THEORETICAL RATES FOR ELECTRON EXCITATION
OF HIGHLY-EXCITED ATOMS

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SUMMARY

Semi-empirical cross-sections and rates are presented for transitions between
highly-excited levels of hydrogen atoms induced by electron impact.

Our results are obtained from classical and semi-classical theories and are
valid whenever the initial and final quantum numbers satisfy \( n, n' \geq 5 \). The
cross-sections are valid for the energies,

\[
\frac{4}{n^2} < \frac{E}{R} \leq (137)^2,
\]

and are at worst in error by about 15 per cent. The rates are valid for the
temperatures,

\[
10^6/n^2 < T/K \leq 3 \times 10^9,
\]

and are at worst in error by about 20 per cent.

Results are presented as simple analytic formulae, and are closer to the
results of Johnson than to other work.

I. INTRODUCTION AND RESULTS

Cross-sections and rate coefficients obtained by methods based on classical
mechanics and the correspondence principle are amongst the more reliable for the
excitation of highly-excited atoms by electrons and have been used for the interpreta-
tion of the radio recombination lines (e.g. Brocklehurst & Seaton (1)). But they
are widely scattered in the literature (Percival & Richards (2), (3), (4) and Richards
(5)) and are not complete. Gee (6) has carried out detailed numerical calculations
which fill the gaps and we are now able to present satisfactory analytic semi-
empirical formulae for both cross-sections and rate coefficients which agree with
these earlier results in their ranges of validity.

The recommended cross-section for excitation of a hydrogen atom at rest,
with equal probability of being in any one of the states of level \( n \), to a state of level
\( n' \), by an incident electron of energy \( E \) is \( \sigma (n \rightarrow n') \). It is given in terms of the
energy \( E = E/R \) in Rydberg units and the geometric cross-section \( n^4 \pi a_0^2 \), where
\( a_0 \) is the Bohr radius by

\[
\frac{E \sigma (n \rightarrow n')}{n^4 \pi a_0^2} = ADL + FGH,
\]
where
\[ s = n' - n > 0 \]  
\[ A = A(n \rightarrow n') = \frac{8}{3s} \left( \frac{n'}{sn} \right)^3 (0.184 - 0.04/s^{2/3}) \left( 1 - \frac{0.2s}{nn'} \right)^{1+2s} \]  
\[ D = \exp \left\{ -1/(nn'E^2) \right\} \]  
\[ L(E) = \ln \left[ \frac{1+0.53E^2nn'}{1+0.4E} \right] \]  
\[ F = [1-0.3sD/(nn')]^{1+2s} \]  
\[ G = 0.5(En^2/n')^3 \]  
\[ H = [C_2(x_-, y) - C_2(x_+, y)] \]  
\[ C_2(x, y) = \frac{x^2 \ln (1+2x/3)}{2y+3x/2} \]  
\[ x_\pm = 2/[En^2(\sqrt{2-n^2/n'^2} \pm 1)] \]  
\[ y = 1/[1-D \ln (18s)/(4s)] \]  
The incident electron energies \( E \) are limited by
\[ 4/n^2 < E \ll 137^2, \]
and the quantum numbers by
\[ s = n' - n > 0 \text{ (excitation)} \]  
\[ n', n \geq 5. \]  

For incident electrons the error in the cross-section is unlikely to exceed 15 per cent provided these conditions are satisfied, and the various checks made suggest that a typical error is 6 per cent.

For de-excitation the detailed balance relation
\[ E'n^2\sigma(n' \rightarrow n) = En^2\sigma(n \rightarrow n') \]  
should be used.

The same result is valid for neutral atoms other than hydrogen, with an additional error which is probably negligible when \( n \) and \( n' \) are both more than four times the highest principal quantum number of all electrons in the ionic core. It is assumed that only one electron is highly excited.

The rate coefficient \( \alpha(n, n') \), in cm\(^3\) s\(^{-1}\), for the same transition due to an electron gas of temperature \( T \), in Kelvins, using the above cross-section is found to be given to within 10 per cent by,
\[ \alpha(n, n') = n^4(J_1+J_2+J_3)/T^{3/2} \text{ cm}^3 \text{ s}^{-1} \]  
where
\[ J_1 = \frac{4}{3} A L \left( \frac{0.85}{\beta} \right) \left( \frac{1}{\beta - \frac{1}{\beta+\beta_1}} \right) \]  
\[ \beta = 10^5 \times 1.58/T \]  
\[ \beta_1 = 1.4(nn')^{1/2} \]

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Theoretical rates for electron excitation

\[ J_2 = \frac{16}{9} \frac{F_1 n'}{y_1} \frac{(\sqrt{2 - n'^2/n''^2} + 1)^3}{(n' + n'')^3 s^3} \frac{\exp(-\beta|\beta_1)}{\beta} \]  
\[ s = n' - n > 0 \]

\[ F_1 = \left( 1 - \frac{0.35}{nn'} \right)^{1+2s} \]

\[ y_1 = (1 - \ln(18s)/4s)^{-1} \]

\[ J_3 = \frac{1}{4} \left( \frac{n''}{n'} \right)^3 \frac{J_4(x)}{(\beta + \beta_1)} \ln \left( 1 + 0.5\beta \xi \right) \]

\[ \xi = 2/\left[ n''(\sqrt{2 - n'^2/n''^2} - 1) \right] \]

\[ x = 0.75 \xi (\beta + \beta_1) \]

\[ J_4(x) = \frac{2}{x^2 + x(1 + e^{-x})} \]

where \( A \) and \( L(x) \) are defined in equations (3) and (5).

This rate coefficient is also to be used for \( n, n' \geq 5 \) and is valid for excitation; the de-excitation rate should be obtained from the detailed balance relation:

\[ \alpha(n', n) = \left( \frac{n}{n'} \right)^2 \exp\{-\beta(E_n - E_n')\} \alpha(n, n'). \]  

The above formula is valid for the ranges of temperatures,

\[ \frac{10^6}{n'^2} < T/K \leq 3 \times 10^9, \]

and the error of \( \alpha \) in this range is unlikely to exceed 20 per cent, the worst errors being at low temperatures.

Computer programs for the cross-sections and rates may be checked against the test values given in Tables 1 and 2.

**Table I**

**Numerical values of the cross-section (1) for** \( n = 100, n' = 101, 102, 103 \) **and** \( n = 5, n' = 7 \) **for various energies**

| \(|E/R| (n = 100)\) | 0.004 | 0.4 | 10 |
|------------------|------|----|----|
| \(E_0(n \rightarrow n+1)\) \(|Rn^4\pi\alpha_0^2\) | 1.241 | 2.983 | 4.962 |
| \(E_0(n \rightarrow n+2)\) \(|Rn^4\pi\alpha_0^2\) | 3.473 | 2.813 | 4.229 |
| \(E_0(n \rightarrow n+3)\) \(|Rn^4\pi\alpha_0^2\) | 1.529 | 7.463 | 1.046 |
| \(E/R (n = 5)\) | 0.2 | 0.6 | 2 |
| \(E_0(5 \rightarrow 7)\) \(|Rn^4\pi\alpha_0^2\) | 1.020 | 2.454 | 4.159 |
TABLE II

Numerical values of the rate (16) for \( n = 100, n' = 101, 102, 103, \) and \( n = 5, n' = 7, \) for various temperatures. The rates are expressed in \( \text{cm}^3 \text{s}^{-1} \)

<table>
<thead>
<tr>
<th>( T/K ) (( n = 100 ))</th>
<th>( 10^3 )</th>
<th>( 10^4 )</th>
<th>( 10^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha(n, n+1) )</td>
<td>9.159 (1)</td>
<td>1.126 (1)</td>
<td>3.924</td>
</tr>
<tr>
<td>( \alpha(n, n+2) )</td>
<td>3.305 (1)</td>
<td>1.337</td>
<td>3.381 (1)</td>
</tr>
<tr>
<td>( \alpha(n, n+3) )</td>
<td>1.741 (1)</td>
<td>3.992 (1)</td>
<td>8.432 (2)</td>
</tr>
<tr>
<td>( T/K ) (( n = 5 ))</td>
<td>( 10^5 )</td>
<td>( 10^6 )</td>
<td>( 10^7 )</td>
</tr>
<tr>
<td>( \alpha(5, 7) )</td>
<td>4.161 (6)</td>
<td>2.773 (6)</td>
<td>1.193 (6)</td>
</tr>
</tbody>
</table>

2. DISCUSSION

The cross-section given in Section 1 is derived from calculations based upon the strong coupling correspondence principle (Percival & Richards (7)). This theory has two fundamental assumptions; first, that strongly-coupled energy levels are approximately equally spaced; second, that the matrix elements of the interaction are well represented by Heisenberg’s form of the correspondence principle.

The strong coupling correspondence principle may be trusted when \( |n-n'|/n \) is small for the following reasons:

R1 Comparisons of exact matrix elements with those calculated using Heisenberg’s form of the correspondence principle show that the error in the latter decreases with \( |\Delta n/n| \) and is about 5 per cent when \( |\Delta n/n| = 0.2 \) (Naccache (8); Richards (5));

R2 the equally-spaced energy level assumption leads to errors of at most 150\( |\Delta n/n| \) per cent;

R3 for an exactly soluble harmonic model of vibrational excitation of molecules the SCCP is in error by about 10 per cent for a \( \nu = 5 \rightarrow 6 \) transition (Clark & Dickinson (9)), and for the rotational excitation of diatomic molecules the SCCP agrees with close-coupling calculations to within 10 per cent for a \( j = 6 \rightarrow 8 \) transition (Dickinson & Richards (10));

R4 for \( 1 \leq |\Delta n| \leq n \) the SCCP agrees with perturbation applied to classical mechanics; this can be shown directly (Percival & Richards (11)) or by numerical computation.

The SCCP applied to electron–hydrogen excitation can be evaluated in closed form only in particular energy regions, where subsidiary approximations are valid (Percival & Richards (3), (4)). For \( \Delta n = 1, 2, 3 \) Gee (6) has evaluated the SCCP numerically and obtained cross-sections without these subsidiary approximations. These numerical results have been checked as follows:

C1 against analytic forms obtained from the SCCP in the energy regions,

\[ \frac{4}{n^2} \ll E \ll \frac{1}{n} \]
\[ \frac{1}{n} \ll E \ll 1 \]

(Percival & Richards (3), (4); Richards (5));

C2 against the Bethe–Born approximation at the high energy region,

\[ E > 1 \]

(Richards (5));
C₃ against classical calculations in the energy region

\[ \frac{4}{n^2} \ll E < \frac{1}{n}, \]

(Banks, Percival & Richards (12));

C₄ against a quantal approximation assuming equally spaced energy levels for \( \Delta n = 1 \) (Presnyakov & Urnov (13), Presnyakov (14));

C₅ against the Seaton–Saraph quantal perturbation theory, adjusted to preserve unitarity, for \( \Delta n = 1 \) (Saraph (15)).

For large \( n, n' \) and \( |\Delta n| \) quantal effects are small except at very high energies, so that pure classical mechanics can be used. For \( |\Delta n| \ll n \) and \( E > \frac{4}{n^2} \) classical perturbation theory is a good approximation to classical mechanics and because of R₄, the analytic forms referred to in C₁ and C₂ are satisfactory for \( 3 < |\Delta n| \ll n \).

For \( \Delta n \) comparable to \( n \) the combined classical theory (Percival (16)) can be used. This combines classical perturbation theory and the binary encounter theory (see Burgess & Percival (17), Banks (18)). It must be emphasized that binary encounter theory on its own is quite inadequate, particularly for \( |\Delta n| = 1 \), even when combined with quantal approximations. This is because adiabatic effects are important for distant collisions. This has been shown explicitly by comparing the cross-sections of Banks (19), obtained by direct numerical integration of the classical equations of motion, with the results of the combined theory. These comparisons show that for \( E > 4/n^2 \) the combined theory is within 20 per cent of the exact classical cross-section.

For low energies \( 4/n^2 < E < 2/n \), the SCCP shows that quantal effects are small for all \( |\Delta n| \), even \( |\Delta n| = 1 \), so that classical mechanics can be used for all \( |\Delta n| \). Consequently the combined theory can be used (Banks et al. (12)).

![Fig. 1. Bethe plot of \( E_0 \) against \( \ln E \) for the 100 → 100 transition. The graphs shown are: (1) Present semi-empirical results, equation (1); (2) Semi-empirical results of Johnson (21); (3) Equally spaced energy level approximation (Presnyakov (14)); (4) Combined theory (Banks, Percival & Richards (12)); (5) Analytic approximation to SCCP (Percival & Richards (3), (4); Richards (5)); (6) Born Approximation (Richards (5)). The crosses are the results of Gee (6) obtained by evaluating the SCCP numerically.](https://academic.oup.com/mnras/article-abstract/175/1/209/2893593)
Fig. 2. Bethe plot of $E\sigma$ against $\ln E$ for the $100 \rightarrow 103$ transitions. The labels to the graphs are as for Fig. 1; results for the equally-spaced energy level approximation (Presnyakov (i4)) are not available for this transition. On this graph curves (4) and (1) are indistinguishable wherever the combined theory is valid.

In Figs 1 and 2 we have drawn the Bethe plots of $E\sigma$ against $\ln E$ for the $100 \rightarrow 101$ and $100 \rightarrow 103$ transitions. In these figures we have shown, where available, the results mentioned in C1–C5; we see that the agreement is satisfactory, suggesting that one can be confident in the estimated errors.

Semi-empirical cross-sections and rates for $n \rightarrow n'$ transitions are available in the literature (Golden & Sampson (20) and Johnson (21)). These results apply to all $n, n'$, but for large quantum numbers do not take account of all of the above-mentioned theories.

Johnson's cross-sections are adequate at intermediate energies, $1/n < E < 1$, but underestimate the cross-section by about 20% at higher and lower energies for $s = 1$, and by factors of 2 and 3 or more for $s = 2$ and 3 and for lower energies. Similarly for large quantum numbers his rates are too low for $s = 1$, the worst errors being at low temperatures; for $s = 3$ they are a factor 7 too small at low ($10^2$ K, $n = 100$) temperatures.

The cross-sections of Golden & Sampson (20) are everywhere too large, and at low energies by an order of magnitude, so that their rates will also be too large, especially at low temperatures.

The methods used here are described fully in the review (11); similar results for protons have been provided by Lodge et al. (22), but these include transitions between all quantum numbers.

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