

Excitation and Ionization of Hydrogen Atoms by Electron Impact

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The classical cross sections of Gryzinski for the excitation and ionization of atomic hydrogen by electron impacts are compared with existing experimental and theoretical cross sections. For excitation from the ground to the first excited states of atomic hydrogen, the classical cross section reproduces the experimental cross section to within a factor of 2 from the excitation threshold to an electron impact energy of about 20 atomic units. For ionization from the ground state of atomic hydrogen, the classical cross section reproduces the experimental cross section to within a factor of 2 from 0.02 atomic units above threshold to about 400 atomic units. A comparison of the classical cross sections with all available Born-approximation cross sections shows that although the classical cross sections are always smaller, they agree quite well with the Born cross sections except at very high energies. However for energies less than 100 atomic units the classical cross sections always agree with the Born cross sections to better than a factor of three. A comparison of experimental "electron-ion" recombination coefficients and theoretical recombination coefficients, obtained by using the classical cross sections, suggests that at low energies, the classical cross sections for transitions between low excited levels cannot be in error by more than a factor of 2.

INTRODUCTION

THE cross sections for excitation and ionization of atoms and molecules by electron impacts are of importance in many physical problems. Quantum-mechanical calculations have been successful in predicting these cross sections for simple atomic systems when the energy of the incident electron is large. For more complicated atomic and molecular systems and for low incident energies, the task of solving the quantum-mechanical scattering equation leads to great analytical and computational difficulties, which have not yet been overcome.

Gryzinski¹ has shown that for a large range of electron scattering problems fair accuracy may be achieved by classical calculations. Compared with quantum-mechanical calculations, the cross sections obtained from classical calculations have the great practical advantages that they have simple analytical forms and may be evaluated rapidly. However, theoretically it is known that the quantum-mechanical scattering equation describes electron scattering processes exactly, although the solution may be difficult to obtain, but it is not as yet known to what extent electron scattering processes may be described by classical mechanics.

Comparisons of experimental and classical cross sections for electron excitation and ionization of a large number of atoms and molecules have already been carried out.¹⁻³ These show that for ionization¹⁻³ the classical theory can usually reproduce the experimental cross sections to better than a factor of 2 in an electron energy range from just above threshold to about 1000 eV. For excitation^{1,3} the situation is not clear, but usually the classical theory reproduces the experimental

cross sections to within a factor of 2 or three over a small energy range above the threshold.

In this paper we compare the classical cross sections for excitation and ionization of atomic hydrogen by electron impacts with available theoretical and experimental data. It is hoped that such a comparison will lead to a better understanding of the possible errors in Gryzinski's classical approximation.

IONIZATION

The cross section for ionization of an atom by electron impacts was first considered classically by Thomson. By assuming that the atomic electron was initially at rest, he obtained a cross section for ionization by electron impacts, which, for a hydrogen atom having principal quantum number n , gives

$$Q_T(n; c) = (1/E_2^2)(E_2/U_n - 1), \quad (1)$$

where $Q_T(n; c)$ is in units of πa_0^2 if, E_2 , the energy of the incident electron, and $U_n = (1/2)(1/n^2)$, the ionization potential of the atomic electron, are in atomic units (27.12 eV).

Using a theory formulated by Chandrasekhar⁴ for stellar encounters, Gryzinski¹ has been able to take into account the initial velocity of the atomic electron and shows that for a hydrogen atom having principal quantum number n and azimuthal quantum number l , the classical cross section for ionization by electron impacts $Q_C(nl; c)$ is given by

$$Q_C(nl; c) = \int_0^\infty f^{nl}(v_e) Q(U_n) dv_e, \quad (2)$$

where $Q(U_n)$ is a function of the ionization potential U_n , the initial energy of the atomic electron E_1 , and the energy of the incident electron E_2 , and where $f^{nl}(v_e)$ is the velocity distribution of the atomic electron. In

¹ M. Gryzinski, Phys. Rev. **115**, 374 (1959).

² S. S. Prasad and K. Prasad, Proc. Phys. Soc. (London) **82**, 655 (1963).

³ V. I. Ochkur and A. M. Petrun'kin, Opt. Spektroskopiya **14**, 457 (1963) [English transl.: Opt. Spectry. (USSR) **14**, 245 (1963)].

⁴ S. Chandrasekhar, Astrophys. J. **93**, 285 (1941).

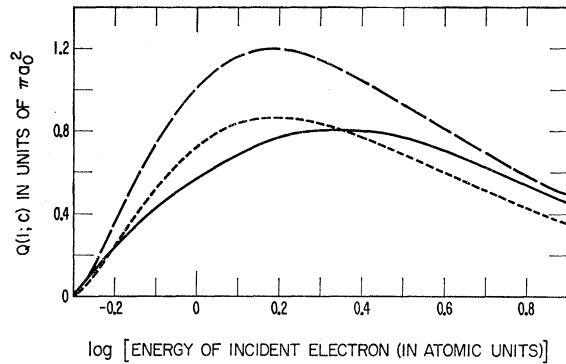


FIG. 1. Cross sections for electron impact ionization of the ground state of atomic hydrogen: — experimental cross section; - - - theoretical cross section, Born approximation; - · - · theoretical cross section, Gryzinski classical approximation.

order to simplify the problem, Gryzinski takes the velocity distribution to be a δ function

$$f^{nl}(v_e) = \delta[v_e - (2U_n/m_e)^{1/2}], \quad (3)$$

and obtains a cross section for ionization, which we will denote by $Q_G(n; c)$, and which is given by

$$Q_G(n; c) = \left\{ \begin{array}{l} \frac{1}{U_n E_2} \left(\frac{E_2}{E_2 + U_n} \right)^{3/2} \left(\frac{5}{3} \frac{2U_n}{E_2} \right) \text{ if } 2U_n \leq E_2, \\ \frac{1}{U_n E_2} \frac{2^{1/2} 4}{3} \left(\frac{E_2 - U_n}{E_2 + U_n} \right)^{3/2} \text{ if } 2U_n \geq E_2 \end{array} \right\}. \quad (4)$$

For the ground state of atomic hydrogen, it has been verified that the cross sections obtained from the exact electron velocity distribution and the δ -function distribution are almost the same, except near the ionization threshold, where the exact distribution gives results which are about twice those of the δ -function distribution.

For ionization from excited states of hydrogen we also expect that the difference between the results obtained by using the two velocity distributions will be very small. However, for the excited states, we note that since each degenerate level has a different velocity distribution, we obtain a different cross section $Q_C(nl; c)$ from Eq. (2) for each degenerate level. As the cross sections obtained from the δ -function distribution take no account of the degenerate levels, we must compare $Q_G(n; c)$ with the average cross section

$$Q_C(n; c) = \frac{1}{n^2} \sum_{l=0}^{n-1} (2l+1) Q_C(nl; c). \quad (5)$$

If we average out the angular parts of the velocity distributions, we can show that at high energies all the $Q_C(nl; c)$ and also $Q_G(n; c)$ tend to $(5/3)(1/U_n E_2)$. Also, if we average over the degenerate levels, we find

that at small energies ϵ above the threshold, the exact distribution cross section tends to $1.13(\epsilon^{3/2}/U_n^{7/2})$ compared with the δ -function distribution cross section which tends to $\frac{2}{3}(\epsilon^{3/2}/U_n^{7/2})$.

The cross section for ionization of the ground state of hydrogen by electron impacts has been measured by several experimental groups.⁵⁻⁷ The agreement between the various measurements is quite good, the maximum difference between them being about 20%. In Fig. 1 we compare the experimental cross section⁵ for ionization of the ground state of hydrogen, $Q(1; c)$, with theoretical cross sections calculated using the first Born approximation⁸ and also calculated from Eq. (4). The agreement between the classical calculations and the experimental measurements is quite good. Apart from a region close to the threshold, the classical cross section does not differ by more than 25% from the experimental cross section. Close to the threshold the classical cross section does not have the correct energy falloff, for at small energies ϵ above the threshold, the experimental cross section varies as 2.12ϵ compared with the classical cross section falloff of $7.5\epsilon^{3/2}$. The cross-section curves cross at $\epsilon=0.12$ atomic units, and the classical cross section is half of the experimental cross section at $\epsilon=0.02$ atomic units.

At large impact energies the Born-approximation cross sections agree with experimental cross sections, and in Fig. 2 we plot the ratio of the ionization cross section obtained from the classical approximation $Q_G(1; c)$ to the cross section obtained from the Born approximation⁸ $Q_B(1; c)$. We see that over a large energy range there is good agreement between $Q_G(1; c)$ and $Q_B(1; c)$. However, as the incident electron energy increases the difference between the Born cross section and the classical cross section increases. This is due to the fact that at large electron energies the classical cross section falls off as $1/E_2$ compared with the correct falloff $\log E_2/E_2$. Nevertheless, by extrapolating from Fig. 2, we estimate that the classical cross section only drops to less than half of the exact cross section for energies above 400 atomic units.

This comparison shows that the classical cross section reproduces the experimental cross section for ionization from the ground state of atomic hydrogen by electron impacts, to within a factor of 2 over an energy range from 0.02 atomic units above the threshold to about 400 atomic units, and to within 25% in an energy range from 0.06 atomic units above the threshold to about 10 atomic units.

For atomic hydrogen the cross section for ionization has only been measured from the ground state, but in

⁵ W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1141 (1958).

⁶ R. L. F. Boyd and A. Boksenberg, *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960).

⁷ E. W. Rothe, L. L. Marino, R. H. Neynaber, and S. M. Trujillo, Phys. Rev. **125**, 582 (1962).

⁸ R. McCarroll, Proc. Phys. Soc. (London) **70**, 460 (1957).

order to give some estimate of the accuracy of the classical cross sections for ionization from excited levels of hydrogen, we also give in Fig. 2 the ratio of $Q_G(2; c)$ to $Q_B(2; c)$, where

$$Q_B(2; c) = \frac{1}{4}[Q_B(2s; c) + 3Q_B(2p; c)], \quad (6)$$

the subscript B is used to denote the Born approximation. Unfortunately, $Q_B(2; c)$ has only been calculated over a very small energy range,^{9,10} and it is not known if the Born-approximation cross section is correct at these energies. However, the good agreement between the classical and Born cross sections suggests that for high energies at least, the classical approximation will give quite good cross sections for ionization from excited states.

EXCITATION

The concept of excitation to a discrete level is in a sense alien to the classical theory which gives directly only the cross section, $Q(n; \epsilon)d\epsilon$ for a collision in which energy between ϵ and $\epsilon + d\epsilon$ is transferred to the target electron. However, if ϵ is in atomic units it may be assumed that the cross section for excitation from a

$$Q_G(n; n') = \frac{1}{(n')^3 E_2 (U_n - U_{n'})^2} \left(\frac{E_2}{E_2 + U_n} \right)^{3/2} \times \left\{ \begin{array}{ll} \frac{1}{3} \frac{(7U_n - 3U_{n'})}{(U_n - U_{n'})} \frac{U_n}{E_2} & \text{if } 2U_n - U_{n'} \leq E_2, \\ \frac{1}{3} \left(\frac{2U_n - U_{n'}}{U_n} \right)^{1/2} \left[\frac{(5U_n - U_{n'})}{(U_n - U_{n'})} + \frac{(U_n - 2U_{n'})}{E_2} \right] \left(1 - \frac{(U_n - U_{n'})}{E_2} \right)^{1/2} & \text{if } 2U_n - U_{n'} \geq E_2, \end{array} \right\}, \quad (8)$$

where $Q_G(n; n')$ is in units of πa_0^2 if, E_2 , the energy of the incident electron, and U_n , and $U_{n'}$, the ionization potentials of the states n and n' are in atomic units.

We note that like the classical cross section for ionization $Q_G(n; c)$, the classical cross section for excitation $Q_G(n; n')$ does not take account of degenerate levels, $Q_G(n; n')$ must be considered as an average value of the cross sections from state n to n' . If $Q(nl; n'l')$ is the cross section for electron excitation from a state with principal quantum n and azimuthal quantum number l to a state with quantum numbers n' and l' , then we must compare $Q_G(n; n')$ with the average cross section

$$Q(n; n') = \frac{1}{n^2} \sum_{l'=0}^{n'-1} \sum_{l=0}^{n-1} (2l+1) Q(nl; n'l'). \quad (9)$$

The only electron excitation cross sections that have been measured experimentally for atomic hydrogen are

⁹ P. Swan, Proc. Phys. Soc. (London) 68, 1157 (1955).

¹⁰ D. McCrea and T. V. M. McKirgan, Proc. Phys. Soc. (London) 75, 235 (1960).

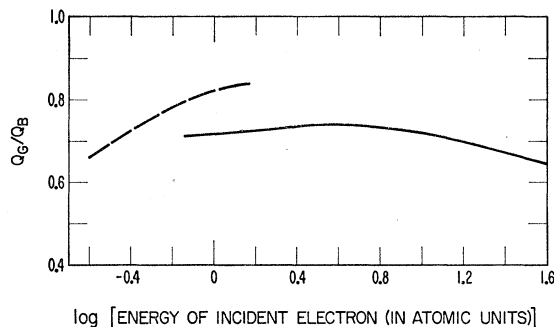


FIG. 2. Ratio of Gryzinski classical approximation cross section to Born-approximation cross section: — ionization of ground state of atomic hydrogen by electron impacts; - - - ionization of first excited state of atomic hydrogen by electron impacts.

state with principal quantum number n to one with principal quantum number n' is

$$Q(n; n') = (n')^{-3} Q(n; \epsilon_{n'n}) (n' > n), \quad (7)$$

where $\epsilon_{n'n}$ is the excitation energy.⁸ Using Gryzinski's expression for $Q(n; \epsilon_{n'n})$ it is then found that in the case of atomic hydrogen, the classical cross section for electron excitation from a state n to n' is given by

the cross sections for excitation from the ground state to the $2s$ and $2p$ states.¹¹ In Fig. 3 we compare the average value of these experimental cross sections $Q(1; 2)$ with the average value of the theoretical cross sections calculated using the first Born approximation,⁸ and also with the cross section calculated from Eq. (8). The agreement between the classical and experimental cross sections for excitation is not as good as for ionization, however in the energy range covered by Fig. 3 the classical and experimental cross sections always agree to better than a factor of 2. For small energies ϵ above the threshold the experimental cross section seems to vary as $2.0\epsilon^{1/2}$ whereas the classical cross section varies as $3.4\epsilon^{1/2}$. This implies that even close to the threshold the classical and experimental cross sections are in quite good agreement; however, recent theoretical work¹² suggests that the cross section is finite at the

¹¹ W. L. Fite, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), p. 421.

¹² R. Damburg and M. Gailitis, Proc. Phys. Soc. (London) 82, 1068 (1963).

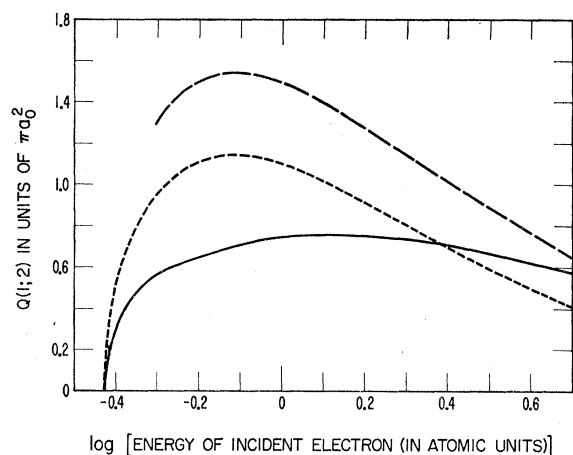


FIG. 3. Cross section for electron impact excitation from the ground to the first excited state of atomic hydrogen: — experimental cross section; — — — theoretical cross section, Born approximation; - · - · - theoretical cross section, Gryzinski classical approximation.

threshold, but this is not at present supported by the experimental measurements.

At large impact energies the Born-approximation cross sections agree with experimental cross sections. In Fig. 4 we plot the ratio of the excitation cross section obtained from the classical approximation $Q_G(1; 2)$ to the average cross section obtained from the Born approximation $Q_B(1; 2)$. We see that only above about 20 atomic units does the classical cross section become less than half the Born cross section. For higher electron energies the difference between the classical and Born approximation cross sections becomes greater as the former falls off as $1/E_2$, while the latter falls off as $\log E_2/E_2$, however, the difference in these fall offs is very slight, and only above 100 atomic units does the classical cross section fall to less than one-third of the Born cross section.

This comparison shows that for excitation from the

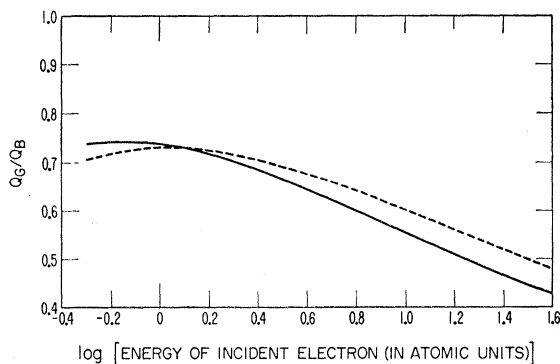


FIG. 4. Ratio of Gryzinski classical approximation cross section to Born approximation cross section: — excitation from $n=1$ to $n=2$ state of atomic hydrogen by electron impacts; - · - · - excitation from $n=1$ to $n=4$ state of atomic hydrogen by electron impacts.

ground state to the first excited states of hydrogen the classical cross section reproduces the experimental cross section to better than a factor of 2 from the threshold to about 20 atomic units.

The cross section for excitation of atomic hydrogen has only been measured experimentally for transitions from the ground to the first excited state. For other transitions in atomic hydrogen, we can get some idea of the validity of the classical theory by comparing the classical cross sections with the Born-approximation cross sections, for we know that the Born approximation is valid at high energies. Unfortunately it is not known at what energies the Born approximation becomes valid. As both $Q_B(1; c)$ and $Q_B(1; 2)$ agree with the experimental cross sections for energies above about 4 atomic units, we can take 4 atomic units as a rough guide for the energy above which the Born approximation becomes valid, however for transitions between excited states the Born approximation may be valid for much lower energies.

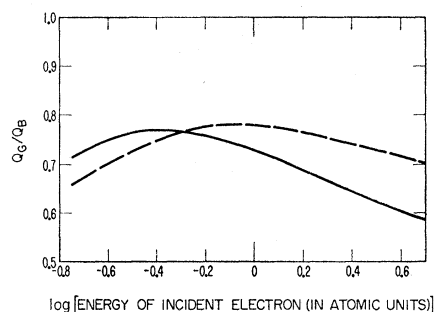


FIG. 5. Ratio of Gryzinski classical approximation cross section to Born approximation cross section: — excitation from $n=2$ to $n=3$ state of atomic hydrogen by electron impacts; - · - · - excitation from $n=2$ to $n=6$ state of atomic hydrogen by electron impacts.

McCarroll⁸ has used the Born approximation to calculate the cross sections for several transitions from the ground state of atomic hydrogen, in Fig. 4 we also plot the ratio $Q_G(1; 4)/Q_B(1; 4)$. At high energies the agreement between $Q_G(1; 4)$ and $Q_B(1; 4)$ is better than that between $Q_G(1; 2)$ and $Q_B(1; 2)$ but not so good as that between $Q_G(1; c)$ and $Q_B(1; c)$; for example, the ratios $Q_G(1; 2)/Q_B(1; 2)$, $Q_G(1; 4)/Q_B(1; 4)$ and $Q_G(1; c)/Q_B(1; c)$ fall below 0.5 at about 20, and 40, and 400 atomic units, respectively. It seems to be a general feature of the classical approximation, that for transitions from a given state it agrees best with the Born approximation for transitions in which the change in the principal quantum number is large.

The Born approximation has also been used to calculate cross sections for transitions from the first excited states of hydrogen.^{10,13} In Fig. 5 we plot $Q_G(2; 3)/Q_B(2; 3)$ and $Q_G(2; 6)/Q_B(2; 6)$. Unfortu-

¹³ T. J. M. Boyd, Proc. Phys. Soc. (London) **72**, 523 (1958).

nately these calculations were carried out over a very limited energy range, but we can see again the general feature that the classical approximation agrees best with the Born approximation for transitions in which the change in the principal quantum number is large. We also note that at high energies the agreement between $Q_G(2; 3)$ and $Q_B(2; 3)$ is not quite so good as the agreement between $Q_G(1; 2)$ and $Q_B(1; 2)$.

Milford and his co-workers¹⁴ have also carried out the formidable task of using the Born approximation to obtain cross sections for the twelve transitions between the degenerate levels of the states with principal quantum numbers 3 and 4. In Fig. 6 we plot $Q_G(3; 4)/Q_B(3; 4)$. At high-impact energies the agreement between $Q_G(3; 4)$ and $Q_B(3; 4)$ is not quite so good as the agreement between $Q_G(2; 3)$ and $Q_B(2; 3)$. However, although $Q_G(3; 4)/Q_B(3; 4)$ falls below 0.5 at 8 atomic units, we see that since the difference between a $1/E_2$ and a $\log E_2/E_2$ falloff is very small, the ratio $Q_G(3; 4)/Q_B(3; 4)$

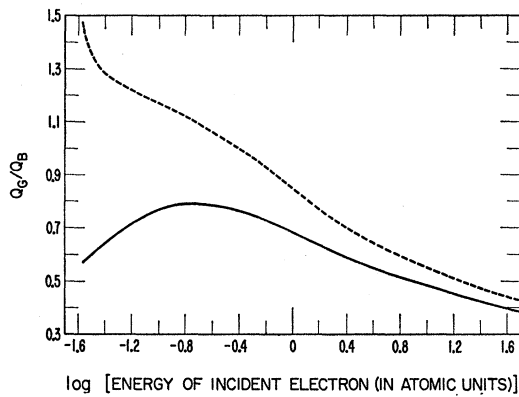


FIG. 6. Ratio of Gryzinski classical approximation cross section to Born-approximation cross section, for excitation from $n=3$ to $n=4$ state of atomic hydrogen by electron impacts: — taking into account all transitions in the Born-approximation cross section; - - - taking into account only main optically allowed transitions in the Born-approximation cross section.

decreases slowly as the energy of the incident electron increases, and only falls below 0.4 at 40 atomic units.

Milford and his co-workers^{15,16} have also used the Born approximation to calculate certain cross sections for the transitions $4 \rightarrow 5$ and $5 \rightarrow 6$. They consider only the main optically allowed transitions in which the azimuthal quantum number l changes by $+1$, since at high energies these transitions have the largest cross sections. However, their calculations on the $3 \rightarrow 4$ transitions show that the other weaker transitions are quite important at low-electron energies. This can be seen clearly in Fig. 6 where we plot the ratio $Q_G(3; 4)/Q_B(3; 4)$ for

¹⁴ G. C. McCoy, S. N. Milford, and J. J. Wahl, Phys. Rev. **119**, 149 (1960).

¹⁵ L. Fisher, S. N. Milford, and F. R. Pomilla, Phys. Rev. **119**, 153 (1960).

¹⁶ S. N. Milford, J. J. Morrissey, and J. H. Scanlon, Phys. Rev. **120**, 1715 (1960).

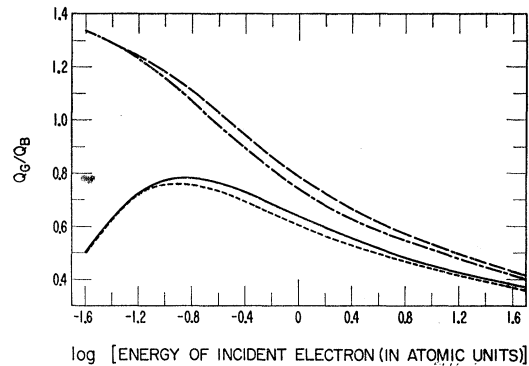


FIG. 7. Ratio of Gryzinski classical approximation cross section to Born-approximation cross section for excitation from $n=4$ to $n=5$ and $n=5$ to $n=6$ states of atomic hydrogen by electron impacts: taking into account all transitions in the Born-approximation cross section, — $n=4$ to $n=5$, - - - $n=5$ to $n=6$; taking into account only main optically allowed transitions in the Born-approximation cross section, - · - · $n=4$ to $n=5$, - - - $n=5$ to $n=6$.

$Q_B(3; 4)$ including all transition, and also for $Q_B(3; 4)$ including only the main optically allowed transitions in which l changes by $+1$. We can take account of the weaker transitions in the case of $4 \rightarrow 5$ and $5 \rightarrow 6$ transitions in a very arbitrary fashion, by assuming that at a given impact energy the weaker transitions will have the same relative effect for the $4 \rightarrow 5$ and $5 \rightarrow 6$ transitions as they have for the $3 \rightarrow 4$ transition.

In Fig. 7 we plot the ratios $Q_G(4; 5)/Q_B(4; 5)$ and $Q_G(5; 6)/Q_B(5; 6)$ for Q_B 's including only the main optically allowed transitions in which l changes by $+1$ and also for Q_B 's in which account is also taken of the other transitions. Although the method of including the weaker transitions is very arbitrary, the ratios in Fig. 7 show the same general trends as the previous ratios. At high energies the agreement between the Born and classical approximations gets slowly worse as the principal quantum number n increases, at least for transitions in which n changes by $+1$, but the difference in the Born- and classical-approximation cross sections

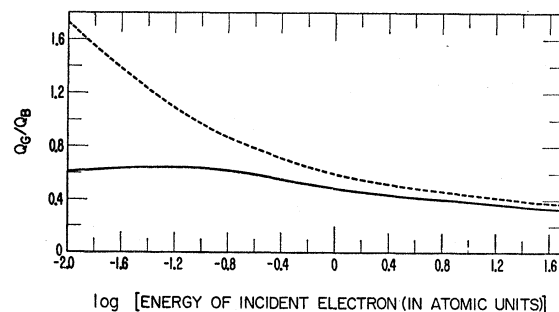


FIG. 8. Ratio of Gryzinski classical-approximation cross section to Bethe-approximation cross section, for excitation from $n=10$ to $n=11$ state of atomic hydrogen by electron impact: — taking into account all transitions in the Bethe-approximation cross section; - - - taking into account only main optically allowed transitions in the Bethe-approximation cross section.

does not increase very quickly as the electron energy increases.

Employing values of $Q_B(10s; 11p)$ and $Q_B(10,9; 11,10)$ calculated at two impact energies McCoyd and Milford¹⁷ have been able to use the Bethe approximation to obtain cross sections for the transitions $10 \rightarrow 11$ for optically allowed transitions in which the azimuthal quantum number l changes by $+1$. In Fig. 8 we plot the ratio $Q_C(10; 11)/Q_B(10; 11)$ for $Q_B(10; 11)$ including only the main optically allowed transitions in which l changes by $+1$, and also for $Q_B(10; 11)$ in which we make allowance for the other transitions in the same manner as for the $4 \rightarrow 5$ and $5 \rightarrow 6$ transitions. Although the method of including the weaker transitions is very arbitrary the ratios in Fig. 8 show the same general trends as the previous ratios.

INDIRECT EXPERIMENTAL INFORMATION

For electron collisions with atomic hydrogen, the only cross sections that have been measured directly are those for transitions from the ground state to the first excited states, and the continuum. No direct experimental data are available on the cross sections for transitions between excited states of hydrogen, however, we can obtain some information about these cross sections from measurements of the populations of the excited states, and the recombination coefficients in a decaying plasma.

If we consider a recombining plasma consisting only of hydrogen atoms, protons and free electrons having a Maxwellian energy distribution of temperature T_e , it can be shown that¹⁸ if $n(c)$ is the number density of free electrons, then the number densities $n(p)$, $n(q) \dots$ of hydrogen atoms in levels with principal quantum numbers p , q, \dots are governed by an infinite set of linear equations which may be written as

$$\begin{aligned} n(p)\{n(c)[K(p,c) + \sum_{q \neq p} K(p,q)] + \sum_{q < p} A(p,q)\} \\ = n(c) \sum_{q \neq p} n(q)K(q,p) + \sum_{q > p} n(q)A(q,p) \\ + n(c)^2\{n(c)K(c,p) + \beta(p)\}, \quad (10) \end{aligned}$$

for all $p > 1$, where $\beta(p)$ is the rate coefficient for radiative recombination, $A(p,q)$ is the Einstein spontaneous emission coefficient, and $K(p,c)$, $K(c,p)$ and $K(p,q)$ are the electronic rate coefficients for ionization, 3-body recombination and excitation or de-excitation, respectively. The K 's are obtained from the electron collision cross sections using

$$K(p,q) = \frac{8\pi}{m_e^{1/2}} \frac{1}{(2\pi kT_e)^{3/2}} \int_{E_p - E_q}^{\infty} Q(p; q) e^{-E/kT_e} E dE. \quad (11)$$

¹⁷ G. C. McCoyd and S. N. Milford, Phys. Rev. **130**, 206 (1963).
¹⁸ D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A267**, 297 (1962); **A270**, 155 (1962).

We also find that the electron recombination coefficient α is given by

$$\begin{aligned} \alpha n^2(c) = -\dot{n}(c) = \dot{n}(1) \\ = n(c) \sum_{q \neq 1} n(q)K(q,1) + \sum_{q > 1} n(q)A(q,1) \\ + n(c)^2\{n(c)K(c,1) + \beta(1)\}. \quad (12) \end{aligned}$$

Bates, Kingston, and McWhirter¹⁸ have indicated how the infinite set of equations can be reduced to a finite set, and have shown that for a wide range of T_e and $n(c)$ the recombination coefficients obtained from Eqs. (10) and (12) will be exact if the A 's, β 's, and K 's are exact. The A 's and β 's have been calculated to high precision; however, even if only the K 's are inaccurate the computed α 's will also be in error.

By considering Eqs. (10) and (12), we see that we would alter both the populations, and also the recombination coefficients by exactly the same amount by either multiplying $n(c)$ by a factor x or by multiplying all the K 's by the same factor x . Hence, if for a given $n(c)$ and T_e we know that all of the K 's are in error by a factor x then we can obtain the correct populations, and recombination coefficient by taking the electron density equal to $xn(c)$. In particular, we find that if collision processes are dominant, the recombination coefficient is proportional to $n(c)$, and so if all of the K 's are in error by a factor of x , then the recombination coefficients will also be in error by a factor of x .

Extensive calculations^{18,19} have been carried out on recombination in a hydrogen plasma employing electron collisional rates calculated using the classical cross sections given by Eqs. (4) and (8). The electron-proton recombination coefficient has also been measured experimentally over a very limited range,²⁰ and in Table I we compare the experimental recombination coefficients with the theoretical recombination coefficients calculated assuming that the Lyman lines are absorbed.¹⁹

Considering the difficulty of measuring the recombination coefficients, and also the possible error in the collisional rate coefficients the agreement between theory and experiment is quite good. We must consider this good agreement as partly fortuitous, since the measured electron temperatures are only accurate to

TABLE I. Comparison of experimental and theoretical recombination coefficients in atomic hydrogen.

Electron density $n(c)$ cm ⁻³	Electron temperature T_e °K	Recombination coefficient α cm ³ sec ⁻¹	
		Experimental	Theoretical
4.7×10^{12}	1300	5.5×10^{-10}	5.0×10^{-10}
7.4×10^{12}	1500	5.8×10^{-10}	3.8×10^{-10}

¹⁹ D. R. Bates and A. E. Kingston, Planetary Space Sci. **11**, 1 (1963).

²⁰ E. Hinnov and J. G. Hirschberg, Phys. Rev. **125**, 795 (1962).

$\pm 25\%$, and since the recombination coefficient varies as $1/T_e^{9/2}$, we would not expect better than a factor of 2 agreement even if the experimental and theoretical recombination coefficients were known exactly. However, the good agreement does suggest that the calculated recombination coefficients are not in error by more than a factor of 2. Since we know that at these temperatures the recombination coefficient is unaffected by the electron collision rates for transitions between the very low or the very high excited states, we can assume that unless there is a large systematic error in the measured electron temperature, the collision rates of the major transitions between the levels $n=4, 5, 6,$ and 7 cannot be in error by more than a factor of 2 at these temperatures.

Since the excited states of helium quickly become hydrogenic as the principal quantum number increases, we would expect that the collisional rates for transitions between excited states in helium will not be greatly different from the rates for the same transitions in hydrogen, and also since the recombination coefficient at low temperatures is almost independent of the collisional rates between very low atomic levels, we would expect that at a given $n(c)$ and T_e the recombination coefficients of hydrogen and helium will not be very different. Relatively extensive laboratory work has been carried out on helium,^{20,21} and in Table II we compare the experimental recombination coefficients for atomic helium with the theoretical recombination coefficients for atomic hydrogen calculated assuming that the Lyman lines are absorbed.¹⁹

The agreement between theory and experiment is quite good; we have 17 tabulated comparisons, and in only one case is there more than a factor of 2 between theory and experiment. Since the agreement between theory and experiment is so good over a wide range of physical conditions, we must conclude that unless there is a large systematic error in the measured temperature, then the theoretical recombination coefficients at low temperatures cannot be in error by more than a factor of 2. In the range covered by these experiments, the theoretical recombination coefficient will have the same error as the theoretical collisional rate coefficients which determine the recombination coefficient. For a given T_e and $n(c)$, it is not easy to say which collisional rate coefficients determine the recombination coefficient, but it is probable that in the range covered by these experiments, the collisional rate coefficients of the main transitions from all of the states from $n=3$ to about $n=10$ help to determine the recombination coefficient at some electron temperature and density, and it is unlikely that these collisional rate coefficients can be in error by a factor of 2 at a temperature at which they are important.

When discussing the population of a state p , it is

²¹ R. W. Motley and A. F. Kuckes, *Proceedings of the Fifth International Conference on Ionic Phenomena, Munich, 1961* (North-Holland Publishing Company, Amsterdam, 1961).

TABLE II. Comparison of experimental and theoretical recombination coefficients in atomic helium.

Electron density $n(c)$ cm^{-3}	Electron temperature T_e °K	Recombination coefficient α $\text{cm}^3\text{sec}^{-1}$	
		Experimental	Theoretical
5.6×10^{13}	3100	4×10^{-11}	7.4×10^{-11}
1.8×10^{13}	2200	1.3×10^{-10}	1.3×10^{-10}
6.2×10^{12}	1500	3.6×10^{-10}	2.8×10^{-10}
2.3×10^{13}	2900	5.3×10^{-11}	5.4×10^{-11}
1.2×10^{13}	2200	1.0×10^{-10}	9.8×10^{-11}
6.6×10^{12}	1700	1.8×10^{-10}	1.8×10^{-10}
3.6×10^{12}	1400	3.3×10^{-10}	2.6×10^{-10}
3.6×10^{13}	2700	7.3×10^{-11}	9.3×10^{-11}
6.2×10^{12}	2400	1.3×10^{-10}	4.4×10^{-11}
3.1×10^{12}	1400	2.7×10^{-10}	2.2×10^{-10}
1.5×10^{12}	1000	5.6×10^{-10}	5.2×10^{-10}
6.5×10^{11}	870	7×10^{-10}	4.8×10^{-10}
1.8×10^{13}	2400	1.3×10^{-10}	9.3×10^{-11}
1.2×10^{13}	2000	1.9×10^{-10}	1.5×10^{-10}
6.1×10^{12}	1500	3.7×10^{-10}	3.0×10^{-10}
3.1×10^{12}	1200	7.3×10^{-10}	4.3×10^{-10}
1.6×10^{12}	760	1.4×10^{-9}	2.0×10^{-9}

more convenient to consider not $n(p)$, but rather the ratio

$$\rho(p) = n(p)/n_B(p), \quad (13)$$

where $n_B(p)$ is the number density of atoms in level p in Saha equilibrium. In Table III we compare some experimental²⁰ and theoretical¹⁹ $\rho(p)$'s.

The agreement between theory and experiment is quite good, and is not inconsistent with the collisional rate coefficients being correct to within a factor of 2. It is also important to note that, since the $\rho(p)$'s vary very rapidly with temperature when they are small,¹⁹ the good agreement between theory and experiment suggests that these measured electron temperatures are not greatly in error.

By considering the energy balance in a magnetically confined plasma, Bates and Kingston²² have shown that if we know the atom temperature and density and the electron density in the plasma, then we can calculate the electron temperature and hence the recombination coefficient. They have reanalyzed the experimental data,²¹ and for several plasmas at different pressures they have compared the theoretical and experimental variation of the recombination coefficient with the electron density. The agreement between theory and experiment is very good, except at low-electron densities, where it is probable that the experimental recombination coefficients are in error, for more recent experiments,²³ at low-electron densities give recombination coefficients which agree with those predicted by theory. It is unfortunate that the recombination coefficients predicted in this way are insensitive to the collisional

²² D. R. Bates and A. E. Kingston, *Proc. Roy. Soc. (London)* **279**, 10 (1964); **279**, 32 (1964).

²³ Yu. M. Aleskovskii and V. L. Granovskii, *Zh. Eksperim. i Teor. Fiz.* **43**, 1253 (1962) [English transl.: *Soviet Phys.—JETP* **16**, 887 (1963)].

TABLE III. Comparison of experimental and theoretical $\rho(p)$'s in helium afterglows.

T_e $n(c)$	1500°K $6.2 \times 10^{13} \text{ cm}^{-3}$ $\rho(p)$		2200°K $1.8 \times 10^{13} \text{ cm}^{-3}$ $\rho(p)$		3100°K $5.6 \times 10^{13} \text{ cm}^{-3}$ $\rho(p)$	
	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical
p						
6	7.5×10^{-1}	7.0×10^{-1}
5	4.1×10^{-1}	4.3×10^{-1}	7.9×10^{-1}	7.1×10^{-1}
4	5.5×10^{-2}	8.8×10^{-2}	3.0×10^{-1}	3.8×10^{-1}	6.3×10^{-1}	6.5×10^{-1}
3	3.0×10^{-4}	5.0×10^{-4}	1.5×10^{-2}	2.0×10^{-2}	1.3×10^{-1}	1.9×10^{-1}

rate coefficients, and give us very little information about the accuracy of the rate coefficients. The reasonable agreement between the theoretical and experimental temperatures does, however, suggest that there is no large systematic error in the measured temperatures.

Bates and Kingston²² show that there is serious disagreement between theory and experiment for one set of recombination coefficients, which were measured in a high-pressure plasma by Motley and Kuckes.²¹ This disagreement is particularly surprising when we consider the reasonable agreement between theory and experiment over the wide range of experimental conditions covered by Tables I and II. It seems probable that this disagreement is caused by a large experimental error in the electron temperatures, for these measured electron temperatures are much larger and increase more rapidly with $n(c)$ than we would expect from either theory or the trend of the measured temperatures at lower pressures.

Because of the experimental error involved in measuring the electron temperature, it is not possible to give precise information about the accuracy of the classical collisional rates; however, unless there is a large systematic error in the measured electron temperature, present experimental evidence from recombination coefficients suggests that the collisional rate coefficients which help determine the recombination coefficients cannot be in error by more than a factor of 2.

CONCLUSION

For ionization from the ground state of atomic hydrogen, the classical cross section of Gryzinski reproduces the experimental cross section to within 25% in an energy range from 0.06 atomic units above the threshold to about 10 atomic units, and to within a factor of 2 from 0.02 atomic units above the threshold to about 400 atomic units. No experimental cross sections have been

measured for ionization from other levels of atomic hydrogen, but a comparison of the classical and Born cross sections for ionization from the $n=2$ states of hydrogen, suggests that at high energies, at least, the classical cross section for ionization from excited levels will not be greatly in error.

For excitation from the ground state of atomic hydrogen to the first excited states, the classical cross section reproduces the experimental cross section to better than a factor of two from the threshold to about 20 atomic units. No experimental cross sections have been measured for other transitions in atomic hydrogen, but a comparison of the classical cross sections with available Born cross sections shows that, although the classical cross sections are always less than Born cross sections, they agree quite well with the Born cross sections over a very large energy range. Only at very high energies is there serious disagreement between the two approximations. This arises because the classical cross sections fall off as $1/E_2$ compared with $\log E_2/E_2$ falloff of the Born cross sections. However, the difference in the two falloffs is so slight that even at 100 atomic units the classical cross section always agrees with the Born cross section to within a factor of 3.

A comparison of experimental recombination coefficients and theoretical recombination coefficients, obtained by using the classical cross sections, suggests that at low energies, the classical cross sections for transitions between low excited levels cannot be in error by more than a factor of 2.

The comparisons made in this paper indicate that classical theory can play a significant role in electron scattering theory, for although we cannot obtain great precision using Gryzinski's classical cross sections, we can obtain much better than order of magnitude estimates for a large number of cross sections with comparatively little effort.