ATOMIC RADIATIVE PROCESSES

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PREFACE

We have witnessed during the past decade a tremendous resurgence of interest in atomic radiative processes. A major reason for this is the laser, which has become an invaluable tool for investigating the interaction of radiation with matter. The laser not only made it possible to refine and improve a number of classic experiments, but also extended the applications to a variety of new nonlinear processes. A prime example is the dynamic Stark effect in which the atom interacts with a strong coherent field during many absorption–emission cycles. The resulting frequency distribution of emitted radiation exhibits sidebands that are not present when broadband radiation is used.

This book is a much revised and expanded version of a series of lectures I gave at the Swiss Institute of Technology in Lausanne, Switzerland. The purpose of the course was to give the students a unified treatment of classical and quantum-mechanical radiation theory together with the description of atomic radiative processes. I have attempted to make the presentation as self-contained as possible. In the derivations all of the essential steps are included and only trivial or straightforward connections are omitted. The development is a gradual one with fairly simple treatments at the beginning and more complicated ones toward the end. This is a theoretical book, and only a few experiments are considered in detail. In a couple of cases I have analyzed an experiment in order to illustrate the theory and to show how the equations relate to experimental results. The reader is directed to a number of review articles in which the experimental aspects are covered.

The book is intended for use in a two-term course. For advanced students some of the introductory chapters may be omitted and a one-term course structured from the last few chapters. The book may also profitably be used by the researcher who wants to calculate a specific process in detail and who is interested in predicting experimental results. The unified treatment of the subject matter should make it easier to compare processes and to extend the theory to new ones.

In the first two chapters, some of the properties of the classical field and its interaction with particles are described, focusing on those aspects needed for a better understanding of the quantum theory. The Hamiltonian formalism is used in order to be able to quantize the field by making only minor modifications. The density of states of the radiation field and the Hamiltonian for the interaction between the field and the particles is also considered.

The theory of atomic radiative processes described in this book relies heavily on the use of Fourier transforms. They are powerful tools in obtaining solutions of time-dependent Schrödinger equations. Coupled differential equations are transformed to coupled linear equations that in most cases can be readily solved. In addition, the description of the transforms in the complex plane gives a great deal of information about the interaction of the radiation field with the atom. In particular, an analysis of the poles of the transforms yields decay rates and frequency shifts. In Chapter 2 a few Fourier transform techniques are introduced and applied to such areas as coherence properties of the field and amplitude and intensity correlations. Many of these classical methods can also be used effectively in the quantum theory.

In Chapter 3 a brief review of the theory of angular momentum is given. The results are useful for evaluating matrix elements and angular momentum selection rules. The properties of irreducible tensors are also discussed. These are used in the expansion of the interaction Hamiltonian, which separates the terms that contain atomic parameters from those that involve the properties of the radiation field.

The quantization of the radiation field is considered in Chapter 4. The system of photon states is derived, and a few of their properties are discussed. The description includes coherent states and their connection with the classical field.

Chapter 5 briefly reviews the description of atomic and field states and their properties in the interaction representation. The contents form the basis for the calculation of amplitudes and probabilities.

The interaction of a two-level atom with single modes of the radiation field is treated in Chapter 6. A convenient way to describe the interaction is to "dress" the atom with the photon states. The procedure allows a much clearer understanding of the evolution of the system. The Fourier transform techniques developed in Chapter 2 are used in describing the coupling of an atom with both rotating and linear fields. Probabilities are calculated by solving amplitudes as well as density matrix equations. The interaction of the atom with the linear field yields a number of interesting results including frequency shifts and multiphoton resonances.

A fairly complete description of spontaneous emission is given in Chapter 7. The presentation starts with Einstein's phenomenological theory, continues with a more accurate description by Weisskopf and Wigner, and is completed with the Fourier transform method applied to both amplitude and density matrix equations.

In Chapter 8 a variety of decay processes are discussed. The techniques and results of the previous chapters are applied to a description of the evolution of coupled atomic states and the frequency distribution of emitted radiation.

The analysis is extended in Chapter 9 to include radiative excitation. Resonance fluorescence with weak incoherent fields is discussed first. The calculation is applied to level-crossing and level-anticrossing effects as well as to optical double resonances. The presence of strong monochromatic radiation leads to a more complicated interaction. The atom goes through many absorption–emission cycles, and the frequency distribution of scattered light shows new features that are due to the coupling of the different cycles. The description of the "dressed" atomic states gives again a good qualitative explanation of the results.

I have purposely kept the reference lists compact. Entries fall into four categories: (1) references of historical interest, (2) books that treat related subject matter in detail, (3) review articles, and (4) references that are pertinent to the presentation.

No attempt has been made to cover all approaches to atomic radiative processes. In many cases there are other methods that use different mathematical tools. The omission of an alternate method does not reflect on its merits. The theory developed here is simply one way to cover coherently a rather incoherent subject.

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1 CLASSICAL ELECTRODYNAMICS

1.1 FORMAL DEVELOPMENT

The calculation of atomic radiative processes requires a description of the atom, the radiation field, and the interaction between the bound electrons of the atom and the field. Both the atom and the radiation field are quantized. The quantization of the atom can be accomplished by quantizing the total action of the system and by examining the Hamilton–Jacobi equation of motion in terms of a series of canonical transformations. The "optical" description of the motion of the generating function leads to the Schrödinger equation for the atom (1.2). The quantization of the radiation field can also be done in a straightforward manner by replacing the classical Poisson brackets of the field components by quantum mechanical commutators. All other aspects of the quantized radiation field can be readily obtained from the classical one. In particular, the quantized version of the vector potential and therefore also of the electric and magnetic fields is very similar in structure to the corresponding classical expressions. The change from the classical to the quantized results can be made by replacing the term that gives the time dependence of the fields at some point in space by an operator that does not depend on time. The spatial dependence of the field quantities is not affected by the quantization procedure. Only those elements of the classical theory that are used in the development of the quantum theory are presented.

The basic equations describing electrodynamical processes are Maxwell's equations together with the Lorentz force. In the absence of dielectric or magnetic media, these equations are

$$\nabla \cdot \mathbf{E} = \rho/\varepsilon_0 \tag{1.1}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{1.2}$$

$$\nabla \times \mathbf{E} + \frac{\partial B}{\partial t} = 0 \tag{1.3}$$

$$\frac{1}{\mu_0} \nabla \times \mathbf{B} - \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} = \mathbf{j} \tag{1.4}$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields, respectively, ρ the electric charge density, and $\mathbf{j}$ the electric current density.

The force acting on a particle with charge e at position $\mathbf{r}$ moving with velocity $\mathbf{v}$ is given by

$$\mathbf{F} = e[\mathbf{E}(\mathbf{r}) + \mathbf{v} \times \mathbf{B}(\mathbf{r})] \tag{1.5}$$

The equations are written in rationalized MKS units. In this system the common units (volt, ampere, coulomb, etc.) are incorporated. The force on a charge e_2 at position $\mathbf{r}_2$ due to another charge e_1 at position $\mathbf{r}_1$ is

$$\mathbf{F} = \frac{e_1 e_2}{4\pi\varepsilon_0} \frac{\mathbf{r}_{12}}{r_{12}^3} \tag{1.6}$$

where $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$. Similarly, the interaction between currents is given by

$$\mathbf{F} = \frac{\mu_0}{4\pi} \iint \frac{\mathbf{j}_1 \times (\mathbf{j}_2 \times \mathbf{r}_{12})}{r_{12}^3} \, d\tau_1 \, d\tau_2 \tag{1.7}$$

where the integrations are over the regions of nonvanishing current densities $\mathbf{j}_1$ and $\mathbf{j}_2$, respectively. If one takes the divergence of Eq. (1.4) and uses Eq. (1.1), one obtains the continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0 \tag{1.8}$$

In taking the divergence one assumes implicitly that the fields are smoothly varying in space and time. Since the divergence of $\mathbf{B}$ is zero [Eq. (1.2)], one can assume the existence of a vector potential such that

$$\mathbf{B} = \nabla \times \mathbf{A} \tag{1.9}$$

This allows us to write

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} - \nabla\phi \tag{1.10}$$