LETTER TO THE EDITOR

Electron-impact excitation of the b $^3\Sigma_u^+$ state of H_2 using the complex Kohn method: R dependence of the cross section

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Abstract. Calculations of electron-impact excitation of the b $^3\Sigma_u^+$ state of H_2 have been carried out using the complex Kohn variational approach. Two-state close-coupling results were obtained with molecular target wavefunctions that properly dissociate to neutral atoms. The R dependence of the fixed-nuclei results was used to obtain the dissociation cross section as a function of the initial vibrational state of H_2.

At low energies, electron-impact dissociation of molecular hydrogen proceeds mainly through excitation of the lowest triplet electronic state (b $^3\Sigma_u^+$), which dissociates to neutral ground-state hydrogen atoms. Cross sections for this process, and particularly their dependence on the initial vibrational quantum number, are required for accurate modelling of hydrogen plasmas. Previous theoretical studies have shown that this cross section is very sensitive to approximations made in the dynamics. Indeed, it is only within the last few years that theoretical calculations have appeared which are in mutual accord (Baluja *et al* 1985, Schneider and Collins 1985, Lima *et al* 1985) and which also agree with experiment (Hall and Andric 1984, Nishimura *et al* 1985). Being spin forbidden, this transition proceeds only through exchange and a relatively small number of symmetry components contribute to the total cross section.

Previous calculations have all been carried out at the equilibrium internuclear separation of H_2. No information, theoretical or experimental, has been available about the dependence of this process on the vibrational temperature of the target molecule. We have therefore extended our earlier treatment (Schneider and Rescigno 1988) to examine the R dependence of the cross section. The results of this investigation are reported in this letter. We begin with a brief description of the complex Kohn variational technique; details of the method have been given elsewhere (Rescigno and Schneider 1988, Schneider and Rescigno 1988). We then describe the calculations we have carried out and present cross sections from near threshold to 30 eV as a function of initial vibrational state.

The electronic problem is solved by using a fixed-nuclei wavefunction of the form

$$\psi_{\Gamma^0} = \sum_\Gamma A(\chi_\Gamma F_{\Gamma\Gamma^0}) + \sum_\mu d_\mu^{\Gamma^0}\oplus_\mu. \tag{1}$$

The χ are electronic target states, A is an antisymmetriser and the F describe the motion of the scattering electron which is incident in a physical channel labelled by Γ^0 and emerges in channel Γ; the functions $\oplus$ are orthonormal three-electron functions

formed from the occupied target orbitals and are used to describe short-range correlation. The effect of these correlation functions can be formally incorporated into an effective optical potential, V_{opt}, by using Feshbach partitioning techniques (Feshbach 1958). Defining Q to be the operator that projects on the functions $\oplus_\mu$ and P its orthogonal complement, we can manipulate the Schrödinger equation in a standard way to produce a modified Hamiltonian,

$$H_{eff} = H_{PP} + (H - E)_{PQ}(E - H)_{QQ}^{-1}(H - E)_{QP} \equiv H_{PP} + V_{opt} \tag{2}$$

and the functions $\oplus_\mu$ are dropped from the trial wavefunction in equation (1):

In the Kohn method, the functions F are further expanded as

$$rF_{\Gamma\Gamma^0}(\boldsymbol{r}) = \sum_l [f_l^\Gamma(r)\delta_{ll^0}\delta_{mm^0}\delta_{\Gamma\Gamma^0} + T_{lml^0m^0}^{\Gamma\Gamma^0}g_l^\Gamma(r)]Y_{lm}(\hat{r}) + \sum_k c_k^{\Gamma\Gamma^0}\varphi_k^\Gamma(\boldsymbol{r}) \tag{3}$$

where the f_l^Γ and g_l^Γ are functions which are regular at $r = 0$ and behave asymptotically as regular and outgoing Ricatti–Bessel functions, Y_{lm} is a spherical harmonic and the φ_k^Γ are a set of square-integrable functions. The entire expansion is symmetry-adapted. The $T_{lml^0m^0}^{\Gamma\Gamma^0}$ are the electronic T-matrix elements from which physical cross sections are determined; they have an implicit R dependence. These coefficients, along with the coefficients $c_k^{\Gamma\Gamma^0}$, are determined variationally by inserting equation (1) into the Kohn variational functional

$$[T^{\Gamma\Gamma^0}] = T^{\Gamma\Gamma^0} - 2 \int \Psi_\Gamma(H_{eff} - E)\Psi_{\Gamma^0} \tag{4}$$

and solving the set of linear equations that result from making it stationary. The fact that outgoing-wave boundary conditions are used ensures that the expression obtained for the T matrix is free of spurious singularities (McCurdy *et al* 1987).

Two states $X\,^1\Sigma_g^+$ and $b\,^3\Sigma_u^+$ are included in equation (1). In practice, the molecular orbitals used to construct these states must be kept orthogonal to the L^2 functions used in expanding the F. Therefore, it is convenient to employ as compact a description of the target states as possible. It is well known that the ground-state Hartree–Fock wavefunction, while providing a reasonable description of the molecule near its equilibrium geometry, does not dissociate properly to neutral atoms. Therefore, we first carried out a multiconfiguration self-consistent field calculation on the ground state using a two-term wavefunction of the form $c_1 1\sigma_g^2 + c_2 1\sigma_u^2$, which does properly dissociate to $H + H$. For the $b\,^3\Sigma_u^+(1\sigma_g 1\sigma_u)$ state, we determine a $1\sigma_u$ orbital by diagonalising the Hamiltonian constructed with the V_{N-1} potential defined by the ground-state $1\sigma_g$ core orbital. This procedure results in a $1\sigma_u$ orbital which is, for small values of R, rather different from the $1\sigma_u$ orbital obtained from the ground-state calculation. Therefore, we then redetermine the ground-state function by performing a two-term configuration-interaction calculation with the original $1\sigma_g$ and the new $1\sigma_u$ orbitals. This procedure gives a ground-state wavefunction which differs very little from the original MCSCF result and provides a simple description of both states in terms of the same two molecular orbitals, which properly become equivalent as $R \to \infty$. Table 1, which compares our calculated $b\,^3\Sigma_u^+ - X\,^1\Sigma_g^+$ energy splittings with the essentially exact results of Kolos and Wolniewicz (1965), shows that our simple procedure is reasonably accurate.

The variational calculations were carried out with basis functions which, in addition to being mutually orthogonal, were also orthogonalised to the target $1\sigma_g$ and $1\sigma_u$ orbitals. In order to relax this strong orthogonality constraint, the correlating configurations $1\sigma_g^2 1\sigma_u$ and $1\sigma_g 1\sigma_u^2$ were used in constructing the optical potentials for the $^2\Sigma_u^+$

Table 1. Electronic energy difference between b $^3\Sigma_u^+$ and ground states of H_2. The 'exact' results are those of Kolos and Wolniewicz (1964). Energies are given in electron volts.

R (au)	This work	Exact
1.0	13.31	13.69
1.2	11.68	12.14
1.4	10.11	10.62
1.6	8.65	9.17
2.0	6.09	6.23
3.0	2.09	2.32
4.0	0.56	0.63

and $^2\Sigma_g^+$ symmetry channels, respectively. Failure to relax these orthogonality constraints between target and scattering orbitals is now known to have led to serious errors in earlier theoretical studies of H_2 dissociation (Chung and Lin 1978, Weatherford 1980). No correlating configurations are needed in $^2\Pi_g$ and $^2\Pi_u$ symmetry. The complex Kohn equations were solved by using scattering basis sets of up to 23 molecular orbitals, constructed from Cartesian Gaussian functions, in each of four symmetries, σ_g, σ_u, π_g, and π_u, along with regular and outgoing-wave Bessel functions up to $l = 12$.

Calculations were performed at internuclear separations between 1.0 and 4.0 au for incident energies of 12, 15, 18, 25 and 30 eV. The results are summarised in tables 2 and 3 in the form of 'fixed-nuclei cross sections' which are defined as

$$\sigma^m(E_0, R) = \frac{1}{k_0^2} \sum_{ll'} |T_{lml'm}(R)|^2. \tag{5}$$

Note that at large R, the $^2\Sigma_g^+$ and $^2\Sigma_u^+$ (as well as the $^2\Pi_g$ and $^2\Pi_u$) contributions to the cross sections approach the same values, as they should. In the large R limit, the problem reduces to exchange scattering from an isolated hydrogen atom.

Table 2. $^2\Sigma$ components of fixed-nuclei cross sections (a_0^2) for excitation of the b $^3\Sigma_u^+$ state of H_2.

R	12 eV	15 eV	18 eV	20 eV	25 eV	30 eV
$^2\Sigma_g^+$ symmetry						
1.0	—	0.2106	0.2946	0.3011	0.2501	0.1850
1.2	0.0389	0.3886	0.4067	0.3812	0.2902	0.1909
1.4	0.4364	0.5373	0.4827	0.4331	0.3063	0.1958
1.6	0.6685	0.6243	0.5187	0.4538	0.3061	0.1948
2.0	0.8670	0.6870	0.5625	0.4746	0.3002	0.1983
3.0	1.2344	0.8979	0.6625	0.5596	0.3804	0.2710
4.0	1.5397	1.2552	0.8235	0.6827	0.4329	0.3144
$^2\Sigma_u^+$ symmetry						
1.0	—	0.5080	0.5095	0.4270	0.2669	0.1667
1.2	0.4513	0.8145	0.6688	0.5548	0.3415	0.2144
1.4	1.1876	1.0479	0.7999	0.6498	0.3999	0.2518
1.6	1.5240	1.2043	0.8660	0.7019	0.4345	0.2774
2.0	1.8053	1.2554	0.8795	0.7219	0.4518	0.3001
3.0	1.6109	1.0825	0.7890	0.6487	0.4229	0.2934
4.0	1.4806	1.1785	0.7974	0.6673	0.4451	0.3189

Table 3. $^2\Pi$ components of fixed-nuclei cross sections (a_0^2) for excitation of the $b^3\Sigma_u^+$ state of H_2.

R	12 eV	15 eV	18 eV	20 eV	25 eV	30 eV
$^2\Pi_g$ symmetry						
1.0	—	0.0999	0.1992	0.1985	0.1451	0.0956
1.2	0.0133	0.2082	0.2577	0.2271	0.1700	0.1106
1.4	0.1453	0.2858	0.2913	0.2666	0.1874	0.1253
1.6	0.2656	0.3420	0.3213	0.2882	0.1998	0.1342
2.0	0.4171	0.4123	0.3558	0.3105	0.2104	0.1412
3.0	0.6032	0.4850	0.3717	0.3108	0.2032	0.1328
4.0	0.5521	0.4488	0.3404	0.2878	0.1894	0.1188
$^2\Pi_u$ symmetry						
1.0	—	0.0006	0.0042	0.0070	0.0113	0.0120
1.2	0.00002	0.0040	0.0101	0.0134	0.0177	0.0171
1.4	0.0024	0.0122	0.0191	0.0225	0.0249	0.0233
1.6	0.0109	0.0236	0.0314	0.0341	0.0341	0.0307
2.0	0.0475	0.0603	0.0653	0.0639	0.0566	0.0477
3.0	0.2067	0.1929	0.1707	0.1554	0.1215	0.0949
4.0	0.3458	0.3111	0.2424	0.2111	0.1686	0.1188

Is it customary to define a rotationally averaged excitation cross section by averaging over the initial and summing over the final rotational levels of the target molecule. On the assumption that these can be taken to be essentially degenerate, we obtain the following expression for the differential cross section, at a particular incident energy E_0:

$$\sigma_{\nu_0 \to k_\nu}(E_0, \theta, \phi) = \int \left| \int \chi_{\nu_0}(R) T(E_0, \theta, \phi; R, \Omega) \chi_{k_\nu}(R)\, \mathrm{d}R \right|^2 \frac{\mathrm{d}\Omega}{4\pi} \qquad (6)$$

where χ_{ν_0} and χ_{k_ν} are the initial (discrete) and final (continuous) vibrational wavefunctions, T is the scattering amplitude and Ω denotes the spherical polar angles of the molecular axis relative to a set of laboratory fixed axes. The final continuum vibrational level is being labelled by k_ν, the relative momentum of the dissociating nuclei. We now make some simplifying approximations. For the final continuum vibrational function we use the classical delta-function approximation which consists of replacing $\chi_{k_\nu}(R)$ by $|\mathrm{d}V/\mathrm{d}R|^{-1/2}\delta(R - R_0^k)$, where R_0^k is the classical turning point on the upper-state potential curve V. The target orientation dependence of the scattering is treated analytically in the usual fashion (Temkin *et al* 1969, Fliflet and McKoy 1980) by expanding the amplitude T in partial waves. The final result for the total cross section, integrated over all accessible levels of the final state, is

$$\sigma(E_0) = \frac{1}{k_0^2} \sum_{l'lm} \int \chi_{\nu_0}(R)^2 |T_{lml'm}|^2\, \mathrm{d}R. \qquad (7)$$

The vibrational wavefunctions were generated numerically using the 'exact' ground-state potential of Kolos and Wolniewicz (1965). The final results are shown in table 4. Incorporation of the R dependence of the scattering amplitude evidently has little effect for $\nu_0 = 0$. Indeed, our values for $\nu_0 = 0$ are in good agreement with previous results. However, the cross sections are seen to increase as a function of initial vibrational excitation. The effect becomes more pronounced as the incident energy decreases.

Table 4. Total cross sections (a_0^2) for excitation of the b $^3\Sigma_u^+$ state of H_2 from various vibrational levels of the ground state.

ν_0	12 eV	15 eV	18 eV	20 eV	25 eV	30 eV
0	1.991	2.227	1.923	1.671	1.139	0.752
1	2.176	2.296	1.959	1.695	1.152	0.768
2	2.400	2.357	1.996	1.725	1.166	0.785
3	2.631	2.428	2.036	1.757	1.185	0.803
4	2.831	2.496	2.076	1.788	1.206	0.821
5	3.011	2.565	2.116	1.820	1.228	0.840
6	3.178	2.638	2.157	1.852	1.252	0.859
7	2.340	2.722	2.202	1.888	1.279	0.880
8	3.507	2.822	2.254	1.928	1.308	0.903
9	3.678	2.942	2.313	1.975	1.341	0.927

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