MARCH, 1928 *PHYSICAL REVIEW* *VOLUME 31*

ON THE QUANTUM THEORY OF THE CAPTURE OF ELECTRONS

BY J. R. OPPENHEIMER*

ABSTRACT

In Section 1 the method of a previous paper[1] is applied to find the rate at which α particles capture electrons from atoms. The mean free path for capture varies roughly with the sixth power of the velocity of the α particle, and in good agreement with Rutherford's experiments.[3] The value of the mean free path is computed for capture in air, and agrees with the experimental value.

In Section 2 the probability of radiative recombination of electrons and protons is computed. The cross section for recombination becomes infinite for small relative velocities with the inverse square of the velocity; for high velocities it is given by $10^{-18}W^{-5/2}$, where W is the energy in volts of the incident electrons.

IN THE collision of an α-particle with an atom, one of the atomic electrons will occasionally be captured by the passing particle. In this capture the electron jumps from one bound orbit to another; and the energy difference in the binding is taken up in the relative translational energy of the two heavy particles. The initial and final states have the same energy; but the wave functions representing them are not strictly orthogonal, since it is possible, though not very likely, that the electron, although "bound" to the atom, be found in the immediate neighborhood of the α-particle. If one writes out the scalar product of the initial and final wave functions, e.g., for hydrogen,

$$\epsilon = \int d\tau \psi_{\mathrm{H}} \psi_{\mathrm{He}^{++}} \psi_{\mathrm{H}^+}{}^* \psi^*{}_{\mathrm{He}^+} \tag{1}$$

where the integral is to be taken over the configuration space, one sees that, for large relative velocities, this becomes very small.[2] The capture thus corresponds to a transition between almost orthogonal states of the same energy, and may be treated by the methods of ref. 1. For this one needs the form of the wave function in the initial state; we shall carry through the calculation for a hydrogen-like atom with arbitrary nuclear charge, and shall consider, subsequently, how, and with what error, this may be applied.

This capture of electrons has been studied both experimentally[3] and theoretically.[4] Our theory will give directly the mean free path for capture as a function of the velocity of the α-particle and the constants of the atom. This has been observed for a considerable range of velocities in air, and will give the most direct check on the theory.

Fowler's theory[4] of the capture is based on considerations radically different from those of this paper. Fowler observes that the loss of the captured

---

* National Research Fellow.

[1] J. R. Oppenheimer, Phys. Rev., Jan. 1928, Section 3. Referred to as ref. 1.

[2] For this the wave functions must be normalized to dE/h. Cf. ref. 1, Eq. 3.

[3] E. Rutherford, Phil. Mag. **47**, 277, 1924. Hdb. d. Physik, xxiv, 177 (1927).

[4] R. H. Fowler, Phil Mag. **47**, 269, and 416 (1924).

electron of the α-particle may be regarded as a process of ionization by collision with one of the atomic electrons. (We shall adduce evidence that the process of loss is not precisely of this kind, but that is here irrelevant). The reverse process to this is a three body collision: two electrons strike the α-particle; one of them is captured, and the other carries off the excess energy. If now one imagines the electrons to form a gas at the temperature appropriate to the velocity of the α-particles, and assumes that the system is in thermodynamic equilibrium at this temperature, one may use the principle of detailed balancing to compute the probability of capture from the probability of loss by ionization; and this latter probability is approximately known from the classical formulae of Bohr. Fowler has carried through the calculations on this basis. They yield, with certain not very unreasonable assumptions, a satisfactory account of the experiments on the ratio of the number of α-particles with a captured electron to the number of bare α-particles in a beam that has been passed through a film of metal.

The theoretical objection to this calculation is that it completely neglects the rôle of the nuclei, and ascribes to the electrons a velocity relative to each other, and relative to the nuclei, which they have not in fact. We shall see later that encounters in which two electrons take part play an unimportant part in the process of capture. Empirically[3] this is confirmed by the fact that the experiments seem to demand a probability of capture proportional to the first power, and not the square, of the electron density. Fowler's formulae may also be applied, with a slight modification, to the evaluation of the mean free path for capture in air. They give results which do not agree nearly as well as those of the present theory with the experiments, and which seem definitely unsatisfactory.

We shall first compute the first order cross section[5] for capture into the normal state by an α-particle of mass M, charge $2e$, and velocity V, for an atom with a single electron of mass m, charge $-e$, and with a nucleus of mass qM, and charge Ze. If we eliminate the motion of the center of gravity of the system as a whole, we may describe the relative motion in terms of the vector $\boldsymbol{R}$ from the center of gravity of the electron and α-particle to the nucleus, and the vector $\boldsymbol{r}$ from this same center of gravity to the electron. The wave function for the initial state, representing a unit stream of α-particles per unit area, is then[6]

$$(2\overline{M}/Kha^3)^{1/2}e^{i(\boldsymbol{K}\cdot\boldsymbol{R})+i\kappa(\boldsymbol{r}\cdot\boldsymbol{R})/R-|\boldsymbol{R}-\boldsymbol{r}|/a} \tag{2}$$

with

$$a=h^2/4\pi^2\mu Ze^2\ ; \qquad \mu=mqM/(m+qM)\ ; \qquad \overline{M}=M^2q/[m+(1+q)M]$$
$$\kappa=2\pi\mu V/h \qquad \boldsymbol{K}=2\pi\overline{M}V/h. \tag{3}$$

---

[5] The probability of capture has the dimensions of an area because the initial wave function (2) is normalized to make the incident flux per unit *area* per unit time unity. $\sigma\cdot\lambda\ =[H]$.

[6] The first two exponential factors give the translational motion of the atom and α-particle; the third gives the motion in the normal state of the atom of the electron about the center of gravity of the atom; the factor is chosen to make the flux of incident α-particles one per unit area per unit time.

The wave function for a final state, with a relative velocity of nucleus and Helium ion $\boldsymbol{V}'$, is

$$1/2(\overline{M}K'/ha_0{}^3\pi^3)^{1/2}e^{i(\boldsymbol{K}'\boldsymbol{R})-2r/a_0} \tag{4}$$

with

$$a_0 = h^2/4\pi^2\mu e^2\ ;\ \boldsymbol{K}' = 2\pi\overline{M}\boldsymbol{V}'/h.$$

This is normalized[7] to $d\nu d\omega$, where $E = h\nu$ is the total energy of the final state, and $d\omega$ is the element of solid angle of the unit vector $\mathbf{s} = \boldsymbol{V}'/V'$. The perturbing energy for the capture is the interaction energy of the α-particle and electron:

$$H_1 = (-2e^2/r)(\mu/m). \tag{6}$$

The matrix component of this which conserves the energy has a velocity $\boldsymbol{V}_1$:

$$\boldsymbol{V}' = \boldsymbol{V}_1\ ;\quad V^2 - V_1{}^2 = (h^2/4\pi^2\mu\overline{M})(1/a^2 - 4/a_0{}^2), \tag{7}$$

and is a function of the direction of $\boldsymbol{V}_1$, or of the vector $\mathbf{s}$:

$$H_1(\mathrm{s}) = (\overline{M}e^2K_1/ka_0{}^3\pi K')(2z^3/\pi)^{1/2}\int d\boldsymbol{R}$$

$$\int d\boldsymbol{r}/r\cdot e i^{[(\boldsymbol{K}\cdot\boldsymbol{R})-(\boldsymbol{K}_1\boldsymbol{R}_1)-\kappa(\boldsymbol{r}\boldsymbol{R})/R]-[2r+|\boldsymbol{R}-\boldsymbol{r})]/a}. \tag{8}$$

If we expand the $|R-r|$ in the exponent for small r/R we get

$$H_1(S) = 2^{11/2}\pi^{1/2}Z^{-3/2}a_0{}^2\overline{M}e^2(K_1/hK)$$
$$\{4-(Z-ia_0\kappa)^2\}^{-1}\{1+a^2(|\boldsymbol{K}_1-\boldsymbol{K}|)^2\}^{-2}. \tag{9}$$

This gives for the first order cross section[8]

$$\sigma_0 = 4\pi^2/h^2\int|H_1(\mathrm{s})|^2 d\omega = \frac{2^{13}\pi^4\overline{M}^2a_0{}^2e^4}{3h^4ZK^2[a_0{}^4\kappa^4+2(4+Z^2)a_0{}^2\kappa^2\cdots]}\cdot \tag{10}$$

We have now to consider the validity of certain of the approximations involved in this calculation. It was shown in ref. 1. that, if the matrix element of H_1 to some other final state—involving a transition which violates the conservation of energy—is much larger than that responsible for the first order effect, second order terms must be considered. The matrix elements of H_1 have maximum values for $\boldsymbol{V}'$ parallel to $\boldsymbol{V}$, and these values are sensibly independent of V'. In this case, therefore, the second order terms are negligible; and they may be shown, in fact, to vanish more rapidly than σ_0 with increasing V. This applies also to transitions to excited states in He$^+$.

In evaluating H_1 we have neglected the term $-2Ze^2/R$, which gives the interaction energy of the nucleus and the α-particle, and which gives rise to the Rutherford scattering. The contribution of this term to the probability

---

[7] Ref. 1, Section 1.

[8] Ref. 1, Section 3, Eq. 7.

of capture is only apparent, and arises from the fact that the wave function for the deflected α-particle and undisturbed atom is not quite orthogonal to that of the deflected α-particle with a captured electron. The contribution of this term to the cross section vanishes more rapidly than σ_0 with increasing V.

The electron may be caught into one of the excited states of He$^+$. The wave functions for these states corresponding to (4) are

$$(1/2\pi)\left\{\frac{\overline{M}K'(2k+1)(k-m)!(n-k-1)!}{2ha_0^3n^2(k+m)![(n+k)!]^3}\right\}^{1/2} e^{i(\boldsymbol{K}\cdot\boldsymbol{R})-2r/na_0}$$

$$L_{n+k}^{(2k+1)}(4r/na_0)P_k^{(m)}(\cos\delta)e^{im\phi} \tag{11}$$

where n, k, m are the three quantum numbers of the He$^+$ orbit. If one uses (11) to estimate the probability of capture into the excited states, one finds that the contribution of states for which $k\neq 0$ vanishes more rapidly than σ_0 by a factor V^{-2}. The only important terms, for large V, for the states n, 0, 0, are those arising from the first term of the Laguerre polynomials. Each such state has a transition probability

$$\sigma_n=\frac{1}{n^3}\frac{2^{13}\pi^4\overline{M}^2a_0^2e^4}{3h^4ZK^2[a_0^4\kappa^4+2(4/n^2+Z^2)a_0^2\kappa^2\cdots]}. \tag{12}$$

For large V the total probability of capture thus becomes

$$\sigma=\sum_{n=2}^{\infty}\sigma_n+\sigma_0=\sum_{n=1}^{\infty}(1/n^3)\sigma_0=1.2\sigma_0. \tag{13}$$

In the evaluation of $H_1(s)$ the exponent $|\boldsymbol{r}-\boldsymbol{R}|$ was expanded:

$$|\boldsymbol{R}-\boldsymbol{r}|\sim R-(\boldsymbol{R}\cdot\boldsymbol{r})/R \tag{14}$$

The integral as it stands is difficult to evaluate, but we may control this approximation by setting

$$|\boldsymbol{R}-\boldsymbol{r}|=\begin{matrix} R-(\boldsymbol{R}\cdot\boldsymbol{r})/R \text{ For } R>r. \\ r-(\boldsymbol{R}\cdot\boldsymbol{r})/r \text{ For } R<r. \end{matrix} \tag{14a}$$

This introduces into the integral over $\boldsymbol{R}$ new terms of the form

$$\kappa^{-3}e^{-1/a_0[2\pm1\pm ia_0\kappa]R}. \tag{15}$$

These vanish more rapidly for large V than the terms retained.

Part of the excess of energy of the electron in its initial state over that in its final state may be given off as spontaneous radiation; this may increase the probability of capture, in particular of capture into the normal state of He$^+$. The cross section for radiative capture is[8]

$$\sigma_r=\int d\omega\int_0^{\nu_0+\nu_1}d\nu(64\pi^4\nu^3/hc^3)\,|P(\bar{\nu},s)|^2;\quad h(\bar{\nu}-\nu)=h\nu_0=E_0 \tag{16}$$

where $\nu_1=(h^2/8\pi^2\mu a_0^2)(Z^2-4)$, and where $\boldsymbol{P}(\bar{\nu},s)$ is that component of the effective electric moment $-e\underline{r}$ of the system which corresponds to a transition to a state of energy $h\bar{\nu}$, and a direction of relative velocity given by the vector $\mathbf{s}$. The resulting matrix integrals differ from H_1 chiefly in having a factor r in place of $2e/r$; and this introduces a factor $\kappa^{-4}e^{-2}$ into the cross section. The ratio of σ_r to σ turns out[9] of the order of magnitude of

$$\sigma_r/\sigma=\nu_1{}^3h^2K/e^2a\overline{M}c^3\kappa^4. \tag{17}$$

For the range to which we shall apply our formulae this is about 10^{-7}. Stimulated radiative transfers do not occur.

These considerations give, for the mean cross section for capture in atomic hydrogen

$$\sigma=1.2\sigma_0=[2\times 10^{-11}/W^2(W+135)] \tag{18}$$

where W is the equivalent electron voltage of the α-particle. This is valid only for velocities for which $50/W$ may be neglected.

For atomic hydrogen captures in which two electrons play a part can not occur. They may occur for other atoms, provided that the sum of the ionization potentials of the two electrons is less than the energy of binding in He^+. But the coupling between the electrons is not very great—compared with the coupling of each to the nucleus—and one may expect such captures to be of the same relative importance as double ionizations in the theory of ionization by collision. One cannot estimate this very accurately without a more detailed knowledge of the periodic and aperiodic wave functions for the atom in question. But Fowler's calculations offer a convenient upper limit, since they make encounters between electrons much more probable than they are in fact, and assume that any electron can absorb any quantum of energy. It will be seen that Fowler's formula gives a cross section for capture by double encounter only about 1/100th of that computed by (10). As has been observed, the probability of the simple capture depends very little on the energy to be taken up by the nucleus.

The most direct way, then, of adapting (18) to experiments on air is to neglect the interaction of the atomic electrons, and use, for the wave function of each electron, that of the normal state of a hydrogen-like atom with such a nuclear charge Z_n as gives the proper ionizing potential for the electron. This yields for λ_c, the mean free path for capture, in air at N.P.T.,

$$\lambda_c{}^{-1}=\Sigma_n(5.4\times 10^8/Z_nW^2)\{W+2764+Z_n{}^2)\}^{-1}. \tag{19}$$

where the summation is to be taken over all the electrons of the "air molecule." The value of λ_c depends only slightly on the ionizing potentials.[10]

[9] To evaluate (16) one may use the property of the normalized wave functions for the motion of the ion: $\int d\omega\int dv\psi_{H^+}(v,\ \mathbf{s},\ \mathbf{R}')\psi_{H^+}{}^*(v,\ \mathbf{s},\ \mathbf{R}'')=\delta(\mathbf{R}'-\mathbf{R}'')$

[10] The oxygen molecule has twelve electrons with Z ranging from 1 to 1.7; and four with $Z=7.5$. The nitrogen molecule has ten electrons with Z ranging from 1.1 to 1.7; and four with $Z=6.5$. Cf. Hdb. d. Physik, xxiii, 756–760, 1926.

For comparison we may quote Fowler's result[11]:

$$\lambda_c^{-1}=2.7\times 10^7\nu_\epsilon^2(e^2h/4n^2VW^2)\{W+104\}^{-1}. \tag{20}$$

Here ν_ϵ is the effective density for double encounters of "loosely bound" electrons. If N be the number of such electrons per molecule, and G be the volume of the molecule, we may set, for air at N.P.T.,

$$\nu\epsilon^2=2.7\times 10^{19}N(N-1)/G\ ;\quad N=10.4\ ;\quad G=6\times 10^{-23}.$$

The numerical values are given in Table I.

TABLE I

V (cm/sec)	λ_c(mm) computed (20)	λ_c(mm) observed (4)	λ_c(mm) computed (19)
(1.) 1.8×10^9	500	2.2	2.3
(2.) 0.9×10^9	4.4	0.037	0.039
(3.) 0.44×10^9	0.042	0.0008	0.0009
Ratio (1./2.)	115	59	57
Ratio (2./3.)	105	46	44

To apply (19) to find the relative concentrations of He^+ and He^{++} in a beam that has passed through air or metal, we must know the probability for the process of loss. There is some evidence that this is not a simple ionization by electron impact. In the first place, since the probability depends upon the square of the matrix component of the perturbing energy, the probability of ionization due to the nucleus should be Z^2 times that for the ionization due to an electron, whereas that due to all the electrons should be Z times that due to a single electron; for heavy atom the nucleus would thus be the more important. The second point is empirical. For the classical theory gives a probability of ionization which falls off with V^{-2}; and one may readily see by writing down the matrix elements that, for large velocities, the quantum mechanics gives this too; this has been established in detail by Elsasser.[12] But experimentally Rutherford finds that the mean free path for loss varies, in a range for which Bohr's formula should hold, as V^1. It may be shown that the ionization due to a colliding dipole falls off less rapidly with increasing V than that due to a simple charge; so that both discrepancies may be resolved by taking for the ionizing particle the core of the atom.

If one uses Bohr's formula for the rate of loss, the method of this section leads to reasonable values for the ratio of the concentrations of He^{++} and He^+. This ratio then varies as V^4, whereas Rutherford finds $V^{4.6}$.

2. The recombination spectrum for electrons and protons may be studied by canonical methods; and one may compute the cross section for re-

[11] Fowler, ref. 4, Eq. 11.

[12] I am indebted to Dr. Elsasser for informing me of his results.

combination from the known wave functions of the hydrogen atom.[13] For, in spite of the fact that the aperiodic wave functions approach those of free particles only when the distance between the particles r is held constant and their relative velocity V is increased indefinitely, and not when V is held constant and r is increased, one can write down an initial wave in terms of these wave functions which, for large r, represents a unit incident beam per unit area, moving with a velocity V in a given direction ($\cos\delta=0$). This turns out to be

$$\Psi_i=2\kappa^{-1}\pi^{1/2}\sum_{k'=0}^{\infty}(k'+1/2)i^{k'}\psi(\nu',k',0) \tag{1}$$

where $\psi(\nu',k',0)$ is the aperiodic wave function for the state $E=h\nu'=\frac{1}{2}mV^2$, orbital angular momentum k', and component of angular momentum parallel to the beam zero, taken real, and normalized to $d\nu'$. For the normal state the wave function is

$$\Psi(0,0,0)=(\pi a_0^3)^{-1/2}e^{-r/a_0}. \tag{2}$$

The interaction energy giving the spontaneous emission may be written

$$H_1=4\pi r(h\nu^3/3c^3)^{1/2} \tag{3}$$

where ν is the frequency of the emitted light. The cross section for radiative recombination to the normal state,

$$\sigma_0=4\pi^2/h^2\left|\int d\tau\ \Psi_i H_1\psi(0,0,0)\right| \tag{4}$$

thus becomes

$$\sigma_0=(2^7\pi e^2h/3m^2c^3g^2)e^{-(4/g)\tan^{-1}g}(1+g^2)^{-2}(1-e^{-2\pi/g})^{-1} \tag{5}$$

where g is the ratio of the initial translational energy of the electron to the energy of ionization of the hydrogen atom. For low velocities the cross section becomes infinite:

$$\sigma_0\sim(2^7\pi e^2h/3e_1^4m^2c^3)g^{-2}. \qquad e_1=2.718\cdots$$

For high velocities it is given by

$$\sigma_0\sim(64e^2h/3m^2c^3)g^{-5}. \tag{7}$$

The extension of (5) to recombination for excited states offers considerable arithmetic difficulties. For high velocities it is easy to modify (7) to take account of the excited states. For, for high velocities, the wave functions of the two body problem approach those for the free particles, and these latter become almost orthogonal to the periodic wave functions, and may be used to evaluate σ. For the initial wave function we may thus take

$$V^{-1/2}e^{i\kappa r\cos\delta}=\kappa^{-1}V^{-1/2}\sum_{k'=0}^{\infty}P_{k'}(\cos\delta)I_{k'}(\kappa r)=\Psi_0 \tag{8}$$

---

[13] Cf. J. R. Oppenheimer, Z. f. Physik, **41**, 268 (1927), Eqs. 46, 47, 29. Further Y. Sugiura, Journ. d. Physique, VI, **7**, 113 (1927) Eq. 15.

with

$$I_{k'}(\kappa r)=\pi i^{k'}\cdot(2k'+1)(2\kappa/r)^{1/2}J_{k'+1/2}(\kappa r). \tag{9}$$

For that of the final state, with the electron bound in an n,k,m orbit, we have

$$\left\{\frac{(2k+1)(k-m)!(n-k-1)!}{\pi n^2a_0{}^3(k+m)![(n+k)!]^3}\right\}^{1/2} e^{-r/na_0}L^{(2k+1)}_{n+k}(2r/na_0)$$
$$P^{(m)}_{k}(\cos\delta)e^{im\phi}=\psi(n,k,m). \tag{10}$$

The *total* cross section for recombination, σ, is then

$$\sigma=4\pi^2/h^2\sum_{n,k,m}\left|\int d\tau\psi_0H_1\psi(n,k,m)\right|^2. \tag{11}$$

Now the selection rule gives $k-k'=\pm1$. With this limitation one may readily verify that the dominant terms for high V have $k=0$, $k'=1$, and that only the first *two* terms of the Laguerre polynomials corresponding to $k=0$ need be retained; all other terms vanish more rapidly with the velocity. Eq. (11) thus reduces to

$$\sigma=(64\pi^4\nu^3e^2/3ch)\sum_{n=1}^{\infty}(16\pi/a_0{}^3n^3V\kappa^2)\left|\int_0^{\infty}r^3drI_1(\kappa r)e^{-r/na_0}(1-(n-1)r/na_0)\right|^2. \tag{12}$$

This yields

$$\sigma=(2^6e^2h/3m^2c^3)g^{-5}\sum_{n=1}^{\infty}n^{-3}=\sigma_0\sum_{n=1}^{\infty}n^{-3} \tag{13}$$

or numerically

$$\sigma=10^{-18}W^{-5/2} \tag{14}$$

with W the electron voltage of the incident beam. For recombination with a bare nucleus of charge Z, σ must be multiplied by Z^5. For recombination from high velocities, and for recombination to the normal state for all velocities, the light emitted is polarized with its electric vector parallel to the electron beam.

Jefferson Physical Laboratory,
Cambridge, Massachusetts,
December 1927.