

COMPUTATION OF THE EFFECTIVE CROSS SECTION FOR THE  
RECOMBINATION OF ELECTRONS WITH HYDROGEN IONS

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ABSTRACT

The quantum-mechanical computation of the cross-section for combination of electrons with a positive point charge has been carried out in polar coordinates. This gives the fraction of the recombination to a final state of total quantum number  $n$  arising from recombination to the substates of different  $l$  values, making possible a comparison of the results with the experimental recombination intensities for alkali vapors to which the theory applies approximately.

**A**N ELECTRON passing by a hydrogen ion with a velocity equivalent to  $V$  volts can undergo a spontaneous transition to one of the states of a hydrogen atom. The probability with which such a process can occur has been treated by Kramers<sup>1</sup> and by Eddington<sup>2</sup> by the methods of the old quantum theory and the correspondence principle. Oppenheimer<sup>3</sup> gives in his treatment of the motion of electrons in a Coulomb field the corresponding wave-mechanical expressions. The following paper gives certain additional calculations and numerical expressions for the probability of capture of electrons.

We recall the definition of the effective cross section of recombination: The decrease of the number  $N_+$  ions per  $\text{cm}^3$  is expressed by

$$\frac{dN_+}{dt} = -\alpha(v) \cdot N_+ \cdot N_- = -q(v) \cdot N_+ \cdot N_-'$$
 (1)

$N_-$  is the number of electrons per  $\text{cm}^3$  having a velocity  $v$  relative to the ions.  $N_-'$  =  $v \cdot N_-$  is the intensity of a stream of  $N_-'$  electrons per  $\text{cm}^2$  per sec.  $\alpha(v)$  is called the coefficient of recombination and  $q(v)$  the effective cross section of recombination.

To find the probability of a transition of such an electron to one of the discrete states with negative energy one computes first the matrix element of the electric moment associated with the transition under consideration. As wave function in the initial state we require a solution  $\psi_k(r, \cos \theta, \phi)$  of the wave equation in the force field of an ion of charge  $Z \cdot e$ , which becomes a plane wave at infinite distance, representing a stream along the  $x$  axis of  $N_-'$  electrons per  $\text{cm}^2$  per sec.:

$$\lim_{r \rightarrow \infty} \psi_k = C \cdot \left\{ e^{i(Z/k a_0)x} + \frac{f(\cos \theta)}{r} \cdot e^{i(Z/k a_0)r} \right\}$$
 (2)

<sup>1</sup> Kramers, Phil. Mag. **46**, 836 (1923).

<sup>2</sup> Eddington, Internal Constitution of Stars, Cambridge (1926).

<sup>3</sup> Oppenheimer, Zeits. f. Physik **55**, 725 (1929).

and

$$\lim C \cdot \frac{h}{2\pi mc} \cdot \text{imag} (\bar{\psi}_k \text{grad } \psi_k) = N_{-}'$$

$$k^2 = \frac{R_v Z^2}{V} \quad (3)$$

$V$  is the energy of the electrons and  $R_v$  is the ionization energy of a hydrogen atom in volts.  $a_0$  is the radius of the first Bohr orbit in hydrogen. In the final state we take the known solution of the wave equation in polar coordinates  $\psi_{n,l,m}(r, \cos \theta, \phi)$ . Then we compute the matrix elements in the complex rectangular coordinates

$$\left. \begin{aligned} x &= r \cos \theta; & X^2(k, nlm) \\ u &= r \sin \theta \cdot e^{i\phi}; & U^2(k, nlm) \\ v &= r \sin \theta \cdot e^{-i\phi}; & V^2(k, nlm) \end{aligned} \right\} = \int \frac{x}{u} \bar{\psi}_k \psi_{nlm} d\tau_x \int \frac{x}{v} \bar{\psi}_k \psi_{nlm} d\tau \quad (4)$$

$$d\tau = \rho^2 \sin \theta d\rho d\theta d\phi$$

The relation between the matrix element  $X(k, nlm)$  and the number of transitions per sec  $q_x(k, nlm)$   $N_{-}'$  giving light of frequency  $\nu_n$  polarized in the  $x$  direction is

$$q_x(k, nlm) \cdot N_{-}' = \frac{64\pi^4}{3} \cdot \left(\frac{\nu_n}{c}\right)^3 \frac{\{\epsilon \cdot X(k, nlm)\}^2}{h} \quad (5)$$

Similar expressions hold for  $u$  and  $v$ . The total cross section for any given state  $n, l$  is

$$\begin{aligned} q(k, nl) &= q_x(k, nl0) + q_u(k, nl-1) + q_v(k, nl+1) \\ &= q_x + 2q_u. \end{aligned}$$

Oppenheimer<sup>4</sup> computed by this method the  $q(k, 10)$  and showed that it is asymptotically, for small velocities of the electron, proportional to  $Z^2/V$ . In a later paper he treated the problem for the excited states in parabolical coordinates<sup>5</sup> using a wave function by Gordon<sup>5</sup> and Temple,<sup>6</sup> which satisfies Eq. (2). This method gives the expression of the total cross section summed over all  $l$ 's with the same  $n$ . The writers made use of the wave function used by Mott<sup>7</sup> for the scattering of  $\alpha$ -particles by nuclei in order to obtain the individual  $q(nl)$ 's. Mott's formula is in this notation:

$$\psi_k = i \cdot \left(\frac{N_{-}' \cdot h}{2\pi Z \epsilon^2}\right)^{1/2} \cdot \frac{k^{1/2} \cdot e^{(k\pi/2) + ik \log \rho}}{\sinh \pi k} \quad (6)$$

$$\sum_{\lambda=0}^{\lambda=\infty} \frac{i^\lambda \cdot (\lambda + i) \cdot P_\lambda(\cos \theta)}{\Gamma(\lambda + 1 + ik)} \cdot \rho^\lambda \cdot \oint e^{\rho z} \cdot \left(z - \frac{i}{2}\right)^{\lambda-k} \cdot \left(z + \frac{i}{2}\right)^{\lambda+ik} \cdot dz$$

<sup>4</sup> Oppenheimer, Phys. Rev. **31**, 349 (1928).

<sup>5</sup> Gordon, Zeits. f. Physik **48**, 180 (1928).

<sup>6</sup> Temple, Proc. Roy. Soc. **121A**, 673 (1928).

<sup>7</sup> Mott, Proc. Roy. Soc. **118A**, 542 (1928).

$\rho = (2Z/ka_0) \cdot r$  and the integral is to be taken along a single contour around  $z = \pm i/2$ . The asymptotic expansion for  $r = \infty$  satisfies Eq. (2), having however in the first exponent an additional slowly varying logarithmic term (see Oppenheimer<sup>4</sup> and Mott<sup>7</sup>). The evaluation of the integrals in Eq. (4) is done following a method given by Fues<sup>8</sup> and used for similar problems by Oppenheimer.<sup>9</sup> At one step one is left with an integral

$$J(k) = \oint \frac{\left(z - \frac{i}{2}\right)^{\lambda - ik} \left(z + \frac{i}{2}\right)^{\lambda + ik}}{\left(-z + \frac{k}{2n}\right)^{l + \lambda + s + 4}} dz$$

to be taken around  $z = k/2n$ . Its evaluation leads to the formulas 7a and 7b. for  $q_x(nl)$  and  $q_u(nl)$ . 7c and 7d are the formulas taken from Oppenheimer's paper.<sup>3</sup>

Abbreviating:  $R$  for the Rydberg constant in frequency units

$$Q(\lambda, \alpha) = \sum_{p=0}^{p=\alpha} \binom{\lambda - ik}{p} \binom{\lambda + ik}{\alpha - p} \left(\frac{n + ik}{-n + ik}\right)^{(\alpha/2) - p},$$

$$S(k, l) = \frac{k^{2l+6}}{k^2(k^2 - 1^2)(k^2 - 2^2) \cdots (k^2 - (l-1)^2)},$$

$$T(k) = \frac{e^{\pi k - 4k \tan^{-1}(n/k)}}{\sinh \pi k},$$

$$D = \frac{32 \cdot \pi^5 \cdot a_0^5 R^2}{3 \cdot Z^2 c^2}$$

$$F(\alpha \beta \gamma) = 1 + \frac{\alpha \cdot \beta}{1 \cdot \gamma} \cdot z + \frac{\alpha(\alpha + 1) \cdot \beta(\beta + 1)}{1 \cdot 2 \cdot \gamma(\gamma + 1)} z^2 + \cdots$$

$$q_x(n, l) = D \cdot \frac{\nu_n}{c} \cdot \frac{(n - l - 1)!}{(2l + 1) \cdot (n + l)! n^{2l+4}} \cdot S(k, l) \cdot T(k) \cdot \left\{ \sum_{s=0}^{s=n-l-1} \left(\frac{2}{n}\right)^s \cdot \left(\frac{R \cdot Z^2}{\nu_n}\right)^{s/2} \cdot \frac{(2l + 2 + s)!}{s!} \binom{n + l}{n - l - 1 - s} \right. \\ \cdot \left[ \frac{4l}{k^2} \frac{RZ^2}{\nu_n} \cdot Q(l - 1, 2l + 2 + s) - \frac{(2l + s + 3)(2l + s + 4)(l + 1)}{(l + ik)(l + 1 + ik)} \right. \\ \left. \left. \cdot Q(l + 1, 2l + 4 + s) \right] \right\}^2 \quad (7a)$$

<sup>8</sup> Fues, Ann. d. Physik **81**, 422 (1926).

<sup>9</sup> Oppenheimer, Zeits. f. Physik **41**, 268 (1927).

$$q_u(n, l) = q_v(n, l) = D \cdot \frac{\nu_n}{c} \cdot \frac{(l+1)!(n-l-1)!}{(l-1)!(2l+1) \cdot (n+l)!n^{2l+4}} S(k, l) \cdot T(k) \cdot \left\{ \sum_{s=0}^{s=n-l-1} \left(\frac{2}{n}\right)^s \left(\frac{R \cdot Z^2}{\nu_n}\right)^{s/2} \cdot \frac{(2l+2+s)!}{s!} \binom{n+l}{n-l-1-s} \right\} \quad (7b)$$

$$\left[ \frac{4}{k^2} \cdot \frac{RZ^2}{\nu_n} O(l-1, 2l+2+s) + \frac{(2l+s+3)(2l+s+4)}{(l+ik)(l+1+ik)} \cdot Q(l+1, 2l+4+s) \right]$$

$$q_z(n) = \sum_{l=0}^{l=n-1} q_x(n, l) = 64D \cdot \frac{\nu_n}{c} \cdot \frac{k^6}{(n^2+k^2)^2} \cdot T(k) \cdot \sum_{s=0}^{s=n-1} \left| (n-s-1) \cdot F\left(-ik, 2+s-n, 1, \frac{-4ink}{(n+ik)^2}\right) - \left(n-s-1 - \frac{2ink}{n+ik}\right) F\left(-ik, 1+s-n, 1, \frac{-4ink}{(n+ik)^2}\right) \right|^2 \quad (7c)$$

$$q_u(n) = q_v(n) = \sum_{n=0}^{n=l-1} q_u(nl) = 64D \cdot \frac{\nu_n}{c} \cdot \frac{(4n)^2 k^{10}}{(n^2+k^2)^4} \cdot T(k). \quad (7d)$$

$$\sum_{s=0}^{s=n-2} (s+1)(n-s-1) \left| F\left(1-ik, 2+s-n, 2, \frac{-4ink}{(n+ik)^2}\right) \right|^2.$$

For electrons whose kinetic energy is small compared with the term value of the final state, we substitute  $w=z/k$  in the integral  $J(k)$  and obtain

$$J(k) = k^{\lambda-l-s-3} \oint \frac{w^{2\lambda} \cdot e^{-1/w} \cdot dw}{\left(-w + \frac{1}{2n}\right)^{l+\lambda+s+4}}.$$

This integral is to be taken around the point  $w=1/2n$  and is independent of  $k$ . Instead of formulas 7a and 7b be obtain 8a and 8b. 8c and 8d are the corresponding asymptotic expressions for  $k=\infty$  of Eq. (7c) and (7d). For all states we obtain  $q=A \cdot 10^{-20} \cdot Z^2/V$  for small  $V$ . Since in experiments on recombination the electron velocities are usually small, these formulas are sufficient in most cases.

Abbreviating

$$K(t, \lambda) = \sum_{\alpha=0}^{\alpha=t} \binom{t}{\alpha} \binom{2\lambda}{\alpha} \frac{\alpha!}{(2n)^\alpha} \cdot \sum_{\beta=0}^{\beta=t-\alpha-1} \binom{t-\alpha}{\beta} \binom{t-\alpha-1}{\beta} \frac{\beta!}{(-2n)^\beta}$$

$$E = \frac{4^7 \cdot \pi^5}{3c^3} \cdot a_0^5 R^3 R_v = 1.24 \times 10^{-19} \text{ cm}^2 \text{ volt}$$

$$M(t, \lambda) = \sum_{\alpha=0}^{\alpha=t} \binom{t}{\alpha} \frac{(-4n)^\alpha}{(\alpha+\lambda)!}$$

we obtain

$$q_x(nl) \sim \frac{E \cdot Z^2}{V} \cdot \frac{(n-l-1)! 16^l \cdot n^{2l+2}}{(2l+1) \cdot (n+l)! e^{4n}} \quad (8a)$$

$$\left\{ \sum_{s=0}^{s=n-l-1} \frac{(4n)^s}{s!} \binom{n+l}{n-l-s-1} [l \cdot R(2l+s+2, l-1) + (l+1) \cdot R(2l+s+4, l+1)] \right\}^2$$

$$q_u(nl) = q_v(nl) \sim \frac{EZ^2}{V} \cdot \frac{l(l+1) \cdot (n-l-1)! 16^l \cdot n^{2l+}}{(2l+1) \cdot (n+l)! e^{4n}} \cdot \left\{ \sum_{s=0}^{s=n-l-1} \frac{(4n)^s}{s!} \binom{n+l}{n-l-s-1} [K(2l+s+2, l-1) - K(2l+s+4, l+1)] \right\}^2 \quad (8b)$$

$$q_x(n) = \sum_{l=0}^{l=n-1} q_x(n, l) \sim \frac{EZ^2}{V} \cdot \frac{1}{4n^2 \cdot e^{4n}} \cdot \sum_{s=0}^{s=n-1} \{ (n-s-1) \cdot M(n-s-2, 0) + (n+s+1) \cdot M(n-s-1, 0) \}^2 \quad (8c)$$

$$q_u(n) = q_v(n) = \sum_{l=0}^{l=n-1} q_u(n, l) \sim \frac{E \cdot Z^2}{V} \cdot \frac{4}{e^{4n}} \cdot \sum_{s=0}^{s=n-2} (s+1) \cdot (n-s-1) \cdot M(n-s-2, 1)^2. \quad (8d)$$

Empirical formulas are generally written in a form

$$q(n, l) = \text{const} \times \frac{1}{V \cdot \nu_{nl}^s}, \quad (9)$$

where  $\nu_{nl}$  is the frequency of the emitted light, given for hydrogen by

$$\nu_{nl} = \nu_n = RZ^2 \left( \frac{1}{n^2} + \frac{1}{k^2} \right). \quad (10)$$

$s=2$  for the  $2P$  band of Cs I (see report on recombination by Mohler<sup>10</sup>). Evaluating Eq. (8) for some of the lower states and abbreviating the algebraic expressions of  $k$  in frequencies according to Eq. (10) one obtains formulas 11, where

$$B = \frac{2 \cdot 4^6 \cdot \pi^5}{3} \cdot \frac{a_0 \cdot R^5 \cdot R_p \cdot Z^6}{c^3}.$$

<sup>10</sup> Mohler, Phys. Rev. Supplement 1, 216 (1929).

$$\left\{ \begin{array}{l}
 1s: q = q_x(10) = B \cdot T(k) \cdot \frac{1}{V \cdot \nu_1^2} \\
 2s: q = q_x(20) = \frac{B \cdot T(k)}{8} \cdot \frac{\nu_1}{V \cdot \nu_2^3} \\
 3s: q = q_x(30) = \frac{B \cdot T(k)}{27} \cdot \frac{\nu_1 \cdot \nu_1^2}{V \cdot \nu_3^5}; i = \left(\frac{27}{7}\right)^{1/2} \sim 2 \\
 2p: q = q_x(21) + 2q_u(21) = B \cdot T(k) \cdot \frac{RZ^2 \left( \frac{1}{36} \frac{\nu_j}{\nu_2} + \frac{1}{8} \right)}{\nu_2^3}; \\
 \qquad \qquad \qquad j = \frac{2}{3}
 \end{array} \right. \quad (11)$$

This shows that the empirical way of writing the formulas involves frequency terms without physical meaning. The general form of the expressions (11) however is similar to Eq. (9), as  $T$  varies only slowly with  $k$ . None of these functions shows any maximum point corresponding to the results of Davis and Barnes experiment,<sup>11</sup> nor do any of the curves for higher states.

From formulas 8a and 8b the constants  $A(nl)$  were computed for some of the lower states. The complexity of the sums increases greatly with larger  $n$ 's. Fig. 1 compares the exact and the asymptotic expressions for the 1s

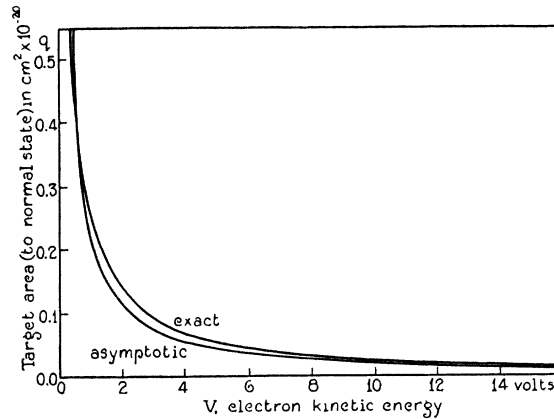


Fig. 1. Exact and asymptotic values of  $q$  for recombination to the 1s state.

state. Table I and Fig. 2 give the values of  $A(n)$  for 1s, 2s, 2p, 3s, . . . , to 5s. The values of  $\sum_l A(nl)$  is given in the last column of Table I and plotted as black dots in Fig. 2. The  $\sum_l A(nl)$  have been computed by summing over the  $A(nl)$  from Eq. (8a) and (8b), and to check it, also directly by Eq. (8c) and (8d). (Oppenheimer's formulas.)

<sup>11</sup> Davis and Barnes, Phys. Rev. **34**, 152 (1929); Barnes, Phys. Rev. **34**, 1224 (1929); **35**, 718 (1930).

TABLE I. Values for  $A(nl)$  and  $A(n) = \sum_{l=0}^{n-1} A(nl)$  in formula  $q(nl) = A(nl) \cdot 10^{-20} \cdot Z^2/V \text{ cm}^2$ .

terms	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	
<i>n</i>	$A(n0)$	$A(n1)$	$A(n2)$	$A(n3)$	$A(n)$
1	.227				.227
2	.0335	.109			.143
3	.0114	.0403	.0520		.104
4	.0053	.0190	.0318	.0254	.0814
5	.0030				

For a comparison of the absolute magnitude of the  $q$ 's with the experimental values obtained from recombination spectra, we compare in Table II the values as given by Mohler<sup>10</sup> for the  $1S$ ,  $2P$  and  $3D$  states of caesium for  $V=0.2$  volts with the states  $2s$ ,  $2p$ ,  $3d$  of hydrogen. There is little justification for picking these hydrogen states as comparison, except that their

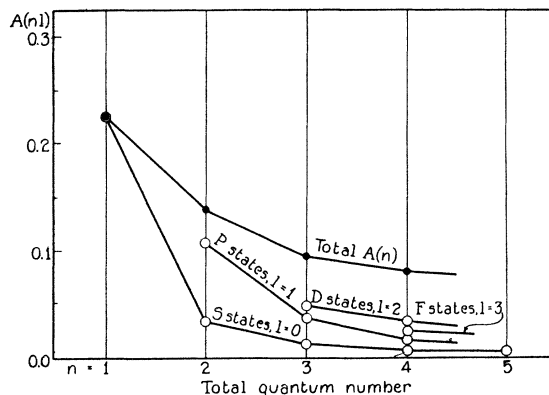


Fig. 2. Values of  $A$  in the formula  $q = A \times 10^{-20} Z^2/V$  for recombination to various states.

*effective* quantum numbers most nearly correspond. For the  $P$  and  $D$  state we have a satisfactory agreement. The discrepancy of the  $1S$  value is to be expected, since it is a highly penetrating orbit, and therefore would differ from a hydrogen-like behavior in a much greater degree than the  $P$  and  $D$  states. A similar disagreement is pointed out by Mohler<sup>10</sup> in comparing the continuous absorption of these states with the theoretical computations for

TABLE II. Comparison of values of  $q$  for  $V=0.2$  volts between caesium (experimental data) and hydrogen (theoretical data).

Cs		H	
term	$q$	term	$q$
$1S$	$0.015 \times 10^{-21} \text{ cm}^2$	$2s$	$1.7 \times 10^{-21} \text{ cm}^2$
$2P$	$6.0 \times 10^{-21} \text{ cm}^2$	$2p$	$5.5 \times 10^{-21} \text{ cm}^2$
$3D$	$6.0 \times 10^{-21} \text{ cm}^2$	$3d$	$2.6 \times 10^{-21} \text{ cm}^2$

the same hydrogen states by Oppenheimer.<sup>9</sup> If one takes the states  $6s$ ,  $6p$  and  $5d$  of hydrogen, whose *true* quantum numbers are the same as for the series electron of Cs in the considered states, the correspondence is improved with respect to the  $S$ -state (it being wrong by a factor 10 instead of 100) but the agreement for the  $P$ - and  $D$ -states is worse by a factor of about 10. This comparison is not given in Table II, because these higher terms have not been computed but only roughly extrapolated

It can not be expected to have any better agreement than this, since the wave function of the series electron in Cs is considerably different from that of any state in hydrogen. It is interesting to see that the best agreement for the  $P$  and  $D$  states is obtained by comparison with hydrogen states of the same effective quantum number.

Attempts to find an expression for the total target area

$$q = \frac{\sum_{n,l} A(nl) \times 10^{-20} \times Z^2}{V}$$

have not been successful.

The experiments by Davis and Barnes<sup>11</sup> can not be explained through spontaneous recombination of the electrons and  $\alpha$ -particles and must therefore be due to some other mechanism.