

Recently Burke *et al* (1983) described an implementation of the R-matrix method (Burke *et al* 1977) using numerically defined basis functions which enabled results to be obtained for the scattering of electrons by nitrogen molecules at low and intermediate scattering energies. Both exchange and charge polarisation effects were included in these calculations without parametrisation. In the present work we extend this method to describe the scattering of low-energy electrons by the H_2^+ ion including the electronic excitation of the target. These are the first *ab initio* results for electron–molecule scattering in which coupling to an excited state is included explicitly together with the use of an optical potential to represent polarisation and residual channel coupling effects. The electron–H_2^+ system is probably the most intensively studied example of electron collisions with a positive molecular ion and is of special interest because of its role in photoionisation of neutral hydrogen (e.g. Robb and Collins 1980) and dissociative recombination of H_2^+ ions (e.g. Giusti-Suzor *et al* 1983).

Calculations of e^-–H_2^+ scattering have been reported within the static exchange approximation by Kelly (1973), Dutta *et al* (1977), Robb and Collins (1980) and Lucchese and McKoy (1981). There have also been polarised orbital calculations by Temkin *et al* (1969) and Temkin and Vasavada (1967) and a series of Kohn variational calculations using a spheroidal coordinate system by Takagi and Nakamura (1980, 1983). In addition there is a considerable body of related work orientated toward a study of the doubly excited autoionising states of H_2 and in particular to determine the position and width of the $1\sigma_u^2\ {}^1\Sigma_g^+$ state, using Feshbach projection operator formalism and Stieltjes moment techniques. Studies of this type have been carried out by Moiseyev and Corcoran (1979), Lesech and Aubert-Frécon (1982), Guberman (1983), Hazi (1979, 1983) and Hazi *et al* (1983).

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Close in spirit to the present work are two recent calculations by Collins and Schneider (1983) and Schneider and Collins (1983) who have applied the linear algebraic equations method (Collins and Schneider 1981, Schneider and Collins 1981, 1982) to describe the electronic excitation of H_2^+. In the first of the two calculations they used both a two-state ($1\sigma_g$, $1\sigma_u$) and a four state ($1\sigma_g$, $1\sigma_u$, $1\Pi_u^+$, $1\Pi_u^-$) close-coupling approximation in order to study channel coupling effects which are not easily included in either the Kohn variational or Feshbach projection formalism approaches. In the second calculation details of the lowest two $^1\Sigma_g^+$ resonances were investigated using a one-state model but including polarisation and correlation effects via an optical potential which was generated by appending 'correlation' functions to the close-coupling expansion. Our approach involves the direct solution of the multicentre R-matrix equations using a two-state close-coupling expansion and numerically defined orbitals to describe the continuum electron. It combines features of both the Collins and Schneider calculations and is the first calculation in which channel coupling effects are explicitly included and polarisation effects are represented by suitable 'correlation' functions without the introduction of arbitrary parameters. We present a detailed comparison of our results using the fixed-nuclei approximation at the equilibrium internuclear separation with those of previous calculations and also report positions and widths of a number of resonances. These results are obtained with a general computer code and demonstrate the efficiency of the R-matrix approach in the case of electronic excitation and therefore suggest that the method will be effective for more complicated systems. Reviews of recent work on the application of R-matrix theory to electron–molecule scattering may be found in papers by Buckley *et al* (1983) and by Burke and Noble (1983). The numerical methods used in the present calculations are similar to those described by Burke *et al* (1983). Modifications include the procedure for generating continuum orbitals (see below) and the way in which the Gailitis (1976) asymptotic expansion is applied. The latter will be described in detail elsewhere (Nesbet and Noble 1984).

2. Theory

The wavefunction for the e–H_2^+ system is expanded within a finite R-matrix sphere of radius 10 au in terms of a close-coupling expansion of the form

$$\Psi(x_1, x_2) = \mathcal{A} \sum_{i=1}^{2} \Phi_i(x_1) F_i(x_2) + \sum_i \phi_i(x_1, x_2) b_i \tag{1}$$

where $x_i = (\boldsymbol{r}_i, \sigma_i)$ represents the space–spin coordinates of the ith electron and $\mathcal{A}$ antisymmetrises the scattered and target electrons. Two states, Φ_i, were retained in the close-coupling expansion corresponding to the ground X $^2\Sigma_g^+$ and first excited $^2\Sigma_u^+$ state of H_2^+. These are represented by LCAO-MO-SCF wavefunctions of Cohen and Bardsley (1980) obtained by varying linear and exponential coefficients within a 1s–2s–2p STO σ basis. We added an extra p_π STO basis function to provide suitable π virtual molecular orbitals. Orbitals F, in equation (1) representing the scattering electron, are formed by taking suitable linear combinations of the occupied target orbitals and additional continuum basis functions whose radial parts are obtained by numerically solving the model scattering problem

$$\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + V_0(r) + k_j^2\right) u_{ij} = 0 \tag{2}$$

subject to the fixed boundary conditions

$$u_{ij}(0)=0$$

$$\frac{a}{u_{ij}(0)}\frac{\mathrm{d}u_{ij}(r)}{\mathrm{d}r}\bigg|_{r=a}=0. \qquad (3)$$

Potential V_0 is taken as the spherical part of the static potential of the target molecule.

This procedure is designed to form an orthonormal set which is complete over a known energy range and is similar to a Lagrange orthogonalisation. It will be described in detail elsewhere (Salvini and Burke 1984). The use of fixed boundary conditions requires the introduction of a Buttle (1967) correction when computing the R matrix. In the present work three or four partial waves are retained for each target state and the continuum basis was chosen to be complete over an energy range up to 11 Ryd. Constants b_i in equation (1) are variational constants while terms ϕ_i represent short-range correlation effects and are formed from the occupied and virtual target orbitals. We have considered two models for the construction of these functions. The first, corresponds to the usual static exchange (SE) model in the case of elastic scattering and consists of freezing the target electron in either the $1\sigma_g$ orbital or $1\sigma_u$ orbital and allowing the second electron to occupy any of the virtual orbitals with the appropriate symmetry for the case under consideration. In the second model, allowance is made for polarisation effects by permitting both electrons to occupy the available virtual orbitals subject only to symmetry constraints. This model will hereafter be referred to as the polarisation or SEP model.

3. Results

Eigenphases have been computed at the equilibrium separation of $R_e = 2.0$ au for all Σ and Π symmetries and for scattering energies up to 2 Ryd. In table 1 we compare $^1\Sigma_g$ eigenphase sums from one-state SE and SEP calculations at a few selected energies with previous results of Luccese and McKoy (1981) obtained by means of an iterative Schwinger variational calculation and also with results of Robb and Collins (1980) using an iterative integral equation method.

Table 1. Comparison of eigenphase sums for single-state calculations in which only the X $^2\Sigma_g^+$ ground state of H_2^+ is retained in the first sum in equation (1).

	Eigenphase sum (rad)					
Energy (Ryd)	a	a	b	c	d	d
0.01	−0.361	−0.357		−0.357	−0.168	−0.164
0.25	−0.386	−0.378	−0.377	−0.381	0.032	0.040
1.00	−0.348	−0.336	−0.352	−0.346	−0.264	−0.252
Number of channels	3	4		6	3	4

[a] Present work SE.
[b] Lucchese and McKoy (1981).
[c] Robb and Collins (1980).
[d] Present work SEP.

The agreement in both cases is excellent and well within the accuracies quoted for these calculations. The results indicate that retaining three partial waves in our calculations is sufficient for scattering energies up to 1 Ryd. This conclusion may also be verified by considering the results shown in figure 1 where we have plotted eigenphase sums as a function of energy for $^1\Sigma_u^+$ symmetry scattering in a two-state SEP model retaining one, two and three partial waves.

In figure 2 we compare eigenphase sums for the $^1\Sigma_g^+$ symmetry computed using the SE and SEP models. It is clear that polarisation effects are much more pronounced in resonance regions than on the background eigenphases. The two resonances shown are shifted to lower energies and tend to be narrower when account is taken of

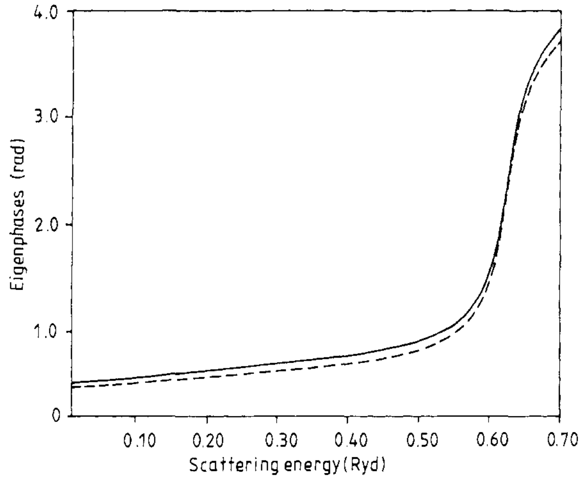

Figure 1. Eigenphase sums in radians as a function of the scattering energy in Rydbergs for e–H_2^+ scattering in the $^1\Sigma_u^+$ symmetry computed using two coupled states and a polarisation model. Broken curve: one partial wave; full curve: including two or three partial waves per target state. These results are indistinguishable.

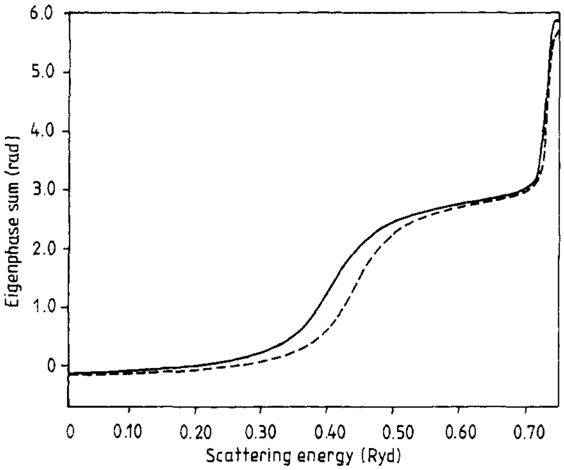

Figure 2. Eigenphase sums in radians as a function of the scattering energy in Rydbergs for e–H_2^+ scattering in the $^1\Sigma_g^+$ symmetry state. Broken curve, static exchange, SE model; full curve, SEP, polarisation model.

polarisation. This effect is more significant for the lower energy resonance than for the resonance at 0.73 Ryd. These resonances are the first two members of a Rydberg series of Feshbach resonances converging towards the excited-state threshold at 0.87 Ryd. This may be seen most clearly in figure 3 which shows our computed eigenphase sums for the $^1\Pi_g$ symmetry in the two-state SEP model. Here the first five members of the Rydberg series are visible and more could be resolved by refining the mesh of energies at which eigenphases are computed. These resonances of course correspond to two-electron excited states of H_2 and therefore have been the subject of many studies, particularly in the case of the $(2p\sigma_u)^2\,{}^1\Sigma_g$ state which plays an important role in the dissociative recombination of H_2^+ ions. We have determined the positions and widths of the two lowest energy resonances below the $^2\Sigma_u^+$ threshold for each of the Σ and Π symmetry states of the scattering system by fitting a Breit–Wigner form with a quadratic background to the computed eigenphase sums. These results are collected in table 2 along with a selection of the results obtained by other workers. The most extensive set of comparable results is that obtained by Takagi and Nakamura (1983) using the Kohn variational principle. The Kohn calculations used a more

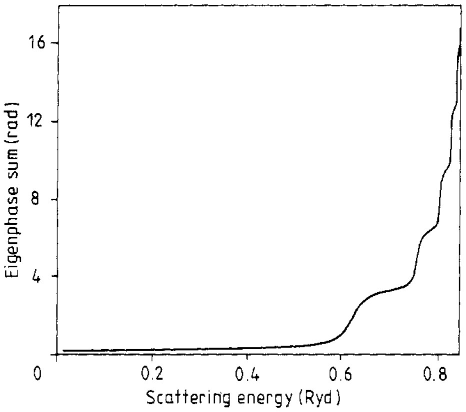

Figure 3. Eigenphase sum in radians as a function of the scattering energy in Rydbergs for e–H_2^+ scattering in the $^1\Pi_g$ symmetry sstate. Polarisation model (SEP) results showing the Rydberg series of resonances converging to the excited-state threshold.

Table 2. Position and width of e–H_2^+ resonances. E_r is the resonance energy measured from the ground state of H_2^+. Γ is the width.

Symmetry	E_r (Ryd)	Γ (Ryd)	E_r (Ryd)	Γ (Ryd)	Reference
$^1\Sigma_g^+$	0.4440	0.095	0.7355	0.010	a
	0.4088	0.106	0.7321	0.010	b
	0.4420	0.104			c
	0.4321	0.114	0.731	0.012	d
	0.395	0.103	0.729	0.011	e
	0.4020	0.118	0.7320		f
	0.4102	0.097			g
			0.727		i
	0.4099		0.7299		j

Table 2. (continued)

Symmetry	E_r (Ryd)	Γ (Ryd)	E_r (Ryd)	Γ (Ryd)	Reference
$^1\Sigma_u^+$	0.6289	0.052			a
	0.6282	0.050	0.7587	0.008	b
	0.6255				c
	0.6228	0.049			d
	0.6248	0.054	0.8004	0.036	f
	0.623	0.054			h
	0.641		0.775		i
	0.6174		0.7737		j
$^1\Pi_u$	0.7622	7.7 (−4)			a
	0.7621	8.1 (−4)	0.8095	4.5 (−4)	b
	0.7590	7.7 (−4)			c
	0.758	8.7 (−4)			d
	0.7764	2.2 (−4)	0.9322	16.4 (−4)	f
	0.759	9.0 (−4)			h
	0.7582		0.8067		j
$^1\Pi_g$	0.6260	0.043			a
	0.6221	0.046	0.7591	0.013	b
	0.6255	0.038			d
	0.6169		0.7578		j
$^3\Sigma_g^+$	0.7883	4.5 (−6)			a
	0.7420	0.023	0.7937	5.0 (−3)	b
	0.731				i
	0.6999		0.7940		j
$^3\Sigma_u^+$	0.6073	6.1 (−4)			a
	0.6026	9.5 (−4)	0.7557	7.0 (−4)	b
	0.6072	7.2 (−4)	0.7656	2.4 (−4)	f
	0.619		0.775		i
	0.5970		0.7715		j
$^3\Pi_u$	0.7583	8.7 (−4)			a
	0.7580	8.9 (−4)	0.8073	4.7 (−4)	b
	0.7706	2.6 (−5)	1.0100	2.8 (−4)	f
	0.7547		0.8049		i
$^3\Pi_g$	0.5951	5.0 (−3)			a
	0.5888	4.1 (−3)	0.7520	8.9 (−4)	b
	0.5877		0.7509		i

[a] Present work SE.

[b] Present work SEP.

[c] Collins and Schneider (1983), 2 coupled states.

[d] Collins and Schneider (1983), 4 coupled states.

[e] Schneider and Collins (1983), optical potential 2.

[f] Tagaki and Nakamura (1983).

[g] Hazi *et al* (1983).

[h] Hazi (1979), as quoted by Collins and Schneider (1983).

[i] Lesech and Aubert-Frécon (1982).

[j] Guberman (1983).

accurate representation of the $^2\Sigma_g^+$ H_2^+ ground state than was used in our own calculations but omitted the $^2\Sigma_u^+$ state. The two sets of results are in good agreement for those resonances lying lowest in energy. However, our results indicate that the second resonance in each symmetry found by Takagi and Nakamura (which is the only survey to date of these states using a scattering method) generally are too high in energy. Indeed some lie above the infinite series of resonances which converge to the $^1\Sigma_u^+$ threshold.

The two-state results of Collins and Schneider (1983) are completely equivalent, apart from minor differences in the orbital basis used, to our SE model results. The very close agreement between these two sets of parameters is therefore a direct check on the numerical accuracy of our work. The 10% differences between the two-state and four-state results of Collins and Schneider provide a rough measure of the errors incurred in omitting the $^2\Pi_u$ state from the close-coupling expansion. However, in the SEP model, the effects of this state are largely accounted for via the correlation terms. This effect is shown by the good agreement between our SEP results and the optical potential 2 results of Schneider and Collins (1983). The results of Hazi (as quoted by Collins and Schneider 1983) and of Hazi *et al* (1983), which we take as representative of those methods using discrete basis-set techniques to calculate resonance parameters directly, are also in good agreement with these results.

Finally table 3 presents a selection of excitation cross sections $Q(1\sigma_g, 1\sigma_u)$ for scattering energies in the range 1–2 Ryd. The SE model results are in good agreement with values quoted by Collins and Schneider (1983).

At energies above the excitation threshold for the $^2\Pi_u$ excited state of H_2^+ which occurs at an energy of 1.35 Ryd, the optical potential we have employed becomes complex and pseudo-resonances may occur. This situation has been discussed for e–N_2 scattering by Burke *et al* (1983) where techniques for averaging over pseudo-resonances first investigated for electron–atom scattering (Burke *et al* 1981) were adapted to the molecular case. In the present work we have again observed the occurrence of pseudo-resonances. However only one pseudo-resonance, with $^1\Pi_u$ symmetry, occurs below 2 Ryd and therefore it is possible to obtain the cross sections given in table 3 without employing an averaging procedure. We omit the $^1\Pi_u$ cross sections which are influenced by the presence of the pseudo-resonance.

Table 3. $^2\Sigma_g^+$–$^2\Sigma_u^+$ excitation cross sections for e–H_2^+ collisions at $R_e = 2.0$ au.

	Excitation cross sections (a_0^2)						
	SE model				SEP model		
Energy (Ryd) = Symmetry	1.0	1.6	2.0	2.0†	1.0	1.6	2.0
$^1\Sigma_g^+$	0.383	0.245	0.192	0.192	0.372	0.243	0.149
$^3\Sigma_g^+$	0.064	0.125	0.122	0.124	0.066	0.131	0.129
$^1\Sigma_u^+$	0.663	0.438	0.324	0.377	0.641	0.406	0.271
$^3\Sigma_u^+$	0.454	0.319	0.240	0.251	0.464	0.326	0.259
$^1\Pi_u$	0.230	0.269	0.234		0.243		
$^3\Pi_u$	0.574	0.437	0.336		0.576	0.428	0.321
$^1\Pi_g$	0.960	0.524	0.391	0.398	0.947	0.485	0.331
$^3\Pi_g$	0.437	0.415	0.381		0.378	0.391	0.361

† Collins and Schneider (1983), 2 states, 3 partial waves.

In summary, we have shown that the R-matrix method formulated in a form appropriate for the treatment of the entire range of small diatomic molecular targets, provides accurate results for the electronic excitation of the hydrogenic ion extremely cheaply despite the use of a simple representation of the target wavefunctions. The model we have used yields scattering observables comparable with other more elaborate and specific procedures and has the advantage that channel coupling and polarisation effects are both explicitly represented. We have presented the first accurate survey of the resonance parameters in the Σ and Π symmetries obtained using a scattering method. The results are sufficiently encouraging that calculations at different internuclear separations are now in progress preparatory to a detailed investigation of vibrational excitation, photoionisation and dissociative recombination processes. These results will be reported in due course along with the application of the method to more challenging molecular systems.

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