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Low-energy electron–H_2^+ collisions: variation of resonance parameters with internuclear separation

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Abstract. The positions and widths of all the low-lying Σ and Π resonances in the electron-H_2^+ collision problem are examined as functions of H_2^+ geometry. The scattering calculations reported are based on the R-matrix method and include both coupled-state and polarisation effects non-empirically. Two- and four-coupled-state calculations are presented. Agreement with many of the previous calculations is found although some published data are found to be in error. Predictions for the $^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$ electronic excitation cross section are also given.

1. Introduction

In a recent paper (Tennyson *et al* 1984, hereafter referred to as I), we reported results on the scattering of low-energy electrons by the H_2^+ ion at its equilibrium internuclear separation ($R = 2a_0$). These results were obtained using the R-matrix method (Burke *et al* 1977) and employed numerical basis functions to represent the continuum orbitals (Burke *et al* 1983, Salvini 1983). The calculations included, without parametrisation, the effects of exchange and charge polarisation as well as coupling to the low-lying $A\,^2\Sigma_u^+$ state of H_2^+. The calculations enabled us to present the first accurate survey of resonance parameters in Σ and Π symmetries obtained using a scattering method for H_2^+ at its equilibrium geometry.

H_2^+ is of fundamental interest in the study of electron-molecule collision processes because of the simple nature of the target and its relationship to photoionisation of hydrogen (e.g. Robb and Collins 1980, Itikawa *et al* 1983) and dissociative recombination (e.g. Giusti-Suzor *et al* 1983). To obtain a full understanding of these processes it is necessary to solve the e-H_2^+ collision problem as a function of H_2^+ separation (R); there remain several unresolved discrepancies in this area. For example, in the $^1\Sigma_g^+$ symmetry, there are significant differences in the calculated widths of the lowest resonance as a function of R (Hazi *et al* 1983) and even some doubt as to whether this resonance is dominated by d- or s-wave scattering (Giusti-Suzor *et al* 1983). Our calculations at $R = 2$ also suggest that some of the published data, especially on higher resonances are unreliable (see I). We believe that our method can resolve these problems.

Therefore we present the first accurate survey of the Σ and Π resonance parameters as a function of H_2^+ internuclear separation. We can thus evaluate the reliability of some of the previous calculations on this topic (e.g. Tagaki and Nakamura 1980, 1983, Hazi 1975, 1979b, 1983, Hazi *et al* 1983, Collins and Schneider 1981, 1983, Sato and

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Hara 1983) as well as presenting data on the second and third resonances in each symmetry, most of which have not previously been considered.

In order to test the reliability of the two-state model used in I and here, we also present calculations which explicitly include the effect of coupling to the $B\,^2\Pi_u$ state of H_2^+. These four-state (configurations: $1\sigma_g^1$, $1\sigma_u^1$, $1\pi_u^{+1}$, $1\pi_u^{-1}$) calculations can then be directly compared with the calculations of Collins and Schneider (1983) who used the linear algebraic approach to perform four-state calculations within the static exchange approximation. Finally, we also present predicted cross sections for the electronic excitation $^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$ as a function of electron scattering energy.

2. Two- and four-state calculations

All calculations reported here used the techniques of I to which the reader is referred for detail. Unless otherwise stated, they were peformed at the static exchange plus polarisation level (the SEP model) with two coupled states and three partial waves per state.

The H_2^+ target was represented by an LCAO-MO-SCF wavefunction comprising three STO for each state, with exponents as optimised by Cohen and Bardsley (1980). For the two-state calculations an extra p_π STO on each H was added to provide suitable π virtual MO to represent polarisation effects. In the four-state calculations, π_g virtual MO were obtained from the complement of the π_u basis of Cohen and Bardsley (1980).

Whilst the representation of the H_2^+ ground state at $R = 2$ is identical with that of I, the use of separately optimised functions for each excited H_2^+ state gives an improved representation of these states. In particular, the threshold of the $A\,^2\Sigma_u^+$ state is lowered by 0.002 Ryd at $R = 2$ in these calculations. The only other significant difference between these and our previous calculations is that an improved, automated procedure was used for fitting the resonances to a Breit-Wigner form (Tennyson and Noble 1984).

Table 1 compares Σ_g^+ resonance parameters obtained with two- and four-state calculations. Results from the only other multistate e-H_2^+ calculation (Collins and Schneider 1983) are given for comparison. The diffuseness of the $B\,^2\Pi_u$ state of H_2^+, and in particular of its Π_g analogue, caused numerical difficulties because of the finite R-matrix sphere; however work is in progress on a more robust numerical basis function code which should ameliorate this problem. Conversely, for two-state calculations we found the results are stable to changes in R-matrix radius. For maximum efficiency, the present calculation used a radius of $10a_0$.

Despite the basis set problems mentioned above, our four-state results are encouraging. Firstly, they are in good agreement with the results of Collins and Schneider (1983), our lower energies being directly attributable to polarisation effects which they neglect. Secondly, the effect of explicitly coupling the $B\,^2\Pi_u$ state is small—less than 0.003 Ryd in all cases—although this leads to comparatively large changes in the predicted widths of the narrow $^3\Sigma_g^+$ resonances. These results suggest that our two-state model is sufficient to give a good representation of low-energy electron-H_2^+ collisions and that in the energy region considered here the contribution from higher electronic states not included via our polarisation potential is small.

Table 2 presents results for $^1\Sigma_g^+$ e-H_2^+ scattering at $R = 2$. The table compares resonance parameters obtained by fitting the total eigenphase sum and fitting only the eigenphase with $l = 2$. Clearly, for all approximations considered, the resonance is

Table 1. Positions and widths of e-H_2^+ resonances at $R = 2\ a_0$. E_{res} is the resonance position measured from the ground state of H_2^+ in Ryd, Γ_{res} is the width in Ryd.

Symmetry		Two-state			Four-state	
		a	b	c	a	c
$^1\Sigma_g$	E_{res}	0.4438	0.4088	0.4057	0.4321	0.4054
	Γ_{res}	0.102	0.106	0.101	0.114	0.110
	E_{res}		0.7321	0.7292		0.7278
	Γ_{res}		0.010	0.0097		0.0124
	E_{res}			0.7951		0.7946
	Γ_{res}			0.0037		0.0047
$^3\Sigma_g$	E_{res}		0.7420	0.7022		0.6996
	Γ_{res}		0.023	8.5×10^{-4}		3.0×10^{-4}
	E_{res}		0.7937	0.7855		0.7848
	Γ_{res}		0.0050	5.8×10^{-6}		9.3×10^{-5}
	E_{res}			0.8056		0.8056
	Γ_{res}			1.8×10^{-5}		2.4×10^{-5}

[a] Collins and Schneider (1983).
[b] Tennyson *et al* (1984); SEP.
[c] This work; SEP.

Table 2. Comparison of parameters for the lowest $^1\Sigma_g^+$ resonance at $R = 2\ a_0$ obtained by fitting (*a*) only the d($l = 2$) eigenphase and (*b*) the full eigenphase sum.

	Two-state				Four-state	
	Static exchange		SEP		SEP	
	d only	Full	d only	Full	d only	Full
E_{res} (Ryd)	0.4418	0.4419	0.4050	0.4057	0.4049	0.4054
Γ_{res} (Ryd)	0.0951	0.0954	0.0982	0.1014	0.1101	0.1104

dominated by the d partial wave. This is in line with the results of previous scattering calculations (e.g. Tagaki and Nakamura 1983) and strongly suggests that the autoionisation of the $1\sigma_u^2$ state of H_2 will lead almost exclusively to the emission of electrons with $l = 2$.

3. Dependence on internuclear separation

Figures 1-8 present resonance positions and widths for e-H_2^+ scattering calculated using a two-state model. These calculations were performed for nine H_2^+ geometries in the range $R = 1.2$-$2.8\ a_0$ with a spacing of $0.2\ a_0$. Included are the results of other workers who have calculated resonance parameters as a function of internuclear separation.

Figure 1 shows resonance positions and widths of $^1\Sigma_g^+$ symmetry. This symmetry is the most intensely studied because of the crossing of the H_2^+ $^2\Sigma_g^+$ ground state and

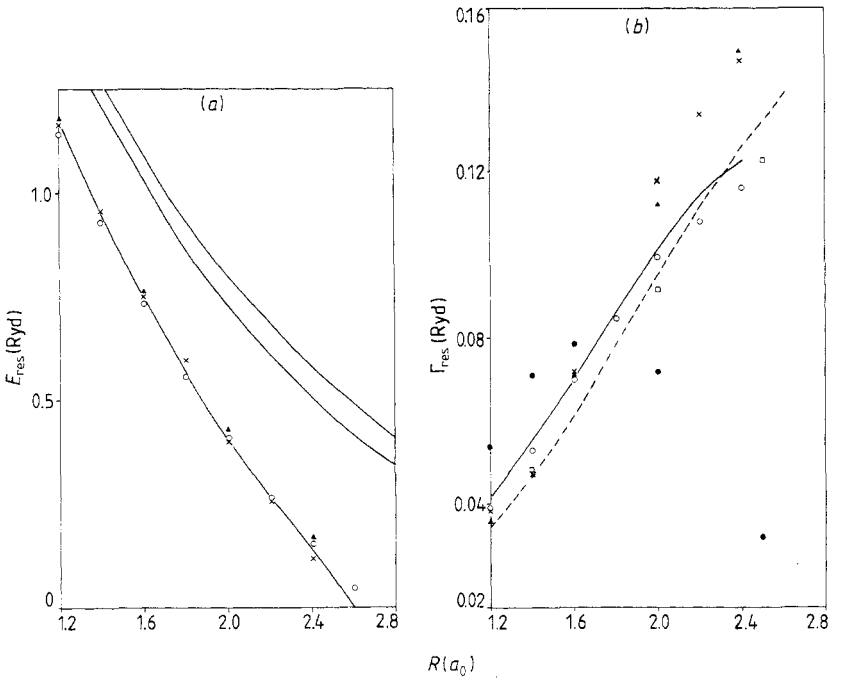

Figure 1. (*a*) Position of lowest three resonances and (*b*) width of lowest resonance of $^1\Sigma_g^+$ symmetry, as a function of H_2^+ separation. Full curve, this work (SEP); broken curve, this work (static exchange); ×, Tagaki and Nakamura (1983); ○, Sato and Hara (1983); ▲, Collins and Schneider (1983) (four-state); □, Hazi *et al* (1983); ●, Bottcher and Docken (1974).

the H_2 $1\sigma_u^2$ state at about $R = 2.6\ a_0$. For this lowest $^1\Sigma_g^+$ potential energy curve (strictly resonance energy curve) there is a good measure of agreement between theoretical calculations so for clarity not all have been included in figure 1(*a*). The situation for the corresponding resonance width (figure 1(*b*)) is less clear. Although the anomalous results of Bottcher and Docken (1974) must be considered discredited, there is still some disagreement between the other theoretical predictions.

Methods of calculation generally divide into two schools: those based on bound-state methods and those based on scattering calculations. The resonance widths of two previous $^1\Sigma_g^+$ e-H_2^+ scattering calculations by Tagaki and Nakamura (1983) and Collins and Schneider (1983) both rise faster with internuclear separation than ours and the other results. However, contrary to usual practise (Hazi 1979a) Tagaki and Nakamura consider partial not total widths. Furthermore, the calculations of Collins and Schneider were performed within the static exchange approximation which partially neglects target polarisation effects.

Our results show much closer agreement with the bound-state results of Hazi *et al* (1983) (well within the 10% accuracy they claim) and of Sato and Hara (1983). This measure of agreement is encouraging and supports our assertions about the accuracy of our method.

An interesting feature of our $^1\Sigma_g^+$ resonance widths is the bend in the curve just before the crossing at $R \sim 2.6\ a_0$. This feature, which appears in slightly enhanced form in our four-state calculations, is caused by polarisation (figure 1(*b*) includes our

static exchange result to illustrate this) and can also be seen in the results of Sato and Hara (1983). The results of Hazi *et al* (1983) are too sparse for any such trend to be detected.

Figure 2 presents results for the $^3\Sigma_g^+$ resonances for which no other geometry-dependent results appear to be available. An interesting feature is that whilst for all other symmetries we have investigated the resonance width increases monotonically with R, the width of the narrow $^3\Sigma_g^+$ resonance shows a shallow minimum in the region $R = 1.8$-$2.0\ a_0$.

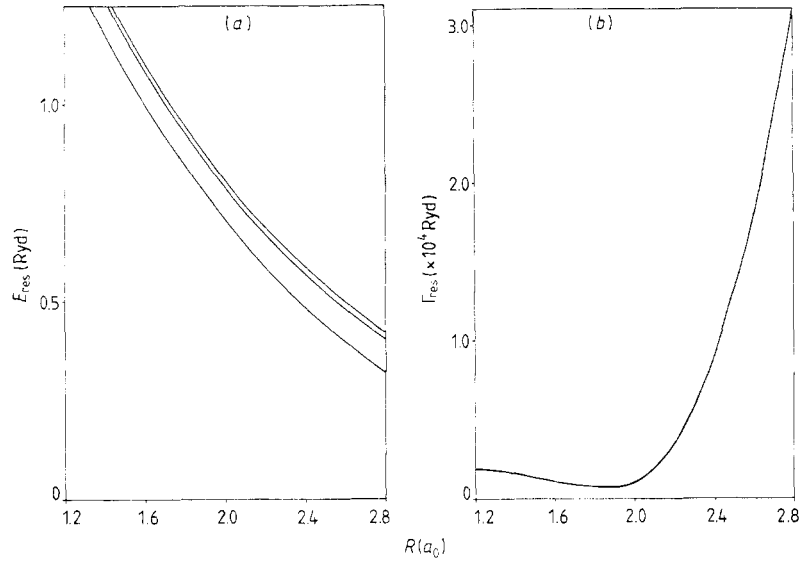

Figure 2. (*a*) Position of lowest three resonances and (*b*) width of lowest resonance of $^3\Sigma_g^+$ symmetry.

Figure 3 compares our results for the $^1\Sigma_u^+$ symmetry with those of Tagaki and Nakamura (1983), Collins and Schneider (1983) and Hazi (1979b, 1983). Although there is a fair agreement between the various calculations about the position of the lowest resonance, our results are consistently lower than the others. For the higher resonances only results due to Tagaki and Nakamura (1983) are available, and, as discussed in I, these are not reliable because of their neglect of coupling to the B $^2\Sigma_u^+$ state of H_2^+.

The $^1\Sigma_u^+$ resonance widths shown in figure 3(*b*) are also in broad agreement, although inclusion of both polarisation and coupled-state effects appears to give resonance widths about 10% narrower. We also note that, perhaps due to more accurate fitting (Tennyson and Noble 1984) or the use of a more stable numerical procedure, our resonance widths are generally smoother functions of R than those published previously.

Figure 4 presents results for the $^3\Sigma_u^+$ symmetry. Again we find fair agreement with Tagaki and Nakamura for the position of the lowest resonance, but a slightly narrower width.

Figures 5 and 6 compare our results for the $^1\Pi_u$ and $^3\Pi_u$ symmetries with those of Hazi (1975) and of Tagaki and Nakamura (1983). The comparison is illuminating.

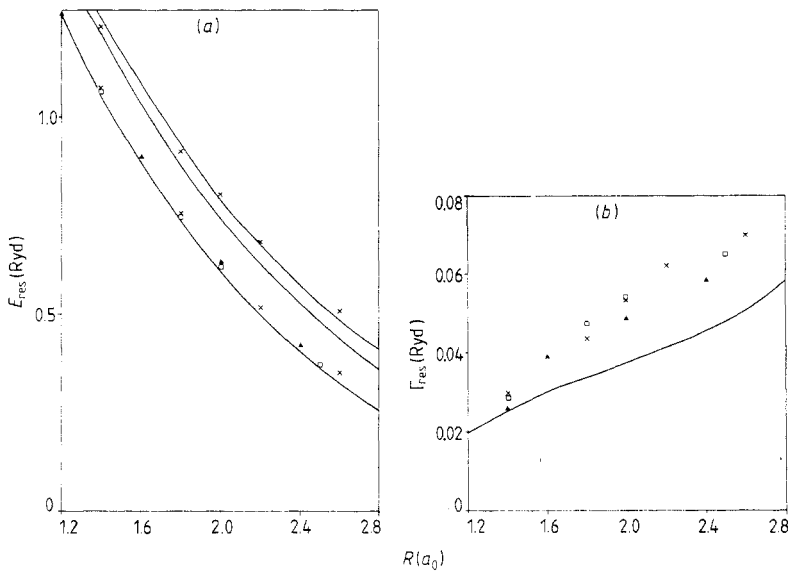

Figure 3. (*a*) Position of lowest three resonances and (*b*) width of lowest resonance of $^1\Sigma_u^+$ symmetry. Full curve, this work (SEP); ×, Tagaki and Nakamura (1983); ▲, Collins and Schneider (1983) (four-state); □, Hazi (1979b, 1983).

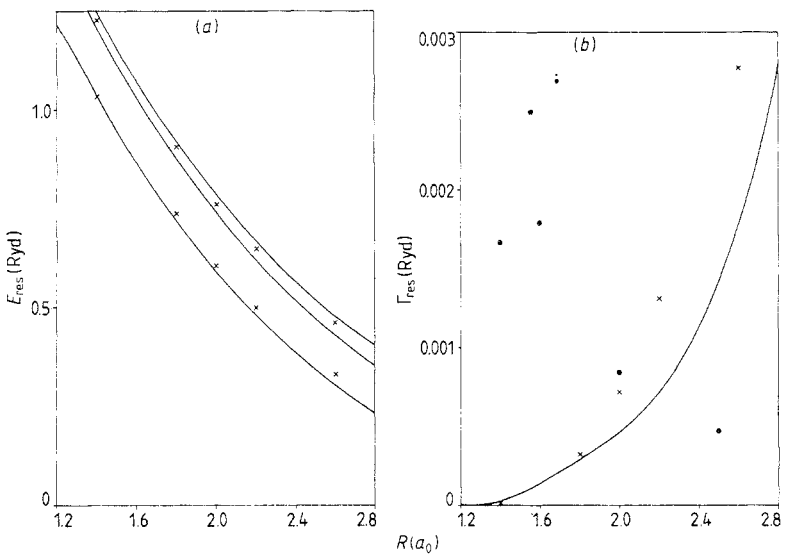

Figure 4. (*a*) Position of lowest three resonances and (*b*) width of lowest resonance of $^3\Sigma_u^+$ symmetry. Full curve, this work (SEP); ×, Tagaki and Nakamura (1983); ●, Bottcher and Docken (1974).

The position of our second $^1\Pi_u$ resonance is in complete agreement with Hazi's (1975) prediction for this resonance. Conversely, the functional form (and magnitude) of both the $^1\Pi_u$ and $^3\Pi_u$ resonance widths predicted by Tagaki and Nakamura (1983) are in complete disagreement with ours. Our resonance widths at $R = 2.0\ a_0$, unlike theirs,

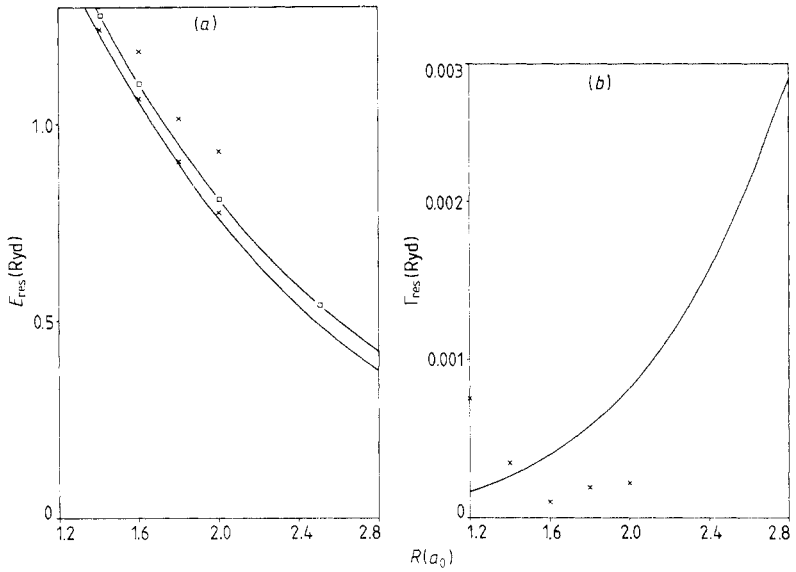

Figure 5. (*a*) Position of lowest two resonances and (*b*) width of lowest resonance of $^1\Pi_u$ symmetry. Full curve, this work (SEP); ×, Tagaki and Nakamura (1983); □, Hazi (1975).

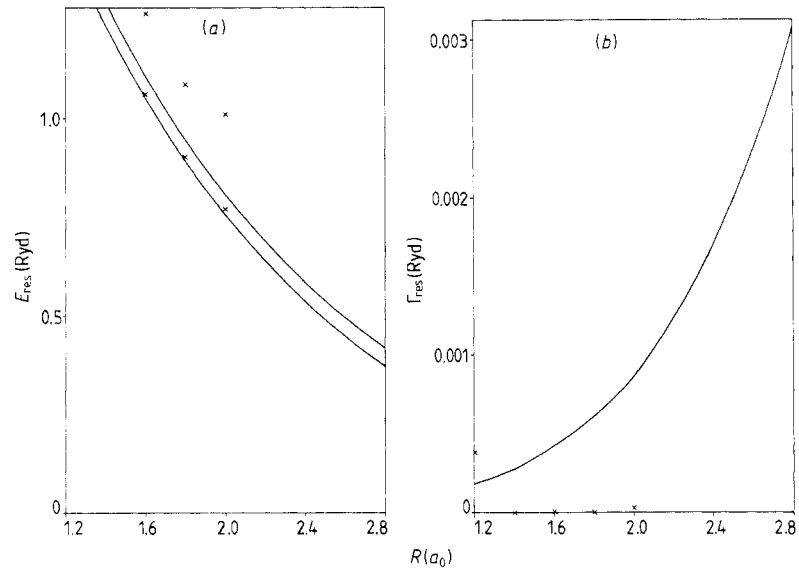

Figure 6. (*a*) Position of lowest two resonances and (*b*) width of lowest resonance of $^3\Pi_u$ symmetry. Full curve, this work (SEP); ×, Tagaki and Nakamura (1983).

are in good agreement with those of other workers (see I). As Tagaki and Nakamura fitted resonance parameters to individual partial waves and not the total eigenphase sums it is possible that they have focused on the wrong partial wave. For Π symmetries, their parameters were obtained by considering only the spheroidal p_π partial wave, whereas our calculations indicate the f_π partial wave is dominant.

Figures 7 and 8 give our results for $^1\Pi_g$ and $^3\Pi_g$ symmetries for which no previous R-dependent data appear to be available, with the exception of calculations by Bottcher and Docken (1974) for $^3\Pi_g$. Their predicted resonances are too wide to be plotted on our figure. We note that the lowest resonance position in both symmetries is low-lying, near that in the $^1\Sigma_u^+$ symmetry, and can be expected to be important in the dissociative recombination process at $R \sim 4\ a_0$.

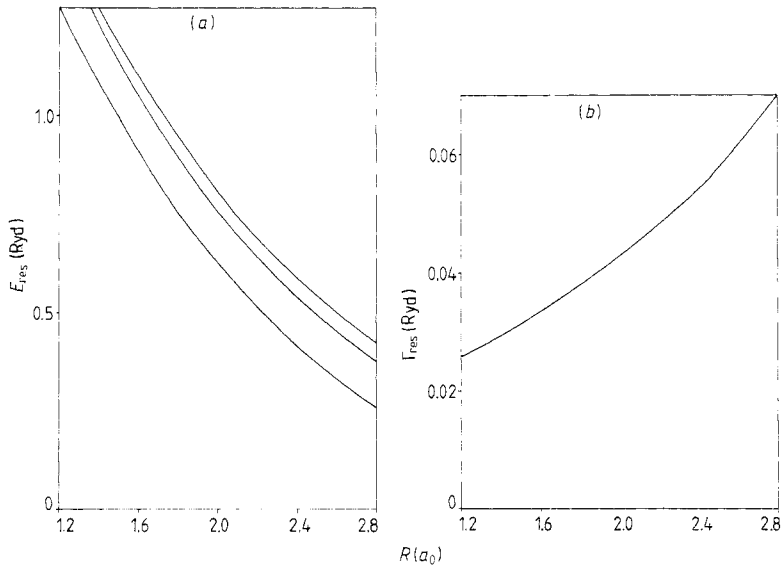

Figure 7. (*a*) Position of lowest three resonances and (*b*) width of lowest resonance of $^1\Pi_g$ symmetry.

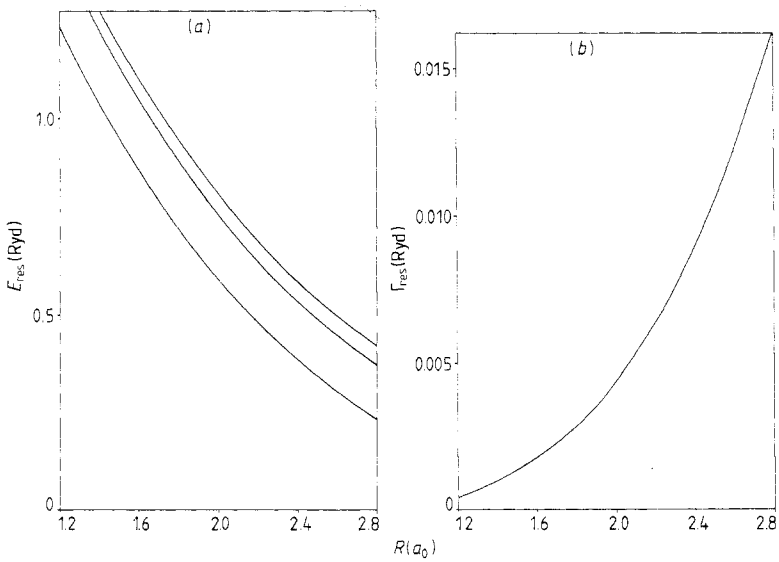

Figure 8. (*a*) Position of lowest three resonances and (*b*) width of lowest resonance of $^3\Pi_g$ symmetry.

4. Electronic excitation

Table 3 shows results for H_2^+ excitation cross sections $Q(^2\sigma_g, ^2\sigma_u)$ for scattering energies below 2 Ryd. For comparison total cross sections calculated within the static exchange approximation by Collins and Schneider (1983) are also shown. In I, their results were found to be in good agreement with static exchange results calculated by our method. The introduction of polarisation can thus be seen to have a relatively small effect on the total electronic excitation cross sections.

Table 3. $^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$ excitation cross sections in a_0^2 for e-H_2^+ collisions at $R = 2.0\ a_0$.

Energy (Ryd)	$^1\Sigma_g$	$^3\Sigma_g$	$^1\Sigma_u$	$^3\Sigma_u$	$^1\Pi_u$	$^3\Pi_u$	$^1\Pi_g$	$^3\Pi_g$	$^1\Delta_g$
0.92	0.388	0.044	0.738	0.416	0.223	0.580	1.081	0.396	0.023
1.0	0.362	0.066	0.524	1.477	0.246	0.588	0.974	0.396	0.033
1.2	0.310	0.115	0.498	0.369	0.280	0.550	0.774	0.406	0.054
1.4	0.267	0.126	0.397	0.322	0.286	0.486	0.634	0.412	0.068
1.6	0.239	0.120	0.444	0.442	0.285	0.432	0.523	0.402	0.075
1.8	0.183	0.128	0.486	0.476	0.289	0.385	0.441	0.390	0.077
2.0	0.166	0.146	0.400	0.323	0.494	0.344	0.378	0.376	0.078

Energy (Ryd)	$^3\Delta_g$	$^1\Delta_u$	$^3\Delta_u$	$^1\Phi_u$	$^3\Phi_u$	$^1\Phi_g$	$^3\Phi_g$	Sum	Total[a]
0.92	0.064	0.136	0.302	0.002	0.005	0.013	0.037	4.45	
1.0	0.094	0.150	0.318	0.007	0.022	0.020	0.055	5.33	4.61
1.2	0.151	0.158	0.332	0.009	0.026	0.036	0.089	4.16	4.51
1.4	0.186	0.155	0.325	0.020	0.060	0.042	0.113	3.90	4.23
1.6	0.201	0.149	0.315	0.031	0.089	0.048	0.127	3.92	3.96
1.8	0.206	0.140	0.302	0.028	0.078	0.051	0.035	3.80	3.74
2.0	0.207	0.130	0.285	0.027	0.076	0.054	0.140	3.60	3.54

[a] Collins and Schneider (1983).

Above the highest threshold explicitly included, the inclusion of polarisation leads to both real and pseudo resonances. Firstly there is an infinite series of resonances converging to the H_2^+ B $^2\Pi_u$ threshold (at 1.345 Ryd for $R = 2.0\ a_0$). The broader of these resonances (e.g. that with $^1\Sigma_u^+$ symmetry at about 1.20 Ryd) will be reproduced by our optical potential. Secondly, above the $^2\Pi_u$ threshold spurious pseudo-resonance effects are possible (Burke *et al* 1981). However, in the present calculations these effects do not appear to be serious and we did not consider it necessary to employ resonance averaging techniques (Salvini *et al* 1984).

5. Conclusions

We have presented a comprehensive survey of the low-lying resonance positions and widths in the e-H_2^+ collision problem as a function of internuclear separation. Comparison of our results with previous calculations where available shows a broad measure of agreement on the lowest resonance position in each symmetry. The only exception to this is the possible misassignment by Hazi (1975) of his $^1\Pi_u$ resonance.

Our calculations also consider the second and third resonance positions and their accuracy has been confirmed by comparison with linear algebraic results (Collins and Schneider 1984) and the excellent agreement with the $^1\Pi_u$ state of Hazi (1975). The only other comparable results for these states is the partial survey due to Tagaki and Nakamura (1983). As was shown in paper I their results constantly give second resonance positions which are too high in energy. This is directly attributable to their neglect of the coupling to the H_2^+ $A\,^2\Sigma_u^+$ state which we include. Indeed their second and third resonances of $^1\Pi_u$ and $^3\Pi_u$ symmetry lie above this state. In contrast our calculation can resolve an arbitrary number of the infinite series of resonances which converge to the $^2\Sigma_u^+$ threshold.

The situation concerning the widths of various resonances is less clear. There are some large variations between the published results and in some cases qualitative differences between functional dependences on H_2^+ geometry. For example, it is important to notice that Tagaki and Nakamura (1981, 1983) calculate partial widths which are not strictly comparable with the total widths presented here.

In the most studied symmetry, $^1\Sigma_g^+$, we predict a slight bend in the resonance width at large H_2^+ separation caused by polarisation effects. This trend, which can also be seen in the widths of Sato and Hara (1983), and in our four-state results and has not previously been commented upon.

In all Σ symmetries our resonance widths are consistently about 10% narrower than those calculated previously using scattering methods. However, these calculations by Tagaki and Nakamura (1983) and Collins and Schneider (1983), at least partially neglect coupled-state and polarisation effects respectively. Our Π symmetry resonance widths are the first accurate results which consider the effects of H_2^+ geometry, although we are in good agreement with the previous results at H_2^+ equilibrium (see I).

Work is now in progress utilising the results presented in this paper to investigate vibrational excitation, photoionisation and dissociative recombination processes, all of which require accurate geometry-dependent data if direct comparisons with experiment are to be made. We are also applying the *R*-matrix method to low-energy electron scattering problems with more demanding (many-electron) targets and in particular to ones in which coupled-state effects might be expected to be significant.

Acknowledgement

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