

## Historic Article

# Elementary processes with two quantum transitions\*

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## Introduction

The first part of this work considers the coaction of two photons in an elementary process. With the help of Dirac's dispersion theory<sup>1</sup>, the probability of a process analogous to the Raman effect, namely the simultaneous emission of two photons, is calculated. It appears that a nonzero probability exists that an excited atom divides its excitation energy into two photons, whose energies in sum prove to be the excitation energy but are otherwise arbitrary. When light falls upon the atom with a frequency smaller than the corresponding atomic eigenfrequency, another stimulated double emission occurs during which the atom divides its energy into one incident and one frequency-difference photon. Kramers and Heisenberg<sup>2</sup> have calculated the probability of this last process according to the correspondence principle.

Additionally, the reversal of this process is considered, namely, where two photons whose frequency-sum equals the excitation frequency of the atom co-act to excite the atom.

Furthermore the behavior of an atom toward scattering particles when it simultaneously has the opportunity to spontaneously emit light is examined. Experimentally, Oldenberg<sup>3</sup> finds a broadening of the resonance line of mercury when he lets the excited atoms collide repeatedly with slow particles. He interprets this through the assumption that a positive or negative part of the excitation energy can be transferred as kinetic energy to the colliding particle, and that the frequency-difference photon is emitted. For this process, a formula analogous to the Raman effect and the double-emission, respectively, is derived here.

Finally, in connection with Franck's work<sup>4</sup>, an attempt is made to explain the excitation-intensity's behavior of spectral lines through collisions with fast electrons via such a double-process.

Franck discusses the behavior of the excitation function of a spectral line, i.e., the intensity as a function of the velocity of the incident electrons. This function is zero for small velocities, until the kinetic energy of the electrons becomes equal to the excitation energy of the respective initial state of the line. It then increases strongly, reaches a maximum at a velocity corresponding to just a few volts above this critical voltage, and then decreases again to zero. This part of the curve has repeatedly been calculated with the ordinary collision theory. One obtains a curve which represents the phenomena well, especially the sudden onset of the function at the critical voltage. For large velocities, the theoretical curve yields a monotonic

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<sup>1</sup> P. A. M. Dirac, *Proc. of R. S.* vol. 114, pp. 143 and 710 (1927).

<sup>2</sup> H. A. Kramers and W. Heisenberg, *Ztschr. f. Physik* **31**, 681 (1925).

<sup>3</sup> O. Oldenberg, *Ztschr. f. Physik* **51**, 605 (1928).

<sup>4</sup> J. Franck, *Ztschr. f. Physik* **47**, 509 (1928).

decrease towards zero. Investigations with fast electrons have shown, however, that the intensity later increases again; it seems to have a flat maximum at an electron-velocity corresponding to about 100 volts for all lines. This maximum corresponds to kinetic energies capable of quite strong ionization; for these energies the theoretical value of the direct collision excitation as well as the extrapolation of the experimental excitation function is already practically zero. The relative intensities of the individual lines are strongly shifted compared to the behavior at small velocities, so that a completely different process appears to underlie the excitation. Franck explains that this phenomenon bears many characteristics of recombination radiation.

However, Franck also shows that this process cannot be actual recombination, primarily since most of the experiment is conducted in such high fields that the released secondary electrons very quickly achieve too high a velocity to become recaptured. Thus Franck interprets this phenomenon via a recombination of the atom with its own electron, a process which can be represented in Bohr's theory as follows: An atomic electron obtains energy from the colliding particle and is thrown into a hyperbolic orbit, i.e., in an orbit with energy higher than the ionization energy. But before it has escaped from a certain impact zone of the atom, it decays via emission of light back into some elliptic orbit, so that the atom now is in an excited state.

Here the question of how such a process can be described according to the principles of quantum mechanics will be discussed. Obviously, then, one can no longer say that the atom recombines before the secondary electron has escaped from a certain impact zone of the atom. But it seems reasonable to attempt an explanation of this phenomenon through a process whereby, simultaneously, in one elementary action, the atom absorbs energy from the colliding electron and emits light, so that it then remains in a state of discrete energy and now is able to emit a spectral line of the discrete spectrum in a second, independent process. Such an interpretation contains strong analogies to the Raman effect, which can also be regarded as the coincidence of two processes in one elementary process. Because such a single process occurs the moment the collision affects the atom, it would explain all phenomena which cannot be interpreted through a recombination radiation.

The calculation yields a non-zero probability for such a process, the character of which will be discussed.

## 1 The coaction of two light quanta in an elementary process

The following calculation closely relates to P. A. M. Dirac's work on emission, absorption, and dispersion.

The interaction of an atom with a radiation field is considered. In order to make the degrees of freedom countable, let the radiation be enclosed in a cubic box of volume  $V$ , which imposes the condition that the light waves are periodically continued outside the box. Later the box is assumed to be infinitely large.

Such a radiation field is equivalent to a system of uncoupled harmonic oscillators, since it is possible to expand the radiation in plane, linearly polarized waves. If  $\mathfrak{A}$  is the vector potential, one has

$$\mathfrak{A} = \sum_{\alpha} q^{\alpha} \mathfrak{A}^{\alpha} = \sum_{\alpha} q^{\alpha} \epsilon^{\alpha} e^{2\pi i \nu_{\alpha} (\mathfrak{s}_x^{\alpha} x + \mathfrak{s}_y^{\alpha} y + \mathfrak{s}_z^{\alpha} z)},$$

where the components of the vectors  $\nu_{\alpha} \mathfrak{s}^{\alpha}$  are determined as usual by integral relations with respect to the size of the box; for each possible vector  $\nu_{\alpha} \mathfrak{s}^{\alpha}$  there are two unit vectors  $\epsilon^{\alpha}$ , orthogonal to each other as well as to  $\mathfrak{s}^{\alpha}$ .

For large cavities the asymptotic number of eigenmodes, whose frequency lies between  $\nu$  and  $\nu + \Delta\nu$ , is

$$Z(\nu) \Delta\nu = \frac{8\pi\nu^2 V}{c^3} \Delta\nu. \quad (1)$$

Maxwell's equations yield the harmonic oscillator differential equation for each quantity  $q^\alpha$ . Subjecting them to quantization, the Hamiltonian of radiation becomes

$$\sum H^\alpha = \sum_\alpha h\nu_\alpha \left( n_\alpha + \frac{1}{2} \right).$$

A state  $s$  of the radiation field is described by noting the states of all oscillators  $s = (n_1 \dots n_\alpha \dots)$ , and the energy difference of two cavity states is

$$h\nu_{ss'} = \sum_\alpha h\nu_\alpha (n_\alpha - n'_\alpha).$$

The matrix elements of  $q^\alpha$  are

$$\left\{ \begin{array}{l} q_{ss'}^\alpha = \sqrt{\frac{hc^2}{2\pi\nu_\alpha V}} (n_\alpha + 1) \quad \text{for } n'_\alpha = n_\alpha + 1, \quad n'_\beta = n_\beta; \\ = \sqrt{\frac{hc^2}{2\pi\nu_\alpha V}} n_\alpha \quad \text{for } n'_\alpha = n_\alpha - 1, \quad n'_\beta = n_\beta; \\ = 0 \quad \text{otherwise.} \end{array} \right. \quad (2)$$

Let an atom with nucleus fixed in space, with Hamiltonian  $H_A$ , with stationary states  $n$  and eigenfrequencies  $\nu_{nn'}$ , interact with the radiation field. Then the Hamiltonian of the total system is

$$H = \sum_\alpha H^\alpha + H_A + H'.$$

The interaction energy  $H'$  is obtained from the Hamiltonian of the electron

$$H_{\text{el}} = \frac{\mathbf{p}^2}{2m} + V(\mathbf{q}) + \frac{e}{mc} (\mathbf{p} \mathfrak{A}) + \frac{e^2}{2mc^2} \mathfrak{A}^2.$$

$\mathbf{p}$  and  $\mathbf{q}$  are the momentum and coordinate vectors, respectively, of an atomic electron;  $V$  is the potential energy of the electron in the atom, and  $\mathfrak{A}$  is the vector potential of the radiation field at the location of the electron. The two-term interaction energy

$$H' = \frac{e}{mc} (\mathbf{p} \mathfrak{A}) + \frac{e^2}{2mc^2} \mathfrak{A}^2$$

is easily transformed into a simpler form. Namely, we consider the action function belonging to  $H_{\text{el}}$

$$L = \dot{\mathbf{q}}\mathbf{p} - H_{\text{el}}$$

and express it as a function of  $\mathbf{q}$  and  $\dot{\mathbf{q}}$  using  $\dot{\mathbf{q}} = \frac{\partial H_{\text{el}}}{\partial \mathbf{p}}$ ,

$$L(\dot{\mathbf{q}}, \mathbf{q}) = \frac{m}{2} \dot{\mathbf{q}}^2 - V(\mathbf{q}) - \frac{e}{c} (\dot{\mathbf{q}} \mathfrak{A}),$$

it is equivalent to another action function

$$\bar{L}(\dot{\mathbf{q}}, \mathbf{q}) = \frac{m}{2} \dot{\mathbf{q}}^2 - V(\mathbf{q}) + \frac{e}{c} \left( \mathbf{q} \frac{d\mathfrak{A}}{dt} \right),$$

which emerged out of the first through addition of the total time-differential  $\frac{d}{dt}(\mathfrak{q}\mathfrak{A})$ . With this we construct the corresponding Hamiltonian  $\bar{H}_{\text{el}}$ , and we obtain

$$\bar{H}_{\text{el}} = \frac{\bar{\mathfrak{p}}^2}{2m} + V(\mathfrak{q}) - \frac{e}{c} \left( \mathfrak{q} \frac{d\mathfrak{A}}{dt} \right).$$

If the wavelength of the light is large compared to the atomic dimension, the spatial variation of  $\mathfrak{A}$  inside the atom can be neglected, so that  $\frac{d\mathfrak{A}}{dt} = \frac{\partial\mathfrak{A}}{\partial t} = \dot{\mathfrak{A}}$ . For the interaction energy, when introducing the electric dipole moment  $\mathfrak{P} = \sum_r e\mathfrak{q}_r$  (the sum ranges over all atomic electrons), one obtains

$$H' = -c^{-1}(\mathfrak{P}\dot{\mathfrak{A}}),$$

where the value of  $\dot{\mathfrak{A}}$  at the position  $x_0, y_0, z_0$  of the atomic center can be used. Because  $\dot{\mathfrak{A}}/c$  is equal to the electric field strength  $\mathfrak{E}$  of the radiation, the interaction energy reduces, under the above assumption, to the potential energy of the electric dipole moment  $\mathfrak{P}$  against the light field.

$H'$  is interpreted as the perturbation energy, and the eigenfunction of the total system is expanded in terms of the eigenfunctions of the unperturbed system,

$$\psi = \sum a_{ns} \psi_{ns}.$$

Assuming that the unperturbed system at time  $t = 0$  is in the state  $n^0, s^0$ , for times that are small compared to the average dwell time, perturbation theory yields for the probability amplitudes  $a_{ns}$  in first order

$$a_{ns}^{(1)} = H'_{ns, n^0 s^0} \frac{1 - e^{2\pi i(\nu_{nn^0} + \nu_{ss^0})t}}{h(\nu_{nn^0} + \nu_{ss^0})},$$

and in second order

$$\left\{ \begin{array}{l} a_{ns}^{(2)} = \sum_{n's'} \frac{H'_{nn'ss'} H'_{n'n^0s's^0}}{h(\nu_{n'n^0} + \nu_{s's^0})} \\ \cdot \left[ \frac{1 - e^{2\pi i(\nu_{nn'} + \nu_{ss'})t}}{h(\nu_{nn'} + \nu_{ss'})} - \frac{1 - e^{2\pi i(\nu_{nn^0} + \nu_{ss^0})t}}{h(\nu_{nn^0} + \nu_{ss^0})} \right] \end{array} \right. \quad (3)$$

The first of these well-known equations yields absorption and emission; the second, besides the Raman effect and dispersion, also yields the effects of simultaneous emission and simultaneous absorption of two photons, which will be investigated here in detail.

In order to first calculate the double emission, let the atom at time  $t = 0$  be in the excited state  $n^0$ , and allow only one strongly excited eigenmode in the cavity

$$\mathfrak{A}^\alpha = \mathfrak{e} e^{2\pi i\nu_\alpha (s_x^\alpha x + s_y^\alpha y + s_z^\alpha z)},$$

whose frequency  $\nu_\alpha$  does not correspond to an eigenfrequency of the atom, i.e.,

$$n_\alpha^0 \gg 1; \quad n_\beta^0 = 0 \quad \text{for } \beta \neq \alpha; \quad \nu_\alpha \neq \nu_{nn'}.$$

Because of the characteristics of the oscillator matrices  $q^\alpha$  (2) in

$$H'_{nn'ss'} = \sum_\alpha \dot{q}_{ss'}^\alpha (\mathfrak{P}_{nn'} \mathfrak{A}^\alpha)$$

$H'_{nn',ss'} H'_{n'n^0s's^0}$  can only then be different from zero if  $s$  emerges out of  $s^0$  either through absorption of one photon  $\nu_\alpha$  of the absorbed frequency and emission of one other arbitrary photon  $\nu_\beta$  – this provides

the *Raman effect* and dispersion – or through emission of two photons. Thus it appears in every case that at fixed  $\nu_\alpha$ , only emission of a specific frequency is possible by conservation of total energy. In order to be able to calculate further for both cases jointly, in the following formulas, whenever there is a double sign, let the upper correspond to the Raman effect and dispersion, and the lower to double emission, respectively. In which case

$$a_{ns}^{(2)} = \frac{\dot{q}_{n_\alpha^0 \pm 1, n_\alpha^0}^\alpha \dot{q}_{1,0}^\beta}{c^2} \sum_{n'} \left[ \frac{(\mathfrak{P}_{nn'} \mathfrak{A}^\alpha)(\mathfrak{P}_{n'n^0} \mathfrak{A}^\beta)}{h(\nu_{n'n^0} + \nu_\beta)} \cdot \left\{ \frac{1 - e^{2\pi i(\nu_{nn'} \mp \nu_\alpha)t}}{h(\nu_{nn'} \mp \nu_\alpha)} - \frac{1 - e^{2\pi i(\nu_{nn^0} + \nu_\beta \mp \nu_\alpha)t}}{h(\nu_{nn^0} + \nu_\beta \mp \nu_\alpha)} \right\} + \frac{(\mathfrak{P}_{nn'} \mathfrak{A}^\beta)(\mathfrak{P}_{n'n^0} \mathfrak{A}^\alpha)}{h(\nu_{n'n^0} \mp \nu_\alpha)} \cdot \left\{ \frac{1 - e^{2\pi i(\nu_{nn'} + \nu_\beta)t}}{h(\nu_{nn'} + \nu_\beta)} - \frac{1 - e^{2\pi i(\nu_{nn^0} + \nu_\beta \mp \nu_\alpha)t}}{h(\nu_{nn^0} + \nu_\beta \mp \nu_\alpha)} \right\} \right]. \quad (4)$$

$a_{ns}^{(2)}$  is only then significantly different from zero when  $\nu_\beta$  lies in the vicinity of a zero of one of the three denominators

$$\nu_{n'n^0} + \nu_\beta, \quad \nu_{nn'} + \nu_\beta, \quad \nu_{nn^0} + \nu_\beta \mp \nu_\alpha.$$

The proximities of the zeros of the first two denominators yield non-zero probabilities for processes in which energy is not conserved, namely for transitions of the atom from  $n^0$  to  $n$  under absorption or emission of a photon of the incident frequency  $\nu_\alpha$  and emission of an eigenfrequency of the atom.

However, these transitions are not consistent with real processes. They arise from a peculiarity of the variation of constants method used here, namely it is assumed that the perturbation energy  $H'$  starts to operate at time zero while in reality it operates continuously. The switching-on process is the reason for the appearance of the anomalous transitions.

Significant, however, is the proximity of the zero of the third denominator which represents the change in total energy in the processes. For such frequencies  $\nu_\beta$  in the vicinity of  $\nu' = \nu_{n^0n} \pm \nu_\alpha$  the additive higher-order terms

$$\frac{1 - e^{2\pi i(\nu_{nn'} \mp \nu_\alpha)t}}{h(\nu_{nn'} \mp \nu_\alpha)}, \quad \frac{1 - e^{2\pi i(\nu_{nn'} + \nu_\beta)t}}{h(\nu_{nn'} + \nu_\beta)}$$

can be neglected, and by also inserting for the matrix elements of the  $q$ 's their values according to (2), one obtains

$$\left\{ \begin{aligned} |a_{ns}^{(2)}|^2 &= \frac{4\pi^2 \hbar^2}{V^2} \left( n_\alpha^0 + \binom{0}{1} \right) \\ &\cdot \left| \sum_{n'} \left( \frac{(\mathfrak{P}_{nn'} \mathbf{e}^\alpha)(\mathfrak{P}_{n'n^0} \mathbf{e}^\beta)}{h(\nu_{n'n^0} + \nu_\beta)} + \frac{(\mathfrak{P}_{nn'} \mathbf{e}^\beta)(\mathfrak{P}_{n'n^0} \mathbf{e}^\alpha)}{h(\nu_{n'n^0} \mp \nu_\alpha)} \right) \right|^2 \\ &\cdot \frac{4 \sin^2 \pi(\nu_{nn^0} + \nu_\beta \mp \nu_\alpha)t}{h^2(\nu_{nn^0} + \nu_\beta \mp \nu_\alpha)^2}. \end{aligned} \right. \quad (5)$$

(The symbol  $\binom{0}{1}$  means that for dispersion and Raman effect it is set to 0, for double emission to 1.) The probability of the process is obtained through summation of  $|a_{ns}^{(2)}|^2$  over all  $\beta$  for which the  $\nu_\beta$  lie in the

proximity of  $\nu'$ . Using as usual, for a large cavity, the transformation from  $\sum_{\beta}$  over the number of all eigenmodes,  $\mathfrak{A}^{\beta}$ , to an integral over  $\int Z(\nu_{\beta})d\nu_{\beta}$ , (1), one obtains, because of the sharp maximum of the integrand at the resonance frequency

$$\begin{aligned} \sum_{\beta} |a_{ns}^{(2)}|^2 &= \frac{8\pi^2 h^2}{V^2} \cdot \frac{1}{3} \left( n_{\alpha}^0 + \binom{0}{1} \right) \\ &\cdot \left| \sum_{n'} \left( \frac{(\mathfrak{P}_{nn'} \mathbf{e}^{\alpha}) \mathfrak{P}_{n'n^0}}{h(\nu_{n'n^0} + \nu_{\beta})} + \frac{\mathfrak{P}_{nn'} (\mathfrak{P}_{n'n^0} \mathbf{e}^{\alpha})}{h(\nu_{n'n^0} \mp \nu_{\alpha})} \right) \right|^2 \\ &\cdot \int Z(\nu_{\beta}) \frac{2 \sin^2 \pi(\nu_{nn^0} + \nu_{\beta} \mp \nu_{\alpha})t}{h^2(\nu_{nn^0} + \nu_{\beta} \mp \nu_{\alpha})^2} d\nu_{\beta}, \\ \sum_{\beta} |a_{ns}^{(2)}|^2 &= \frac{64\pi^4 \nu'^3}{3hc^3} \cdot \frac{2\pi h \nu_{\alpha} \left( n_{\alpha}^0 + \binom{0}{1} \right)}{V} \\ &\cdot \left| \sum_{n'} \left( \frac{(\mathfrak{P}_{nn'} \mathbf{e}^{\alpha}) \mathfrak{P}_{n'n^0}}{h(\nu_{n'n} \pm \nu_{\alpha})} + \frac{\mathfrak{P}_{nn'} (\mathfrak{P}_{n'n^0} \mathbf{e}^{\alpha})}{h(\nu_{n'n^0} \mp \nu_{\alpha})} \right) \right|^2 t. \end{aligned}$$

This formula only makes sense if  $\nu' > 0$ . Thus double emission is only possible if  $\nu_{n^0 n} > 0$ , and if  $\nu_{\alpha} < \nu_{n^0 n}$  for the incident frequency.

If one assumes that a spectral line of finite width is incident – rather than that only a single eigenfunction of the cavity is strongly excited at the beginning – and if in the case of the double emission one considers the probability of the emission of  $\nu_{\alpha}$  not exactly into the one eigenmode  $\mathfrak{A}^{\alpha}$ , but instead in a narrow frequency range  $\Delta\nu$ , the above formula must also be summed over all eigenmodes  $\mathfrak{A}^{\alpha}$  with frequency between  $\nu$  and  $\nu + \Delta\nu$ . Using the function  $\varrho(\nu)$  of the mean monochromatic radiation density, defined via

$$V\varrho(\nu)\Delta\nu = \sum_{\nu < \nu_{\alpha} < \nu + \Delta\nu} h\nu_{\alpha} n_{\alpha}^0, \quad (6)$$

one obtains

$$\begin{cases} w_{nn^0}^{de} = \frac{64\pi^4 \nu'^3}{3hc^3} 2\pi \left( \varrho(\nu) + \frac{8\pi\nu^3 h}{c^3} \right) \Delta\nu \\ \cdot \frac{1}{3} \left| \sum_{n'} \left( \frac{\mathfrak{P}_{nn'} \mathfrak{P}_{n'n^0}}{h(\nu_{n'n} - \nu)} + \frac{\mathfrak{P}_{nn'} \mathfrak{P}_{n'n^0}}{h(\nu_{n'n^0} + \nu)} \right) \right|^2 \end{cases} \quad (7)$$

for the probability of the double emission per unit time. Thus it appears that in vacant cavities a finite probability exists for spontaneous, simultaneous emission of two photons, and indeed all frequency divisions are possible. If the incident light has the frequency  $\nu$ , then the ratio of the induced emission at frequency  $\nu'$  – with respect to its intensity – behaves as if a virtual oscillator with the moment

$$\mathfrak{P}_{nn^0}^{\alpha} = \sqrt{2\pi\varrho(\nu)} p_{nn^0}^{\alpha}$$

where

$$p_{nn^0}^{\alpha} = \sum_{n'} \left( \frac{(\mathfrak{P}_{nn'} \mathbf{e}) \mathfrak{P}_{n'n^0}}{h(\nu_{n'n} - \nu)} + \frac{\mathfrak{P}_{nn'} (\mathfrak{P}_{n'n^0} \mathbf{e})}{h(\nu_{n'n^0} + \nu)} \right) \quad (8)$$

spontaneously emits the frequency  $\nu'$ . The magnitude of the induced double emission for normal radiation densities is considerably smaller than the corresponding spontaneous double emission. (The ratio is the same as between ordinary induced and spontaneous emission.) This formula (8) is fully analogous to the one for the Raman effect, in which the relevant moment is

$$\mathbf{p}_{nn^0}^r = \sum_{n'} \left( \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon})(\mathfrak{P}_{n'n^0})}{h(\nu_{n'n} + \nu)} + \frac{\mathfrak{P}_{nn'}(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon})}{h(\nu_{n'n^0} - \nu)} \right).$$

Since the observed intensity additionally depends on the number of the atoms in the initial state, which in this case is an excited state, the phenomenon will be hardly observable because of the strong spontaneous emission. Perhaps, however, the effect could be found for meta-stable states where the spontaneous emission probability,  $|P_{nn^0}|^2$ , is small.

In contrast, the inverse process of the double absorption is proportional to the number of the atoms in the ground state. Essentially the calculations in this case proceed analogously. Only this time let the initial state  $n^0$  of the atom be, say, the ground state, and before the switching-on of the perturbation in the cavity let it contain only light of two narrow frequency ranges: of the mean frequencies  $\nu$  and  $\nu'$ , respectively, whose average frequency sum is equal to an eigenfrequency of the atom,  $\nu + \nu' = \nu_{nn^0}$ . The eigenfunctions of each frequency range shall have equal directions of propagation  $\mathfrak{s}$  and  $\mathfrak{s}'$ , and equal polarization  $\boldsymbol{\epsilon}$  and  $\boldsymbol{\epsilon}'$ , respectively.

Based on the same considerations as above, the amplitude of the probability of the transition from  $n^0$  to  $n$ ,  $a_{ns}^2$ , (3) is then only significantly different from zero when the cavity state  $s$  emerges out of  $s^0$  through absorption of a photon  $\nu_\alpha$  out of the frequency range  $\nu$  and another one  $\nu_\beta$  out of the frequency range  $\nu'$ . For such transitions, neglecting the corresponding higher order terms as in (5),

$$\begin{aligned} a_{ns}^{(2)} &= c^{-2} \dot{\mathfrak{q}}_{n_\alpha^0-1, n_\alpha^0}^\alpha \dot{\mathfrak{q}}_{n_\beta^0-1, n_\beta^0}^\beta \\ &\cdot \sum \left[ \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon}^\beta)(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon}^\alpha)}{h(\nu_{n'n^0} - \nu_\alpha)} + \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon}^\alpha)(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon}^\beta)}{h(\nu_{n'n^0} - \nu_\beta)} \right] \frac{1 - e^{2\pi i(\nu_{nn^0} - \nu_\alpha - \nu_\beta)t}}{h(\nu_{nn^0} - \nu_\alpha - \nu_\beta)} \\ &= \frac{2\pi h}{V} \sqrt{n_\alpha^0 \nu_\alpha n_\beta^0 \nu_\beta} \\ &\cdot \sum_{n'} \left[ \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon}')(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon})}{h(\nu_{n'n^0} - \nu_\alpha)} + \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon})(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon}')}{h(\nu_{n'n^0} - \nu_\beta)} \right] \frac{1 - e^{2\pi i(\nu_{nn^0} - \nu_\alpha - \nu_\beta)t}}{h(\nu_{nn^0} - \nu_\alpha - \nu_\beta)}. \end{aligned}$$

One obtains the probability of the process by summation of  $|a_{ns}^{(2)}|^2$  over  $s$ , i.e., in a large cavity by integration over  $\nu_\alpha$  and  $\nu_\beta$ . Using again the function  $\varrho(\nu)$  defined in (6), i.e., the monochromatic radiation density per unit volume, and because of the sharp resonance for  $\nu_\alpha + \nu_\beta = \nu_{nn^0}$ , one obtains using standard methods

$$\begin{aligned} \sum_s |a_{ns}^{(2)}|^2 &= 4\pi^2 \cdot \left| \sum_{n'} \left( \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon}')(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon})}{h(\nu_{n'n^0} - \nu)} + \frac{(\mathfrak{P}_{nn'} \boldsymbol{\epsilon})(\mathfrak{P}_{n'n^0} \boldsymbol{\epsilon}')}{h(\nu_{n'n^0} - \nu')} \right) \right|^2 \\ &\cdot \int \varrho(\nu_\alpha) \varrho(\nu_\beta) \frac{4 \sin^2 \pi(\nu_{nn^0} - \nu_\alpha - \nu_\beta)t}{h^2(\nu_{nn^0} - \nu_\alpha - \nu_\beta)^2} d\nu_\alpha d\nu_\beta. \\ w_{nn^0}^{d_\alpha} &= \frac{16\pi^4}{h^2} \int \varrho(\nu_{nn^0} - \nu) \varrho(\nu) d\nu |\mathbf{p}^\alpha \boldsymbol{\epsilon}'|^2, \end{aligned} \quad (9)$$

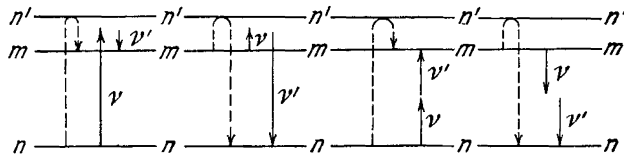
where  $\mathbf{p}^\alpha$  means the vector defined in (8). The integral ranges over the width of one of the incident spectral lines. It appears, however, that the probability of simultaneous absorption is smaller than that of simultaneous emission at normal intensities. The ratio of the probabilities of double emission to double absorption

is the same as in normal emission and absorption. Therefore the processes will not perturb the radiation equilibrium.

The frequency of this process of simultaneous absorption is increased by the fact that it is proportional to the number of atoms in the ground state. But then again the quadratic dependency on the light density acts unfavorably, so that for observation certainly large light intensities are necessary.

It should be mentioned that, similar to the Raman effect, both processes discussed above behave as if two events, each of which does not satisfy energy conservation, happen in one process: The atom jumps under emission or absorption of a frequency  $\nu$  from state  $n^0$  to an intermediate state  $n'$  and from there under emission or absorption of a frequency  $\nu'$  into the final state  $n$ .

All processes are schematically compared again here, for the sake of simplicity, in such a way that all transitions are shown between two states  $n$  and  $m$ , for which  $\nu_{mn} > 0$ .  $n'$  is the arbitrary intermediate state. Figs. 1 and 2 represent the Stokes and the anti-Stokes case of the Raman effect, respectively, Fig. 3 the double absorption and Fig. 4 the double emission.



**Fig. 1–4** The dashed lines represent the behavior of the atom; upward arrows mean absorbed, downward arrows mean emitted photons.

## 2 The coaction of light and collision in an elementary process

The coaction of light and incident particles – such as electrons – on an atom is considered here.

The electron waves are enclosed in a cubic box of volume  $V$ , which imposes the same conditions on them as for the radiation, namely they are periodically continued outside the box.

Without any interaction, the energy of the electrons is just the kinetic energy  $T$ , and the eigenfunctions are plane waves

$$\psi_{\kappa} = \frac{1}{\sqrt{V}} e^{\frac{2\pi i}{h}(\mathbf{p}_{\kappa}^x x + \mathbf{p}_{\kappa}^y y + \mathbf{p}_{\kappa}^z z)},$$

where the components of  $\mathbf{p}_{\kappa}$  are specified as usual by integral relations to the size of the box; the number of eigenmodes, whose energy  $E_{\kappa}$  lies between  $E$  and  $E + \Delta E$  and whose momentum vector  $\mathbf{p}_{\kappa}$  lies in the solid angle  $\Delta\omega_{\mathbf{p}}$ , is

$$N(E)\Delta E\Delta\omega_{\mathbf{p}} = \frac{m}{h^3} V \sqrt{2mE} \Delta E \Delta\omega_{\mathbf{p}}. \quad (10)$$

The interaction of such a field of free electrons and a radiation field with an atom will be investigated. The Hamiltonian of the total system is

$$H = H_A + \sum_{\alpha} H^{\alpha} + T + H',$$

where the interaction energy  $H'$  decomposes into two parts,

$$H' = V + U,$$

where the first one,  $V$ , means the interaction energy between atom and radiation,

$$V = -c^{-1}(\mathfrak{P} \dot{\mathfrak{A}})$$



and the second one,  $U$ , means the interaction between atom and electron, which can be taken, for example, as the Coulomb field. The interaction between radiation and electron is neglected here.

The probability amplitudes  $a_{n\kappa s}$  are examined in the same way as before, namely only such processes are studied for which at the beginning there is no radiation in the cavity, i.e., which are pure emission processes. Let there be only *one* electron with the energy  $E_0 = \frac{p_{\kappa^0}^2}{2m}$  in the box, and at the beginning the atom is assumed to be in either the excited or the unexcited state  $n^0$ .

Since  $V$  does not depend on the coordinate of the electron and  $U$  does not depend on the radiation, a matrix element of  $H'$  becomes

$$H'_{n\kappa s; n'\kappa' s'} = V_{n s; n' s'} \delta_{\kappa \kappa'} + U_{n\kappa; n'\kappa'} \delta_{s s'},$$

and thus in first order the transition probability additively separates into the effect of light only and collisions only. The coaction of both can first be obtained in second order.

Because of the characteristics of the perturbation potentials the probability amplitude in second order is then

$$\left\{ \begin{aligned} a_{n\kappa s}^{(2)} &= a_{n\kappa}^{(2)} \delta_{s s^0} + a_{n s}^{(2)} \delta_{\kappa \kappa^0} \\ &+ \sum_{n'} \left[ \frac{U_{n n' \kappa \kappa^0} V_{n' n^0 s s^0}}{h(\nu_{n' n^0} + \nu_{s s^0})} \right. \\ &\cdot \left( \frac{1 - e^{\frac{2\pi i}{h}(h\nu_{n n'} + E_{\kappa} - E_0)t}}{h\nu_{n n'} + E_{\kappa} - E_0} - \frac{1 - e^{\frac{2\pi i}{h}(h\nu_{n n^0} + h\nu_{s s^0} + E_{\kappa} - E_0)t}}{h(\nu_{n n^0} + \nu_{\alpha}) + E_{\kappa} - E_0} \right) \\ &+ \frac{V_{n n' s s^0} U_{n' n^0 \kappa \kappa^0}}{h\nu_{n' n^0} + E_{\kappa} - E_0} \\ &\cdot \left. \left( \frac{1 - e^{2\pi i(\nu_{n n'} + \nu_{s s^0})t}}{h(\nu_{n n'} + \nu_{s s^0})} - \frac{1 - e^{\frac{2\pi i}{h}(h\nu_{n n^0} + h\nu_{s s^0} + E_{\kappa} - E_0)t}}{h(\nu_{n n^0} + \nu_{s s^0}) + E_{\kappa} - E_0} \right) \right]. \end{aligned} \right. \quad (11)$$

Here the terms  $a_{n s}^{(2)} \delta_{s s^0}$  and  $a_{n\kappa}^{(2)} \delta_{\kappa \kappa^0}$  are the contributions which are generated in second order through collisions only or through radiation only, respectively. For processes to which in fact both light and colliding particles contribute, i.e., processes for which  $k$  and  $s$  are changed, they are zero.

The probability of the emission of light, whose frequency  $\nu$  is not equal to an eigenfrequency of the atom, is investigated. For the same reasons as in the previous paragraph  $a_{n\kappa s}^{(2)}$  is only significantly different from zero for such states  $\kappa, s$  for which energy is approximately conserved, i.e., for which  $h\nu_{n n^0} + h\nu_{\alpha} + E_{\kappa} - E_0$  is small; for such states the additive higher order terms

$$\frac{1 - e^{\frac{2\pi i}{h}(h\nu_{n n'} + E_{\kappa} - E_0)t}}{h\nu_{n n'} + E_{\kappa} - E_0}, \quad \frac{1 - e^{2\pi i(\nu_{n n'} + \nu_{\alpha})t}}{h(\nu_{n n'} + \nu_{\alpha})}$$

can be neglected. Hence

$$\left\{ \begin{aligned} a_{n\kappa s}^{(2)} &= \sqrt{\frac{2\pi h\nu_{\alpha}}{V}} \sum_{n'} \left( \frac{U_{n n' \kappa \kappa^0} (\mathfrak{P}_{n' n^0} \mathfrak{A}^{\alpha})}{h(\nu_{n' n^0} + \nu_{\alpha})} \right. \\ &\left. + \frac{(\mathfrak{P}_{n n'} \mathfrak{A}^{\alpha}) U_{n' n^0 \kappa \kappa^0}}{h\nu_{n' n^0} + E_{\kappa} - E_0} \right) \frac{1 - e^{\frac{2\pi i}{h}(h\nu_{n n^0} + h\nu_{\alpha} + E_{\kappa} - E_0)t}}{h\nu_{n n^0} + h\nu_{\alpha} + E_{\kappa} - E_0}. \end{aligned} \right. \quad (12)$$

In order to obtain the probability of emission of light of the mean frequency  $\nu$  in a narrow frequency range  $\Delta\nu$  in the atomic transition from the state  $n^0$  to the state  $n$ ,  $|a_{n\kappa s}^{(2)}|^2$  is to be multiplied by the number

of eigenfunctions in the range  $\Delta\nu$ , i.e.,  $Z(\nu)\Delta\nu$ , and to be summed over all  $\varkappa$ , which for a large cavity transforms into an integral over  $N(E)dE$  [compare (10)].

Because of the sharp maximum of the integrand, one obtains as usual

$$\begin{aligned} \sum_{s\Delta\nu} \sum_{\varkappa} \left| a_{n\varkappa s}^{(2)} \right|^2 &= \frac{2\pi h\nu}{V} Z(\nu) \\ &\cdot \frac{1}{3} \int \left| \sum_{n'} \left( \frac{U_{nn'\varkappa\varkappa^0} \mathfrak{P}_{n'n^0}}{h(\nu_{n'n^0} + \nu)} + \frac{\mathfrak{P}_{nn'} U_{n'n^0\varkappa\varkappa^0}}{h\nu_{n'n^0} + E_{\varkappa} - E_0} \right) \right|^2 d\omega_{p\varkappa} \\ &\int N(E) \frac{2 - 2 \cos 2\pi(\nu_{nn^0} + \nu_{\alpha} + \frac{E_{\varkappa} - E_0}{h})t}{(h\nu_{nn^0} + h\nu_{\alpha} + E - E_0)^2} dE \\ &= \frac{8\pi^3}{3V} \nu Z(\nu) N(E_0 - h(\nu_{nn^0} + \nu_{\alpha})) \cdot \Delta\nu \cdot t \\ &\int \left| \sum_{n'} \left( \frac{\mathfrak{P}_{n'n^0} U_{nn'\varkappa\varkappa^0}}{h(\nu_{n'n^0} + \nu)} + \frac{\mathfrak{P}_{nn'} U_{n'n^0\varkappa\varkappa^0}}{h(\nu_{n'n} - \nu)} \right) \right|^2 d\omega_{p\varkappa}. \end{aligned}$$

This probability is normalized by a density  $1/V$  of the incident electrons. Relating it instead to a current of incident electrons with current density equal to one, the result is also to be multiplied by

$$\frac{V}{v_0} = \frac{V}{\sqrt{\frac{2}{m} E_0}}.$$

Finally inserting the values for  $Z$  and  $N$ , one obtains for the probability of the sought coaction

$$\left\{ \begin{aligned} w_{nn^0} &= \frac{64\pi^4}{3} \frac{\nu^3 m^2}{h^3 c^3} \sqrt{1 - \frac{h(\nu_{nn^0} + \nu_{\alpha})}{E_0}} V^2 \\ &\int \left| \sum_{n'} \left( \frac{U_{nn'\varkappa\varkappa^0} \mathfrak{P}_{n'n^0}}{h(\nu_{n'n^0} + \nu)} + \frac{\mathfrak{P}_{nn'} U_{n'n^0\varkappa\varkappa^0}}{h(\nu_{n'n^0} - \nu)} \right) \right|^2 d\omega_{p\varkappa}. \end{aligned} \right. \quad (13)$$

The result is independent of the box's size  $V$ , since  $U_{n'n^0\varkappa\varkappa^0}$  is inversely proportional to  $V$ .

In particular, let  $n^0$  be an excited and  $n$  a lower lying state of the atom, i.e.,  $\nu_{n^0 n} > 0$ . It then appears, that in the transition from  $n^0$  to  $n$ , the atom can emit frequencies  $\nu$  which are larger or smaller than the excitation frequency  $\nu_{n^0 n}$ . The probability appears to be greater when only small amounts of energy are transferred to the incident particle, i.e., when the frequency  $\nu$  lies near  $\nu_{n^0 n}$ , because in the above equation in the sum over  $n'$  there are, among others, terms in which  $n' = n^0$  or  $n' = n$ . The corresponding terms take the values

$$\begin{aligned} &\frac{\mathfrak{P}_{nn^0} U_{n^0 n^0 \varkappa \varkappa^0}}{h(\nu_{n^0 n} - \nu)} \quad \text{for } n' = n^0, \\ &\frac{\mathfrak{P}_{nn^0} U_{nn \varkappa \varkappa^0}}{h(\nu_{nn^0} + \nu)} \quad \text{for } n' = n. \end{aligned}$$

Both of these terms provide a resonance for  $\nu = \nu_{n^0 n}$ . When  $\nu$  lies near  $\nu_{n^0 n}$ , they will outweigh all others by far. This resonance does not exist in the corresponding formula for the Raman effect and the double emission, respectively. This result appears to agree with the experimental results by Oldenberg.

For the phenomenon of the excitation radiation mentioned in the introduction, the initial conditions essentially are the same as before: at the start of the process let the atom be in an initial state  $n^0$ , which

for instance may be the ground state, but let the kinetic energy  $E_0 = \frac{v_{\infty 0}^2}{2m}$  of the incident electron now be significantly greater than the ionization energy of the atom.

The probability of the transition of the atom to a state  $n$  in the discrete spectrum is considered, and it will be shown that there is a possibility that the atom reaches this state via a detour through the continuous spectrum.

In order to calculate the probability of such a process, it is necessary to resort once more to formula (11). By the sum over  $n'$  the integral  $dE'$  over the continuous spectrum is always implied. The approximation which led from (11) to (12) is not legitimate here, since the denominator of some of the neglected terms can now become zero, even when energy conservation is preserved. Nevertheless, as a result of the initial conditions, some simplifications are possible.

Since  $n^0$  represents the ground state of the atom and  $s^0$  the vacant cavity, it follows that  $\nu_{n^0 n} > 0$ , and  $\nu_{s^0 s} = \nu_{\alpha} > 0$ . Hence the denominators  $\nu_{n'n^0} + \nu$  of the first sum in (11) will always be large, whereas all three denominators can be zero simultaneously in the second sum. If we devote our attention to such processes only, the last term will by far outweigh the first, and therefore alone represents the dominant feature of the phenomenon.

Hence essentially

$$a_{n\kappa s}^{(2)} = \sqrt{\frac{2\pi\hbar\nu_{\alpha}}{V}} \sum_{n'} \frac{(\mathfrak{P}_{nn'}\mathfrak{A}^{\alpha})U_{n'n^0\kappa\kappa^0}}{h\nu_{n'n^0} + E_{\kappa} - E_0} \cdot \left[ \frac{1 - e^{2\pi i(\nu_{nn'} + \nu_{\alpha})t}}{h(\nu_{nn'} + \nu_{\alpha})} - \frac{1 - e^{\frac{2\pi i}{\hbar}(h\nu_{nn^0} + h\nu_{\alpha} + E_{\kappa} - E_0)t}}{h(\nu_{nn^0} + \nu_{\alpha}) + E_{\kappa} - E_0} \right].$$

A formal transformation brings it to the form

$$a_{n\kappa s}^{(2)} = \sqrt{\frac{2\pi\hbar\nu_{\alpha}}{V}} \cdot \frac{1}{h(\nu_{nn^0} + \nu_{\alpha}) + E_{\kappa} - E_0} \sum_{n'} (\mathfrak{P}_{nn'}\mathfrak{A}^{\alpha})U_{n'n^0\kappa\kappa^0} \cdot \left[ \frac{1 - e^{-2\pi i\left(\nu_{n'n^0} + \frac{E_{\kappa} - E_0}{\hbar}\right)t}}{h\nu_{n'n^0} + E_{\kappa} - E_0} \cdot e^{2\pi i\left(\nu_{nn^0} + \nu_{\alpha} + \frac{E_{\kappa} - E_0}{\hbar}\right)t} - \frac{1 - e^{2\pi i(\nu_{nn'} + \nu_{\alpha})t}}{h(\nu_{nn'} + \nu_{\alpha})} \right].$$

Here too, in the summation over  $n'$  and integration over  $dE'$ , respectively, consideration should mainly be given to those terms in which one of the denominators is small. If the resonance positions lie in the continuum, the integrand has strong maxima for  $\nu_{E'n^0} = E_0 - E_{\kappa}$  and  $\nu_{E'n} = \nu_{\alpha}$ , respectively, and is small at greater distance. Because the product  $\mathfrak{P}_{nE'}U_{E'n^0\kappa\kappa^0}$  is slowly varying in the small, relevant frequency range, one can replace it by its value at the resonance frequency and evaluate the integral approximately. For the range of discrete eigenfunctions it is an error to interpolate the discrete values  $\mathfrak{P}_{nn'}$ ,  $U_{n'n^0\kappa\kappa^0}$  in  $n'$  via a continuous function of  $E'$  and replace the summation by an integration. Later one sees, in the special case of large velocities of the colliding particle considered here, that this error is marginal because  $h\nu_{E'n^0}$ ,  $h\nu_{E'n}$  energy changes occur mostly where the resonance frequencies really lie in the continuum.

Hence approximately

$$a_{n\kappa s}^{(2)} = \sqrt{\frac{2\pi\hbar\nu_{\alpha}}{V}} \frac{1}{h(\nu_{nn^0} + \nu_{\alpha}) + E_{\kappa} - E_0} \left[ (\mathfrak{P}_{nE^1}\mathfrak{A}^{\alpha})U_{E^1n^0\kappa\kappa^0} \cdot e^{2\pi i\left(\nu_{nn^0} + \nu_{\alpha} + \frac{E_{\kappa} - E_0}{\hbar}\right)t} \int \frac{1 - e^{-2\pi i\left(\frac{E_{\kappa} - E_0}{\hbar} + \nu_{E'n^0}\right)t}}{\nu_{E'n^0} + \frac{E_{\kappa} - E_0}{\hbar}} d\nu_{E'n^0} + (\mathfrak{P}_{nE^2}\mathfrak{A}^{\alpha})U_{E^2n^0\kappa\kappa^0} \int \frac{1 - e^{2\pi i(\nu_{nE'} + \nu_{\alpha})t}}{\nu_{nE'} + \nu_{\alpha}} d\nu_{nE'} \right]$$

$$= \sqrt{\frac{2\pi\hbar\nu_\alpha}{V}} \frac{i\pi}{\hbar(\nu_{nn^0} + \nu_\alpha) + E_\varkappa - E_0} \left[ (\mathfrak{P}_{nE^1}\mathfrak{A}^\alpha)U_{E^1n^0\varkappa\varkappa^0} \cdot e^{2\pi i\left(\nu_{nn^0} + \nu_\alpha + \frac{E_\varkappa - E_0}{\hbar}\right)t} + (\mathfrak{P}_{nE^2}\mathfrak{A}^\alpha)U_{E^2n^0\varkappa\varkappa^0} \right].$$

Thereby the atomic states  $E^1$ ,  $E^2$  are the positions of the resonance, determined as functions of  $\varkappa$  and  $s$  so that

$$\hbar\nu_{E^1n^0} + E_\varkappa - E_0 = 0, \quad \nu_{nE^2} + \nu_\alpha = 0. \quad (14)$$

In order to obtain the probability of the atom's transition from the state  $n^0$  to the state  $n$ ,  $|a_{ns\varkappa}^{(2)}|^2$  is to be summed over  $\varkappa$  and  $s$ . First the summation over  $\varkappa$ , which for large cavities transforms, as before, to an integral over  $N(E)dE_\varkappa dw_\varkappa$  [compare (10)], is carried out. Again, only the frequency range needs to be considered for which the denominator, which represents the conservation of total energy for the process, is small and because for this frequency the atomic states  $E^1$  and  $E^2$  are the same,  $E^1 = E^2 = E$ , one obtains

$$\left\{ \begin{aligned} \sum_{\varkappa} |a_{ns\varkappa}^{(2)}|^2 &= \frac{2\pi^3\hbar\nu_\alpha}{V} N(E_0 - \hbar\nu_{En^0}) |\mathfrak{P}_{nE}\mathfrak{A}^\alpha|^2 \\ &\cdot \int |U_{En^0\varkappa\varkappa^0}|^2 d\omega_{\mathbf{p}_\varkappa} \cdot \frac{4\pi^2}{\hbar} \cdot t. \end{aligned} \right. \quad (15)$$

Thereby due to (14), the state  $E$  and the energy release of the incident electron,  $E_\varkappa - E_0$ , is determined as a function of  $s$ , i.e.,  $\nu_\alpha$ , that

$$\hbar\nu_{nn^0} + \hbar\nu_\alpha + E_\varkappa - E_0 = 0, \quad E_0 - E_\varkappa = \hbar\nu_{En^0}, \quad \nu_\alpha = \nu_{En}. \quad (16)$$

Formula (15) is the probability that the atom decays into the state  $n$ , and in doing so emits a photon of frequency  $\nu_\alpha = \nu_{En}$  into the eigenmode  $\mathfrak{A}^\alpha$  of the cavity. The formulae (16) show that this process behaves as if two separate events, each satisfying energy conservation, occur in one process, namely ionization of the atom through collision whereby the electron releases the energy  $\hbar\nu_{En^0}$ , and subsequent recombination under emission of the frequency  $\nu_\alpha = \nu_{En}$ .

In order to obtain the total probability of the atom's transition into the state  $n$ , (15) is to be summed over all  $s$  corresponding to all  $\alpha$ , which transforms, as in the first paragraph, to an integration over  $Z(\nu_\alpha)d\nu_\alpha$ . If the probability is again finally related to the current density of one electron per second through a cross section perpendicular to the propagation direction of the electrons, rather than to the density  $1/V$  of incident electrons, one has to multiply by  $\frac{Vm}{\sqrt{2mE_0}}$ ; hence for the transition probability of the atom from  $n^0$  to  $n$  one obtains

$$\begin{aligned} w_{nn^0} &= \frac{8\pi^5}{3} \sqrt{\frac{m}{2E_0}} \int \nu_{En} Z(\nu_{En}) |P_{nE}|^2 N(E_0 - \hbar\nu_{En^0})^2 \int |U_{En^0\varkappa\varkappa^0}|^2 d\omega_\varkappa d\nu_{En} \\ &= \frac{64\pi^6 m^2}{3h^3 c^3} V^2 \int \nu_{En}^3 |P_{nE}|^2 \sqrt{1 - \frac{\hbar\nu_{En^0}}{E_0}} \int |U_{En^0\varkappa\varkappa^0}|^2 d\omega_\varkappa d\nu_{En}. \end{aligned}$$

Moreover, expressing the matrix elements in this formula through the emission coefficient

$$A_{nE} = \frac{64\pi^4 \nu_{En}^3}{3hc^3} |P_{nE}|^2$$

and through the theoretical value of the collision ionization probability [see, e.g., Born<sup>5</sup>], which in this notation reads

$$S_{En^0} = \frac{4\pi^2 m^2}{h^4} \sqrt{1 - \frac{h\nu_{En^0}}{E_0}} V^2 \int |U_{En^0 \rightarrow \infty}|^2 d\omega_{\mathbf{p}_\infty},$$

one obtains the final formula

$$w_{nn^0} = \frac{h}{4} \int A_{nE} S_{En^0} dE. \quad (17)$$

It subsequently appears that the previous *ansatz* regarding the interpolation of the discrete matrix elements through a continuous function of energy was justified because the probability of the collision excitation in the discrete spectrum, at large velocities of the incident electrons, is small and is only significant for transitions into the continuum – a conclusion which can be drawn, for example, from Born's formulae. It is therefore also sufficient in the final formula to extend the integral only over the continuum.

This process of collision ionization and simultaneous recombination is analogous to the process mentioned by Franck and discussed in the Introduction. That it really consists of a uniform process, and not of two processes independent of each other, follows from the proportionality of the frequency with  $t$ . In contrast, the consecutive occurrence of two independent processes – perhaps the excitation through collision and later light-emission after a dwell time of  $10^{-8}$  sec – must for times which are small compared to  $10^{-8}$ , and for these the calculation is valid, always be proportional to  $t^2$ .

This formula represents the probability of the excitation of the state  $n$  through collision with a fast electron. The atom can then emit the lines of the discrete spectrum in a second, independent process. Formula (17) explains that the maximum of the intensities of these lines lies in the region where the total ionization  $\int S_{En^0} dE$  is large. Moreover, it clarifies the full displacement of the intensities compared to the direct collision excitation, for which the excitation of the state  $n$  is proportional to a matrix element  $|U_{nn^0 \rightarrow \infty}|^2$ , and hence qualitatively reproduces the phenomena mentioned in the Introduction.

Finally, an estimate of the order of magnitude of the probability of an excitation relative to the ionization probability shall be given.

The total probability is

$$w_I = \int S_{En^0} dE,$$

and thus

$$\frac{w_{nn^0}}{w_I} = \frac{h}{4} \frac{\int A_{nE} S_{En^0} dE}{\int S_{En^0} dE}.$$

Denoting by  $\bar{A}$  an average of  $A_{nE}$ , one has

$$w_{nn^0} \simeq \frac{h}{4} \bar{A} \int S_{En^0} dE,$$

and

$$\frac{w_{nn^0}}{w_I} \simeq \frac{h}{4} \bar{A}.$$

Now

$$\int A_{nE} dE \simeq \bar{A} \Delta E$$

<sup>5</sup> M. Born, Ztschr. f. Physik **38**, 803 (1926); Nachrichten der Göttinger Ges. der Wissenschaften 1926, p. 146.

is the emission coefficient for the entire continuum, of the same order of magnitude as the emission coefficient for a line of the discrete spectrum. And the latter represents the reciprocal of the average dwell time, i.e., about  $10^8 \text{ sec}^{-1}$ .

Hence

$$\bar{A} \simeq \frac{10^8}{\Delta E}$$

and

$$\frac{w_{nn^0}}{w_I} \simeq \frac{h \cdot 10^8}{\Delta E} = \frac{10^8}{\Delta \nu}.$$

Because the width of the continuous spectrum is about

$$\Delta \nu = 10^{15} \text{ sec}^{-1},$$

one finds

$$\frac{w_{nn^0}}{w_I} \simeq \frac{10^8}{10^{15}} \simeq 10^{-7}.$$

This is a very rough estimate. A more accurate consideration of the behavior of this transition probability, however, is only to be obtained through a numerical evaluation of the matrix elements  $P_{nE}$ ,  $U_{En^0}$ , for instance, for hydrogen.

The fraction  $\frac{w_{nn^0}}{w_I}$  represents the number of atoms, which make transitions through a single-step double process directly into the state  $n$ , relative to the number of ionized atoms. Experimentally measured is the intensity of a line, for example, the resonance line  $\nu_{n^1n^0}$ . Because the atoms, which are brought into a higher state  $n$ , can mostly also emit the resonance line  $\nu_{n^1n^0}$ , the observed intensity is not only proportional to  $w_{n^1n^0}$ , but will also depend on the transition probability  $w_{nn^0}$  into all higher states.

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