1
Introduction

The purpose of this book is to present a unified account of the exciting developments in the field of quantum electronics which have occurred during the last two decades. Following introductory chapters on electromagnetism and quantum mechanics, the basic processes involving the interaction of radiation and atoms are discussed in some detail. We believe that a thorough understanding of this material is essential for later chapters.

However, in order that the reader shall not lose sight of our ultimate objective, we present here a brief historical introduction showing how our understanding of light and matter has developed since the end of the nineteenth century. It is hoped that this will allow the student to set the material which follows in the proper context and will give him or her an appreciation of the beauty and fascination of the field of optical physics.

1.1. Planck's radiation law

By the end of the nineteenth century the development of the wave theory of light, commenced by Young and Fresnel, seemed to have reached its culmination in the brilliant theoretical work of Maxwell. In another branch of physics the theory of heat leading on to the kinetic theory of gases and to statistical mechanics as developed by Clausius, Boltzmann, Maxwell, and Gibbs also seemed to be complete in most of its essential points. This encouraged Michelson to write in 1899:

'The more important fundamental laws and facts of physical science have all been discovered, and these are so firmly established that the possibility of their ever being supplanted in consequence of new discoveries is exceedingly remote.'

There was, however, an unresolved discrepancy in the theory of black-body radiation. In fact the solution of this apparently minor problem by Planck (1901) was to be

the starting point of the quantum theory and of our present understanding of the structure of atoms and molecules.

Following the work of Kirchhoff on the connection between emission and absorption coefficients, it had been proved that the radiation inside a totally enclosed cavity maintained at a uniform temperature was a function of the temperature alone and was identical with the radiation which would be emitted by a perfectly black body at the same temperature. The spectral distribution of the radiation had been investigated experimentally and it was found that the intensity increased slowly with decreasing frequency until it reached a peak, after which it decreased very rapidly (Fig.1.1). However, all attempts to derive an equation giving the intensity as a function of frequency had failed. The most convincing approach made by Rayleigh and Jeans on the basis of classical thermodynamics gave the result

$$\rho(\omega) = \frac{\omega^2}{\pi^2 c^3} kT , \qquad (1.1)$$

where $\rho(\omega)\, d\omega$ represents the energy of radiation per unit volume in the angular frequency range between ω and $\omega+d\omega$. The term kT in equation (1.1) comes from the equipartition of energy applied to a linear oscillator which is assumed to act as the emitter or absorber of radiation of frequency $\omega/2\pi$. We see from equation (1.1) and Fig. 1.1 that the intensity predicted by the Rayleigh-Jeans law increases indefinitely at higher frequencies, the well-known ultraviolet catastrophe, in complete contradiction with the experimental results.

Planck realized that the difficulty lay in the principle of equipartition which could only be circumvented by a complete departure from classical mechanics. He postulated that an oscillator of frequency $\omega/2\pi$, instead of being able to assume all possible energy values, could exist only in one of a set of equally spaced energy levels having the values $0, \hbar\omega, 2\hbar\omega, \ldots, m\hbar\omega, \ldots$. m is an integer and $\hbar = h/2\pi$, where h is a constant now known as Planck's constant.

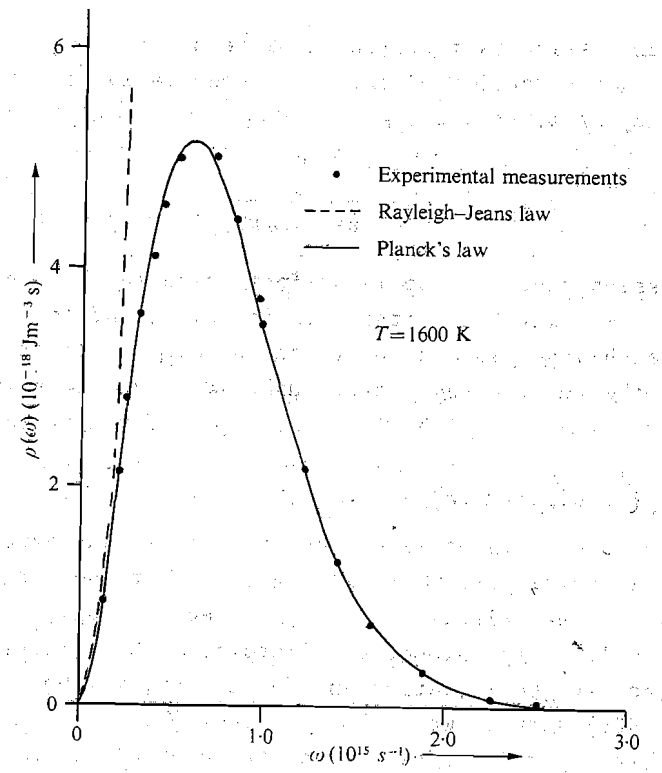

Fig.1.1. Energy density of black-body radiation as a function of the angular frequency ω

The unit of energy $\hbar\omega$, which cannot be further subdivided, Planck called a *quantum*. If we now assume that the probability of finding an oscillator with the energy $m\hbar\omega$ is given by the Boltzmann factor $\exp(-m\hbar\omega/kT)$, then the average energy of an oscillator is given by

$$\bar{\varepsilon} = \frac{\sum_{m=0}^{\infty} m\hbar\omega \exp(-m\hbar\omega/kT)}{\sum_{m=0}^{\infty} \exp(-m\hbar\omega/kT)} = \frac{\hbar\omega}{\exp(\hbar\omega/kT)-1} . \qquad (1.2)$$

When this expression is inserted in place of kT in equation (1.1), the energy density of the black-body radiation at the frequency $\omega/2\pi$ becomes

$$\rho(\omega) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{\exp(\hbar\omega/kT)-1} . \qquad (1.3)$$

This expression proved to be in perfect agreement with experiment when $\hbar$ was given a certain finite value, and the classical Rayleigh-Jeans law was obtained only in the limit as $\hbar \to 0$. Thus the turn of the century ushered in Planck's law and with it the birth of the quantum theory of radiation.

1.2. *The photoelectric effect*

In spite of this agreement between theory and experiment, not all physicists were willing to accept the quantum hypothesis. Indeed Planck himself believed initially that it applied only to the atomic oscillators in the cavity walls and not to the radiation inside the cavity. However, Einstein (1905) soon showed that the quantum theory could explain certain puzzling features of the photoelectric effect in a very simple way.

The emission of electrons from the surface of a metal which is illuminated by ultraviolet light was discovered by Hertz in 1887. Later experiments by Lenard showed that when the intensity of the incident light was changed, without altering its spectral distribution, the kinetic energy of the ejected electrons remained constant and only the number emitted varied. We now know that at very low intensities the rate of emission can become so small that only a few electrons per second are ejected. In this limit, it appears as if all the energy in the light wave falling on the surface would have to be concentrated on a single electron in order to give it the observed kinetic energy. This seems to be at variance with classical electrodynamics, for the energy in a light wave is usually assumed to be distributed uniformly across the wavefront.

To resolve this difficulty, Einstein made the bold hypothesis that the energy in the radiation field actually existed as discrete quanta, now called *photons*, each having an energy of $\hbar\omega$ and that in interactions between light and matter this energy is essentially localized at one electron. In the photoelectric effect an electron at the surface of the metal gains an energy $\hbar\omega$ by the absorption of a photon and the maximum kinetic energy of the ejected electron is observed to be

$$\frac{1}{2} m v_{max}^2 = \hbar\omega - e\phi \qquad (1.4)$$

where ϕ is the work function of the surface measured in electron volts. According to this theory the rate of emission of photoelectrons will be proportional to the flux of quanta incident upon the surface, in agreement with Lenard's experiments. Moreover Einstein's theory predicts that the maximum kinetic energy of the photoelectrons should be a linear function of the frequency of the incident light. This was later confirmed experimentally by Millikan (1916), and led to a value of $\hbar$ which agreed to within 0.5 per cent with the value derived by fitting equation (1.3) to the black-body spectrum. With this clarification of the quantum aspects of the interaction of light and matter, the stage was then set for further advances in the field of atomic spectroscopy.

1.3. *Early atomic spectroscopy*

The spectroscopy of gases had been studied since the middle of the nineteenth century, first with prism spectroscopes and later with spectrographs using diffraction gratings. Atoms excited in gas discharges were found to emit spectra consisting of many sharp lines of definite frequency, in contrast to the continuous spectra emitted by black-body sources or by solids at high temperatures. Although most atoms had very complicated spectra, that of

hydrogen was relatively simple and in 1885 Balmer discovered an empirical formula which fitted the wavelengths of the visible lines to surprisingly high accuracy. For many purposes it is more convenient to work with the wavenumbers, $\tilde{\nu}$, which are related to the wavelengths *in vacuo*, λ_{vac}, by $\tilde{\nu}=1/\lambda_{vac}$. The Balmer formula for hydrogen then becomes

$$\tilde{\nu} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{1.5}$$

where n is an integer taking the values 3, 4, 5, ... and R_H is a constant having the value 109 677·58 cm^{-1}. Further work by Rydberg in the 1890s showed that the lines of the alkali metals could be classified into a number of spectral series, each of which was described by a similar formula

$$\tilde{\nu} = \tilde{\nu}_\infty - \frac{R}{(n-d)^2} \tag{1.6}$$

where n is again an integer and d is a constant. The Rydberg constant, R, was shown to have the same value, to within 0·05 per cent, for all elements and for the first time indicated a common link between the spectra of different chemical elements.

In both the Balmer and the Rydberg formulae the wavenumber of a spectral line is given by the difference of two quantities. In 1908 Ritz showed experimentally that in any spectrum it was possible to set up tables of quantities called terms, having dimensions of cm^{-1}, such that the wavenumbers of the observed spectral lines could be written as the difference of two terms. This is known as the Ritz combination principle. In hydrogen, new spectral series were predicted with lines given by

$$\tilde{\nu} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

where m and n are integers and m is fixed for a given series. When, in the same year, Paschen discovered one of these new series in the infrared region, the principle received striking

confirmation.

These spectral lines at precisely related frequencies seemed to be in violent disagreement with the picture of the atom proposed by Rutherford (1911) to explain experiments on the scattering of α-particles. In this model, described more clearly by Bohr (1913), the atom was assumed to consist of a massive positively-charged nucleus, radius $\approx 10^{-12}$cm, which was surrounded by a cloud of negatively-charged electrons moving in orbits of radius $\approx 10^{-8}$cm. But according to classical mechanics, an electron moving in the Coulomb field of the nucleus would radiate electromagnetic energy at the frequency of its orbital motion. As the electron lost energy it would slowly spiral into the nucleus, emitting radiation of continuously increasing frequency. Obviously this did not happen in real atoms for they are observed to be stable in their normal state and to radiate only certain discrete frequencies when excited. The first major step forward in the solution of this problem was taken by Bohr (1913).

1.4. *The postulates of Bohr's theory of atomic structure*

In order to develop a quantitative theory of the hydrogen atom, Bohr put forward three basic postulates.

Postulate 1. *A bound atomic or molecular system can exist* only in certain discrete energy levels denoted by the values $E_1, E_2, \ldots, E_i, \ldots$. These energies are determined by superimposing certain quantum conditions (Postulate 3) on to classical mechanics.

Postulate 2. In the absence of any interaction with radiation, the atomic system will continue to exist permanently in one of the allowed energy levels which are therefore called stationary states. The emission or absorption of radiation is connected with a process in which the atom passes from one stationary state to another. In emission, the energy lost by the atomic system appears as energy in the radiation field and the frequency of the light emitted is given by

$$\hbar\omega_{ji} = E_j - E_i \tag{1.7}$$

where $\hbar$ is Planck's constant divided by 2π. The energy in the radiation field appears in the form of a photon and, following Einstein's hypothesis, has many of the characteristics of a material particle. In absorption, a photon is removed from the radiation field and the atom makes a transition from a lower to a higher energy level.

These two postulates were confirmed in the following year by the experiments of Franck and Hertz (1914) on the critical potentials of atoms. They found that when atoms were bombarded with a monoenergetic beam of electrons, only elastic collisions occurred at low energies. As the accelerating voltage is increased, a point is reached at which the electrons have sufficient kinetic energy to raise the atoms to the lowest excited energy level. Inelastic collisions occur and the atoms start to emit light in the transition connecting the lowest excited state to the ground level. As the electron energy is increased again, further excitation thresholds are reached and the spectrum of the atom appears line by line. Finally the bombarding electrons have sufficient energy to release an electron from the atom, so ionizing the gas. These experiments provide a direct, although rather imprecise, measurement of the energy levels and ionization potentials of atoms.

These two postulates also explain the existence of spectral terms and the Ritz combination principle. We see from equation (1.7) that the wavenumbers of spectral lines are given by differences of quantities of the form E_i/hc. These must therefore be the spectral terms. Thus the work of the spectroscopists in deducing the terms from the observed spectra immediately provides one with a table of atomic energy levels. Following this important clarification and the later development of selection rules for radiative transitions, the classification and analysis of atomic and molecular spectra proceeded rapidly. Energy-level tables are now available for the majority of atoms, ions, and simple

molecules, although the analyses of the complex spectra of the rare earth metals and of highly-ionized atoms are still often incomplete.

Postulate 3. For the hydrogen atom Bohr assumed that the electron moved in circular orbits about the nucleus under the influence of the Coulomb attraction. The allowed circular orbits were then determined simply by the requirement that the angular momentum of the electron should be an integral multiple of $\hbar$. This restricts the energies of the hydrogen atom, in states of angular momentum $n\hbar$, to the quantized values

$$E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\mu e^4}{2\hbar^2}\frac{1}{n^2}, \tag{1.8}$$

where ε_0 is the permittivity of free space and μ is the reduced mass of the electron, given by $\mu = m/(1+m/M)$ where m and M are the masses of the electron and proton respectively. Not only do the predicted energy levels have the $1/n^2$ dependence, in agreement with the formulae for the wavenumbers of the lines of the Lyman, Balmer, and Paschen series in hydrogen, but the empirical Rydberg constant is, for the first time, given in terms of atomic constants:

$$R_H = \frac{\mu e^4}{(4\pi\varepsilon_0)^2\, 4\pi\hbar^3 c} \tag{1.9}$$

When this expression is evaluated, it agrees with the spectroscopic value within the combined errors of the various constants involved.

1.5. *Development of quantum mechanics*

This tremendous accomplishment of Bohr stimulated other theoreticians, and soon Sommerfeld (1916) had generalized Bohr's quantum conditions and applied the results to elliptical orbits in the hydrogen atom. By including relativistic effects he was able to interpret many of the details of the hydrogen fine structure. The introduction of an additional quantum number describing the allowed orientations

of the orbits in space also gave a partial explanation of the observed Zeeman effect. However, one of the most important theoretical developments was Bohr's own correspondence principle. This states that in the limit of large quantum numbers, the results of quantum theory must be in agreement with the physical laws deduced from a combination of classical mechanics and electromagnetism. When this principle was combined with the relations connecting the transition probabilities for spontaneous and stimulated transitions derived by Einstein (1917), many of the results of the modern theory of radiation were obtained.

However, the old quantum theory was incomplete. It gave no definite basis for the calculation of the relative or absolute intensities of spectral lines. It also failed to give satisfactory results when attempts were made to calculate the energy levels of atoms containing more than one electron. Even in an apparently simple atom like helium, numerous attempts to calculate the energy of the ground state failed to reach agreement with the experimentally determined value.

The starting point of a new quantum theory of atoms was the hypothesis put forward by de Broglie (1924) that a particle moving with linear momentum p has associated with it a wave whose wavelength is given by

$$\lambda = h/p. \tag{1.10}$$

This idea was improved and extended by Schrödinger (1926) and led to the development of the equation which now bears his name. Almost simultaneously Heisenberg (1925) developed a theory of matrix mechanics which was soon shown to be mathematically equivalent to Schrödinger's wave mechanics. The development of the quantum theory of atomic structure and a review of some of the important results are continued in Chapter 3. We therefore now turn our attention to the development of the quantum theory of radiation processes.

1.6. *Interaction of atoms and radiation 1926-39*

In the period between 1926 and 1939 the development of our understanding of radiation processes parallels the development of the theory of atomic and molecular structure. Many of the results which had been derived by the use of the correspondence principle and the old quantum theory were re-derived in a more rigorous and satisfactory manner. The quantum-mechanical expression for the refractive index of a gas or vapour is an example of this type of progress. In hydrogenic systems the rates of radiative transitions were calculated and the theoretical lifetimes of the different excited levels were derived. In other atoms only approximate estimates of the transition probabilities were possible, but the lifetime measurements made by canal rays and fluorescence from atomic beams were not sufficiently accurate to demand more refined calculations.

Thus by 1939, it appeared once again that the understanding of atoms and light was almost complete, although it is true that in many cases satisfactory agreement between theory and experiment was only reached with the use of the more sophisticated techniques developed after the end of the second world war. A relativistically-invariant theory of one-electron atoms which included the effects of electron spin in a consistent manner had been developed by Dirac. This appeared to be the final solution to the problem of the hydrogen atom. However, it should be remembered that a few experimentalists were not entirely happy and questioned whether the Dirac theory of the fine structure was completely correct. There was therefore a need to develop new experimental techniques which would increase the accuracy of fine and hyperfine-structure measurements.

1.7. *Optical physics since 1945*

The work on radar and radio communications carried out during the second world war proved to be of immense assistance to one of the new spectroscopic techniques. This was

the magnetic resonance method first applied by Rabi *et al.* (1939) to atomic beams, and extended after the war to liquids and solids by Bloch, Purcell, and their colleagues (Bloch *et al.* 1946; Purcell *et al.* 1946). The first major shock to atomic physics came, however, when Lamb and Retherford (1947) applied this new technique to metastable hydrogen atoms and showed that the $2^2S_{\frac{1}{2}}$ and $2^2P_{\frac{1}{2}}$ levels of atomic hydrogen were not degenerate as predicted by the Dirac theory. This experiment stimulated the development of the theory of quantum electrodynamics and led to the precise calculation of radiative corrections to atomic energy levels. Further applications of the magnetic resonance method were opened up by the invention of the optical double resonance and optical pumping techniques by Kastler and his pupils in Paris (Brossel and Kastler (1949), Kastler (1950)). The extraordinary precision of these experiments has enabled a detailed study of the interactions of atoms with light and radio waves to be made, and has revealed subtle new effects which were previously hidden or unsuspected.

More recently the invention of microwave masers and of lasers operating at optical frequencies has transformed the field of optical physics in a remarkable way. In solid state physics, Franken's demonstration of the frequency doubling of ruby laser light immediately opened up a new field of non-linear optics. In atomic and molecular physics the applications of laser radiation were initially less rapid and spectacular. However, following the development of narrow-bandwidth tunable dye lasers in 1970, the interest in this field of research has experienced an explosive growth which as yet shows no signs of slowing down.

1.8. The present situation (1975)

We now believe that quantum mechanics, extended where necessary by quantum electrodynamics, is able to explain satisfactorily all features of the energy-level structure of atoms and molecules. Precise and detailed calculations of the energy levels of many atoms have now been made, and

there is generally excellent agreement with the empirical data obtained by spectroscopists. Similarly, we now believe that we have a good understanding of the processes involving the interaction of atoms with light, at least for experiments involving incoherent light or coherent radiation of low intensity. However, the effects of coherent, high intensity, radio- and optical-frequency radiation on atoms and molecules are at present only partially understood. Thus a great deal of experimental and theoretical work on the non-linear optics and spectroscopy of gases is currently in progress.

It is therefore safe only to say that this book is an attempt to present the state of our knowledge of the interaction of atoms and radiation as it exists now. In certain areas, theory and experiment dove-tail so neatly together that these processes must be considered to be well understood. In other areas, disagreement exists or work is still in progress and we should certainly be prepared for further surprises and unexpected developments in the future.

Problems

1.1. By considering the electromagnetic field confined within a large cubical box having perfectly reflecting sides, show that the number of modes of the radiation field per unit volume in the angular frequency range between ω and $\omega+d\omega$ is $\omega^2 d\omega/\pi^2 c^3$.

1.2. (a) From Planck's expression, equation (1.3), show that the angular frequency at which the energy density of black-body radiation is a maximum at a fixed temperature is proportional to the temperature. This is Wien's displacement law.

(b) By integrating equation (1.3) over all frequencies, show that the total energy density of black-body radiation is proportional to T^4 and that the constant of proportionality is given by

$$\sigma' = \frac{4\sigma}{c} = \frac{\pi^2 k^4}{15 c^3 \hbar^3} = 7{\cdot}565 \times 10^{-16}\ \mathrm{J\ m^{-3}\ K^{-4}}$$

This is the Stefan-Boltzmann law. $\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$

1.3. A classical model of a one-electron atom consists of a positive charge of amount $+e$ uniformly distributed throughout the volume of a sphere, radius R, together with a point electron of charge $-e$ which is free to move within the sphere. Show that the electron will oscillate about its equilibrium position with simple harmonic motion and find the frequency of oscillation, $\omega_0/2\pi$.

If the atomic radius R is equal to the radius of the first Bohr orbit, $a_0 = 4\pi\varepsilon_0\hbar^2/me^2$, show that ω_0 is twice the Rydberg angular frequency,

$$\omega_R = \frac{1}{2}\left(\frac{e^2}{4\pi\varepsilon_0 m a_0^3}\right)^{1/2}$$

1.4. In air, Ångström determined the wavelengths of the spectral lines of the visible series of atomic hydrogen as

H_α	6562·10 Å
H_β	4860·74 Å
H_γ	4340·10 Å
H_δ	4101·20 Å

Show that these lines are accurately described by the Balmer formula and from them calculate a value for the Rydberg constant, R_H. The refractive index of air in the visible region of the spectrum may be taken as 1·00028 at standard temperature and pressure.

By replacing the factor $1/2^2$ in equation (1.5) by $1/1^2$ and $1/3^2$ in turn, calculate the wavelengths *in vacuo* of the first four lines of the Lyman and Paschen series respectively.

1.5. Using the Bohr formula, equation (1.8), and the modern value of the Rydberg constant,

$R_\infty = 109\ 737\ \mathrm{cm^{-1}} \equiv 13{\cdot}6$ eV, construct energy-level diagrams for atomic hydrogen and singly-ionized helium to the same scale.

1.6. Show that as $n \to \infty$, the frequency of radiation emitted by a hydrogen atom in the transition from a level of principal quantum number n to one of quantum number $n-1$ tends to the frequency of the orbital motion of the electron as deduced from classical mechanics.

This is an illustration of Bohr's Correspondence Principle.

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Chapters 1 and 2 give an account of the historical development of modern physics and the references suggested on p.47 are particularly useful.

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2

Review of classical electrodynamics

This chapter gives a concise account of those sections of classical electromagnetism which we shall require later. We commence by introducing Maxwell's equations for time-dependent electric and magnetic fields and from them derive the electromagnetic wave equation. The properties and polarization of plane electromagnetic waves are examined and expressions for the energy flux and energy density obtained. We then introduce the scalar and vector potentials and discuss the radiation of electromagnetic waves by time-varying distributions of current and charge. This enables explicit expressions for the fields produced by oscillating electric and magnetic dipoles to be obtained. We derive expressions for the rate at which these dipoles radiate energy and angular momentum which will later be fundamental to our treatment of the spontaneous emission of radiation by excited atoms. Finally, we consider the radiation fields of electric quadrupole charge distributions and show how the angular distribution and rate of radiation differ from those of dipole sources.

2.1. *Maxwell's equations*

We now recognize that many apparently unrelated physical phenomena such as γ-rays, X-rays, visible light, thermal radiation, and radio waves are all forms of electromagnetic radiation, having frequencies ranging from 10^{20} Hz for γ-rays to 10^4 Hz for radio waves. The idea that electromagnetic waves could be propagated through space was first suggested by Faraday and was later confirmed by the brilliant theoretical work of Maxwell published in 1864. Maxwell started from the basic laws of electricity and magnetism for macroscopic phenomena, which, when stated in their differential form in the rationalized M.K.S. system are as follows: