International Journal of Theoretical Physics, Vol. 33, No. 7, 1994

Theory of Atomic Spectral Emission Intensity

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Received June 11, 1993

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, electrodynamics, and statistical physics. Quantum rules lead to revision of the conventional principle of local thermal equilibrium of matter and radiation. Study of electrodynamics suggests absence of spectral emission from fractions of the numbers of atoms and ions in a plasma due to radiative inhibition caused by electromagnetic force fields. Statistical probability methods are extended by the statement: A macroscopic physical system develops in the most probable of all conceivable ways consistent with the constraining conditions for the system. The crucial role of statistical physics in transforming quantum logic into common sense logic is stressed. The theory is strongly supported by experimental evidence.

1. 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, in 1859, introduced the statistical concept of distribution function. Boltzmann, in 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 in 1902.

The embryo of quantum statistical physics was created when Planck in 1900 presented his blackbody radiation formula. Einstein in 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 (Kuhn, 1978).

Bohr's 1915 theory of the atom postulated discrete internal energy levels, and spectral lines were explained by light-quantum emissions with

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0020-7748/94/0700-1479$07.00/0

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 used by Einstein in 1916 to give what seems to be the very first description of a macroscopic physical system in a quantum statistical physics formulation.

In this work Einstein (1917) 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 ε_n was considered and the atoms of a gaseous sample were assumed to populate the levels n in proportion to $W_n = P_n \exp(-\varepsilon_n/kT)$ 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 upgoing photon-absorbing atomic jumps and of downgoing 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 (Dirac, 1930). The statement of the relationship of these fundamental atomic constants more than 10 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 (Herzberg, 1944). This is identical to one of Einstein's (1917) original assumptions 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 semiclassically 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 constituent 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. This will be the basis of a description of the macroscopic sample as an assembly of such microsystems.

The main subject of this paper is intensity of spectral lines. Spectral line emission occurs when the atom makes jumps from higher to lower internal energy eigenstates. We may therefore simply consider the internal states of the atom only, neglecting kinematic effects resulting from motion of the atom. The interaction of the atom with the external field may then be described by the internal atomic electron four-current (electric current and charge) coupling with the external electromagnetic field. Details of this description in the framework of quantum electrodynamics are studied in Yngström (1988).

The electromagnetic field can always be split into two separate parts in a relativistically covariant manner. These are a pure radiation field (photons) and a generalized Coulomb field (electric and magnetic fields of force). The well-known radiative transitions of the atom are caused by the coupling of the atomic electrons with the radiation field.

The generalized Coulomb interaction is described by the coupling of the atomic electron four-current with the four-currents of the sources of the external field. When this coupling is weak the internal atomic energy eigenstates are perturbed by the well-known Zeeman and Stark effects. In case the coupling becomes strong one may think of the atom as having formed compound states with ambient particles (electrons, ions, and atoms). This picture of the Coulomb interaction appears perhaps best in collisional processes. In contrast to photon interaction, the Coulomb interaction is not instantaneous. In inelastic collisions the atom is carried from one energy eigenstate to another in some time interval. During this time the atom passes through intermediate transitional states with unobservable internal energy.

All this means that the spectral emission from the atom is quenched. Since the sum of all transition probabilities from a state is unity, the generalized Coulomb force transitions compete with the spectral transitions. The unit value of the total sum of spectral transition probabilities from an internal energy eigenstate of the atom in a pure radiational external field is decreased by the value of the sum of Coulomb transition probabilities in a general external electromagnetic field.

Quenching of spectral emission intensity has been observed in various plasma experiments. In a recent report (Chung *et al.*, 1989) references to contemporary and earlier work on quenching phenomena are discussed. In most papers quenching is attributed to changing spontaneous emission probability rate. In this paper quenching is claimed to result from competition between transition modes. The radiative rates of direct transitions between atomic discrete states are overall quenched by the Coulomb forces in comparison to the transition rates 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.

Photon emission may occur during the Coulomb transitions. This emission is of higher order than the spectral emission. Emission from intermediate transitional atomic states should thus be quite weak and one may hence also speak of these states as being nonradiative.

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 Φ describing a momentary internal atomic state

$$\Phi = \sum c_n \varphi_n + b\psi \tag{1}$$

where φ_n are orthonormal discrete energy eigenfunctions and ψ symbolizes transitional states. ψ and Φ are not defined with mathematical rigor (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 ψ orthogonal to the φ's. We thus have

$$(\Phi, \Phi) = \sum |c_n|^2 + |b|^2 = 1 \tag{2}$$

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

$$\sum |c_n|^2 = 1 - |b|^2 \leq 1 \tag{3}$$

Transitions between the states φ_n are coupled with emission and absorption of photons. In neglecting possible but very unlikely radiative transitions within the "state" ψ we can interpret equation (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 Φ. At every instant we thus imagine that the sample is an assembly of N atoms described microscopically by a set of Φ's. A large number of instants in a certain time interval defines an ensemble of such assemblies described by a "superset" of Φ'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 quasimacroscopic 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 $1 - e^{-\alpha}$ as the mean values of the ensemble averages of $c_n c_m^*$ and $|b|^2$, respectively. The condition expressed by equation (3) can now be written

$$\sum w_{nn} = \mathrm{Tr}\, w = e^{-\alpha} \tag{4}$$

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 intermediate transitional states. The radiative N_R assembly gives rise to an atomic emission line spectrum, while the N_V atoms may be termed nonradiative in disregard of possible interactions with emission of a weak continuous spectral background. We then have

$$N = N_R + N_V \tag{5}$$

$$N_R = Ne^{-\alpha} \tag{6}$$

$$N_R = \sum_j N_j \tag{7}$$

with N_j being the average population number of the energy level ε_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 nonradiative intermediate states. As pointed out in the 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 quasifree 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 downgoing 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

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

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

An upgoing 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 (Herzberg, 1944), we have

$$P_i M_{fi} = P_f M_{if} \tag{9}$$

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 ε, 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 quasifree 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

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

Combining (8)–(10) yields

$$\frac{P_i}{P_f} = \frac{P_{if}}{P_{fi}} = \frac{1/P_{fi}}{1/P_{if}} \tag{11}$$

Since the lifetime of a level is equal to the inverse of the rate of transition away from the level, we see from equation (11) that the ratio of the lifetimes 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 (1917) result is obtained in our framework. The atom is assumed to obey the Maxwell–Boltzmann relative probability distribution

$$W_k = P_k\, e^{-\varepsilon_k/kT} \tag{12}$$

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

$$P_{if} = nM_{if} \tag{13}$$

which together with (8) and (9) are identical to Einstein's original relations for the *A* and *B* coefficients. Einstein's equilibrium condition is now expressed by the relation

$$W_i P_{fi} = W_f P_{if} \tag{14}$$

which is claimed to express the equality of probability rates of upgoing and downgoing atomic transitions.

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

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

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

$$N_j = P_j N_R \tag{15}$$

with $\sum_j P_j = 1$. Equation (15) then provides together with equations (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 α.

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 atom. Energy is conveyed steadily to these atoms by an external agent. This causes spontaneous 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

$$S = E/T + \text{const} \tag{16}$$

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 equation (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

$$N_R = \sum_j N_j = \text{const} \tag{17a}$$

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

$$N_V = \text{const} \tag{17b}$$

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

$$\sum_j N_j \varepsilon_j = \text{const} \tag{18a}$$

and

$$N_V \bar{\varepsilon}_V = \text{const} \tag{18b}$$

In (18b) we have introduced the average energy $\bar{\varepsilon}_V$ of the nonradiative atoms N_V. We shall also introduce the average energy $\bar{\varepsilon}$ of the radiative atoms N_R by the relation

$$N_R \bar{\varepsilon} = \sum_j N_j \varepsilon_j \tag{19}$$

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 ε_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 ε_j is P_j. Hence the *a priori* probability for N_j atoms to occupy ε_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

$$\ln W = -N_V \ln \frac{N_V}{N} - \sum_j N_j \ln \frac{N_j}{NP_j} + \ln C \tag{20}$$

According to Boltzmann this is connected to entropy S by

$$S = k \ln W \tag{21}$$

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 δN, δN_j, and δN_V with $\delta N = \sum \delta N_j + \delta N_V$. We get from equation (20)

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

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),

$$\delta N_V \ln \frac{N_V}{N} + \sum_j \delta N_j \ln \frac{N_j}{NP_j} = 0 \tag{23}$$

Our constraints (17) and (18) yield the subsidiary conditions $\sum_j \delta N_j = 0$, $\sum_j \delta N_j \varepsilon_j = 0$, and $\delta N_V = 0$ for the variations of (23).

Introducing undetermined Lagrange multipliers γ, α, and κ, we obtain the solution of (23), compatible with the constraints, from

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

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

$$\delta E = kT\, \delta \ln W \tag{25}$$

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 $\delta\bar{\varepsilon} = \delta\bar{\varepsilon}_V = 0$. This brings eventually constraint (18b) into proper consideration.

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

$$\delta E = \delta N_V \bar{\varepsilon}_V + \delta N_R \bar{\varepsilon} \tag{26}$$

or

$$\delta E = \delta N_V \bar{\varepsilon}_V + \sum_j \delta N_j \varepsilon_j \tag{27}$$

In standard formulations of thermodynamics there is usually a term $\delta N \mu$ that contributes to the energy variation δE by the chemical potential μ. Such a potential is not defined in the present formulation since we consider only internal atomic degrees of freedom. On the other hand, we might interpret $\bar{\varepsilon}_V$ as playing the role of μ for the atoms N_V.

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

$$\delta E = kT\left(\delta N_V \gamma + \delta N_R \alpha + \sum_j \delta N_j \varepsilon_j \kappa \right) \tag{28}$$

This expression for δE 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. Together with equation (19) this implies that the constraints (17a) and (18a) are equivalent. All this leads to the conclusion that equation (28) must be identical to equation (26). Thus the multiplier κ is zero and

$$\alpha = \frac{\bar{\varepsilon}}{kT}$$

$$\gamma = \frac{\bar{\varepsilon}_V}{kT}$$

From equation (24) we then get

$$N_j = P_j N e^{-\bar{\varepsilon}/kT} = P_j N_R \tag{29}$$

$$N_V = N e^{-\bar{\varepsilon}_V/kT} = N(1 - e^{-\bar{\varepsilon}/kT}) \tag{30}$$

where the second equal signs follow from using equations (5)–(7).

Using equation (19), we have

$$N_R \bar{\varepsilon} = \sum_j \varepsilon_j N_j = \sum_j P_j \varepsilon_j N_R$$

with the last step following from (29).

We thus have

$$\bar{\varepsilon} = \sum_j P_j \varepsilon_j \tag{31}$$

i.e., $\bar{\varepsilon}$ 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 are close to the ionization level of an atom, $\bar{\varepsilon}$ may in practice be well approximated by the value of the ionization energy.

Returning to (30), we find

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

which may be interpreted as stating that the average Coulomb interaction energy is $-kT \ln[\exp(\bar{\varepsilon}/kT) - 1]$. 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

$$P_j A_{kj} = P_k A_{jk} \tag{33}$$

When $\varepsilon_j > \varepsilon_k$ the transition $j \to k$ will be accompanied by the emission of a photon $h\nu_{jk}$,

$$h\nu_{jk} = \varepsilon_j - \varepsilon_k \tag{34}$$

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

$$I'_{jk} = h\nu_{jk} N_j A_{kj} \tag{35}$$

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 nonzero 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 practicing 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 toward 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 ε_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 ε_j may thus be considered being made by one atom out of N_j atoms.

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

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

This transition probability might appear strange since it depends on a power of Δt instead of the 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 Δt.

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

$$Q = \prod_{j=1}^{n} \prod_{k=1}^{j} Q_{kj} \tag{37}$$

where n denotes the highest energy level.

If the rate of energy emission is W, the energy emitted by the atoms in time Δt is

$$W\Delta t = \sum_{j=2}^{n} \sum_{k=1}^{j} N_{kj}(\varepsilon_j - \varepsilon_k) \tag{38}$$

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

$$\delta \ln Q = \sum_{j>k} \delta N_{kj} \ln \frac{N_j A_{kj}\,\Delta t}{N_{kj}} \tag{39}$$

A maximum of Q is attained when $\delta \ln Q = 0$. With no constraining condition for the variations δN_{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 δN_{kj} subject to

$$\sum_{j>k} \delta N_{kj}(\varepsilon_j - \varepsilon_k) = 0$$

The sought solution is

$$N_{kj} = \Delta t\, N_j A_{kj}\, e^{-\beta(\varepsilon_j - \varepsilon_k)} \tag{40}$$

where β is a Lagrange multiplier. Inserting expression (40) for N_{kj} into equation (39) yields

$$\delta \ln Q = \beta \sum_{j>k} \delta N_{kj}(\varepsilon_j - \varepsilon_k) = \beta \sum_{j>k} \delta N_{kj} h\nu_{jk} \tag{41}$$

valid for arbitrary δN_{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

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

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

$$\beta = \frac{1}{kT_p} \tag{43}$$

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

$$\delta S = \frac{1}{T} \sum_i \delta N_i \varepsilon_i$$

with

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

Hence

$$\delta S = \frac{1}{T} \sum_{j>k} \delta N_{kj}(\varepsilon_k - \varepsilon_j) \tag{44}$$

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 $T_p = T$. Equation (43) then becomes $\beta = 1/kT$ and equation (40) yields the photon emission formula

$$N_{kj} = \Delta t N_j A_{kj}\, e^{-h\nu_{jk}/kT} \tag{45}$$

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 spacelike 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 Δt. The total number of transitions is then

$$I_{kj} = N_{kj} + S_{kj} \tag{46}$$

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

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

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. Equation (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

$$\begin{aligned} \ln R_{kj} &= \ln \frac{(N_{kj} + S_{kj})!}{N_{kj}!\, S_{kj}!} \\ &= (N_{kj} + S_{kj}) \ln(N_{kj} + S_{kj}) - S_{kj} \ln S_{kj} - N_{kj} \ln N_{kj} \end{aligned}$$

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

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

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

$$R = \prod_{j>k} R_{kj} \tag{49}$$

The maximum probability principle is now applied to R as follows. Performing variations δS_{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

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

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

From equation (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

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

The steady-state condition of equal rates of downgoing and upgoing transitions, i.e., $I_{kj} = I_{jk}$, implies by (51)

$$N_k A_{jk} = N_j A_{kj} \tag{52}$$

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 equation (29); $N_i = N_R P_i$. The steady-state condition thus provides 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 equation (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:

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

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

7. DISCUSSION OF PHOTON EMISSION

The *a priori* number of atomic jumps $j \to k$ is $N_j A_{kj}\, \Delta t$ and the actually occurring number of jumps is I_{kj}. The ratio $I_{kj}/N_j A_{kj}\, \Delta t$ is then the average number of times that each *a priori* jump occurs in time Δt. 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 $I_{kj}/N_j A_{kj}\,\Delta t$. Instead of an even distribution of actual jumps I_{kj} over the *a priori* jumps $N_j A_{kj}\,\Delta t$ we must then consider all possible distributions. The total number of ways of such distributions is

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

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

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

This variation applied to the pertaining emitted photons is described by

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

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 Δt is

$$S(\Delta t) = k \ln D \tag{57}$$

At entropy maximum we thus have the thermodynamic relation

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

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

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

with $\delta \ln D$ given by (55). With the simplification $N_j A_{kj}\,\Delta t = Z_{kj}$ we have

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

With regard to certain experimental results to be discussed in the concluding section we shall consider a generalized variation of $\ln D$. Equation (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

$$\delta \ln D = \sum_{j>k} \delta I_{kj} \ln \frac{Z_{kj}}{I_{kj}} \tag{61}$$

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 equation (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

$$I_{kj} = Z_{kj}\, e^{-h\nu_{jk}/kT} \tag{62}$$

The condition $Z_{kj} \gg I_{kj}$ limits the validity of equation (62) to cases where $h\nu_{jk} \gg kT$. This condition alone yields equation (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 Δt 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.

8. CONCLUSION

The present theory of atomic spectral emission was presented in outline at the 1984 FACSS meeting (Yngström, 1985). The work was initiated by experimental observations which indicated that spectral line intensity fluctuations depend strongly on wavelength. These observations were made by B. Thelin and were first reported in connection with the theoretical presentation in 1984 (Thelin, 1985).

Thelin's method of fluctuation analysis is used in Thelin (1986*a*) to demonstrate exponential dependence on $h\nu$ of spectral intensity, and evidence for such dependence on $\bar{\varepsilon} + h\nu$ is given by Thelin (1987, 1988*a,b*). 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 $J = \bar{\varepsilon}$.

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 (Thelin and Yngström, 1986). This work is presented in more detail in Yngström and Thelin (1990), where also a strict mathematical derivation of Thelin's analysis method is given. A recent work (Yngström, 1994) shows very good support for the new intensity formula from detection limit data of ionic spectral lines.

The fluctuation method of analysis has provided evidence for the validity of formula (62) in the study of auroral emissions (Thelin, 1986*b*). 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

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

by writing

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

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

Results in Thelin (1988*c*) 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 $h\nu$.

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.

NOTE ADDED IN PROOF

In agreement with the new intensity formula presented in this paper, the principle of maximum entropy for spontaneously emitted radiation from material bodies in well-defined thermal states has recently been shown (Bekenstein and Schiffer, 1994) to imply that the radiation intensity is a fraction of the Planck radiation intensity.

ACKNOWLEDGMENTS

Many stimulating discussions of spectroscopic experiments with Dr. Bo Thelin are gratefully acknowledged. I thank Prof. Bengt Hultqvist for much encouragement and for his kind hospitality at this institute. Leave of absence granted by the Local School Board of Gällivare is acknowledged. I thank my friend Birgit Sandahl for valuable linguistic criticism.

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