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LETTER TO THE EDITOR

Electronic excitation of the b $^3\Sigma_u^+$ state of H_2 using the *R*-matrix method

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Abstract. The electronic excitation of the repulsive b $^3\Sigma_u^+$ state of H_2 from the ground state is studied using the *R*-matrix method. Correlation and polarisation effects are included *ab initio*. Results are compared with other theoretical work. While previous calculations appear to underestimate the cross section, good agreement is obtained with the results of the linear algebraic method and the Schwinger multichannel formulation. We also present elastic scattering cross sections in the same approximation and compare our results with other work. We obtain satisfactory agreement with experimental results.

The study of the X $^1\Sigma_g^+ \rightarrow$ b $^3\Sigma_u^+$ transition in H_2 provides a sensitive test of various theories because, being spin forbidden, this process can only occur through exchange. The process has been studied in the distorted-wave approximation (Fliflet and McKoy 1980) and the Ochkur–Rudge approximation (Cartwright and Kuppermann 1967). There are various two-state close-coupling approximations (Chung and Lin 1978, Weatherford 1980, Lima *et al* 1984, 1985, Schneider and Collins 1985). The calculations of Chung and Lin (1978) and Weatherford (1980) make no allowance for correlation and polarisation effects. These effects are however included by Lima *et al* (1984, 1985) in the Schwinger multichannel variational formulation, and by Schneider and Collins (1985) in the linear algebraic method (LAM).

The Ochkur–Rudge and distorted-wave methods are expected to be valid at high impact energies. At low and intermediate electron energies, they show results which may be even qualitatively incorrect (Lee and McKoy 1983). The close-coupling calculations of Chung and Lin (1978) and Weatherford (1980) were performed at the two-state static-exchange level. Since the transition under study is a short-range process, the correlation and polarisation terms which they omit can be expected to play significant roles. In the linear algebraic method (LAM), Collins and Schneider (1983) introduce exchange and polarisation contributions to the full interaction via separable expansions of the Feshbach optical potential. Using this method, they calculated the cross sections with which we compare our results and also the results of Schneider and Collins (1985). This method is closest in spirit to the present work.

We use the *R*-matrix method of Burke *et al* (1977) which has recently been reviewed by Burke and Noble (1983). This method has yielded reliable results for the electronic excitation of H_2^+ (Tennyson and Noble 1985). We expand the wavefunction for the

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e-H_2 system within a finite R-matrix sphere of radius 10 au in the form

$$\Psi(x_1, x_2, x_3) = \mathscr{A} \sum_{i=1}^{2} \Phi_i(x_1, x_2) F_i(x_3) + \sum_i b_i \phi_i(x_1, x_2, x_3) \tag{1}$$

where $x_i = (\boldsymbol{r}_i, \sigma_i)$ represents the space-spin coordinates of the ith electron and $\mathscr{A}$ is an anti-symmetriser. Two states $X\,{}^1\Sigma_g^+$ and $b\,{}^3\Sigma_u^+$ of H_2 are included in the first expansion. These states, at the H_2 equilibrium distance $R = 1.4\ a_0$, are represented by an LCAO-MO-SCF wavefunction, which was constructed using the 1s-2s-2p STO σ basis of Fraga and Ransil (1961). This basis was augmented by one $2p\pi$ STO function (with the $2p\sigma$ exponent) on each H to provide virtual molecular orbitals for polarisation effects. The functions F in equation (1) describe the radial motion of the scattering electron. These are obtained numerically by solving a one-dimensional model scattering problem (Salvini 1983).

The continuum basis was chosen to be complete over an energy range up to 3.0 Ryd. We retained the lowest three partial waves for each of the target states.

The terms ϕ_i in equation (1) are L^2 configurations of three electrons which are formed from the occupied and virtual target orbitals. These represent the short-range correlation effects. In the static-exchange (SE) model, two electrons are frozen in either $1\sigma_g^2$ or $1\sigma_g^1\,1\sigma_u^1$ configurations and the third electron occupies any of the virtual orbitals appropriate for the overall symmetry of the system. In the static-exchange polarisation (SEP) model, one electron is frozen in a $1\sigma_g$ or $1\sigma_u$ orbital and the other two electrons occupy virtual orbitals within the constraints of symmetry. The b_i are coefficients which are determined variationally.

In figure 1, we present the results of elastic scattering from the ground state of H_2 using our SEP model and compare the results with the LAM results of Collins and Schneider (1983) and of Lima *et al* (1984) calculated in the Schwinger multichannel formulation. We show the experimental results of total cross sections measured by Hoffman *et al* (1982), Dalba *et al* (1980) and Jones (1985). Beyond 0.35 Ryd, we are in good agreement with the experimental results of Jones (1985). In the energy region between 0.15 and 0.35 Ryd, there is some disagreement among the various experiments.

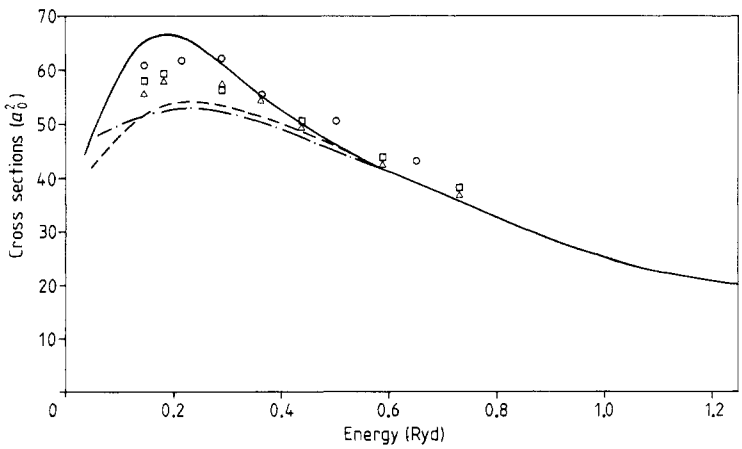

Figure 1. Elastic scattering cross sections for electron impact on the $X\,{}^1\Sigma_g^+$ state of H_2: ——, two-state SEP; □, Dalba *et al* (1980) experiment; △, Jones (1985) experiment; ○, Hoffman *et al* (1982) experiment; - - -, Collins and Schneider (1983); — · —, Lima *et al* (1984).

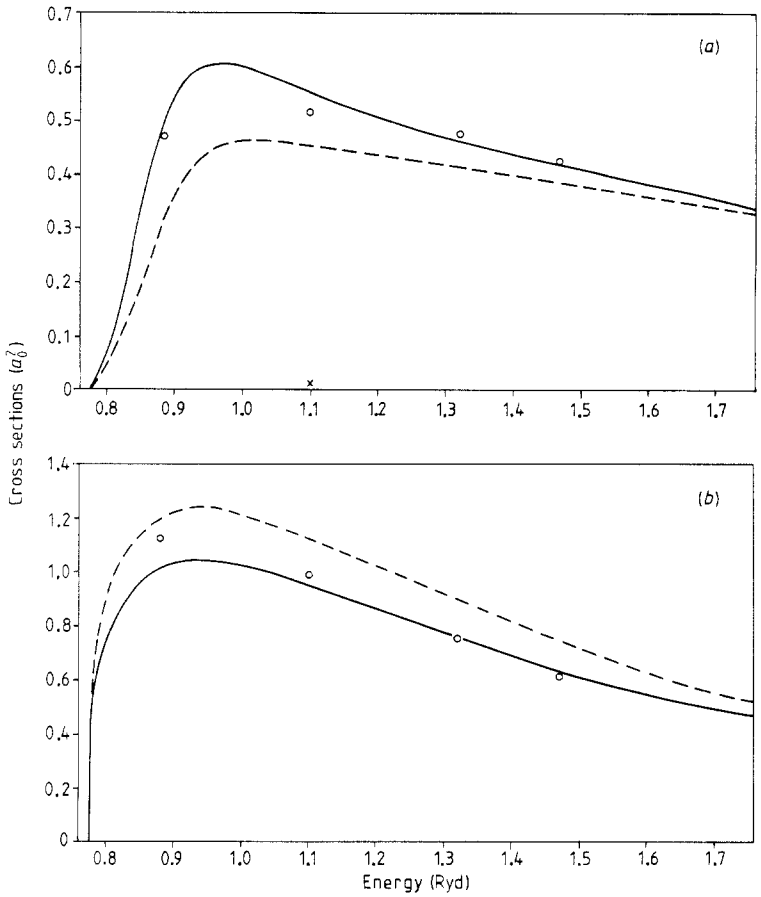

Figure 2. Cross sections for $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ in H_2 for (*a*) $^2\Sigma_g$ symmetry, (*b*) $^2\Sigma_u$ symmetry: ——, two-state SEP; - - -, two-state SE; ×, Chung and Lin (1978); ○, Schneider and Collins (1985).

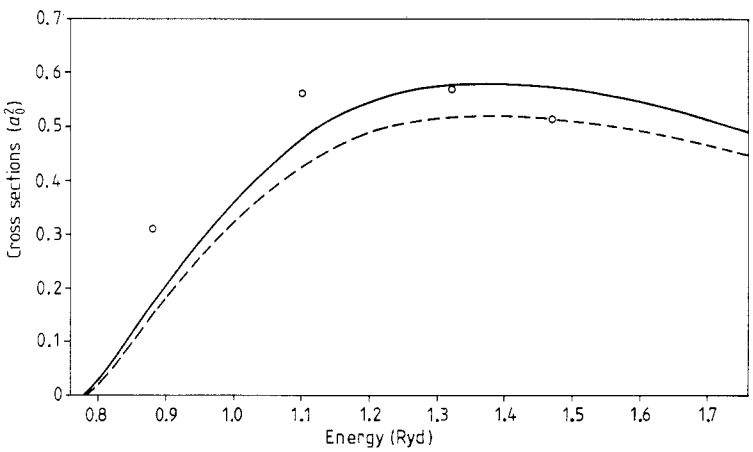

Figure 3. Cross sections for $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ in H_2 for $^2\Pi_g$ symmetry: ——, two-state SEP; - - -, two-state SE; ○, Schneider and Collins (1985).

Our results tend to overestimate the experimental measurements whereas the other theoretical results illustrated tend to underestimate them.

In figure 2, we compare our results of SE and SEP models for excitation of the b $^3\Sigma_u^+$ state with the two-state results of Chung and Lin (1978) and LAM results of Schneider and Collins (1985) for the symmetries $^2\Sigma_g$ and $^2\Sigma_u$. The inclusion of polarisation effects increases the cross section for the $^2\Sigma_g$ symmetry and decreases it by an almost complementary amount for $^2\Sigma_u$ symmetry. For all these symmetries our SEP results are in good agreement with LAM results; our values for the cross sections agree to within

Table 1. X $^1\Sigma_g^+ \rightarrow$ b $^3\Sigma_u^+$ excitation cross sections in a_0^2 for e-H_2 collisions at $R = 1.4\ a_0$.

Energy (Ryd)	$^2\Sigma_g$	$^2\Sigma_u$	$^2\Pi_u$	$^2\Pi_g$	$^2\Delta_g$	$^2\Delta_u$	Sum
0.78	0.0183	0.4717	0.0000	0.0074	0.000 00	0.000 00	0.4974
0.82	0.1768	0.8380	0.0005	0.0634	0.000 00	0.000 04	1.0787
0.86	0.3914	0.9735	0.0017	0.1341	0.000 00	0.000 17	1.5009
0.90	0.5438	1.0278	0.0035	0.2053	0.000 01	0.000 40	1.7808
0.92	0.5826	1.0382	0.0047	0.2395	0.000 02	0.000 55	1.8656
0.94	0.6018	1.0412	0.0059	0.2723	0.000 03	0.000 72	1.9220
0.96	0.6077	1.0388	0.0073	0.3037	0.000 04	0.000 91	1.9585
0.98	0.6054	1.0323	0.0087	0.3335	0.000 06	0.001 11	1.9811
1.00	0.5987	1.0288	0.0102	0.3616	0.000 08	0.001 33	1.9947
1.04	0.5799	0.9977	0.0133	0.4130	0.000 12	0.001 82	2.0058
1.10	0.5512	0.9515	0.0182	0.4772	0.000 20	0.002 62	2.0009
1.20	0.5102	0.8656	0.0262	0.5491	0.000 38	0.004 10	1.9556
1.30	0.4743	0.7763	0.0340	0.5801	0.000 62	0.005 63	1.8709
1.50	0.4138	0.6123	0.0471	0.5674	0.001 19	0.008 31	1.6501
1.80	0.3272	0.4406	0.0578	0.4791	0.002 11	0.010 75	1.3176
2.00	0.2680	0.3673	0.0619	0.4038	0.002 60	0.011 60	1.1152

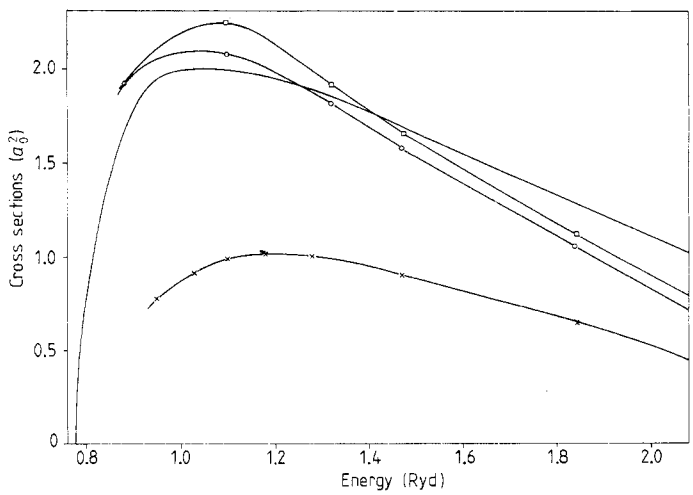

Figure 4. Cross sections for X $^1\Sigma_g^+ \rightarrow$ b $^3\Sigma_u^+$ in e-H_2 summed over all symmetries: ——, two-state SEP; ×, Chung and Lin (1978); ○, Schneider and Collins (1985); □, Lima *et al* (1985).

20%. In sharp contrast to this, the results of Chung and Lin lie very much lower. This we attribute to the neglect of correlation and polarisation effects in their calculations.

In figure 3, we compare our results for $^2\Pi_g$ symmetry with LAM results. The agreement is again satisfactory considering that the two methods are quite different in their numerical approach. In figure 4, we show the summed cross sections for all the symmetries and compare our results with other workers. As expected, our results again lie closer to the LAM results and those of Lima *et al* (1985) than the results of Chung and Lin (1978). We present the cross sections for this excitation process in table 1 for all the symmetries considered in this work. It is apparent from table 1 that we have obtained converged results.

We conclude that the correlation and polarisation effects are important for the calculation of cross sections for the process $X\ ^1\Sigma_g^+ \rightarrow b\ ^3\Sigma_u^+$ in H_2. The neglect of these effects in earlier calculations yields estimates significantly too low.

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