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IN ATOMIC RADIATIVE EMISSION**

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ON THE ROLE OF COULOMB FORCES IN ATOMIC RADIATIVE EMISSION

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Abstract

It is shown how the generalized Coulomb interaction (electric and magnetic fields of force) competes with the radiative interaction causing overall inhibition of the radiative capability of atoms and ions in a gaseous sample of matter. Basic quantum mechanical aspects of the electromagnetic interaction are discussed in a heuristic introduction followed by a more precise treatment in the formalism of relativistic quantum electrodynamics.

Introduction

The subject of this paper will be introduced by considering a tentative, heuristic description of the physics of one of the atoms in a macroscopic sample of matter in the gaseous state. It will be presupposed that the action on the atom by its environment is purely electromagnetic. Then the consideration will be confined to a physical system composed of a single atom in a general external electromagnetic field.

The electromagnetic field can always be split into a pure radiation field and a generalized Coulomb field in a relativistically covariant manner. The radiation field can be quantized into photons, while the Coulomb field cannot be given a description in terms of real quanta. As was emphasized by F. Rohrlich in Boulder 1980 [1], pure radiative processes are very well described by conventional QED while, to a large extent, processes involving the Coulomb field have not been understood. The usual methods of perturbation theory are inadequate for describing the full importance of the Coulomb field. Although QED has been proved to be completely renormalizable, faithful representations in Hilbert space of the generalized Coulomb field do not seem to have been found. This is in sharp contrast to the successful device of Fock space to represent the radiation field.

We thus have to consider two kinds of external electromagnetic action on the atom. According to fundamental principles of quantum theory each interaction process occurs with a certain probability per unit time. This can be expressed in terms of the wellknown Feynman-Dyson expansion of $|\langle \beta | U(t_2, t_1) | \alpha \rangle|^2$, the probability of transition from state $|\alpha\rangle$ to $|\beta\rangle$ in the time interval $t_2 - t_1$. In particular, there is always a non-zero probability that $|\beta\rangle$ is the same physical state as $|\alpha\rangle$, i.e. interaction may not at all cause observable effects.

Suppose the initial state $|\alpha\rangle$ is an eigenstate of a Hamiltonian operator E . Thus $|\alpha\rangle$ is assigned a value of energy in a certain sense and $|\alpha\rangle$ will then be called a unistate. As time passes the initial state will develop into $U|\alpha\rangle$. If $[U, E] \neq 0$ the state $U|\alpha\rangle$

will contain a superposition of eigenstates of E . The U -operator then describes interaction causing transitions of the initial unistate into a linear combination of unistates. In this multistate each unistate appears with a certain probability determined by the U -operator.

Imagine that we observe the atom during a certain time interval. The atom may then be found in discrete eigenstates of its internal (electron) energy. These eigenstates are those of the free, unperturbed atom and quasi-free states perturbed by weak action of the external, generalized Coulomb field (Stark and Zeeman effects). In some instants we might observe the atom making jumps between such eigenstates emitting or absorbing a photon. These processes are the well-known radiative atomic transitions.

Less known are processes involving strong action on the atom by the external Coulomb field. In contrast to the radiative, photon interaction this interaction is not instantaneous. The Coulomb field (electric and magnetic force) acts continuously on the atom during lapses of time. This action may become so strong that the atom forms a bound state with the sources of the external Coulomb field.

The atom will then be bound to the external sources by continuous exchange of energy. The energy of the bound atom cannot be specified precisely. The atom is in a multistate; a quantum mechanical superposition of unistates labelled by a continuous energy parameter.

This action of the Coulomb field may cause non-radiative atomic transitions between discrete energy eigenstates via intermediate bound states. The interaction may also result in ionized states of the atom. These states may simply be included in our discussion by letting the word "atom" signify all pertaining ions when not stated otherwise. For example, the concept of atomic unistate will thus also refer to all possible ionic unistates.

The composition of the multistate of the bound atom is continuous-

ly changing with time because of the Coulomb forces. The bound state may also change by the emission of photons. Such photons will be in quantum multistates labelled by energy values in the atomic bound state energy range. This radiation resembles the so-called Bremsstrahlung and one may argue that the probability of such processes is much smaller than the probability of corresponding Coulomb transitions.

The non-radiative transitions within the bound state presumably dominate over the radiative ones owing to much larger available phase spaces. In radiative transition amplitudes the four-momenta of the emitted photons are restricted because of the photon mass being zero while there is no such a priori restriction of the four-momentum transfers in corresponding non-radiative transition amplitudes.

Our consideration has thus brought us to the following conclusions. The state of our atom must be considered a quantum mechanical multistate which is composed of discrete eigenstates of its electronic internal energy and of bound states with continuous internal energy. The photons emitted by the atom will then also be in multistates. Upon detection by a spectrometer they will give rise to a line spectrum with a weak background of a continuous spectrum. The radiation emanating from one atom in a spectral sample thus represents the whole spectrum of the atom and its ions.

The spectral lines are due to radiative transitions between free and quasi-free states and the continuous spectrum is due to emission from bound states. The bound states are almost non-radiative. The strong Coulomb interaction quenches the radiative transitions of the atom. The weak Coulomb interaction on the other hand may counteract this effect by resonant coupling of discrete internal energy levels leading to enhanced radiative transition probabilities. In comparison to the line spectrum from atoms in a pure radiation field and with negligible external Coulomb interaction the spectral lines would be split and might have different relative intensities.

2. QED of atom in external EM-field.

We shall now formulate our introductory heuristic discussion more precisely by using the frame-work of quantum electrodynamics -QED. Let us then employ a Furry-Dirac interaction picture for our atom. We imagine that we have obtained a representation of all the discrete energy eigenstates of the free atom. In principle a well-defined (regularized) atomic electron current density operator $j(x)$ can then be constructed in the Hilbert space spanned by these eigenstates. The operator $j(x)$ induces the electron transitions that correspond to the atom making jumps between its energy levels.

The external field is given by a four-vector $A(x)$ which may be written

$$A(x) = a(x) + \int D_R(x-x')J(x')d^4x' , \quad (1)$$

the sum of the radiation field $a(x)$ and the Coulomb field $c(x)$ from the retarded external electric current density $J(x')$;

$$c(x) = \int D_R(x-x')J(x')d^4x' . \quad (2)$$

The atom interacts with its environment by coupling its electron current $j(x)$ with the external field $A(x)$. This is expressed by the interaction Hamiltonian

$$H(t) = \int j(x) \cdot A(x)d^3x \quad (3)$$

where $j \cdot A$ is the usual four-vector scalar product of j and A .

By Eqns (1-3) we have

$$H(t) = R(t)+V(t) \quad (4)$$

$$R(t) = \int j(x) \cdot a(x)d^3x \quad (5)$$

$$V(t) = \int j(x) \cdot c(x)d^3x = \iint D_R(x-x')j(x) \cdot J(x')d^4x'd^3x \quad (6)$$

If the external field would be a pure radiation field our interaction Hamiltonian would be equal to $R(t)$. This would yield the well-known theory of radiative transitions for the atom. The physical states would be vectors in the Hilbert space spanned by the direct products of all energy eigenstates of the free atom with photon states. The photon states would be the Fock vectors for photons with energy values determined by the differences in energy value of the atomic eigenstates. In this space the operator $R(t)$ causes energy jumps of the atom accompanied by emission or absorption of photons.

We shall denote these atom-photon state vectors with greek letters $|\alpha\rangle$, $|\beta\rangle$, $|\gamma\rangle$ The Coulomb interaction Hamiltonian $V(t)$ would be defined as an operator in this space if $c(x)$ were represented by a well-defined c-number field.

Let us assume that our macroscopic system is described in terms of a statistical ensemble. Then the ensemble average of the regularized quantum mechanical expectation values of the current density operator $J(x')$ may be used as the c-number representation of $J(x')$. In this way the external Coulomb field $c(x)$ defined in Eqn (2) will be represented by a macroscopic c-number vector field. The Coulomb interaction Hamiltonian $V(t)$ given by Eqn (6) will be an operator defined in the Hilbert space $\{ |\alpha\rangle \}$.

The last conclusion is strictly valid under the condition that we use our constrained representation of $j(x)$ being the transition current for jumps of the free atom between its discrete energy levels. In this formulation we thus neglect issues of perturbation of energy levels, possible atomic intermediate and bound states. We shall see that our simplified approach enables us to obtain an important result concerning competition between radiative transitions and non-radiative transitions of an atom in an external electromagnetic field. The competition appears solely as a consequence of fundamental principles of QED and its principal features seem to be demonstrated convincingly enough in our simplified formulation.

3. The U-matrix and transition probability.

The time development operator in the interaction picture is

$$U(t_2, t_1) = T: \exp - \frac{i}{\hbar} \int_{t_1}^{t_2} [R(t)+V(t)]dt: . \quad (7)$$

This is the Dyson solution of the Schrödinger equation

$$\frac{\partial}{\partial t_2} U(t_2, t_1) = -\frac{i}{\hbar} [R(t_2)+V(t_2)] U(t_2, t_1). \quad (8)$$

U is unitary, $U^\dagger = U^{-1}$, and satisfies the group properties $U(t_2, \tau)U(\tau, t_1) = U(t_2, t_1)$ and $U(\tau, \tau) = 1$ for arbitrary τ .

Let us introduce the operator

$$W(t_2, t_1) = T: \exp - \frac{i}{\hbar} \int_{t_1}^{t_2} V(t)dt: . \quad (9)$$

Then a solution of Eqn (8) is given by

$$U(t_2, t_1) = W(t_2, \tau) T: \exp - \frac{i}{\hbar} \int_{t_1}^{t_2} W(\tau, t) R(t) W(t, \tau) dt: W(\tau, t_1) \quad (10)$$

with arbitrary τ .

Let us write D_2 for $\frac{\partial}{\partial t_2}$. Straightforward use of Eqn (10) yields

$$\begin{aligned} D_2 U(t_2, t_1) &= [D_2 W(t_2, \tau)] \cdot W(\tau, t_2) U(t_2, t_1) + \\ &+ W(t_2, \tau) \cdot [D_2 T: \exp - \frac{i}{\hbar} \int_{t_1}^{t_2} W(\tau, t) R(t) W(t, \tau) dt:] W(\tau, t_1) \\ &= -\frac{i}{\hbar} V(t_2) U(t_2, t_1) + W(t_2, \tau) \cdot -\frac{i}{\hbar} W(\tau, t_2) R(t_2) W(t_2, \tau) \times \\ &\times W(\tau, t_2) U(t_2, t_1) . \end{aligned}$$

$$D_2 U(t_2, t_1) = -\frac{i}{\hbar} [R(t_2)+V(t_2)] U(t_2, t_1).$$

Thus Eqn (10) is proved to be solution of Eqn (8).

Let us now put $\tau=t_2$ in Eqn (10) obtaining

$$U(t_2, t_1) = T: \exp - \frac{i}{\hbar} \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt : W(t_2, t_1). \quad (11)$$

In this way we have obtained an expression for the U-matrix where pure Coulomb processes are described by the non-radiative factor $W(t_2, t_1)$ while all radiative processes are expressed by

$$\text{the factor } T: \exp - \frac{i}{\hbar} \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt :.$$

The factorization of the U-matrix as expressed by Eqn (11) describes competition between our two different kinds of interaction. This effect will easily be seen when we represent the current $j(x)$ by the free atomic transition current and use the macroscopic c-number representation of $J(x)$ according to the simplification adopted in the previous Section.

Let us then consider the probability for transition from state $|\alpha\rangle$ to $|\beta\rangle$ with the atom making an energy-lowering jump under the emission of a photon with energy equal to the energy loss of the atom. We shall then consider the process only to first order in the radiative interaction $R(t)$, i.e. with

$$U(t_2, t_1) = [1 - \frac{i}{\hbar} \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt] W(t_2, t_1). \quad (12)$$

The transition probability will then be expressed by

$$\begin{aligned} & | \langle \beta | U(t_2, t_1) | \alpha \rangle |^2 = \\ & \frac{1}{\hbar^2} | \langle \beta | \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt W(t_2, t_1) | \alpha \rangle |^2 \\ & = \frac{1}{\hbar^2} | \sum_{\gamma} \langle \beta | \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt | \gamma \rangle \langle \gamma | W(t_2, t_1) | \alpha \rangle |^2 \quad (13) \end{aligned}$$

after inserting the complete set of (intermediate) states $|\gamma\rangle$.

By (13) and (5) our radiative process is governed by the terms

$$\begin{aligned}
 & \langle B | \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt | \gamma \rangle = \\
 & = \langle B | \int_{t_1}^{t_2} \int a(x) \cdot W(t_2, t) j(x) W(t, t_2) d^3x dt | \gamma \rangle. \quad (14)
 \end{aligned}$$

Each one of these terms is multiplied by $\langle \gamma | W(t_2, t_1) | \alpha \rangle$, which may be non-zero only in case $|\gamma\rangle$ contains the same photon state as $|\alpha\rangle$, since W , by definition in (9) and (6), has no photon operator. The transition current operator $j(x)$ is changed according to $j(x) \rightarrow j_W(x) = W(t_2, t) j(x) W(t, t_2)$ which is a unitary transformation since $W(t_2, t) = W^*(t, t_2)$.

With an unimportant loss of generality we may assume that our photon can only be emitted in the particular atomic jump of the transition $|\alpha\rangle \rightarrow |\beta\rangle$ (uniqueness of spectral line). The energy spectrum of $a(x)$ in (14) is then fixed to the single energy value of our photon. The integration in expression (14) then also fixes the contributing energy spectrum of the transition current operator $j_W(x)$ to be equal to this photon energy.

In general, this single energy value of the spectrum of $j_W(x)$ is the sum of the atomic energy change in the transition $|\gamma\rangle \rightarrow |\beta\rangle$ and the simultaneous energy transfer to the external field sources. If $|\gamma\rangle = |\alpha\rangle$ there is no external energy transfer. If $|\gamma\rangle \neq |\alpha\rangle$ the photon emission occurs together with Coulomb interaction of the atom with the external sources. These latter transitions are thus the results of electromagnetic interaction of high order and have therefore much smaller probability amplitudes than the "direct" transition in the case $|\gamma\rangle = |\alpha\rangle$. This is the Bremsstrahlung case discussed in the Introduction and we may assume generally that the transition probability can be approximated by neglecting all intermediate states but $|\alpha\rangle$ in expression (13).

The general arguments of the preceding paragraph may be replaced by the following reasoning in our simplified representation of operators. Since we represent $j(x)$ by the free atomic transition

current our photon can only couple with the current for the transition $|\alpha\rangle \rightarrow |\beta\rangle$. This means that the operator $R(t)$ is simply represented by $|\beta\rangle\langle\beta| R(t) |\alpha\rangle\langle\alpha|$. The radiative transition probability amplitude of Eqn (14) may thus be written

$$\int_{t_1}^{t_2} \langle\beta|W(t_2,t)|\beta\rangle\langle\beta|R(t)|\alpha\rangle\langle\alpha|W(t,t_2)|\gamma\rangle dt.$$

In this expression the term $\langle\alpha|W(t,t_2)|\gamma\rangle$ contains an exponential function of $\frac{i}{\hbar} V(\alpha,\gamma)(t-t_2)$, where $V(\alpha,\gamma)$ is the energy transfer in the transition $|\gamma\rangle \rightarrow |\alpha\rangle$. This statement is based on noting that $j(x)$ and $c(x)$ in expression (6) for $V(t)$ are supposed to have well-defined Fourier expansions in energy-momentum space. The Fourier energy dependent exponents will survive in the Dyson expansion of $W(t,t_2)$ and give rise to the energy transfer dependent exponential function above.

The term $\langle\alpha|W(t,t_2)|\gamma\rangle$ thus oscillates with t when $|\gamma\rangle \neq |\alpha\rangle$. In the simplified representation now discussed there is no counter-oscillating term in the radiative transition probability amplitude. With reference to the Riemann-Lebesgue lemma we may thus neglect the terms with $|\gamma\rangle \neq |\alpha\rangle$ when performing the integration over t in our radiative amplitude.

Our transition probability is thus expressed by

$$\begin{aligned} | \langle U(t_2, t_1) \rangle |^2 &= \frac{1}{\hbar^2} \left| \langle \beta | \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt | \alpha \rangle \langle \alpha | W | \alpha \rangle \right|^2 \\ &= \frac{1}{\hbar^2} \left| \langle \beta | \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt | \alpha \rangle \right|^2 \cdot \left| \langle \alpha | W(t_2, t_1) | \alpha \rangle \right|^2. \quad (15) \end{aligned}$$

Now $\left| \langle \alpha | W(t_2, t_1) | \alpha \rangle \right|^2 = \langle \alpha | W | \alpha \rangle \langle \alpha | W^\dagger | \alpha \rangle$ and

$$1 = \langle \alpha | W W^\dagger | \alpha \rangle = \sum_{\gamma} \langle \alpha | W | \gamma \rangle \langle \gamma | W^\dagger | \alpha \rangle \quad \text{yield}$$

$$\left| \langle \alpha | W | \alpha \rangle \right|^2 = 1 - \sum_{\gamma \neq \alpha} \left| \langle \alpha | W | \gamma \rangle \right|^2 \leq 1. \quad (16)$$

When this inequality is used in (15) we find that the radiative transition probability is subject to the condition

$$|\langle \beta | U(t_2, t_1) | \alpha \rangle|^2 \leq \frac{1}{\hbar^2} \left| \langle \beta | \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_1) dt | \alpha \rangle \right|^2. \quad (17)$$

The current-current Coulomb coupling (6) in W causes nonradiative exchange of energy between the atomic electron current and the external currents. The initial state $|\alpha\rangle$ is thereby partly brought into states that contribute very little to the particular radiative emission. The "radiatively active" norm of $|\alpha\rangle$ is diminished by the fractional factor $|\langle \alpha | W_{21} | \alpha \rangle|$. This factor might become very small in case the external current J carries excessive electric charge as happens, for example, when the electron density is high. The contribution of high energy transfer terms in the sum $\sum_{\gamma \neq \alpha} |\langle \alpha | W_{21} | \gamma \rangle|^2$ would presumably grow with increasing external current density whereby the inequality (16) and hence also (17) would be strongly satisfied.

Let us write Eqn (12) in the form

$$U(t_2, t_1) = W(t_2, t_1) - \frac{i}{\hbar} \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_1) dt.$$

This expression for the U -operator leads to the formula

$$\begin{aligned} |\langle \beta | U(t_2, t_1) | \alpha \rangle|^2 &= \\ &= \frac{1}{\hbar^2} \left| \int_{t_1}^{t_2} \langle \beta | W(t_2, t) | \beta \rangle \langle \beta | R(t) | \alpha \rangle \langle \alpha | W(t, t_1) | \alpha \rangle dt \right|^2 \end{aligned} \quad (18)$$

after using the previously adopted simplified representation of $R(t)$. Eqn (18) shows that the matrix element $\langle \beta | R(t) | \alpha \rangle$ for a "direct" radiative transition is multiplied by the number $\langle \beta | W(t_2, t) | \beta \rangle \langle \alpha | W(t, t_1) | \alpha \rangle$ the absolute value of which is smaller than unity. Hence, Eqn (18) implies the same conclusion as Eqn (17); the nonradiative Coulomb interaction causes overall quenching of radiative atomic interaction.

Our formulae show that the relative values of radiative transition probabilities of an atom in a Coulomb field might differ from those of the free atom. Spectral line intensity ratios are affected. The overall Coulomb quenching might be compensated for some transitions by resonant coupling of the external Coulomb field with the atom.

The conclusions of this Section rest upon some-what "hand-waving" arguments. A more refined treatment would require a much larger complete set of states $| \gamma \rangle$ to span the Hilbert space. That would mean expansion of the atomic unistate space by taking Stark and Zeeman effects into account and inclusion of bound states. The representation of j would be generalized and the frequency distribution of spectral lines would have to be considered. In Section 4 a series expansion of the radiative transition operator is presented that might be useful in the study of all these issues.

In spite of the limitations introduced by our simplified representation of physical states and operators it seems that the principal feature of radiative inhibition caused by the Coulomb interaction has been demonstrated quite convincingly.

4. Series expansion of the radiative transition operator.

For the purpose of explicit calculations the following series expansion of the radiative transition operator in Eqn (12) may be useful

$$\begin{aligned}
 & -\frac{i}{\hbar} \int_{t_1}^{t_2} W(t_2, t) R(t) W(t, t_2) dt = \\
 & = -\frac{i}{\hbar} \int_{t_1}^{t_2} R dt + \sum_{k=1}^{\infty} \frac{(-i)^{k+1}}{\hbar (k+1)!} T: \left(\int_{t_1}^{t_2} V dt, \right)^k \int_{t_1}^{t_2} R dt :^k \quad (19)
 \end{aligned}$$

The derivation of this expression with its infinite series of retarded commutators cannot easily be rendered in print. However, the correctness of Eqn (19) can be proved in a straightforward manner by using the standard rules for time derivatives of time-ordered quantities in the expression for $U(t_2, t_1)$ obtained from Eqn (12) after inserting expression (19). In this way we will find that the Schrödinger equation for U is satisfied to first order in R and Eqn (19) is established.

After inserting (19) we can write (12) in the form

$$U(t_2, t_1) = [1 + R_{21}(1) + \sum_{k=1}^{\infty} R_{21}(k+1)] W(t_2, t_1), \quad (20)$$

$$R_{21}(1) = -\frac{i}{\hbar} \int_{t_1}^{t_2} R(t) dt, \text{ and}$$

$$\begin{aligned}
 R_{21}(k+1) = & \left(-\frac{i}{\hbar}\right)^{k+1} \int_{t_1}^{t_2} dt'_{k+1} \int_{t_1}^{t'_{k+1}} dt'_k \dots \int_{t_1}^{t'_3} dt'_2 \int_{t_1}^{t'_2} dt'_1 \times \\
 & \times [V(t'_k + 1), [V(t'_k), \dots [V(t'_2), R(t'_1)] \dots]] .
 \end{aligned}$$

By the T-product definition the last expression is equivalent to the k :th term of the sum on the right hand side of (19). Its derivative with respect to t_2 is

$$\begin{aligned}
 D_2 R_{21}(k+1) = & \left(-\frac{i}{\hbar}\right)^{k+1} \int_{t_1}^{t_2} dt'_k \dots \int_{t_1}^{t'_3} dt'_2 \int_{t_1}^{t'_2} dt'_1 \times \\
 & \times [V(t_2), [V(t'_k), \dots [V(t'_2), R(t'_1)] \dots]]
 \end{aligned}$$

which is equivalent to

$$D_2 R_{21}(k+1) = \left[-\frac{i}{\hbar} V(t_2), R_{21}(k) \right]$$

from which follows

$$D_2 \sum_{k=1}^{\infty} R_{21}(k+1) = \left[-\frac{i}{\hbar} V(t_2), 1 + R_{21}(1) + \sum_{k=1}^{\infty} R_{21}(k+1) \right]. \quad (21)$$

We have

$$D_2 R_{21}(1) = -\frac{i}{\hbar} R(t_2)$$

which to first order in R can be written

$$D_2 R_{21}(1) = -\frac{i}{\hbar} R(t_2) \left[1 + R_{21}(1) + \sum_{k=1}^{\infty} R_{21}(k+1) \right]. \quad (22)$$

Using the relations (21) and (22) together with

$D_2 W(t_2, t_1) = -\frac{i}{\hbar} V(t_2) W(t_2, t_1)$ when taking the t_2 derivative of Eqn (20) we obtain the Schrödinger equation

$$D_2 U(t_2, t_1) = -\frac{i}{\hbar} [R(t_2) + V(t_2)] U(t_2, t_1).$$

Concluding discussion

A general theorem of quantum field theory was expressed by Eqn (10) and its application by (11) and (12) to QED led to the conclusion stating that the generalized Coulomb interaction competes with the ordinary radiative interaction. This causes overall inhibition of the radiative capability of atoms and ions.

In a simplified formalism the inhibition was expressed by showing that the radiatively active norm of a discrete eigenstate of energy is diminished by a fractional factor which is determined by the Coulomb interaction. In a more general interpretation we may express this by saying that the initial energy eigenstate partly develops into highly non-radiative states. These we may classify as bound states coupled by the Coulomb field to the ambient electric charges and currents.

The quantum mechanical state of our "one atom in external field" system is a superposition of all the discrete internal energy eigenstates of the atom and its ions plus bound states. This picture of the state of one atom being a quantum mechanical superposition of all its possible states has thus emerged from a microscopic point of view.

From a macroscopic point of view we may obviously consider our sample of gaseous matter as an assembly of microscopic "one atom" systems. The quantum mechanical properties of our "one atom" system are then the fundamental a priori conditions for a quantum statistical physics description of the macroscopic system. That description is obtained by considering an ensemble of our "one atom" assemblies. The assembly defined by taking the ensemble average in accordance with relevant macroscopic constraints is then a representative of the macroscopic physical system.

The microscopic a priori radiative properties of atoms and ions imply that the representative assembly is split into several distinct assemblies. There are assemblies specified by average occupation numbers of discrete internal energy levels of atoms

and ions. Such an assembly is radiative. It is the source of a characteristic emission line spectrum. The existence of highly non-radiative bound states implies that a fraction of the total number of elements in each atomic and ionic population belongs to a non-radiative assembly. This kind of assembly may be specified by an average population number and average energy only since the energy value of a member of a bound state assembly is unobservable.

The conclusions of the previous paragraph constitute a cornerstone of a new theory of spectral line emission presented in 1984 [2]. The theory predicts that the ratio of the number of radiatively active members to the total number of members of a specific atomic or ionic population is given by the factor $\exp(-\bar{\epsilon}/kT)$. $\bar{\epsilon}$ is the arithmetic mean energy value of the discrete levels and equals with good approximation the ionization energy of the element. T is the temperature pertaining to the internal degree of freedom defined by the discrete energy level ladder. The theory has been very well confirmed by experimental data analysis [3,4,5], and its detailed derivation is given in [6]. Observation in plasmas of what seems to be evidence for the Coulomb force quenching of radiative emission has recently been reported in [7].

When $\bar{\epsilon} \gg kT$ the radiative capability factor $\exp(-\bar{\epsilon}/kT)$ is very small. A large fraction of matter constituents for which this condition is fulfilled will thus be practically dark.

The results reported in this paper may be important not only for the calculation of transition probabilities of atoms and ions. The general theorem of Eqn (10) may also be very useful in considering competition effects of nuclear forces analogously to our present study of electromagnetic forces.

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