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THEORY OF ATOMIC SPECTRAL  
EMISSION INTENSITY

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Theory of Atomic Spectral Emission Intensity

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Abstract

The theoretical derivation of a new spectral line intensity formula for atomic radiative emission is presented. The theory is based on first principles of quantum physics and statistical physics. It is argued that the formulation of the theory provides a very good example of the manner in which quantum logic transforms into common sense logic. The theory is strongly supported by experimental evidence.

## Introduction

The fundamental principles of classical statistical physics were mainly established in works by Maxwell, Boltzmann, and Gibbs. In considering the kinetic theory of gases, Maxwell (1859) introduced the statistical concept of distribution function. Boltzmann (1872) used the probability measure of distributions to give a statistical interpretation of entropy and the second law of thermodynamics. Credit for authorship of statistical ensemble theory is given to Gibbs (1902).

The embryo of quantum statistical physics was created when Planck (1900) presented his black body radiation formula. Einstein (1906) showed that a necessary ingredient of Planck's theory was the existence of light-quanta with energy  $h\nu$ , and in 1908 Einstein's light-quanta successfully explained the photoelectric effect [1].

Bohr's theory of the atom (1915) postulated discrete internal energy levels and spectral lines were explained by light-quantum emissions with energy equal to the energy loss of the atom making jumps from higher to lower energy levels. Einstein's light-quantum hypothesis had thus been linked to a quantum hypothesis of the atom. This link was very soon (1916) used by Einstein to give what seems to be the very first description of a macroscopic physical system in a quantum statistical physics formulation.

In this work [2] Einstein introduced his famous radiative emission and absorption coefficients  $A$  and  $B$  respectively of an atom. Only the internal atomic degree of freedom over the range of discrete energy values  $\epsilon_n$  was considered and the atoms of a gaseous sample were assumed to populate the levels  $n$  in proportion to  $W_n = P_n \exp(-\epsilon_n/kT)$  with  $P_n$  a statistical weight. This (Boltzmann) distribution was referred to as the farthest reaching generalization of Maxwell's velocity distribution law. (We shall throughout use the term "atom" for a gaseous constituent instead of Einstein's "molecule"). The  $A$  and  $B$  coefficients were used to write down the probability of elementary emission and absorption processes for "radiation bundles", i.e. photons.

In particular Einstein considered atomic jumps between two energy levels with accompanying emission or absorption of photons with energy  $h\nu$  equal to the energy difference of the two atomic levels. It was assumed that in a macroscopic system the total number of each kind of radiative process was simply equal to the product of the probability of each particular elementary process and the population number of the initial atomic level. Imposing equilibrium demanded equality between the total number of up-going photon absorbing atomic jumps and of down-going photon emitting atomic jumps. This led to the photons being distributed according to Planck's formula—in Einstein's somewhat emotional phrasing "es ergab sich auf diesem Wege die Plancksche Formel in verblüffend einfacher und allgemeiner Weise" (in this way the Planck formula emerged in an amazingly simple and general manner).

Einstein obtained his coefficients by reasoning in terms of classical electrodynamics. The correctness of the coefficients was first strictly verified by Dirac in the late 1920s in his quantum mechanics formulation of radiation theory [3]. The statement of the relationship of these fundamental atomic constants more than ten years before this relationship was actually understood is considered one of Einstein's great achievements.

Einstein's generalization of the Maxwell distribution into the so-called Boltzmann distribution of atoms over discrete energy levels is most frequently referred to as the condition for local thermal equilibrium (LTE). This concept has been used by spectroscopists ever since the 1920s as the basis of an intensity formula for optical emission from spectroscopic samples. The intensity of an atomic emission line is assumed to be proportional to the Einstein A coefficient of the emission and the Boltzmann population number of the upper level of the pertaining atomic transition [4]. This is identical to one of Einstein's original assumptions of Ref. [2] and application of Einstein's absorption rule in the limit of complete reabsorption of the radiation emitted according to the intensity formula leads, of course, to the Einstein equilibrium of matter and Planck radiation.

Einstein's original formulation of quantum statistical physics of

gaseous matter in interaction with radiation was thus adopted as a basic principle of optical emission spectroscopy. We have noted that his principle was formulated quite long before the advent of quantum mechanics. It is also important to note that although Maxwell's statistical distribution was invoked conceptually, Boltzmann's fundamental probability principle for determining the distributions and their time development actually occurring in Nature was not considered in particular. All this renders ample reason for scrutinizing the theory of optical emission from a spectroscopic sample.

The results of such a scrutiny will be presented in this paper. It turns out that fundamental principles of quantum mechanics and quantum field theory for microphysics, together with averaging procedures and maximum probability principles of quantum statistical distributions for macrophysics, suggest the abandonment of the principle of LTE. Arguments based on the concept of quantum mechanical state do not imply the semi-classically founded Einstein equilibrium.

## 2. Microscopic and macroscopic laws of physics

This Section will be devoted to a conceptual discussion. Some apparently vague points will be clarified in the subsequent Section.

We have learnt that the special logic of quantum mechanics applies to the microscopic world. We should also realize that this special logic need not be understood directly in macroscopic logical terms. What we need is a logical bridge to translate the microscopic laws into the laws of events in the macroscopic world. The apparent controversy between quantum mechanics and common sense causes debates from time to time. I think much would be gained if in such debates it could be agreed that the microscopic and macroscopic worlds considered separately are described by incompatible logical systems. The main topic of this paper will furnish a very good example of the way the microscopic quantum logic is translated into macroscopic "common sense" logic.

A macroscopic physical system may be thought of as being an assembly of microscopic subsystems. A subsystem is then composed of a basic microscopic constituent (particle) in interaction with the rest of the macroscopic system via microscopic fields of force. This microphysical system is supposed to be described by quantum mechanics.

We can solve (at least in principle) the quantum mechanical problem posed by a basic microsystem and thus determine all its possible states. Since we have a system with interaction the state, in general, is a quantum mechanical superposition of all possible states. The basic physical properties of this microsystem determine a priori conditions for the construction of assemblies that may represent the macroscopic system in a statistical physics description.

We thus form all assemblies of subsystems taking care of the microphysical a priori conditions and the constraints of the macroscopic physical system. These assemblies constitute a statistical ensemble. The actual macroscopic state is represented by

an assembly that is found by averaging over the ensemble. This representative assembly must, following Boltzmann, be chosen as being the most probable assembly of all those consistent with the macroscopic constraints.

Our basic microscopic constituent is described by a superposition of base states that span the space of the possible quantum mechanical states. By a fundamental postulate of quantum mechanics the superposition defines the probability of observing the constituent in each base state. This is the kernel of the microscopic logic; the constituent is simultaneously in many possible states but is found in one state upon observation.

The translation of this into the macroscopic logic is achieved in the process of forming the representative assembly for the macroscopic system. A priori we have the microscopic base states at our disposal in determining properties of the macroscopic system. For instance, we may ask how many basic constituents there are on an average in a particular base state. This is a meaningful question since every measurement of this number provides a definite result and the average number of constituents is thereby determined (this might presuppose some kind of stationarity condition).

The results of measurements of all average macroscopic quantities should, of course, agree with the results obtained theoretically for the representative assembly. When this requirement of consistency is fulfilled we can say that the representative assembly expresses physics from the view of quantum mechanics as well as classical physics. From the classical, macroscopic view the basic constituents are on an average distributed in definite numbers over base states. From the microscopic, quantum mechanical view every basic constituent is occupying every base state according to a probability distribution. The ensemble concept of statistical physics thus provides complementary logical descriptions of macroscopic systems in terms of both classical physics and quantum mechanics.

### 3. Micro- and macrophysics of gaseous sample

Let us now put the discussion of the preceding Section into a more concrete form. We shall then consider a macroscopic sample of matter in the gaseous state. In general the constituents of such a sample are molecules, atoms, and ions. We shall confine the discussion to a subsample consisting of one kind of constituents which we shall speak of as "atoms". Our results will apply to any one of such subsamples. From the way we treat this problem it will be obvious how to obtain a description of the whole sample.

Our sample is supposed to be in a stationary state. Energy is pumped into the sample at a steady rate and this energy is emitted from the sample in the form of electromagnetic radiation, photons. Our sample may thus be a spectral lamp or any other steadily shining gaseous body.

Let us then consider the physics of one of the atoms in the macroscopic sample. We shall presuppose that the action by the macroscopic environment on our atom is purely electromagnetic. Then our object of study is a microsystem consisting of one atom in an external electromagnetic field. The macroscopic sample can evidently be described as an assembly of such microsystems.

The physics of the microsystem can be expressed in the formalism of relativistic quantum electrodynamics (QED). This is done in my paper Ref.[5] and I shall here give a brief review of the results of that paper.

The interaction in the microsystem is given by the atomic electron four-current coupling with the four-vector potential of the external field. The field can always be split into two parts in a relativistically covariant fashion. These are a pure radiation field (photon field) and a generalized Coulomb field (electric and magnetic fields of force). The coupling with the radiation field describes the well-known radiative transitions of the atom. The interaction with the Coulomb field causes highly non-radiative transitions of the atom via intermediate bound states. Bound

states are formed by strong coupling of the atomic electron current with the source currents of the external Coulomb field. Transitions among these states might cause emission of weak, continuous radiation resembling so-called Bremsstrahlung.

The quantum mechanical state of the atom is in general a superposition of discrete internal energy eigenstates (states of the free atom and free states perturbed by the Zeemann and Stark effects) and unspecifiable bound states. It turns out that radiative rates of direct transitions between discrete states are overall quenched by the Coulomb forces in comparison to corresponding transitions of the free atom in a pure radiation field. The quenching may be compensated for some transitions by resonant Coulomb force enhancement of radiative transition rates.

The Coulomb interaction thus introduces very important quantum mechanical a priori conditions for the construction of an assembly for the representation of the macroscopic sample. We shall now proceed with this construction and see how these microscopic conditions will be expressed in macroscopic terms.

The principal features of the atom in the microsystem can be stated symbolically in terms of a wave function  $\Phi$  describing a momentary internal atomic state

$$\Phi = \sum c_n \varphi_n + b\psi, \quad (1)$$

where  $\varphi_n$  are orthonormal discrete energy eigenfunctions and  $\psi$  symbolizes bound states.  $\psi$  and  $\Phi$  are not defined with mathematical rigour (it may not be possible to define them in ordinary Hilbert space) but for the benefit of physical interpretation we treat them formally as normalized wave functions with  $\psi$  orthogonal to the  $\varphi$ 's. We thus have

$$(\Phi, \Phi) = \sum |c_n|^2 + |b|^2 = 1. \quad (2)$$

This equation is interpreted by saying that  $|c_n|^2$  is the probability of observing the atom in an eigenstate of energy  $\epsilon_n$ . The probability of observing the atom having definite energy is  $\sum |c_n|^2$  which by Eqn (2) satisfies

$$\sum |c_n|^2 = 1 - |b|^2 \leq 1. \quad (3)$$

Transitions between the states  $\varphi_n$  are coupled with emission and absorption of photons. In neglecting possible but very unlikely radiative transitions within the "state"  $\psi$  we can interpret Eqn (3) as stating that the probability of the atom being observed in a radiative state is smaller than unity.

Suppose we have  $N$  atoms in the macroscopic sample. The momentary internal state of each atom is supposed to be given formally by a definite  $\phi$ . At every instant we thus imagine that the sample is an assembly of  $N$  atoms described microscopically by a set of  $\phi$ 's. A large number of instants in a certain time interval defines an ensemble of such assemblies described by a "superset" of  $\phi$ 's. The average values of  $c_n c_m^*$  and  $|b|^2$  for each atom can then in principle be determined from this superset.

The sample is assumed to be in a stationary state. By this is meant that the macroscopic properties of the sample are determined by well-defined time average measurements. The time averaging is then done over a time interval which is long in comparison to the characteristic periods of the fluctuations of all macroscopic quantities needed for a complete macroscopic description of the sample.

The atoms are moving around randomly in the gaseous sample. This suggests that they are all coupled with the same external field on the time average discussed in the preceding paragraph. This suggestion could be called quasi-macroscopic since it involves neglect of the quantum mechanical uncertainty. This uncertainty might show up in different values for ensemble superset averages of  $c_n c_m^*$  and  $|b|^2$  of different atoms. All this, however, implies that well-defined mean values of these ensemble averages exist when the ensemble is constructed in accordance with the macroscopic conditions for time averaging.

In this way we eventually construct a statistical density matrix  $w_{nm}$  and a statistical density scalar  $1 - e^{-\alpha}$  being the mean values of the ensemble averages of  $c_n c_m^*$  and  $|b|^2$  respectively. The condition expressed by Eqn (2) can now be written

$$\sum w_{nn} = \text{Tr} w = e^{-\alpha} \quad (4)$$

where, of course,  $\alpha \geq 0$ .

The representative assembly for our macroscopic gaseous sample can now be described as follows. The assembly of  $N$  atoms is split into two distinct assemblies. One of these is composed of  $N_R$  atoms which have discrete internal energy values. These atoms can emit and absorb photons by making jumps between the energy levels. The other distinct assembly is formed by  $N_V$  atoms in bound states. This population of atoms is highly non-radiative. The radiative  $N_R$  assembly gives rise to an atomic emission line spectrum while the  $N_V$  atoms create a weak continuous spectral back-ground.

We then have the relations

$$N = N_R + N_V, \quad (5)$$

$$N_R = N \cdot e^{-\alpha}, \quad (6)$$

$$N_R = \sum_j N_j \quad (7)$$

with  $N_j$  being the average population number of the energy level  $\epsilon_j$ . These relations comprise a macroscopic picture of our sample. The distribution  $\{N_j\}$  is in principle defined by the result of experiments designed to observe such a distribution. In other words, the relations (5-7) should be considered statements of interpreting experimental results.

This interpretation is the legitimate basis for the use of concepts like number of atoms on a discrete energy level, number of atoms jumping between such levels, and number of particles in non-radiative intermediate states. As pointed out in preceding context, the microscopic "real" picture is the quantum mechanical one stating that every atom is in all its possible states according to a probability distribution.

The relations (5-7) will thus be used as a starting point for the formulation in terms of statistical physics to describe our macroscopic sample of gaseous matter. We shall devote the next section to the study of pure radiative processes in order to find microscopic conditions that might impose constraints on the radiative distribution  $\{N_j\}$ . In this way the starting point for the statistical physics description will be assumed to be completely settled.

#### 4. Atom in radiation field

Let us now consider the interaction of the atom with the radiation field in our microsystem. We shall then only consider the discrete quasi-free states of the atom, i.e. the possible effect of the Coulomb forces is limited to splitting of discrete levels and influencing radiative transition rates between such levels.

We assume that there exists a spontaneous transition rate  $M_{fi}$  for the down-going jump  $|i\rangle \rightarrow |f\rangle$  under the emission of a photon of energy  $h\nu$  in the initial state. As is well-known the rate of the above transition is

$$P_{fi} = (n+1) M_{fi} \quad (8)$$

when there are  $n$  photons  $h\nu$  in the initial state.

An up-going jump  $|f\rangle \rightarrow |i\rangle$  under absorption of a photon  $h\nu$  is governed by a rate given by  $M_{if}$  times the number of photons initially present.

The two discrete levels are assumed to have statistical weights  $P_i$  and  $P_f$  respectively. According to standard radiation theory [6] we have

$$P_i M_{fi} = P_f M_{if}. \quad (9)$$

We recall that our macroscopic sample is in a stationary state so that the quantities  $P$  and  $M$  of our microscopic system may be looked upon as representative mean values of the assembly of "one atom" microsystems constituting the macroscopic physical system. Again we state that the average influence of the Coulomb forces is assumed to be included in the microscopic quantities  $\epsilon$ ,  $P$  and  $M$ . In this way we may argue that we can use a formulation analogous to the standard theory of a single atom in a pure radiation field when treating radiative jumps of the quasi-free atom between its discrete energy levels in the microsystem.

Let us assume that the microsystem is initially in the atomic eigenstate  $|i\rangle$  with  $n$  photons  $h\nu$ . The transition probability per unit time to the state  $|f\rangle$  with  $n+1$  photons is given by (8).

Since we have  $n+1$  photons with the state  $|f\rangle$  the transition rate back to state  $|i\rangle$  with  $n$  photons will be given by

$$P_{if} = (n+1) M_{if}. \quad (10)$$

Combining (8), (9) and (10) yields

$$\frac{P_i}{P_f} = \frac{P_{if}}{P_{fi}} = \frac{1/P_{fi}}{1/P_{if}}. \quad (11)$$

Since the life-time of a level is equal to the inverse of the rate of transition away from the level, we see from Eqn (11) that the ratio of the life-times equals the ratio of the corresponding statistical weights. This means that the probability of observing the atom in one of its discrete levels is simply proportional to the statistical weight of the level.

Performing this analysis for all pairs of levels connected by direct radiative transitions yields the important result that the atom is in interaction equilibrium with any radiation field when its radiative state is a superposition of the discrete energy eigenstates weighted according to the statistical weights of corresponding energy levels.

Let us now see how Einstein's result of Ref.[2] is obtained in our framework. The atom is assumed to obey the Maxwell-Boltzmann relative probability distribution

$$W_k = P_k \cdot e^{-\epsilon_k/kT} \quad (12)$$

in a constant radiation field, i.e. the energy distribution of photons is fixed. In our notation this means that Eqn (10) is changed into

$$P_{if} = n \cdot M_{if}, \quad (13)$$

which, together with (8) and (9), is identical to Einstein's original relations for the A and B coefficients.

Einstein's equilibrium condition is now expressed by the relation

$$W_i P_{fi} = W_f P_{if} \quad (14)$$

which is claimed to express equality of probability rates of up-going and down-going atomic transitions.

Combining all these equations (8, 9, 12, 13, 14) yields

$$n = \frac{1}{e^{(\epsilon_i - \epsilon_f)/kT} - 1} = \frac{1}{e^{h\nu/kT} - 1}$$

which is Planck's radiation formula. After the assumption of the generalized Maxwell-Boltzmann probability distribution for the atom over internal energy levels this "amazing" Einstein result thus appears as a consequence of neglecting the influence of one photon.

By employing the concept of quantum mechanical state to our microsystem we have found that the probability of observing the atom in a discrete eigenstate of energy is proportional to the statistical weight of the eigenstate. This microscopic a priori condition then suggests that the assembly representing our macroscopic sample can be described macroscopically by

$$N_j = P_j N_R \quad (15)$$

with  $\sum_j P_j = 1$ . Eqn (15) then provides together with Eqns (5-7) the basis for a statistical physics description of our sample. In the next Section we shall use standard combinatorial methods to connect these relations to thermodynamic quantities and determine the value of the constant  $\alpha$ .

### 5. Thermodynamics of stationary gaseous sample.

The macroscopic properties of the sample under study were stated in Section 3. We consider a subsample of one kind of atoms. Energy is conveyed steadily to these atoms by an external agent. This causes emission of spectral radiation at a constant rate from the radiatively active atoms. For convenience we may think of a typical experiment in optical emission spectroscopy - a spectral lamp is shining steadily and the intensities of spectral lines are measured.

We consider only the degree of freedom defined by the internal (electron) states of the atom. With respect to this degree of freedom the atoms have total internal energy  $E$  and entropy  $S$ . We have

$$S = E/T + \text{const.} \quad (16)$$

and (16) will obviously be the one and only possible thermodynamic relation in terms of internal atomic quantities. The electron temperature  $T$  of the atom is defined by (16).

Our sample consists of a fixed number  $N$  of atoms. By Eqn (7) these are split into two distinct populations  $N_V$  and  $N_R$ . The  $N_R$  atoms emit the observed spectral lines. A necessary condition for the steadiness of the spectral intensity is the macroscopic constraint

$$N_R = \sum_j N_j = \text{const.} \quad (17a)$$

Since  $N$  is fixed we then also have by (5)

$$N_V = \text{const.} \quad (17b)$$

The steady state of our sample implies that the internal energy is constant. We then have the auxiliary constraints

$$\sum_j N_j \epsilon_j = \text{const.} \quad (18a)$$

and

$$N_V \bar{\epsilon}_V = \text{const.} \quad (18b)$$

In (18b) we have introduced the average energy  $\bar{\epsilon}_V$  of the non-radiative atoms  $N_V$ . We shall also introduce the average energy  $\bar{\epsilon}$

of the radiative atoms  $N_R$  by the relation

$$N_R \bar{\epsilon} = \sum_j N_j \epsilon_j. \quad (19)$$

Let us then determine the distribution  $\{N_j, N_V\}$  which is most probable under the constraints, i.e. find the maximum of entropy when (17) and (18) are satisfied.

The radiative atoms can be selected in  $\binom{N}{N_R}$  ways from the total number of  $N$  atoms. These  $N_R$  atoms can be distributed in  $N_R! \prod_j 1/N_j!$  ways over the levels  $\epsilon_j$ .

In this last combinatorial the division by  $N_j!$  is motivated by the fact that a permutation of particle labels does not change the physical state.

The a priori probability for an atom of the set  $N_R$  to occupy  $\epsilon_j$  is  $P_j$ . Hence the a priori probability for  $N_j$  atoms to occupy  $\epsilon_j$  will be  $P_j^{N_j}$ . These numbers are then the probabilities by which each way of distribution must be weighted in order to obtain the expression for the probability of the distribution.

All this leads to the following expression for the probability  $W$  of a distribution of our atoms:

$$W = C \binom{N}{N_R} N_R! \prod_j \frac{P_j^{N_j}}{N_j!} = C \frac{N!}{N_V!} \prod_j \frac{P_j^{N_j}}{N_j!},$$

where  $C$  is a normalization constant and the relation (5),  $N = N_R + N_V$ , has been used.

The Stirling formula  $\ln X! = X \ln X/e$  for factorials when  $X \gg 1$  applied to the preceding expression yields

$$\ln W = -N_V \ln \frac{N_V}{N} - \sum_j N_j \ln \frac{N_j}{N P_j} + \ln C. \quad (20)$$

According to Boltzmann this is connected to entropy  $S$  by

$$S = k \ln W. \quad (21)$$

The macroscopic state of the physical system is by Boltzmann's

principle the most probable of all conceivable states. This is the state with maximum entropy. We thus determine the maximum of  $\ln W$  by considering the result of variations  $\delta N$ ,  $\delta N_j$  and  $\delta N_V$  with  $\delta N = \sum \delta N_j + \delta N_V$ . We get from Eqn (20)

$$\delta \ln W = -\delta N_V \ln \frac{N_V}{N} - \sum_j \delta N_j \ln \frac{N_j}{NP_j} \quad (22)$$

A second variation shows that  $\delta^2 \ln W < 0$  which means that any extremum value of  $\ln W$  is a maximum. By putting  $\delta \ln W = 0$  in (22) we thus obtain the condition for maximum of entropy as defined by (21),

$$\delta N_V \ln \frac{N_V}{N} + \sum_j \delta N_j \ln \frac{N_j}{NP_j} = 0. \quad (23)$$

Our constraints (17) and (18) yield the subsidiary conditions

$$\sum_j \delta N_j = 0, \quad \sum_j \delta N_j \epsilon_j = 0, \quad \text{and} \quad \delta N_V = 0$$

for the variations of (23).

Introducing undetermined Lagrange multipliers  $\gamma$ ,  $\alpha$ , and  $\kappa$  we obtain the solution of (23), compatible with the constraints, from

$$-\delta N_V \ln \frac{N_V}{N} - \sum_j \delta N_j \ln \frac{N_j}{NP_j} = \delta N_V \gamma + \sum_j \delta N_j (\alpha + \epsilon_j \kappa). \quad (24)$$

From Eqn (21) we have  $\delta S = k \delta \ln W$  and from Eqn (16)  $\delta S = \delta E/T$ .

Hence,

$$\delta E = kT \delta \ln W. \quad (25)$$

The equations (22), (24), and (25) are valid for arbitrary variations from the steady state at entropy maximum. Let us now limit the variations by imposing the conditions  $\delta \bar{E} = \delta \bar{E}_V = 0$ .

This brings eventually constraint (18b) into proper consideration.

The average energy quantities  $\bar{E}_V$  and  $\bar{E}$  were defined in (18b) and (19). The total energy variation  $\delta E$  may thus be expressed by

$$\delta E = \delta N_V \bar{E}_V + \delta N_R \bar{E} \quad (26)$$

or

$$\delta E = \delta N_V \bar{\epsilon}_V + \sum_j \delta N_j \epsilon_j. \quad (27)$$

In standard formulations of thermodynamics there is usually a term  $\delta N\mu$  that contributes to the energy variation  $\delta E$  by the chemical potential  $\mu$ . Such a potential cannot exist in the present formulation since we consider only internal atomic degrees of freedom.

From equations (17a), (22), (24), and (25) we have

$$\delta E = kT(\delta N_V \gamma + \delta N_R \alpha + \sum_j \delta N_j \epsilon_j \kappa). \quad (28)$$

This expression for  $\delta E$  must be identical to either (26) or (27). Mathematically, of course, any linear combination of the two expressions (26) and (27) could be made identical to (28). That would, however, leave the Lagrange multipliers undetermined.

In the previous Section we found that the microscopic a priori conditions suggested the distribution (15), i.e.  $N_j = N_R P_j$ , for the radiative atoms. This suggestion will be firmly established in the next Section. All this leads to the conclusion that Eqn (28) must be identical to Eqn (26). Thus the multiplier  $\kappa$  is zero and

$$\alpha = \frac{\bar{\epsilon}}{kT},$$

$$\gamma = \frac{\bar{\epsilon}_V}{kT}.$$

From Eqn (24) we then get

$$N_j = P_j N e^{-\bar{\epsilon}/kT} = P_j N_R, \quad (29)$$

$$N_V = N e^{-\bar{\epsilon}_V/kT} = N(1 - e^{-\bar{\epsilon}/kT}), \quad (30)$$

where the second equal sign steps follow from using the equations (5), (6) and (7).

Using Eqn (19) we have

$$N_R \bar{\epsilon} = \sum_j \epsilon_j N_j = \sum_j P_j \epsilon_j N_R$$

with the last step following from (29).

We thus have

$$\bar{\epsilon} = \sum_j P_j \epsilon_j \quad (31)$$

i.e.  $\bar{\epsilon}$  is equal to the arithmetic mean of the values of all discrete energy levels each counted as many times as degeneracy implies. Since usually a very large part of the levels is close to the ionization level of an atom,  $\bar{\epsilon}$  may in practice be well approximated by the value of the ionization energy.

Returning to (30) we find

$$\bar{\epsilon}_V = \bar{\epsilon} - kT \ln(e^{\bar{\epsilon}/kT} - 1) \quad (32)$$

which may be interpreted as stating that the average Coulomb interaction energy is  $-kT \ln(e^{\bar{\epsilon}/kT} - 1)$ .

In concluding this Section we may state that with our present formulation of the thermodynamics we have obtained complete consistency with the microscopic a priori constraints imposed by the Coulomb forces and the radiative interaction.

## 6. Intensity of spectral emission lines.

Suppose the average probability per unit time for one atom in our sample of making a radiative transition between the discrete states  $|j\rangle$  and  $|k\rangle$  is  $A_{kj}$ . This is in principle a mean value of the microscopic a priori transition rate that was denoted by  $P_{kj}$  in Section 4. We have

$$P_j A_{kj} = P_k A_{jk}. \quad (33)$$

When  $\epsilon_j > \epsilon_k$  the transition  $j \rightarrow k$  will be accompanied by the emission of a photon  $h\nu_{jk}$

$$h\nu_{jk} = \epsilon_j - \epsilon_k. \quad (34)$$

If the average number of atoms on the energy level  $\epsilon_j$  is  $N_j$  one would expect the total average number of jumps  $j \rightarrow k$  per unit time to be simply  $N_j A_{kj}$ , i.e. the accompanying rate of energy emission  $I'_{jk}$  would be

$$I'_{jk} = h\nu_{jk} N_j A_{kj} \quad (35)$$

The emission formula (35) is based on the assumption that the action of the macroscopic system is simply the sum of the actions of the microscopic subsystems. This is almost certainly valid when there are no macroscopic constraints governing the physical system. When there are such constraints we must determine by probability analysis the most probable way of macroscopic action which is consistent with the a priori microscopic constraints. In doing so we extend Boltzmann's fundamental maximum probability principle: The development of a macroscopic physical system almost always occurs in the most probable of all conceivable ways consistent with the constraining conditions for the system. The words "almost always" express that there are very small non-zero probabilities of odd events happening in Nature.

The importance of taking macroscopic constraints into consideration may be illustrated by the following imagined shooting experiment. Suppose a marksman practising rifle-shooting at a standard target at a certain range hits the target with 50% of his shots - the average result of ten shots thus being five

bullet-holes in the target. Now suppose ten marksmen of this very same shooting skill simultaneously fire one shot each at a common single target. What will the average number of target hits be of such collective rounds of ten shots? The correct answer is not the number five. The number must be smaller than five because now each bullet competes with nine others in its flight towards the target. The caliber of the bullets determines a constraint at the collective shooting which is absent at the individual shooting. When firing the shots one by one the holes in the target can overlap while the holes from bullets arriving simultaneously at the target cannot overlap. At the collective shooting rounds the whole target area is not accessible to a bullet.

This experiment might be considered a parabolic description of our physical problem. The counting of bullet-holes corresponds to our counting of emitted photons. Answering the shooting quiz by the number five is equivalent to writing the formula (35) for photons emitted from the spectral sample. Completion of the parabolic interpretation could imply that the constraint of a fixed rate of energy emission from the sample would yield a formula predicting a rate of emission differing from (35). We shall see that this is indeed the result of the following probability analysis.

Let us consider the energy levels  $\epsilon_j$  with average numbers  $N_j$  of atoms. Atoms jumping away from a level are constantly replaced by atoms jumping to this level. In this way the numbers  $N_j$  are fixed in our steadily shining sample. Every single jump from  $\epsilon_j$  may thus be considered being made by one atom out of  $N_j$  atoms.

Suppose the number of down-going transitions  $j \rightarrow k$  is  $N_{kj}$  in the time interval  $\Delta t$ . Assuming that these transitions occur independently we find that the probability of this event is proportional to  $Q_{kj}$  given by

$$Q_{kj} = \binom{N_j}{N_{kj}} \cdot (A_{kj} \Delta t)^{N_{kj}}.$$

We can always adjust  $\Delta t$  so that  $N_k \gg N_{kj} \gg 1$  which permits us

to write  $Q_{kj}$  in the form

$$Q_{kj} = \frac{(N_j A_{kj} \Delta t)^{N_{kj}}}{N_{kj}!} . \quad (36)$$

This transition probability might appear strange since it depends on a power of  $\Delta t$  instead of accustomed linear dependence. To avoid possible confusion on this point one must bear in mind that  $Q_{kj}$  is the probability for exactly  $N_{kj}$  transitions in time  $\Delta t$ .

The probability for all transitions  $\{N_{kj}\}$  during  $\Delta t$  will be

$$Q = \prod_{j=2}^n \prod_{k=1}^j Q_{kj} \quad (37)$$

where  $n$  denotes the highest energy level.

If the rate of energy emission is  $W$ , the energy emitted by the atoms in time  $\Delta t$  is

$$W\Delta t = \sum_{j=2}^n \sum_{k=1}^j N_{kj} (\epsilon_j - \epsilon_k) . \quad (38)$$

We shall now determine the values of  $N_{kj}$  yielding the most probable transition pattern compatible with a fixed rate of energy emission.

We have from (37) and (36)

$$\ln Q = \sum_{j>k} \ln Q_{kj} = \sum_{j>k} N_{kj} \ln \frac{N_j A_{kj} \Delta t}{N_{kj}/e}$$

from which we obtain

$$\delta \ln Q = \sum_{j>k} \delta N_{kj} \ln \frac{N_j A_{kj} \Delta t}{N_{kj}} . \quad (39)$$

A maximum of  $Q$  is attained when  $\delta \ln Q = 0$ . With no constraining condition for the variations  $\delta N_{kj}$  we would thus by (39) have this maximum when  $N_{kj} = N_j A_{kj} \Delta t$ , which is the emission formula (35). In our approach, however, the constraint  $\delta(W\Delta t) = 0$  must be satisfied together with  $\delta \ln Q = 0$ .

By (38) and (39) we thus seek a solution  $\{N_{kj}\}$  of the equation  $\delta \ln Q = 0$ , i.e.

$$\sum_{j>k} \delta N_{kj} \ln \frac{N_j A_{kj} \Delta t}{N_{kj}} = 0,$$

with the variations  $\delta N_{kj}$  subject to

$$\sum_{j>k} \delta N_{kj} (\epsilon_j - \epsilon_k) = 0.$$

The sought solution is

$$N_{kj} = \Delta t N_j A_{kj} e^{-B(\epsilon_j - \epsilon_k)} \quad (40)$$

where  $B$  is a Lagrange multiplier.

Inserting expression (40) for  $N_{kj}$  into Eqn (39) yields

$$\delta \ln Q = B \sum_{j>k} \delta N_{kj} (\epsilon_j - \epsilon_k) = B \sum_{j>k} \delta N_{kj} h\nu_{jk} \quad (41)$$

valid for arbitrary  $\delta N_{kj}$ . If we assume that entropy  $S_p$  can be related to the photons with total energy  $\sum N_{kj} h\nu_{jk}$  and temperature  $T_p$  we have

$$\delta S_p = \frac{1}{T_p} \sum_{j>k} \delta N_{kj} h\nu_{jk}. \quad (42)$$

The photon distribution  $\{N_{kj}\}$  given by (40) was obtained by determining the maximum of the probability function  $Q$ . By Boltzmann's fundamental principle this suggests the relation

$$\delta S_p = k \delta \ln Q.$$

Comparison with (41) and (42) leads to

$$B = \frac{1}{kT_p}. \quad (43)$$

Suppose we consider the variation expressed by (42) being a reversible fluctuation from the stationary state of the sample. The entropy of the atoms would then change according to

$$\delta S = \frac{1}{T} \sum_i \delta N_i \epsilon_i \text{ with}$$

$\delta N_i = \sum_{j>i} \delta N_{ij} - \sum_{k<i} \delta N_{ki}$ . Hence,

$$\delta S = \frac{1}{T} \sum_{j>k} \delta N_{kj} (\epsilon_k - \epsilon_j). \quad (44)$$

Since we consider a reversible (adiabatic) fluctuation the total entropy of the  $[N_i]$  atoms and the  $[N_{kj}]$  photons must not change. Thus

$$\delta S + \delta S_p = 0$$

which is valid according to (42) and (44) if  $T_p = T$ . Eqn (43) then becomes  $\beta = 1/kT$  and Eqn (40) yields the photon emission formula

$$N_{kj} = \Delta t N_j A_{kj} e^{-h\nu_{jk}/kT}. \quad (45)$$

We recall that our formula (45) is the result of the assumption that the transitions are independent. In terms of relativity theory these events of transitions have space-like separation, i.e. no physical signal can connect them. We may thus say that out of a total set of transitions  $I_{kj}$  we have selected a set of causally unconnected transitions  $N_{kj}$ . Evidently such a selection can always be made.

A well-known mechanism of causal connection is the process of stimulated emission. Suppose causal connections between transitions give rise to a number  $S_{kj}$  of extra transitions besides  $N_{kj}$  in the time interval  $\Delta t$ . The total number of transitions is then

$$I_{kj} = N_{kj} + S_{kj}. \quad (46)$$

The number of ways  $R_{kj}$  for this division of  $I_{kj}$  is

$$R_{kj} = \binom{I_{kj}}{S_{kj}} = \binom{I_{kj}}{N_{kj}} = \frac{(N_{kj} + S_{kj})!}{N_{kj}! S_{kj}!}. \quad (47)$$

The trivial symmetry of  $R_{kj}$  with respect to  $S_{kj}$  and  $N_{kj}$  exhibited in (47) proves that the division (46) of  $I_{kj}$  is quite unambiguous. Eqn (47) expresses that the number of ways for selecting the independent transitions equals the number of ways for all arbitrarily dependent extra transitions. There is thus no logical

possibility for the existence of further extra transitions besides  $S_{kj}$ .

From (47) we get by Stirling's rule

$$\ln R_{kj} = \ln \frac{(N_{kj} + S_{kj})!}{N_{kj}! S_{kj}!} = (N_{kj} + S_{kj}) \ln(N_{kj} + S_{kj}) - S_{kj} \ln S_{kj} - N_{kj} \ln N_{kj}.$$

Variations  $\delta S_{kj}$  with  $\delta N_{kj} = 0$  yield

$$\delta \ln R_{kj} = \delta S_{kj} \ln \left(1 + \frac{N_{kj}}{S_{kj}}\right). \quad (48)$$

The probability of  $S_{kj}$  extra transitions besides the transitions  $N_{kj}$  already determined by (45) will be proportional to

$$R = \prod_{j>k} R_{kj}. \quad (49)$$

The maximum probability principle is now applied to  $R$  as follows. Performing variations  $\delta S_{kj}$  subject to the constraint of a fixed rate of energy emission,

$$\sum_{j>k} \delta S_{kj} h\nu_{jk} = 0,$$

yields by (48) and (49) the equation

$$\delta \ln R = \sum_{j>k} \delta S_{kj} \ln \left(1 + \frac{N_{kj}}{S_{kj}}\right) = 0$$

for a maximum of  $R$ . We thus obtain from these two equations

$$\ln \left(1 + \frac{N_{kj}}{S_{kj}}\right) = \beta h\nu_{jk}. \quad (50)$$

The same thermodynamical arguments as were used to obtain the emission formula (45) will also now show that the Lagrange multiplier  $\beta$  equals  $1/kT$ .

From Eqn (50) we obtain

$$S_{kj} = \frac{N_{kj}}{e^{h\nu_{jk}/kT} - 1},$$

and, after using (45), we finally obtain the formula for total emission

$$I_{kj} = N_{kj} + S_{kj} = \frac{\Delta t N_j A_{kj}}{e^{h\nu_{jk}/kT} - 1}. \quad (51)$$

The up-going transitions  $I_{jk}$  are supposed to be accompanied by absorption of energy quanta from the field created by the external pumping agent. These quanta must have energy  $h\nu_{jk}$  and may thus be counted in the same way as the emitted photons. In effect, photons are emitted from the pump, absorbed and emitted again by the atoms. We may then consider the up-going transitions as being time-reversed down-going transitions. Since the interaction is purely electromagnetic we have invariance under time-reversal [6].

All this means that the number of up-going transitions in time  $\Delta t$  will be given by (51) with  $j$  and  $k$  interchanged. The steady state condition of equal rates of down-going and up-going transitions, i.e.  $I_{kj} = I_{jk}$ , then requires

$$N_k A_{jk} = N_j A_{kj}. \quad (52)$$

By comparing (52) with the standard relation  $P_k A_{jk} = P_j A_{kj}$  we find

$$\frac{N_k}{N_j} = \frac{P_k}{P_j}$$

which is consistent with Eqn (29);  $N_i = N_R P_i$ . The steady state condition together with time-reversal invariance thus provide an alternative way of concluding that the discrete energy levels are populated in proportion to their statistical weights.

Our results from Section 5 - (29) and (31) - together with Eqn (51) of this Section may now be summarized in a formula for the intensity of optical spectral emission lines in units of energy per unit time:

$$I(h\nu_{jk}) = \frac{BNh\nu_{jk} P_j A_{kj} e^{-\bar{E}/kT}}{e^{h\nu_{jk}/kT} - 1}, \quad (53)$$

where  $B$  is a parameter depending on properties of the experimental design.

## 7. Discussion of photon emission

The a priori number of atomic jumps  $j \rightarrow k$  is  $N_j A_{jk} \Delta t$  and the actually occurring number of jumps is  $I_{kj}$ . The ratio  $I_{kj}/N_j A_{jk} \Delta t$  is then the average number of times that each a priori jump occurs in time  $\Delta t$ . The transition probability rate  $A_{kj}$  is an average of all possible momentarily and locally attained values. This implies that the a priori jumps actually occur various numbers of times deviating from the average number  $I_{kj}/N_j A_{jk} \Delta t$ . Instead of an even distribution of actual jumps  $I_{kj}$  over the a priori jumps  $N_j A_{jk} \Delta t$  we must then consider all possible distributions. The total number of ways of such distributions is

$$D_{kj} = \frac{(N_j A_{jk} \Delta t - 1 + I_{kj})!}{(N_j A_{jk} \Delta t - 1)! I_{kj}!} \quad (54)$$

This rather tentative reasoning has thus led to the well-known combinatorial  $D_{kj}$  for Bose-Einstein particles  $I_{kj}$ . If we neglect  $-1$  in (54) and form the variational equation for  $\ln D = \sum \ln D_{kj}$  in the usual manner we obtain

$$\delta \ln D = \sum_{j>k} \delta I_{kj} \ln \left( 1 + \frac{N_j A_{jk} \Delta t}{I_{kj}} \right). \quad (55)$$

This variation applied to the pertaining emitted photons is described by

$$\delta(W\Delta t) = \sum_{j>k} \delta I_{kj} h\nu_{jk}. \quad (56)$$

The maximum of  $\ln D$  at fixed energy emission is obtained when  $\delta \ln D$  and  $\delta(W\Delta t)$  are both zero. This gives the total emission formula (51) for  $I_{kj}$ . We may thus assume that the entropy  $S(\Delta t)$  of the photons emitted in the time interval  $\Delta t$  is

$$S(\Delta t) = k \ln D. \quad (57)$$

At entropy maximum we thus have the thermodynamic relation

$$\delta S(\Delta t) = \frac{1}{T} \delta(W\Delta t), \quad (58)$$

which by (56) and (57) is equivalent to

$$\delta \ln D = \frac{1}{kT} \sum_{j>k} \delta I_{kj} h\nu_{jk} \quad (59)$$

with  $\delta \ln D$  given by (55).

With the simplification  $N_j A_{kj} \Delta t = Z_{kj}$  we have

$$\ln D = \sum_{j>k} \left[ (Z_{kj} + I_{kj}) \ln \left( 1 + \frac{Z_{kj}}{I_{kj}} \right) - Z_{kj} \ln \frac{Z_{kj}}{I_{kj}} \right]. \quad (60)$$

With regard to certain experimental results to be discussed in the concluding Section we shall consider a generalized variation of  $\ln D$ . Eqn (60) yields

$$\delta \ln D = \sum_{j>k} \left[ \delta I_{jk} \ln \left( 1 + \frac{Z_{kj}}{I_{kj}} \right) + \delta Z_{kj} \ln \left( 1 + \frac{I_{kj}}{Z_{kj}} \right) \right].$$

If  $Z_{kj} \gg I_{kj}$  and the values of  $\{\delta Z_{kj}\}$  are reasonably bounded we will obtain

$$\delta \ln D = \sum_{j>k} \delta I_{kj} \ln \frac{Z_{kj}}{I_{kj}}. \quad (61)$$

We thus see that this generalized variation of  $\ln D$  may be expressed in variations of the photon numbers  $I_{kj}$  only. Because of this and since the definition of photon entropy in Eqn (57) has not been violated the relation (61) is compatible with (58) and (59). Thus we have

$$\sum_{j>k} \delta I_{kj} \ln \frac{Z_{kj}}{I_{kj}} = \sum_{j>k} \delta I_{kj} h\nu_{jk} / kT$$

which implies the photon emission formula

$$I_{kj} = Z_{kj} e^{-h\nu_{jk}/kT}. \quad (62)$$

The condition  $Z_{kj} \gg I_{kj}$  limits the validity of Eqn (62) to cases where  $h\nu_{jk} \gg kT$ . This condition alone yields Eqn (62) directly from the photon emission formula (51).

The point of our roundabout derivation of formula (62) is the suggestion that the formula is valid for quite general atomic distributions  $\{N_j\}$ . Our previous assumption of a steady state of the spectral sample was not used to derive (62). Hence, this result could apply to samples with fluctuations of the number of

particles as well as of the external energy pumping rate. Our "roundabout" derivation indicates that this presupposes properly bounded fluctuations during the photon registration time  $\Delta t$  so that meaningful mean values of the quantities  $T$ ,  $N_j$ , and  $A_{kj}$  then exist. All this might be summarized bluntly in stating again that photon emission "always" occurs in the most probable way.

## Conclusion

The present theory of atomic spectral emission was presented in outline at the 1984 FACSS meeting [7]. The work was initiated by experimental observations which indicated that spectral line intensity fluctuations depend strongly on wave length. These observations were made by B. Thelin and were first reported in connection with the theoretical presentation in 1984 [8].

Thelin's method of fluctuation analysis is used in [9] to demonstrate exponential dependence on  $h\nu$  of spectral intensity, and evidence for such dependence on  $\bar{\epsilon} + h\nu$  is given by Thelin in [10, 11, 12,]. In these papers the intensity formula (53) is assumed to be well approximated by

$$I = C e^{- (J+h\nu)/kT}$$

with the ionization energy  $J = \bar{\epsilon}$ .

The analysis method is based on study of the fluctuations of spectral line intensity ratios obtained from repeated simultaneous measurements of various spectral lines.

Strong evidence for formula (53) was obtained by analyzing tabulated data for electric dipole emission lines [13]. This work is presented in more detail in Ref. [14], where also a strict mathematical derivation of Thelin's analysis method is given.

The fluctuation method of analysis has provided evidence for the validity of formula (62) in the study of auroral emissions [15]. In these observations the auroral spectral sample is very large and is subject to fluctuations in size, electron temperature, and external energy input. Arguments for the validity of formula (62) in such a turbulent case were discussed in Section 7. We may once again discuss this and consider the result of variation of

$$I = Z e^{-h\nu/kT}$$

by writing

$$\frac{\delta I}{I} = \frac{\delta Z}{Z} - \frac{h\nu}{k} \delta T^{-1}.$$

From this expression we see that in case  $h\nu \gg kT$  the quantity  $\left| \frac{h\nu}{k} \delta T^{-1} \right| = \frac{h\nu}{kT} \left| \frac{\delta T}{T} \right|$  might be the dominating source of relative intensity fluctuations, since we may assume that  $\left| \frac{\delta T}{T} \right|$  and  $\left| \frac{\delta Z}{Z} \right|$  are of equal orders of magnitude.

Results from analyses of optical emission data from expanding barium clouds released by rockets in the upper atmosphere also support the suggestion that the intensity of these emissions depends mainly on an exponential function of  $h\nu$  [16].

All this experimental evidence supports convincingly the new atomic spectral intensity formula. Although the formula is new, the theoretical arguments used to obtain it cannot be considered quite new. The theory presented here seems to possess much strength since its foundation consists of well-known and well-established basic principles of physics.

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