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Part I

Introduction

1

The Principles of Fluorescence

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1.1 Luminescence

Although this chapter is concerned primarily with the fluorescence process it is important to understand that fluorescence is one of several phenomena that give rise to the collective term *luminescence*. Broadly speaking, luminescence is defined as the emission of light by a substance, where the emitted light cannot be attributed to incandescence, that is, thermal radiation. In the case of fluorescence, light is emitted from a substance after it has been irradiated, usually with visible or ultraviolet light. There are other important kinds of luminescences and some of these are described in the following paragraphs.

Phosphorescence is a light emission that often lasts minutes or sometimes hours after irradiation. The slow release of light characterized by phosphorescence is the result of the storage of energy in *metastable* states and is often thermally activated. In this instance "metastable" refers to the local stability of an energy state with respect to surrounding systems that exhibit a different energy state. *Photoluminescence* is a more general term that encompasses both fluorescence and phosphorescence.

Chemiluminescence is light emitted during cold chemical reactions whereas *bioluminescence* is essentially chemiluminescence from living organisms. *Thermoluminescence* is a type of phosphorescence but one that occurs at elevated temperatures. Thermoluminescence is not related to incandescence, as thermal excitation is used to initiate the release of energy from another source.

Electroluminescence is light emission initiated by electric influences. For example, in cathodoluminescence, the emission of light is initiated by excitation with an electron beam. *Radioluminescence* is caused by excitation with nuclear radiation or X-rays, whereas *triboluminescence* occurs when certain materials are mechanically altered, such as when fractured or polished.

Although several investigators reported luminescence phenomena during the 17th and 18th centuries, it was British scientist Sir George G. Stokes (1852) who first described "fluorescence" in his reference to the light-emitting properties of the mineral fluorite (fluorspar). It was not until the discovery of the electron by Sir Joseph John Thomson (1897a,b) and the discovery of the quantized nature of matter by Planck (1900, 1902) and light by Einstein (1905) that our comprehension of matter and energy was spectacularly

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revolutionized, and indeed it is the current theory of quantum mechanics that underpins our understanding of the fluorescence process.

1.2 The Relevance of Quantum Mechanics and Electronic Theory

Wave–particle duality is a central concept for our current understanding of modern quantum mechanics (Anastopoulos, 2008). The fact that particles and matter exhibit both wave and particle-like properties helps us to explain their behavior at the quantum scale. To appreciate *how* light interacts with matter, it is important first to consider the nature of light and the role of matter in terms of electronic structure. Unfortunately, an in-depth discussion pertaining to quantum theory and the magnificent discoveries throughout the history of science is beyond the scope of this chapter. However, for readers to gain an insight into *how* light can interact with matter in ways that result in the emission of light it is necessary first to consider the nature of light and how matter is organized in terms of electronic structure. Although there have been monumental discoveries over the ages, all of which have contributed to our understanding of the universe, for simplification this chapter focuses attention toward scientific discoveries achieved throughout late 19th and the 20th centuries.

1.2.1 Wave–Particle Duality and Quantization of Energy and Matter

During the early 19th century, atoms were the smallest particles known, and were believed to be indestructible and indeed indivisible, as such the knowledge of subatomic particles and their role in energy transfer processes in light–matter interactions were unknown. Many of the early advancements in electromagnetic theory were achieved owing to curiosity surrounding the phenomena of magnetism, electricity, and light.

1.2.1.1 Subatomic Particles

In 1838, Michael Faraday passed an electric current through a glass tube containing rarefied air (partially emptied). Faraday observed an arc of light emanating from the negative electrode (cathode) almost reaching the positive electrode (anode). These so-called cathode rays, what we now know to be electron beams, were the subject of great interest (Faraday 1844; Dahl, 1997). Shortly after the work of Faraday, in 1839, the French physicist Edmund Becquerel, who was fascinated by the properties of light, observed that certain materials produced electricity (the emission of electrons) when exposed to sunlight (Becquerel 1839). In 1857, German physicist Heinrich Geissler repeated Faraday's experiment but this time he was able to evacuate more air from specially designed glass tubes (10^{-3} atmospheres) using an improved pump. Geissler found that, instead of an arc, the light glow filled the tube completely (Dahl, 1997). James Clerks Maxwell's work regarding the nature of electromagnetic fields paved the way for a greater understanding of the nature of light, and between 1862 and 1864 Maxwell demonstrated that electric and magnetic fields propagated through space, in wave forms, at the speed of light. From this, Maxwell deduced (Maxwell's equations) that electricity, magnetism and light were all manifestations of the same phenomenon, and in 1865 proposed a unifying theory of electromagnetism through his publication “A dynamical theory of the electromagnetic field.” In 1876, the German physicist Eugen Goldstein coined the phrase *cathode rays* when he demonstrated that the glow from the cathode cast a shadow (Hedenus, 2002). The English scientist Sir William Crookes developed the first cathode ray tube during the 1870s with high vacuums. Using these tubes he was able to demonstrate that luminescence rays appearing within the tube actually carried energy from the cathode to the anode. Crookes also deflected these cathode rays using magnetism and showed that the cathode beam behaved as if it were negatively charged. In 1879, he proposed that these observations could be explained by a fourth state of matter in which negatively charged molecules were projected at high velocities from the cathode. Crookes termed this proposed fourth state “radiant matter” (Crookes, 1879; Eliezer & Eliezer, 2001).

Edmund Becquerel’s work and the conversion of light into electricity were of great interest to the German physicist Heinrich Hertz. In 1887, before the discovery of the electron, Hertz performed experiments demonstrating that an electric spark across an air gap between two electrodes is more easily emitted when ultraviolet light is shone on the cathode. Finally, in 1897, in his experiments investigating how gases at low temperatures conducted electricity, J. J. Thomson proved that cathode rays were composed of negatively charged *particles* that we now know as electrons, and that these particles were much lighter than the smallest ions known at that time, hydrogen. These observations (Thomson, 1897a,b), along with the accidental discovery of radioactivity from studies performed on natural fluorescing minerals by Antoine Henri Becquerel (1896) at the same time, provided evidence that atoms are not indestructible and that they are composed of *subatomic* particles. Thomson realized that because many atoms appeared to be electrically, other “positively charged” subatomic particles must also exist within the atom. It was in 1903 that Thomson postulated that individual atoms were spheres of “uniform positive electrification,” scattered with electrons rather like “currants” in a bun.

1.2.1.2 Quantized Matter and Energy

Before the discovery of the electron and the possibility of further subatomic particles, matter was known to have mass, chemical and electromagnetic properties. In the main, the aspects of matter that gave rise to many of the observed chemical and electrical properties were still largely unknown during the late 19th century. It was generally accepted that the arrangement of matter involved the presence of tiny oscillating particles (invisible to the naked eye) and that it was these oscillating properties that gave rise to observed chemical and physical properties. In 1894 Wilhelm Wien used theories about heat, and also Maxwell’s electromagnetic theories, to account for the relationship between wavelength distribution and radiated heat energy from a theoretical body of matter that absorbed *all* radiation (black-body). In 1896 Wilhelm Wien performed experiments designed to understand the spectral radiance of electromagnetic radiation from a black body in thermodynamic equilibrium (within a cavity). Wien presented his laws of thermal radiation work in a Nobel lecture given in December 1911 (Wien, 1911). Wien’s Law accurately predicts

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the behavior of black-body radiation at high frequencies (short wavelengths) but fails to predict accurately the behavior of black-body radiation at low frequencies (longer wavelengths). Max Planck, who is considered by many to be the founder of quantum mechanics, discovered that the intensity of electromagnetic radiation emitted by a black body is dependent on *both* the frequency of the radiation (the color of light) and the temperature of the emitting body. Planck (1900) stated that the energy of the charged oscillators in a black body must be *quantized* and that electromagnetic energy can be emitted only in a quantized form. This is to say that the energy (E) can only ever be a multiple of an elementary unit given by the equation

$$E = h\nu \tag{1.1}$$

where h is Planck's constant, and ν (the Greek letter nu) is the frequency of the oscillator. This later became known as the Planck postulate. The assumption that electromagnetic radiation (light) is quantized allowed Planck to derive a mathematical formula that could be applied to the *entire* electromagnetic spectrum, unlike Wien's Law, which was true only for short wavelengths (UV-Vis). At the time, Planck believed that the quantization of energy applied only to the tiny oscillators related to matter under investigation and made no assumption that light itself is quantized. Planck's concern was one of solving the mathematical problem highlighted earlier by Wien rather than proposing a fundamental change in the understanding of the world. Despite this, Planck's postulate was to help transform our understanding of the world and universe in which we exist.

The photoelectric effect is the phenomenon whereby electrons are emitted from material, such as metals, nonmetals, liquids, and gases as a direct consequence of their absorption of energy The achievements of Hertz in observing the photoelectric effect were very important as it paved the way for Johann Elster and Hans Geistel to pioneer the reliable production of photoelectric devices at the turn of the 20th century. These photoelectric devices could accurately measure the intensity of light far beyond the capability of the human eye. In 1902 before the discovery of the electron, Philipp Eduard Anton von Lenard observed that the energy of individual emitted particles from a cathode ray increased with the frequency of the light rather than the intensity of light (Philipp Lenard – Biography). At the time this postulate was in direct conflict with James Clerk Maxwell's electromagnetic wave theory, which predicts that the energy of the electromagnetic wave would be proportional to the intensity of the radiation as opposed to frequency. In 1905, Albert Einstein described light as being composed of discrete quanta (what we now know as photons), rather than as a continuous wave of energy. Using Max Planck's theory of black-body radiation, Einstein theorized that the energy in each quantum of light was equal to the frequency multiplied by a constant (later named Planck's constant). Therefore a photon above a threshold frequency has the required energy to eject a single electron. This work led to the theory of unity, which took into account that both electromagnetic waves and subatomic particles possessed properties both of particles and electromagnetic waves, the so-called wave–particle duality (Einstein, 1905).

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In 1903, just before Einstein's theory of unity, Thomson postulated that individual atoms were spheres of "uniform positive electrification," scattered with electrons rather like "currants" in a bun. Thomson also realized that because many atoms appeared to be electrically neutral, other "positively charged" subatomic particles must also exist within the atom. Shortly after this proposed model of Thomson, in 1910 Lord Ernest Rutherford and his researchers led to the proposition that an atoms mass must be concentrated at its center, that is, the nucleus (Rutherford, 1911). Much of Rutherford's work was complemented by the Danish physicist Neils Bohr, who, in 1913, proposed that electrons exist in *quantized* states. Bohr's physical model postulated that the energy of these quantized states was determined by the angular momentum (motion through space) of the electron's orbit about the nucleus. Quantized states do not vary "continuously" but rather in permitted quantum leaps, that is, between precise values. Furthermore, electrons were free to leap between these states, or orbits, by the emission or absorption of photons at discrete frequencies. Bohr used the notion of quantized orbits to account for the emitted spectral lines of hydrogen atoms. Although momentous in our understanding of physics, Bohr's model failed to predict the observed relative intensities of spectral lines, and more importantly the spectra of more complex atoms with fine and hyperfine structure. Despite the shortfalls of Bohr's theory, which was constrained to the simplest known atom, hydrogen, the notion that an atom is a dense nucleus of positive charge surrounded by lower-mass orbiting electrons was an established idea by 1914.

Bohr's initial model (Bohr, 1922) helped scientists advance our understanding of chemical bonding between atoms and better understand the quantum state. In 1916, American scientist Gilbert Newton Lewis proposed the idea of the covalent chemical bond, in which the bond between two atoms is maintained by a pair of "shared" electrons. The work of Lewis was elaborated further in 1919 by the American chemist Irving Langmuir. Langmuir suggested that all electrons were distributed in consecutive spherical "shells" of equal thickness. Langmuir further divided these shells into a number of cells each containing one pair of electrons. Using this model Langmuir was able to explain the chemical properties of all elements in the periodic table according to the periodic law, which states that the chemical properties of the elements are periodic functions of their atomic numbers.

In 1923, Walter Heitler and Fitz London fully explained electron-pair formation and chemical bonding in terms of quantum mechanics (Heitler and London, 1927). In the same year the French physicist Louise de Broglie proposed that wave–particle duality applied not only to photons, but also to electrons and every other subatomic physical system; this work was published in his PhD thesis in 1924. Austrian physicist Wolfgang Pauli (1925) observed that the shell-like structure of the atom could be explained by a set of four parameters that define every quantum energy state, as long as each state was inhabited by no more than a single electron.

These parameters are:

- Principle quantum number, n. In Bohr's model this number largely determines the energy level and the average distance of an electron from the nucleus.

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- Magnetic quantum number, *l*, which represents the orbital angular momentum and describes the number of possible angular momentum states.
- Azimuthal quantum number, *m*, where azimuthal represents the angular measurement in a spherical coordinate system.
- Spin quantum number, *s*. This number represents the intrinsic angular momentum.

It is important to note that matters are further complicated because for each principle quantum number value (n) there are $n - 1$ values for l. In addition, when s is taken into consideration for any quantum value n then there are a total of $2n^2$ states of the same energy possible. This prohibition against more than one electron occupying the same quantum energy state became known as the Pauli exclusion principle (Pauli, 1925, 1926; Massimi, 2005).

1.2.1.3 Copenhagen Interpretation

The work of Louise de Broglie in 1923 linked wavelength, frequency, and momentum, and de Broglie formulated the theory that any moving subatomic particle or object had an associated wave. This theory saw the birth of wave mechanics (*mécanique ondulatoire*), a mathematical unifying of the physics of energy (wave) and matter (particle). In 1925 an explanation of the spin quantum number (the fourth parameter), which had been shown to have two distinct possible values, was provided by the Dutch physicists George Uhlenbeck and Abraham Goudsmit when they suggested that an electron, in addition to the angular momentum of its orbit, could possess an intrinsic angular momentum. This property became known as spin and explained the previously mysterious splitting of spectral lines observed with a high-resolution spectrograph; this phenomenon is known as fine structure splitting.

In Copenhagen between 1925 and 1927, in an attempt to overcome the physical constraints and limitations of his theories, Bohr collaborated with the German physicists Werner Heisenberg and Max Born and the Austrian physicist Erwin Schrödinger to develop the use of abstract mathematical and theoretical formulations instead of physical empirical experiments. This was an important shift in scientific thinking, the main thrust of which was to explain the observations of everyday life and observation through mathematics, the so-called ‘matrix mechanics (Born et al., 1925; Born and Jordan, 1925; Heisenberg, 1925). These models utilized matrices (rectangular array of numbers) to describe properties such as momentum, energy, and position as opposed to ordinary numbers. In 1927, Heisenberg published the uncertainty principle. The Heisenberg uncertainty principle gives an insight into the nature of the quantum system itself and states that it is impossible to simultaneously know the momentum and position of a quantum object (e.g., electron) with perfect accuracy. Furthermore, Heisenberg continued to show that the more precisely one property is measured, the less precisely the other *can* be measured. The very act of observing a particle at any one point in time and space will change the behavior of that particle within the quantum system. Therefore the uncertainty principle is not concerned about the limitations of scientists or measurement techniques, but is a mere description of the nature of the quantum system itself. Consequently, it is not possible to know the values of all of the properties of the system at the same time and therefore the unknown properties must be described in terms of probability. Erwin Schrödinger used de Broglie's concepts on wave mechanics to describe the time dependence of a physical quantum state. Schrödinger's attempt to describe how a quantum state changes over time assumed that because all matter has wave-like properties, then all physical quantum states could be explained using wave functions. Initially there was much debate concerning what the wave function (ψ) of the equation was. It is now generally accepted that a wave function is a probability distribution (Born interpretation). The Schrödinger equation is used extensively in modern quantum mechanics to discover the allowed energy levels of quantum mechanical systems (e.g., atoms, molecules, and transistors). Schrödinger (1926a,b) is seen by many as the most significant contributor to the wave theory of matter.

These attempts by Bohr, Heisenberg, Born, and Schrödinger to interpret experimental observations through mathematical formulations became known as the Copenhagen interpretation.

The principles of the Copenhagen interpretation state that

- All quantum systems can be completely described by wave functions.
- The description of nature is probabilistic.
- Matter has wave–particle duality and experiments can determine only if matter is behaving either as a particle or as a wave.
- It is not possible to know the values of all of the properties of any system at the same time. Therefore, the unknown properties can be described only in terms of probability (Heisenberg's uncertainty principle).

1.2.2 Chemical Bonding and Molecular Orbitals

The interactions between electrons and orbitals within atoms ultimately lead to chemical bonding and the formation of molecules, and it is these interactions that are mostly responsible for the absorption and light-emitting properties of molecules. Because this book is principally concerned with the properties of dissolved organic fluorophores, it is necessary to focus our attention on the nature of chemical bonding and molecular orbitals. The theory of covalent bonding, as proposed by Gilbert Lewis in 1916, states that a covalent bond involves the sharing of two electrons between two atoms. However, this theory predated the theory of quantum mechanics, and currently there are two basic models that have been developed to explain how electrons are shared by atoms, the valence bond (VB) theory and molecular orbital (MO) theory (Hückel, 1930, 1931, 1932; Pauling, 1931, 1940). Both of these theories introduce wave functions from quantum mechanical theory. The following sections discuss the nature of bonding albeit in a limited way. Useful underpinning reading can be found from most modern chemistry textbooks (Atkins, 2007; Atkins et al., 2009; Brady, 2011).

According to the Bohr theory (1922), all electrons in the same orbit (shell) have the same energy. However, we now know that with the exception of electrons in the first orbit that this is not the case. Therefore the energy orbitals within atoms (**s, p**, **d**, and **f**) also possess sublevels (principle quantum number) of energy. Owing to the wave–particle duality of electrons it is impossible to pinpoint their exact position; instead we can only consider the probability of finding an electron in a region of space. The probability (expressed as the volume around a nucleus in which an electron is 90% probable to be found) is referred to as the atomic orbital. The orbital of **s** electrons is spherical (**s** orbital). There are three different **p** orbitals ($\mathbf{p}_x$, $\mathbf{p}_y$, and $\mathbf{p}_z$), which have equal energies but different directions in space. These are often described as dumbbell orbitals. For electrons at higher energies, **d** and **f** orbits become available. These orbitals are more complex and numerous than the orbits observed for **s** and **p** electrons.

The distribution of electronic charge throughout the axis of a chemical bond is important. In covalent bonding the region where the value of an orbital wave function (ψ) equals zero (or is very low), defines a region of space within the system where there is zero electron density. This is known as a nodal plane, and quantum theory indicates that molecular orbitals with identical symmetries mix, and the wave functions for $\mathbf{s} + \mathbf{s}$ and $\mathbf{p}_z + \mathbf{p}_z$ become blended. The extent of this mixing (or blending) depends on the relative energies of the molecular orbitals involved and is extremely important for determining the number of nodal planes and distribution of energy within molecular bonding orbitals. This mixing of wave functions is termed resonance. Typically, molecules exist as a number of atoms bonded together via covalent bonding, and the collective arrangement of these atoms is such that the overall molecular structure is electrically neutral. Within this structure, all outermost electrons of the atoms involved are paired with other electrons, either in bonds or lone pairs. These outer electrons are termed *valence electrons* and are very influential in determining how atoms interact with each other (reactivity).

Lewis's original theory could not take into account the shape adopted by molecules. Gillespie and Nyholm (1957) developed the currently accepted modern theory of chemical bond formation (MO and VB theories), which uses the valence-shell electron pair repulsion model (VSEPR) to account for molecular structure (Gillespie, 1970). VSEPR states that molecular shape is caused by repulsions between electron pairs in the valence shell.

1.2.2.1 Sigma Bonds (σ Bonds)

Sigma bonds (σ bonds) are the strongest type of covalent chemical bond and are perhaps best illustrated in simple diatomic molecules such as H_2, F_2, Cl_2, Br_2, and I_2. Sigma bonding in diatomic molecules is always symmetrical with respect to the rotation about the bond axis (nucleus to nucleus). Therefore common σ bonds can be represented as $\mathbf{s} + \mathbf{s}$, $\mathbf{p}_z + \mathbf{p}_z$, $\mathbf{s} + \mathbf{p}_z$, and $\mathbf{d}_z{}^2 + \mathbf{d}_z{}^2$ (where z is defined as the axis of the bond). In σ covalent bonding the two "shared" electrons can either originate from the same atom, in which case the σ bond is covalent, or from each atom, where the σ bond is termed a coordinate covalent bond. For homo diatomic molecules, bonding σ orbitals have no nodal planes between the bonded atoms, whereas in the case of hetero diatomic atoms forming a covalent bond (where one atom is more electronegative than the other) the electron pair will spend more time closer to that atom. This is termed a polar covalent bond.