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Impact-Parameter Treatment of Hydrogen-Hydrogen Excitation Collisions. II. Four-State Approximation*

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An impact-parameter treatment is carried out for the processes H(1s) + H(1s) → H(1s) + H(2s or 2p) with incident hydrogen-atom energies E in the range 360 eV $\leq E \leq$ 100 keV. Full account is taken of distortion, back coupling, rotational coupling, and the virtual transition sequence $1s \rightleftharpoons 2p \rightleftharpoons 2s$. Comparison with previous two-state calculations, which included only the effects of distortion and back coupling, shows that the presence of the optically allowed 1s-2p transition increases the 1s-2s cross section at all energies, augmenting it by as much as 73% at 360 eV, and contributes relatively less with energy increase. For excitation of the 2p-magnetic components, rotational coupling and the inclusion of the optically forbidden channel influence the cross sections only slightly and in opposite senses for energies above 6 keV, while for lower energies their combined effect is to decrease severely the excitation probabilities. The percentage polarization of the emitted radiation is also evaluated.

I. INTRODUCTION

Recently, Flannery[1] calculated the $n=2$ and 3 single-excitation cross sections describing collisions between two hydrogen atoms initially in their ground states. A two-state version of the impact-parameter treatment was used. The 1s-2p excitation probability is larger than that of the 1s-2s transition, and hence it is to be expected that the inclusion of the optically allowed channel will influence the forbidden-transition probability, although the reverse situation is presumably less important. Also during the collision there is a natural tendency, especially for intermediate encounters with impact parameter ρ in the range $\rho_1 < \rho < \rho_2$, for the quantization axis of the atoms, which is fixed in the two-state treatment, to follow the rotation of the internuclear line. This tendency becomes less for distant collisions, $\rho > \rho_2$, because the perturbation is then not sufficiently strong to separate the degenerate magnetic substates, and also for close collisions, $\rho < \rho_1$, because the quantization axis of the atomic eigenfunctions is reluctant to follow the rapid rotation of the internuclear line. These effects can be introduced into the theoretical description by including couplings between the magnetic m substates. This procedure effectively bridges the gap between the two extreme cases of the two-state approximation, with its constantly fixed quantization axis, and the perturbed stationary state[2] or perturbed rotating-atom[3] methods, in which the axis of the quantization is taken to follow always the rotating internuclear line.

In this paper, the influence of this "rotation" coupling together with the virtual transition sequence, represented by $1s \rightleftharpoons 2p_0 \rightleftharpoons 2p_{+1} \rightleftharpoons 2p_{-1} \rightleftharpoons 2s$, is examined for the case of the 2s and 2p single excitations in an H-H collision. Distortion and back-coupling effects are included, but exchange effects are neglected.

II. THEORY

In describing a collision between two hydrogen atoms, we can assume that the incident atom travels with constant velocity v in the positive direction along a line distant ρ, the impact parameter, from the Z axis of a fixed cylindrical coordinate system; the target atom being at rest at the origin. The impact-parameter method[4] results in the following set of coupled equations:

$$i\hbar \frac{\partial a_r}{\partial Z} = \frac{1}{v} \sum_{s=1}^{S} a_s(Z) \exp[i(m_r - m_s)\Phi]\, V_{rs}(\vec{R}) \exp i\left(\frac{\epsilon_r - \epsilon_s}{\hbar v}\right) Z; \quad r = 1, 2, \ldots, 5 \tag{1}$$

subject to the condition $|a_s(-\infty)| = \delta_{1s}$, with the zero of time chosen so that $Z = vt$. The potential matrix elements $V_{rs}(\vec{R})$ are given by

$$V_{rs}(\vec{R}) = \int \psi_r^*(\vec{r}_1, \vec{r}_2) \mathcal{V} \psi_s(\vec{r}_1, \vec{r}_2)\, d\vec{r}_1 d\vec{r}_2 , \tag{2}$$

where $\psi_\alpha(\vec{r}_1, \vec{r}_2)$ represents a set of atomic eigenfunctions of energy ϵ_s, describing two *isolated* hydrogen atoms, one of which remains in the ground state and the other ($\alpha = 1, 2, \ldots, 5$) in one of the $1s$, $2pm (m = 0, +1, -1)$, and $2s$ states. The inclusion of the phase factor $\exp[i(m_r - m_s)\Phi]$ in Eq. (1), m_r being the magnetic quantum number of state r quantized with respect to the Z axis, effectively removes any Φ dependence from the coefficients a_r. The instantaneous electrostatic interaction between the two hydrogen atoms is

$$\mathcal{V}(\vec{R}, \vec{r}_1, \vec{r}_2) = \frac{e^2}{|\vec{R}+\vec{r}_1-\vec{r}_2|} - \frac{e^2}{|\vec{R}-\vec{r}_2|} - \frac{e^2}{|\vec{R}+\vec{r}_1|} + \frac{e^2}{R} , \tag{3}$$

with $\vec{R} \equiv (\rho, Z, \Phi)$ as the nuclear separation, so that $R^2 = \rho^2 + v^2 t^2$, and with $\vec{r}_i$ as the distance of each orbital electron from its parent nucleus of charge e. The probability of excitation of the target from state 1 to α is $\mathcal{P}_{1,\alpha}(\rho) = |a_\alpha(\infty)|^2$, which is independent[1] of the phase angle Φ, and hence the cross section describing excitation is

$$Q_{1\alpha}(v) = 2\pi \int_0^\infty \mathcal{P}_{1,\alpha}(\rho)\rho d\rho . \tag{4}$$

If we neglect exchange effects, we can write the basis set as

$$\psi_\alpha(\vec{r}_1, \vec{r}_2) = \phi_{nlm}(\vec{r}_1)\phi_{1s}(\vec{r}_2) , \tag{5}$$

where $\phi_{nlm}(\vec{r})$ denotes wave functions for the hydrogen atom. Then the matrix elements coupling each of the excited channels with the initial channel 1 and with each other have been calculated[1,5] (as analytical functions of $\vec{R}$) by an integral technique previously described. The off-diagonal potential matrix elements cause the transition, while the diagonal ones distort the wavelength of the rectilinear motion. The virtual-transition and rotational elements can be similarly evaluated to yield, on omitting the phase dependance $\exp[i(m_s - m_r)\Phi]$,

$$\begin{aligned} &V^{1s,1s}_{2p_0,2p_{-1}} = V_{24} = (3/\sqrt{2})\, \mathcal{J}^2_{2p,2p}(R) \sin\theta\cos\theta = -V_{23} , \quad V^{1s,1s}_{2p_0,2s} = V_{25} = \mathcal{J}^1_{2s,2p}(R)\cos\theta , \\ &V^{1s,1s}_{2p_1,2p_{-1}} = V_{34} = -(\tfrac{3}{2})\, \mathcal{J}^2_{2p,2p}(R)\sin^2\theta , \quad V^{1s,1s}_{2p_{-1},2s} = V_{45} = (1/\sqrt{2})\, \mathcal{J}^1_{2s,2p}(R)\sin\theta = -V_{35} , \end{aligned} \tag{6}$$

where $\cos\theta(t) = \hat{R}(t=-\infty)\cdot\hat{R}(t)$ and where the radial potentials, in atomic units, are given by

$$\mathcal{J}^1_{2s,2p}(R) = e^{-R}\left(\frac{83}{81R^2} + \frac{83}{81R} - \frac{7}{6} + \frac{R}{2} - \frac{7R^2}{72}\right) - \frac{e^{-2R}}{81}\left(\frac{83}{R^2} + \frac{166}{R} + 30\right) \tag{7}$$

and

$$\mathcal{J}^2_{2p,2p}(R) = e^{-R}\left(\frac{38}{81R^3} + \frac{38}{81R^2} - \frac{7}{243R} - \frac{5}{27} + \frac{11R}{108} - \frac{7R^2}{216}\right) - \frac{2e^{-2R}}{243}\left(\frac{57}{R^3} + \frac{114}{R^2} + \frac{82}{R} + 12\right) . \tag{8}$$

The superscripts of the $\mathcal{J}$'s refer to the total orbital angular momentum L, and the subscripts and superscripts of V denote composite initial and final quantum numbers of electron 1 of the target H and electron 2 of the incident H, respectively. The equality of the magnitudes of all couplings to the $2p_1$ and $2p_{-1}$ states, which provide equal distortion terms, results in equal probabilities for the $2p_1$ and $2p_{-1}$ excitations, as expected also from the spatial symmetry of the collision. Hence, the five-state approximation reduces to, in effect, a four-state approximation described by the modified equations; in matrix representation

$$i\begin{bmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \dot{a}_4 \\ \dot{a}_5 \end{bmatrix} = \begin{bmatrix} V_{11} & V_{12}e^{i\epsilon t} & 2^{\frac{1}{2}}V_{14}e^{i\epsilon t} & V_{15}e^{i\epsilon t} \\ V_{12}e^{-i\epsilon t} & V_{22} & 2^{\frac{1}{2}}V_{24} & V_{25} \\ 2^{\frac{1}{2}}V_{14}e^{-i\epsilon t} & 2^{\frac{1}{2}}V_{24} & (V_{44}-V_{34}) & 2^{\frac{1}{2}}V_{45} \\ V_{15}e^{-i\epsilon t} & V_{25} & 2^{\frac{1}{2}}V_{45} & V_{55} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_4 \\ a_5 \end{bmatrix} \tag{9}$$

subject to unit normalization, and $\epsilon = \frac{3}{8}$ a.u. The effect of the $2p_1$-$2p_{-1}$ coupling V_{34} is to modify the equal amounts of distortion, $V_{33} = V_{44}$, created by the $2p_{\pm 1}$ states. Also, the s-p coupling for single excitations in hydrogen is short range, in contradiction to that assumed by Dose,[6] who invoked a long-range effect to justify its neglect. It is only when both the target and projectile neutral atoms suffer excitations to p states that a long-range R^{-3} interaction potential is in evidence.[5]

TABLE I. Cross sections for the process H(1s) + H(1s) → H(1s) + H(2s, 2p_0, or 2$p_{\pm 1}$). Here v is the incident atom velocity in atomic units (1 a.u. = 2.19×10^8 cm/sec). Incident atom energy $E = 25\ v^2$ keV. Also $Q(nl_m)$ are the four-state cross sections in units of $a_0^2 (= 0.28 \times 10^{-16}\ \text{cm}^2)$ for excitations of individual magnetic components of the $H(nl)$ level. And $\sigma(nl_m)$ are the two-state cross sections in units of $a_0^2 (= 0.28 \times 10^{-16}\ \text{cm}^2)$ for excitation of individual magnetic components of the $H(nl)$ level. The exponents give the power of 10 by which the entry must be multiplied.

v(a.u.)	$Q(2s)$	$\sigma(2s)$	$Q(2p_0)$	$\sigma(2p_0)$	$Q(2p_1)$	$\sigma(2p_1)$
2	2.26^{-2}	2.20^{-2}	6.42^{-3}	6.27^{-3}	2.50^{-2}	2.51^{-2}
1.8	2.78^{-2}	2.71^{-2}	9.50^{-3}	9.23^{-3}	3.01^{-2}	3.02^{-2}
1.6	3.51^{-2}	3.40^{-2}	1.46^{-2}	1.42^{-2}	3.68^{-2}	3.69^{-2}
1.4	4.57^{-2}	4.40^{-2}	2.35^{-2}	2.28^{-2}	4.56^{-2}	4.58^{-2}
1.2	6.16^{-2}	5.90^{-2}	3.97^{-2}	3.87^{-2}	5.74^{-2}	5.77^{-2}
1.0	8.71^{-2}	8.26^{-2}	7.07^{-2}	6.95^{-2}	7.26^{-2}	7.32^{-2}
0.8	1.30^{-1}	1.21^{-1}	1.31^{-1}	1.29^{-1}	8.94^{-2}	9.07^{-2}
0.6	1.98^{-1}	1.80^{-1}	2.31^{-1}	2.29^{-1}	9.58^{-2}	9.90^{-2}
0.5	2.32^{-1}	2.06^{-1}	2.70^{-1}	2.70^{-1}	8.39^{-2}	8.85^{-2}
0.4	2.25^{-1}	1.94^{-1}	2.36^{-1}	2.39^{-1}	5.36^{-2}	5.95^{-2}
0.3	1.14^{-1}	9.63^{-2}	8.86^{-2}	9.05^{-2}	1.49^{-2}	1.90^{-2}
0.2	4.93^{-3}	4.03^{-3}	3.99^{-3}	3.70^{-3}	3.36^{-4}	6.54^{-4}
0.18	1.90^{-3}	1.35^{-3}	2.03^{-3}	2.31^{-3}	1.14^{-4}	2.19^{-4}
0.16	7.81^{-4}	5.03^{-4}	7.44^{-4}	1.01^{-3}	3.50^{-5}	7.43^{-5}
0.14	1.94^{-4}	1.31^{-4}	1.40^{-4}	1.98^{-4}	6.97^{-6}	1.90^{-5}
0.12	3.78^{-5}	2.19^{-5}	1.97^{-5}	3.31^{-5}	6.82^{-7}	2.49^{-6}

III. RESULTS AND DISCUSSION

By solving Eq. (9) to give the probabilities and by using Eq. (4) for the cross sections, we have carried out four-state calculations (with an error of < 0.5%) in the energy interval 360 eV ≤ E ≤ 100 keV for the collision processes

$$\text{H}(1s) + \text{H}(1s) \rightarrow \text{H}(1s) + \text{H}(2s, 2p_0, \text{ or } 2p_{\pm 1}).$$

The results are displayed in Table I, together with the comparison results of the two-state treatment. The 2s-excitation cross sections are increased over the entire energy range, while the total 2p cross sections are decreased only at the lower energies. From knowledge of the contributions to the cross sections from various impact-parameter ranges, we observed that close collisions ($\rho < 2$ a.u.) contribute relatively more to the 2s than to the 2p_0, and relatively more to the 2p_0 than to the 2$p_{\pm 1}$ cross sections. For the 1s-2s transition, the virtual-state coupling increases the contribution from all encounters at all energies. The combined effect of the optically forbidden transition and rotational coupling on the 1s-2p excitations is a decrease in the contributions from close encounters and an increase in those from distant ones. This results in an overall increase of the 2p_0 cross sections (at energies above 6 keV) and a decrease in the 2$p_{\pm 1}$ cross sections at all energies. The net effect is a slight increase of the total 2p cross section at high energies and a reduction at energies below 25 keV. As Table II shows, the percentage polarization of the emitted radiation is less strongly affected.

The impact parameters ρ_1, less than which the quantization axis of the atoms is unable to follow the rapid rotation of the internuclear line, and ρ_2,

TABLE II. Percentage polarization of radiation emitted from H(2p) formed by the process H(1s) + H(1s) → H(1s) + H(2p). Here v is the incident atom velocity in atomic units (1 a.u. = 2.19×10^8 cm/sec). Incident atom energy $E = 25\ v^2$ keV. And P_i is the polarization percentages derived from excitation cross sections evaluated by use of the ith-state approximation.

v(a.u.)	P_2	P_4
2.0	−17.6	−17.4
1.8	−15.9	−15.6
1.6	−13.5	−13.1
1.4	−10.4	−10.0
1.2	−6.3	−5.8
1.0	−0.9	−0.4
0.8	6.0	6.6
0.6	14.5	15.2
0.5	19.0	20.1
0.4	23.2	24.4
0.3	25.4	28.2
0.2	28.7	34.5
0.18	33.8	37.0
0.16	35.6	38.0_1
0.14	33.7	38.0_3
0.12	35.5	39.2

beyond which the perturbation is insufficient to cause separation of the magnetic substates, decrease and increase, respectively, as the energy is lowered. This observation is a direct manifestation of the tendency for the collision complex to assume molecular characteristics. Thus, the interesting influence of rotational coupling becomes most marked precisely in the energy region where calculations become prohibitively time consuming owing to the rapid oscillations associated with a low incident velocity. In this context, it would prove useful to reformulate the impact-parameter method in an effort to obviate this computational hazard.

In conclusion, the presence of the optically allowed channel increases the 2*s* cross section from about 5% at 25 keV to 73% at 360 eV, while rotational coupling decreases the 2*p* cross sections from 1% to 45% for the same energy interval. These effects assume increasing importance as the energy falls below 360 eV, where also nuclear- and electronic-exchange effects and directional changes[7] of the projectile that result from the distortion terms would need to be considered. All these refinements in the existing impact-parameter treatment would necessitate heavy numerical work.

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