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Excitation of Atomic Hydrogen by Protons

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Excitation cross sections for protons incident on atomic hydrogen are calculated by a nonadiabatic method. This consists of expanding the wave function in the spherical harmonics of the target, giving rise to an infinite set of coupled two-dimensional equations. These are solved numerically in the approximation which retains only S and P states of the target.

INTRODUCTION

A LARGE discrepancy exists between the theoretical and experimental cross sections for the $1s$–$2p$ excitation of atomic hydrogen by proton impact. Measurements,[1] which have been made in the 1–30-keV energy range, give cross sections about twice as great as those of the most elaborate theoretical calculation[2] which uses the close coupling method with $1s$, $2s$, and $2p$ states in both direct and rearrangement channels. Since the computed cross section is little altered by the inclusion of the $3s$ and $3p$ states it appears likely that coupling with further bound states will be small and that the continuum may play a crucial role in the excitation process. This possibility is investigated in the present paper using a variant of Temkin's nonadiabatic theory,[3] which consists of expanding the total wave function in spherical harmonics about the target proton. This gives rise to an infinite set of coupled two-dimensional equations. The nonadiabatic method consists of solving these equations sequentially as an increasing number of terms are retained in the expansion.

At high energies the method should converge reasonably rapidly since the continuum is well represented in the two-dimensional amplitudes. However, at low energies, where charge exchange is important, the convergence will probably be slow since an adequate description of rearrangement requires a large number of angular momenta.

The original application of this technique to a scattering problem was made by Temkin who considered the s-wave electron-hydrogen collision. Here, the "infinitely" massive proton is taken as the origin of a coordinate system so that a single two-dimensional function can describe both direct and rearrangement amplitudes, $\Psi^{\pm}(r_1, r_2) = \Phi(r_1, r_2) \pm \Phi(r_2, r_1)$. This, together with the symmetry of the Pauli principle, greatly enhanced the convergence of Temkin's expansion. Unfortunately, in the proton-hydrogen problem, direct and rearrangement amplitudes must be centered about different origins (the two protons), and the symmetry of the problem cannot be exploited in a simple way.

THEORY

We use the well-known impact parameter method in which the protons are treated as classical particles of infinite mass. Let $\mathbf{r} = (r, \theta, \phi)$ and $\mathbf{R} = (R, \Theta, \Phi)$ be the position vectors of the electron and incident proton relative to the stationary target proton which is located at the origin of a fixed coordinate system. The incident proton moves along a line parallel to and at a distance ρ from the z axis, with a constant velocity v.

The time-dependent Schrödinger equation for the electron is (in atomic units)

$$(\tfrac{1}{2}\nabla^2 + i(\partial/\partial t) + r^{-1} + |\,\mathbf{r}-\mathbf{R}\,|^{-1} - R^{-1})\Psi(\mathbf{r}, t) = 0. \qquad (1)$$

We have retained the interproton potential so that at large separations the perturbation tends rapidly to zero.

Taking advantage of the fact that the spherical harmonics $Y_{lm}(\theta, \phi)$ are eigenfunctions of

$$\begin{aligned}((\sin^2\theta)^{-1}(\partial^2/\partial\phi^2) + (\sin\theta)^{-1}(\partial/\partial\theta)\ \sin\theta(\partial/\partial\theta))&\\ \times Y_{lm}(\theta, \phi) = -l(l+1)\,Y_{lm}(\theta, \phi),& \qquad (2)\end{aligned}$$

we expand the wave function

$$\Psi(\mathbf{r}, t) = r^{-1}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\mathfrak{L}_{lm}(r, t)\,Y_{lm}(\theta, \phi) \qquad (3)$$

and the perturbation

$$-|\,\mathbf{R}-\mathbf{r}\,|^{-1} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{\gamma_l(r, R)}{2l+1}\,Y_{lm}(\theta, \phi)\,Y_{lm}^*(\Theta, \Phi), \qquad (4)$$

where

$$\begin{aligned}\gamma_l(r, R) &= -r^l/R^{l+1} \quad \text{for} \quad r<R\\ &= -R^l/r^{l+1} \quad \text{for} \quad r>R. \qquad (5)\end{aligned}$$

Substitution of these expressions in (1) gives, after some conventional manipulation, an infinite set of coupled equations

$$\begin{aligned}\left(\frac{1}{2}\frac{\partial^2}{\partial r^2} + r^{-1} - R^{-1} - \frac{l(l+1)}{r^2} + i\frac{\partial}{\partial t}\right)\mathfrak{L}_{lm}(r, t)&\\ = \sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2} F\begin{pmatrix} l & l_2 \\ m & m_2\end{pmatrix}\mathfrak{L}_{l_2 m_2}(r, t),& \qquad (6)\end{aligned}$$

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[1] R. F. Stebbings, R. A. Young, C. L. Oxley, and H. Ehrhardt, Phys. Rev. **138**, A1312 (1965).

[2] L. Wilets and D. F. Gallaher, Phys. Rev. **147**, 13 (1966).

[3] A. Temkin, Phys. Rev. **126**, 130 (1962).

where

$$F\begin{pmatrix} l & l_2 \\ m & m_2 \end{pmatrix}=4\pi \sum_{l_1=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \frac{\gamma_{l_1}^*(r, R)}{2l_1+1} Y_{l_1m_1}(\Theta, \Phi) J\begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2 \end{pmatrix} \tag{7}$$

and

$$J\begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2 \end{pmatrix}=\int_{-1}^{1} d(\cos\theta) \int_0^{2\pi} d\phi\, Y_{lm}^*(\theta, \phi)\, Y_{l_1m_1}(\theta, \phi)\, Y_{l_2m_2}(\theta, \phi)$$

$$=(-)^m \left(\frac{(2l+1)(2l_1+1)}{4\pi(2l_2+1)}\right)^{1/2} (ll_100 \mid l_20)\,(ll_1-mm_1 \mid l_2-m_2). \tag{8}$$

The second expression of Eq. (8) is in terms of Clebsch–Gordan coefficients.

For a collision in which the hydrogen atom is initially in a state with quantum numbers $n_0l_0m_0$, Eq. (6) must be solved subject to the boundary conditions

$$\mathcal{L}_{lm}(0, t) = \lim_{r\to\infty} \mathcal{L}_{lm}(r, t) = 0,$$

$$\lim_{t\to-\infty} \mathcal{L}_{lm}(r, t) = R_{n_0l_0}(r) \exp(it/2n_0^2)\, \delta_{ll_0}\delta_{mm_0}, \tag{9}$$

where $R_{n_0l_0}(r)$ is r times the normalized hydrogenic radial function.

If we make the expansion

$$\mathcal{L}_{lm}(r, t) = \left(\sum_{n=l+1}^{\infty} + \int dk\right) \alpha_{nlm}(t) \exp\left(\frac{it}{2n^2}\right) R_{nl}(r), \tag{10}$$

then the probability of excitation to a final state with quantum numbers nlm is

$$P_{nlm} = \lim_{t\to\infty} \mid \alpha_{nlm}(t) \mid^2 \tag{11}$$

and the corresponding cross section is

$$Q_{nlm} = 2\pi \int_0^{\infty} P_{nlm}\rho d\rho. \tag{12}$$

The expansion coefficients may be obtained from a knowledge of $\mathcal{L}_{lm}(r, t)$ either by direct projection from Eq. (10),

$$\alpha_{nlm}(t) = \exp\left(-\frac{it}{2n^2}\right) \int_0^{\infty} R_{nl}(r) \mathcal{L}_{lm}(t) dr, \tag{13}$$

or by substituting (10) into (6) and making use of the relation

$$\left(\frac{1}{2}\frac{\partial^2}{\partial r^2} + r^{-1} - \frac{l(l+1)}{r^2} + i\frac{\partial}{\partial t}\right) R_{nl}(r) \exp\left(\frac{it}{2n^2}\right) = 0, \tag{14}$$

which gives the integral formula

$$\alpha_{nlm}(t) = \delta_{nn_0}\delta_{ll_0}\delta_{mm_0} - i\int_{-\infty}^{t} dt' \exp\left(-\frac{it}{2n^2}\right) \int_0^{\infty} R_{nl}(r) dr \left[R^{-1} + \sum_{l_2=0}^{\infty} \sum_{m_2=-l_2}^{l_2} F\begin{pmatrix} l & l_2 \\ m & m_2 \end{pmatrix}\right] \mathcal{L}_{l_2m_2}(r, t). \tag{15}$$

It is clearly impossible to solve the above set of equations without making some drastic approximations. The most natural way to proceed is to neglect all but a very few of the functions $\mathcal{L}_{lm}(r, t)$ in Eq. (6) and to solve this finite set of equations numerically with the appropriate boundary conditions. The simplest case is the zeroth-order or S-wave problem in which only $\mathcal{L}_{00}(r, t)$ is retained. In the first-order or p-wave problem we neglect all the $\mathcal{L}_{lm}(r, t)$ except those with $l=1$ and $l=0$. In general the nth-order problem is that in which only those functions with $l=n$ or less are retained in Eq. (6). The assumption of the nonadiabatic method is that the excitation probabilities P_{nlm} will eventually converge to the correct result as the order of the problem is increased. At low energies, where charge exchange becomes important, the convergence may well be slow since an adequate description of rearrangement requires very many angular momenta in the present formulation.

ZEROTH-ORDER APPROXIMATION

Neglecting all terms in (6) with $l=1$ or greater gives the s-wave equation

$$[\tfrac{1}{2}(\partial^2/\partial r^2) + i(\partial/\partial t) + V(r, t)]\mathcal{L}_{00}^{(0)}(r, t) = 0, \tag{16}$$

where

$$V(r, t) = 1/r \quad \text{for } r<R$$

$$= 2/r - 1/R \quad \text{for } r>R. \tag{17}$$

The approximation defined above for $\mathcal{L}_{00}^{(0)}(r, t)$ closely resembles the zeroth-order problem of Temkin's nonadiabatic theory.[3] As in Temkin's application, Eq. (16) has a clear physical interpretation. Initially the electron sees only the charge of the target proton. When the electron cloud is penetrated by the incident proton, the electron sees a doubly charged nucleus. Thus a temporary helium ion is formed which decays as the moving proton emerges from the electron cloud.

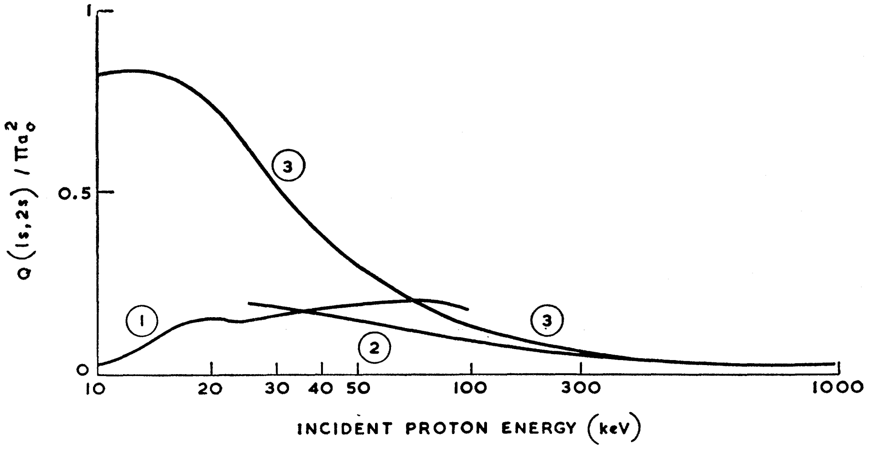

FIG. 1. The $1s$–$2s$ excitation cross section for protons incident on atomic hydrogen. (1) Close coupling from Wilets and Gallaher (Ref. 2). (2) Nonadiabatic zeroth-order results. (3) Nonadiabatic first-order results.

The boundary conditions at infinity (9) are awkward to handle numerically and it was found more convenient to make the transformations

$$\mathcal{L}_{00}^{(0)}(r,t)=\exp(it/2)\chi(\xi,\tau),$$

$$\tau=\tan^{-1}(vt/\rho),\qquad \xi=\tan^{-1}(r),\tag{18}$$

thus placing the entire problem within a box $-\frac{1}{2}\pi\leq\tau\leq\frac{1}{2}\pi$, $0\leq\xi\leq\frac{1}{2}\pi$. The boundary conditions at infinity may now be simply stated

$$\chi(\xi,-\tfrac{1}{2}\pi)=2\tan(\xi)\exp(-\tan\xi),$$

$$\chi(0,\tau)=\chi(\tfrac{1}{2}\pi,\tau)=0.\tag{19}$$

The finite (central) difference equation corresponding to (16) is

$$A\chi=K,\tag{20}$$

where A is a complex tridiagonal matrix, χ is a column vector representing the solution at some value of τ, and K depends on previous values of τ. Using a noniterative technique developed by one of us,[4] Eq. (20) may be directly inverted and $\chi(\xi,\tau_i)$ obtained from a knowledge of $\chi(\xi,\tau_{i-1})$. Since the initial condition at $\tau=-\frac{1}{2}\pi$ is given by (19) a numerical solution may be developed over the entire region $-\frac{1}{2}\pi\leq\tau\leq\frac{1}{2}\pi$.

Calculations were performed on the laboratory's

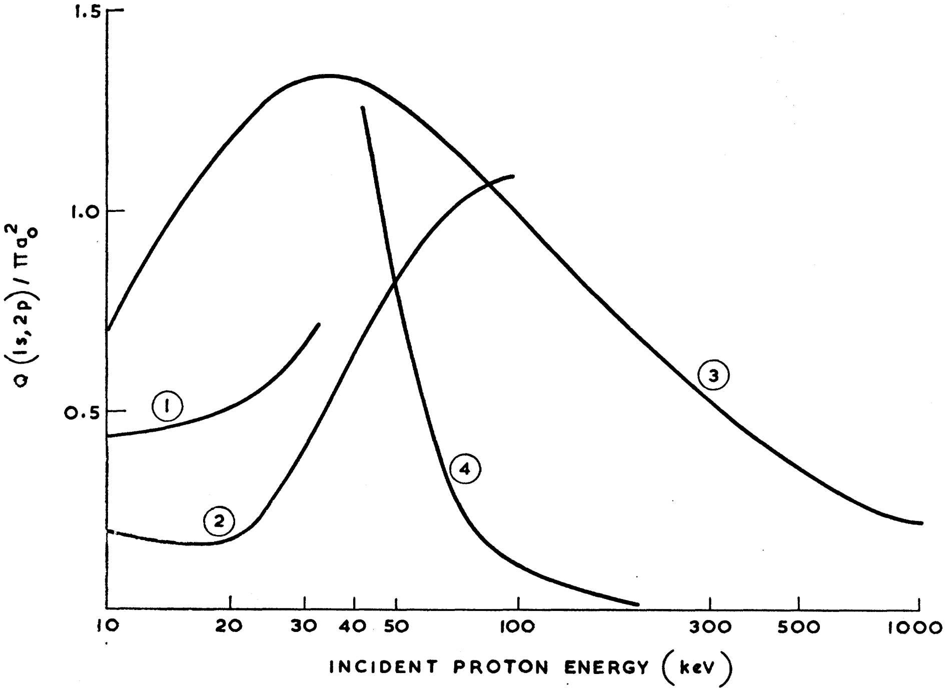

FIG. 2. The $1s$–$2p$ excitation cross section for protons incident on atomic hydrogen. (1) Experimental results of Stebbings *et al.* (Ref. 1). (2) Close coupling ($1s\,|\,2s\,|\,2p$) with rearrangements from Wilets and Gallaher (Ref. 2). (3) Present nonadiabatic calculation. (4) Charge exchange from Wilets and Gallaher (Ref. 2).

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[4] A. Temkin and E. C. Sullivan, National Aeronautics and Space Administration Technical Note No. D-1702, 1963 (unpublished).

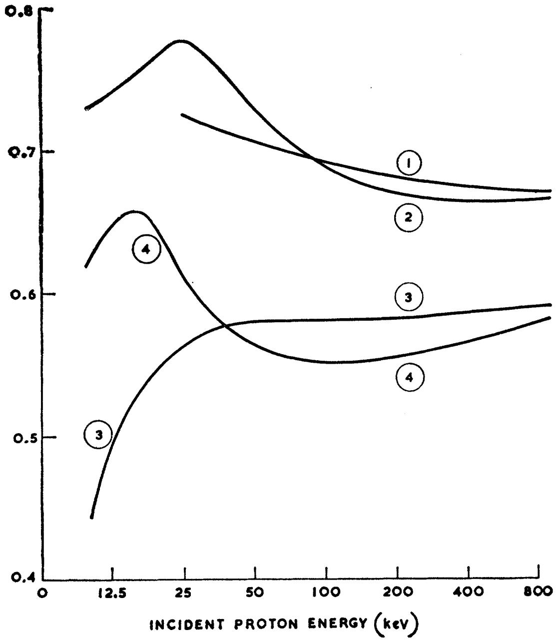

FIG. 3. $[2^3Q(3x)]/[3^3Q(2x)]$. (1) $x=s$ in the zeroth-order approximation. (2) $x=s$ in the first-order approximation. (3) $x=p_0$ in the first-order approximation. (4) $x=p_{\pm 1}$ in the first-order approximation.

IBM 7094/7040 computer using a 400×400 point mesh on the ξ, τ plane. The unitarity requirement

$$\int_0^{\pi/2} |\chi(\xi,\tau)|^2 \sec^2\xi d\xi = 1 \qquad (21)$$

was confirmed to a very high degree of accuracy except for values of τ close to $\frac{1}{2}\pi$ where it was occasionally violated by as much as 2%. This was due to an accumulated instability in χ which greatly inhibited the convergence of the excitation probabilities $P_{n00} = |\alpha_{n00}(\tau)|^2$ when computed using Eq. (13). However, the instability had an insignificant effect on the values of $|\alpha_{n00}(t)|^2$ computed from (15) which depends on the entire history of χ rather than upon its instantaneous value at $\tau=\frac{1}{2}\pi$.

TABLE I. Excitation cross sections in units of $(\pi a_0^2/n^3)$ calculated in the zeroth-order approximation.

	Energy (keV)					
n	25	50	100	200	400	800
2	1.68	1.17	0.718	0.395	0.209	0.108
3	1.22	0.827	0.495	0.269	0.141	0.0725
4	1.10	0.741	0.445	0.238	0.125	0.0639
5	1.05	0.705	0.412	0.225	0.118	0.0604
6	1.03	0.687	0.402	0.219	0.114	0.0587
7	1.01	0.676	0.394	0.215	0.113	0.0576
QI	0.269	0.222	0.133	0.0718	0.037	0.0188
R[a]	0.665	0.853	0.928	0.970	1.03	...

[a] R = (Close coupling $1s$–$2s$ cross section)/(Nonadiabatic $1s$–$2s$ cross section). See Ref. 5.

Cross sections were computed using (11), (12), and (15), and the results are given in Table I. Q_I corresponds to the s-wave contribution to the ionization cross section and was computed from

$$Q_I = 2\int_0^\infty \rho d\rho \{1 - \sum_{n=1}^{\infty} |\alpha_n(\pi/2)|^2\}, \qquad (22)$$

where the complete sum was formed by extrapolating above $n=7$. Since the zeroth-order problem corresponds to the complete expansion in target s states it is clear that any close coupling calculation which retains only s states of the target must be an approximation to the zeroth-order problem. Table I should therefore be useful in studying the convergence of the close coupling expansion. Lovell and McElroy[5] have calculated the $1s$–$2s$ excitation cross section in the $1s/2s$ close coupling approximation and the ratio of their results to those of the nonadiabatic theory form the bottom row of

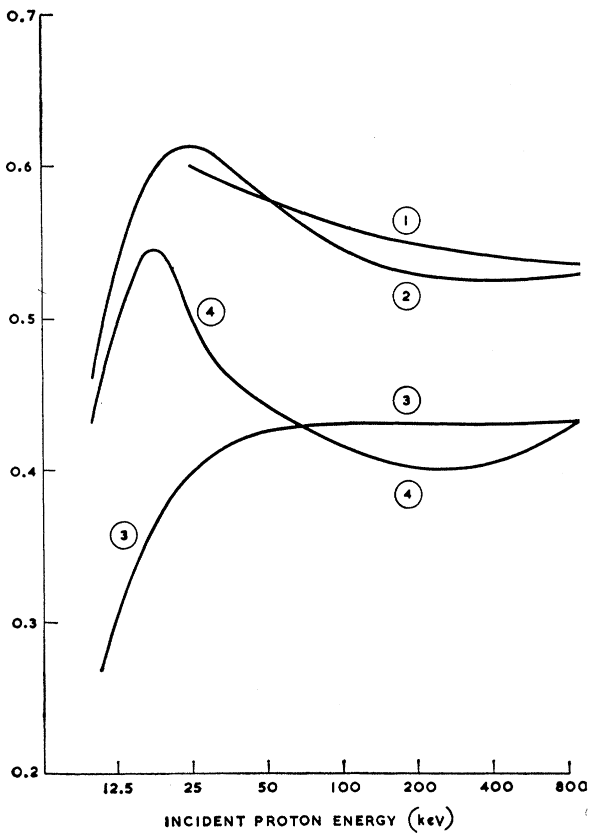

FIG. 4. $[2^3Q(7x)]/[7^3Q(2x)]$. (1) $x=s$ in the zeroth-order approximation. (2) $x=s$ in the first-order approximation. (3) $x=p_0$ in the first-order approximation. (3) $x=p_0$ in the first-order approximation. (4) $x=p_{\pm 1}$ in the first-order approximation.

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[5] S. E. Lovell and M. B. McElroy, Proc. Roy. Soc. (London) **A283**, 100 (1965).

Table I. Unfortunately the corresponding 1*s*/2*s*/3*s* calculation has not been reported.

FIRST-ORDER APPROXIMATION

Here we retain only those terms of (6) with $l=0$ and $l=1$. This gives four coupled equations linking the amplitudes $\mathcal{L}_{0,0}^{(1)}$, $\mathcal{L}_{1,0}^{(1)}$, $\mathcal{L}_{1,-1}^{(1)}$, and $\mathcal{L}_{1,+1}^{(1)}$. However, the combination $\mathcal{L}_{1,-1}^{(1)}\exp(-i\Phi)+\mathcal{L}_{1+1}^{(1)}\exp(+i\Phi)$ is not coupled to the other functions and since the hydrogen atom is initially in a 1*s* state we have

$$\mathcal{L}_{1-1}^{(1)}\exp(-i\Phi)+\mathcal{L}_{1,+1}^{(1)}\exp(+i\Phi)=0. \tag{23}$$

Taking the linear combination $\mathcal{L}_{1\mp1}^{(1)}$ defined by

$$\mathcal{L}_{1,\pm1}^{(1)}=(1/\sqrt{2})\left(\mathcal{L}_{1,-1}^{(1)}\exp(-i\Phi)-\mathcal{L}_{1,1}^{(1)}\exp(+i\Phi)\right), \tag{24}$$

we find that the remaining functions must satisfy the equations

$$\begin{aligned}
\left(\frac{1}{2}\frac{\partial^2}{\partial r^2}+i\frac{\partial}{\partial t}+V(r,R)\right)\mathcal{L}_{0,0}^{(1)}&=\frac{\gamma_1}{\sqrt{3}}\left(\frac{vt}{R}\right)\mathcal{L}_{1,0}^{(1)}+\frac{\gamma_1}{\sqrt{3}}\frac{\rho}{R}\mathcal{L}_{1,\pm1}^{(1)},\\
\left(\frac{1}{2}\frac{\partial^2}{\partial r^2}+i\frac{\partial}{\partial r}+V(r,R)-\frac{1}{r^2}-\frac{\gamma_2}{5}\frac{(2v^2t^2-\rho^2)}{R^2}\right)\mathcal{L}_{1,0}^{(1)}&=\frac{\gamma_1}{\sqrt{3}}\left(\frac{vt}{R}\right)\mathcal{L}_{0,0}+\tfrac{3}{5}\gamma_2\frac{\rho vt}{R^2}\mathcal{L}_{1,\pm1}^{(1)},\\
\left[\frac{1}{2}\frac{\partial^2}{\partial r^2}+i\frac{\partial}{\partial t}+V(r,R)-\frac{1}{r^2}-\frac{\gamma_2}{5}\left(\frac{2\rho^2-v^2t^2}{R^2}\right)\right]\mathcal{L}_{1\pm1}^{(1)}&=\frac{\gamma_1}{\sqrt{3}}\frac{\rho}{R}\mathcal{L}_{0,0}+\tfrac{3}{5}\gamma_2\frac{\rho vt}{R^2}\mathcal{L}_{1,0}^{(1)}.
\end{aligned} \tag{25}$$

Since Eq. (25) retains all target *P* states it accounts for the entire long-range polarizability of the hydrogen atom. Again, any close coupling calculation which retains only *S* and *P* states of the target must form an approximation to (25). The first-order approximation should provide an accurate representation of the exact wave function at energies where coupling with rearrangement states is unimportant. As illustrated in Fig. 1 this circumstance should hold at energies slightly in excess of 100 keV.

TABLE II. Cross sections for excitation of the $N=2$ level of the atomic hydrogen by protons calculated in the first-order approximation.

Energy (keV)	1*s*–2*s*	$2^3\times\sigma/(\pi a_0^2)$ 1*s*–2p_0	1*s*–2$p_{\pm1}$
10	6.6	2.0	3.7
20	5.9	4.4	5.0
25	4.9	5.1	5.2
50	2.4	5.7	4.5
100	1.07	5.1	3.3
200	0.50	3.8	1.83
400	0.24	2.5	0.97
800	0.114	1.55	0.46

Equation (25) was solved numerically by a method similar to that described above for the zeroth-order problem and the results are shown in Figs. 1 to 4, and in Table II. That the experimental cross sections of Fig. 2 lie between those of the nonadiabatic and close-coupling calculations is consistent with the observation that the two theories take account of quite different effects. The nonadiabatic calculation takes full account of coupling with higher bound states and ionization states of the target but completely neglects coupling with rearrangement states while the close-coupling calculation does precisely the opposite. Moreover, at low energies, charge exchange removes a substantial portion of the available probability so that the nonadiabatic cross sections may be expected to be too large.

The similarity of Figs. 3 and 4 shows that the n^3 law holds fairly well over the entire energy range.

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