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COMPARISON BETWEEN THE CLASSICAL AND
QUANTUM THEORIES OF INCOHERENT SCATTERING

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COMPARISON BETWEEN THE CLASSICAL AND QUANTUM THEORIES
OF INCOHERENT SCATTERING

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ABSTRACT

The incoherent scattering of light by a volume of gas can be treated by classical methods in a straight forward manner. Certain difficulties are pointed out in the wave mechanical treatment of the same problem and a solution of the difficulty is proposed.

АННОТАЦИЯ

Некогерентное рассеяние света в газах может быть рассчитано простым образом классическими методами. Показываются трудности, возникающие при рассмотрении этой проблемы в свете волновой механики и предлагается метода для устранения этих трудностей.

KIVONAT

A fény inkoherens szórása gázokban a klasszikus módszerekkel egyszerűen számolható. Megmutatjuk ennek a problémának hullámmechanikai tárgyalásában fellépő nehézségeket és javaslatot teszünk azok megoldására.

INTRODUCTION

The passage of a beam of light through an optical medium can be treated classically supposing the atoms of the medium to be point oscillators. The incident beam produces thus forced oscillations. Each atom is thus under the influence of the field of the primary wave and that of the fields produced by the oscillators. Interference between the primary field and that of the oscillators produces the field of the refracted beam.

More precisely if the atoms are sufficiently regularly distributed and their distances are very small as compared with the wave length λ of the incident beam then we obtain as the result of the interaction thus described the beams which are also obtained from classical optics. If the atoms are irregularly distributed as e.g. in the case of a gas - then the radiation of the field produced by the atoms has an incoherent component spreading into all directions which is caused by the density fluctuations; the latter process is the Rayleigh scattering. The intensity of the scattered radiation depends on the measure of the density fluctuations and thus this intensity can be made use of to determine the number of scattering centres, thus to determine Loschmidt's number L .

It is an interesting problem how the scattering of the radiation by an ensemble of atoms can be treated in accord with wave mechanics. The difficulty arises if we suppose /as this was elaborated in more detail in a previous publication/ that the atoms of a gas inside a container are bound to spread about uniformly over the region of the container. Regarding wave mechanical treatment of the problem we have thus to expect that the superposition of the /spread out/ wave function of the atoms of the gas produces density fluctuations which are equivalent to those which arise from the random positions of point atoms. The scattering of the incident beam in the wave mechanical picture is thus obtained as the scattering on a continuous medium the density of which shows fluctuations more or less equivalent to the density fluctuations of a gas expected from the classical picture based on the kinetic theory of gases.

The problem is, however, by no means trivial. So as to show the problematics we give first a short account of the classical theory of Rayleigh scattering using a method developed by us in an earlier publica-

tion^{1/}. We give this derivation firstly because it leads to the correct results in a comparatively simple manner but also because this method can be employed successfully in the wave mechanical treatment of the problem.

CLASSICAL THEORY OF RAYLEIGH SCATTERING

Consider a volume of gas containing N atoms. Suppose an electromagnetic plane wave with electrical field strengths

$$\underline{E}(\underline{r}, t) = \underline{E}_0 \cos(\underline{k} \underline{r} - \omega t + \varphi) \quad /1/$$

to fall upon it. An atom in a position \underline{r}' at the time t' will have an induced dipole moment

$$\underline{\Pi}(\underline{r}', t') = \kappa \underline{E}_0 \cos(\underline{k} \underline{r}' - \omega t' + \bar{\varphi}) \quad /2/$$

where κ is the polarizability of the atom* and

$$\delta\varphi = \bar{\varphi} - \varphi$$

the phase shift between the incident field and the forced oscillation depends on the frequency ω and also on the nature of the atoms.

The radiation field of the atom in a point \underline{r} at t has an electrical field strength which is in a good approximation

$$\left. \begin{aligned} \underline{E}(\underline{r}', \underline{r}, t) &= \frac{\underline{s} \times (\underline{s} \times \underline{E}_0)}{s^3} \frac{\kappa}{\lambda^2} \cos(\underline{k} \underline{s}' - \omega t' + \bar{\varphi}) \\ \underline{s} &= \underline{r} - \underline{r}' & t' &= t - s/c \end{aligned} \right\} \quad /3/$$

If the N atoms of the gas are placed in points $\underline{r}' = \underline{r}^{(1)}, \underline{r}^{(2)}, \dots, \underline{r}^{(N)}$ then the total field in a point \underline{r} at t can be written

$$\underline{E}(\underline{r}, t) = \sum_{n=1}^N \underline{E}(\underline{r}^{(n)}; (\underline{r}, t)) \quad /4/$$

In the expression /4/ we have taken into account only the action of the outer field upon the atoms of the gas. In an exact treatment it would be necessary to take into consideration also the action of the radiation fields of the N atoms upon each of the atoms.

*The polarization κ is meant to be the effective polarization which is affected by the known depolarization effects of the ensemble of atoms. We shall return to these questions in another publication.

If we consider the radiation energy from a gas we can neglect the effect of this interaction upon itself except in the region of the primary beam and of those secondary beams which we expect from classical optics. As can be seen as the result of the more detailed analysis the self-interaction is responsible for the extinction of the part of the primary beam which otherwise would come out of the medium and for the production of the refracted and reflected beams. The latter considerations are, however, unimportant for our purposes.

So as to obtain the fluctuations of intensity of the radiation field let us divide the volume of the gas into $M \gg N$ cells $\delta \underline{r}'_m$ $m = 1, 2, \dots, M$. The cells should be so small that most of them contain no atom about, N cells contain one atom and those which contain more than one atom should be negligible in number.

Using this subdivision we can write in place of /4/

$$\underline{E}(\underline{r}, t) = \sum_{m=1}^M \epsilon_m \underline{E}(\underline{r}_m; \underline{r}, t), \quad /5/$$

where

$$\epsilon_m = \begin{cases} 1 & \text{if the } m\text{-th cell contains an atom} \\ 0 & \text{if the } m\text{-th cell is empty.} \end{cases}$$

\underline{r}_m is the coordinate vector of the atom inside $\delta^3 \underline{r}_m$. Introducing a density distribution $\rho(\underline{r}')$ so that

$$N \rho(\underline{r}') \delta^3 \underline{r} = \delta n(\underline{r}') \quad /6/$$

is the approximate number of atoms in $\delta^3 \underline{r}'$ then the sum /5/ can be replaced by an integral and we have

$$\underline{E}(\underline{r}, t) = N \int \rho(\underline{r}') \underline{E}(\underline{r}'; \underline{r}, t) d^3 \underline{r}'. \quad /7/$$

Since the total number of atoms is N we have

$$\int \rho(\underline{r}') d^3 \underline{r}' \quad /7a/$$

Relation /7/ gives the intensity of the secondary radiation which were to be expected if the gas could be taken to have a continuous density $\rho(\underline{r}')$. /The action of the secondary field upon the atoms is neglected in /7//.

We can introduce the probability concept if we take $\rho(\underline{r}')$ to be a probability density. We can thus suppose the ϵ_m to be stochastic variables thus we suppose

$$\epsilon_m = \begin{cases} 1 & \text{with a probability } N\rho(\underline{r}_m)\delta^3\underline{r}_m \\ 0 & \text{" " " " } 1 - N\rho(\underline{r}_m)\delta^3\underline{r}_m \end{cases} \quad /8/$$

The generating function of the distribution /8/ can be written

$$L_m(v) = (1 - N\rho(\underline{r}_m)\delta^3\underline{r}_m + e^v N\rho(\underline{r}_m)\delta^3\underline{r}_m),$$

thus the logarithmic generating function neglecting higher order terms

$$M_m(v) = \ln L_m(v) = N\rho(\underline{r}_m)(e^v - 1). \quad /9/$$

Taking the ϵ_m to be independent stochastic variables we see from /5/ that $\underline{E}(\underline{r}, t)$ can be taken as a linear combination of these variables.

The distribution $P(\underline{r}, t; \underline{E})$ is thus the folding of the distributions $P_m(\underline{r}, t; \underline{E}_m)$ of the probability that radiation emerging from the m-th cell should contribute an amount \underline{E}_m to the field strength \underline{E} . Using the ordinary rules of folding we obtain for the logarithmic generating functions $M(\underline{E}; \underline{v})$

$$M(\underline{E}, \underline{v}) = \sum M_m(\underline{v}\underline{E}(\underline{r}_m; \underline{r}, t)). \quad /10/$$

Thus with the help of /9/ and replacing the sum by an integral

$$M(\underline{E}; \underline{v}) = N \int \rho(\underline{r}') (e^{\underline{v}\underline{E}(\underline{r}'; \underline{r}, t)} - 1) d^3\underline{r}'. \quad /11/$$

The above generating function contains three parameters $\underline{v} = v_1, v_2, v_3$; derivations into v_k give the moments of the components E_k of \underline{E} . We have thus

$$\langle \underline{E} \rangle = \left(\frac{\partial M}{\partial \underline{v}} \right)_{\underline{v}=0} = N \int \rho(\underline{r}') \underline{E}(\underline{r}'; \underline{r}, t) d^3\underline{r}'. \quad /12/$$

Comparing /12/ and /7/ we see that the expected value of the stochastic ensemble /5/ is equal to the value of the field strength emitted by a smoothed out distribution with density $N\rho(\underline{r}')$. Since $\underline{E}(\underline{r}'; \underline{r}, t)$ varies harmonically with \underline{r}' the right hand side of /12/ vanishes for most values of \underline{r} /exceptions are the directions of the various optical beams/. We have thus

$$\langle \underline{E} \rangle = 0 \quad \text{/in most directions/} \quad /13/$$

In the regions where /13/ is valid, we have thus

$$\langle \underline{E}^2 \rangle = \langle (\delta \underline{E})^2 \rangle = (\nabla_{\underline{v}}^2 M)_{\underline{v}=0}$$

thus

$$\langle \underline{E}^2 \rangle = N \int \rho(\underline{r}') E^2(\underline{r}; \underline{r}', t) d^3 \underline{r}' \quad /14/$$

From /3/ and /14/ we find

$$\langle \underline{E}^2 \rangle = \frac{N \kappa^2 E_0^2}{\lambda} a(\underline{r}), \quad /15/$$

where

$$a(\underline{r}) = \int \rho(\underline{r}') \cos^2(\underline{k} \cdot \underline{r}' - \omega t' + \varphi) \frac{d^3 \underline{r}'}{|\underline{r} - \underline{r}'|^2}$$

the average value of the \cos^2 is in very good approximation, therefore

$$a(\underline{r}) = \frac{1}{2} \int \frac{\rho(\underline{r}') d^3 \underline{r}'}{|\underline{r} - \underline{r}'|^2} \quad /16/$$

We can write

$$\frac{1}{4\pi} \langle \underline{E}^2 \rangle = I_R, \quad /17/$$

where I_R is the intensity of the scattered radiation. Note, that $\langle \underline{E}^2 \rangle$ does not depend noticeably on the time; this does not contradict the fact, that the electric vector of the radiation field oscillates with the frequency ω . Indeed, extending our calculation we find, e.g.

$$\left\langle \left(\frac{\partial \underline{E}}{\partial t} \right)^2 \right\rangle = \omega^2 \langle \underline{E}^2 \rangle$$

thus the time derivative of \underline{E} has an expected value which is in accord with the fact the actual \underline{E} value oscillates harmonically with the frequency ω and only the expected value $\langle \underline{E}^2 \rangle$ - obtained by averaging over the various configurations of the atoms - is constant in time.

The refractive index of the medium is obtained from classical considerations as

$$n = 1 + 2\pi \kappa \rho(\underline{r}).$$

Taking the average density

$$\bar{\rho} = N/V \quad /V \text{ volume of the gas/}$$

we have

$$n - 1 = \frac{2\pi n N}{V} \quad /18/$$

From /15/ /17/ and /18/ we find

$$\frac{N}{V} = \frac{(n-1)^2 V a(\underline{r})}{4\pi\lambda^4} \frac{I_O}{I_R} \quad \text{with} \quad I_O = \frac{1}{4\pi} t_O^{-2} \quad /19/$$

thus the ratio of the incident intensity and the scattered intensity leads to the determination of N/V the density of atoms.

THE WAVE MECHANICAL TREATMENT OF THE SCATTERED RADIATION

The wave mechanical treatment of the problem starts necessarily with the determination of the wave function representing the ensemble of N atoms enclosed into a container. Let us consider for the sake of simplicity H-atoms thus we can write for the wave function $\bar{\Psi}(\underline{r}^{(1)}, \underline{r}^{(2)})$ where

$$\underline{r}^{(k)} = \underline{r}_1^{(k)}, \underline{r}_2^{(k)}, \dots, \underline{r}_N^{(k)} \quad k = 1, 2$$

The upper index 1 referring to the proton as the upper index 2 to electron. The three dimensional electron density is thus obtained

$$\bar{\rho}(\underline{r}) = \sum_{k=1}^N \int \bar{\Psi}(\underline{r}^{(1)}, \underline{r}^{(2)}) \delta(\underline{r} - \underline{r}_k^{(2)}) d\underline{r}^{(1)} d\underline{r}^{(2)} \quad /20/$$

An electromagnetic field of the form /1/ can be introduced as a perturbation into the $2N$ body wave equation. A simple calculation shows that this perturbation produces current densities in the electron cloud which densities can be attributed to a continuous electric polarization of density $\pi(\underline{r}', t) \bar{\rho}(\underline{r}')$. Thus the radiation is such as if we had atoms distributed with an average density $\bar{\rho}(\underline{r}')$. The problem of the wave mechanical interpretation of the Rayleigh scattering reduces to show that $\bar{\rho}(\underline{r}')$ behaves just as the fluctuating density of an ensemble of N atoms.

THE CHOICE OF THE WAVE FUNCTION

When looking for the wave function of the ensemble of N atoms we can start from a solution $\psi(\underline{r}^{(1)}, \underline{r}^{(2)}, t)$ of the H-equation with appropriate boundary condition. Since ψ must be anti symmetric in any pair of variables $\underline{r}_k^{(1)}, \underline{r}_\ell^{(1)}$ respectively $\underline{r}_k^{(2)}, \underline{r}_\ell^{(2)}$ we can write e.g.

$$\bar{\psi}(\underline{r}^{(1)}, \underline{r}^{(2)}) = \det \psi_{k\ell} \quad /21/$$

where

$$\psi_{k\ell} = \psi(\underline{r}_k^{(1)}, \underline{r}_\ell^{(2)}) \quad k, \ell = 1, 2, \dots, N$$

If $\psi_{k\ell}$ is a standing wave enclosed in the box then the wave function $\bar{\psi}$ thus obtained represents very nearly constant electron density and thus the system behaves rather like a crystal than a gas and no noticeable incoherent scattered intensity is to be expected.

The fact that the rather symmetrical wave function /21/ does not lead to the observed behaviour of the gas draws attention to the fact - which we have pointed out already in a previous publication - namely that a physical system containing several bodies can be represented mathematically by a large number of wave functions which, however, lead to very different expected behaviours of the physical system.

The wave function which describes adequately a many body problem has to be chosen carefully so as to give results in agreement with observations. The method of how to select the wave function in actual case is not known. It seems to us that this selection can be carried out with the help of a kind of correspondence principle. That the selections thus obtained are not arbitrary and the selections can be seen if we find that the same wave function can be used to interpret different phenomena.

When choosing the wave function of the N atom ensemble we have to remark that according to the classical theory of the gas the atoms have a thermal distribution of well-known form and that the latter is verified directly by experiment. The wave function describing the ensemble must therefore contain somehow the thermal distribution.

Let us write $\psi(\underline{K}, \underline{r}^{(1)}, \underline{r}^{(2)})$ for the wave function representing a standing wave with wave vector \underline{K} inside the container. If the container is a cube with sides L , then the components of \underline{K} are integral multiples of L . The electron density in the standing wave is

$$\bar{\rho}(\underline{k}, \underline{r}) = e \int |\psi(\underline{k}, \underline{r}^{(1)}, \underline{r})|^2 d^3 \underline{r}^{(1)}$$

itself a harmonically oscillating function of the coordinates.

The wave function

$$\bar{\Psi}(\underline{k}, \underline{r}^{(1)}, \underline{r}^{(2)}) = \det \psi_{k\ell}(\underline{k})$$

describes thus rather a regular lattice of H-atoms than a gas containing N atoms. We can, however, consider an ensemble where the atoms /considered classically/ have wave vectors $\underline{k}^{(1)}, \underline{k}^{(2)}, \dots, \underline{k}^{(N)}$. The wave functions belonging to different wave vectors are very nearly orthogonal therefore we obtain the normalized wave function

$$\bar{\Psi}(\underline{r}^{(1)}, \underline{r}^{(2)}) = \frac{1}{\sqrt{N}} \sum_{n=1}^N (\underline{k}^{(n)}; \underline{r}^{(1)}, \underline{r}^{(2)})$$

which corresponds to a system of atoms with wave vector $\underline{k}^{(n)}$ $n = 1, 2, \dots, N$. The electron density can thus be written

$$\rho(\underline{r}) = \sum_{n=1}^N \bar{\rho}(\underline{k}^{(n)}, \underline{r}) .$$

Considering the wave functions as discrete points in the momentum space, we can write

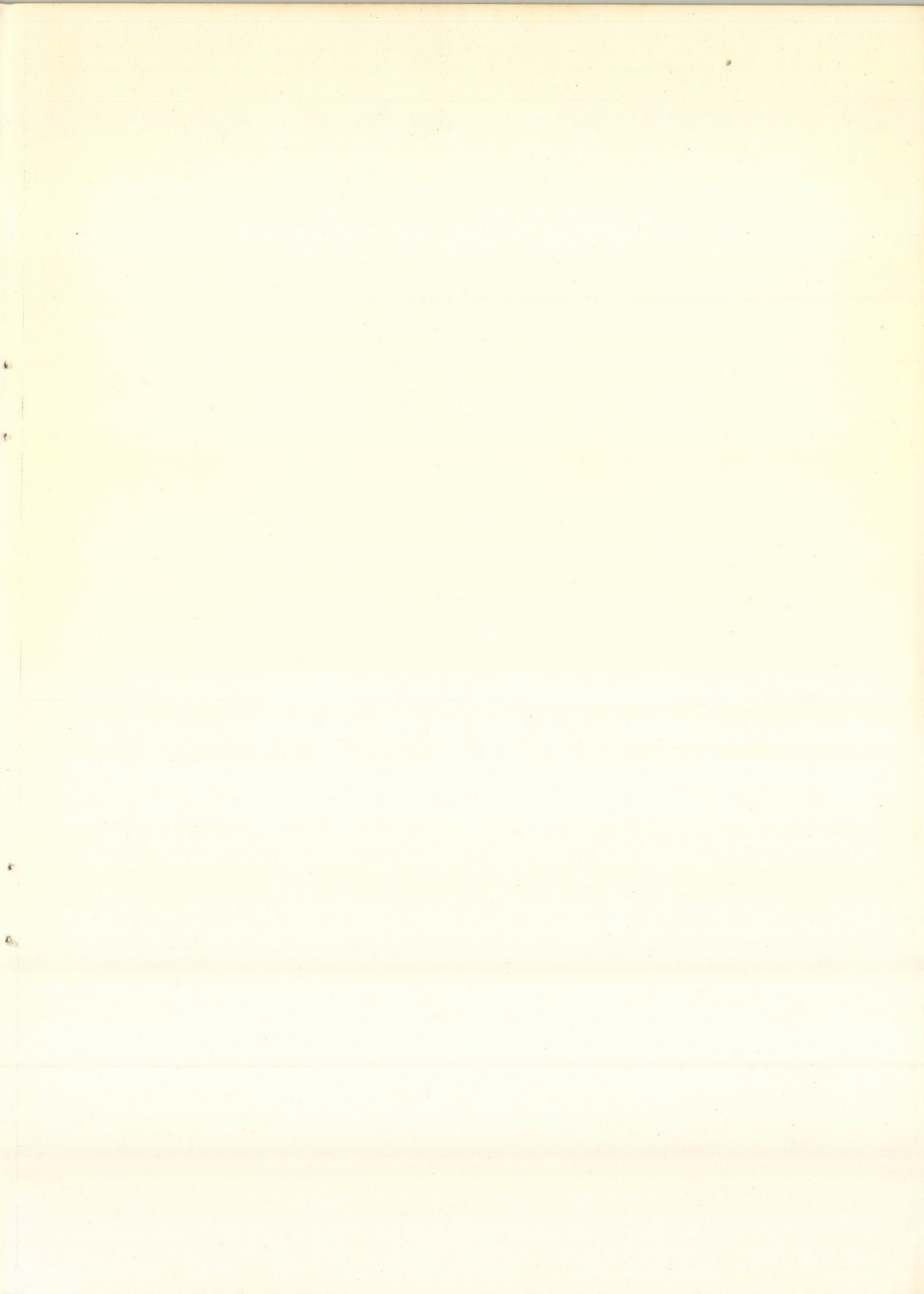
$$\rho(\underline{r}) = \sum_{m=1}^N \epsilon_m \bar{\rho}(\underline{k}^{(m)}; \underline{r})$$

where the sum is to be extended over all wave vectors $\underline{k}^{(m)}$ giving standing waves. The factors ϵ_m are zero with N exceptions, the N standing waves corresponding to the atomic states.

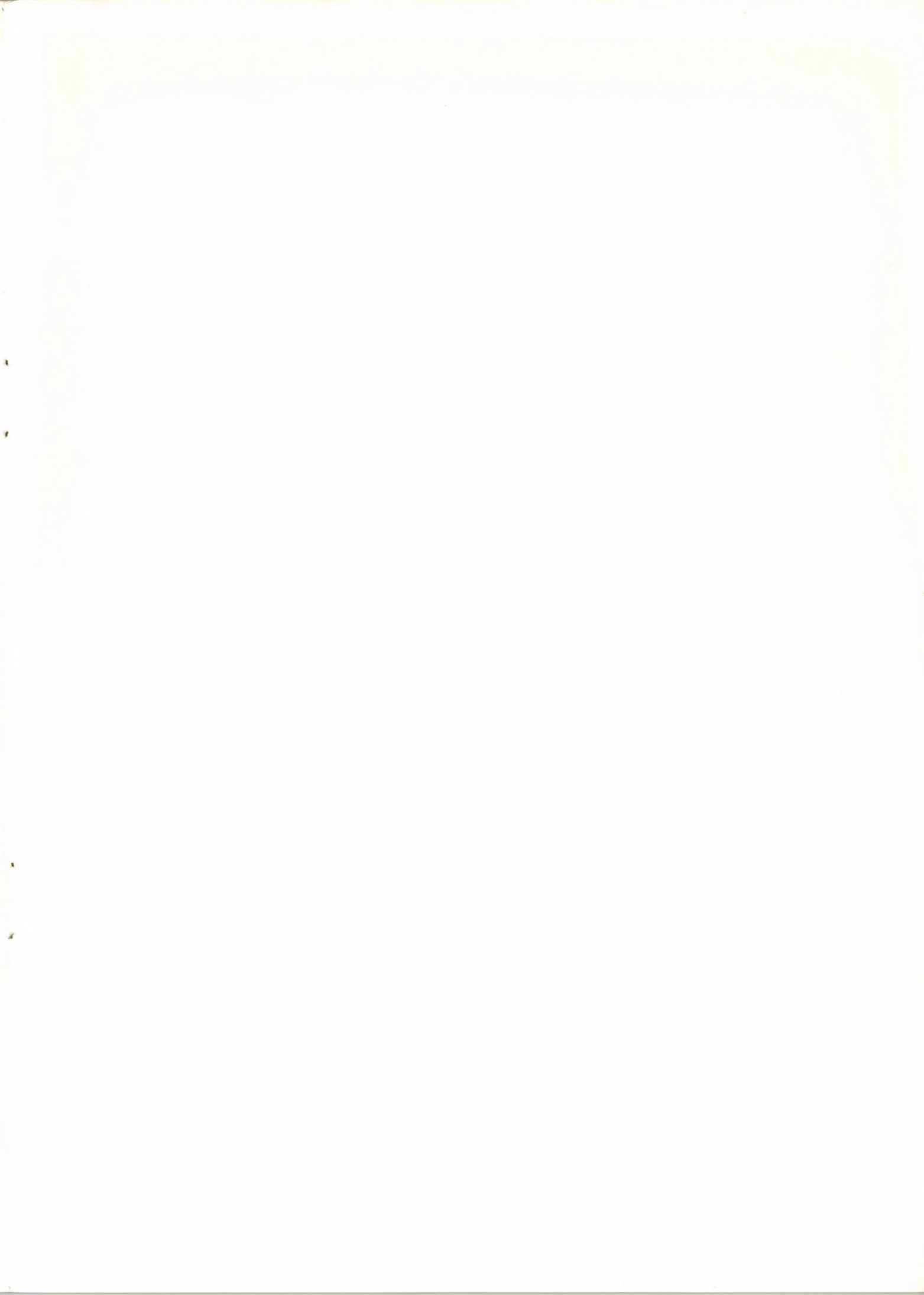
Supposing that the standing waves are selected at random from the possible states we can take /as in the classical case/ the ϵ_m to be independent stochastic variables and the probability $P(\underline{r}; \rho)$ to find a density ρ in a point \underline{r} has a logarithmic generating function.

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