Foundations of
Molecular Quantum Electrodynamics

R. GUY WOOLLEY

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This book presents a comprehensive account of molecular quantum electrodynamics from the perspectives of physics and theoretical chemistry. The first part of the book establishes the essential concepts underlying classical electrodynamics, using the tools of Lagrangian and Hamiltonian mechanics. The second part focuses on the fundamentals of quantum mechanics, particularly how they relate to, and influence, chemical and molecular processes. The special case of the Coulomb Hamiltonian (including the celebrated Born–Oppenheimer approximation) is given a modern treatment. The final part of the book is devoted to non-relativistic quantum electrodynamics and describes in detail its impact upon our understanding of atoms and molecules, and their interaction with light. Particular attention is paid to the Power–Zienau–Woolley (PZW) representations, and both perturbative and non-perturbative approaches to QED calculation are discussed. This book is ideal for graduate students and researchers in chemical and molecular physics, quantum chemistry, and theoretical chemistry.

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To Anne, Claire and Euan

Au terme dernier, vous m'apprenez que cet
univers prestigieux et bariolé se réduit à l'atome
et que l'atome lui-même se réduit à l'électron.
Tout ceci est bon et j'attends que vous continuiez.
Mais vous me parle d'un invisible système
planétaire où des électrons gravitent autour d'un
noyau. Vous m'expliquez ce monde avec une
image. Je reconnais alors que vous en êtes
venus à la poesie: je ne connaîtrai jamais.
Ai-je le temps de m'en indigner ?
Vous avez déjà changé de théorie.
Ainsi cette science qui devait tout m'apprendre
finit dans l'hypothèse, cette lucidité sombre
dans la métaphore, cette incertitude se résout en œuvre d'art.

Albert Camus, *Le mythe de Sisyphe*, © Éditions Gallimard

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Preface

The book begins with an account of how chemistry came about as a science and hit on a structural conception to account for the empirical facts of chemical reactions in terms of the spatial arrangement of atoms. Such an approach is to be contrasted with that of physics, which is founded on a mechanical description of natural phenomena. The basic unit of chemistry is the atom; however, not enough is known about their 'interactions' to formulate a 'mathematical chemistry' beyond stoichiometry, and so recourse has long been taken to subatomic structure in terms of electrons and nuclei. Such particles have the additional physical property of electric charge, and a combination of electrodynamics and quantum theory is unavoidable in a fundamental physical account. These two contrasting methodologies collided in the early twentieth century when physics advanced into what had hitherto been the province of the chemist. In the author's opinion the resulting tension has never been resolved satisfactorily. An exploration of how that tension arises and where it persists seems a good enough reason to try to describe the 'known knowns' and the 'known unknowns' in this story. Although some of the principal features of quantum chemistry will feature, this is not another book about quantum chemistry, a subject for which there is already an extensive textbook, monograph and journal literature.

The book is divided into three parts: 'The Classical World', 'Quantum Theory', and 'Non-relativistic Quantum Electrodynamics'. After the historical account of the development of chemical thought, the next three chapters in Part I summarise some essential facts about classical electrodynamics, starting from Maxwell's explanation of electromagnetic phenomena in terms of the fields **E** and **B** – the electric and magnetic fields, respectively. Throughout the book extensive use will be made of auxiliary variables to describe the field (the field potentials) and the charge–current density of the charged particles (the polarisation fields), and a recurring theme is the need to keep in mind that the auxiliary variables are arbitrary and unphysical. Chapter 2 describes classical electromagnetism; looking ahead to a hoped-for quantum theory, it is important that the combined system of charged particles and electromagnetic field can be described by the mechanical schemes devised by Lagrange ('Lagrangian mechanics') and Hamilton ('Hamiltonian mechanics'), and these are developed in Chapter 3. Chapter 4 is concerned with the formal description of the electromagnetic field in the absence of charges in terms of a collection of independent harmonic oscillators using the Hamiltonian scheme.

Part II of the book introduces the ideas of the quantum theory. Quantum mechanics is the general dynamical theory of physical systems according to the quantum laws when temperature is ignored; in other words, it is a $T = 0$ theory. Chapter 5 gives

an outline of the basic quantum mechanical formalism and concepts, while Chapter 6 reviews methods for approximate calculations that have proved to be useful in the present context, and includes some introductory remarks about the finite temperature theory. Chapter 7 describes the quantisation of the free electromagnetic field both in terms of photons (the 'particle' description) and through reinterpretation of the field variables as quantum mechanical operators (the 'wave' description); they are entirely equivalent. Chapter 8 is concerned with the quantum mechanics of a collection of electrons and nuclei when only electrostatic interactions between the charges are considered – based on the so-called Coulomb Hamiltonian. This has been much studied in physics (the 'many-body problem') and, of course, is of central importance for the physics of atoms and molecules. For the latter a 'clamped-nuclei' formulation is ubiquitous. The assumption that the nuclei, even if identical, can be regarded as fixed, distinguishable classical charges is commonly justified by reference to some version of the celebrated 'Born–Oppenheimer approximation' which is given close scrutiny.

Part III is devoted to non-relativistic quantum electrodynamics (QED) understood as the quantum mechanics of a closed collection of charges interacting with the electromagnetic field, finishing with what it might mean for atoms and molecules given that they are described as collections of electrons and nuclei; this is where the 'known unknowns' become prominent as we cycle back to the first chapter. Chapter 9 examines how quantisation of the combined system of charges and field may be carried out, paying special attention to the gauge transformations associated with the vector potential, and a dual description in terms of polarisation fields. Chapter 10 describes the perturbation theory approach to QED, based on choosing the 'unperturbed' reference system as an idealised 'free field' and an atomic system in the absence of electromagnetic radiation. Chapter 11 gives some introductory remarks on the non-perturbative investigations of non-relativistic QED Hamiltonians that are of active interest in mathematical physics. Finally, in Chapter 12 we confront this mathematically sophisticated account of the building blocks of atoms with what the chemists have found with molecules.

I am indebted to Akbar Salam and Brian Sutcliffe, who gave me much valuable commentary on the early draft of this book; naturally, I am solely responsible for errors that remain. My heartfelt thanks for the love and support of my family and their indulgence over the period of its writing. Many thanks also to my editors, Sarah Armstrong and Nicholas Gibbons of Cambridge University Press, for their encouragement and advice.

PART I

THE CLASSICAL WORLD

Introduction

1.1 The Origins of Chemistry

Chemistry is concerned with the composition and properties of matter, and with the transformations of matter that can occur spontaneously or under the action of heat, radiation or other sources of energy. It emerged as a science in recognisably modern form at the end of the eighteenth century. From the results of chemical experiments, the chemist singles out a particular class of materials that have characteristic and invariant properties. This is done through the use of the classical separation procedures – crystallisation, distillation, sublimation and so on – that involve a phase transition. Such materials are called pure substances and may be of two kinds: elements and compounds. A pure substance is an idealisation since perfect purity is never achieved in practice.

Formally, elements may be defined as substances which have not been converted either by the action of heat, radiation or chemical reaction with other substances, or small electrical voltages, into any simpler substance. Compounds are formed from the chemical combination of the elements, and have properties that are invariably different from the properties of the constituent elements; they are also homogeneous. These statements derive from antiquity; thus from Aristotle [1]:

> An element, we take it, is a body into which other bodies may be analysed, present in them potentially or in actuality (which of these, is still disputable), and not itself divisible into bodies different in form.

Similar statements can be found in Boyle and in Lomonosov, for example; they gain significance when the notion of 'simpler' substance is explicated. A substantial account of the history and philosophy of these ideas can be found in a recent Handbook [2].

In the seventeenth century, a scientific attitude emerged that is recognisably 'modern'; it aimed to describe the physical aspects of the natural world through analytical procedures of classification and systematisation in order to find explanations of natural phenomena in purely naturalistic terms [3]. The underlying mechanical philosophy[1] was grounded firmly in a picture of a world of physical objects endowed with

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[1] The idea that the physical world is a complex machine that could, in principle, be built by a skilled artisan.

well-defined fixed properties that can be described in mathematical terms – shape, size, position, number and so on. It can be seen as a return to the mathematical ideals of the Pythagoreans and of Plato, and a renewal of the ideas of the early Greek atomists, for example Democritus. There was quite explicitly a movement against the still prevailing Aristotelian system of the scholastic philosophers which was closely connected with the religious authorities. The prime movers of this revolution were Galileo and Descartes; both sought a quantitative approach to physics through the use of mathematics applied to mechanical or corpuscular models that would replace a philosophical tradition that had originated in antiquity.

The scientific revolution initiated by Galileo with its quantitative approach to physics represented a fundamental shift from the organism to the machine as the model in terms of which the physical world should be understood. However, the belief that this understanding was founded on 'ultimate explanations' rooted in principles that appear self-evident was demolished by Newton's account in the *Principia* of the physical world based on universal gravitation. Action-at-a-distance (gravity) cannot be reconciled with a strict mechanistic philosophy, instead the goals of science became focused on finding the best theoretical account of experience and experiment, in preference to reliance on common-sense notions of the world. As far as chemistry is concerned, this shift in outlook did not take place until more than a century later.[2] Alchemy was regarded with increasing scepticism throughout the eighteenth century partly due to the accumulation of empirical evidence that spoke against transmutation of metals, but nevertheless aspects of it such as the interpretation of chemical properties in terms of alchemical 'principles' and the phlogiston ideas of Becher and Stahl lingered on.

Eventually the new view of physics prevailed comprehensively; the significance of this for chemistry was the recognition that the alchemical 'principles' and phlogiston could not survive the Newtonian imperative. On the other hand a mathematical formulation of chemical laws on Newtonian lines was never achieved. The phlogiston chemists did have some success in distinguishing between mixtures and pure substances (including some of the elements in the modern sense) by experimental means; this was also true of the later alchemists but to a much more limited extent. Thereby they discovered that there were limits to the amount of separation of a starting material that could be achieved by repeated crystallisation and distillation, and that the end products of these physical separation procedures often had characteristic physical properties such as boiling point, melting point[3] and crystal morphology by which different substances could be recognised. Once it became possible to distinguish reliably between different substances, systematic chemical experimentation could be carried out. Two enduring features emerge from such practice:

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[2] Lavoisier notably took a steam engine as a model for describing a living body [4]. Newton's lengthy absorption in alchemy, contemporary with his novel physics, had been imbued with the organic ideas of growth and maturation [5], [6].

[3] The German physicist and instrument maker, D. G. Fahrenheit, invented the mercury thermometer in 1714 and devised the temperature scale that bears his name shortly after [7].

1. Chemical transformations generally bring about changes in the properties of substances.
2. Substances vary widely in their chemical reactivity when in contact with other substances.

The change in attitude that accompanied the emergence of chemistry as a science can be seen in Lavoisier's *Traité élémentaire de chemie*; he recognised that differences in masses were experimentally accessible and proposed that the elements should be characterised by their gravimetric properties. He produced a reasonably correct and extensive list of elements with their modern names [8]. Lavoisier was by no means the first chemist to have investigated the weight relationships of reagents and products in chemical transformations. He was, however, the first person to publish an account of how such information could serve as the basis of a systematic analytical approach to chemistry. Even so, light and 'caloric' were still included in his list of elements despite their imponderable nature and the impossibility of isolating 'caloric' experimentally in its free state. After Lavoisier, an element came to be understood as a pure substance that formed products of greater weight than itself in all chemical changes which it underwent. The significance of the implementation of this new meaning for the concept of 'element' was that (a) elements and compounds could be recognised experimentally by a physical property and (b) it then became apparent that the characteristic properties of the elements did not persist in their compounds. This is in stark contrast with the mythical conception it displaced.

The characteristic chemical notion of a pure substance is based on an ideal conception of the chemical and physical properties of matter and their changes under specified experimental conditions (pressure, temperature, in inert containers etc.). Physical properties belong to materials in isolation from other materials and are those properties that can be observed without conversion of the material into other substances, whereas chemical properties refer to the chemical reactions that materials undergo. There we have a fundamental distinction between the goals of chemistry and physics. The core activity of the chemist is the experimental preparation of chemical compounds – *chemical synthesis* – and their characterisation – *chemical analysis*.

This first chapter gives an account of the historical development of the atomic–molecular conception of chemistry that led to the fundamental chemical idea of molecular structure. This is the overarching idea that opens the way to a systematic account of the experimental facts of chemistry; it is a microscopic interpretation in terms of the 'smallest particle' of an element, the 'atom', but does not require any detailed physical description of an 'atom'. There is a parallel history of the search in physics for the characterisation of the 'atom', and a central question for science is how/whether these two histories might be unified. Physics is based on dynamics and requires rules governing the interactions between basic 'particles'. It ascribes a fundamental role to the notions of energy and time, concepts entirely lacking from a structural account. In the absence of a theoretical formulation of the interactions of atoms sufficient for describing chemistry, recourse was taken more than a hundred years ago to subatomic structure – the discovery that atoms were composite entities

comprised of positive (nuclei) and negative (electrons) charged particles – as a basis for a physical account of molecular properties. It is thus inevitable than a physical understanding of chemistry must involve some version of quantum theory and the electrodynamics of charged particles. This book is devoted to things we know about non-relativistic electrodynamics that seem relevant to such a unification which remains controversial. There are also 'known unknowns' to be identified along the way, and from this vantage point the 'unknown unknowns' may be uncovered in the future [9].

1.2 Stoichiometry and Atoms

Measurements of changes in weight – stoichiometry[4] – are a characteristic feature of the quantitative study of chemical reactions; such measurements reveal one of the most important facts about the chemical combination of substances, namely that it generally involves fixed and definite proportions by weight of the reacting substances. These changes in weight are found to be subject to two fundamental laws:

Law of conservation of mass: (A. Lavoisier, 1789)

L1 No change in the total weight of all the substances taking part in any chemical process has ever been observed in a closed system.

Law of definite proportions: (J. L. Proust, 1799)

L2 A particular chemical compound always contains the same elements united together in the same proportions by weight.

The *chemical equivalent* (or *equivalent weight*) of an element is the number of parts by weight of it which combines with, or replaces eight parts by weight of oxygen or the chemical equivalent of any other element; the choice of eight parts by weight of oxygen is purely conventional. By direct chemical reaction and the careful weighing of reagents and products, one can determine accurate equivalents directly. Depending on the physical conditions under which reactions are carried out, one may find significantly different equivalent weights for the *same* element corresponding to the formation of several chemically distinct pure substances. These findings are summarised in the laws of chemical combination [10]:

Law of multiple proportions: (J. Dalton, 1803)

L3 If two elements combine to form more than one compound the different weights of one which combine with the same weight of the other are in the ratio of simple whole numbers.

Let $E[A, n]$ be the equivalent weight of element A in compound n [11]; if we consider the different binary compounds formed by elements A and B, the Law of Multiple Proportions implies

$$\frac{E[A, i]}{E[B, i]} \;=\; \omega_{ij} \, \frac{E[A, j]}{E[B, j]}, \tag{1.1}$$

where ω_{ij} is a simple fraction.

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[4] From Greek $\sigma\tau o\iota\chi\varepsilon\tilde{\iota}o\nu$ – *stoicheion* – an element.

Law of reciprocal proportions: (J. Richter, 1792)

L4 The proportions by weight in which two elements respectively combine with a third element are in a simple ratio to the proportion by weight in which the two elements combine with one another.

In the notation just introduced this means

$$\frac{E[Y,YZ]}{E[Z,YZ]} = \frac{m}{n}\left(\frac{E[Y,XY]/E[X,XY]}{E[Z,XZ]/E[X,XZ]}\right), \tag{1.2}$$

where m and n are small integers. On the other hand, a knowledge of the proportions by weight of the elements in a given pure substance is not sufficient information to fix the chemical identity of the substance since there may be several, or many, compounds with the same proportions by weight of their elemental constituents; for example, this is true of many hydrocarbon substances which are chemically distinct yet contain one part by weight of hydrogen to twelve parts by weight of carbon, for example, acetylene, benzene, vinylbenzene, cyclooctatetraene and so on. In these cases, there are distinct compounds formed by two elements that exhibit constant chemical equivalents.

At the beginning of the nineteenth century, the chemical elements were given a microscopic interpretation in terms of Dalton's atomic hypothesis that marks the beginning of chemical theory. The impetus for this new insight came from Dalton's investigations of the properties of mixtures of gases and their solubility in water, and his interest in meteorology. The constant composition of the atmosphere was explained by Lavoisier, Berthollet, Davy and other prominent chemists as being due to a loose chemical combination between its elements. Dalton, who had made a detailed study of the *Principia*, combined Newton's atomic picture of fluids with his own ideas about heat to argue correctly that the atmosphere was a physical mixture of gases. His interest in the mechanism of mixing (and solution) of gases prompted him to determine the relative sizes of the atoms of the gases, and for this purpose he had first to determine their relative weights [12], [13]. Only later did he attempt to apply his atomic theory to chemical experiments; his success in correctly deducing the formulae of the oxides of nitrogen (N_2O, NO, NO_2) led him to state the law of multiple proportions.

Henceforth, the elements were to be regarded as being composed of microscopic building blocks, atoms, which were indestructible and had invariable properties, notably weight, characteristic of the individual elements. Similarly, compounds came to be thought of in terms of definite combinations of atoms that we now call molecules. All molecules of the same chemical substance are exactly similar as regards size, mass and so on. If this were not so, it would be possible to separate the molecules of different types by chemical processes of fractionation, whereas Dalton himself found that successively separated fractions of a gaseous substance were exactly similar. Dalton's idea is different from historically earlier interpretations of the atomic concept such as that of early Greeks, like Democritus, or of Boyle and Newton.

Nearly 50 years of confusion followed Dalton until the Sicilian chemist Cannizzaro outlined [14] a method whereby one could reliably determine a consistent set of weights of different kinds of atoms from the stoichiometric data associated with

a set of chemical reactions, and he used this method to define the atomic composition of molecules. Cannizzaro's argument was based on Avogadro's hypothesis that equal volumes of gases at the same pressure and temperature contain equal numbers of molecules. From the mathematical point of view, the problem is indeterminate in the sense that one cannot exclude the possibility that the 'true' atomic weights are actually integer submultiples of those proposed. Cannizzaro offered a partial remedy by observing that the probability that one has the 'true' weights is increased by increasing the amount of data about stoichiometric relations. It is the case that a complete account of the mathematical relations that represent stoichiometry does not require any assumption about atoms [15].

Another limitation is that stoichiometry is concerned only with the changes in weight that occur in chemical reactions; it says nothing about the changes in other properties that accompany chemical transformations. Equally, the original atomic theory could say nothing about the chemical affinity of atoms, why some atoms combine and others do not, nor give any explanation of the restriction to simple fractions in the laws of chemical combination of atoms. Affinity had been a major problem for the phlogiston chemists which was not resolved by Dalton's atomism; only much later with the aid of a structural conception of chemical substances would it be amenable to elucidation. That said, this account of stoichiometry was a major theoretical achievement in classical chemistry based on the atomic/molecular conception of matter.

1.3 Molecular Structure and Chemical Bonds

Having sorted out ideas about elements and compounds in terms of atoms and molecules, attention shifted to synthesis – the making of new compounds – and progress thereafter was rapid, especially in the chemistry of compounds containing the element carbon, what we call organic chemistry. It seems pertinent to recognise that the synthesis of new substances has been the principal experimental activity of chemists for more than 200 years. The number of known pure organic and inorganic substances has grown from a few hundred in 1800 to several hundred million today, with a doubling time of about 13 years that had been remarkably constant over the whole span of two centuries [16]. In order to keep track of the growth of experimental results, more and more transformations of compounds into other compounds, some kind of theoretical framework was needed. In the nineteenth century, the only known forces of attraction that might hold atoms together were the electromagnetic and gravitational forces, but these were seen to be absolutely useless for chemistry and so were given up in favour of a basic structural principle. The development of the interpretation of chemical experiments in terms of molecular structure was a highly original step for chemists to take since it had nothing to do with the then known physics based on the Newtonian ideal of the mathematical specification of the forces responsible for the observed motions of matter. It was one of the most far-reaching steps ever taken in science. G. N. Lewis once wrote [17]

> No generalization of science, even if we include those capable of exact mathematical statement, has ever achieved a greater success in assembling in a simple way a multitude of heterogeneous observations than this group of ideas which we call structural theory.

In the 1850s the idea of atoms having autonomous valencies had developed, and this led Frankland to his conception of a chemical bond [18], [19]. He wrote [20]

> By the term *bond*, I intend merely to give a more concrete expression to what has received various names from different chemists, such as atomicity, an atomic power, and an equivalence. A monad is represented as an element having one bond, a dyad as an element having two bonds, *etc*. It is scarcely necessary to remark by this term I do not intend to convey the idea of a material connection between the elements of a compound, the bonds actually holding the atoms of a chemical compound being, as regards their nature much more like those which connect the members of our solar system.

The idea of representing a bond as a straight line joining atomic symbols is probably due to Crum Brown. Frankland, with due acknowledgement, adopted Crum Brown's representation which put circles round the atom symbols, but by 1867 the circles had been dropped and more or less modern chemical notation became widespread.

There is a long history in chemistry of the view that chemical combination is due to electrical forces. In the early nineteenth century, Berzelius attempted to systematise the chemical knowledge of his time in an electrochemical theory which took Volta's ideas of galvanic action in a battery as its starting point [21]. The rise of organic chemistry, in which the combination of atoms was not obviously of an electrical kind, led to the eclipse of his approach; the theory of types and the theory of radicals both bid to replace it. Later, it was recognised that Berzelius' idea that the quantity of electricity collected in each atom of different elements depended on their mutual electrochemical differences and controlled their chemical affinity was contradicted by the laws of electrolysis discovered by Faraday. The electrical theory of chemical combination was revived and expanded by von Helmholtz in his celebrated 1881 Faraday lecture [22].

In 1875 van 't Hoff published a famous booklet which marks the beginning of stereochemistry [23]. Following a suggestion of Wislicenus, van 't Hoff proposed that molecules were microscopic material objects in the ordinary three-dimensional space of our sensory experience with physicochemical properties that could be accounted for in terms of their three-dimensional structures. For example, if the four valencies of the carbon atom were supposed to be directed towards the corners of a tetrahedron, there was a perfect correspondence between predicted and experimentally prepared isomers, and a beautiful structural explanation for the occurrence of optical activity. It is natural to extend this hypothesis to all molecules and to suppose that optically active molecules are simply distinguished from other species in that they possess structures that are dissymmetric. Here there is a clear implication for the dimensionality of the 'molecular space'. In a two-dimensional world there would be two forms of the molecule CH_2X_2, whereas only one such compound is known. On the other hand, molecules

such as C-abde exist in two forms; these facts require a three-dimensional arrange-ment of the 'bonds'. Evidently, no picture of the atom is required for this construction; indeed molecular structures can be reduced to suitably labeled points (atoms) joined by lines (bonds). Moreover, van 't Hoff's identification of ordinary physical space as the space supporting these structures is optional; any Euclidean 3-space will do. For van 't Hoff, stereochemistry was part of an argument to give a proof of the physical reality of molecules; molecules could not be perceived directly simply because of the limitations inherent in our senses.

Atomic structure seems first to have been related to valency when both Mendeléev and Meyer observed, independently, in 1869 how valency was correlated with posi-tion in the periodic table [24]. There was however no agreement about the nature of atoms. In the same year as van 't Hoff inaugurated stereochemistry with his advo-cacy of the tetrahedral bonding about the carbon atom, Maxwell gave strong support to Lord Kelvin's vortex model of the atom [25] because it offered an atomic model which had permanence in magnitude, the capacity for internal motion or vibration (which Maxwell linked to the spectroscopy of gases), and a sufficient amount of pos-sible characteristics to account for the differences between atoms of different kinds [26].

From the second half of the nineteenth century onwards, the attribution of phys-ical reality to atoms and molecules was highly controversial because of its obvious metaphysical character. While the realist position was advocated strongly by chemists such as van 't Hoff, and physicists such as Maxwell and Boltzmann, it was criticised severely by other noted scientists such as Duhem and Ostwald whose scientific phi-losophy was related to the positivism of Mach; for them atoms were fictions of the mind, and they preferred to restrict their discussions to the macroscopic domain. Yet again, others preferred to maintain a sharp distinction between what they regarded as objective knowledge and what was only probably known or speculative; for exam-ple, Kekulé did not share the strong conviction of his student van 't Hoff about the structural model, but Kekulé was nevertheless an effective user of the model.

On the other hand, chemists had made a change that brought their thinking much more into line with the customary approach in physics; from the 1860s onwards, induc-tive argument was replaced by a deductive model based on the formulation and testing of hypotheses [27]. Another important point to keep in mind is that chemistry at the start of the nineteenth century was a science of the transformation of substances (Lavoisier), whereas by the end of the century it had become a science of the trans-formations of molecules (van 't Hoff), so much so that practitioners of the chemical sciences now often do not distinguish between substances and molecules.

Thus over a period of many years, chemists developed a chemical language – a sys-tem of signs and conventions for their use – which gave them a representation of their fundamental postulate that atoms are the building blocks of matter; molecules are built up using atoms like the letters of an alphabet. A molecule in chemistry is seen as a struc-ture, as a semi-rigid collection of atoms held together by chemical bonds. So not only can the numbers of different kinds of atoms in a molecule be counted, but their disposi-tion with respect to each other can be imagined, and this leads to pictures of molecules.

The laws that govern the relative dispositions of the atoms in three-dimensional space are the classical valency rules which provide the syntax of chemical structural formulae. In particular, they specify the combinations of atoms that can be realised under 'ordinary' conditions. Valency, the capacity of an atom for stable combination with other atoms, is thus a constitutive property of the atom not requiring further explanation.

To each pure substance there corresponds a structural molecular formula; and conversely, to each molecular formula there corresponds a unique pure substance. It is absolutely fundamental to the way chemists think that there is a direct relationship between specific features of a molecular structure and the chemical properties of the substance to which it corresponds. Of especial importance is the local structure in a molecule involving a few atoms coordinated to a specified centre, for this results in the characteristic notion of a functional group; the presence of such groups in a molecule expresses the specific properties of the corresponding substance (acid, base, oxidant etc.) which, however, is realised only experimentally in an appropriate reaction context.

Furthermore, each pure substance can be referred to one or several categories of chemical reactivity, and can be transformed into other substances which fall successively in other categories. The structural formula of a molecule summarises or represents the connection between the spatial organisation of the atoms and a given set of chemical reactions that the corresponding substance may participate in. This set includes not only the reactions required for its analysis and for its synthesis, but also potential reactions that have not yet been carried out experimentally. This leads to a fundamental distinction between the chemical and physical properties of substances; while the latter can be dealt with by the standard 'isolated object' approach of physics, the chemical properties of a substance make sense only in the context of the network that describes its chemical relationships, actual and potential, with other substances. Since there is no apparent limit in principle to the (exponential) growth in the number of new substances, the chemical network may not be bounded.

1.4 Atomic Structure and Chemistry

The first tentative steps towards a theory of the chemical bond followed Thomson's discovery of the electron in the late 1890s and his claim that the electron was a universal constituent of atoms. There were several independent measurements of the charge/mass ratio of cathode rays contemporary with Thomson's announcement in 1897; crucially, however, he was the first to measure the charge on the electron in an experiment with his student Rutherford using the Wilson cloud chamber device invented in Cambridge [28]. Thomson initially favoured a uniform distribution of positive charge inside an 'atomic sphere' with solely negatively charged electrons – the so-called 'plum pudding model' of an atom. He had found that the mass of the electron was about 1/1700 of the mass of the hydrogen atom, and since he assumed the positive charge distribution contributed no mass to the atom, this implied that atoms must contain thousands of electrons [29].

In his Romanes Lecture (1902), Lodge suggested that chemical combination must be the result of the pairing of oppositely charged ions, for (quoted in Stranges, [30])

> It becomes a reasonable hypothesis to surmise that the whole of the atom may be built up of positive and negative electrons interleaved together, and of nothing else; an active or charged ion having one negative electron in excess or defect, but the neutral atom having an exact number of pairs.

The notion of positive and negative electrons was an early 'solution' to the evident problem of the electroneutrality of the atom, and also its stability since a positive charge is needed to keep the electrons together [31]. Earnshaw's theorem in classical electrostatics implies that a collection of charges interacting purely through Coulomb's inverse square law cannot have an equilibrium configuration, and so must be moving [32]; on the other hand, classical electrodynamics implies that moving charges must generally lose energy by radiation.[5]

In 1906, Thomson showed that the number of electrons in an atom is of similar magnitude to the relative atomic mass of the corresponding substance, and that the mass of the carriers of positive electricity could not be small compared to the total mass of the atomic electrons. These conclusions came from three independent theoretical results: firstly, a formula he derived for the refractive index of a monatomic gas; secondly, his formula for the absorption of β-particles in matter; and thirdly, the cross section,[6] σ, for the scattering of X-rays by gases [33]:

$$\sigma = \frac{8\pi}{3} \left(\frac{1}{4\pi\varepsilon_0} \frac{e^2}{m_e c^2} \right)^2 . \tag{1.3}$$

Thus, the hydrogen atom could contain only one electron.

The use of a potential energy surface (PES) as key to understanding the dynamics of molecules can be glimpsed in the beginnings of chemical reaction rate theory more than a century ago that go beyond the purely thermodynamic considerations of van 't Hoff and Duhem, and in the first attempts to understand molecular ('band') spectra in dynamical terms in the same period. As early as 1892, Lord Rayleigh had pointed out that the absence of broadening of the spectral lines of molecular gases due to molecular rotation was an outstanding difficulty for spectroscopic theory [34]. The lack of continuous bands in the spectra of gases was taken as clear evidence of a radical failure of either classical mechanics or classical electrodynamics, or both. Later Bjerrum developed Rayleigh's approach to show that the width of infrared absorption bands should be of the order of magnitude to be expected from the superposition of molecular rotations on molecular vibrations [35], [36]. Thus, for a diatomic molecule, Bjerrum found that an absorption band in a molecular gas at thermal equilibrium should be a doublet separated by a frequency interval of

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[5] See Appendix C where the classical field of a moving charge is investigated.

[6] Known now as the low-energy (Thomson) limit of the Compton scattering cross section calculated according to Quantum Electrodynamics (QED). e and m_e are the charge and mass parameters of the electron, respectively, c is the speed of light and ε_0 the permittivity of vacuum.

$$\Delta v \approx \frac{1}{\pi}\sqrt{\frac{2k_BT}{I}}, \tag{1.4}$$

where I is the molecular moment of inertia, T is the temperature in Kelvin and k_B is Boltzmann's constant.

The idea of basing a theory of chemical reactions (chemical dynamics) on an energy function that varies with the configurations of the participating molecules seems to be due to Marcelin. In his last published work, his thesis, Marcelin showed how the Boltzmann distribution for a system in thermal equilibrium and statistical mechanics can be used to describe the rate, v, of a chemical reaction [37]. The same work was republished in the Annales de Physique shortly after his death [38].[7] His fundamental result can be expressed, in modern terms, as

$$v = M\big(e^{-\Delta G^{\#}_{+}/RT} - e^{-\Delta G^{\#}_{-}/RT}\big), \tag{1.5}$$

where R is the molar gas constant (Avogadro's number, N_A times k_B), T is the temperature in Kelvin, the subscripts $+, -$ refer to the forward and reverse reactions and $\Delta G^{\#}$ is the change in the molar Gibbs (free) energy in going from the initial $(+)$ or final $(-)$ state to the 'activated state'. The pre-exponential factor M is obtained formally from statistical mechanics. Marcelin gave several derivations of this result using both thermodynamic arguments and also the statistical mechanics he had learnt from Gibbs' famous memoir [39].

The most interesting aspect of Marcelin's account is the suggestion that molecules can have more degrees of freedom than those of simple point material particles. In this perspective, a molecule can be assigned a set of coordinates $\mathbf{q} = q_1, q_2, \ldots, q_n$, and their corresponding canonical momenta $\mathbf{p} = p_1, p_2, \ldots p_n$. Then the instantaneous state of the molecule is associated with a 'representative' point in the canonical phase space $\mathcal{P}$ of dimension $2n$, and so as the position, speed or structure of the molecule changes, its representative point traces a trajectory in the $2n$-dimensional phase space [37].

In his phase space representation of a chemical reaction, the transformation of reactant molecules into product molecules was viewed in terms of the passage of a set of trajectories associated with the 'active' molecules through a 'critical surface' $\mathcal{S}$ in $\mathcal{P}$ that divides $\mathcal{P}$ into two parts, one part being associated with the reactants, the other with the products. According to Marcelin, for passage through this surface it is required[8] [37]

> [une molécule] il faudra [....] qu'elle atteigne une certaine région de l'éspace sous une obliquité convenable, que sa vitesse dépasse une certain limite, que sa structure interne corresponde à une configuration instable, etc. ....

Although this discussion looks familiar, it does so only because of the modern interpretation we put upon it. It is important to note that nowhere did Marcelin elaborate on how the canonical variables were to be chosen, nor even how n could be fixed in any given case. The words 'atom', 'electron' and 'nucleus' do not appear anywhere in his

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[7] René Marcelin was killed in action fighting for France in September 1914.
[8] that a molecule must reach a certain region of space at a suitable angle, that its speed must exceed a certain limit, that its internal structure must correspond to an unstable configuration etc. ....

thesis, in which respect he seems to have followed the scientific philosophy of Gibbs [40] and his countryman Duhem [41]. On other pages in the thesis, Marcelin refered to the 'structure' (also 'architecture') of a molecule and to molecular 'oscillations' but never otherwise invoked the structural conception of a molecule due to van 't Hoff, although he was very well aware of van 't Hoff's physical chemistry.

The activity of physicists in what hitherto had been the province of chemists did not pass unremarked. At the 1909 meeting of the British Association for the Advancement of Science (BAAS), the distinguished organic chemist Armstrong offered them some fairly pointed advice [42]:

> Now that physical inquiry is largely chemical, now that physicists are regular excursionists into our territory, it is essential that our methods and our criteria are understood by them. I make this remark advisedly, as it appears to me that, of late years, while affecting almost to dictate a policy to us, physicists have taken less and less pain to make themselves acquainted with the subject matter of chemistry, especially with our methods of arriving at the root conceptions of structure and the properties as conditioned by structure. It is a serious matter that chemistry should be so neglected by physicists.

Thomson was one of very few physicists with a serious interest in studying the role of electrons in chemistry, and his penchant for qualitative arguments took him steadily away from the mainstream of physics. The 'plum-pudding' model became of purely historical interest when a completely novel conception was introduced by Rutherford in 1911; he successfully explained the back-scattering of α-particles by a thin gold foil in terms of his notion of the atomic nucleus where most of the atomic mass, and all of the positive charge in the atom resided [43]. The nucleus is negligibly small in comparison with the dimensions of an atom (10^{-5}:1). Almost immediately, the astronomer Nicholson proposed a 'planetary' model of the atom,[9] in which electrons orbit the positively charged nucleus [45], [46]. If electrons are placed in a circular orbit of radius a with angular velocity ω, an energetic equilibrium is obtained when the centrifugal force on a specified electron is balanced by the attractive force of the nucleus less the repulsions of the other electrons. Critically, however, with more than one electron the orbit does not have dynamical stability. Nicholson's calculations were directed towards a hypothetical atom he believed was responsible for the spectra of nebulae; this atom, called 'Nebulium', could not be identified with any terrestrial atom. The notion has long been consigned to obscurity, though the calculations proved significant in the following decade.

As an example, consider the helium atom modelled as a pair of electrons in a circular orbit about a nucleus with charge $q = 2e$ which for simplicity is regarded as immobile; then there are six degrees of freedom. The equilibrium arrangement has the electrons on opposite sides of the nucleus in steady motion in the same direction. The modes can be classified as in-plane and perpendicular to the plane of the orbit. One in-plane mode

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[9] Nicholson was inspired by Maxwell's account of the rings of Saturn [44]; although electrostatics and gravitation are described by the same inverse square law, a crucial difference is that the electrons repel each other while the 'particles' in Saturn's rings experience only attractive forces. This leads to a marked difference in the requirements for the stability of particle orbits.

is unstable; if the electrons are subject to a perturbation in the orbital plane directed at right angles to the line joining the pair, the electrons do not return to the equilibrium configuration, but instead move apart exponentially. This is the typical behaviour of multielectron systems. Notice also that the classical mechanics is quite incomplete since the preceding argument leads to an equation involving the combination $a^2\omega^3$ so that another statement is required to fix either the angular velocity or the radius a. The only parameters available in the Newtonian mechanics of the problem are the charge and mass of the electron, and these are not enough to construct units of length, mass and time required for a complete physical theory. If the velocity of light is admitted, in recognition of electromagnetic phenomena in the atomic regime, then a characteristic length (the classical electron radius) can be constructed,

$$r_e = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{m_e c^2}, \tag{1.6}$$

which, to within a numerical factor, is the square root of the Thomson scattering cross section, (1.3). Its magnitude, however, is $\sim 10^{-15}$ m, far too small to be a characteristic length for atoms and molecules.

Two quite different remedies for this situation were proposed in 1913. Bohr linked atomic structure to Planck's constant, h, the quantum of action. While accepting the correctness of Nicholson's calculations, he proposed the following remarkable hypothesis [47], [48]:

> In any molecular system consisting of positive nuclei and electrons in which the nuclei are at rest relative to each other and the electrons move in circular orbits, the angular momentum of every electron round the centre of its orbit will in the permanent state[10] of the system be equal to $h/2\pi$, where h is Planck's constant.

For each orbit this gives

$$ma^2\omega = \frac{h}{2\pi} \equiv \hbar, \tag{1.7}$$

which is sufficient to fix the radius of the orbit and the frequency ω. The quantisation of the angular momentum is supposed to trump the classical dynamical instability of the orbits in multielectron systems. For the hydrogen atom, Bohr found $2a \approx 1.1 \times 10^{-10}$ m and $\omega \approx 6.2 \times 10^{15}$ s^{-1}. Bohr further took it that higher-energy electron orbits were associated with integer multiples of the quantised angular momentum. This leads to a system of discrete energy levels, and he identified the observed spectral frequencies $\{\nu\}$ with *transitions* between these energy levels according to the quantum law (an expression of the conservation of energy):

$$h\nu_{nm} = E_n - E_m. \tag{1.8}$$

The theory gives quantitative agreement with the observed sequence of spectral lines of atomic hydrogen known as the Balmer and Paschen series, and offers the prediction (verified later) of other series in the IR and UV parts of the spectrum. The same theory applies to He$^+$ with a simple modification of the nuclear charge and the reduced

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[10] In modern terms, the ground state.

mass of the electron–nucleus pair. In companion papers, Bohr gave a qualitative dis-
cussion of multielectron atoms [49] and of the hydrogen molecule [50]. These justly
famous papers are commonly referred to now as 'Bohr's trilogy'. In the following years,
Bohr developed his approach and gave a comprehensive account of atomic spectra and
the periodic table. He was centrally involved in the development of quantum theory
and was acutely aware of the paradoxes it entailed prior to the discovery of quantum
mechanics; Bohr received the Nobel Prize in Physics in 1922 [51].

Shortly after Bohr's introduction of the idea of stationary state energy levels in atoms
determined by Planck's constant h, similar ideas were developed for the vibrations
and rotations of more general molecules. Molecular structure was expressed in terms
of a mechanical model (for example, the dumbbell model of a diatomic molecule or
the symmetric top model of a polyatomic molecule) amenable to classical dynamical
calculations supplemented by 'quantum conditions'[11] [52], [54], and this led to rapid
progress in the understanding of molecular spectra.

In the same year as the appearance of Bohr's trilogy, Thomson took an entirely
different view; he argued that because of the instability problem of classical orbits in
an electrostatic field every electron would have to have its own orbit, and hence an
extremely complicated picture of an atom would ensue that would be useless for the
needs of chemistry. He therefore proposed a modification of electrostatics [54],

> In considering the forces which may exist in the atom, we must remember that we
> cannot assume that the forces due to the charges of electricity inside the atom are of
> exactly the same character as those given by the ordinary laws of Electrostatics; these
> laws may merely represent the average effect of a large number of such charges, and
> in the process of averaging some of the peculiarities possessed by the individuals may
> disappear.

His proposal was that the force law between a nucleus of charge Ze and an electron
a distance r apart is expressed by the equation

$$F = \frac{Ze^2}{4\pi\varepsilon_0 r^2}\left(1 - \frac{l}{r}\right), \tag{1.9}$$

where the length, l, is a characteristic atomic constant of order 10^{-10} m. With such a
force law, a number of electrons can be in stable equilibrium around a nucleus without
having to be assigned to orbits of the Bohr type; instead it leads to a model of the atom
with a size of the order of l in which electrons are static. It is noteworthy that Thomson
made no reference to the hydrogen atom, and no reference to Bohr and Rutherford
[55]. The model was of no consequence in physics; however, Thomson made use of it to
develop a systematic discussion of the facts of chemistry and ideas about valency which
were congenial to chemists in the UK and USA. Thomson thought his formulation
provided a unification of chemistry and physics; his mature ideas were recorded in his
Franklin lectures delivered in 1923 [56].

One of Thomson's admirers in the USA was Noyes, editor of the *Journal of the Amer-
ican Chemical Society* between 1902 and 1917, and a person like Lewis of considerable

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[11] This is the approach that we now refer to as the Old Quantum Theory.

influence. In 1917, Noyes reviewed recent developments in ideas about valency in terms of electronic models and wrote [57]

> Physicists in general have directed their attention to rotating or rapidly moving electrons and to the relation between these and spectral lines, the disintegration of atoms and other phenomena involving individual atoms. Chemists, on the other hand, following the suggestion of J. J. Thomson, have considered chiefly the role which the valence electrons probably play in the combination of atoms.

Ideas about the electronic structure of atoms very similar to those of Lodge also formed in the mind of Lewis, but they were not published until 1916,[12] after the Bohr atom ideas had become prominent in physics. It was Lewis' skilful combination of electronic ideas with traditional notions of the bond that proved so persuasive to chemists. In his 1923 book, Lewis wrote the following about the development of his theory [17]:

> In the year 1902 …, I formed an idea of the inner structure of the atom which, although it contained certain crudities, I have ever since regarded as representing essentially the arrangement of electrons in the atom …
>   The main features of this theory of atomic structure are as follows:
>
> 1. The electrons in an atom are arranged in concentric cubes.
> 2. A neutral atom of each element contains one more electron than a neutral atom of the element next preceding.
> 3. The cube of eight electrons is reached in the atoms of the rare gases, and this cube becomes in some sense the kernel about which the larger cube of electrons of the next period is built.
> 4. The electrons of an outer incomplete cube may be given to another atom, as in Mg^{++}, or enough electrons may be taken from other atoms to complete the cube, as in Cl^-, thus accounting for 'positive and negative valence'.

The model of the atom that is presupposed here is a static one inspired by the work of Thomson. In his 1916 paper, Lewis introduced a new idea and a new means of representation, and these are quite unambiguously Lewis' contributions alone [59]. The new idea was the 'rule of two' in which he asserted that the occurrence of electrons in molecules in even numbers was pretty much universal. The new means of representation was the method of symbolising electrons by dots which is now so familiar to us. The ability to make the correspondence of a pair of dots between two atom symbols and the bond was extremely attractive to working chemists. It is obvious that these ideas owe absolutely nothing to quantum theory, and certainly nothing to Bohr. It would be wrong to believe that this was because those involved in the developments here did not know what was going on in physics; they knew very well and were, on the whole, pretty sceptical about them. At a meeting of the AAAS in New York in December 1916, Lewis devoted his address to the idea of a static atom and commented that [61]:

> Unless we are willing, under the onslaught of quantum theories, to throw over all the basic principles of physical science, we must conclude that the electron in the Bohr

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[12] The priority in publication of the 'octet rule' is actually by Abegg in 1904 [58]. Lewis did not publish until 1916 at about the same time as Kossel, who had arrived at very similar conclusions [59], [60].

atom not only ceases to obey Coulomb's law, but exerts no influence whatsoever upon another charged particle at any distance.

Lewis considered this absence of effect logically and scientifically objectionable for "that state of motion which produces no physical effect whatsoever may better be called a state of rest" [59]. He was not alone in his scepticism; efforts continued for a decade after Bohr's hydrogen atom paper to get a theory in which the electrons in an atom remained still and were distributed at the corners of a cube. In his Nobel lecture in 1922, however, Bohr delivered a sharp attack on static atom theories, pointing out that in view of Earnshaw's theorem in electrostatics [32], [51],

> Statical positions of equilibrium for the electron are in fact not possible in cases where the forces between the electrons and the nucleus even approximately obey the laws that hold for the attractions and repulsions between electrical charges.

He also suggested that the developing quantum theory offered the possibility of relating the properties of the elements and the experimental results concerning the constituents of atoms, something that was quite beyond the statical atom models. By this Bohr meant physical properties; his examples demonstrate the periodicity (in the sense of the periodic table) of the elements. There is nothing about chemical bonding and valency.

This was clearly, at the very least, an uncomfortable situation, and Sidgwick attempted to avoid the difficulty by shifting the argument away from atomic structure as such, to the idea of molecular structure in which pairs of electrons had common orbits of the Bohr–Sommerfeld type involving the molecular nuclei. He seems to have been the first chemist to point out that it was possible to imagine a dynamical situation in which a pair of electrons could hold a pair of nuclei together; this suggestion was made at a meeting of the Faraday Society in Cambridge in 1923 [62]. At that meeting, Lewis gave an introductory address in which he signaled his accession to a similar point of view which shortly afterwards was elaborated in book form [17]. Lewis was clearly still unhappy with quantum theory, for in the closing pages of his book he could not resist referring to it as "the entering wedge of scientific Bolshevism."

The dynamical model described by Sidgwick had contemporaneously been discussed in terms of the Old Quantum Theory by Pauli and by Nordheim who attempted to classify the various sorts of orbits satisfying the 'quantum conditions' that were possible for electrons shared by two nuclei [63], [64]. Their calculations were unsuccessful as indeed were contemporary calculations on the Bohr stationary states of the helium atom. We noted earlier that the Bohr model of the helium atom is dynamically unstable; a similar behaviour is found with H_2. Nordheim investigated the forces between two hydrogen atoms as they approach each other adiabatically in various orientations consistent with the quantum conditions. Before the atoms get close enough for the attractive and repulsive forces to balance out, a sudden discontinuous change in the electron orbits takes place and the electrons cease to revolve solely round their parent nuclei. Nordheim was unable to find an interatomic distance at which the energy of the combined system was less than that of the separated atoms. At the end of his paper Nordheim wrote [64]

> dass eine rein adiabatische Annäherung nicht zu einer Bindung führen kann, da sich die Atome zwar anfangs anziehen, dann aber infolge der Stosswirkung in genan derselben Weise auseinanderfliegen müssen.

Paraphrased, this means that a purely adiabatic approximation cannot describe the formation of bonds between atoms because if they come together adiabatically, they can just as easily separate.

The parlous situation regarding the application of the Old Quantum Theory to atomic and molecular systems shortly before the discovery of quantum mechanics is dealt with in the books by Sommerfeld [65] and Born [66]; for example, Sommerfeld expressed his hopes as follows:

> To the future falls the task of working out *a complete topology of the interior of the atom* and, beyond this, a system of mathematical chemistry, that is one which will tell us the exact position of the electrons in the atomic envelope and how this qualifies the atom to form molecules and to enter into chemical compounds.
>
> The subject of mathematical physics has been in existence for more than one hundred years; a system of mathematical chemistry that can achieve what we have just mentioned, that can shed light on the still very obscure conception of valency and can, at least in typical cases, predict the reactions that must occur, is only on the point of being created.

He introduced his detailed account of the Bohr models for He, H_2 and H_2^+ with the following words:

> The following calculations concern models that are indeed interesting from the historical aspect but that cannot be maintained empirically and theoretically.

In Sommerfeld's view, chemical bonding and valency remained a mystery that the developing quantum theory had not illuminated [65].

Following the discovery of quantum mechanics by Heisenberg [67], a consistent account of the structure of the atom was rapidly realised, and all previous conceptions of the atom became untenable. By the time Sidgwick published his book (1927), he had decided to face the consequences of the quantum revolution in physics. The preface to his book begins [68]:

> This book aims at giving a general account of the principles of valency and molecular constitution founded on the Rutherford-Bohr atom.… In developing the theory of valency there are two courses open to the chemist. He may use symbols with no definite physical connotation … or he may adopt the concepts of atomic physics, … and try to explain chemical facts in terms of these. But if he takes the latter course, as is done in this book, he must accept the physical conclusions in full ….

But he was clearly uneasy when he acknowledged the newly published work of Schrödinger:

> It has yet given no proof that the physical concepts which led (him) to his fundamental differential equation should be taken so literally as to be incompatible with the conceptions of the nature of electrons and nuclei to which the work of the last thirty years has led.

Even at this date, there was still refusal from some distinguished chemists at what had developed in the conception of the nature of matter. Henry Armstrong was still an outspoken critic, writing in 1927 [69]:

> On p. 414 [Nature (1927), vol 120], Prof W. L. Bragg asserts that 'In sodium chloride there appear to be no molecules represented by NaCl. The equality in number of sodium and chlorine atoms is arrived at by a chess-board pattern of these atoms; it is a result of geometry and not of a pairing-off of the atoms.' This statement is more than 'repugnant to common sense'. It is absurd to the n th degree, not chemical cricket. Chemistry is neither chess nor geometry, whatever X-ray physics may be. Such unjustified aspersion of the molecular character of our most necessary condiment must not be allowed any longer to pass unchallenged. A little study of the Apostle Paul may be recommended to Prof. Bragg, as a necessary preliminary even to X-ray work, especially as the doctrine has been insistently advocated at the recent Flat Races at Leeds, that science is the pursuit of truth. It were time that chemists took charge of chemistry once more and protected neophytes against the worship of false gods: at least taught them to ask for something more than chess-board evidence.

Armstrong evidently failed to appreciate that the solid state was qualitatively different from fluids where his organic chemistry flourished, but also that Bragg had accepted completely the chemist's classical notion of structure in the atomic domain; there was nothing in what Bragg had done that had anything to do with the developing quantum theory.

Heitler and London's paper on the quantum chemistry of the H_2 molecule according to Schrödinger's wave mechanics appeared in the same year [70]. In contrast to the earlier investigations of Pauli and Nordheim using the Old Quantum Theory methods, the new quantum mechanics based on adiabatic approach of the atoms yielded a bound molecular ground state; key to London's approach was the fundamental notion that as the nuclei moved they acted as adiabatic parameters in the electronic wave function [71]. Thus quantum chemistry was initiated as an *electronic structure theory*. Shortly before the publication of the Heitler and London paper, Sidgwick had sent London a copy of his new book seeking comment on the consistency of the Lewis-inspired approach and the new developments in wave mechanics; while London praised the book, he preferred his own approach. According to his biographer, London, as a new university teacher, had written recently to Schrödinger suggesting that he did not think quantum mechanics was necessary for chemists' understanding of chemical processes; indeed he thought that a course in quantum mechanics for chemists might frighten them [72].

It fell to Pauling to attempt a reconciliation between the Lewis theory and the approach made by Heitler and London through the development of the Valence Bond model of electronic structure. This he did in a series of papers published between 1928 and 1933 and whose conclusions are brought together in his book, dedicated to Lewis and published in 1939 [73]. In this enormously influential book, Pauling had a clear programme:

> I formed the opinion that, even though much of the recent progress in structural chemistry has been due to quantum mechanics, it should be possible to describe the new developments in a thorough-going and satisfactory manner without the use of advanced mathematics. A small part only of the body of contributions of quantum mechanics to chemistry has been purely quantum mechanical in character; …. The advances which have been made have been in the main the result of essentially chemical arguments, …. The principal contribution of quantum mechanics to chemistry has been the suggestion of new ideas, such as resonance.

Pauling started his exposition from the idea of the electron pair bond as envisaged by Lewis and showed how this can be understood in the context of the Heitler–London calculation as being due to strong orbital overlap. Introducing the idea of orbital hybridisation, he then used the idea of maximum overlap in discussing bonding generally. It should not be thought, however, that all were as convinced as was Pauling in the correspondence between perfect pairing and the bond. Mulliken arrived at very different conclusions from the standpoint of Molecular Orbital theory. He devoted his 1931 review to a description of molecular structure in terms of molecular orbitals, and at the end of the last section, felt constrained to write [74]:

> The fact that valence electrons almost always occur in pairs in saturated molecules appears to have after all no fundamental connection with the existence of chemical binding. … A clearer understanding of molecular structure … can often be obtained by dropping all together the idea of atoms or ions held together by valence forces, and adopting the molecular point of view, which regards each molecule as a distinct individual built up of nuclei and electrons.

For Mulliken at least, it was clearly somewhat doubtful even then that the bond was either necessary for, or explicable in terms of the quantum mechanics required to account for chemical binding. At issue here was a question of interpretation rather than technique, for both methods had provided a basis for useful calculations; moreover, from the technical point of view it was soon shown that the two methods could be extended to give ultimately the same description of the electronic structure of the H_2 molecule [75]. Later this proof was extended to the general case of the polyatomic molecule [76], so that the choice of method depended on convenience rather than a point of principle.

1.5 Chemical Physics and Quantum Chemistry

The scope of quantum chemistry in its first two decades can be gauged from two famous books which showed the development of a wide-ranging formalism, although practical calculations were strongly limited by the sheer complexity of the requisite wave-mechanical calculations [77], [78]. What transformed the subject was the development and widening availability of electronic computers in the years after WWII [79]. The successes and contributions of quantum chemistry to modern chemistry are well

known and need not be detailed here; a comprehensive overview of the whole subject can be found in a recent Handbook [80]. Quantum chemistry is widely thought to be an explicit justification of Dirac's original claim that quantum mechanics could be used directly and quantitatively to describe the facts of chemistry if only the computations could be done. It is worth reminding ourselves of what Dirac wrote and its context. Dirac started by remarking (in 1929) that quantum mechanics had been nearly completed, the remaining problem being essentially its relationship with relativity ideas [81]. He continued:

> These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

The evidence for such a claim was really rather slight, probably amounting to little more than the work of Heitler and London [70] on the electronic structure of the hydrogen molecule,[13] but nevertheless it has been regarded as 'received wisdom' ever since. As we shall see (§5.3.3), an evident irony is that the claim was made in the introduction to a justly famous paper showing the far-reaching implications of permutation symmetry in the new quantum mechanics for systems of identical particles.

Chemistry relies on the atom as its basic unit; however, there is no sufficient account of interactions between atoms that could serve as a fundamental basis for theoretical chemistry. Thus chemical physics and quantum chemistry invoke sub-atomic structure and rely on Schrödinger's equation and an appropriate Hamiltonian for atoms and molecules which are taken to be composed of charged particles, electrons and nuclei. The following quotation comments on the 'derivation' of the wave equation for the hydrogen atom [77]:

> On observing that there is a formal relation between this [Schrödinger] wave equation and the classical energy equation for a system of two particles of different masses and charges, we seize on this as providing a simple, easy, and familiar way of describing the system, and we say that the hydrogen atom consists of two particles, the electron and proton, which attract each other according to Coulomb's inverse-square law. Actually we do not know that the electron and proton attract each other in the same way that two macroscopic electrically charged bodies do, inasmuch as the force between two particles in a hydrogen atom has never been directly measured. All that we do know is that the wave equation for the hydrogen atom bears a certain formal relation to the classical dynamical equations for a system of two particles attracting each other in this way.

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[13] Doubtless Dirac was aware of the then recent work of Born and Oppenheimer (1927).

The wave equation for the hydrogen atom with the Hamiltonian based on purely (Coulombic) electrostatic forces between the charged particles yields definite formulae for discrete energy levels expressed in terms of fundamental constants including values for the electron and proton masses and their charges; if we substitute the experimentally determined values (obtained from other experiments), remarkable agreement with spectroscopic data is achieved.

A fundamental theory of atoms and molecules is expected to justify such a result; the restriction to electrostatics is, however, no more than a practical ansatz that can be traced back to the Bohr theory of the atom [47], [48]. Of course, the model did not survive the discovery of quantum mechanics, but it left a seemingly permanent imprint; the quantum theory that developed from it is fundamentally spectroscopic in nature (energy levels, transition matrix elements, the S-matrix, response functions etc.). Bohr's model is mainly remembered for his introduction of Planck's constant, h, and the resulting quantisation of the angular momentum. Much less remarked on today is that Bohr made a decisive break with classical electrodynamics. In modern terms, the idea is this; formally one fixes the gauge of the vector potential, $\mathbf{A}$, by the Coulomb gauge condition,

$$\boldsymbol{\nabla} \cdot \mathbf{A} = 0, \tag{1.10}$$

and it then follows easily that the longitudinal part of the electric field strength due to the electrons and nuclei can be expressed entirely in terms of their coordinates and gives rise to the familiar static Coulomb potential in the Hamiltonian. 'Radiation reaction' due to the transverse part of their electromagnetic field is simply discarded ad hoc, and the role of the radiation field is demoted to the status of an 'external' perturbation inducing transitions between Bohr's stationary states. For a system of charged particles with purely electrostatic interactions, this leads to the so-called 'Coulomb Hamiltonian' and the miracle of quantisation sweeps away the pathologies of its classical ancestor, as demonstrated by the Kato–Rellich theorem [82], [83]. However, when electromagnetic radiation is admitted the situation is much more complicated because of 'self interactions' which lead to formally infinite 'electromagnetic masses' for the charges [84].

Since we are dealing with charged particles, a fundamental theory of atoms and molecules must presumably be based on their electrodynamics, and so we require electrodynamics formulated in terms of Hamiltonian dynamics, since this is the route to Schrödinger's equation. It is conventional to begin with a classical description knowing that the canonical quantisation scheme due to Dirac, based on the correspondence

$$i\hbar \text{ classical Poisson} - \text{bracket} \rightarrow \text{ quantum commutator}, \tag{1.11}$$

is a standard procedure for obtaining a quantum theory from a classical analogue that has been cast in Hamiltonian form, and this is the route we shall follow. It has long been recognised, however, that the scheme involves analogy which may not be reliable, since the resulting quantum theory may or may not turn out to be satisfactory. The classical theory is thus no more than a recognisable starting point towards a quantum theory, the required endpoint.

The usual discussion in the literature of classical electrodynamics concentrates on the Lorentz force for the dynamics of the charges, with fields obtained from the relevant (retarded) solutions of the Maxwell equations; much of the discussion is concerned with aligning the theory with special relativity which is an obvious priority in general physics. In classical electrodynamics, the limiting case of point charged particles is pathological, and a major goal of the theory is the treatment of the infinities that arise. For example, the Coulomb energy is divergent for a classical point charge, as will be shown in Chapter 2.

In some sense, this means that the notion of a point particle carrying electric charge is simply inconsistent with classical physics. We now know from quantum mechanics that classical physics cannot be used for lengths shorter than about the reduced Compton wavelength ($\lambda_C = \hbar/m_0 c$) for the particle; according to the uncertainty principle, this corresponds to energies greater than the pair production threshold. It is known that maintaining explicit Lorentz invariance and gauge invariance provides the best route to making sense of the divergences that plague the electrodynamics of point charged particles.

Atoms and molecules are characterised minimally by the specification of a definite number of nuclei and electrons. There is no known theory of a system with a fixed finite number of particles interacting through the electromagnetic force that accommodates gauge invariance and is covariant under Lorentz transformations, so that any general account of atoms and molecules will be 'non-relativistic' to some degree. It is usually accepted that the first step in transforming to a Hamiltonian description is to ensure that Newton's law of motion for the charges with the Lorentz force, and the Maxwell equations for the field, are recovered as Lagrangian equations of motion. There is then a standard calculation for the determination of the associated Hamiltonian. This is the subject matter of Chapter 3.

It is important to note that the customary starting point for classical Lagrangian electrodynamics involves symbols for the electric charges $\{e_n\}$ and masses $\{m_n\}$ of the particles which are merely parameters that cannot be assumed to have the experimentally determined values. There is a subtle change of viewpoint here; the original equations of motion, modelled on macroscopic classical electrodynamics, describe the electromagnetic fields associated with prescribed sources through Maxwell's equations, while Newton's laws are used to describe the motion of charged particles in a prescribed electromagnetic field. The Lagrangian formalism, however, describes a closed system for which $\partial L/\partial t = 0$, so that by the usual arguments the Hamiltonian H is the constant energy of the whole system.

For comparison with experimental data, the parameter e is required to be the experimentally observed charge of a particle; a gauge-invariant theory guarantees charge conservation and at non-relativistic energies there are no physical processes that can modify the value of e. This is true in both classical and quantum theories. The situation with the mass parameter m for a particle is quite different since there is a charge–field interaction that leads to an 'electromagnetic mass' additional to the 'mechanical mass' m. It is possible for the 'electromagnetic mass' (due to self-interaction) to become arbitrarily large and this requires m to be negative so that the observed mass = mechanical

mass + electromagnetic mass has its observed (positive) value. This pathology certainly occurs in the point charge limit and is the origin of so-called 'runaway' solutions in the classical equations of motion for the charged particles. A feature of the runaway solution is that it has an essential singularity at $e = 0$, so there is no possibility of constructing solutions of the interacting charge and field system that pass smoothly into the solutions of the non-interacting system as $e \to 0$. Some of these problems are inherited by the quantum theory resulting from canonical quantisation of non-relativistic classical electrodynamics.

From the point of view of fundamental theory, it is clear that there is a considerable gulf between Bohr's picture which is the basis for the usual perturbation theory procedures, and the actual characterisation of the non-relativistic QED Hamiltonian H for a collection of charged particles. The conventional perturbation theory of optical physics assumes that the Hilbert space of the full system is the same as that for the 'free' reference system (atoms/molecules and EM field without coupling), as in ordinary quantum mechanics, so that the diagonalisation of the full Hamiltonian, H, expressed in the reference system basis can be expressed as a certain unitary transformation. If one takes the charges to be 'point particles', this is never the case; the usual remedy is to smooth out point charges, which is physically plausible for nuclei, but not so evident for electrons. In the presence of electromagnetic radiation, all the discrete energy levels of the atomic system become thresholds of continuous spectra; they are said to be 'embedded' eigenvalues (resonances). The fate of these discrete states of isolated atoms/molecules thus requires the perturbation theory of *continuous* spectra. A short introduction to these ideas is given in Chapter 11.

As for treating the field as an 'external' perturbation, this is commonly implemented by assuming that the electromagnetic field variables in the Hamiltonian are classical variables. But if the electromagnetic field is regarded as a physical system, it clearly has a specific Hamiltonian which has to be quantum mechanical if all its properties are to be described. That does not contradict the fact that one can realise *states* of the field that have some of the same statistical properties (mean correlation functions of the field) as in Maxwell's classical electrodynamics, and so might be called 'classical states'.

A fundamental shift in chemical perspective occurred during the years either side of World War II. By and large, the historical approach to molecular structure was highly successful for organic chemistry, even though there were puzzles and anomalies that had to be regarded as 'special cases', for example, concerning the structural formulae for polycyclic hydrocarbons such as anthracene; it was much less successful for inorganic compounds. For this reason, the systematic use of physical methods of structure determination, especially X-ray and electron diffraction techniques, in organic chemistry textbooks was much delayed with respect to those of inorganic chemistry and did not become widespread until the late 1950s [85], [86]. This change in methodology seemed to imply a fundamental revision in the notion of molecular structure from being a hypothesis that encoded the actual and potential chemistry of a substance (the set of chemical reactions a substance may participate in) to being an experimental observable to be measured by a physical technique.

Most of the physical techniques of structure determination fall under the general heading of spectroscopy, that is, they involve the monitoring of some kind of radiation that has previously interacted with the chemical substance. With the passage of time, it has become evident that the experimental results derived from these techniques are quite generally either reported directly in terms of classical molecular structure models (e.g. diffraction experiments, microwave spectroscopy, dielectric properties) or in terms of correlations with classical structural features (e.g. infrared, visible-UV, NMR spectroscopies). There is, however, an important distinction to be made. Classical structural formulae deliberately suppress detailed geometric information and instead focus on the configuration (or conformation) of the functional groups so as to convey the relevant information about the position of the substance in the chemical network. The precise structural diagrams derived from physical measurements do not identify functional groups per se and hence do not encode the chemistry of the substance; for that one must refer back to the older conception of a molecule.

While it is widely believed that this change in orientation of the basis for molecular structure is an inevitable outcome of the development of modern physical theory applied to molecular systems, a more reasonable view is that a far-reaching reinterpretation of these experiments has been made for reasons that are largely independent of any requirements of physics (specifically quantum mechanics). Looking back, it is apparent that Armstrong's appeal to physicists [42], quoted in §1.4, was never heard, but equally Sidgwick's claim [68] that the chemist "must accept the physical conclusions in full" does not describe how things have turned out. It is also quite clear that the success of chemistry based on the conception of molecular structure initiated by van 't Hoff is quite independent of the physical nature of the atom which, as we have seen in this chapter, underwent very radical revisions up to the discovery of quantum mechanics. In other words, rather than the seamless integration of chemical theory into physics, all that has happened is that the nineteenth-century rupture between chemistry and physics has been patched over in the framework of quantum chemistry.

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2 Classical Electromagnetism

2.1 Introduction

Classical physics is the body of knowledge about physics created from the time of Newton in the seventeenth century until the end of the nineteenth century. The core of it is undoubtedly the mechanics of 'particles' created by Newton that is given mathematical form in his famous laws of motion. When the volume of a body is unimportant for the physics, its motion can be specified by giving the position of a point. A particle is characterised purely by its mass, M. As time passes, the point particle follows a path called its orbit under the influence of the forces that act on it. If there are no forces, the particle remains in a state of uniform (unaccelerated) motion and is said to be free. All motion is relative, but before Einstein time was self-evidently absolute. A key notion, due originally to Galileo, is that the laws of motion are the same in all unaccelerated ('inertial') reference frames; the coordinate transformations that relate any two such frames are called Galilean transformations. Collectively, they form an abstract symmetry group usually known as the Galilean group (see §2.3.1).

In the nineteenth century, the property of electric charge was recognised as another attribute of material bodies, and this led to the first researches into electrical and magnetic phenomena such as the characterisation of the force law associated with a system of charges at rest (Coulomb, Gauss), and forces associated with electrical conductors and magnets (Ampère, Biot and Savart, Ørsted). Electromagnetic theory was given a radically new direction by Faraday, who focused attention on the space surrounding electrical conductors and magnets; his lines of force are the first expression of the idea of the electromagnetic field as a primary entity that carries energy, momentum and force. Faraday, however, lacked the mathematical tools required to turn his ideas into a quantitative theory.

This step was taken by Maxwell who showed that the known electrical and magnetic phenomena, and the properties of light, were encompassed by his famous system of equations in which electric and magnetic fields appear as the dependent variables [1]. Maxwell's development of electrodynamics marks a decisive shift away from the Newtonian ideal of a dynamical theory of material points based on ordinary differential equations supplemented by initial conditions. The electromagnetic field is described by continuous functions of space and time that satisfy partial differential equations

to which must be adjoined appropriate boundary conditions. These are the celebrated Maxwell equations with which we shall begin.

Since our main interest is to develop a quantum theory of processes involving atoms and molecules in electromagnetic fields, the goal of the next two chapters is to show how classical electrodynamics can be given an Hamiltonian formulation such that the Maxwell equations are just Hamilton's equations of motion. The standard procedure of canonical quantisation as developed by Dirac then gives a corresponding quantum theory for the field and its sources which are taken to form a closed dynamical system.

2.2 Maxwell's Theory

A charge density ρ and a current density $\mathbf{j}$ are sources of the electromagnetic field. The sources and the field in a given inertial frame are related by the Maxwell equations which in the usual vector calculus notation, originally due to Heaviside [2], [3], take the form

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0, \tag{2.1}$$

$$\boldsymbol{\nabla} \wedge \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{2.2}$$

$$\varepsilon_0 \boldsymbol{\nabla} \cdot \mathbf{E} = \rho, \tag{2.3}$$

$$\boldsymbol{\nabla} \wedge \mathbf{B} - \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} = \mu_0 \mathbf{j}; \tag{2.4}$$

here $\mathbf{E}$ is the electric field intensity, $\mathbf{B}$ is the magnetic induction and c is the speed of light. These equations hold at every point in space ($\mathbf{x}$) and time (t). With this understanding, $\mathbf{x}$ and t can be suppressed in the field equations to simplify the notation. We use S.I. units throughout so that $\mathbf{E}$ and $c\mathbf{B}$ have the same dimensions. Equation (2.1) is the statement that there are no free magnetic charges, while Eq. (2.2) describes electromagnetic induction (Faraday, Lenz). Coulomb's Law and Gauss's theorem in electrostatics are covered by (2.3) which is generally valid for space- and time-dependent charge density and electric field, while (2.4) gives Ampère's Law. The appearance of the displacement current, $c^{-2}\partial \mathbf{E}/\partial t$, in (2.4) is a crucial modification due to Maxwell himself; it is essential both for the description of light as an electromagnetic phenomenon, and for the expression of local conservation of electric charge.

The Maxwell equations involve two fundamental constants characterising the electrical permittivity (ε_0) and magnetic permeability (μ_0) of free space; they are related by the equation

$$\varepsilon_0 \mu_0 c^2 = 1. \tag{2.5}$$

In the electrodynamics of continuous media, ε_0 and μ_0 must be multiplied by the dielectric constant (ε) and permeability (μ), respectively, of the medium, and it is customary

to replace $\mathbf{E}$ and $\mathbf{B}$ by modified fields $\mathbf{D}$ and $\mathbf{H}$. As we are aiming at a microscopic theory of charged particles interacting with the field, we shall continue with the notation in Eqs. (2.1)–(2.4).

Two important symmetry operations are space inversion, or parity, denoted by P and time reversal denoted by T; by considering the experimental arrangements that generate electric and magnetic fields, it is easily seen that the electric field intensity $\mathbf{E}$ changes sign under P and is invariant under T; $\mathbf{E}$ is a time-even polar vector. On the other hand, the magnetic induction $\mathbf{B}$ is unchanged by the parity operation P but changes sign under time reversal T; hence, the magnetic induction $\mathbf{B}$ is a time-odd axial vector. It then follows that the Maxwell equations (2.1)–(2.4) are invariant under the separate operations of P and T [4]. If Maxwell's equations are to be valid in all inertial reference frames, one must give up Galilean relativity for electromagnetism; this fact led Einstein to the remarkable conclusion that there is no absolute notion of simultaneity (as there is in Newton's mechanics), and thence to special relativity. The symmetry group of transformations between different inertial frames is called the Poincaré group; the Galilean group can be thought of as a limiting case of the Poincaré group appropriate for particles with speeds $v \ll c$ (cf. Chapter 3).

It is a classical result that the Maxwell equations for the free field imply conservation laws for 15 mechanical quantities because they admit a larger group of symmetries than those required for invariance under Lorentz transformations [5], [6]. The additional symmetries describe the conformal or angle-preserving transformations in space-time, which are generated by dilations, $x_\mu \rightarrow \lambda \, x_\mu$, and inversions, $x_\mu \rightarrow x_\mu/x^2$, where λ is a real scalar, and x^2 is given by (2.84). These are symmetries because the Maxwell equations provide no intrinsic length scales which only arise through interactions with charged particles. The Poincaré group essential for special relativity is a subgroup of the infinite dimensional Lie Group SO(4,2) that describes conformal symmetry.

When first derivatives of the fields are admitted, many more conserved currents can be defined [7], [8]. As an example, consider the following scalar quantity:

$$\xi = \frac{1}{2}\varepsilon_0\big(\mathbf{E} \cdot (\boldsymbol{\nabla} \wedge \mathbf{E}) + c^2\mathbf{B} \cdot (\boldsymbol{\nabla} \wedge \mathbf{B})\big). \tag{2.6}$$

Calculation of its time derivative yields

$$\frac{\partial \xi}{\partial t} = -\frac{1}{2}\varepsilon_0 c^2 \boldsymbol{\nabla} \cdot \big(\mathbf{E} \wedge (\boldsymbol{\nabla} \wedge \mathbf{B}) - \mathbf{B} \wedge (\boldsymbol{\nabla} \wedge \mathbf{E})\big) \equiv -\boldsymbol{\nabla} \cdot \mathbf{J}^{(Z)}, \tag{2.7}$$

which shows that ξ is the spatial density of a conserved quantity. The flux of the conserved quantity is the vector field $\mathbf{J}^{(Z)}$; it is directed along the propagation direction of the electromagnetic wave. ξ and $\mathbf{J}^{(Z)}$ are components of a third-rank tensor quantity originally called the 'zilch' tensor [9]. A characteristic of these additional conserved quantities is that they are generally restricted to the free field since they do not survive interactions, and it was originally believed that the zilch tensor had no physical significance [10]. More recently, the quantity ξ has been proposed as a candidate [11], [12] for the 'optical chirality' of laser light beams that carry orbital angular momentum ('twisted light'), though ξ does not have the dimensions of a true angular momentum [13]. A connection between the zilch tensor and the Stokes parameter description of

the polarisation properties of electromagnetic radiation was, however, recognised and will be described in Chapter 4 [9], [14]; the Stokes parameters can be quantised to give the Stokes operators, so this correspondence is also valid in the quantum theory of radiation (see Chapter 7).

Two important results are easily derived using standard vector identities. Since DivCurl vanishes, we obtain from (2.2),

$$\mathbf{\nabla} \cdot \frac{\partial \mathbf{B}}{\partial t} = \frac{\partial}{\partial t}\left(\mathbf{\nabla} \cdot \mathbf{B}\right) = 0. \tag{2.8}$$

Thus (2.1) is independent of time at every point in space. Equations (2.1) and (2.2) are evidently independent of the sources and are kinematical statements about the electromagnetic field. By a similar argument, we infer from (2.3) to (2.5) that

$$\frac{\partial \rho}{\partial t} + \mathbf{\nabla} \cdot \mathbf{j} = 0. \tag{2.9}$$

This important relation is the equation of continuity that expresses charge conservation at every point $(\mathbf{x},t)$. This may be seen as follows: if we integrate the equation of continuity (2.9) over a volume Ω with fixed boundaries, we obtain

$$\int_{\Omega} \mathbf{\nabla} \cdot \mathbf{j}\,\mathrm{d}^3\mathbf{x} = \int_{S}\mathbf{j}\cdot\,\mathrm{d}^2\mathbf{S} = -\int_{\Omega}\frac{\partial \rho}{\partial t}\,\mathrm{d}^3\mathbf{x} = -\frac{\partial}{\partial t}\int_{\Omega}\rho\,\mathrm{d}^3\mathbf{x} = -\frac{\partial q_{\Omega}}{\partial t}, \tag{2.10}$$

that is, the flux of charge through the boundary surface S is precisely equal to the rate of change of charge inside Ω; no net charge is created or destroyed. This is the law of conservation of electric charge.

All ordinary matter on a macroscopic scale is found to remain electrically neutral at all temperatures to a very high degree of accuracy.[1] Its coupling to the electromagnetic field is characterised by a quantity we call electric charge. The laws of electrolysis established by Faraday when combined with the atomic theory of matter imply that electricity at the atomic level is discrete [16], [17]; in ordinary matter, charge is found in positive or negative integral multiples of a basic unit of charge ($e = 1.602 \times 10^{-19}$ Coulombs). Apart from movement of charge from one volume to another, creation and destruction of pairs of particles with opposite charges is allowed by the law (2.10). Particles with masses m_k moving slowly compared to the speed of light, however, obey Galilean kinematics and are subject to the law of conservation of mass:

$$M = \sum_{k} N_k m_k = \text{constant}. \tag{2.11}$$

Since, in general, there are no rational relations between the masses $\{m_k\}$, the constancy of M implies that the particle numbers $\{N_k\}$ are also constant. Hence, particle number (and with it charge) is absolutely conserved in Galilean invariant theories; this holds in both classical and quantum mechanics. Pair creation is a feature specifically of relativistic quantum mechanics.

As shown in Appendix B, a vector field $\mathbf{U}(\mathbf{x})$ can always be decomposed into orthogonal parts that are called the longitudinal and transverse components. Thus, for the

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[1] This represents a precision of 1 part in 10^{10} for $v/c \sim 10^{-3}$ [15].

electric field intensity we can write

$$\mathbf{E} = \mathbf{E}^{\parallel} + \mathbf{E}^{\perp}, \quad \mathbf{E}^{\perp} \cdot \mathbf{E}^{\parallel} = 0, \tag{2.12}$$

where the orthogonal components satisfy

$$\boldsymbol{\nabla} \cdot \mathbf{E}^{\perp} = 0, \qquad \text{transverse}, \tag{2.13}$$

$$\boldsymbol{\nabla} \wedge \mathbf{E}^{\parallel} = 0 \qquad \text{longitudinal}. \tag{2.14}$$

The magnetic induction is always transverse (2.1). From (2.3), (2.13) and (2.14) we see that the charge density ρ is responsible for the longitudinal component of the electric field intensity.

Maxwell's system of coupled first-order equations may be transformed directly into a pair of uncoupled inhomogeneous second-order equations,

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{Y} = \mathbf{C_Y}(\mathbf{j},\rho), \tag{2.15}$$

with $\mathbf{Y} = \mathbf{E}$ or $\mathbf{B}$. The source terms $\mathbf{C_Y}$ are

$$\mathbf{C_E} = \left(\mu_0\frac{\partial \mathbf{j}}{\partial t} + \frac{1}{\varepsilon_0}\boldsymbol{\nabla}\rho\right), \quad \mathbf{C_B} = -\mu_0\boldsymbol{\nabla}\wedge\mathbf{j}. \tag{2.16}$$

The pairs $(\rho,\mathbf{j})$ and $(\mathbf{E},\mathbf{B})$ are required to be continuous functions of space and time with continuous derivatives such that space and time differentiation is commutative for them.

It follows that in a region of space where there are no charges or currents the electromagnetic fields satisfy a *wave equation*,

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{Y} = \mathbf{0}, \quad \mathbf{Y} = \mathbf{E},\mathbf{B}, \tag{2.17}$$

from which Maxwell's constant c can be identified as the speed of the wave motion. Electromagnetic waves are purely transverse since (cf. (2.1), (2.3))

$$\boldsymbol{\nabla}\cdot\mathbf{B} = \boldsymbol{\nabla}\cdot\mathbf{E} = 0. \tag{2.18}$$

These equations define the free field.

A *plane wave* has the special property of depending on the time t and one spatial coordinate, say z, which we call the propagation direction. The spatial derivatives in the plane transverse to the direction of travel vanish, and the wave equation (2.17) simplifies to

$$\frac{\partial^2 Y}{\partial z^2} - \frac{1}{c^2}\frac{\partial^2 Y}{\partial t^2} = 0, \tag{2.19}$$

where Y is any component of $\mathbf{E}$ and $\mathbf{B}$. This equation has solutions of the form

$$Y = Y_1(z-ct) + Y_2(z+ct). \tag{2.20}$$

Elementary calculation shows that the functions Y_1 and Y_2 are trigonometric functions, so that, for example,

$$Y = Y^{(0)}\cos(kz - \omega t), \tag{2.21}$$

where $Y^{(0)}$ is an integration constant and $\omega = kc$ is a solution. The displacement $\mathbf{Y}$ of a travelling-plane electromagnetic wave moving in an arbitrary direction at the point $(\mathbf{x}, t)$ can be represented as

$$\mathbf{Y}(\mathbf{x}, t) = \mathbf{Y}^{(0)} e^{i(\mathbf{k}\cdot\mathbf{x} - \omega t)}, \tag{2.22}$$

where $\mathbf{Y}^0$ is an arbitrary complex-valued constant vector and the wave vector $\mathbf{k}$ has magnitude ω/c.

Putting the solution (2.22) into Maxwell's equations for the free field (2.2), (2.4) yields the important relations for plane waves:

$$\mathbf{E} = -c\,\hat{\mathbf{k}} \wedge \mathbf{B}, \quad \mathbf{B} = \frac{1}{c}\,\hat{\mathbf{k}} \wedge \mathbf{E}. \tag{2.23}$$

Thus, the fields are orthogonal to each other and to $\mathbf{k}$ in agreement with (2.18). For each $\mathbf{k}$ we introduce two unit vectors in the plane at right angles to $\mathbf{k}$, that is, tangent to the sphere of fixed $|\mathbf{k}|$, for example

$$\hat{\boldsymbol{\varepsilon}}(\mathbf{k})_1 = \frac{(k_2, -k_1, 0)}{\sqrt{k_1^2 + k_2^2}}, \tag{2.24}$$

$$\hat{\boldsymbol{\varepsilon}}(\mathbf{k})_1 \wedge \hat{\boldsymbol{\varepsilon}}(\mathbf{k})_2 = \hat{\mathbf{n}}, \tag{2.25}$$

where $\hat{\mathbf{n}} = \mathbf{k}/|\mathbf{k}|$ is directed along the direction labelled 3. We call the $\hat{\boldsymbol{\varepsilon}}(\mathbf{k})_i$, $i = 1, 2$ the *polarisation* vectors for the mode $\mathbf{k}$. It is not possible to choose a continuous basis of polarisation vectors for every possible value of $\mathbf{k}$, essentially because of the topological fact captured by Poincaré's 'can't comb the hairs on a sphere' theorem [18], but this is usually of no consequence since the arbitrary polarisation vectors are unobservable. An important property is their sum rule [19], [20],

$$\sum_{\lambda=1,2} \hat{\varepsilon}(\mathbf{k})_{\lambda i} \hat{\varepsilon}(\mathbf{k})_{\lambda j} = \delta_{ij} - \frac{k_i k_j}{k^2} \equiv \mathcal{B}(\mathbf{k})_{ij}, \tag{2.26}$$

which is a function that is discontinuous only at $k = 0$.

At any instant in time, the electric field vector of a plane wave travelling in the z-direction has components given by

$$\begin{aligned}
E_x &= E_1^{(0)} \cos(kz - \omega t) \\
E_y &= E_2^{(0)} \cos(kz - \omega t + \alpha) \\
E_z &= 0,
\end{aligned} \tag{2.27}$$

and the three parameters $\{E_1^{(0)}, E_2^{(0)}, \alpha\}$ can be used to characterise the polarisation of the wave. For example, at any point along a circularly polarised wave, the electric field $\mathbf{E}$ maintains a fixed magnitude but has a direction that rotates in space with a constant angular frequency. Hence, the tip of the $\mathbf{E}$-vector traces out a circle, and the components (E_x, E_y) of $\mathbf{E}$ oscillate with the same amplitude, $E_1^{(0)} = E_2^{(0)}$, but with a phase difference of $\pm\pi/2$. If the tip of the $\mathbf{E}$-vector rotates in a clockwise sense when viewed by an observer receiving the wave, it is said to be right-circularly polarised; if anticlockwise, it is left-circularly polarised. If $E_1^{(0)} = E_2^{(0)}$ and the phase difference is

zero, the resultant is linear polarisation. Otherwise, if $E_1^{(0)} \neq E_2^{(0)}$, the polarisation is elliptical.

2.2.1 The Mechanical Properties of the Electromagnetic Field

We now consider the mechanical properties of the electromagnetic field. The electromagnetic energy in unit volume – the energy density – is defined to be

$$E = \frac{1}{2}\varepsilon_0 \left(\mathbf{E} \cdot \mathbf{E} + c^2 \mathbf{B} \cdot \mathbf{B}\right), \tag{2.28}$$

and is such that its volume integral is the energy content in the specified volume,

$$\mathcal{E} = \int_\Omega E \, \mathrm{d}^3 \mathbf{x}. \tag{2.29}$$

Consider a time-dependent electromagnetic field; the rate of change of the energy density is

$$\frac{\partial E}{\partial t} = \varepsilon_0 \left(\mathbf{E} \cdot \frac{\partial \mathbf{E}}{\partial t} + c^2 \, \mathbf{B} \cdot \frac{\partial \mathbf{B}}{\partial t} \right). \tag{2.30}$$

The time derivatives in this equation may be expressed in terms of the space derivatives of the fields, and the sources, using the Maxwell equations (2.2) and (2.4), and with the aid of an obvious vector identity there results Poynting's theorem,

$$\frac{\partial E}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{S} = -\,\mathbf{j} \cdot \mathbf{E}, \tag{2.31}$$

where we have defined the Poynting vector $\mathbf{S}$ for the field by

$$\mathbf{S} = \varepsilon_0 c^2 \, (\mathbf{E} \wedge \mathbf{B}). \tag{2.32}$$

Only the real part of the electromagnetic field is required for classical electromagnetism; the real part can always be trivially separated out after linear operations. Moreover, physical quantities determined from quadratic combinations of the field vectors are evaluated as time averages over a cycle for which the cycle average theorem holds, provided the time dependence is harmonic [20], [21]:

$$\overline{(\Re \mathbf{X})(\Re \mathbf{Y})} = \tfrac{1}{2}\, \Re(\mathbf{X}\mathbf{Y}^*). \tag{2.33}$$

As an example, the intensity of a plane wave is the time average of the magnitude of the Poynting vector, $|\mathbf{S}|$, over one cycle; for the plane wave, since the wave is harmonic, this is simply $\frac{1}{2}|\mathbf{S}|$, where

$$|\mathbf{S}| = \varepsilon_0 c^2 |\mathbf{E} \wedge \mathbf{B}| = \varepsilon_0 c |\mathbf{E} \wedge \hat{\mathbf{k}} \wedge \mathbf{E}| = \varepsilon_0 c |\mathbf{E}^{(0)}|^2. \tag{2.34}$$

The fields $\mathbf{E}$ and $\mathbf{B}$ contribute equally to the average energy of the plane wave which is $\frac{1}{2}c|\mathbf{S}|$, that is, c times the intensity. $\mathbf{S}$ is along the direction of $\mathbf{k}$.

Similarly, the flux $\mathbf{J}^{(Z)}$, (2.7), obtained from the zilch tensor, is also collinear with $\mathbf{k}$; an elementary calculation using (2.27) shows that

$$\mathbf{J}^{(Z)} = \omega E_1^{(0)} E_2^{(0)} \sin(\alpha) \, \hat{\mathbf{k}}. \tag{2.35}$$