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Impact-Parameter Treatment of Hydrogen-Hydrogen Excitation Collisions. I. Two-State Approximation

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The impact-parameter versions of the full two-state and the Born approximations are used to calculate the $n = 2$ and 3 single-excitation cross sections describing collisions between two ground-state hydrogen atoms. Effects similar to those encountered by Bates in his distortion calculations of the $2s$ and $2p$ excitations of hydrogen by proton impact are observed. Cross sections for excitation up to the $4s$ state are also provided by using the Born approximation. The percentage polarization of impact radiation emitted is evaluated.

I. INTRODUCTION

Knowledge of inelastic cross sections for collisions between heavy particles is important in interpreting the aurorae, airglow, and the luminosity accompanying a meteor trail. At present there is no direct method available for calculating excitation cross sections over the entire energy range of the colliding particles. However, two

approximations, in principle, different and valid in mutually exclusive regions, are useful. The perturbed stationary state (PSS) method[1] describes the formation of a quasimolecule by molecular wave functions that tend to the initial and final states of the colliding atoms at infinite separation; the kinetic energy of relative motion, assumed small, is responsible for the transition. This adiabatic procedure is the continuum analog

of the Born-Oppenheimer method for dealing with molecular bound states. In the limit of high energy and weak interaction, the collision can be described by the Born approximation,[2] in which the instantaneous electrostatic interaction averaged over the initial and final atomic states of the separated atoms causes the transition.

Bates[3] has pointed out that the PSS method, which involves molecular eigenfunctions that are naturally quantized with respect to the internuclear axis, does not tend in the limit of high energy and weak interaction to the Born approximation when the atomic states are spatially degenerate and are quantized relative to an axis fixed in space. Moreover, close encounters are important in neutral-neutral excitations,[4] and the quantization axis in the PSS method is so constrained to follow the resulting rapid rotation of the internuclear line that the method cannot properly describe the physical situation. The PSS method is also unreliable for treating distant encounters,[4] since the interaction then is not sufficiently strong to resolve spatial degeneracies. These defects are theoretically remedied[5] by including coupling between the degenerate states, i.e., a linear combination of $\Sigma, \Pi, \Delta, \ldots$ wave functions, in which the coefficients depend on the orientation angles of the internuclear axis, is used instead of a single molecular eigenfunction. This modification results in coupled equations that virtually destroy the value of the PSS method, and hence effort has been directed mainly toward improvement of the Born approximation for intermediate and low energies rather than to the removal of unphysical constraints inherent in the PSS method.

The wave and impact-parameter versions[2] of the Born approximation are essentially equivalent[6] for treating heavy-particle collisions when the cross section is summed over final-state and averaged over initial-state degeneracies. While the wave treatment readily leads to closed expressions for the cross section in the case of H-H collisions, the impact-parameter formulation does not, although valuable physical insight into the collision process is gained.

A suitable improvement is obtained by allow-

ing the relative motion to be distorted from the plane-wave or rectilinear-path description by including both wavelength and directional changes due to the influence of the averaged initial- and final-state interactions. Bates[7] has shown that for proton-hydrogen 2s and 2p excitation, wavelength distortion, effected in the impact-parameter treatment by replacing the unperturbed by the perturbed eigen-energies, leads to much smaller cross sections at moderate velocities than those calculated by Bates and Griffing[8] using the Born wave treatment. Also, Bates and Boyd[9] conclude that change of direction is only important for very slow heavy-particle collisions.

Because of the large number of partial waves entering into a refined wave treatment, attention shall be confined to the impact-parameter version.

The present paper, in which we have isolated the effects of distortion and back coupling, represents the beginning of a systematic attempt to ascertain which particular matrix elements, other than that in the Born approximation, assume importance as the velocity of the collision is lowered. The inclusion of gerade symmetry effects, which arise from the identity of the nuclei in the H-H collision, entails the evaluation of an almost similar set of matrix elements that are encountered in a consideration of electron exchange in the hydrogen molecule. The evaluation of these two-electron two-center exchange integrals is a formidable task that is further complicated by the appearance of velocity-dependent phase factors associated with the translational motion of the electrons. Hence exchange effects will be neglected because of the heavy computational labor involved with their investigation. The evaluation[10] of the direct Coulomb integrals as analytical functions of the nuclear separation has permitted the present impact-parameter calculations to be carried out with relative ease.

Accordingly, a two-state calculation is performed for the $n = 2$ and 3 single excitations involving two hydrogen atoms initially in their ground state; i.e., distortion and back coupling to the initial state will be investigated, and exchange effects will be neglected. The Born cross section for the 1s-4s transition will also be included.

II. THEORY

The impact-parameter method is semiquantal in that the colliding particles are taken to follow a classical or rectilinear trajectory, while the probability of excitation is calculated from quantum mechanics. Let the target hydrogen atom be at the origin of a fixed set of cylindrical coordinates and assume the incident hydrogen atom to move with constant velocity v in the positive direction along a line distant ρ, the impact parameter, from the Z axis. The total electronic wave function evolves in time according to Dirac's theory of variation of constants[2] as

$$\Psi_n(\vec{r}_1, \vec{r}_2, t) = \sum_s a_{ns}(t) \psi_s(\vec{r}_1, \vec{r}_2) \exp(i\epsilon_s t/\hbar), \tag{1}$$

where $\psi_s(\vec{r}_1, \vec{r}_2)$ represents a complete set of atomic eigenfunctions of energy ϵ_s, describing two isolated hydrogen atoms, and $\vec{r}_i$ the distance of each orbital electron from its parent nucleus. Substituting (1) in the Schrödinger equation and proceeding in the customary manner[2] leads to an infinite set of coupled, first-order differential equations. These reduce, in the two-state approximation where couplings to states other than the initial 1 and final 2 are ignored, to the following set:

$$i\hbar \frac{\partial a_{1m}(Z)}{\partial Z} = \frac{1}{v} \sum_{s=1}^{2} a_{1s}(Z) V_{ms}(\vec{R}) \exp\left(i\frac{\epsilon_m - \epsilon_s}{\hbar v}\right) Z, \quad m = 1, 2 \quad, \tag{2}$$

subject to the condition $|a_{1s}(-\infty)| = \delta_{1s}$, with the zero of time chosen so that $Z = vt$. The matrix elements are defined by

$$V_{ms}(\vec{R}) = \int \psi_m^*(\vec{r}_1, \vec{r}_2) \, \mathcal{v} \, \psi_s(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \langle \psi_m | \mathcal{v} | \psi_s \rangle, \tag{3}$$

in which the instantaneous electrostatic interaction between two hydrogen atoms is

$$\mathcal{v}(\vec{R}, \vec{r}_1, \vec{r}_2) = e^2/|\vec{R} + \vec{r}_1 - \vec{r}_2| - e^2/|\vec{R} - \vec{r}_2| - e^2/|\vec{R} + \vec{r}_1| + e^2/R \quad, \tag{4}$$

with $\vec{R} \equiv (\rho, Z, \Phi)$ as the nuclear separation; such that $R^2 = \rho^2 + v^2 t^2$. The probability of excitation from state 1 to 2 is $\mathcal{P}_{1,2}(\rho) = |a_{12}(\infty)|^2$, and hence the excitation cross section is

$$Q_{12}(v) = \int_0^{2\pi} \int_0^{\infty} |a_{12}(\infty)|^2 \rho \, d\rho \, d\Phi. \tag{5a}$$

If the back-coupling term $V_{12}a_{12}$ is small (as in the case of a weak transition) and is neglected in (2), then the pair of equations decouple and reduce to the distortion approximation. If, in addition, the diagonal terms V_{mm} are assumed negligible, then Born's approximation results. Detailed balance given as $\mathcal{P}_{1,2} = \mathcal{P}_{2,1}$ is satisfied in all cases. The inclusion of the back-coupling term conserves initial- and final-state populations, thereby ensuring excitation probabilities that do not exceed unity.

Let the basis set describing two hydrogen atoms at infinite separation, exchange not included, be

$$\psi_s(\vec{r}_1, \vec{r}_2) = \phi_{nlm}(\vec{r}_1) \phi_{n'l'm'}(\vec{r}_2), \tag{6}$$

where each hydrogen wave function is written, in atomic units, as

$$\phi_{nlm}(\vec{r}) = e^{-r/n} \sum_{k=0}^{k_1 = n-l-1} (-1)^k A_k^{nl} r^{k+l} Y_{lm}(\hat{r}), \tag{7}$$

with $Y_{lm}(\hat{r})$ as the normalized spherical harmonic and

$$A_k^{nl} \{[(n+l)! (n-l-1)!]^{\frac{1}{2}}/(n-l-1-k)! (2l+1+k)! k!\} 2^{k+l+1}/n^{k+l+2} \tag{8}$$

For the process

$$H(1s) + H(1s) \rightarrow H(1s) + H(n, l, m), \tag{9}$$

we can show (see Appendix) that the off-diagonal coupling potential between the initial and final states can

be written analytically as

$$
V_{1s,nlm}^{1s,1s}(\vec{R}) = 4\pi^{\frac{1}{2}}\left\{ \sum_{k=0}^{k_1} (-1)^l A_k^{nl} J_{ll}^{kk}(R) \right\} Y_{lm}(\hat{R}),
$$

(10)

where, in general,

$$
J_{Ll}^{Kk}(R) = 2^L(K+1)!\left(1 - \frac{\partial}{\partial\beta}\right)R^L\left(\frac{d}{RdR}\right)^L \frac{1}{R}\sum_{p=1}^{p_1}\frac{(2\alpha)^{K+3-2p}}{(p-1)!(K+3-2p)!}\left(\frac{\partial}{\partial\alpha^2}\right)^{K+L+2-p}\frac{e^{-\alpha R}-e^{-\beta R}}{\beta^2-\alpha^2},
$$

(11)

with $\alpha = 1 + 1/n$, β set equal to 2 after the β differentiation is performed, and $p_1 = (K+2)/2, (K+3)/2$, for K even or odd, respectively. 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. These potentials, for $nl = 2s$, $2p$, $3s$, $3p$, $3d$, and $4s$, have been explicitly determined by Flannery and Levy[10] as functions of $\vec{R}$. The diagonal matrix elements, i.e., the static potential averaged over each initial and final state, can be similarly evaluated by using Eq. (A.8) of the Appendix to yield

$$
V_{nlm,nlm}^{1s,1s}(\vec{R}) = e^{-2R}\left(1 + \frac{1}{R}\right) + 4\pi\sum_{L=0}^{2l}(-1)^m \mathcal{I}_{nl}^{L}(R)D(llL,m-m0)Y_{L0}(\hat{R}),
$$

(12)

with

$$
\mathcal{I}_{nl}^{L}(R) = \sum_{k,k'=0}^{k_1} A_k^{nl}A_{k'}^{nl}J_{Ll}^{Kk}(R), \quad K = k+k'+2l-L, \quad \alpha = 2/n,
$$

(13)

$$
D(ll'L,mm'M) = \int Y_{lm}(\Omega)Y_{l'm'}(\Omega)Y_{LM}^*(\Omega)d\Omega = \left\{\frac{(2l+1)(2l'+1)}{4\pi(2L+1)}\right\}^{\frac{1}{2}}C(ll'L,000)C(ll'L,mm'M),
$$

(14)

where the C's are the Clebsch-Gordan coefficients and $Y_{lm}^* = (-1)^m Y_{l-m}$ represents the phase convention. The projection of the total orbital angular momentum L along the Z axis is M. The formulas (12) to (14) have been applied up to and including the $n=3$ shell, and it is observed that the radial potential can be expressed as

$$
\mathcal{I}_{nl}^{L}(R) = e^{-\alpha R}\sum_{s=-(L+1)}^{2(n-1)}\lambda_s R^s - e^{-2R}\sum_{t=-(L+1)}^{0}\mu_t R^t, \quad n \neq 1.
$$

(15)

As previously noted,[10] a convenient check on the coefficients λ and μ is that as R approaches zero, $\mathcal{I}_{nl}^{L}(R)$ tends to the correct united-atom limit $\mathcal{I}_{nl}^{L}(0)\delta_{L0}$, which can be easily evaluated. This observation provides the following matrix relationship between the μ_t and certain λ_s:

$$
\begin{bmatrix} \lambda_0 - \mathcal{I}_{nl}^{L}(0)\delta_{L0} \\ \\ \lambda_{-1} \\ \\ \vdots \\ \\ \lambda_{-(L+1)} \end{bmatrix} = \begin{bmatrix} 1 & -\gamma & \gamma^2/2! & \cdots & \frac{(-\gamma)^{L+1}}{(L+1)!} \\ \\ 0 & 1 & -\gamma & \cdots & \frac{(-\gamma)^L}{L!} \\ \vdots & \vdots & \vdots & & \vdots \\ \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix} \begin{bmatrix} \mu_0 \\ \\ \mu_{-1} \\ \\ \vdots \\ \\ \mu_{-(L+1)} \end{bmatrix}
$$

(16)

where $\gamma = \beta - \alpha$. The coefficients of Eq. (15) are displayed in Table I.

TABLE I. Diagonal radial potentials.

$$\mathcal{G}_{nl}^{L}(R) = C_1\left[e^{-2R/n}\sum_{s=-(L+1)}^{2(n-1)}\lambda_s R^s - C_2\,e^{-2R}\sum_{t=-(L+1)}^{0}\mu_t R^t\right].$$

nl	L	C_1	$-\lambda_4$	λ_3	$-\lambda_2$	λ_1	$-\lambda_0$	λ_{-1}	λ_{-2}	λ_{-3}	λ_{-4}	λ_{-5}	C_2	μ_0	μ_{-1}	μ_{-2}	μ_{-3}	μ_{-4}	μ_{-5}
$2s$	0	$2^{-3}\times3^{-4}$	⋯	⋯	63	450	1338	1672	⋯	⋯	⋯	⋯	8	45	209	⋯	⋯	⋯	⋯
$3s$	0	2^{-8}	$\frac{272}{3^7}$	$\frac{1892}{3^6}$	$\frac{1649}{3^4}$	$\frac{2077}{3^3}$	$\frac{44133}{2^5\times3^2}$	$\frac{17621}{2^7}$	⋯	⋯	⋯	⋯	2^{-7}	4172	17621	⋯	⋯	⋯	⋯
$2p$	0	$2^{-3}\times3^{-5}$	⋯	⋯	63	198	558	664	⋯	⋯	⋯	⋯	8	15	83	⋯	⋯	⋯	⋯
$2p$	2	$2^{-3}\times3^{-5}$	⋯	⋯	63	198	360	-56	912	912	⋯	⋯	16	12	82	114	57	⋯	⋯
$3p$	0	2^{-9}	$\frac{272}{3^7}$	$\frac{1348}{3^6}$	$\frac{785}{3^4}$	$\frac{671}{3^3}$	$\frac{13741}{2^5\times3^2}$	$\frac{5245}{2^7}$	⋯	⋯	⋯	⋯	2^{-7}	1036	5245	⋯	⋯	⋯	⋯
$3p$	2	2^{-9}	$\frac{272}{3^7}$	$\frac{1348}{3^6}$	$\frac{253}{3^3}$	$\frac{532}{3^3}$	$\frac{5561}{2^5\times3^2}$	$-\frac{2563}{2^7}$	$\frac{10299}{2^8}$	$\frac{30897}{2^9}$	⋯	⋯	3×2^{-9}	2320	14892	20598	10299	⋯	⋯
$3d$	0	2^{-9}	$\frac{272}{5\cdot3^7}$	$\frac{52}{3^6}$	$\frac{87}{3^5}$	$\frac{23}{3^3}$	$\frac{457}{2^5\times3^2}$	$\frac{169}{2^7}$	⋯	⋯	⋯	⋯	2^{-7}	28	169	⋯	⋯	⋯	⋯
$3d$	2	$5^{-1}\times2^{-9}$	$\frac{272}{3^7}$	$\frac{260}{3^6}$	$\frac{119}{3^4}$	$\frac{80}{3^3}$	$\frac{793}{2^5\times3^2}$	$-\frac{371}{2^7}$	$\frac{1419}{2^8}$	$\frac{4257}{2^9}$	⋯	⋯	3×2^{-9}	272	2028	2838	1419	⋯	⋯
$3d$	4	2^{-9}	$\frac{272}{5\times3^7}$	$\frac{52}{3^6}$	$\frac{35}{3^5}$	$-\frac{1}{3^4}$	$-\frac{211}{2^5\times3^2}$	$\frac{231}{2^7\times3^2}$	-5	$-\frac{585}{2^9}$	$\frac{29295}{2^{10}}$	$\frac{87885}{2^{11}}$	$3^3\times2^{-11}$	64	688	2720	5700	6510	3255

M. R. FLANNERY

The probability of exciting any of the m substates of the level nl is

$$\mathcal{P}_{1s,nl}^{1s,1s}(\rho) = \sum_{m=-l}^{l} \mathcal{P}_{1s,nlm}^{1s,1s}(\rho) = \mathcal{P}_{1s,nl0}^{1s,1s}(\rho) + 2 \sum_{m=1}^{l} \mathcal{P}_{1s,nlm}^{1s,1s}(\rho) \tag{17}$$

because of the equality of the absolute magnitudes of the potentials coupling the initial state with each of of the two $|m|$ states, which also provide equal amounts of distortion. Hence equal probabilities for excitation of the substates m and $-m$ result.[11] The above l partial probabilities can be shown to be independent of any phase factor $\exp i(m'-m)\,\Phi$ (occurring in $V_{nlm,n'l'm'}^{1s,1s}$), thus allowing Eq. (5) to be rewritten as

$$Q_{1s,nl}(v) = 2\pi \int \mathcal{P}_{1s,nl}^{1s,1s}(\rho)\rho\,d\rho = Q_{1s,nl0}(v) + 2 \sum_{m=1}^{l} Q_{1s,nlm}(v), \tag{5b}$$

which is apparent also from the spatial symmetry of the collision.

Finally, if the kinetic energy E of the incident atom is expressed in keV, and v in atomic units, then

$$E = 25v^2 \text{ keV}. \tag{18}$$

III. RESULTS AND DISCUSSION

Two-state and Born calculations have been carried out (with an error of $<0.5\%$) in the energy interval $1 \leq E \leq 100$ keV for the collision processes

$$H(1s) + H(1s) \rightarrow H(1s)$$

$$+ H(2s; 2p0, \pm 1, 3s; \ 3p0, \pm 1; \ 3d0, \pm 1, \pm 2),$$

$$\tag{19}$$

where the fixed Z axis is taken as the axis of quantization of the atoms. When the Born cross sections are summed over the spatial degeneracies, they agree exactly with the Born-wave calculations of Bates and Griffing,[8] in which the atoms are referred to a Z axis taken along the momentum transfer direction (such that only $\Delta m = 0$ transitions are permitted). In addition, the Born cross section was evaluated for the $1s$-$4s$ transition. From Tables II–V, we observe that inclusion of all the two-state couplings leads to a decrease in the total cross sections, which therefore approach at high energies to the Born values from below, with the exception of the np results, which tend to the Born limit from above. The combined influence of distortion and back coupling is qualitatively different at high energy for different $|m|$ substates. It increases the $np0$, $3d \pm 1$ and decreases the ns, $np \pm 1$, $3d0 \pm 2$ excitations, the effects almost cancelling on summation over spatial degeneracies. The cross-section maxima have been generally shifted to higher energies.

TABLE II. Process: $H(1s) + H(1s) \rightarrow H(1s) + H(ns)$. $Q(ns)$: Two-state cross sections in units of a_0^2. $\sigma(ns)$: Born cross sections in units a_0^2. The index gives the power of 10 by which the entry must be multiplied.

v (a.u.)	$Q(2s)$	$\sigma(2s)$	$Q(3s)$	$\sigma(3s)$	$\sigma(4s)$
2	2.20^{-2}	2.24^{-2}	5.64^{-3}	5.75^{-3}	2.29^{-3}
1.8	2.71^{-2}	2.76^{-2}	6.95^{-3}	7.10^{-3}	2.84^{-3}
1.6	3.40^{-2}	3.49^{-2}	8.74^{-3}	8.97^{-3}	3.61^{-3}
1.4	4.40^{-2}	4.56^{-2}	1.13^{-2}	1.17^{-2}	4.71^{-3}
1.2	5.90^{-2}	6.20^{-2}	1.51^{-2}	1.59^{-2}	6.40^{-3}
1.0	8.26^{-2}	8.90^{-2}	2.10^{-2}	2.28^{-2}	9.17^{-3}
0.8	1.21^{-1}	1.37^{-1}	3.04^{-2}	3.50^{-2}	1.40^{-2}
0.6	1.80^{-1}	2.32^{-1}	4.26^{-2}	5.74^{-2}	2.27^{-2}
0.5	2.06^{-1}	3.07^{-1}	4.52^{-2}	7.28^{-2}	2.83^{-2}
0.4	1.94^{-1}	3.90^{-1}	3.61^{-2}	8.39^{-2}	3.14^{-2}
0.3	9.63^{-2}	4.01^{-1}	1.19^{-2}	6.98^{-2}	2.42^{-2}
0.2	4.03^{-3}	1.91^{-1}	1.72^{-4}	2.24^{-2}	6.83^{-3}

TABLE III. Process: $H(1s) + H(1s) \rightarrow H(1s) + H(2p)$. $Q(nlm)$: Two-state cross sections in units of a_0^2. $\sigma(nlm)$: Born cross sections in units of a_0^2. The index gives the power of 10 by which the entry must be multiplied.

v (a.u.)	$Q(2p_0)$	$\sigma(2p_0)$	$Q(2p_1)$	$\sigma(2p_1)$	$Q(2p)$	$\sigma(2p)$
2	6.27^{-3}	4.56^{-3}	2.51^{-2}	2.54^{-2}	5.64^{-2}	5.55^{-2}
1.8	9.23^{-3}	6.79^{-3}	3.02^{-2}	3.08^{-2}	6.96^{-2}	6.84^{-2}
1.6	1.42^{-2}	1.05^{-2}	3.69^{-2}	3.78^{-2}	8.80^{-2}	8.62^{-2}
1.4	2.28^{-2}	1.71^{-2}	4.58^{-2}	4.74^{-2}	1.14^{-1}	1.12^{-1}
1.2	3.87^{-2}	2.94^{-2}	5.77^{-2}	6.04^{-2}	1.54^{-1}	1.50^{-1}
1.0	6.95^{-2}	5.40^{-2}	7.32^{-2}	7.82^{-2}	2.16^{-1}	2.10^{-1}
0.8	1.29^{-1}	1.06^{-1}	9.07^{-2}	1.01^{-1}	3.10^{-1}	3.07^{-1}
0.6	2.29^{-1}	2.11^{-1}	9.90^{-2}	1.21^{-1}	4.27^{-1}	4.53^{-1}
0.5	2.70^{-1}	2.83^{-1}	8.85^{-2}	1.20^{-1}	4.47^{-1}	5.23^{-1}
0.4	2.39^{-1}	3.31^{-1}	5.95^{-2}	9.93^{-2}	3.58^{-1}	5.30^{-1}
0.3	9.05^{-2}	2.65^{-1}	1.90^{-2}	5.39^{-2}	1.29^{-1}	3.72^{-1}
0.2	3.70^{-3}	7.23^{-2}	6.54^{-4}	9.84^{-3}	5.07^{-3}	9.20^{-2}

The variation of the excitation probability $\mathcal{P}_{1,2}(\rho)$ with impact parameter is a more sensitive gauge of any trends or apparent anomalies in the cross section. It shows that close encounters contribute relatively more to the optically forbidden transitions than to the optically allowed transitions, and hence distortion, which affects close encounters more strongly than it does distant ones, influences the $1s$-ns and $1s$-nd transitions more than it does the $1s$-np transitions. It shows also that for the $1s$-ns excitations, distortion decreases, at all energies, the contribution of near head-on collisions, the change becoming less with increase of the impact parameter. For intermediate and high energies, the contributions of close impacts to the $np0$ and $3d \pm 1$ excitation probabilities are substantially increased, and those of distant encounters are somewhat decreased for $np0$ and increased for $3d \pm 1$. The reverse situation occurs for the $np \pm 1$, $3d0 \pm 2$

excitations. At low velocities, the contributions of all encounters for all transitions are reduced. Thus the role of distortion and back coupling in H-H excitations is similar to the case of the $1s$-$2s$ and $2p$ transitions in the H^+-H system already analyzed by Bates.[7] We also observe that distortion has a stronger influence on the higher n levels (for a given l) than on the lower ones.

The rotational axis approximation in which the axis of quantization of the atoms is taken along the internuclear axis [hence, only $\Delta m = 0$ transitions are allowed[3] when ψ_S is given by Eq. (6)] was also examined. In the high-energy range, the resulting cross section is overestimated (owing to the neglect of coupling between the m substates) and considerably underestimated for low energies. For s-s transitions, the cross sections are, of course, identical with those in Table II. If $|\Delta m| > 0$ transitions are to be permitted, then ψ_S must involve perturbed or molecu-

TABLE IV. Process: $H(1s) + H(1s) \rightarrow H(1s) + H(3p)$. $Q(nlm)$: Two-state cross sections in units of a_0^2. $\sigma(nlm)$: Born cross sections in units of a_0^2. The index gives the power of 10 by which the entry must be multiplied.

v (a.u.)	$Q(3p_0)$	$\sigma(3p_0)$	$Q(3p_1)$	$\sigma(3p_1)$	$Q(3p)$	$\sigma(3p)$
2.0	1.95^{-3}	1.41^{-3}	6.60^{-3}	6.75^{-3}	1.52^{-2}	1.49^{-2}
1.8	2.88^{-3}	2.10^{-3}	7.91^{-3}	8.14^{-3}	1.87^{-2}	1.84^{-2}
1.6	4.40^{-3}	3.25^{-3}	9.60^{-3}	9.94^{-3}	2.36^{-2}	2.31^{-2}
1.4	7.02^{-3}	5.25^{-3}	1.18^{-2}	1.24^{-2}	3.06^{-2}	3.00^{-2}
1.2	1.17^{-2}	8.96^{-3}	1.46^{-2}	1.56^{-2}	4.09^{-2}	4.01^{-2}
1.0	2.04^{-2}	1.62^{-2}	1.80^{-2}	1.98^{-2}	5.64^{-2}	5.58^{-2}
0.8	3.61^{-2}	3.09^{-2}	2.11^{-2}	2.46^{-2}	7.83^{-2}	8.00^{-2}
0.6	5.67^{-2}	5.75^{-2}	2.03^{-2}	2.70^{-2}	9.73^{-2}	1.12^{-1}
0.5	5.85^{-2}	7.12^{-2}	1.60^{-2}	2.46^{-2}	9.04^{-2}	1.21^{-1}
0.4	4.04^{-2}	7.19^{-2}	8.45^{-3}	1.77^{-2}	5.73^{-2}	1.07^{-1}
0.3	9.10^{-3}	4.39^{-2}	1.62^{-3}	7.51^{-3}	1.23^{-3}	5.89^{-2}
0.2	2.54^{-4}	7.61^{-3}	2.18^{-5}	9.17^{-4}	3.03^{-4}	9.44^{-3}

TABLE V. Process: $H(1s) + H(1s) \rightarrow H(1s) + H(3d)$. $Q(nlm)$: Two-state cross sections in units of a_0^2. $\sigma(nlm)$: Born cross sections in units of a_0^2. The index gives the power of 10 by which the entry must be multiplied.

v (a.u.)	$Q(3d_0)$	$\sigma(3d_0)$	$Q(3d_1)$	$\sigma(3d_1)$	$Q(3d_2)$	$\sigma(3d_2)$	$Q(3d)$	$\sigma(3d)$
2	1.78^{-4}	2.12^{-4}	1.75^{-4}	1.60^{-4}	4.42^{-4}	4.46^{-4}	1.41^{-3}	1.42^{-3}
1.8	1.90^{-4}	2.36^{-4}	2.53^{-4}	2.31^{-4}	5.22^{-4}	5.28^{-4}	1.74^{-3}	1.75^{-3}
1.6	2.00^{-4}	2.62^{-4}	3.78^{-4}	3.48^{-4}	6.22^{-4}	6.31^{-4}	2.20^{-3}	2.22^{-3}
1.4	2.16^{-4}	2.90^{-4}	5.84^{-4}	5.38^{-4}	7.44^{-4}	7.58^{-4}	2.87^{-3}	2.88^{-3}
1.2	2.63^{-4}	3.39^{-4}	9.29^{-4}	8.63^{-4}	8.85^{-4}	9.08^{-4}	3.89^{-3}	3.88^{-3}
1.0	4.55^{-4}	4.81^{-4}	1.50^{-3}	1.41^{-3}	1.02^{-3}	1.06^{-3}	5.50^{-3}	5.43^{-3}
0.8	1.15^{-3}	9.55^{-4}	2.35^{-3}	2.27^{-3}	1.08^{-3}	1.16^{-3}	8.01^{-3}	7.81^{-3}
0.6	2.94^{-3}	2.35^{-3}	3.01^{-3}	3.14^{-3}	8.68^{-4}	9.93^{-4}	1.07^{-2}	1.06^{-2}
0.5	3.74^{-3}	3.28^{-3}	2.67^{-3}	3.06^{-3}	5.91^{-4}	7.43^{-4}	1.03^{-2}	1.09^{-2}
0.4	3.02^{-3}	3.42^{-3}	1.53^{-3}	2.17^{-3}	2.58^{-4}	3.92^{-4}	6.60^{-3}	8.54^{-3}
0.3	7.58^{-4}	1.83^{-3}	3.01^{-4}	7.90^{-4}	3.87^{-5}	1.04^{-4}	1.44^{-3}	3.62^{-3}
0.2	1.34^{-5}	2.03^{-4}	3.94^{-6}	6.22^{-5}	3.21^{-7}	5.82^{-6}	2.19^{-5}	3.39^{-4}

lar wave functions, which procedure results in the perturbed rotating atom (PRA) or PSS methods, respectively.

The polarization of light emitted in a particular direction owing to optical transitions from states of hydrogen collisionally excited depends on the relative probability of excitations of the magnetic sublevels of the upper states concerned. With the hydrogen beam directed along the Z axis, the direction of observation along the X axis, and with the intensities of emitted light with electric vector along the Z and Y axes taken as $I^{\parallel}$ and $I^{\perp}$, respectively, the percentage polarization is

$$P = 100(I^{\parallel} - I^{\perp})/(I^{\parallel} + I^{\perp}). \tag{20}$$

For the case of np and nd levels, Percival and Seaton[12] have shown that when fine structure is included and hyperfine structure excluded, Eq. (20) can be written in terms of the collision cross section Q_m for excitation of a particular magnetic substate as

$$P = \frac{300(Q_0 - Q_1)}{7Q_0 + 11Q_1}, \qquad np \text{ levels}, \tag{21a}$$

$$P = \frac{300(Q_0 + Q_1 - 2Q_2)}{5Q_0 + 9Q_1 + 6Q_2}, \qquad nd \text{ levels}. \tag{21b}$$

The entries in Table VI provide the percentage polarization of light emitted from the $2p$, $3p$, and $3d$ levels. In particular, the $2p$ results and those calculated by Gallaher and Wilets[13] for H excitation by proton collisions exhibit similar variation with energy, although differing considerably in magnitude from one another. This observation may well provide a means of distinguishing between excitation of hydrogen by either proton or hydrogen impact.

In conclusion, the reliability of the Born cross sections when summed over spatial degeneracies for energies above 25 keV is mainly due to the anomalous effect of distortion and the relatively weak influence of back coupling, although the determined polarization fractions will not agree with those of the two-state calculation. For lower energies, the Born approximation severely overestimates the collision cross sections, when the influence of distortion and back-coupling becomes increasingly important.

ACKNOWLEDGMENTS

TABLE VI. Percentage polarization.

v (a.u.)	Level		
	$2p$	$3p$	$3d$
2.0	−17.6	−16.2	−31.2
1.8	−15.9	−14.7	−28.4
1.6	−13.5	−11.4	−24.5
1.4	−10.4	−8.0	−19.1
1.2	−6.3	−4.8	−11.6
1.0	−0.9	2.1	−1.3
0.8	6.0	9.3	12.0
0.6	14.5	17.6	26.9
0.5	19.0	21.8	33.9
0.4	23.2	25.5	39.8
0.3	25.4	27.5	43.7
0.2	28.7	34.6	48.0

APPENDIX

To facilitate the evaluation of the potential matrix elements as analytical functions of $\vec{R}$, we consider the following integral:

$$s(k,n,l;\vec{q}) = \int e^{-\alpha r} r^{k+l} e^{-i\vec{q}\cdot\vec{r}} Y_{lm}(\hat{r})d\vec{r} \ . \tag{A.1}$$

Substituting

$$e^{-i\vec{q}\cdot\vec{r}} = 4\pi \sum_{l,m} i^l Y_{lm}(\hat{q})Y^*_{lm}(\hat{r})\left(\frac{q}{r}\right)^l \left(\frac{d}{qdq}\right)^l \frac{\sin qr}{qr} \tag{A.2}$$

and using the standard integral

$$\int_0^\infty x^{n-1} e^{-\alpha x} \sin\beta x\, dx = \frac{(n-1)!}{(\alpha^2+\beta^2)^{n/2}} \sin\left(n\tan^{-1}\frac{\beta}{\alpha}\right) , \tag{A.3}$$

together with the finite expansion

$$\sin m\theta = \sin\theta\left[2^{n-1}\cos^{n-1}\theta - \binom{n-2}{1}2^{n-3}\cos^{n-3}\theta + \binom{n-3}{2}2^{n-5}\cos^{n-5}\theta - \cdots\right] , \tag{A.4}$$

in which $\binom{n}{r}$ are binomial coefficients, we find, on completion of the q differentiation, that

$$s(k,n,l;\vec{q}) = 4\pi(-2iq)^l(k+1)! Y_{lm}(\hat{q})\sum_{p=1}^{p_{max}}\frac{(-1)^{p+1}(k+l+2-p)!}{(p-1)!(k+3-2p)!}\frac{(2\alpha)^{k+3-2p}}{(\alpha^2+q^2)^{k+l+3-p}} \tag{A.5}$$

with $p_{max} = (k+2)/2$, $(k+3)/2$ for k even or odd, respectively. We note that

$$\psi(\vec{q}) = (2\pi)^{-\frac{3}{2}}\sum_{k=0}^{k_1}(-1)^k A_k^{nl}\, s(k,n,l;\vec{q}) \tag{A.6}$$

provides an alternative expression for the hydrogenic momentum wave functions first worked out by Podolsky and Pauling[14] in terms of Gegenbauer functions.

The following formula for the generalized form-factor $F_{ij}(\vec{q})$ for hydrogen is obtained immediately:

$$F_{ij}(\vec{q}) = \int \phi_{nlm}(\vec{r})\phi_{n'l'm'}(\vec{r})e^{i\vec{q}\cdot\vec{r}}d\vec{r} = 4\pi\sum_{k,k'=0}^{k_1,k_1'}(-1)^{k+k'}A_k^{nl}A_{k'}^{n'l'}$$

$$\times \sum_{L,M}(2iq)^L(K+1)! D(ll'L,mm'M)Y_{LM}(\hat{q})\sum_{p=1}^{p_1}\frac{(-1)^{p+1}(K+L+2-p)!(2\alpha)^{K+3-2p}}{(p-1)!(K+3-2p)!(\alpha^2+q^2)^{K+L+3-p}} , \tag{A.7}$$

with $\alpha = 1/n + 1/n'$, $\phi^*_{nlm} = (-1)^m \phi_{nl-m}$, and the remaining notation as defined in text. The use of (A.7) results in the following expression for the interaction matrix element:

$$\left\langle \phi_{nlm}(\vec{r}_1)\phi_{1s}(\vec{r}_2)\left| \frac{1}{|\vec{R}+\vec{r}_1-\vec{r}_2|} - \frac{1}{|\vec{R}-\vec{r}_2|} \right| \phi_{n'l'm'}(\vec{r}_1)\phi_{1s}(\vec{r}_2)\right\rangle$$

$$= 4\pi\left(1-\frac{\partial}{\partial\beta}\right)\sum_{k,k'=0}^{k_1,k_1'}A_k^{nl}A_{k'}^{n'l'}\sum_{LM}(-1)^{l+l'}2^L(K+1)!(-1)^m D(ll'L,-mm'M)$$

$$\times Y_{LM}(\hat{R})R^L \left(\frac{d}{RdR}\right)^L \frac{1}{R} \sum_{p=1}^{p_1} \frac{(2\alpha)^{K+3-2p}}{(p-1)!\,(K+3-2p)!} \left(\frac{\partial}{\partial\alpha^2}\right)^{K+L+2-p} \frac{e^{-\alpha R}-e^{-\beta R}}{\beta^2-\alpha^2} \ , \quad (A.8)$$

where the Fourier transform relationship

$$\frac{1}{|\vec{R}-\vec{r}|} = \frac{1}{2\pi^2}\int \frac{e^{i\vec{q}\cdot(\vec{R}-\vec{r})}}{q^2}\,d\vec{q} \qquad\qquad (A.9)$$

is used for the static interaction.

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$$c_{nn'}(t) = a_{nn'}(t)\,\exp i(m'-m)\,\Phi\,\exp i\int_0^t V_{n'n'}(t)dt\,,$$

and thus the probability of excitation from state n to n' becomes

$$\mathcal{P}_{n,n'}(\rho) = |a_{nn'}(\infty)|^2 = |c_{nn'}(\infty)|^2\,.$$

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